# Priority 2
# Determinand Identification Guide

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by

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# Priority 2
# Determinand Identification Guide

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# PRIORITY 2 DETERMINAND IDENTIFICATION GUIDE

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**SUMMARY**

To demonstrate chemical compliance with the *Drinking-Water Standards for New Zealand* (DWSNZ), water suppliers are required to monitor Priority 2 determinands present in their supplies at concentrations exceeding 50% of their maximum acceptable value (MAV). Drinking-water suppliers are now responsible for identifying these determinands.

Identifying chemical hazards in a drinking-water supply and designing sampling programmes to assess the extent of the risk they present, should be part of a drinking-water supply's public health risk management plan (PHRMP). Consequently, identifying Priority 2 determinands links to the review cycle of a water supply's PHRMP.

This guide for drinking-water suppliers and drinking-water assessors (DWA), defines how the procedure for the identification of Priority 2 determinands fits into the PHRMP review cycle and the way Priority 2 determinands are to be identified. The water supplier designs and provides the DWA with a sampling programme stating the determinands for which samples will be taken, and the location and timing of the sampling.

The guide provides tools to guide water suppliers and DWAs in the identification of Priority 2 determinands (except cyanotoxins[1]) using a qualitative assessment of the likelihood of them being present in the water supply. At least two samples must be collected for each determinand being assessed, and the guide contains instructions on where and when samples for each determinand should be taken.

The first part of the guide provides concise guidance on the Priority 2 determinand identification procedure and is followed by an appendix containing more detailed information explaining the reasons for the way in which the procedure is structured.

[1] Cyanobacterial toxins are not covered by the process described in the handbook because their concentrations can change so rapidly that testing for them infrequently is of no value.

# 1 INTRODUCTION

To demonstrate compliance with the *Drinking-Water Standards for New Zealand 2005 (Revised 2008)* (DWSNZ) drinking-water suppliers must monitor chemical determinands assigned to their water supplies as Priority 2 determinands. Initially, the Ministry of Health identified Priority 2 determinands for water suppliers to begin the process.

Identifying chemical hazards in a water supply logically fits with public health risk management plan (PHRMP) preparation. Consequently, from the time a water supply is required to comply with Sections 69s and 69ZC of the Health Act 1956, identifying a water supply's Priority 2 determinands becomes the responsibility of the water supplier.

Small and neighbourhood drinking water supplies are not required to prepare a PHRMP, although their preparation by those supplies is recommended. As a result, this protocol will only apply to those supplies if the Medical Officer of Health has required a PHRMP to be prepared for a supply under section 69ZA of the Health Act 1956. The Medical Officer of Health may require a PHRMP to be prepared if he or she has evidence of a chemical determinand being present in the water at a concentration greater than 50% of its maximum acceptable value (MAV).

This guide provides drinking-water suppliers with information to guide them through the identification of a water supply's Priority 2 determinands using a qualitative assessment of the likelihood of them being present in the water supply. It will also assist drinking-water assessors (DWAs) to assess the adequacy of sampling programmes prepared by water suppliers, and to assign Priority 2 determinands to water supplies.

The guide discusses Priority 2 determinand *identification* only and is *not* concerned with compliance monitoring. To help maintain the distinction between these two activities, the collection of samples for Priority 2 determinand identification is referred to as "sampling". The collection of samples for demonstrating compliance with the DWSNZ is referred to as "monitoring".

This guide is a quick reference for Priority 2 determinand identification. Further detail is contained in the appendix. The guide contains the following sections:

- Priority 2 determinand identification and the PHRMP review cycle
- identification process overview
- what to sample for
- when and where to sample.

## 2 PRIORITY 2 DETERMINAND IDENTIFICATION AND THE PHRMP REVIEW CYCLE

Figure 1 shows how preparing a water supplier's sampling programme for identifying Priority 2 determinands, implementing the programme and monitoring the resulting Priority 2 determinands for compliance with the DWSNZ fit with the PHRMP review process.

Notable features of Figure 1 are:

a) the sampling programme for Priority 2 determinand identification is prepared as part of the revision of a water supply's PHRMP, and will occur at least every five years

b) once the sampling programme is prepared and approved, it is implemented and may take up to 12 months to complete

c) a DWA assesses the sampling results when they are available and assigns Priority 2 determinands to the water supply as appropriate

d) once assigned to the water supply, the need to undertake compliance monitoring for Priority 2 determinands is included in the revised PHRMP that is approved by a DWA

e) compliance monitoring of the Priority 2 determinands contained in the PHRMP may begin at anytime, but no later than the start of the next financial year after the revised PHRMP is implemented, to help the drinking-water supplier budget for monitoring costs.

The same process for identifying Priority 2 determinands is followed when a PHRMP is first prepared for a supply. The PHRMP submitted to a DWA for approval must include the Priority 2 determinands that have been officially assigned to the supply as the result of the identification sampling programme.

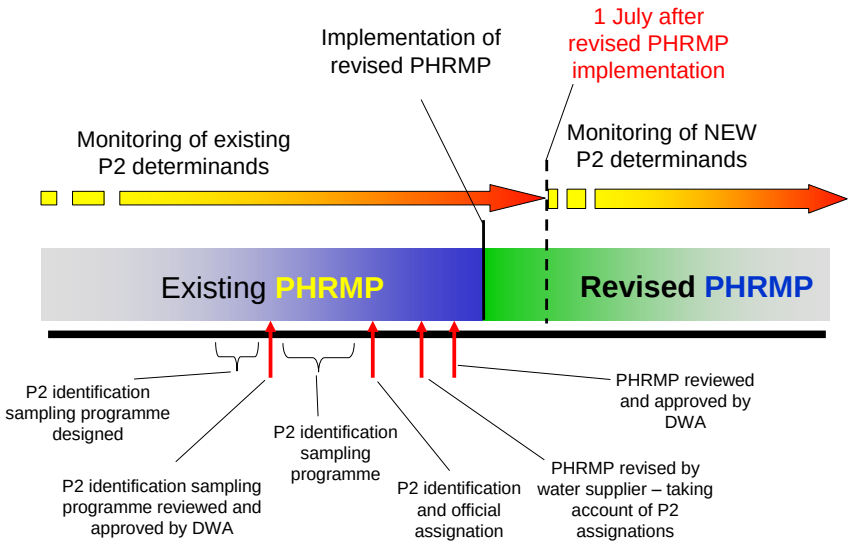
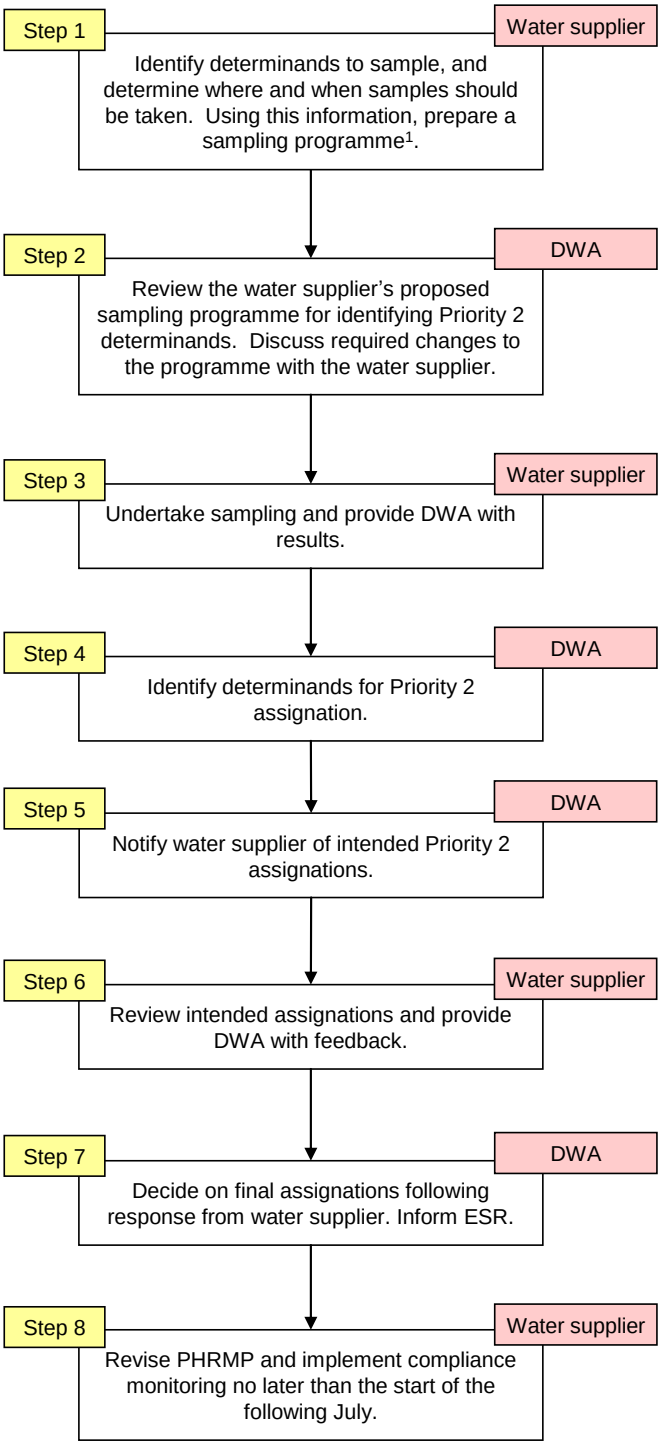



**Figure 1 Timeline depicting the way Priority 2 determinand identification fits within the PHRMP review cycle**

## 3 IDENTIFICATION PROCESS OVERVIEW

Figure 2 shows the steps involved in Priority 2 determinand identification and assignation.




[1] Help can be obtained from the Drinking-Water Assistance Programme Facilitator

**Figure 2 Steps for Priority 2 determinand identification and assignation. Water suppliers and DWAs are involved in this process. The pink box at each step shows which of these groups is/are responsible for the step.**

Detail of the Priority 2 determinand identification process (see also Section A2).

Step 1. The water supplier prepares a sampling programme by:

- identifying the determinands to include in the programme using their knowledge of the supply catchment/recharge zone, the decision guides and the activities table to complete the check-sheet
- determining where samples will be taken
- scheduling when samples will be taken – a minimum of two samples is required.

Step 2. The DWA reviews the sampling programme prepared by the water supplier to ensure that the determinands included in the programme cover the possible chemical hazards to the supply. The DWA works from the check-sheet prepared by the water supplier, checking this against their (the DWA's) knowledge of the water supply and its catchment/recharge zone, the decision guides and the activities table.

Step 3. Once the revised PHRMP is implemented, the water supplier applies their sampling programme. When all sampling results are available, the supplier sends them to the DWA (within 10 working days of receiving the last result).

