

Chapter 10: Chemical compliance

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10.1 Introduction

As well as compliance issues, this chapter provides some information on the sources, occurrences, and management related to the chemical determinands covered by the *Drinking-water Standards for New Zealand 2005* (revised 2008) (DWSNZ). The World Health Organization's *Guidelines for Drinking-water Quality* have been drawn on extensively (WHO 2004a/2011).

This chapter discusses the current and potential risks of chemical contamination of drinking-water. Risks associated with or originating in the raw water are discussed in Chapter 3: Source Waters. This chapter explains the methods used to derive the Maximum Acceptable Values (MAVs) for chemical determinands of health significance and provides detailed information on how to apply the DWSNZ to these determinands. Section 10.2 addresses the basis of the changes to the MAVs from their earlier values.

Tables 2.2 and 2.3 in the DWSNZ list the MAVs for chemical determinands of health significance. Some chemical determinands that may affect water quality but have no health significance are discussed in Chapter 18: Aesthetic Considerations.

Some chemical determinands found in drinking-water are beneficial – see WHO (2005).

Information is given on the planning and implementation of monitoring programmes for chemical determinands and assessment of results according to the DWSNZ, and how and why to carry out discretionary monitoring. Examples are provided.

The individual chemical determinands are described in detail in the Datasheets in Volume 3. Many of these may have possible health or aesthetic concerns but do not have a MAV or a GV.

The removal of chemical determinands of health concern from water is discussed where possible in the individual datasheets, and in the various treatment chapters. For example, Chapter 13 includes a section on lime softening and ion exchange; Chapter 14 includes a section on the use of adsorption processes such as activated alumina and activated carbon. Section 19.3.4 of Chapter 19 covers point-of-use and point-of-entry treatment systems. AWWA (1995) discusses fluoridation; see full list of AWWA Standards on <http://www.awwa.org/files/Resources/Standards/StandardsSpreadsheet.xls>.

10.1.1 Maximum Acceptable Value (MAV)

The MAV of a chemical determinand is the concentration of that determinand which does not result in any significant risk to the health of a 70 kg consumer over a lifetime of consumption of two litres of the water a day.

For genotoxic carcinogens the MAV represents an excess lifetime cancer risk, usually amounting to one extra incidence of cancer per 100,000 people drinking water containing the determinand in question at the MAV for 70 years (ie, an assessed risk of 10^{-5}).

The MAVs (section 2 of the DWSNZ) provide the benchmark whereby the public health safety of the drinking-water is assessed, ie, if the determinands in the drinking-water occur at concentrations less than their MAV, the water is considered safe. The other sections of the DWSNZ describe how to demonstrate compliance with the DWSNZ.

The derivation of the MAVs is explained in the datasheets.

Some MAVs are called provisional. This may be because the WHO considered that the available data are not precise enough to develop a MAV, but that there are health concerns related to the determinand, so they derived a provisional guideline value. In some cases WHO (2004a) decided that some determinands no longer needed a guideline value; in most cases the 2005 DWSNZ retained the MAV but called it provisional. The 2008 revision deleted most of these. Some substances, eg, some pesticides, have more relevance in New Zealand so a provisional MAV was developed despite there being no WHO guideline value (eg, azinphos methyl), or a different guideline value (eg, 1080) in WHO (2004a).

In summary, a provisional MAV is an estimated safe value based on the best toxicological information available to date, but that limitations with the derivation of the value are acknowledged and there may be the need to revise this when new information arrives. Therefore provisional MAVs should be treated in the same way as other MAVs with regard to consequences of P2 status and exceedence.

Guidance values for short-term exposures (STEVs) are now being developed by the WHO, the USEPA and other organisations, for a small number of substances that are used in significant quantities and are frequently implicated in an emergency as a consequence of spills, usually to surface water sources. See sections 10.2.5.1 and 10.2.5.4. Where available, these values appear in the datasheets. The 2008 revision includes short-term MAVs for cyanide, nitrate and nitrite. STEVs will appear in the datasheets.

Drinking water standards in England and Wales are now set out in European and UK legislation. They are called Prescribed Concentrations or Values (PCVs). Many are different from the WHO Guideline Values (DWI 2010a). Where relevant, PCVs are shown in the datasheets.

The most commonly used method to test for compliance is by chemical analysis and comparison with the relevant MAVs. Most of the chemicals likely to be of concern have a MAV, but with more than 100,000 chemicals in commercial use and many more natural compounds, chemical testing of regulated chemicals alone may be insufficient to identify all potential hazards, so additional methods may be required. EnHealth (2012a) proposes that biological testing is also conducted as part of an integrated approach to assessment of water quality based on a weight-of-evidence approach. The options are discussed.

10.2 Chemical determinands of health significance

10.2.1 Background

With respect to chemical determinands, the current DWSNZ (2008 revision) arises from a revision of the DWSNZ published in 2000 and 2005. This revision incorporates current scientific, national and international information, based largely on WHO (2004a) and subsequent rolling revisions.

The DWSNZ lists over 100 chemical determinands with MAVs or PMAVs. Refer to the previous section and to Chapter 1: Introduction, section 1.6.2 for information about MAVs. Where relevant, the DWSNZ and the Australian Drinking Water Guidelines (NHMRC, NRMMC 2004/2011) have recalculated the WHO Guidelines Values (GV) to a 70 kg bodyweight basis from the 60 kg used by the WHO. This increase in body weight results in a nominal 16 percent increase in MAV values, however, this increase is not always apparent in the MAV because of rounding effects. As discussed below, some determinands are not dependent on adult body weight: some calculations are independent of bodyweight, and others, (lead, short-term nitrite and DDT and its isomers) are calculated using bodyweight and water consumption values for children or infants; details appear on the datasheets.

The WHO (2004a) guideline value lists include a number of provisional guideline values. These have been established based on the practical level of treatment achievability or analytical achievability. In these cases, the guideline value is higher than the calculated health-based value. Uncertainty in the toxicological basis for the guideline may also result in its designation as provisional.

The 2005 DWSNZ contained MAVs for 50 determinands not listed in WHO (2004a). These were given provisional MAVs. Most of these determinands are organic compounds, including a large number of pesticides. The basis for their inclusion was the assumption that registration of a pesticide for use in New Zealand may ultimately result in contamination of drinking-water supply. Where WHO (2004a) considered that a chemical determinand is unlikely to appear in drinking-water at a concentration of health significance, it has been removed from the DWSNZ 2008 revision, and datasheets have been modified or prepared accordingly.

New Zealand toxicologists recalculated the boron MAV (for the 2000 DWSNZ). It became 1.4 mg/L, cf the WHO GV of 0.5 mg/L. The basis for this difference is explained in the datasheet. Subsequent to the 2008 DWSNZ, WHO (in 2011) revised their GV for several determinands, eg, boron to 2.4 mg/L. The MoH has yet to devise an acceptable procedure for updating MAVs without having to rewrite the Standards, along with the extensive consultation period that the public seems to expect these days.

Because of the extensive list of determinands, a risk-based approach should be used to evaluate the health significance of these determinands in a particular water supply, using available information relating to contaminants likely to be present in the water supply catchment (see Chapter 3: Source Waters). Details on the derivations are provided in the datasheets.

The 2005 DWSNZ also included a table of determinands for which health concerns have been raised, but for which no MAVs have been set (Table A2.2, DWSNZ 2005). This table was removed from the 2008 revision, but information is retained (or expanded) in the datasheets.

WHO (2004a) notes that:

Only a few chemicals have been shown to cause widespread health effects in humans as a consequence of exposure through drinking-water when they are present in excessive quantities. These include fluoride and arsenic. Human health effects have also been demonstrated in some areas associated with lead (from domestic plumbing), and there is concern because of the potential extent of exposure to selenium and uranium in some areas at concentrations of human health significance. These constituents should be taken into consideration as part of any priority-setting process.

Drinking-water may be only a minor contributor to the overall intake of a particular chemical, and in some circumstances controlling the levels in drinking-water, at potentially considerable expense, may have little impact on overall exposure. Drinking-water risk management strategies should therefore be considered in conjunction with other potential sources of human exposure.

Guidance is provided in the supporting document *Chemical Safety of Drinking-water* (WHO 2004b) on how to undertake prioritisation of chemicals in drinking-water. This deals with issues including:

- the probability of exposure (including the period of exposure) of the consumer to the chemical
- the concentration of the chemical that is likely to give rise to health effects
- the evidence of health effects or exposure arising through drinking-water, as opposed to other sources, and relative ease of control of the different sources of exposure.

The application of a risk-based approach is addressed in Chapter 3: Source Waters in relation to assessing potential sources of contaminants.

