



Priority 2 and Priority 3 Chemical Determinands Identification Guide



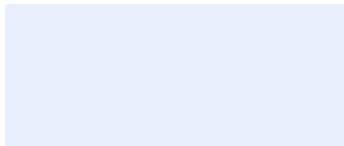
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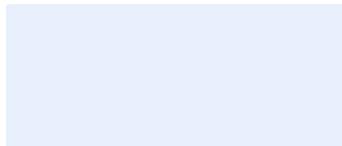
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EXECUTIVE SUMMARY

To demonstrate chemical compliance with the *Drinking-Water Standards for New Zealand (DWSNZ)*, water suppliers are required to monitor determinands present in their supplies at concentrations exceeding 50% of their maximum acceptable value (MAV). These are termed Priority 2 determinands. Drinking-water suppliers are now responsible for identifying these determinands. Priority 3 determinands are determinands present at concentrations less than or equal to their MAV. Water suppliers should also undertake monitoring to check that these determinands do not need to be reclassified as Priority 2.

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 water safety plan (WSP). Consequently, identifying Priority 2 and Priority 3 determinands links to the review cycle of a water supply's WSP.

This guide for drinking-water suppliers and drinking-water assessors (DWA), defines how the procedure for the identification of Priority 2 and Priority 3 determinands fits into the WSP review cycle and the way these determinands can 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 help water suppliers and DWAs in the identification of Priority 2 and Priority 3 determinands (except cyanotoxins¹) 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 and Priority 3 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.

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1. INTRODUCTION

[The Health Act 1956, s69Z, requires water suppliers supplying water from minor, medium or large water supplies to prepare and implement water safety plans². Water safety plans have to identify the public health risks (if any) associated a water supply (s69Z(2)(a)(i)). These risks may arise from microbiological, chemical or radiological hazards. This guide is concerned with the management of chemical hazards.

The *Drinking-Water Standards for New Zealand 2005 (Revised 2008)* (DWSNZ) is one of the tools by which the public health risk associated with water supplies is managed. The DWSNZ identifies four possible priority classes. However, only microbiological hazards can be classed as Priority 1 determinands, leaving Priorities 2 to 4 for the classification of chemical determinands. Priority 4 includes determinands known not to be likely to occur in a water supply, consequently water safety plans should focus on Priority 2 and 3 chemical determinands.

Two key parts of managing the chemical risk to a water supply are identification of the health-significant determinands in the water, and determination of their concentration to allow their classification as Priority 2 or Priority 3. This guide sets out a protocol for both these things.

The guide aims to help drinking-water suppliers and drinking-water assessors (DWAs) with the identification of Priority 2 and 3 determinands using a qualitative assessment of which determinands are likely to be present in a water supply.

Generally, Priority 3 determinands do not have to be sampled to show compliance with the DWSNZ. However, there are situations in which sampling for them is a necessary part of good public health risk management. The guide provides **recommendations** for monitoring Priority 3 determinands, because no requirements for sampling Priority 3 determinands are contained in the DWSNZ.

The guide is not concerned with the compliance monitoring required for Priority 2 determinands. This is separate from the protocol set out here. The requirements are contained in the DWSNZ.

Priority 2 determinands are only officially assigned to supplies serving more than 500 people. However, if the water supplier wishes, Priority 2 determinand assignments may be made to smaller supplies.

[Notes:

- *Sampling of determinands that have been classified as Priority 2 or Priority 3 determinands is referred to as “monitoring” in this guide. The collection of samples for the purpose of identifying Priority 2 and 3 determinands is termed “sampling”.]*
- *For brevity, the process by which health-significant determinands are identified as Priority 2 or Priority 3 determinands is referred to in this guide as ‘determinand identification’.]*

² Small and neighbourhood drinking water supplies are not required to prepare a water safety plan, 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 water safety plan to be prepared for a supply under section 69ZA of the Health Act 1956. The Medical Officer of Health may require a water safety plan 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).

1.1 THE GUIDE'S CONTENT

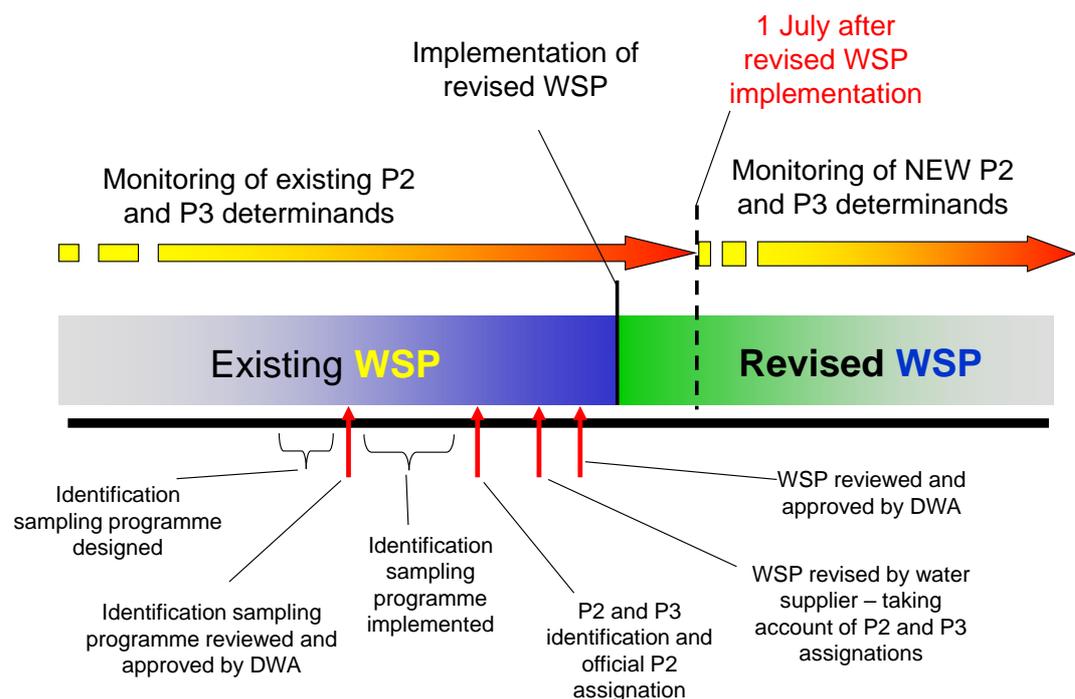
The guide is a quick reference for Priority 2 and Priority 3 determinand identification. Further detail is contained in the appendix. The guide contains the following sections:

- Priority 2 and 3 determinand identification and the water safety plan review cycle
- identification process overview
- what to sample for
- when and where to sample.
- monitoring Priority 3 determinands.

2. CO-ORDINATION WITH THE WATER SAFETY PLAN REVIEW CYCLE

Error! Reference source not found. shows how preparing a water supplier's sampling programme for identifying Priority 2 and 3 determinands, implementing the programme and monitoring the resulting Priority 2 determinands for compliance with the DWSNZ fit with the water safety plan review process. Section **Error! Reference source not found.** explains the steps identified in **Error! Reference source not found.**

FIGURE 1: Timeline depicting the way determinand identification fits within the water safety plan (WSP) review cycle



There are several notable features of **Error! Reference source not found.**

- The sampling programme for determinand identification is prepared as part of the revision of a water supply's water safety plan, and will occur at least every five years.
- Once the sampling programme is prepared and approved, it is implemented and may take up to 12 months to complete.
- A DWA assesses the sampling results when they are available and assigns Priority 2 determinands to the water supply as appropriate. The DWA will also say whether monitoring of any Priority 3 determinands should be undertaken to check that they are unlikely to reappear in the supply at potentially health significant concentrations.
- Once assigned to the water supply, the need to undertake compliance monitoring for Priority 2 determinands is included in the revised water safety plan that is

approved by a DWA. Any monitoring of Priority 3 determinands is also included in the revised water safety plan.