Step 4. The DWA reviews the results and identifies any determinand found to be present in the water at a concentration greater than 50% of its MAV. These will be assigned to the water supply as Priority 2 determinands, as well as any existing Priority 2 determinands, unless the water supplier can provide an adequate reason why they should not.

Step 5. Within 15 working days of receiving the sampling results, the DWA notifies the water supplier of the outcome of their review and whether they propose to assign the determinands identified in Step 4 as Priority 2 determinands to the supply.

Step 6. Within 10 working days, the water supplier responds, with supporting information[2], if they disagree with the proposed assignations.

Step 7. The DWA finalises the Priority 2 determinand assignations for the supply and informs the water supplier and ESR.

Step 8. The water supplier revises their PHRMP and implements compliance monitoring of the assigned Priority 2 determinands no later than the start of the following financial year[3].

[2] Supporting information needs to show why the test result, which was greater than 50% of the MAV, was atypical of the water quality and very unlikely to occur again. If there is doubt over the result being atypical, the DWA may consider classifying the determinand as a Priority 3 determinand provided the water supplier undertakes sampling (at a reduced frequency from compliance monitoring) to gather more data on the water quality.

## 4 WHAT TO SAMPLE FOR

To help both water suppliers and DWAs in identifying determinands to sample for, the guide provides three types of supporting material.

a) Decision guides (Section 4.1)

   The decision guides are flow diagrams that help the user to decide which determinands to include in the water supply's sampling programme, based on the water supply's characteristics, in particular its catchment or recharge zone.

b) Activities table (Section 4.2)

   This table helps the user decide which determinands may arise in a water supply because of human activities in the water supply's catchment or recharge zone. It provides a list of possible activities and records the determinands that may arise from these activities.

c) Priority 2 determinands identification check-sheet (Section 4.4)

   Once completed, the check-sheet records the path followed by the water supplier through each of the decision guides. This standardised form will simplify the process of selecting which determinands to include in the supply's sampling programme. It also enables the DWA to understand the water supplier's reasons for selecting the determinands for their sampling programme.

The determinands to include in the sampling programme come from three groups.

**Group 1:** **Determinands that *must* be included** (see also Section A3.2)

- Arsenic
- Barium
- Manganese
- Selenium

These must be included in a sampling programme at least once every five years.

Fluoride has been found to occur naturally at a concentration more than 50% of its MAV in very few water sources. Consequently, it is not included in Group 1, although a check for it is recommended. Fluoride is assigned to a *fluoridating* water supply as a Priority 2 determinand without the need for inclusion in the Priority 2 determinand identification process.

[3] Compliance monitoring for the period required by the DWSNZ, that is, until all samples taken during a year's compliance monitoring are shown not to contain the determinand at a concentration exceeding 50% of its MAV.

**Group 2: Determinands that *may* be included and can be identified using the decision guides alone**

- Boron (naturally-occurring) (see also Section A3.3.1)
- Heavy metals (naturally-occurring) (see also Section A3.3.2)
- Disinfection by-products (see also Section A3.3.3)
- Water treatment chemical contaminants (see also Section A3.3.4)

The appropriate decision guide will indicate whether these determinands need to be sampled and, if there is a group of determinands, which determinands must be sampled.

**Group 3: Determinands that *may* be included and are identified using the decision guides and the activities table**

- Determinands arising from human activities in the catchment/recharge zone (see also Section A3.3.5)

The decision guide for this group of determinands shows whether the activity is close enough to the supply's abstraction point that contaminants from it may be a concern. For those activities that are close enough, refer to the activities-determinands table to identify the determinands to include in the sampling programme. There is no requirement to monitor determinands in the sampling programme if they duplicate some of the naturally-occurring determinands from groups 1 and 2.

The sampling programme must allow for two samples to be taken for each tested determinand.

Priority 2 determinands already being monitored for compliance purposes do not need to be included in sampling for Priority 2 determinand identification. Compliance data will show whether they need to remain as a Priority 2 determinand.

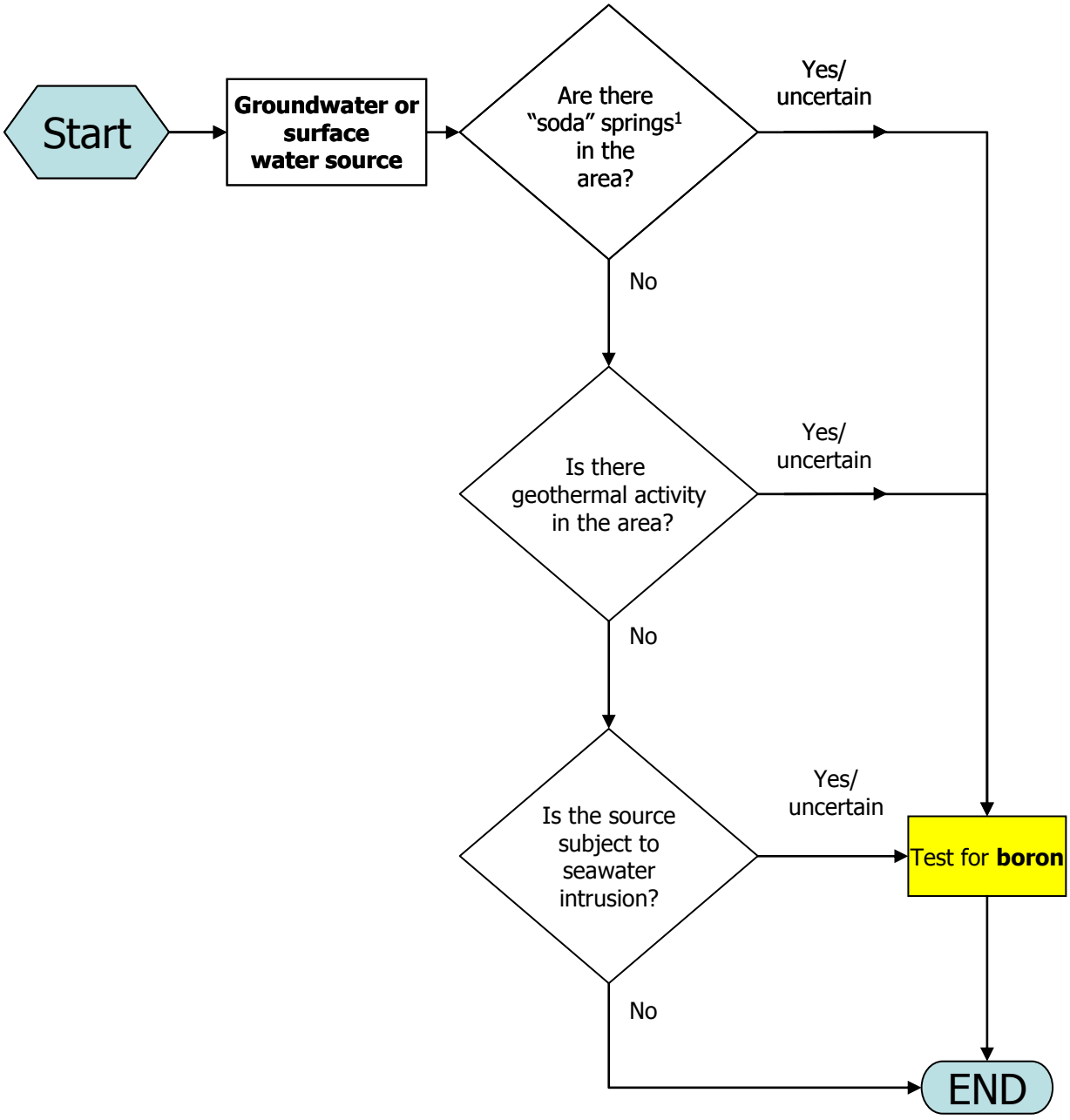
Radiological determinands (see also Section A3.6) need only be sampled once every 10 years, and this only needs to be done for groundwaters not under the influence of surface water. A single sample only is required on each occasion. The radiological determinands to test for are:

- total alpha activity
- total beta activity
- radon.

Potassium measurements may need to be made to correct the total beta activity for a potassium-40 contribution.

## 4.1 Decision Guides

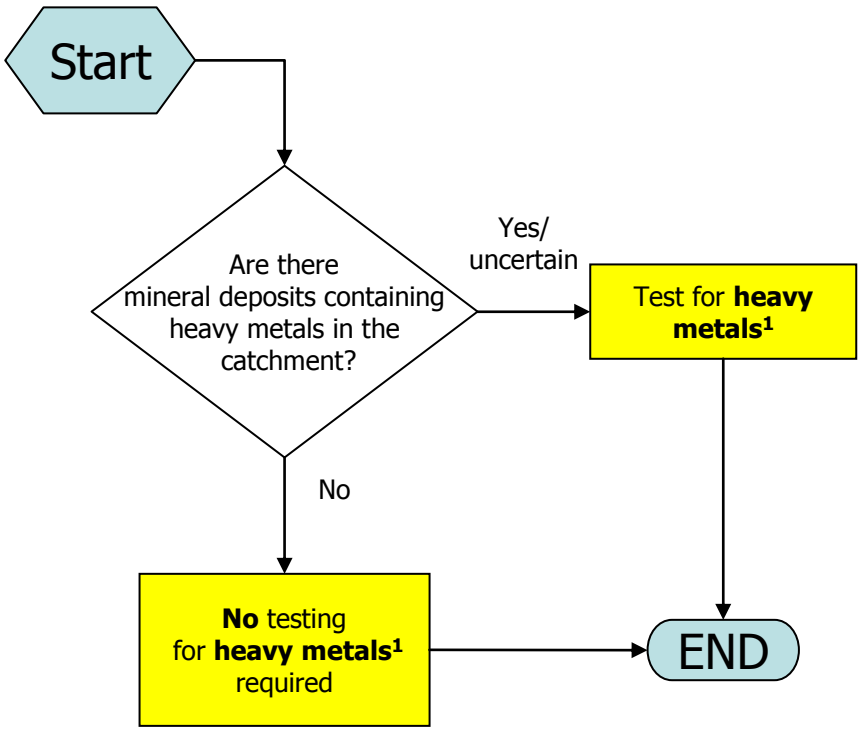
**Decision Guide - Boron (naturally-occurring)**