Risk management issues related to trace organics and fluoridation are addressed in the:

- MoH Public Health Risk Management Plan Guide PHRMP Ref. P8.4: Treatment Processes – Trace Organics Removal, and in
- MoH Public Health Risk Management Plan Guide PHRMP Ref. P9: Treatment Processes – Fluoridation.

See also WHO 2007 *Chemical Safety of Drinking-water: Assessing priorities for risk management*.

The United Nations Environment Programme, International Labour Organisation and World Health Organization jointly sponsored a project within the International Programme on Chemical Safety (IPCS) on the harmonisation of approaches to the assessment of risk from exposure to chemicals. They produced a booklet *IPCS Risk Assessment Terminology* (IPCS 2004).

Personal care products and domestic cleaning products are a diverse range of products that contain vast numbers of different chemicals. These chemicals may have the potential to reach drinking water supplies via release into the environment through typical use and entry to sewerage and subsequent treatment. Published studies on the occurrence of these substances demonstrate that trace amounts can reach drinking water. DWI (2014a) assessed approximately 690 chemicals; thirty-three were identified during the data collation and prioritisation exercise as having a high potential for reaching drinking water supplies. The potential concentration of these chemicals in drinking water was then modelled. Ten of the thirty-three prioritised chemicals were predicted to produce levels of maximum exposure through drinking water and bathing close to or greater than would be anticipated through their intended use. Where relevant, further information is included in individual datasheets.

10.2.2 Inorganic chemicals of health significance

The inorganic determinands of health significance are listed in Table 2.2 of the DWSNZ. Of these chemicals, the ones most often occurring in health significant concentrations in New Zealand drinking-water supplies are metals from corrosion of fittings,¹ and arsenic, boron and nitrate. Arsenic and boron occur naturally in geothermal fluids or sometimes in association with marine sediments, whereas nitrate concentrations are increased by intensive agricultural activity.

The inorganic determinands of health significance listed in the DWSNZ are predominantly metals. These may be present in the source water or may enter the water in the distribution system, or from the plumbing.

The main natural contributors of metals to source water in New Zealand are geothermal fluids and the leaching of minerals and rocks. Natural sources, especially geothermal, are well known for arsenic, antimony and mercury, and may also be important in localised areas for lead. Generally these determinands can be avoided in the source water selection process; otherwise specialised treatment may be necessary. The USEPA has some useful information about arsenic at <http://water.epa.gov/lawsregs/rulesregs/sdwa/arsenic/compliance.cfm>

Leaching of contaminants from landfill sites or industrial contamination is a recognised source of metals to source waters, although uncommon in New Zealand.

Metals appearing in the source water may be present as free soluble ions, precipitated compounds, ions complexed with organic matter, or as compounds adsorbed on particles. Complexation with organic matter can present treatment problems for those metals that are conventionally removed by oxidation/precipitation, because of the difficulty in destroying the soluble complexes to allow oxidation and precipitation of the metal.

¹ Note that the legislative responsibility for drinking-water quality beyond the point of supply to a property comes under the Building Act 2004 (http://www.med.govt.nz/buslt/bus_pol/building/review/)

Dissolution of metals in the distribution system by corrosive water can lead to the concentrations of metals reaching the consumer being higher than was originally present in the raw water (eg, copper, lead, nickel). Sections 10.2.6, 10.3.3 and 10.3.4 discuss the effects of corrosion of plumbing materials further. In this situation aggressiveness (plumbosolvency), which has no MAV itself, has an indirect effect on the determinands of health significance. Corrosion products may result from the dissolution of pipes (eg, copper, lead), or solders used in plumbing joints (eg, iron, zinc, lead, cadmium, antimony). Internationally, the lead component of solder has reduced; for example, the Canadian Standard CSA B125.1 limited the lead content of solder to 0.2 percent in 1986. The National Plumbing Code of Canada officially prohibited lead solders from being used in new plumbing or in repairs to plumbing for drinking water supplies in the 1990. The most common replacements for lead solders are tin-antimony, tin-copper and tin-silver solders. In Australia plumbing products are required to be certified to WaterMark and AS/NZS 4020:2005; and/or have low lead content or be lead free, when renovating or building.

There have been suggestions that fluoridation accelerates corrosion; CDC (2013) states that water fluoridation will not increase water corrosion or cause lead to leach (dissolve) from pipes and household plumbing fixtures. Metals (eg, zinc, barium, lead) may also be leached from plasticisers or stabilisers in the polymeric materials used in many modern water systems (eg, vinyl chloride).

A MoH report (2012) includes results of 511 drinking water samples taken from schools that operate their own water supply; 41 percent of samples exceeded 50 percent of the MAV for lead. This was due to dissolution from the reticulation and/or in the case of roof catchment, from components of the rainwater collection system, such as lead-head nails, lead flashings and lead soldered storage tanks. The report itemised abatement options.

Some inorganic disinfection by-products are contained in Table 2.2 of the DWSNZ. Organic disinfection by-products were the first types of disinfection by-product found, and are still the predominant compounds that cause concern when chlorine is used for disinfection.

Monochloramine is produced as a by-product if ammonia is present in water being chlorinated. It may also be used as a disinfectant in its own right. Since the introduction of chlorine dioxide and ozone as disinfectants a number of new inorganic disinfection by-products arising from these disinfectants have also been identified. Inorganic by-products may arise from the reaction of the disinfectant with other inorganic or organic constituents in the water (bromate, chlorite), or as a by-product of the process used to generate the disinfectant (chlorate, chlorite). The inorganic disinfection by-product that has been identified most widely in New Zealand drinking waters is chlorate, which is most often present as a decomposition product of hypochlorite solutions.

Disinfectants and their by-products are discussed in Chapter 15: Treatment Processes, Disinfection. Most disinfection by-products have a datasheet.

The remaining compounds contained in Table 2.2 are a miscellaneous collection of non-metallic substances. They may be present in water from natural and agricultural sources (eg, nitrate/nitrite), sometimes of geothermal origin (eg, boron), from intentional addition as a preventive health measure (fluoride), or from contamination by human activities (eg, cyanide, nitrate/ nitrite).

Health Canada (2000) commissioned NSF International to review contaminant occurrences from chemicals used in water treatment. Several metals were listed, with lead being the most persistent offender. DWI (2013) published "Potential Contaminants in Drinking Water Treatment Chemicals: Final Report". DWI (2014) published "Brass fittings – A source of lead in drinking water". Many of the findings appear in the datasheet for lead.

DWI (2016) summarised a study of the leaching of lead and nickel from brass fittings. Amongst their finding were:

- low lead brass fittings (<0.25 percent lead) have been shown to yield less lead than corresponding 'high lead' brass fittings (2.0 percent to 3.5 percent lead)
- however, the low lead taps tested did yield relatively high quantities of nickel
- it was also found that the relatively high lead brass ferrules (up to 6.0 percent lead) were relatively low yielding
- it was demonstrated that phosphate dosing reduces leaching of nickel and zinc in addition to lead
- it was shown that high yields of lead and nickel come from new brass fittings, fittings that have been empty of water for some time and from fittings that have held stagnating water. Flushing before use is recommended for these situations.

Some inorganic determinands, when in low concentrations, may also have health implications, but do not currently have WHO GVs or DWSNZ MAVs. Chapter 12 of WHO (2005) discusses these. The main focus in setting standards has been on the toxicological properties of contaminants. Nevertheless, some studies have attempted to define the minimum content of essential elements or total dissolved solids (TDS) in drinking-water, and some countries have included requirements or guidelines for selected substances in their drinking-water regulations. The issue is relevant not only where drinking-water is obtained by desalination (if not adequately re-mineralised) but also where home treatment or central water treatment reduces the content of important minerals, eg, by softening, and when low-mineral bottled water is consumed.

Sufficient evidence is now available to confirm the health consequences from drinking-water deficient in calcium or magnesium. Many studies show that a higher content of magnesium in drinking-water is related to decreased risks for cardiovascular disease (CVD) and especially for sudden death from CVD. This relationship has been described independently in epidemiological studies with different study designs, performed in different areas, different populations, and at different times. The consistent epidemiological observations are supported by the data from autopsy, clinical, and animal studies. Biological plausibility for a protective effect of magnesium is substantial, but the specificity is less evident due to the multifactorial aetiology of CVD. In addition to an increased risk of sudden death, it has been suggested that intake of water low in magnesium may be associated with a higher risk of motor neuronal

disease, pregnancy disorders (so-called preeclampsia), sudden death in infants, and some types of cancer. Recent studies suggest that the intake of soft water, ie, water low in calcium, is associated with a higher risk of fracture in children, certain neurodegenerative diseases, pre-term birth and low weight at birth and some types of cancer. Furthermore, the possible role of water calcium in the development of CVD cannot be excluded. It is possible that as more information becomes available, recommended minimum levels will be established for some determinands.