- e. Compliance monitoring of the Priority 2 determinands and monitoring of Priority 3 determinands contained in the water safety plan may begin at any time, but no later than the start of the next financial year after the revised water safety plan is implemented. This is to help the drinking-water supplier budget for monitoring costs.

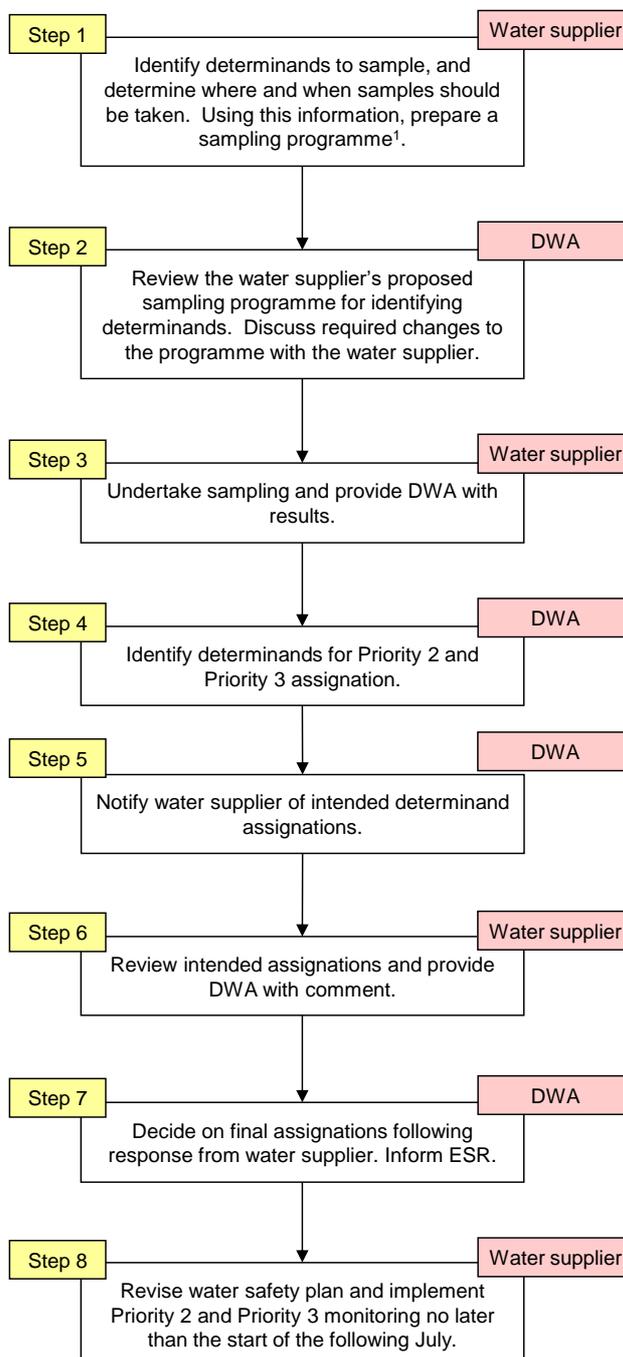
The same process for identifying determinands is followed when a water safety plan is first prepared for a supply. The water safety plan submitted to a DWA for approval must include the Priority 2 determinands that have been officially assigned to the supply and Priority 3 determinands identified for monitoring.

3. DETERMINAND IDENTIFICATION PROCESS OVERVIEW

3.1 STEPS AND RESPONSIBILITIES

Error! Reference source not found. shows the steps involved in the identification of potential chemical hazards in drinking water supplies and their priority class assignment. Water suppliers and DWAs are involved in this process. The pink box at each step shows which of these groups is responsible for the step.

Figure 2: Steps for determinand identification and assignation



Detail of the 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 (see Section 4.4)
 - 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. 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 uses **Error! Reference source not found.** to identify which determinands they propose be classed as Priority 2 and 3. The sampling frequency for Priority 3 determinand monitoring is also determined. Priority 3 monitoring is for risk management purposes not compliance.
- Step 5. Within 15 working days of receiving the sampling results, the DWA notifies the water supplier of the outcome of their review and which determinands identified in Step 4 they propose be assigned to the supply as Priority 2 and 3 determinands.
- Step 6. Within 10 working days, the water supplier responds, with supporting information³, if they disagree with the proposed Priority 2 and 3 designations.
- Step 7. The DWA finalises the determinand assignments for the supply and informs the water supplier and ESR.
- Step 8. The water supplier revises their water safety plan and implements compliance monitoring Priority 2 determinands and monitoring of Priority 3 determinands no later than the start of the following financial year⁴.

³ 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 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.