Note: 1 Springs high in sodium and bicarbonate/carbonate

## Decision Guide – Heavy metals (naturally-occurring)

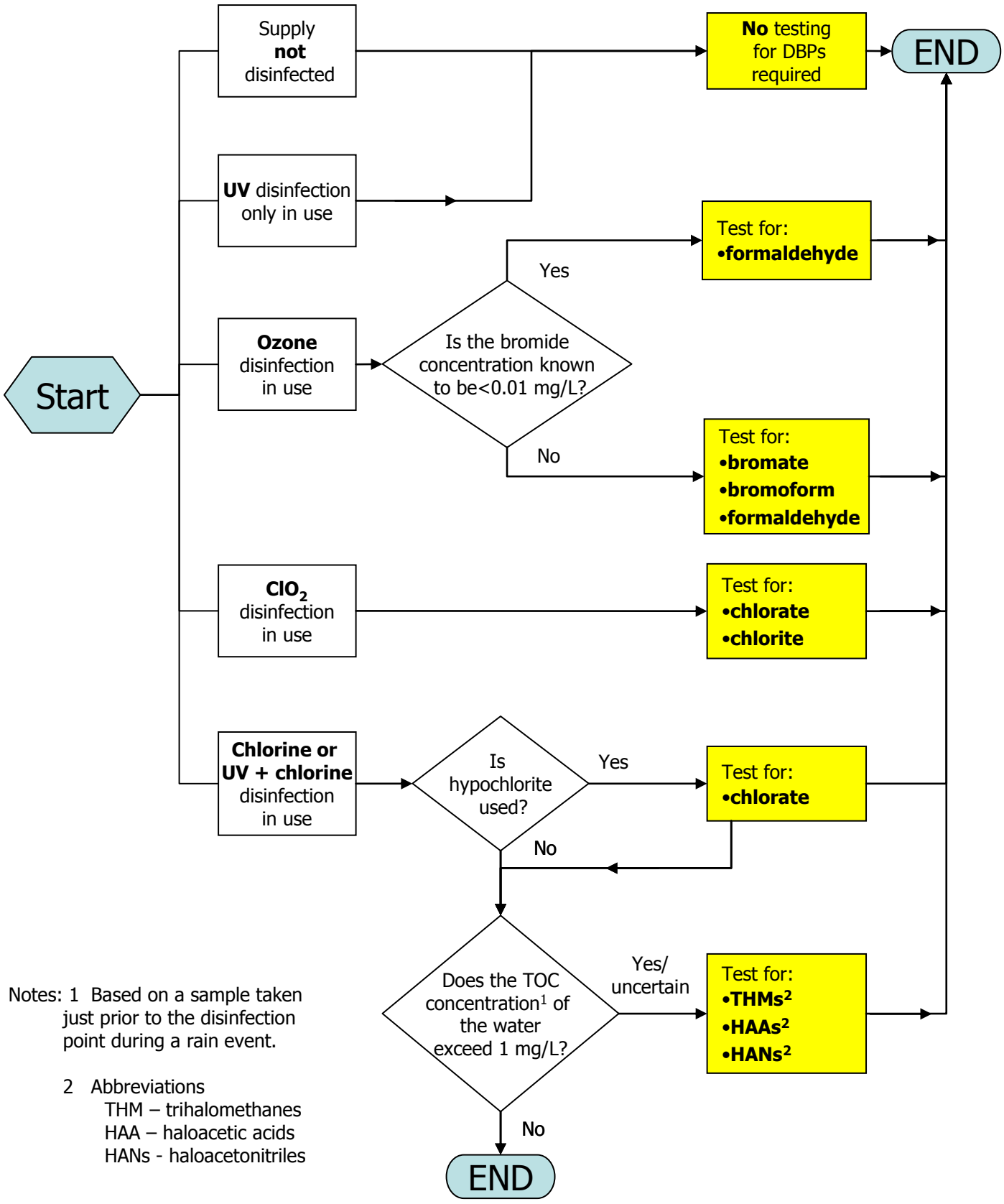
This guide is not for heavy metals arising from plumbosolvent waters, or for heavy metals arising from industrial operations.




Note: 1 "Heavy metals" includes:

- antimony
- cadmium
- copper
- lead
- nickel
- mercury

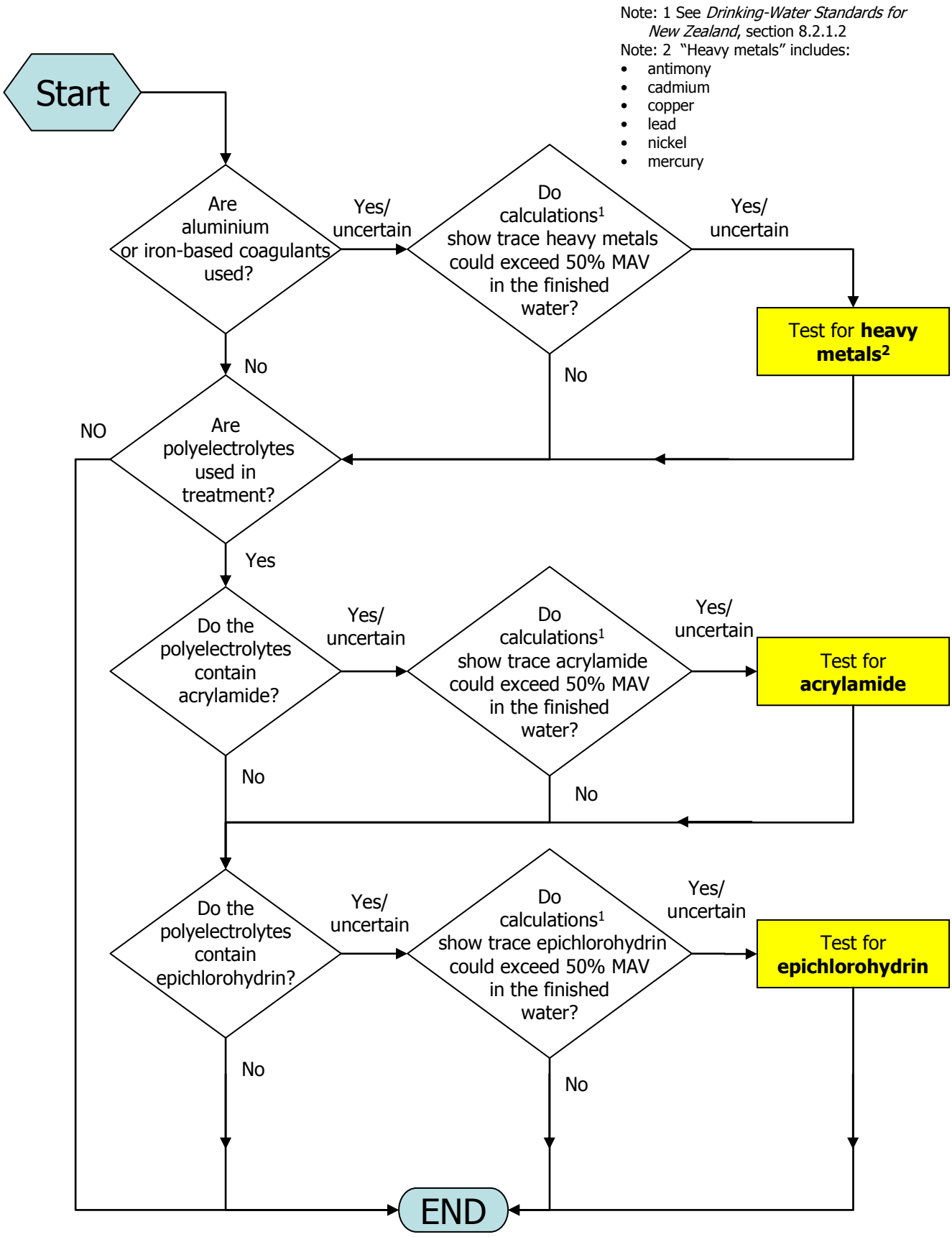
## Decision Guide - Disinfection By-products



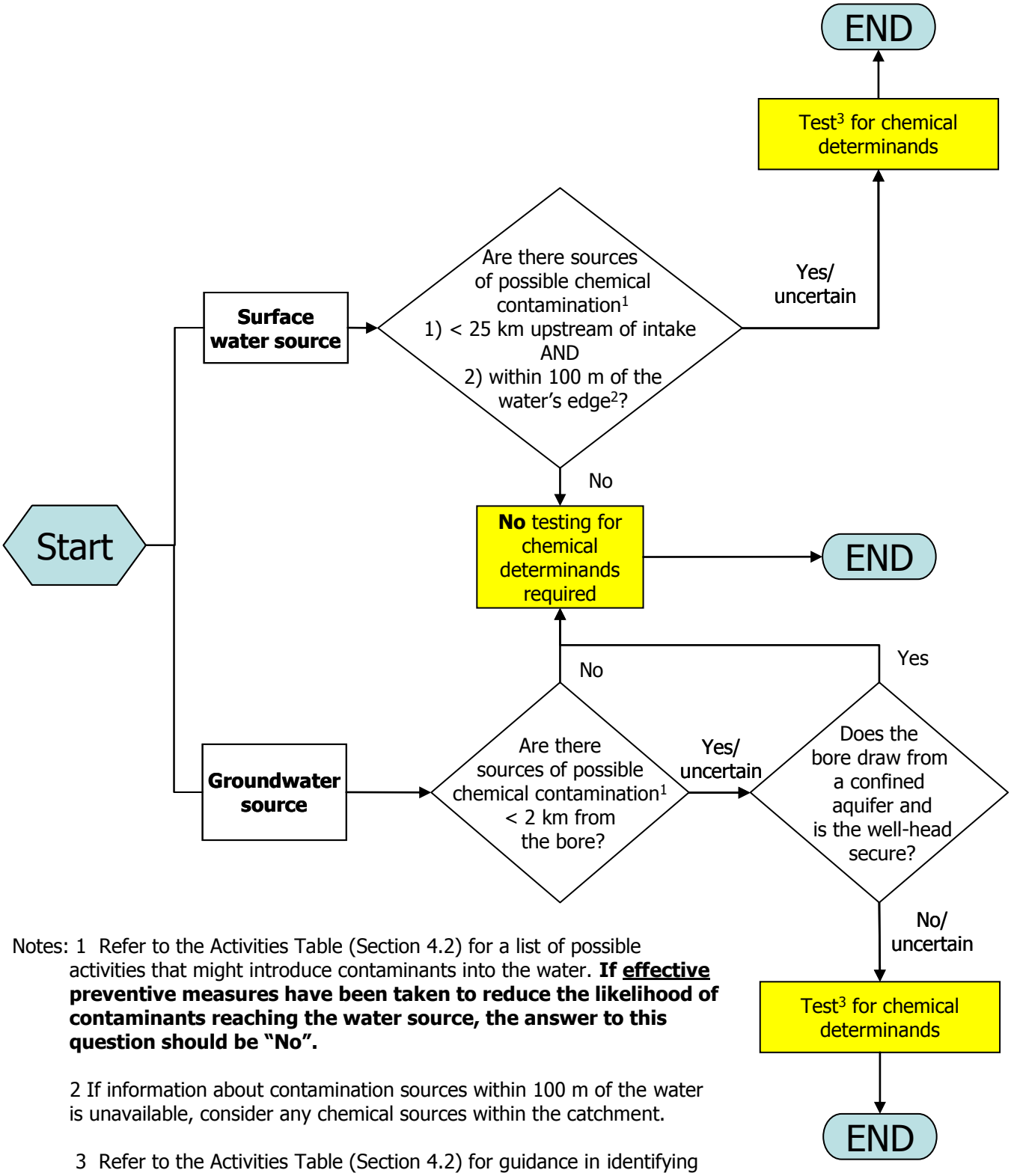

Notes: 1 Based on a sample taken just prior to the disinfection point during a rain event.