Most New Zealand water supplies are taken from surface sources and most contain relatively low levels of calcium and magnesium compared with European and North American supplies. WHO (2005) suggests a minimum for magnesium of 10 mg/L and for calcium, a minimum of 20 mg/L. Typical surface water supplies in New Zealand contain about 2 mg/L Mg and 12 mg/L Ca.

10.2.3 Organic determinands of health significance and pesticides

Introduction

A large number of organic determinands of health significance has been identified in drinking-waters around the world.

Pesticides and other organic determinands with MAVs have been tabulated together in Table 2.3 of the DWSNZ. Not all of the determinands listed in Table 2.3 were being used in New Zealand at the time the DWSNZ were prepared. They are included to cover the possibility of their use in the future. Others, such as DDT and its isomers and dieldrin, are no longer registered for use in New Zealand. As a result, there are still a few stockpiles of unused pesticides in various parts of the country. These stockpiles, and residues in soil, are a potential contributor of pesticides to source waters of drinking-water supplies, so MAVs for these compounds have been retained.

Adsorption

Some pesticides and other organic determinands can be removed from water by adsorption techniques. The most common treatment process uses powdered or granular activated carbon. This is discussed in Chapter 14.

Aeration

Air stripping involves the transfer of volatile compounds from water to air. The higher the vapour pressure of the compound the more it is amenable to air stripping. Consequently, air stripping is the technology of choice for compounds with high Henry's law constant (high vapour pressure and low solubility in water). Henry's law constants can be called air-water partition coefficients. There are several types of air stripping devices which provide high exchange surface area (interface) between water and air, with low energy consumption, to facilitate the mass transfer of the VOCs from water to air. WRF (2014) reports the results of aeration trials on the removal of several volatile organic contaminants from water. The VOCs' removal efficiencies were studied

by collecting operational data from pilot plant operations, under various air-to-water ratios (53–652), three different temperatures (4, 12, and 20°C), and 1 to 6 trays in series. Henry's law constants can be found at <http://www.henrys-law.org/henry-3.0.pdf>. Aeration is also discussed briefly in Chapters 12 and 18.

Some groundwaters have been found to contain traces of the more persistent pesticides that were formerly used in New Zealand but which have been withdrawn from use for some years. Other organic contaminants, such as pentachlorophenol (PCP), may leach to groundwater or surface waters from (now disused) timber treatment sites and storage areas, just as PAHs have raised concerns at old coal gas plants.

Pesticides have several properties that affect their ability to leach to groundwater, as follows:

K_{oc}

This property refers to how tightly and quickly the pesticide binds to organic particles in the soil. A higher number indicates a greater tendency for the pesticide to bind to organic matter and thus a lesser tendency to leach with the soil water.

Persistence (T₅₀)

Pesticides are degraded primarily by sunlight, soil microbes, and chemicals in the soil. The combination of these factors determines persistence, or how long the pesticide remains in the soil. Persistence is usually measured in terms of half-life (T₅₀), or the time it takes for half of the applied chemical to break down. The greater the persistence of a pesticide, the more likely it is to leach to groundwater.

Rate of application (R)

Different amounts of each pesticide are required to control target weeds, insects, or diseases. Generally, the chance of leaching increases when pesticides are applied at a higher rate.

Application method (F)

Pesticides may be incorporated into the soil by mixing, applied to the soil surface, or applied to growing plants or seeds. To leach through the soil, a chemical first has to reach the soil. Pesticides applied to plants can be absorbed by the plant or broken down by sunlight, reducing the potential for leaching. Pesticides applied to the soil surface can also be broken down by sunlight before reaching the soil surface. Of the three methods of application, soil incorporation provides the greatest opportunity for leaching because all of the chemical is placed in the soil.

$$\text{Pesticide Leaching Potential (PLP)} = (T_{50} \times R \times F) / K_{oc}$$

A table of leaching potentials for several common pesticides has been published by North Carolina Cooperative Extension Service, see References.

Persistent organic pollutants (POPs)

POPs are chemicals that:

- are extremely stable and persist in the environment
- bio-accumulate in organisms and food chains
- are toxic to humans and animals and have chronic effects such as disruption of reproductive, immune and endocrine systems, as well as being carcinogenic
- are transported in the environment over long distances to places far from the points of release.

With the evidence that POPs are transported to regions where they have never been used or produced, the international community decided in 1997 to work towards the establishment of a Convention that will serve as an international, legally binding instrument to reduce and/or eliminate releases of twelve POPs, as identified in the UNEP Governing Council Decision 19/13C. The initial list of POPs contains the nine pesticides that are listed below. The decision also includes PCBs (mainly used in electrical equipment) and two combustion by-products, dioxins and furans. The UNEP Governing Council also requested that criteria and a procedure be developed to identify further POPs as candidates for international action. This request has been complied with and more substances are therefore likely to be included in the list.

The nine pesticides in the initial list of the Stockholm Convention on POPs are: aldrin, chlordane, DDT, dieldrin, endrin, hexachlorobenzene, heptachlor, mirex and toxaphene. Along with PCBs, dioxin and furan, this original list comprised 'the dirty dozen'. None of those pesticides is currently registered by ERMA for use in New Zealand.

In May 2009 another nine chemicals (or groups of chemicals) were added to the POP list. These were (see ICS 2009):

- lindane (1)
- its by-products alpha hexachlorocyclohexane (2) and beta hexachlorocyclohexane (3)
- the flame retardants hexabromodiphenyl ether/heptabromodiphenyl ether (4), tetrabromodiphenyl ether/pentabromodiphenyl ether (5) and hexabromobiphenyl (6)
- the pesticide chlordecone (7)
- the industrial chemicals pentachlorobenzene (8) and perfluorooctane sulfonic acid, its salts, and perfluorooctane sulfonyl fluoride (9).

Datasheets have been prepared for the POPs.

Pesticides

Pesticides with MAVs appear in Table 2.3 of the DWSNZ; some may also exert taste and odour so will appear in Table 2.5 too (aesthetic determinands). MAVs have been established for only a small fraction of the pesticides registered for use in New Zealand. The health risk of currently used pesticides that do not have a MAV, together with any new pesticides, will be reviewed for inclusion in the DWSNZ at a later date. Datasheets for pesticides with MAVs appear in Volume 3, along with a large number without a MAV, in fact all pesticides registered for use in New Zealand now have a datasheet.

Many of the early pesticides were very toxic and killed a wide range of pests and many plants or animals that were not pests. Many of them and/or their degradation products were also persistent in the environment, and some showed excessive signs of bioaccumulation. The WHO developed GVs for these, and they were adopted into the DWSNZ with MAVs. The MAVs have been retained despite the pesticide no longer being registered for use because residues are still being found, years later. Instead of having broad toxic properties, many newer pesticides target biochemical pathways specific to the type of pest being controlled; they are usually applied at lower rates, and are usually less persistent in the environment too. Datasheets have been prepared for these newer pesticides. Deriving a MAV for non-persistent pesticides is not particularly relevant because they are generally used seasonally (resulting in possible acute exposure), whereas a MAV is based on the consumption of two litres of water per day for a lifetime (chronic exposure). Acute limits are receiving international attention, and will be introduced in New Zealand in the future – see sections 10.2.5.1 and 10.2.5.4.

In the four national surveys of pesticides in groundwater and various regional monitoring programmes (MAF 2006), concentrations of individual pesticides were generally low compared with their MAVs. Pesticides exceeded the MAV in less than 1 percent of sampled wells. Six pesticides: atrazine, bromacil, cyanazine, dieldrin, MCPA and mecoprop were detected in groundwater samples in concentrations higher than their MAV, but no pesticides have been detected above their MAV in community drinking-water supplies. Dieldrin was identified at rates exceeding 50 percent of the MAV in two distribution zones that serve a total population of 360. It was also found at 33 percent of its MAV in a drinking-water supply serving 7860 people. Concentrations of four herbicides (simazine, 2,4,5-T, terbutylazine and triclopyr) were also detected, but at rates below 5 percent of their MAV.

With respect to groundwater resources, 33 different pesticides have been detected in New Zealand aquifers. Most of the pesticides detected were herbicides; 26 different active ingredients were found. Triazines, and specifically simazine, occurred most frequently, with alachlor, bromacil and some phenoxy hormones also occurring repeatedly. The non-herbicide chemicals found most frequently were diazinon, procymidone and some organophosphates (MAF 2006). Refer to the individual datasheets for further information.