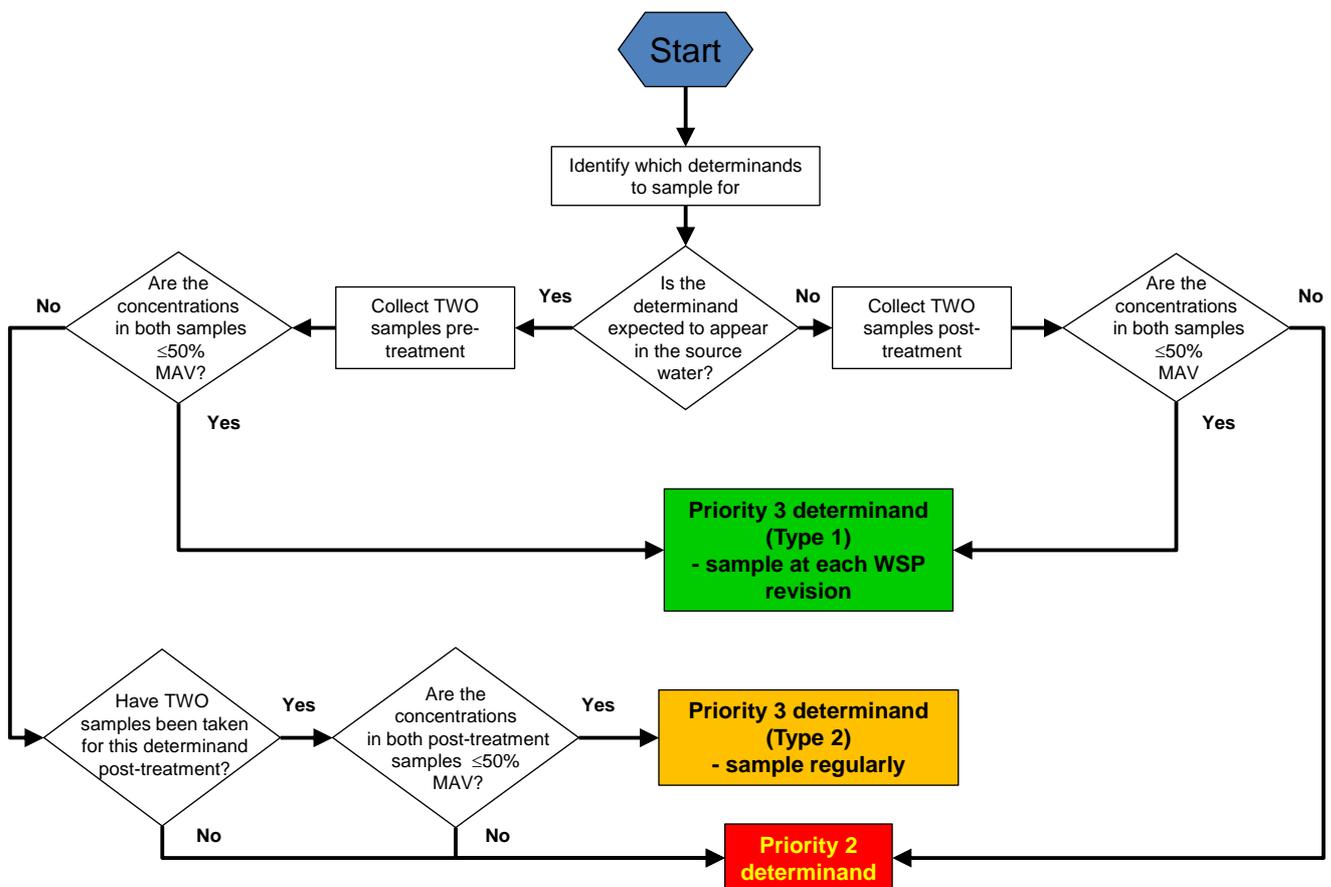
3.2 ASSIGNING PRIORITY CLASSES FROM SAMPLING RESULTS

Sections **Error! Reference source not found.** and 5 describe how to determine which determinands need to be included in the sampling programme, and when and where they are to be taken.

Figure 3 sets out the procedure for making priority assignments based on the sampling results

Figure 3: Use of sampling results from the identification programme to make priority assignments.

Refer to Section 0 for the sampling frequencies of Priority 3 determinand monitoring



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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. Determinand 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 should 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.

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

- Boron (naturally-occurring) (see also Section A3.3)
- Heavy metals (naturally-occurring) (see also Section A3.3)
- Disinfection by-products (see also Section A3.3)
- Water treatment chemical contaminants (see also Section A3.3)

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)

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 determinand identification. Compliance data will show whether they need to remain as a Priority 2 determinand.

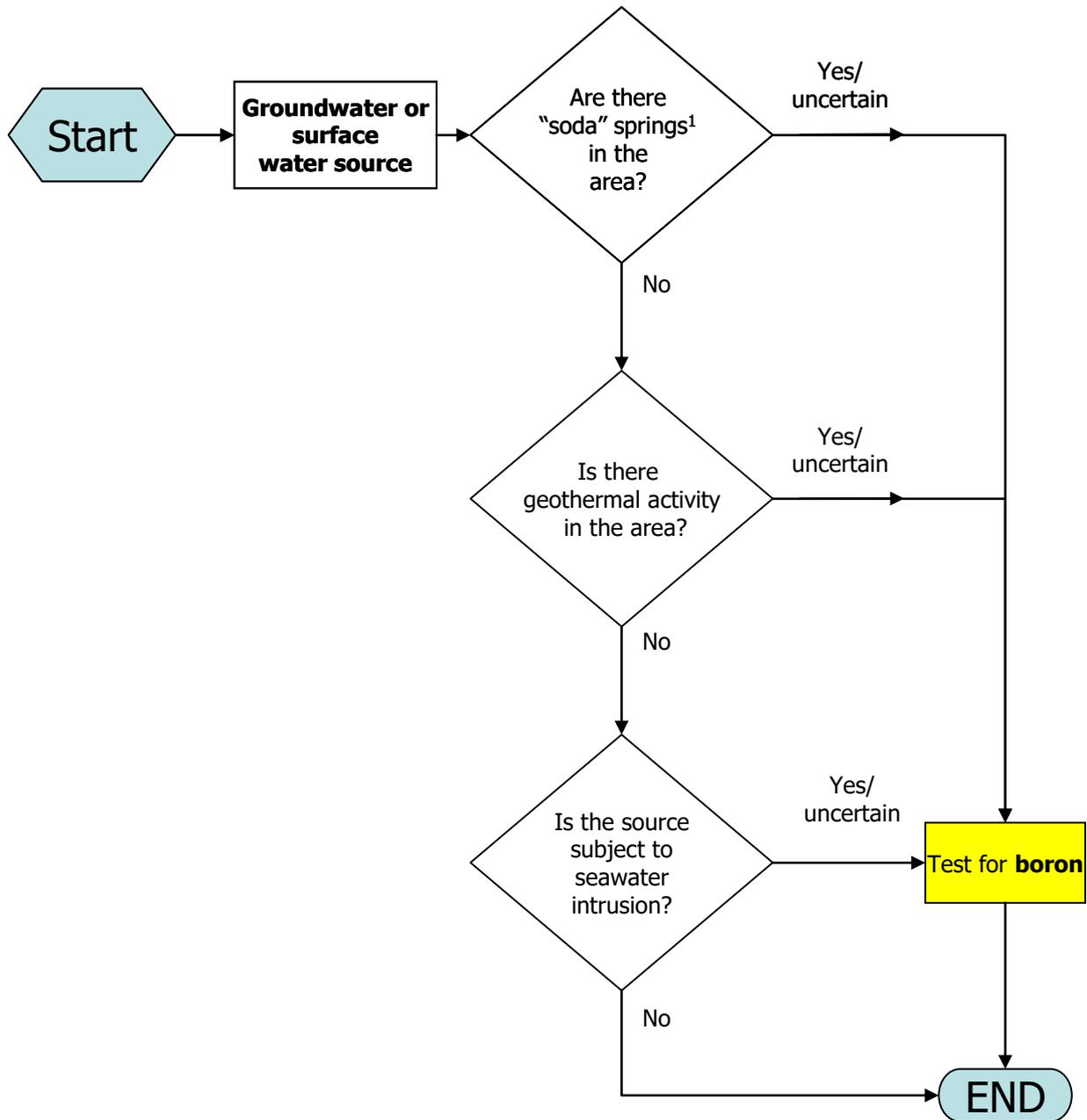
Radiological determinands (see also Section A3.6) need only be sampled once every 10 years, and this only needs to be done for groundwaters not under the influence of surface water. A single sample only is required on each occasion. The radiological determinands to test for are:

- 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

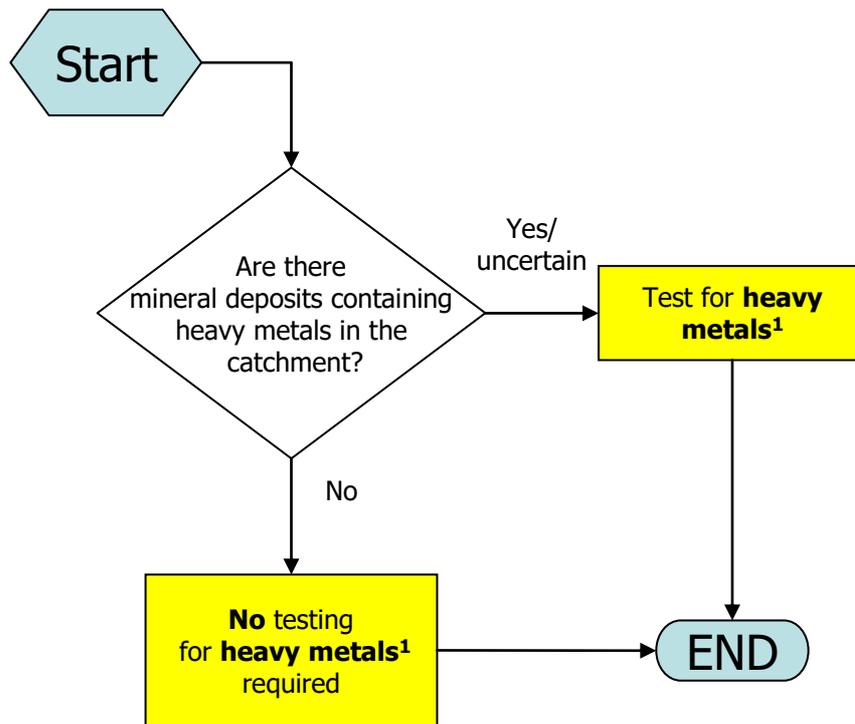
Decision Guide - Boron (naturally-occurring)