2 Abbreviations
THM – trihalomethanes
HAA – haloacetic acids
HANs - haloacetonitriles

## Decision Guide – Contaminants in treatment chemicals



## Decision Guide - Chemical determinands arising from human activity




Notes: 1 Refer to the Activities Table (Section 4.2) for a list of possible activities that might introduce contaminants into the water. **If <u>effective</u> preventive measures have been taken to reduce the likelihood of contaminants reaching the water source, the answer to this question should be "No".**

2 If information about contamination sources within 100 m of the water is unavailable, consider any chemical sources within the catchment.

3 Refer to the Activities Table (Section 4.2) for guidance in identifying which determinands to monitor, based on the contaminating activity.

.

## 4.2 Activities Table

Abbreviations: DBP – disinfection by-products; EDTA – ethylene diamine tetraacetic acid.

| Land use category | Activity | Contaminating material | Possible health-significant determinands | Comment |
|---|---|---|---|---|
| **1. Agriculture** | Use of pesticides | Range of pesticides, metals | Pesticides, copper | |
| | Use of artificial fertilizers | Range of artificial fertilizers | Nitrate, cadmium | • Cadmium is a contaminant of superphosphate |
| | Use of manure as fertilizer | Manure | Nitrate, copper | |
| | Fuel storage and use | Petrol, diesel | Industrial solvents (benzene, toluene, xylene, ethylbenzene) | |
| | Silage production | Silage leachate | Nitrate | |
| | Dairy shed operation | Washwater | Nitrate | • Chlorine and monochloramine may also be present, but they are unlikely to reach concentrations of concern |
| | Spray irrigation of effluent | Effluent | Nitrate, copper | • Levels of contaminants from well-operated effluent ponds should be low |
| | Effluent pond operation | Effluent | | |
| | Grazing animals | Manure deposited in pasture | | |

| Land use category | Activity | Contaminating material | Possible health-significant determinands | Comment |
|---|---|---|---|---|
| **2. Forestry** | Sewage sludge application | Sewage | Nitrate, heavy metals | |
| | Use of pesticides | Range of pesticides | Pesticides | |
| | Use of poisons (feral animal control) | Poisoned baits | Cyanide, 1080 | • Determine which poisons are in use before selecting determinands to monitor<br>• Events involving 1080 should be treated as a chemical spillage. Preventive measures need to be taken as soon as contamination is believed to have occurred, and sampling for 1080 needs to be undertaken as soon as possible after the contamination event. 1080 decomposes relatively rapidly – its half life in water is about 24 hours |
| | Use and maintenance of vehicles | Petrol, diesel, oil | Industrial solvents (benzene, toluene, xylene, ethylbenzene) | |
| | Fuel storage | Petrol, diesel | | |
| **3. Mining and quarrying** | Use and maintenance of vehicles | Petrol, diesel, oil | Industrial solvents (benzene, toluene, xylene, ethylbenzene) | |
| | Fuel storage | Petrol, diesel | | |
| | Ore extraction | Extraction chemicals | Cyanide, heavy metals | • The metals of concern will depend on the composition of the ore |
| | Collection and treatment of acid mine drainage | Mine drainage | Heavy metals | • The metals of concern will depend on the composition of the ore |

| Land use category | Activity | Contaminating material | Possible health-significant determinands | Comment |
|---|---|---|---|---|
| **4. Industry and commerce** (Heavy and light industry) | Ceramics | Glazes | Heavy metals, boron | |
| | Cold storage | Refrigerants | Nitrate | |
| | Drum reconditioning | Range of organic and inorganic chemicals, degreasers, detergents | Industrial solvents, heavy metals | |
| | Electronics | Alkalis, acids, cyanides, solvents, metals | Cyanide, heavy metals, industrial solvents (tetrachloroethene, trichloroethane, toluene) | |
| | Fertilizer/agrichemical production | Fertilizers and pesticides | Nitrate, pesticides | |
| | Foundries | Acids, metals, fluxes | Heavy metals, nitrate | • Nitric acid may give rise to nitrate |
| | Furniture production | Glues, polishes, paints | Industrial solvents (toluene, dichloromethane) | |

| Land use category | Activity | Contaminating material | Possible health-significant determinands | Comment |
|---|---|---|---|---|
| | Meat and milk processing | Processing effluent including cleaning chemicals | Nitrate | • Chlorine and monochloramine may also be present, but they are unlikely to reach concentrations of concern |
| | Metal cleaning/electroplating | Cleaning and plating chemicals, metals, acids | Cyanide, heavy metals, industrial solvents, nitrate, EDTA | • Nitric acid may give rise to nitrate |
| | Paper making | Bleaching chemicals, caustic soda | Chlorate, DBPs | • In this situation, DBPs may be formed in the source water before chlorine at the water treatment plant comes in contact with the water. The quantities of chlorinated organic compounds (eg, DBPs) should be small in a well-run plant |
| | Printing | Solvents, inks, dyes | Industrial solvents (eg, dichloromethane, toluene, xylene) | |
| | Product storage | Fumigants | 1,3-dichloropropene, cyanide | • The nature of the fumigation will determine which fumigants are a concern |
| | Resins | Range of organic chemicals | Formaldehyde | |

| Land use category | Activity | Contaminating material | Possible health-significant determinands | Comment |
|---|---|---|---|---|
| | Rubbers and plastics | Solvents, plasticisers, paints and other organic substances | Industrial chemicals, (formaldehyde, di(2-ethylhexyl)phthalate), cyanide | |
| | Tanning | Tanning chemicals | Chromium | |
| | Wood processing | Preservatives and other treatment chemicals | Pentachlorophenol, copper, chromium, arsenic, boron, chlorpyriphos, benzo(α)pyrene | |
| | Wool scouring | Degreasing agents, pesticides | Pesticides (including chlorpyriphos, diazinon) | • The classes of pesticides likely to be derived from wool are organophosphates, synthetic pyrethroids, insect growth regulators |
| **4. Industry and Commerce** (Commerce and Community) | Car washes | Soaps, detergents, waxes, oil | Benzo(α)pyrene | |
| | Cemeteries | Embalming fluids, bodies, coffin construction materials, fertilizers | Formaldehyde, arsenic, mercury, lead, copper, nitrate | • The properties of the soil and age of the cemetery, *inter alia*, will influence the nature of contaminants in the groundwater |
| | Defence establishments | Disinfectants, human waste, chemical dumps, fuel and oil | Chlorine, industrial chemicals (including, benzene, toluene, xylene, ethylbenzene) | |
| | Dry cleaning | Dry cleaning chemicals | Industrial solvents (tetrachloroethene, | |

| Land use category | Activity | Contaminating material | Possible health-significant determinands | Comment |
|---|---|---|---|---|
| | | | trichloroethane) | |
| | Hospital | Disinfectants, biological waste, radiological waste, other miscellaneous chemicals | Formaldehyde, chlorine | • Reticulation of waste disposal should eliminate the hazards associated with this activity |
| | Laboratories (school, medical and research) | Disinfectants, biological waste, other miscellaneous chemicals | Formaldehyde | • Chlorine and monochloramine may also be present, but they are unlikely to reach concentrations of concern |
| | Laundromats | Detergents, bleaches, dyes | | • Chlorine and monochloramine may also be present, but they are unlikely to reach concentrations of concern |
| | Offices | Detergents, solvents | Industrial solvents | |
| | Photographic processing | Photographic processing chemicals | Cyanide | |
| | Prisons | Disinfectants, human waste | Nitrate | • Only a possible concern if sewage is treated and discharged on-site<br>• Chlorine and monochloramine may also be present, but they are unlikely to reach concentrations of concern |
| | Scrap yards | Petroleum products, solvents, metals, acids, alkalis | Heavy metals, industrial chemicals, benzo(α)pyrene | |
| | Swimming pools | Disinfectants, other pool treatment chemicals, | DBPs | • In this situation, DBPs may be formed in the source water before chlorine at the water |

| Land use category | Activity | Contaminating material | Possible health-significant determinands | Comment |
|---|---|---|---|---|
| | | human waste | | treatment plant comes in contact with the water. The quantities of chlorinated organic compounds (eg, DBPs) should be small in a well-run plant<br>• Chlorine and monochloramine may also be present, but they are unlikely to reach concentrations of concern |
| **4. Industry and commerce** (Transport , storage and utilities) | Airport operation | Fuels, fire-fighting foams, solvents, de-icing substances, fumigants | Industrial chemicals | |
| | Fuel storage and sale | Fuel storage and sale | Industrial solvents (benzene, toluene, xylene, ethylbenzene) | |
| | Railway operation | Spraying of tracks, diesel and oil leaks, human waste (if toilet effluent is vented onto tracks) | Pesticides, benzo(α)pyrene, nitrate | • Spills of cargo carried by rail may result in a wide range of contaminants being introduced into water *if there is a pathway to the source water* |
| | Road transport | Asphalt, fuel and oil leaks, chemicals for roadside weed control, metals | Benzo(α)pyrene, industrial solvents (benzene, toluene, xylene, ethylbenzene), herbicides, heavy metals | • Spills of cargo carried by road may result in a wide range of contaminants being introduced into water *if there is a pathway to the source water* |
| | Sewerage reticulation | Sewage (human waste, trade waste) | Nitrate, heavy metals, industrial chemicals | • A wide range of industrial and domestic contaminants may be present in sewage |
| | Sewage treatment | | | |

| Land use category | Activity | Contaminating material | Possible health-significant determinands | Comment |
|---|---|---|---|---|
| | Stock effluent and camper van effluent disposal facilities | Animal and human waste | Nitrate, heavy metals | |
| | Tyre storage | Tyres | Benzo(α)pyrene | |
| **5. Open space** | Car parks | Fuel and oil leaks, asphalt surface | Industrial solvents (benzene, toluene, xylene, ethylbenzene), benzo(α)pyrene | |
| | Clay target clubs | Lead shot | Lead, benzo(α)pyrene | |
| | Disposal of stormwater run-off | Fuel and oil spills and other contaminants on asphalt road surfaces, faecal material from animals, weed and pest control chemicals, fertilizers, metals | Nitrate, pesticides, industrial solvents (benzene, toluene, xylene, ethylbenzene), heavy metals | |
| | Golf courses | Chemicals used for course up-keep(fertilizer, pesticides); fuel storage | Nitrate, pesticides, industrial solvents (benzene, toluene, xylene, ethylbenzene) | |
| | Recreational parks | Fertilizers, weed control chemicals, fuel and oil from vehicles | | |
| | Sports fields | Fertilizers, weed control chemicals, fuel and oil | | |