In general, groundwater contamination is more likely in shallow, unconfined aquifers with permeable soils and high groundwater recharge. This is supported by the results from Canterbury, where a high percentage of wells (87 percent) were shallow (<30 m depth), and wells where pesticides had been found were shallower than 18 m. But pesticides have also been detected in deep wells, eg, in the Pukekohe area the mobile and very persistent herbicide picloram (up to 0.0009 mg/L) has frequently been detected in a well that is 64.5 m deep and cased to 39.5 m. The vulnerability of the Edendale aquifer to groundwater contamination is related to its high recharge rate of 300–400 mm/y due to high annual rainfall coupled with a low evapotranspiration rate. The widespread use of soak holes for stormwater disposal further increases the vulnerability of this aquifer (MAF 2006).

Water suppliers drawing from catchments that have a high usage of pesticides may consider adding granular activated carbon filters to the treatment process for regular use, or storing powdered activated carbon on site for emergency use. Trials are needed to select the most effective grade of carbon. The use of activated carbon is discussed in Chapter 9: Cyanobacteria Compliance, in section 9.7.2.3 and Table 9.5; Chapter 14: Filtration Processes, in section 14.7; and in Chapter 18: Aesthetic Considerations, section 18.3 under the heading of taste and odour.

The way in which pesticides are used is prescribed in their terms of registration, which in some cases may restrict their use near bodies of water. Nevertheless, contamination of drinking-water sources may possibly occur by accident, or emergency use.

The pattern of pesticide use can be highly variable. Apart from normal seasonal change and crop use, it can depend on the weather; for example, during warm, dry weather more insecticides are used, and during humid weather more fungicides may be used. Pesticide usage depends largely on land use, or the area different crops cover. If the crop changes, the pesticides may too. Also, new products can come on to the market and become dominant, briefly, or for years. For example, azoxystrobin, a fungicide used in cereals arrived on the market in about 1997, and by 2000 in the UK was widely used on wheat. But as disease resistance started to develop and new strobilurin fungicides, such as pyraclostrobin, came to the market, its use declined. Atrazine, a herbicide used in maize was withdrawn in the UK in 2007. Immediately following its withdrawal there was an increase in use of terbuthylazine (from nothing in 2008 to 18,000 kg active substance in 2010), and a 10-fold increase in the use of mesotrione (DEFRA 2013).

Disinfection by-products

Table 2.3 of the DWSNZ contains organic compounds of health significance (and that have a MAV) that arise from varying sources. The most frequently detected members of this group in New Zealand drinking-waters are the disinfection by-products, the type and concentration of which depend on the disinfectant used along with many other factors such as the natural organic matter content, pH, temperature and reaction time. Chapter 15: Treatment Processes, Disinfection, section 15.4 provides an outline of the factors that affect the formation of disinfection by-products. The datasheets discuss the types of by-products formed from the use of different disinfectants. Some chemicals primarily formed as disinfection by-products may also have industrial sources, not very common in New Zealand though.

Chlorination is the most extensively used disinfection process in New Zealand, indeed in the world. Information about the concentrations of some of its by-products in the country's water supplies was first obtained in the late 1980s. The predominant by-products of chlorination are trihalomethanes and haloacetic acids. In addition to chlorinated by-products, chlorine also forms by-products containing bromine when bromide is present in the water, even at quite low concentrations. This occurs as the result of chlorine oxidising bromide to bromine which is a lot more reactive. WRF (2015) discusses the use of aeration in the clearwell to reduce the concentration of volatile DBPs.

A balance needs to be found between microbiological safety and the risks posed by disinfection by-product formation. Although the microbiological quality of the water must not be sacrificed for the sake of reducing disinfection by-product formation, awareness of the factors controlling disinfection by-product formation will allow their production to be minimised while still maintaining good microbiological quality. Apart from the actual removal of natural organic matter from the raw water, the biggest single step in the reduction of DBPs has been the switch from prechlorination to postchlorination.

The disinfection by-products of ozonation are small, oxygen-rich organic molecules, such as aldehydes and ketones. Brominated compounds may arise if bromide is present in the source water.

Chlorine dioxide treatment may form halogenated by-products if there is a residual of chlorine present from the generation process.

DWI (2015) discusses disinfection by-products attributed to UV disinfection; see Chapter 15.

General organic chemicals

The polycyclic aromatic hydrocarbons (PAHs) are now represented in Table 2.3 of the DWSNZ by only benzo[a]pyrene. These organic compounds are characteristic of the incomplete combustion of organic material. They may be present in source waters, or arise in the distribution system by being leached from coal tar-lined pipes – not common in New Zealand now.

Another major group of organic compounds in Table 2.3 with a natural source is the cyanobacterial toxins. Their appearance in water, and the organisms from which they are derived, are discussed in Chapter 9. Cyanobacteria grow as phytoplankton (free-swimming or suspended) in lakes, large rivers and domestic sewage oxidation ponds, and can also attach to river cobbles as epiphytes or benthic organisms.

The remaining compounds in Table 2.3 of the DWSNZ are, for the most part, industrial in origin. Their appearance in drinking-water water is therefore indicative of the contamination of the source water and the reason for their appearance should be investigated. New Zealand, not being particularly industrial, means many are not likely to be found in our source waters. Some however may appear as the result of water treatment processes (acrylamide), or by leaching of distribution system materials, eg, the plasticisers di(2-ethylhexyl)adipate and di(2-ethylhexyl)phthalate from plastic pipes.

Health Canada (2000) commissioned NSF International to review contaminant occurrences from treatment chemicals. Several organic substances were listed, with dimethylamine being the most persistent offender. It is an impurity in polyelectrolytes. There is no MAV in the DWSNZ for dimethylamine, but a datasheet appears in Volume 3. WHO (2004) does not have a guideline value either. Because of its frequency in drinking-water, Health Canada proposed a maximum level of 0.05 mg/L, whereas NSF proposed 0.12 mg/L.

See Ahern (2008) for a discussion on organic chemicals (including pesticides) that may be in use in New Zealand. This was updated – see Auckland City (2016); this report discusses flame retardants, plasticisers, surfactants, perfluorinated compounds, musk fragrances, pesticides, pharmaceuticals, steroid oestrogen, personal care products, preservatives, and corrosion inhibitors. These are also covered in the datasheets, in much more detail.

10.2.4 Health risk from toxic chemicals

Once a toxic chemical enters the body its effect is determined by the interplay of absorption, distribution, metabolism and excretion. The nature, number, severity and/or prevalence of specific effects generally increase with increasing dose, and sometimes depends on the age, sex and condition of the consumer.

Absorption of toxic chemicals across body membranes and into the bloodstream can occur in the gastro-intestinal tract, lungs and through the skin, with the gastro-intestinal tract being the main site of entry for drinking-water. Most chemicals must be absorbed once they enter the gastro-intestinal tract in order to exert their toxic effect. Following absorption, distribution of the toxicant to various organs depends on the ease with which it crosses cell membranes, its affinity for various tissues and the blood flow through the organ. In some instances, metabolism of a chemical creates a more toxic chemical than the original while in other instances it does not change, or reduces, the chemical's toxicity. Because lipid-soluble compounds are reabsorbed in the kidney and intestine due to their ability to cross cell membranes, the body metabolises these toxicants into water-soluble compounds that can be excreted easily. The major routes of excretion for chemicals from drinking-water are through the kidney and biliary system (liver) although some excretion may also occur through the lungs, gastro-intestinal tract, milk, sweat and saliva.

Local toxic effects may be produced when a material comes into contact with a body surface. Systemic effects occur when material is absorbed from a contaminated site and is disseminated by the circulatory system to cause toxic injury in various organs and tissues far from the site of primary contamination. Systemic effects may be produced by the parent material that is absorbed, or by conversion products following absorption. They may be restricted to one organ or tissue system, or affect multiple organs and tissues. Many materials may cause both local and systemic toxicity.

Health effects caused by exposure to toxic chemicals are generally classified in the following categories: organ-specific; neurological/behavioural; reproductive/developmental/teratological; carcinogenic/mutagenic. Effects may be prolonged or short-term, reversible or irreversible, immediate or delayed, single or multiple.

Toxic chemicals fall into two categories:

- all non-carcinogenic compounds and a number of carcinogenic compounds where the effects are observed only above a certain threshold dose with no effects observed below this threshold
- genotoxic carcinogens that do not appear to have a threshold for toxic effects to occur.

A different approach is used for the derivation of the MAV depending on the category in which the chemical is placed.

The International Agency for Research on Cancer (IARC) has classified a large number of compounds according to their carcinogenicity to humans. WHO has evaluated each compound that has been shown to be a carcinogen on a case-by-case basis and the reasoning behind their classification and derivation of the MAV for the carcinogens is given in section 10.2.5.2.