Note: 1 Springs high in sodium and bicarbonate/carbonate

Decision Guide – Heavy metals (naturally-occurring)

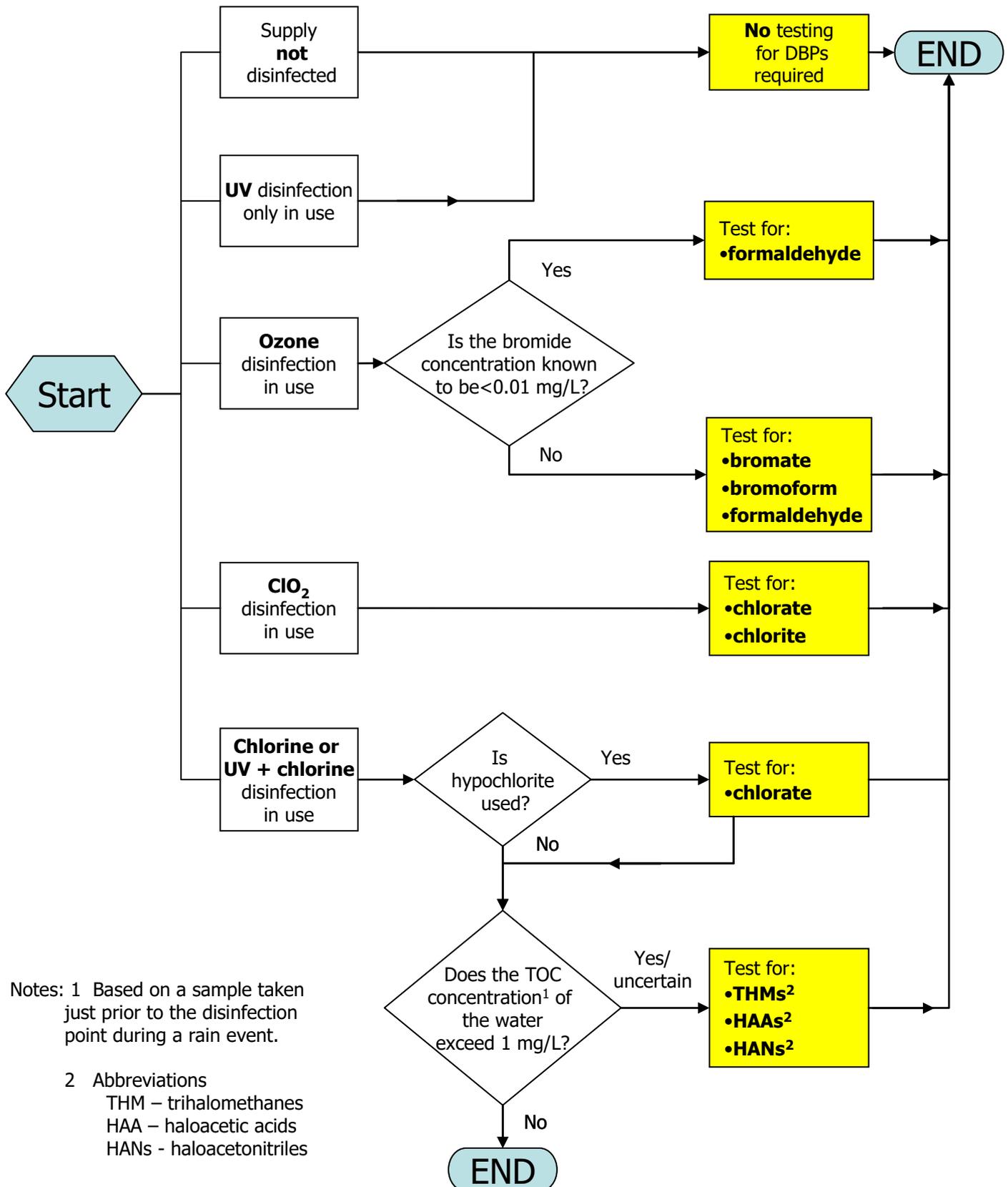
This guide is not for heavy metals arising from plumbosolvent waters, or for heavy metals arising from industrial operations.



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

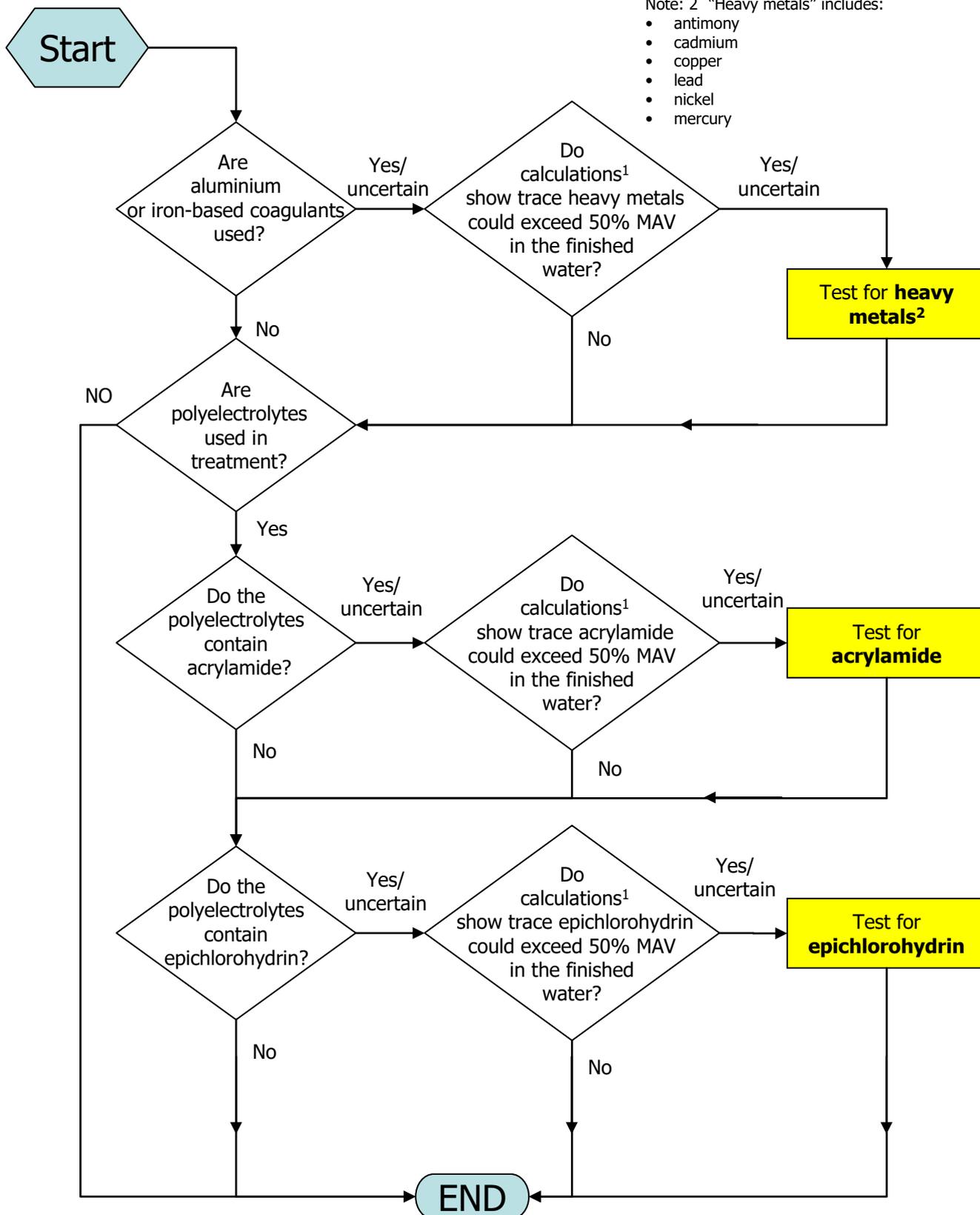
THM – trihalomethanes
 HAA – haloacetic acids
 HANs - haloacetonitriles