| Land use category | Activity | Contaminating material | Possible health-significant determinands | Comment |
|---|---|---|---|---|
| | | from vehicles | | |
| **6. Residential** (urban, lifestyle block, rural) | Disposal of household waste | Household chemicals, garden chemicals, petrol, diesel and oil | Heavy metals, industrial chemicals (benzene, toluene, xylene, ethylbenzene), nitrate, pesticides | • The contamination risk associated with this activity is likely to be small because of their small scale |
| | Use of fertilizers | Fertilizers | Nitrate, cadmium | |
| | Keeping pets or livestock (lifestyle blocks) | Animal waste, pest control chemicals | Nitrate, pesticides | |
| | Fuel storage | Petrol, diesel, oils | Industrial solvents (benzene, toluene, xylene, ethylbenzene) | |
| | On-site disposal of sewage | Human waste, detergents | Nitrate | |
| | Weed and pest control | Pesticides | Pesticides | |
| **7. Vacant land** | Illegal dumping | Wide range of possible chemicals | Heavy metals, industrial chemicals (benzene, toluene, xylene, ethylbenzene), nitrate, pesticides | |
| **8. Landfill** | Disposal of industrial waste | Wide range of possible chemicals | Heavy metals, industrial chemicals | |

| Land use category | Activity | Contaminating material | Possible health-significant determinands | Comment |
|---|---|---|---|---|
| | | | (benzene, toluene, xylene, ethylbenzene), nitrate, pesticides cyanide | |
| | Disposal of waste from water and wastewater treatment systems | Waste sludge (which includes treatment chemicals) | Heavy metals, acrylamide, epichlorohydrin | |
| | Disposal of household waste | Household chemicals, garden chemicals, petrol, diesel and oil | Heavy metals, industrial chemicals (benzene, toluene, xylene, ethylbenzene), nitrate, pesticides | • Which contaminants are present will depend on how well the landfill system is controlled |
| **9. Fishing** | Onshore aquaculture | Faecal matter, pesticides | Pesticides, nitrate | |
| **10. Conservation land** | On-site sewage disposal | Human waste | Nitrate | |
| | Disposal of domestic waste | Tin cans | Heavy metals | • Burial of cans if they are not taken off site |
| | Feral animal control | Poisons | Cyanide, 1080 | • Check to determine which poisons are in use before selecting determinands to monitor<br>• Events involving 1080 should be treated as a chemical spillage. Preventive measures need |

| Land use category | Activity | Contaminating material | Possible health-significant determinands | Comment |
|---|---|---|---|---|
| | | | | to be taken as soon as contamination is believed to have occurred, and sampling for 1080 needs to be undertaken as soon as possible after the contamination event. 1080 decomposes relatively rapidly[4]. |

[4] The primary route of degradation is microbial defluoridation. Laboratory studies of 1080 have shown half-lives from very much less than 24 hours to eight days – Appendix C of the ERMA review of 1080 (2007.) (Application for the Reassessment of a Hazardous Substance under Section 63 of the Hazardous Substances and New Organisms Act 1996. Application Number: HRE05002), http://www.epa.govt.nz/about-us/monitoring/1080/Pages/default.aspx.

### 4.3 Analyses needed

Where the activities table identifies groups of determinands as potential public health concerns, the required analyses are given below.

| Determinand group in activities-determinands table | Analyses required |
|---|---|
| Pesticides | • Trace pesticide suite (multi-residue)<br>• Trace acid herbicide suite |
| Herbicides | • Trace acid herbicide suite |
| Industrial chemicals | • Semi-volatile organic compounds (SVOC)<br>• Volatile organic compounds (VOC) |
| Industrial solvents | • Volatile organic compounds (VOC) |
| Heavy metals | • Antimony, cadmium, chromium, copper, lead, mercury, nickel |

## 4.4 Check-sheet

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# Check-sheet for Priority 2 Chemical Determinand Identification

This check-sheet is to assist both water suppliers and drinking-water assessors decide which determinands to include in a water supply's sampling plan for Priority 2 determinand identification. The check-sheet sets out the criteria for inclusion of determinands in the sampling plan. It should be used in conjunction with the decision guides and the Activities Table in the *Priority 2 Chemical Identification Guide* .

Should Page 2 not provide enough space for recording human activities that might introduce health significant determinands into the water, copy the page and append it to the others.

For all determinand classes, except those arising from human activity, tick the determinands to include in the sampling plan. For determinands arising from human activity, write the determinand names or determinand group names from the Activities Table on the dotted lines.

**Determinand Class**

**Determinands to include in sampling plan**

Compulsory →
- Arsenic
- Barium
- Manganese
- Selenium

Year last tested for, if not included: ……

Naturally-occurring heavy metals

Heavy metal deposits present ?

NO ☐ →

YES ☐ →
- Antimony
- Cadmium
- Chromium
- Copper
- Lead
- Nickel
- Mercury

Naturally-occurring boron

Soda springs in area?

NO ☐ →

YES ☐

Geothermal activity in area?

NO ☐ →

YES ☐ →
- Boron

Seawater intrusion?

NO ☐ →

YES ☐

**Determinand Class**

**Determinands to include in sampling plan**

## Determinands arising from human activity

**List contaminant sources:**

- within 25 km of intake and within 100 m of the water's edge

OR

- less than 2 km from the bore

Are there any factors that would make contamination from the source unlikely?

If a determinand group is listed in the Activities Table (Section 4.2), use the group name here. A listing of all determinands in the group is not required.

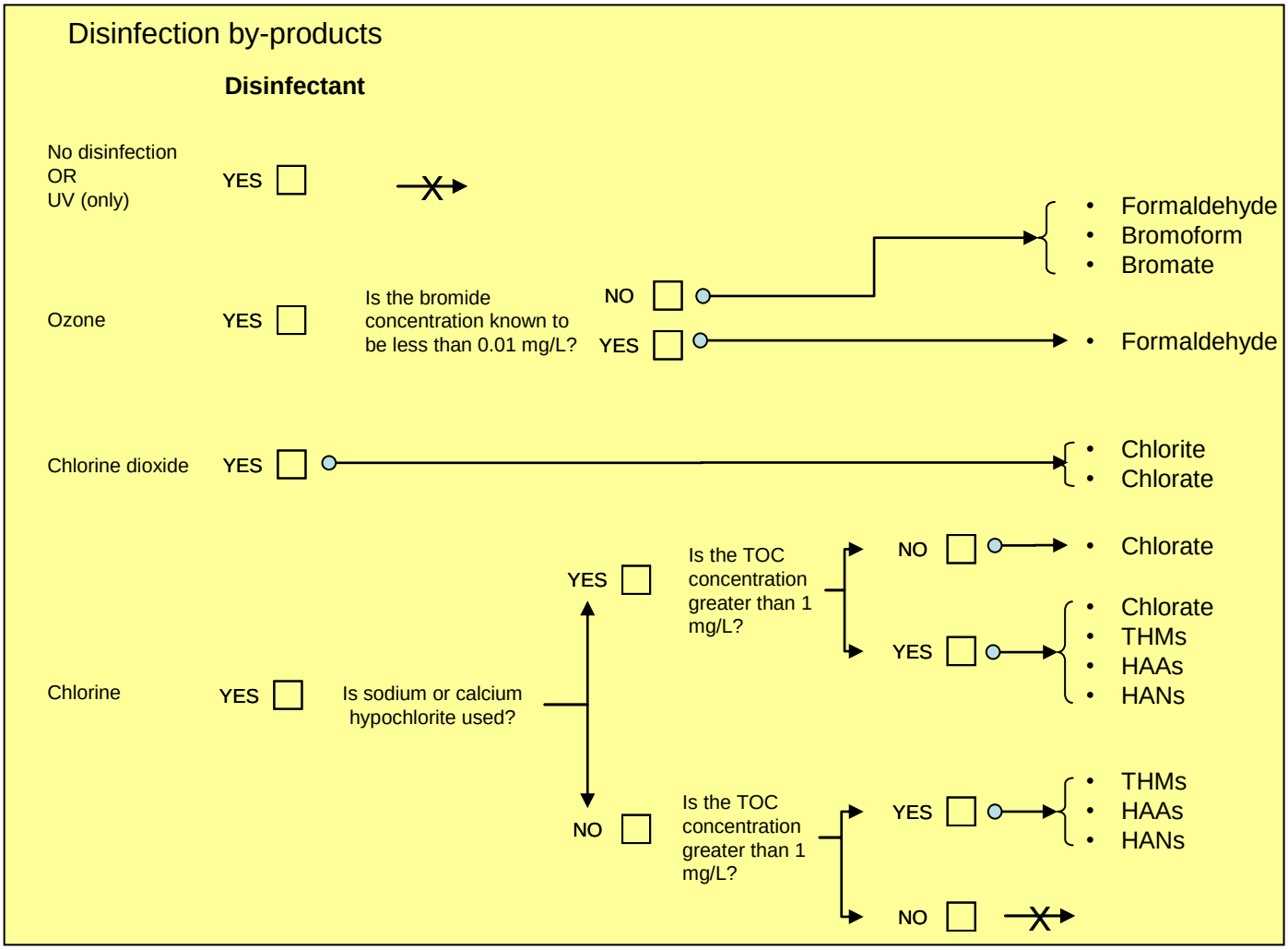
| | |
|---|---|
| | NO ☐ YES ☐ |
| | NO ☐ YES ☐ |
| | NO ☐ YES ☐ |
| | NO ☐ YES ☐ |
| | NO ☐ YES ☐ |
| | NO ☐ YES ☐ |
| | NO ☐ YES ☐ |
| | NO ☐ YES ☐ |