MAF (2006) states that WHO has yet to resolve how to deal with the impact of mixtures of pesticides in drinking-water on human health (see section 10.2.5.3 for developments). Groundwater surveys in New Zealand have revealed that most contamination occurs as mixtures, such as a range of triazine herbicides, whereas most toxicity and exposure assessments are based on controlled experiments with only one contaminant. The European Commission (EC) produced a non-specific guideline for pesticides in drinking water of 0.0001 mg/L per pesticide and 0.0005 mg/L for the total of pesticide residues in a sample (EC Directive 80/778, 1980), but the standard for total pesticides was not based on toxicological studies.

Another uncertainty is that most water monitoring programmes do not include pesticide degradation products, some of which are equally toxic or even more toxic and also more polar, thus more mobile than the corresponding parent compounds. However, there are generally no established standards for metabolites, even though metabolites may have similar effects to their parent compounds (MAF 2006).

MAF (2006) added that an emerging concern is the interference of some chemicals with endocrine systems. Some of the most frequently detected pesticides (simazine and atrazine) are suspected endocrine disruptors. At present this issue is controversial. This, and the matters mentioned above, will probably be addressed by the WHO, and therefore the DWSNZ, in the future.

The World Health Organization keeps up to date with emerging issues, publishing peer-reviewed reports which are available from the internet; the topic of pharmaceuticals in drinking water is a recent example (WHO 2011a). An important observation was that raw sewage and wastewater effluents are a major source of pharmaceuticals found in surface waters. Keep up to date on emerging issues by looking at www.who.int/water_sanitation_health

WRF (2015a) reviewed the literature associating bladder cancer with chlorination disinfection by-products.

10.2.5 Derivation of MAVs for chemicals of health significance

The MAVs for most of the chemical determinands included in the DWSNZ have been adapted from the assessments of the toxicity of drinking-water contaminants published in the *Guidelines for Drinking-Water Quality* (WHO 2004a) and subsequent rolling revisions, see section 1.6.2 of these Guidelines. The information in the sections describing the derivation of the MAVs (sections 10.2.5.1 and 10.2.5.2) has been taken from this source. WHO has used published reports from the open peer reviewed literature, information submitted by governments and other parties, and unpublished proprietary data to develop the guidelines. WHO has used expert judgement to select the most suitable experimental animal study on which to base the extrapolation and the derivation of each of their guideline values.

Toxicity testing identifies toxicants by their biological activity and/or their effect on biological systems. Toxicity can be tested at the cellular level with *in vitro* bioassays, and in whole organisms with *in vivo* bioassays. If testing demonstrates that toxicity is possible, an epidemiological study of the exposed population may be warranted to check whether the contaminant has resulted in human health effects. Although epidemiology is a more relevant measure of human health than *in vitro* and *in vivo* testing, designing and conducting these types of studies for detecting the effect of drinking-water on human health can be both challenging and time-consuming.

A fundamental principle of toxicology is that, for a chemical administered to a genetically homogeneous population of animals from the same species, the proportion exhibiting a particular toxic effect will increase as the dose increases. For many toxic effects, except genotoxic carcinogens, there is a dose below which no effect or response can be elicited, referred to as the 'threshold dose'. The threshold concept, a corollary of the dose-response relationship, is important. It implies that it is possible to determine a 'no observed effect level' (NOEL), which can be used as the basis for assigning 'safe levels' for exposure.

The basis of the derivation of the MAVs is information on the health effects resulting from exposure to the chemicals. Such information comes from studies on human populations or on laboratory animals. Toxicity studies using animals are most commonly used but their value is generally limited due to the relatively small number of animals used, the relatively high doses administered and the need to extrapolate the results of these studies to human populations subject to low doses. Epidemiological studies, studies of health effects following exposure to chemicals on human populations, are available less often and are sometimes of reduced value because of the lack of quantitative information on the concentrations to which the people have been exposed or to what else the populations have been simultaneously exposed.

10.2.5.1 Derivation of MAVs based on a tolerable daily intake approach

For most kinds of toxicity, it is generally believed that there is a dose below which no adverse effects will occur. The MAVs for the determinands that are non-carcinogenic or non-genotoxic carcinogens have been calculated on the basis of a tolerable daily intake (TDI) approach. This is also called an acceptable daily intake (ADI).

The overall process for deriving the MAVs is presented in the following sections. Information has been assessed to select the most suitable study to use as the basis for choosing a NOAEL (no observed adverse effects level) or, if that is not available, a LOAEL (lowest observable adverse effect level). Sometimes the literature refers to the NOEL (no observed effects level). This value is divided by an uncertainty factor (UF) reflecting the level of uncertainty associated with the NOAEL or LOAEL to determine a tolerable daily intake (TDI). The MAV is determined by multiplying this value by the average weight of a person (BW) and by the proportion (P) of the TDI that a person is likely to ingest in drinking-water, and by dividing by the average volume of water that a person will drink during one day (C). Definitions appear at the end of section 10.2.5.1.

$$\text{TDI} = \frac{\text{NOAEL (LOAEL)}}{\text{UF}} \text{ and } \text{MAV} = \frac{\text{TDI} \times \text{BW} \times \text{P}}{\text{C}}$$

In the individual datasheets the derivation of the MAV of each chemical which has been based on a TDI approach is shown as a combination of the above two equations as shown below:

$$\text{MAV} = \frac{\text{NOAEL/LOAEL} \times \text{BW} \times \text{P}}{\text{UF} \times \text{C}}$$

where:

TDI/ADI:	tolerable/acceptable daily intake (mg/kg body weight/day)
NOAEL:	no observable adverse effect level
LOAEL:	lowest observable adverse effect level
MAV:	Maximum Acceptable Value in mg/L
BW:	body weight (70 kg for adult; 10 kg for two-year old children; 10 kg calculation is used for infants for DDT + isomers and 5 kg is used for lead and short-term nitrite)
P:	proportion of tolerable daily intake attributable to drinking-water
C:	the average volume of water consumed per day (adults two litres; children one litre; infant 0.75 litre)
UF:	uncertainty factor

In general MAVs calculated by the above equation have been rounded to one significant figure using the following rules:

- if the second and third significant figures were between 01 and 50 inclusive the MAV was rounded down
- if the second and third significant figures were >50 the MAV was rounded up.

Calculation of MAVs

For non-carcinogenic and non-genotoxic carcinogens, the TDI approach is used to calculate the MAVs. TDIs are regarded as representing a tolerable intake for a lifetime. In summary, this involves:

- 1 a no observed adverse effects level (NOAEL) or lowest observed adverse effects level (LOAEL) is obtained from animal or human studies
- 2 the uncertainty factor (UF) associated with the NOAEL or LOAEL is selected. Most lie between 100–1000
- 3 the TDI equals the NOAEL (or LOAEL) divided by the UF, the units being mg per kg of body weight per day
- 4 the MAV equals the TDI times body weight times the proportion of the TDI that comes from drinking water, divided by the volume drunk.

There are exceptions to this approach, such as nitrate. The primary health concern regarding nitrate and nitrite is the formation of methaemoglobinaemia, so-called blue-baby syndrome. The derivation is based on epidemiological studies, methaemoglobinaemia was not reported in infants in areas where drinking-water consistently contained less than 50 mg of nitrate per litre; see datasheet for further information. Nitrate is reduced to nitrite in the stomach of infants, and nitrite is able to oxidise haemoglobin (Hb) to methaemoglobin (metHb), which is unable to transport oxygen around the body. WHO (2004a) concluded that extensive epidemiological data support the current guideline value for nitrate-nitrogen of 10 mg/litre, but stated that this value should be expressed not on the basis of nitrate-nitrogen but on the basis of nitrate itself, which is the chemical entity of concern to health.

The calculations showing the derivation of the MAVs are included on the datasheets.

Definition of terms

Toxicity studies

Acute toxicity studies evaluate single-dose effects. Sub-chronic toxicity studies evaluate short-term, repeat-dose effects. Chronic toxicity studies evaluate long-term, repeat-dose effects, often covering the lifespan of the test animal. Reproductive toxicity studies are designed to provide general information about the effects of a test substance on reproductive performance in both male and female animals (this includes teratogenicity studies which cover the adverse effects on the developing embryo and foetus). Developmental toxicity studies examine the spectrum of possible in-utero outcomes. Genotoxicity studies are designed to determine whether test chemicals can perturb genetic material to cause gene or chromosome mutations. Carcinogenic studies observe test animals for a major portion of their lifespan for neoplastic lesions during or after exposure to various doses of a test substance by an appropriate route.