Decision Guide – Contaminants in treatment chemicals

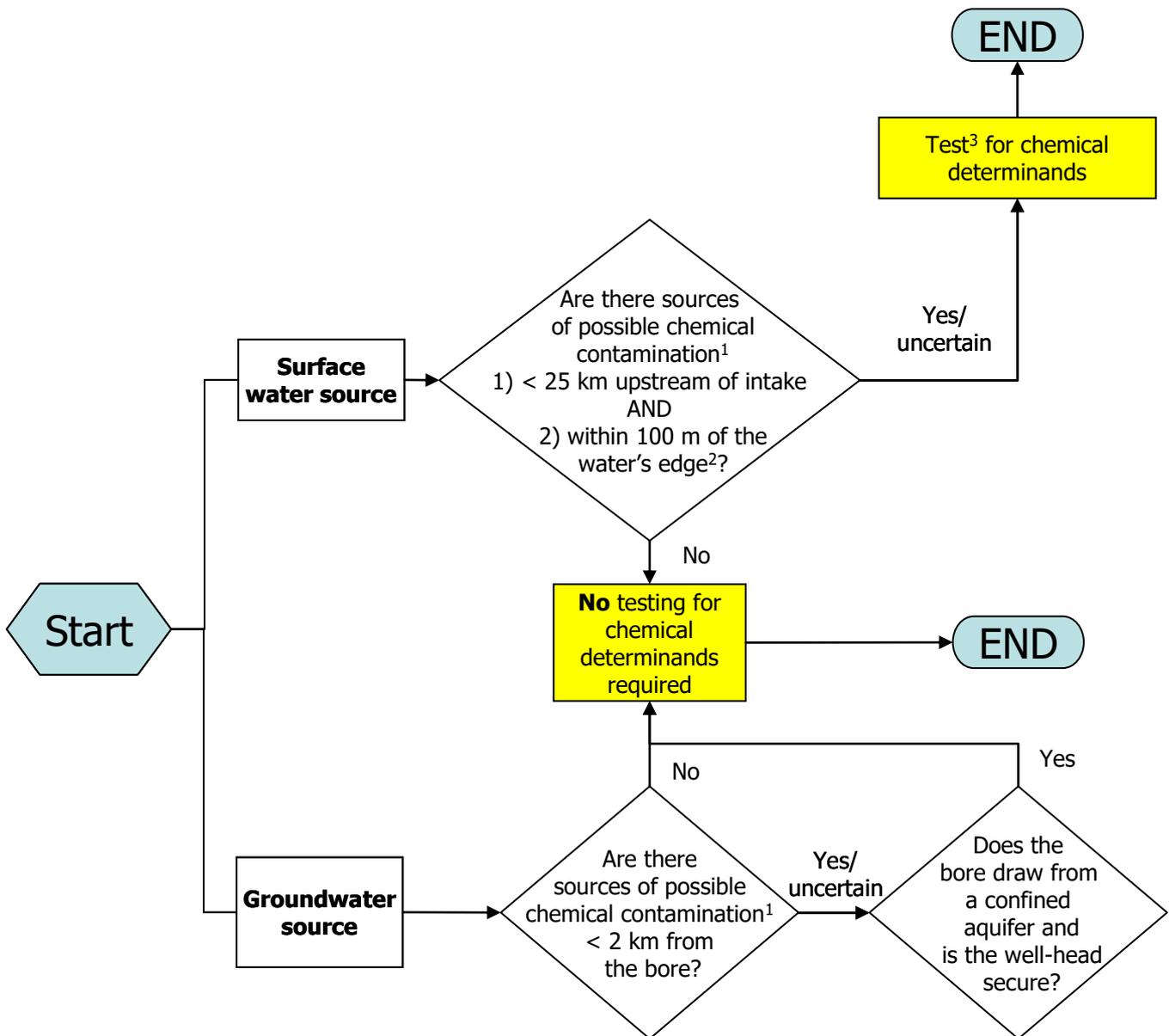
Note: 1 See *Drinking-Water Standards for New Zealand*, section 8.2.1.2

Note: 2 "Heavy metals" includes:

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



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 effective 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 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/agricultural 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)	
	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

Land use category	Activity	Contaminating material	Possible health-significant determinands	Comment
	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	
	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, chlorpyrifos, benzo(a)pyrene	
	Wool scouring	Degreasing agents, pesticides	Pesticides (including chlorpyrifos, diazinon)	The classes of pesticides likely to be derived from wool are organophosphates, synthetic pyrethroids, insect growth regulators

Land use category	Activity	Contaminating material	Possible health-significant determinands	Comment
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, <i>inter alia</i> , 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, 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

Land use category	Activity	Contaminating material	Possible health-significant determinands	Comment
				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, human waste	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. 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 <i>if there is a pathway to the source water</i>
	Road transport	Asphalt, fuel and oil leaks, chemicals for roadside weed control, metals	Benzo(α)pyrene, industrial solvents (benzene, toluene, xylene, ethylbenzene),	Spills of cargo carried by road may result in a wide range of contaminants being introduced into water <i>if there is a pathway to the source water</i>

Land use category	Activity	Contaminating material	Possible health-significant determinands	Comment
			herbicides, heavy metals	
	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			
	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		

Land use category	Activity	Contaminating material	Possible health-significant determinands	Comment
	Sports fields	Fertilizers, weed control chemicals, fuel and oil 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	

Land use category	Activity	Contaminating material	Possible health-significant determinands	Comment
8. Landfill	Disposal of industrial waste	Wide range of possible chemicals	Heavy metals, industrial chemicals (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	

Land use category	Activity	Contaminating material	Possible health-significant determinands	Comment
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 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 ⁵ .