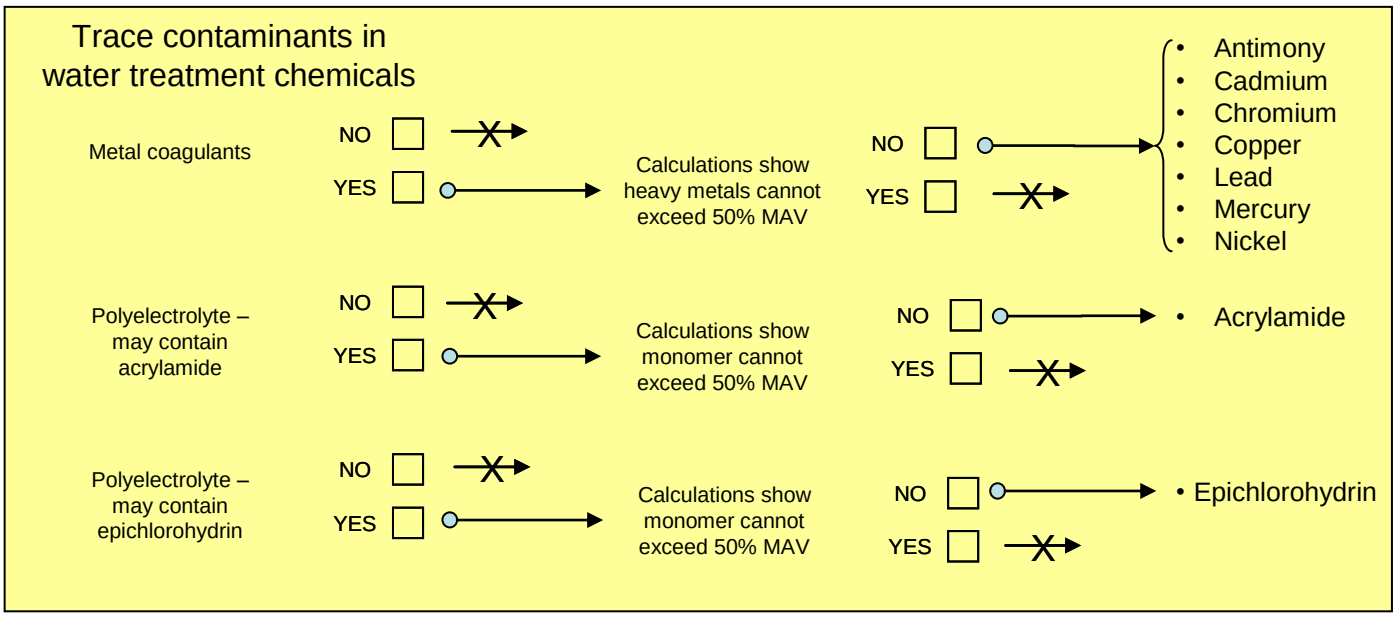
Refer to the Activities Table (Section 4.2) →

- ……
- ……
- ……
- ……
- ……
- ……
- ……
- ……
- ……
- ……
- ……
- ……
- ……
- ……
- ……
- ……
- ……
- ……
- ……
- ……

**Determinand Class**

**Determinands to include in sampling plan**



## 5 WHEN AND WHERE TO SAMPLE

(See also Section A4)

| Determinand | Sampling location | Sampling time or season | Additional notes |
|---|---|---|---|
| Heavy metals – antimony, cadmium, copper, lead, mercury, nickel | Anywhere in the reticulation or from the water leaving the treatment plant | No specific time or season, but there must be at least two months between the samples | Samples must be taken from a well-flushed tap to avoid detecting metals derived from the dissolution of plumbing fittings |
| Acrylamide, epichlorohydrin | Anywhere in the reticulation or from the water leaving the treatment plant | Anytime when the polyelectrolyte is in use, but there must be at least two months between the samples | |
| Arsenic, boron | Anywhere in the reticulation or from the water leaving the treatment plant | No specific time or season, unless the source is subject to seawater intrusion, in which case samples should be collected at about high tide. There must be at least two months between the samples | |
| Barium, fluoride, selenium | Anywhere in the reticulation or from the water leaving the treatment plant | No specific time or season, but there must be at least two months between the samples | |
| Manganese | Anywhere in the reticulation | No specific time or season, but there must be at least two months between the samples | Some variation within the reticulation is possible, so that on each sampling occasion, samples should be taken from at least **three** locations in the reticulation<br><br>If complaints about manganese are associated with high flows in the reticulation (eg, hydrant flushing), samples should be taken at these times, and at locations where complaints have arisen |
| Nitrate | Anywhere in the reticulation or from the water leaving the treatment plant | September/October. Take the second sample the following September/October | In some parts of the country, nitrate concentrations are highest when the spring thaw flushes nitrate into the groundwater |

| Determinand | Sampling location | Sampling time or season | Additional notes |
|---|---|---|---|
| Disinfection by-products (DBPs) | At the extremities of the reticulation system, that is, as far from the treatment plant as possible. Sample chlorate anywhere after the treatment plant | In autumn, after a rain event that has visibly increased the colour (organic content) of the water<br><br>Sample for chlorate just before a new container of hypochlorite is brought into use | Sufficient delay should be allowed after the rain event to allow the slug of treated water, potentially containing raised DBP concentrations, to reach the reticulation extremities. The FAC[5] residual at the extremities must be at its normal level, which in any event must not be less than 0.1 mg/L |
| Pesticides, herbicides | Anywhere in the reticulation, or from the water leaving the treatment plant | During the two seasons/periods when agrichemicals are most used in the catchment/recharge zone, with an interval of at least two months between samples. | |
| Industrial chemicals | Anywhere in the reticulation, or from the water leaving the treatment plant | No specific time, unless industry operations make the presence of the determinands more likely at some times than others. If practicable, there must be at least two months between the samples | |
| Radiological determinands | Anywhere in the reticulation, or from the water leaving the treatment plant | One sample at any time | Not required for surface water |

[5] Free available chlorine

# Appendix

## Background to Priority 2 determinand identification

## A1 INTRODUCTION

The *Drinking-Water Standards for New Zealand 2005 (Revised 2008)* (DWSNZ) lists 115 chemical determinands and three radiological determinands of health significance. Many of the chemical determinands are trace organic chemicals and analysis for them is expensive. Moreover, the presence of chemical and radiological determinands of health significance in drinking-water is influenced by factors that may vary among supplies. Consequently, requiring drinking-water suppliers to monitor all listed chemical and radiological determinands is unnecessary and expensive.

The need to avoid unnecessary monitoring is recognised by the DWSNZ and has been addressed by creating priority classes. The priority class system ensures that only determinands (microbiological, chemical and radiological) of health significance that are likely to be present in drinking-water at potentially health significant concentrations are monitored. This protects public health while conserving scarce resources.

Under the priority classification system, Priority 2 determinands only need to be monitored if it is believed they may be present in the water. This priority class may contain, microbiological, chemical and radiological determinands, although in practice it includes only chemical determinands. Between 1995 and 2004, the Ministry of Health's Priority 2 Chemical Determinands Identification Programme assessed drinking-water supplies to identify which chemical determinands needed to be assigned to them as Priority 2 determinands. For chemical compliance with the DWSNZ, a water supplier is required to monitor Priority 2 determinands assigned to their water supply.

The Health Act 1956 requires water suppliers to prepare and implement public health risk management plans (PHRMPs). Part of maintaining a satisfactory PHRMP is the continuing identification of hazards that could present a threat to the health of drinking-water consumers. This includes the identification of Priority 2 determinands. The Ministry of Health initiated the identification of Priority 2 determinands for water suppliers through the centralised programme described above. Now, water suppliers will be responsible for identifying chemicals of health concern in their own water supplies as the drinking-water sections of the Health Act 1956 come into force for their supplies.

Small and neighbourhood drinking water supplies are not required to prepare a PHRMP, although their preparation by those supplies is recommended. As a result, this protocol will only apply to those supplies if the Medical Officer of Health has required a PHRMP to be prepared for a supply under section 69ZA of the Health Act 1956. The Medical Officer of Health may require a PHRMP to be prepared if he or she has evidence of a chemical determinand being present in the water at a concentration greater than 50% of its maximum acceptable value (MAV).

This guide defines, for drinking-water suppliers and drinking-water assessors (DWA), the procedure by which Priority 2 determinands are to be identified. Part of the procedure requires a brief sampling programme focused on those determinands considered likely to enter the water supply. This document also provides guidance on identifying which determinands should be included in the sampling programme. It focuses on identifying Priority 2 determinands, not compliance monitoring subsequent to identification.

To distinguish between the collection of data for Priority 2 determinand identification and the water testing requirements for compliance once a determinand has been assigned to a supply, this guide refers to the monitoring undertaken for determinand identification as *sampling* or the *sampling programme*, and the terms *monitoring*, or *monitoring programme* refer to compliance monitoring.

When identifying Priority 2 determinands, the drinking-water supplier is concerned with chronic[6] exposure of their consumers to chemical or radiological hazards. Acute[7] exposure to hazards through accidents or natural disasters is not covered in this guide. The procedure explained here is unsuitable for monitoring acute exposure.

Section A2 sets out the overall protocol to be followed for Priority 2 determinand identification. The protocol involves water suppliers and DWAs, and includes planning, sampling data assessment and official assignation to the water supply of any Priority 2 determinands identified.

Section A3 discusses how determinands can be identified for sampling. While the water supplier may consider sampling for a broad range of determinands, this section describes a way to reduce the number of determinands being sampled.

Section A4 discusses when and where samples should be taken for sampling the determinands identified in Section 3.

[6] Chronic exposure is exposure over a long period of time, usually to low concentrations. For the purposes of setting almost all MAVs for chemical determinands, the exposure period is assumed to be a lifetime of 70 years.

[7] For the purposes of the handbook, acute exposure is exposure for a short period, usually to high concentrations.

## A2 IDENTIFYING PRIORITY 2 DETERMINANDS AND MAKING ASSIGNATIONS

To assign a Priority 2 determinand to a drinking-water supply, evidence is needed that the determinand sometimes exceeds 50% of its MAV. This evidence is obtained from a brief (two samples only) sampling programme. To avoid the sampling programme having to encompass all the determinands listed in the DWSNZ, a simplified assessment of the risk factors that may lead to the presence of health-significant determinands in the water supply is used to focus on the determinands of primary concern.

Section 4 summarises the six steps from the start of the process when the water supplier designs their sampling programme to the assignment of Priority 2 determinands to the supply. These steps are discussed in more detail next.

Step 1 The water supplier prepares a sampling programme

The programme has to state which determinands will be tested for and when and where samples will be taken. The water supplier can identify which determinands need to be included in the programme using their knowledge of their catchment or recharge zone[8] and the tools provided in the guide. The Ministry of Health-recognised laboratory the water supplier will use for the analyses must also be identified.

Evidence from past national surveillance of drinking-water quality indicates that some determinands are unlikely to be detectable in New Zealand drinking waters at health-significant concentrations. The decision guides (Section 4.1) and the check-sheet (Section 4.4) which is based on the guides, focus on the determinands or groups of determinands that past experience has shown are more likely to arise.

The check-sheet is intended as a guide for water suppliers, keeping them focused on the determinands of possible concern. It ensures that the reasons for selecting these determinands for sampling, or not selecting them, are recorded. This helps both the water supplier and the DWA when the DWA reviews the sampling programme.

The water supplier may seek assistance from their Drinking-Water Assistance Programme facilitator in preparing their sampling programme.

Step 2 The DWA reviews and approves the water supplier's proposed sampling programme.