Tolerable daily intake

The TDI is an estimate of the amount of a substance in food and drinking-water, expressed on a body weight basis (mg/kg or mg/kg of body weight) that can be ingested on a daily basis over a lifetime without appreciable health risk, that is, TDI is an assessment of chronic effects. The TDI is based on the lowest NOAEL obtained in studies on the most sensitive species.

As TDIs are regarded as representing a tolerable intake for a lifetime, they are not so precise that they cannot be exceeded for short periods of time. A short-term exposure to levels exceeding the TDI (within reason) is not a cause for concern provided the individual's intake averaged over longer periods of time does not appreciably exceed the level set. The large uncertainty factors generally involved in establishing a TDI serve to provide assurance that exposure exceeding the TDI for short periods is unlikely to have any deleterious effects upon health. However, consideration should be given to any acute toxic effects that may occur if the TDI is substantially exceeded for short periods of time. See section 10.2.5.4 for a discussion on short-term exposure limits.

ADI refers to the acceptable daily intake and means the same as TDI.

Chronic reference dose (cRfD)

The USEPA defines chronic reference dose (cRfD or sometimes just RfD) as 'an estimate, with uncertainty spanning perhaps an order of magnitude, of a daily oral exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects (other than cancer) during a lifetime'. If the value is adjusted due to a sensitive sector of the population, it is called population adjusted dose (PAD). This chronic reference dose would appear to be the same as tolerable/acceptable daily intake (TDI/ADI).

Acute reference dose (ARfD)

The acute reference dose or ARfD (an expression used by the USEPA and more recently the WHO) is the maximum quantity of an agricultural or other chemical that can safely be consumed as a single, isolated, event.² The ARfD is derived from the lowest single or short-term dose which causes no effect in the most sensitive species of experimental animal tested, together with a safety factor which reflects the quality of the toxicological database and takes into account the variability in responses between species and individuals.

Drinking water equivalent level (DWEL)

The USEPA also uses the concept of drinking water equivalent level or DWEL, which is defined as 'a lifetime exposure concentration protective of adverse, non-cancer health effects that assumes all of the exposure to a contaminant is from the drinking water'.

² Note some definitions use 'a day' instead of 'single event'. See section 10.2.5.4 for further discussion.

Human Health Benchmarks for Pesticides (HHBPs)

The USEPA (in 2012) developed the concept of Human Health Benchmarks for Pesticides (HHBPs); acute or one-day HHBPs, chronic or lifetime (non-cancer) HHBPs, and carcinogenic HHBPs. HHBPs are the concentrations in water at or below which adverse health effects are not anticipated from one-day or lifetime exposures. Chronic HHBPs are similar to our MAVs. Acute or one-day HHBPs are in essence, short-term MAVs. See <http://iaspub.epa.gov/apex/pesticides/f?p=HHBP:home> and <http://www.epa.gov/sites/production/files/2015-10/documents/hh-benchmarks-techdoc.pdf>

Minimal risk levels (MRLs)

The US Department of Health and Human Services, Agency for Toxic Substances & Disease Registry (ATSDR: latest Oct 2015) has developed minimal risk levels (MRLs) which are similar to the USEPA's reference dose (RfD), ie, an estimate of the daily human exposure to a hazardous substance that is likely to be without appreciable risk of adverse non-cancer health effects over a specified duration of exposure. ATSDR uses the no observed adverse effect level/uncertainty factor (NOAEL/UF) approach to derive MRLs for hazardous substances. They are set below levels that, based on current information, might cause adverse health effects in the people most sensitive to such substance induced effects. MRLs are derived for acute (1 to 14 days), intermediate (15 to 364 days), and chronic (365 days and longer) exposure durations, and for the oral and inhalation routes of exposure.

No observed adverse effect level (NOAEL) and lowest observed adverse effect level (LOAEL)

The NOAEL is defined as the highest dose level or concentration of a chemical in a single study, found by experiment or observation, which causes no detectable adverse health effect. If a NOAEL is not available, a LOAEL may be used to derive the MAV. The LOAEL is the lowest dose or concentration of a chemical in a single study, found by experiment or observation that causes a detectable adverse health effect.

Some studies record the largest dose at which no effects are observed is identified. This dose level is called the 'No observable effect level', or NOEL.

Uncertainty factors

Uncertainty factors are used to correct both the NOAEL and LOAEL for the uncertainties intrinsic to extrapolation between animal studies and human populations or from a small human group to the general population. In the derivation of their drinking-water guidelines, WHO has applied uncertainty factors to the NOAEL or LOAEL selected using the approach outlined below:

Source of uncertainty	Factor
Interspecies variation (animals to human)	1–10
Intraspecies variation (individual variations)	1–10
Adequacy of studies or database	10
Nature and severity of effect	1–10

The datasheets for the chemical contaminants explain the reason for the selection of the uncertainty factor for each compound. The method of computation of MAVs from NOAELs and LOAELs has to allow for a number of uncertainties, including:

- the animal species on which the study was based may be less sensitive than humans
- some humans are more sensitive than others
- some animals within the species used to derive the toxicity data may be more sensitive to the effects of a chemical than the particular animals used for the tests.

If adverse effects are observed at all dose levels tested, an additional uncertainty factor is usually applied, because the NOAEL, by definition, would be lower than the LOAEL, had it been observed.

Situations where the nature and severity of effect might warrant an additional uncertainty factor include studies where the end-point was malformation of a foetus or where the end-point determining the NOAEL was directly related to possible carcinogenicity.

The uncertainty factor is determined by multiplying together the factors from each of the four sources. Typically, uncertainty factors lie between 100 and 1000. Uncertainty factors do not exceed 10,000 because the MAV would cease to have meaning as a health-effect value.

Human body weight

To calculate the MAVs it has been assumed that the average weight of a New Zealand adult is 70 kg. This is also the figure used in the *Australian Drinking-Water Guidelines* (NHMRC 2004/2011). WHO (2004a) has calculated its guideline values using an adult weight of 60 kg due to the lower adult weights commonly found in developing countries. As mentioned earlier, some MAVs are based on the effects on children, where a body weight of 10 kg has been used.

Proportion of intake from drinking-water

The intake of the compounds covered in the drinking-water standards can occur from food, air, skin absorption, pharmaceuticals and other products, as well as from drinking-water. Therefore it is necessary to determine what proportion of the total human intake is likely to occur as a result of consuming water.

Wherever possible, WHO used data concerning the proportion of total intake normally ingested in drinking-water (based on mean levels in food, air and drinking-water) or intakes estimated on the basis of consideration of physical and chemical properties were used in the derivation of the WHO guideline values. Where such information was not available, an arbitrary (default) value of 10 percent for drinking-water was used. This default value is, in most cases, sufficient to account for additional routes of intake (ie, inhalation and dermal absorption) of contaminants in water.

Volume of drinking-water consumed

An assumed water intake of two litres per day for adults is commonly used by WHO and regulators in computing drinking-water guidelines and standards. WHO (2003) reviewed water consumption and hydration needs under a variety of conditions, retaining the two litres per day. Physical exertion, especially in extreme heat, can significantly increase water requirements. Sweat rates can reach 3–4 L/h, with variations in rate depending upon work/exercise intensity and duration, age, sex, lactation/pregnancy, training and conditioning, heat acclimatisation, air temperature, humidity, wind velocity, cloud cover and, clothing. The 2 L/d consumption rate is considered appropriate for New Zealand conditions.

Recent material from Australia discusses many of the above points: *Environmental Health Risk Assessment: Guidelines for assessing human health risks from environmental hazards (EnHealth 2012 update)*.

[http://www.health.gov.au/internet/main/publishing.nsf/content/804F8795BABFB1C7CA256F1900045479/\\$File/DoHA-EHRA-120910.pdf](http://www.health.gov.au/internet/main/publishing.nsf/content/804F8795BABFB1C7CA256F1900045479/$File/DoHA-EHRA-120910.pdf)

10.2.5.2 Derivation of MAVs for potentially carcinogenic compounds

The International Agency for Research on Cancer (IARC) has evaluated available evidence to classify chemical substances with respect to their potential carcinogenic risk to humans into the following groups:

- Group 1: the agent is carcinogenic to humans
- Group 2A: the agent is probably carcinogenic to humans
- Group 2B: the agent is possibly carcinogenic to humans
- Group 3: the agent is not classifiable as to its carcinogenicity to humans
- Group 4: the agent is probably not carcinogenic to humans.