⁵ 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 table	Analyses required
Pesticides	<ul style="list-style-type: none">• Trace pesticide suite (multi-residue)• Trace acid herbicide suite
Herbicides	<ul style="list-style-type: none">• Trace acid herbicide suite
Industrial chemicals	<ul style="list-style-type: none">• Semi-volatile organic compounds (SVOC)• Volatile organic compounds (VOC)
Industrial solvents	<ul style="list-style-type: none">• Volatile organic compounds (VOC)
Heavy metals	<ul style="list-style-type: none">• Antimony, cadmium, chromium, copper, lead, mercury, nickel

4.4 CHECK-SHEET

Check-sheet for 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 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 and Priority 3 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

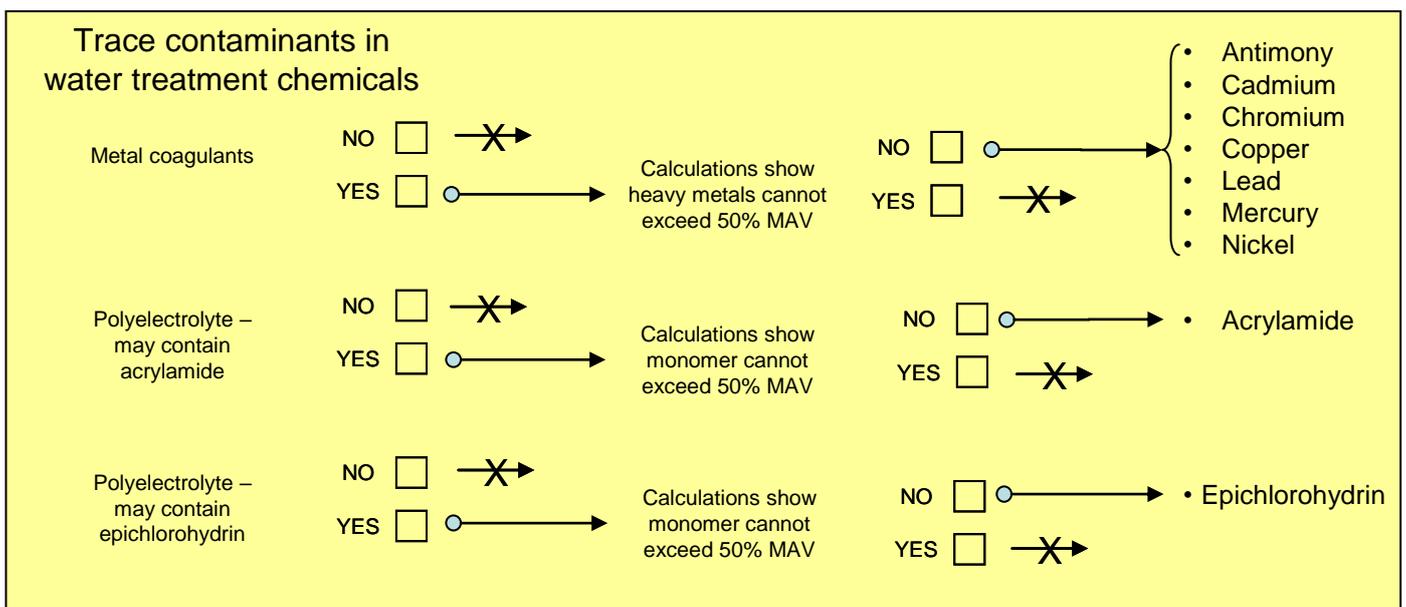
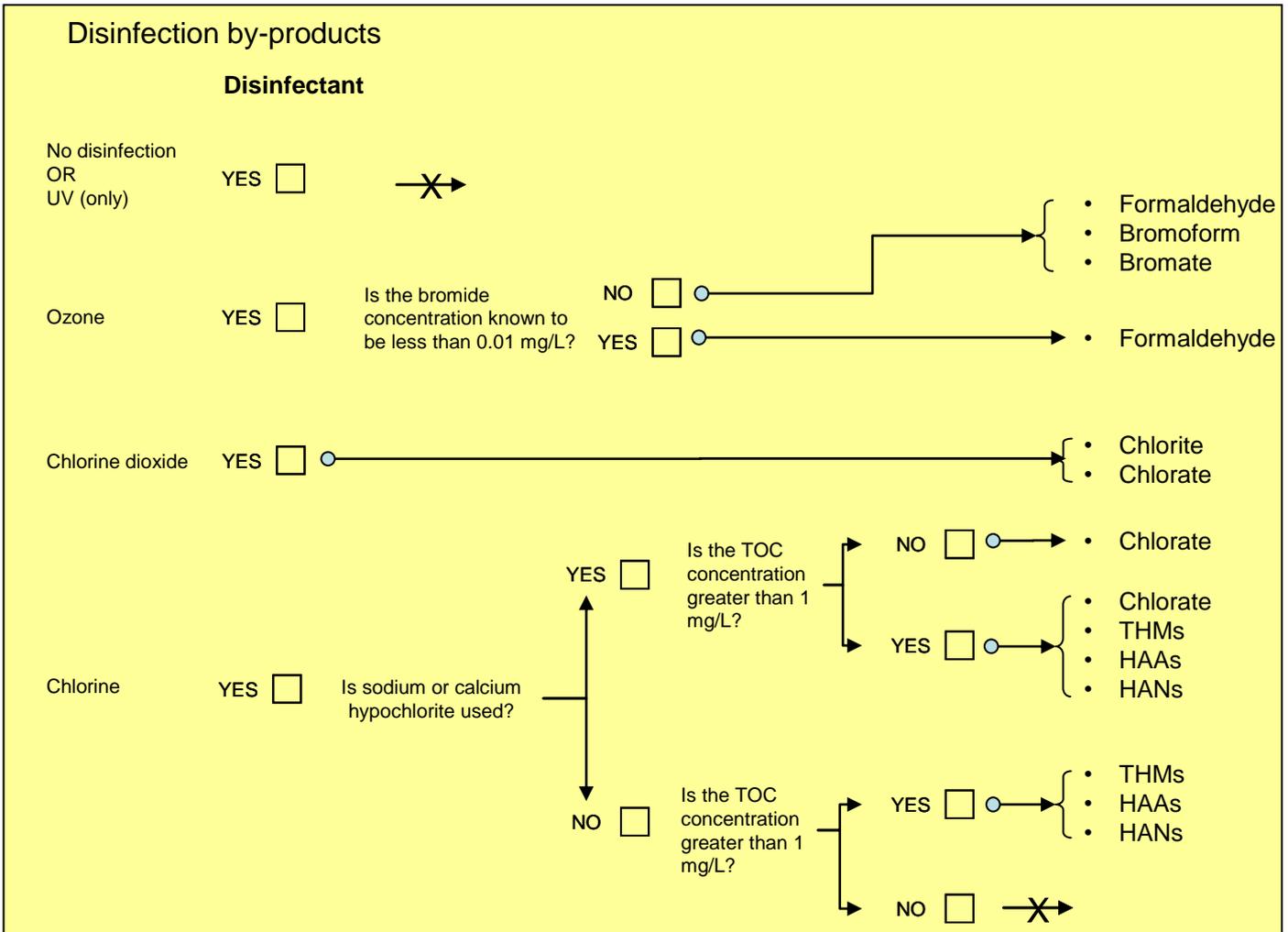
<p>Compulsory —————→</p> <p>Year last tested for, if not included:</p>	<ul style="list-style-type: none"> • Arsenic • Barium • Manganese • Selenium
---	--