Priority 2 determinand identification is part of the hazard identification water suppliers need to undertake when preparing or reviewing their PHRMPs. Thus, the frequency of identifying Priority 2 determinands for a water supply is determined by the frequency at which the water supplier chooses to review the PHRMP (which is no less frequently than five yearly).

The water supplier's proposed sampling programme for identifying Priority 2 determinands is reviewed by the DWA, before the sampling programme is implemented.

[8] The area overlying an aquifer through which the water passes to the aquifer.

In reviewing the sampling programme, the DWA needs to consider the adequacy of its three main components – when and where samples will be taken, and what determinands will be tested for in the samples.

To adequately assess the water supplier's selection of determinands to be included in the sampling programme, the DWA needs to be familiar with the water supply and the risk factors within it that may lead to contamination, and to have received the check-sheet completed by the water supplier. The logic the water supplier has used for the selection will be evident from the check-sheet, and the DWA can check this against their own knowledge of the water supply.

The DWA may seek ESR's opinion regarding their assessment of the programme *if there is some aspect of the supply that makes designing the sampling programme difficult.*

Step 3 The water supplier undertakes the sampling and provides the DWA with the results.

The water supplier carries out the sampling, ensuring that their approved sampling programme is followed. Once both results for each determinand are available (a minimum of two samples per determinand is required), the water supplier provides the DWA with the results within 10 working days of receiving the last result for the suite of determinands.

Step 4 The DWA reviews the results and identifies the Priority 2 determinands.

The DWA examines the analytical results, and identifies any determinand for which *either* result exceeds 50% of its MAV. These determinands will be assigned to the drinking-water supply as Priority 2 determinands, unless the water supplier can provide a good reason why they should not be assigned (see Step 5). The DWA may wish to confer with ESR *if there is a difficulty evaluating the information provided by the water supplier*.

Step 5 The DWA notifies the water supplier of the intended Priority 2 determinand assignations.

The DWA notifies the water supplier of the intended Priority 2 determinand assignations within 15 working days of receiving the results and gives the water supplier 10 working days to respond. This should be a formality as the water supplier will already be aware of the test results.

Official Priority 2 determinand assignations are only made to water supply zones serving more than 500 people[9].

Step 6 The water supplier responds to the proposed assignations.

Should the water supplier consider that there is good reason why any of the intended assignations should not be made official, they need to support their case with information showing why the test result, which was greater than

[9] Water suppliers responsible for water supplies serving 500 or fewer people may wish to monitor the concentrations of determinands that have been shown to exceed 50% of their MAV for their own purposes, but there is no official Priority 2 assignation and monitoring is not mandatory.

50% of the MAV, was atypical of the water quality and very unlikely to occur again.

Step 7 The DWA makes the assignations official.

The DWA reaches a final decision regarding the Priority 2 determinand assignations for the supply. Should the water supplier, as part of Step 6, disagree with the intended assignation, and agreement between the water supplier and the DWA cannot be reached, the Ministry of Health will adjudicate and resolve the situation.

Once the final assignations are decided, this information is provided to ESR for recording in the national database, Water Information New Zealand.

Step 8 The water supplier revises their PHRMP and implements Priority 2 determinand compliance monitoring.

The water supplier includes the newly assigned Priority 2 determinands, and the need to undertake compliance monitoring, in their revised PHRMP. Once the revised PHRMP is approved by a DWA and implemented, compliance monitoring for the assigned Priority 2 determinands can begin immediately, but *must* begin no later than the start of the next financial year after the revised PHRMP is implemented.

## A3 WHICH DETERMINANDS TO ASSESS

### A3.1 Introduction

Where possible, the protocol for Priority 2 determinand identification uses a risk-based approach to identify which determinands to include in the sampling programme. The protocol uses existing knowledge about supply characteristics and the likely presence of determinands in a water supply to ensure sampling focuses only on those determinands that may be a concern. The water supplier may add to this minimum list.

This section helps drinking-water suppliers and DWAs decide which determinands should be assessed.

Chemical and radiological determinands can be divided into two groups:

a) those that *have to be* assessed each time the Priority 2 assignations to the supply are reviewed

b) those that *may need to be* assessed depending on the likelihood of their presence in the water.

### A3.2 Determinands that *have to* be assessed when Priority 2 determinands are being identified

The determinands contained in this group are:

- arsenic
- barium
- manganese
- selenium.

They must be included in a sampling programme once every five years. As a result, if a water supplier reviews their PHRMP more frequently, they may choose not to include them in their sampling programme with every review, or they may choose to include only some from the list.

Determinands fall into this category for one, or more, of several reasons.

a) Changes in their concentrations may occur slowly.

   For these determinands it is difficult to tell whether previously low concentrations will remain so, or reach a level of health significance. Determinands with concentrations that depend on the slow weathering of rocks and minerals may be in this class.

b) Slight differences in environmental conditions can cause large variations in their concentrations.

   Risk factors may indicate the likelihood of these determinands being present in a water, but cannot reliably indicate whether their concentrations will exceed 50% of their MAV – an example is manganese.

c) The risk factors that lead to the presence of the determinand in water are poorly understood.

For example, the likelihood of finding unacceptably high concentrations of arsenic in a water source is generally greater in geothermal regions than non-geothermal regions. However, some groundwater sources well removed from geothermal activity contain elevated arsenic concentrations. Barium is another determinand for which the factors influencing its presence in New Zealand water supplies are unknown.

The factors leading to the occurrence of naturally-occurring fluoride are unknown. However, because there are very few water supplies containing naturally-occurring fluoride that exceeds 50% of its MAV, fluoride is not included in this group of determinands. Sampling for it is recommended.

### A3.3 Determinands that *may need* to be assessed

As part of PHRMP development, drinking-water suppliers should gather information about possible contaminant sources in the catchments or recharge zones of their source waters, treatment chemicals and reticulation networks. In relation to catchments and recharge zones, both historical and existing contaminant sources should be considered. The more detailed the information collected, the more specific monitoring and analytical requirements can be, which will minimise monitoring costs.

The determinands discussed in this section are included in the sampling programme on the basis of risk factors, which help in identifying situations in which their presence in the water is unlikely and sampling unnecessary. The determinands in this category are:

- boron (naturally-occurring)
- heavy metals (naturally-occurring)
- disinfection by-products (DBP)
- water treatment chemical contaminants
- determinands arising from human activities in the catchment or recharge zone.

Decision guides (Section 4.1) are provided for each of these determinands or determinand groups to help the water supplier decide whether they should be included in the sampling programme. There is a broad spectrum of determinands that could be included within the last group of determinands. To help the water supplier identify when determinands should be monitored within this group, the guide contains an activities table (Section Y), which identifies determinands to include, based on the activities that might lead to their presence in drinking-water.

As noted under Step 1 in Section A2, past surveillance programmes have found that some determinands listed in the DWSNZ are not detected in New Zealand's drinking waters at concentrations greater than 50% of their MAV. The tools provided in the guide for selecting determinands for sampling do not focus on these determinands. However, some are included in the activities table either explicitly (eg, cyanide), or implicitly in the multi-determinand analytical methods used for detecting pesticides and industrial chemicals. Thus, although there is no evidence for them being a concern to date, the periodic reassessment of Priority 2 determinands may detect them should their concentrations increase in future.

Cyanobacterial toxins are not included in any of the decision guides or the activities table because their concentrations can change so rapidly that testing for them infrequently, as is done in identifying most Priority 2 determinands, is of no value. High frequency sampling is needed when they are likely to be present in association with algal bloom development. See Section 7 of the DWSNZ for advice on managing cyanobacteria and cyanotoxins.

### A3.3.1 Boron (naturally-occurring)

Since the 1995 edition of the DWSNZ, the MAV for boron has been raised from 0.3 mg/L to 1.4 mg/L. As a result, the number of water supplies in which the boron concentration exceeds 50% of its MAV has markedly decreased.

The boron decision guide considers three possible features of a water supply that may signal raised boron concentrations:

a) "soda" springs, which contain high concentrations of sodium bicarbonate/carbonate, also tend to contain raised boron concentrations

b) waters in geothermal areas can contain raised boron concentrations (as well as raised arsenic concentrations)

c) seawater contains boron (at approximately 4.5 mg/L), so seawater intrusion into groundwaters (or surface waters if the source is near a river mouth) can raise boron concentrations in the water supply, although it is unlikely that seawater intrusion alone would result in a MAV exceedance because the salinity of the water would render it unpalatable.

### A3.3.2 Heavy metals (naturally-occurring)

For this the guide, the suite of "heavy metals" includes antimony, cadmium copper, lead and nickel. Although mercury is a heavy metal, for reasons of practicality it is considered as separate from this suite.

The corrosion of plumbing fittings is the main source of metals in New Zealand's drinking-water. Very few water supplies contain heavy metals in their source water and even then, the concentrations are very low. Sampling for the heavy metal suite is only recommended in the decision guide if sources of heavy metal may exist in the catchment or recharge zone. Mineral deposits or mining activities are taken as evidence of possible natural sources of heavy metals.

Mercury deposits are found in a handful of locations in New Zealand. Mercury at concentrations of potential health concern has been found in very few samples. Sample containers and preservation for mercury are different from those for the other heavy metals. Consequently, it is separated from the others in the decision guide to avoid unnecessary analytical costs.

### A3.3.3 Disinfection by-products

Members of several families of compounds can form when disinfectants react with naturally-occurring substances (often substances derived from rotting vegetation) in water. The nature of the disinfectant determines what types of by-product form, as does the concentration of bromide in the water. Higher concentrations of bromide increase the likelihood of the formation of DBPs containing bromine.

The decision guide's first step is to identify the disinfectant in use, which leads to the identification of the determinands most likely to be formed by the disinfectant. In the case of ozone, reaction with organic matter can form formaldehyde. Bromate and bromoform can form when the water contains bromide. If bromide concentration data for the water are unavailable, the presence of bromide should be assumed. For chlorination, a screen for trihalomethanes, haloacetic acids and haloacetonitriles is needed. If the water supplier is certain that the maximum total organic carbon (TOC) concentration in the water is less than 1 mg/L, then DBP formation is unlikely to reach levels of potential health concern (50% MAV).

Chlorate arising from hypochlorite use is classified as a DBP, but it is not formed by the same types of reaction that form the trihalomethanes and haloacetic acids. As a result, the use of hypochlorites, rather than gas chlorine, is the primary indicator of whether testing for chlorate is necessary. The TOC concentration of the water is irrelevant with respect to chlorate formation.

### A3.3.4 Determinands introduced with water treatment chemicals

The decision guide provided for DBPs that may be formed during treatment also covers chlorate that is introduced into the water in hypochlorite disinfectant.

Other determinands that are potential trace contaminants in treatment chemicals may also be introduced into the water. These include acrylamide and epichlorohydrin, which are monomers of polyelectrolytes, and heavy metals, which may be present in trace quantities in metal-based coagulants.