The International Agency for Research on Cancer (IARC) is part of the World Health Organization. IARC's mission is to coordinate and conduct research on the causes of human cancer, the mechanisms of carcinogenesis, and to develop scientific strategies for cancer prevention and control. The Agency is involved in both epidemiological and laboratory research and disseminates scientific information through publications, meetings, courses, and fellowships.

A more detailed description of these classifications is presented in the IARC classification near the end of this subsection, and any other available information was taken into consideration in establishing the WHO drinking-water guidelines.

It is generally considered that the initiating event in the process of chemical carcinogenesis is the mutation in the genetic material (DNA) of somatic cells (ie, cells other than ova and sperm). Because the genotoxic mechanism theoretically does not have a threshold, there is a probability of harm at any level of exposure. Therefore the use of a threshold approach (see section 10.2.5) is considered inappropriate and mathematical low-dose risk extrapolation has been used. Non-threshold models assume linearity between the lowest experimentally derived dose and the zero dose.

This implies that there is a calculable probability of an adverse effect (risk) no matter how small the dose.

However, there are carcinogens that are capable of producing tumours in animals or humans without exerting genotoxic activity, but acting through an indirect mechanism. It is generally believed that a threshold dose exists for these non-genotoxic carcinogens.

Each compound that has been shown to be a carcinogen has been evaluated on a case-by-case basis, taking into account the evidence of genotoxicity, the range of species affected, and the relevance to humans of the tumours observed in experimental animals. For carcinogens for which there is convincing evidence to suggest a non-genotoxic mechanism, MAVs were calculated using the threshold approach explained in section 10.2.5.1 for the non-carcinogens.

WHO determined the guidelines for genotoxic carcinogens generally using the linearised multistage model. This model extrapolates the dose-response relationship observed at higher doses to the risk that may be associated with lower concentrations.

The IARC Classification of the Carcinogenicity of Compounds (ex IARC Monograph No. 54)

Group 1: The agent (mixture) is carcinogenic to humans. The exposure circumstance entails exposures that are carcinogenic to humans.	This category is used when there is <i>sufficient evidence</i> of carcinogenicity in humans. Exceptionally, an agent (mixture) may be placed in this category when evidence in humans is less than sufficient but there is <i>sufficient evidence</i> of carcinogenicity in experimental animals and strong evidence in exposed humans that the agent (mixture) acts through a relevant mechanism of carcinogenicity.
Group 2	This category includes agents, mixtures and exposure circumstances for which, at one extreme, the degree of carcinogenicity in humans is almost sufficient, as well as those for which, at the other extreme, there are no human data but for which there is evidence of carcinogenicity in experimental animals. Agents, mixtures, and exposure circumstances are assigned to either group 2A (probably carcinogenic to humans) or group 2B (possibly carcinogenic to humans) on the basis of epidemiological and experimental evidence of carcinogenicity and other relevant data.
Group 2A: The agent (mixture) is probably carcinogenic to humans. The exposure circumstance entails exposures that are probably carcinogenic to humans.	This category is used when there is <i>limited evidence</i> of carcinogenicity in humans and <i>sufficient evidence</i> of carcinogenicity in experimental animals. In some cases, an agent (mixture) may be classified in this category when there is <i>inadequate evidence</i> of carcinogenicity in humans and <i>sufficient evidence</i> of carcinogenicity in experimental animals and strong evidence that the carcinogenesis is mediated by a mechanism that also operates in humans. Exceptionally, an agent, mixture, or exposure circumstance may be classified in this category solely on the basis of <i>limited evidence</i> of carcinogenicity in humans.
Group 2B: The agent (mixture) is possibly carcinogenic to humans. The exposure circumstance entails exposures that are possibly carcinogenic to humans.	This category is used for agents, mixtures and exposure circumstances for which there is <i>limited evidence</i> of carcinogenicity in humans and less than <i>sufficient evidence</i> of carcinogenicity in experimental animals. It may also be used when there is <i>inadequate evidence</i> of carcinogenicity in humans but there is <i>sufficient evidence</i> of carcinogenicity in experimental animals. In some instances, an agent, mixture or exposure circumstance for which there is <i>inadequate evidence</i> of carcinogenicity in humans, but <i>limited evidence</i> of carcinogenicity in experimental animals together with supporting evidence from other relevant data may be placed in this group.

The IARC Classification of the Carcinogenicity of Compounds (ex IARC Monograph No. 54)

Group 3: The agent (mixture or exposure circumstance) is not classifiable as to its carcinogenicity to humans.	This category is used most commonly for agents, mixtures, and exposure circumstances for which the evidence of carcinogenicity is inadequate in humans and inadequate or limited in experimental animals. Exceptionally, agents (mixtures) for which the evidence of carcinogenicity is inadequate in humans but sufficient in experimental animals may be placed in this category when there is strong evidence that the mechanism of carcinogenicity in experimental animals does not operate in humans. Agents, mixtures and exposure circumstances that do not fall into any other group are also placed in this category.
Group 4: The agent (mixture) is probably not carcinogenic to humans.	This category is used for agents or mixtures for which there is <i>evidence suggesting lack of carcinogenicity</i> in humans and in experimental animals. In some instances, agents or mixtures for which there is <i>inadequate evidence</i> of carcinogenicity in humans but <i>evidence suggesting lack of carcinogenicity</i> in experimental animals, consistently and strongly supported by a broad range of other relevant data, may be classified in this group.

A number of uncertainties are involved in this type of derivation. The models used are conservative and tend to overestimate rather than underestimate the risk, thus providing a greater degree of protection. The MAVs selected for most genotoxic carcinogens are associated with an estimated excess lifetime cancer risk of 10^{-5} . This means there is a risk of one additional cancer per 100,000 people ingesting drinking-water containing the substance at the same concentration as the MAV for 70 years. Concentrations associated with estimated excess lifetime cancer risks of 10^{-4} and 10^{-6} can be calculated by multiplying and dividing, respectively, the MAV by 10.

10.2.5.3 Exposure to more than one chemical

Policy and risk management processes are primarily focused on the safety of individual chemicals. However, the general population is exposed to a wide range and number of chemicals in all media and there is growing concern around recognition of the potential for a combined adverse effect when chemicals occur together. Assessing the combined risks to human health from exposure to chemical mixtures is much more complex than for single entities. The main challenges faced by regulators are how to determine the degree to which humans are co-exposed to chemicals, what interactions may occur among these, and what specific human health impacts are associated with the chemical mixtures.

There are no generally accepted procedures for estimating the risk arising for simultaneous exposure to more than one chemical.

Groups of chemicals that may exert an additive common effect include the:

- triazine pesticides and their metabolites: atrazine, cyanazine, propazine, simazine and terbutylazine
- N-methyl carbamates pesticides: aldicarb, bendiocarb, carbaryl, carbofuran, formetanate, methiocarb, methomyl, oxamyl, pirimicarb and propoxur
- large chemical groups such as the dioxins, PCBs, PAHs, groups of pharmaceuticals, chlorinated aromatics, microcystins, perfluorinated chemicals, and VOCs
- groups of disinfection by-products that have a similar composition or toxic effects, such as the THMs, HAAs and HANs.

WHO (2017a) discusses these issues and includes case studies for pharmaceuticals, microcystins, oestrogens, and N-methyl carbamates. These are discussed further in the datasheets.

For trihalomethanes (THMs), the WHO (Guidelines 2011) has used the approach of summing the ratios of the concentration of each determinand to its respective MAV. The THMs are bromodichloromethane, bromoform, chloroform and dibromochloromethane. If the sum of the ratios exceeds 1.0 the MAV for THMs has been exceeded. See example calculation in the trihalomethane datasheet.

This approach is generalised in section 8.2.1 of the DWSNZ to cover other groups of substances with similar health effects. Families of disinfection by-products, such as the haloacetic acids (HAAs) and haloacetonitriles (HANs) should be handled in this manner. In using this approach no individual determinand may have exceeded its MAV, but the group together may exceed the MAV of one. WHO (2011) states that the sum of the ratio approach should also be used for nitrate and nitrite; however, in reality, the concentration of nitrite in New Zealand waters is usually so low that it has little effect in the outcome.

The approach of summing the ratios only applies to those determinands with a MAV. That is despite only three of the nine potential haloacetic acids having a MAV and only two of the 10 potential haloacetonitriles having a MAV.

When a determinand is reported to be less than its limit of detection (LoD), a value equal to half the LoD should be used in the calculation. This pragmatic solution takes into account both practical and statistical considerations rather than being 'scientifically defensible'. There are three main options in doing the calculation when <LoDs (non-detects) have been reported:

- a) replacing less than LoD values with zero
- b) replacing less than LoD values with the LoD
- c) replacing less than LoD values with a figure >0 and $<LOD$.