<p>Naturally-occurring heavy metals</p>	<p>Heavy metal deposits present ?</p> <p>NO <input type="checkbox"/> —X→</p> <p>YES <input type="checkbox"/> ●————→</p>	<ul style="list-style-type: none"> • Antimony • Cadmium • Chromium • Copper • Lead • Nickel • Mercury
--	---	--

<p>Naturally-occurring boron</p>	<p>Soda springs in area? NO <input type="checkbox"/> —X→</p> <p>YES <input type="checkbox"/> ●————→</p> <p>Geothermal activity in area? NO <input type="checkbox"/> —X→</p> <p>YES <input type="checkbox"/> ●————→</p> <p>Seawater intrusion? NO <input type="checkbox"/> —X→</p> <p>YES <input type="checkbox"/> ●————→</p>	<ul style="list-style-type: none"> • Boron
---	--	---

Determinand Class

Determinands to include in sampling plan



5. WHEN AND WHERE TO SAMPLE

(See also Section A4)

Sampling locations and timing are explained in the table below. Except for determinands that will only be found in treated waters, all determinands should first be sampled in the source water. If the concentration of a determinand exceeds 50% of its MAV in the source water, samples may be taken from the treated water. This is to determine whether the treatment process reduces the determinand's concentration to less than 50% of its MAV.

Any samples taken from treated water (ie, water leaving the treatment plant or in the distribution zone) must be collected at the locations specified in the DWSNZ (although these samples are not for compliance purposes).

Determinand	Sampling Location		Sampling time or season	Additional notes
	Pre-treatment	Post-treatment		
Heavy metals – antimony, cadmium, copper, lead, mercury, nickel	Yes	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	NA	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	Yes	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	Yes	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	

Determinand	Sampling Location		Sampling time or season	Additional notes
	Pre-treatment	Post-treatment		
Manganese	Yes	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 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	Yes	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
Disinfection by-products (DBPs)	NA	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 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 ⁶ residual at the extremities must be at its normal level, which in any event must not be less than 0.1 mg/L

⁶ Free available chlorine

Determinand	Sampling Location		Sampling time or season	Additional notes
	Pre-treatment	Post-treatment		
Pesticides, herbicides	Yes	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	Yes	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	Yes	Anywhere in the reticulation, or from the water leaving the treatment plant	One sample at any time	Not required for surface water

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6. PRIORITY 3 DETERMINAND MONITORING

(See also Section A4.4)

This section discusses the monitoring of Priority 3 determinands once they have been identified.

Error! Reference source not found. identifies two types of Priority 3 determinands. The distinction is made on the basis of how frequently samples for the determinand need to be taken in a satisfactory monitoring programme. The sampling frequencies are given in the table below.

Priority 3 Determinand	Likelihood of determinand concentration exceeding 50% MAV	Frequency of sampling
Type 1	Low ($\leq 50\%$ MAV in source)	Two samples collected as part of the identification programme undertaken before each water safety plan revision
Type 2	Higher ($> 50\%$ MAV in source)	Annually, or preferably, 6 monthly. DWA to decide on frequency based on the likelihood of the determinand concentration increasing. Greater or lesser frequencies may be set at the DWA's discretion.

The frequency of sampling reflects the likelihood that the concentration of the Priority 3 determinand will rise above 50% of its MAV before the next repeat of the identification process. As explained in Section **Error! Reference source not found.**, an identification process must be undertaken in time for each revision of the water safety plan.

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APPENDIX A: BACKGROUND FOR THE 'PRIORITY 2 AND PRIORITY 3 CHEMICAL IDENTIFICATION GUIDELINES'

A.1 INTRODUCTION

The Health Act 1956, s69Z, requires water suppliers supplying water from minor, medium and large water supplies to prepare and implement water safety plans (WSPs). Water safety plans have to identify the public health risks (if any) associated with a water supply (s69Z(2)(a)(i)). These risks may arise from microbiological, chemical or radiological hazards. Part of maintaining a satisfactory WSP is the continuing identification of hazards that could present a threat to the health of drinking-water consumers. This includes the identification of chemical determinands of potential public health significance

The *Drinking-Water Standards for New Zealand 2005 (Revised 2008)* (DWSNZ) is another tool by which the public health risk associated with water supplies is managed. The 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 in 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, four possible priority classes are identified. Only microbiological hazards can be classed as Priority 1 determinands, leaving Priorities 2 to 4 for the classification of chemical determinands. Priority 4 includes determinands known not to be likely to occur in a water supply. As a result, water safety plans should focus on managing Priority 2 and 3 chemical determinands.

A chemical determinand is assigned to a water supply as a Priority 2 determinand if there is evidence that it is present at a concentration greater than 50% of its maximum acceptable value (MAV). 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 Ministry of Health initiated the identification of Priority 2 determinands for water suppliers through the centralised programme described above. Now, water suppliers are 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.

During the process of identifying Priority 2 determinands, a water supplier may also identify chemical determinands in their water supply that are present at concentrations equal to or less than their MAV in the reticulated drinking-water. These determinands are classified as Priority 3 determinands. Generally, they do not need to be monitored to show compliance

with the DWSNZ. However, the concentrations of these determinands cannot be assumed to remain indefinitely equal to, or less than, their MAV. For example, where a determinand is present at high concentrations in the source water, its concentration in the distribution zone may be reduced to a level less than 50% of the MAV by treatment. Changes in the efficacy of the treatment could result in an increase in the determinand's concentration in the reticulated water.

For chemical risks to be well managed Priority 3 determinands should be monitored. This monitoring is part of good public health risk management and not a compliance requirement of the DWSNZ. The frequency at which monitoring samples should be taken depends on the likelihood of the determinand's concentration increasing.

Through the process of identifying Priority 2 determinands, Priority 3 determinands are also identified. This guide sets out a protocol for identifying which health-significant determinands are present in the water and which of these two priority classes they should be assigned to. The guide provides **recommendations** for monitoring Priority 3 determinands, because no requirements for sampling Priority 3 determinands are contained in the DWSNZ. The guide is not concerned with the compliance monitoring required for Priority 2 determinands. This is separate from the protocol set out here. The requirements are contained in the DWSNZ.

Small and neighbourhood drinking water supplies (those serving between 25 and 500 people) are not required to prepare a WSP, 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 WSP to be prepared for a supply under section 69ZA of the Health Act 1956. The Medical Officer of Health may require a WSP 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). Priority 2 determinands are only officially assigned to supplies serving more than 500 people. However, if the water supplier wishes, Priority 2 determinand assignments may be made to smaller supplies.

The guide defines, for drinking-water suppliers and drinking-water assessors (DWA), the procedure for identifying Priority 2 and Priority 3 determinands. 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 provides guidance on the monitoring of Priority 3 determinands, as this is not done by the DWSNZ, as it is for Priority 2 determinands.

When identifying chemical determinands of potential health significance, the drinking-water supplier is concerned with chronic⁷ exposure of their consumers to chemical or radiological hazards. Acute⁸ exposure to hazards through accidents or natural disasters is not covered in this guide. The procedure explained here is unsuitable for acute exposure.

Section A2 sets out the overall protocol to be followed for Priority 2 and Priority 3 determinand identification. The protocol involves water suppliers and DWAs, and includes planning, sampling data assessment and official assignment to the water supply of any Priority 2 determinands identified.

⁷ 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.

⁸ For the purposes of the handbook, acute exposure is exposure for a short period, usually to high concentrations.

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.