These determinands do not need to be included in the identification sampling programme if the treatment chemicals are not used, or if calculations show the final concentration in the water to be less than 50% of the MAV. The concentration in the finished water can be calculated as follows:

$$\left[\frac{\text{Percentage of contaminant in treatment chemical}}{100}\right] \times \left[\text{Contaminant concentration of treatment chemical in dosing solution (weight/volume)}\right] \times \left[\frac{\text{Dose rate of dosing solution (volume/time)}}{\text{Flow rate of water through the treatment plant (volume/time)}}\right] = \text{Contaminant concentration in finished water (weight/volume)}$$

### A3.3.5 Chemical determinands arising from human activity

The decision guide for chemical determinands arising from human activity asks if there are "… sources of possible chemical contamination …" in either the catchment or recharge zone. The word "possible" is included to allow for steps to have been taken to ensure that a potential source of contaminants is unlikely to affect the water supply's source water. For example, a chemical storage facility may be located on an impermeable pad and surrounded by a bund. Provided such steps can be identified, this helps to avoid unnecessary testing.

Once the decision guide for determinands arising from human activity has been used to determine whether a possible source of pollution could contaminate the water, the activities table is used to identify the chemical determinands to be tested for.

The chemical determinands likely to arise from human activity will depend on the nature of the activity. The activities table lists a group of land uses and the activities associated with each land use. For each activity, chemical determinands considered health significant are listed. Should chemicals be in use in an activity that could contaminate

the water and the chemicals have not been identified in the table and/or do not have a MAV, the water supplier and DWA should seek advice about the need to test for the chemical.

*Historical information*

The Priority 2 Chemical Determinands Identification Programme detected agrichemicals or industrial chemicals in very few samples. When concentrations of these classes of compound exceeded 50% of their MAV, it was due to unusual circumstances. However, greater use of agrichemicals or more industrial development and their associated waste streams could increase the likelihood of agrichemicals or industrial chemicals being present in the water. Consequently, checks for them, if they are potential contaminants, would be prudent unless they fall outside the selection criteria used in the decision guide.

*Analyses required*

In the activities table, some determinands are specifically identified. However, sometimes specific determinands cannot be identified and a generic group of determinands, such as pesticides, is listed. The analytical packages that the water supplier should request for determinand groups are listed in Section 5.3 of the guide.

At the time of preparing the guide, hydrocarbon recovery from geological formations using hydraulic fracturing (fracking) was being used in only one region in New Zealand (Taranaki). Use of fracking may increase in the future. Should this type of operation be encountered, the list of determinands covered by fuel storage in the activities table, and arsenic, is the minimum suite of determinands that should be included in a sampling programme. The company carrying out the operation should be approached to determine other potential contaminants.

The DWSNZ contain MAVs for nitrate and nitrite. Nitrite is an intermediate formed during the conversion of ammonia and nitrate, and under the oxidising conditions usually present in a water supply (due to water chlorination, if nothing else[10]) nitrite is rapidly converted to nitrate. Although nitrite could be formed during some of the activities listed in the activities table, it is not listed in the determinands to include in the sampling programme. Analysis for nitrate should be sufficient for a water supply, unless the nitrate concentration is well in excess of the MAV, or there is a high ammonia concentration in the water. In either case, an analysis for nitrite should also be undertaken.

### A3.4 Miscellaneous determinands

While the decision guides and activities table attempt to identify the main sources of chemical determinands, some contaminant sources may have been overlooked. Water suppliers should make a mental check of their supplies, from source through treatment to reticulation to identify contaminant sources and the nature of the determinands they may release into the water.

### A3.5 Previous Priority 2 assignations

Where a Priority 2 determinand has previously been assigned to a drinking-water supply, but has been reclassified as a Priority 3 or Priority 4 determinand, the water supplier

[10] In the presence of sufficient chlorine, the primary product of the reaction between ammonia and chlorine is nitrogen gas, although some nitrate is formed as a by-product. In the absence of chlorine, the oxidation of ammonia to nitrate is achieved by microbes. The rate of this reaction will depend on the conditions, but may be slow.

should include this determinand in their sampling programme, except when the reclassification resulted from a major change in the supply. Usually, such changes would be the use of a different source or a substantial modification to the treatment train. In these instances, there is no reason to believe that the original Priority 2 determinands still apply to the supply.

If a determinand is an existing Priority 2 determinand and monthly compliance monitoring is in progress, data from this monitoring will show whether the determinand needs to remain as a Priority 2 determinand. Consequently, determinands already being monitored for compliance purposes do not need to be included in sampling for Priority 2 determinand identification.

Fluoride must be included as a Priority 2 determinand in fluoridated supplies and consequently must be monitored for compliance purposes. It is assigned to a supply as a Priority 2 determinand without the need for inclusion in the Priority 2 determinand identification process.

### A3.6 Radiological determinands

Radiological determinands are only assigned to groundwaters that are not under the influence of surface waters. Guidance cannot be given for determining which of these groundwaters are more likely to contain radiological determinands. For this reason, every 10 years, samples should be taken from groundwaters not under the influence of surface waters, and analysed for all three radiological determinands (total alpha activity, total beta activity and radon). Potassium *may* also need to be determined in the water, if the MAV for beta emitters is exceeded, to assess whether potassium-40 is contributing to the total beta activity[11].

[11] The MAV for total beta activity excludes the contribution from potassium-40.

## A4 SAMPLING BACKGROUND INFORMATION

### A4.1 Introduction

Continuous monitoring of a determinand in a water supply is not possible for most chemicals. To understand the potential risk to health created by a determinand, the water supplier and DWA rely on discrete sample collection. The more frequently samples can be taken, the better our understanding of the range over which the chemical concentration may vary. A single sample provides information about the chemical's concentration at one point in time. It tells nothing about the variability of the chemical's concentration.

Assigning chemical determinands as Priority 2 determinands to a supply allows resources to be focused on these (Priority 2) determinands. As a result, once a determinand has been assigned as a Priority 2 determinand, more frequent monitoring (monthly, or weekly, in the cases of fluoride and chlorine) than the sampling used to identify the Priority 2 determinand is required for compliance purposes. More frequent monitoring yields a clearer picture of the determinand's threat to health. This sampling frequency is not required during the process of identifying Priority 2 determinands. Only two samples are required for Priority 2 determinand identification.

The difficulty with collecting only two samples for Priority 2 determinand identification is that a reliable indication of the determinand's concentration range cannot necessarily be obtained. To compensate for this shortcoming, the samples need to be taken at a time and place during which the determinand's concentration, if variable, is likely to be at its highest.

This section provides guidance on selecting sampling times and locations when monitoring for Priority 2 determinand identification. Section 6 of the guide contains a summary of the sampling times and locations for specific determinands or determinand groups.

### A4.2 When to sample

The question of when to sample becomes important if a determinand's concentration is likely to change. The concentration of a determinand may change for different reasons and on different timescales. These reasons include:

a) season (periodic, but relatively long timescale)

b) weather conditions (random, possibly short timescale)

c) factors related to human activities that affect the determinand's concentration, for example, a daily industrial or farming activity that releases contaminants into a water source, (periodic, short timescale).

Although two samples need to be collected for each determinand being sampled, this does not mean that all determinands have to be sampled at the same time. Factors affecting the times when determinands are at their highest concentration can be different for the different determinands, and different sampling times may be required to accommodate this.

The summary table in Section 4 states that the timing of sampling for some determinands is not critical, but for these determinands, at least two months between samples must be allowed, in case there is unexpected variability in concentration.

A4.2.1 Determinands unlikely to show substantial temporal variability

The concentrations of determinands that are released into water by slow natural processes (usually geological in nature) may change slowly. While their concentrations need to be determined to check for long-term trends, the selection of a sampling time over the course of one years' assessment is not critical, so that samples for these determinands can be taken at any time.

A4.2.2 Determinands with random temporal variability

Determinands that show temporal variability fall into two groups. For some determinands we do not know why their concentration changes. Guidance on when to sample for these determinands cannot be given, because the times when their concentrations will be greatest are unpredictable. Samples for these determinands can be taken at any time that is convenient.

The second group contains determinands with concentrations that do not change predictably, but for which we can identify at least one factor that increases their concentrations. Determinands with concentration increases linked to rain events, such as DBPs, are an example of determinands in this group. Temperature is another factor overlying the effect of rain events on DBP formation. As a result, maximum concentrations of DBPs are expected during rain events in late summer or autumn.

When chlorate is to be sampled because of hypochlorite use, season and rain events do not need to be considered. For this determinand, the age of the hypochlorite solution used to treat the water is important – the older the solution the higher chlorate concentration. Samples should be taken when an old container of hypochlorite is about to be replaced.

A4.2.3 Determinands likely to show periodic variability

Determinands with seasonally influenced concentrations fall into this group. In some instances the seasonal influence is clearly linked to natural processes, for example, the increase in groundwater nitrate concentrations with the spring thaw. Other determinands, such as agrichemicals, appear to change in concentration in association with human activity, although natural cycles are the underlying cause of the human activity.

## A4.3 Where to sample

Knowing how, or if, determinand concentrations may change as they move through the water supply from the source to the consumer is necessary for selecting sampling locations.

A4.3.1 Determinands expected to be removed by treatment

Some determinands of health significance may be present in the source water, but the treatment processes are designed to remove them. Although they are not expected in the treated water, samples for these determinands should be taken after treatment to check that the removal is satisfactory.

Temporary treatment failure could result in the passage of these determinands into the reticulated water. Such a situation is more akin to a chemical spillage, that is, it is short-term, and Priority 2 determinand assignations are not made on this basis. It should be investigated as if it were a spillage, through more frequent sampling until the problem is resolved. The water supplier's PHRMP should cover the protocol for dealing with treatment failures.

A4.3.2 Determinands with concentrations that are unlikely to change through the reticulation network

Samples for determinands that are unlikely to change in concentration once the water has left the treatment plant can be taken at any location following treatment. This is the case whether or not their concentrations have been reduced by treatment.

A4.3.3 Determinands with concentrations that may change through the reticulation network

The most commonly occurring determinands to change in concentration through the reticulation network are DBPs. Concentrations of DBPs tend to increase with time after the disinfectant is added to the water. This means that, in general, their concentration will increase with distance from the treatment plant. Consequently, samples for DBPs should be taken at the extremities of the reticulation network. The exception is chlorate that is introduced into the water with hypochlorite solution and will not change in concentration once the water leaves the treatment plant.

Manganese is another common determinand that may vary in concentration through the reticulation network. Variations in the concentration of manganese may result from its deposition in low flow parts of the network. As a result, samples should be collected at random locations, unless there are specific parts of the system where manganese concentrations are known to increase sometimes.