[Notes:

Sampling of determinands that have been classified as Priority 2 or Priority 3 determinands is referred to as “monitoring” in this guide. The collection of samples for the purpose of identifying Priority 2 and 3 determinands is termed “sampling”.]

For brevity, the process by which health-significant determinands are identified as Priority 2 or Priority 3 determinands is referred to in this guide as ‘determinand identification’.

A.2 IDENTIFYING PRIORITY 2 AND 3 DETERMINANDS AND MAKING ASSIGNATIONS

To assign a determinand to a drinking-water supply with Priority 2 or Priority 3 classification, evidence is needed to show whether the determinand sometimes exceeds 50% of its MAV. The 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.

This section summarises the eight steps from the start of the process when the water supplier designs their sampling programme, to the assignment of determinands to the supply and the revision of the WSP to include any new monitoring requirements. 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 zone⁹ 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 most 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.

⁹ The area overlying an aquifer through which the water passes to the aquifer.

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.

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

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

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 and Priority 3 determinands.

The DWA examines the analytical results, and identifies any determinand for which *either* result from the two samples taken 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.*

Determinands that are detected, but at concentrations less than, or equal to, 50% of their MAVs, are assigned as Priority 3 to the supply.

Error! Reference source not found. shows how the results of sampling are used to decide whether a determinand should be assigned as a Priority 2 or Priority 3 determinand. Priority 2 determinands are assigned on the basis of the concentration to which consumers are exposed, unless a post-treatment sample is not taken. The type of Priority 3 classification (Type 1 or 2) depends on the results from samples taken pre-treatment and post-treatment. When neither sample provides evidence of the determinand exceeding 50% of its MAV, the

classification is a Priority 3 Type 1. Alternatively, if the post-treatment concentration is less than 50% of the MAV, but the pre-treatment sample exceeds 50% of the MAV, the classification is Priority 3 Type 2. For this classification more frequent sampling is recommended because a decline in treatment performance could result in consumers being exposed to concentrations greater than 50% of the MAV.

Step 5 The DWA notifies the water supplier of the intended Priority 2 and Priority 3 determinand assignments.

The DWA notifies the water supplier of the intended assignments 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 assignments are generally only made to water supply zones serving more than 500 people, however, a determinand can be assigned to a smaller supply as an official Priority 2 determinand, if the water supplier wishes.

Step 6 The water supplier responds to the proposed assignments.

Should the water supplier consider that there is good reason why any of the intended Priority 2 assignments should not be made official, they need to support their case with information showing why the test result, which was greater than 50% of the MAV, was atypical of the water quality and very unlikely to occur again.

Step 7 The DWA makes the assignments official.

The DWA reaches a final decision regarding the Priority 2 determinand assignments for the supply. Should the water supplier, as part of Step 6, disagree with the intended assignment, 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 assignments are decided, this information is provided to ESR for recording in the national drinking-water database.

Step 8 The water supplier revises their WSP and implements Priority 2 determinand compliance monitoring and appropriate monitoring for any Priority 3 determinands.

The water supplier includes the compliance monitoring for any assigned Priority 2 determinands, and monitoring for any Priority 3 determinands, in their revised WSP. Once the revised WSP 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 WSP is implemented. Any Priority 3 determinand monitoring recommended should also start before the start of the next financial year.

A.3 WHICH DETERMINANDS TO ASSESS

A.3.1 Introduction

Where possible, the protocol for 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 chemical risks to the supply are reviewed
- b. those that *may need to be* assessed depending on the likelihood of their presence in the water.

A.3.2 Determinands that have to be assessed when identifying chemical determinands

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 WSP 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.

A.3.3 Determinands that may need to be assessed

As part of WSP 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 4.2), 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.

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.

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.

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.

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:

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

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

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 4.3 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 else¹⁰) 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.

A.3.4 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.

A.3.5 Previous Priority 2 assignments

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 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.

A.3.6 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 activity¹¹.

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.

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

A.4 SAMPLING BACKGROUND INFORMATION

A.4.1 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 and Priority 3 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 determinands. Only two samples are required for determinand identification.

The difficulty with collecting only two samples for 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 place where, and time when, the determinand's concentration, if variable, is likely to be at its highest.

This section provides guidance on selecting sampling times and locations when sampling for determinand identification. Section 5 of the guide contains a summary of the sampling times and locations for specific determinands or determinand groups.

A.4.2 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 vary with the determinand, and different sampling times may be required to accommodate this.

The table in Section 5 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.

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 not vary greatly, or they do change, this is likely to happen 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 year's assessment is not critical, so that samples for these determinands can be taken at any time.

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.

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.

A.4.3 Where to sample

On each of the two occasions a sample is taken during the chemical identification process, at least one sample must be taken pre-treatment, unless the determinand cannot be present in the water prior to treatment (eg, disinfection by-products or monomers present in polyelectrolytes). This is important for helping to decide the frequency of sampling for any Priority 3 determinands identified, as discussed below.

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.

Determinands not expected to be removed by treatment, or where there is no treatment

On each sampling occasion, two samples taken before treatment (or from the source) are required when there is no reason to believe that the determinand's concentration will change between the source water and the distribution system. If the determinand's concentration exceeds 50% of its MAV in either sample, the determinand will be assigned as a Priority 2 determinand.

Determinands expected to be removed by treatment

Some determinands of health significance may be present in the source water, but treatment processes may remove them. In these situations, two samples should be taken post treatment in addition to the pre-treatment samples. The results from the post-treatment samples are used to decide whether the determinand should be classified as a Priority 2 or Priority 3 determinand. If the post-treatment sample result leads to a Priority 3 classification, the pre-treatment sample is used to decide on whether the Priority 3 determinand should be classified as Type 1 or Type 2 (see section A4.4).

When the pre-treatment concentration is greater than 50% of the MAV, 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 assignments 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 WSP should cover the protocol for dealing with treatment failures.

Determinands with concentrations that are unlikely to change through the distribution zone

When samples need to be taken from the distribution zone, the appropriate location depends on whether the determinand is likely to change in concentration as the water travels through the 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.

Determinands with concentrations that may change through the distribution zone

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 sometimes to increase.

A.4.4 Monitoring Priority 3 determinands

(See Section 0)

The DWSNZ state that a water supplier does not have to monitor Priority 3 determinands (DWSNZ, s3.3.3). However, the section acknowledges that water suppliers should undertake sampling programmes, as part of good risk management, to assess whether Priority 3 determinands should be elevated to Priority 2 classification. S 8.2.2 of the DWSNZ also allows DWAs to require determinands to be monitored for a period after Priority 2 determinands have been reclassified as Priority 3 determinands, if the reason for the reduction in concentration is not obvious.

Error! Reference source not found. in the Guide introduces the concept of Type 1 and Type 2 Priority 3 determinands. This distinguishes between Priority 3 determinands that are unlikely to markedly increase in concentration because they are not present at elevated concentrations anywhere else in the supply (Type 1), and those that are present in the source water at elevated concentrations (Type 2). In the latter situation gradual deterioration in treatment performance may result in consumers being exposed to a concentration equivalent to a Priority 2.

Sampling for Type 1 Priority 3 determinands is ideally undertaken in step with the WSP review cycle, during determinand identification. However, to take account of the greater likelihood of Priority 3 Type 2 determinands increasing in concentration in the distribution zone, annual, or preferably, six-monthly sampling is recommended. The DWA is given discretion to modify these recommended frequencies to make allowance for the situation, such as the water supplier's ability to afford relatively frequent sampling.



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