Option a) reduces the risk of false positives and gives the water supplier the benefit of doubt

Option b) reduces the risk of false negatives and gives the consumer the benefit of doubt, and

Option c) choosing a value equal to half the LoD is a compromise between the two.

This is discussed further in the Appendix in Chapter 1 where it states that case a) above is appropriate if there are not a lot of "less thans". There is basically no solution if "less than values" predominate. A solution is offered for the intermediate situation.

Choosing a laboratory or analytical procedure with the lowest LoD will reduce the chance of these determinands becoming a P2.

10.2.5.4 Short-term exposure values (STEVs)

See section 10.2.5.1 for some definitions.

The WHO *Guidelines* (WHO 2017) discuss health-based values for use in emergencies. Section 8.7.5 includes:

Health-based values for acute and short-term exposures (called acute and short-term health-based values) can be derived for any chemicals that are used in significant quantities and are involved in an emergency, such as a spill into surface water sources. JMPR has provided guidance on the setting of acute reference doses (ARfDs) for pesticides (Solecki et al 2005). These ARfDs can be used as a basis for deriving acute health-based values for pesticides in drinking-water, and the general guidance can also be applied to derive ARfDs for other chemicals. The JMPR ARfD is usually established to cover the whole population, and must be adequate to protect the embryo or foetus from possible in utero effects. An ARfD based on developmental (embryo/foetal) effects, which applies to women of childbearing age only, may be conservative and not relevant to other population subgroups.

The ARfD can be defined as the amount of a chemical, normally expressed on a body weight basis that can be ingested in a period of 24 hours or less without appreciable health risk to the consumer. Most of the scientific concepts applicable to the setting of ADIs or TDIs for chronic exposure apply equally to the setting of ARfDs. The toxicological end-points most relevant for a single or one-day exposure should be selected. For ARfDs for pesticides, possible relevant end-points include haematotoxicity (including methaemoglobin formation), immunotoxicity, acute neurotoxicity, liver and kidney toxicity (observed in single-dose studies or early in repeated-dose studies), endocrine effects and developmental effects. The most relevant or adequate study in which these end-points have been determined (in the most sensitive species or most vulnerable subgroup) is selected, and NOAELs are established. The most relevant end-point providing the lowest NOAEL is then used in the derivation of the ARfD. Uncertainty factors are used to extrapolate from experimental animal data to the average human and to allow for variation in sensitivity within the human population. An ARfD derived in such a manner can then be used to establish an acute health-based value by allocating 100 percent of the ARfD to drinking-water, as follows:

$$\text{acute health-based value} = \text{ARfD} \times \text{Rfbw} \times \text{D} \times \text{C}$$

where:

- bw = body weight (60 kg for adult, 10 kg for children, 5 kg for infants)
- P = fraction of the ARfD allocated to drinking-water (100%)
- C = daily drinking-water consumption (2 L for adults, 1 L for children, 0.75 L for bottle-fed infants).

[For the common situation in New Zealand, ie, for a 70 kg adult, the STEV is ARfD x 35.]

However, available data sets do not allow the accurate evaluation of the acute toxicity for a number of compounds of interest. If appropriate single-dose or short-term data are lacking, an end-point from a repeated-dose toxicity study can be used. This is likely to be a more conservative approach, and this should be clearly stated in the health-based value derivation. When a substance has been spilt into a drinking-water source, contamination may be present for a period longer than 24 hours, but is not usually present for longer than a few days. Under these circumstances, the use of data from repeated-dose toxicity studies is appropriate to derive a short-term health-based value (using the approach outlined in section 8.2.2). As the period of exposure used in these studies will often be much longer than a few days, this, too, is likely to be a conservative approach.

Where there is a need for a rapid response, and suitable data are not available to establish an ARfD but a guideline value or health-based value is available for the chemical of concern, a pragmatic approach would be to allocate a higher proportion of the ADI or TDI to drinking-water. As the ADI or TDI is intended to be protective of lifetime exposure, small exceedances of the ADI or TDI for short periods will not be of significant concern for health. In these circumstances, it would be reasonable to allow 100 percent of the ADI or TDI to come from drinking-water for a short period.

10.2.5.5 Preparation of and response to short-term exposures

Water suppliers need to address the risks of short-term exposures in their WSPs (see Chapter 2 Management of Community Supplies, section 2.2.2 Risk health risk management plans) and contingency plans (see section 2.2.3 Contingency planning). Short-term exposure values (STEVs) and/or ARfDs are included in most of the chemical datasheets.

A chemical spill or accidental discharge may lead to MAVs or short-term limits being exceeded. Section 3.1.2 of the DWSNZ discusses major transgressions, and includes the following paragraph:

Major transgressions are serious. The water supplier must carry out the actions specified in the DWSNZ immediately, which includes informing the DWA so the DWA can help to identify the steps needed to protect consumers. In the case of a major transgression, a medical officer of health may issue a water supplier with a compliance order to take appropriate action to protect public health under section 69ZZH of the Act.

The following general checklist may assist in assessing the degree and duration of risk following a spill of a chemical determinant of health significance. The WSP needs to address the following issues if spills or accidental discharges can affect raw water.

a) The risk

- What chemicals are stored, used, discharged or transported in the catchment?
- Are the users aware of the risk caused by the chemical(s); have alternatives been considered?
- Do those responsible have adequate controls in place to minimise the risks?

- Are procedures in place for water suppliers being advised of incidents?
- Is the local HazMat Coordination Committee active?

b) The spill

- What was spilt, and where (bankside point discharge or other)?
- If to land, is groundwater also at risk?
- What volume and concentration was spilt, when, and at what rate did it discharge?
- If more than one chemical involved, are effects additive? See section 10.2.5.3.
- Does the water supplier and regional council have an appropriate contingency plan in place?

c) The source water

- Is it a lake/reservoir, stream/river, roof or groundwater source?
- Are there any tributaries between the spill and the intake?
- What are the current flow and dispersion characteristics of the source water?
- How long will the spill take to reach the intake and how long will it take to pass?
- What is the water temperature, pH, turbidity?

d) The chemical(s)

- Is it a single substance, or a mixture?
- Does the chemical have a MAV, STEV, or other health advisory such as TDI (ADI)?
- Or is it likely to give rise to taste/odour complaints?
- What is its water solubility, or does it volatilise, sink or float?
- Is it likely to adhere to particles (its K_{ow}) and is it mobile in soils?
- What are its evaporation, hydrolysis, photolysis rates in the source water?
- What are its biological uptake rates and bacterial degradation rates?
- What degradation products are formed and are they toxic?
- Which laboratories can analyse the chemicals concerned?
- How long does it take to obtain a result?

e) The treatment process

- Can the substance be prevented from entering the intake, eg, with booms or absorbents?
- Can abstraction be stopped until the chemical has passed the intake?
- Can a different abstraction point or off-river storage be used?
- How much of the chemical will be removed by the standard treatment process?
- Will it interfere with the treatment process or react with WTP chemicals?
- Can the treatment process be modified in time, eg, is activated carbon available?
- Can contaminated stored water be run to waste?

f) The distribution system

- What is the estimated concentration of the substances concerned?
- How long will it remain in the distribution system?
- What measures can be taken if the concentration or duration is excessive?

g) Need for a desk study

- Until the chemicals have been identified, assume a worst case.
- Raw and final water concentrations will vary so testing samples may not be practicable.
- Test results may not be available for a few days.
- Is a STEV or other health advisory available, or can one be calculated quickly?
- An idea of likely concentrations can be estimated by taking into account items in a) to f).

10.2.6 Plumbosolvent water

Health-significant metals, usually heavy metals, often appear in drinking-water. From 1995 to 2000, the Priority 2 Chemical Determinands Identification Programme assessed 859 distribution zones, 393 (46 percent) of which were found to contain at least one heavy metal (antimony, cadmium, copper, lead or nickel) at a concentration in excess of its MAV in the first flush of water taken from the sampling point (Nokes and Davies 2000). The metals most frequently detected were lead and nickel.

These metals are rarely present in New Zealand source waters; it is much more common for them to appear in the water as the result of dissolution of materials within the reticulation network, or from the plumbing materials used in consumers' premises. Control of metal concentrations in the water supplied to the consumers' premises is the responsibility of the water supplier, either through source water selection, the use of suitable treatment processes or changes to the materials used in the reticulation network. Metals found to be present in the *reticulated* water at potentially health-significant concentrations (greater than 50 percent of their MAV) are therefore assigned as Priority 2b determinands to the supply concerned.

Materials from which plumbing fittings are made also influence the concentrations of metals present in drinking water. This source of metals (from fittings already installed) is outside the water supplier's direct control, and heavy metal Priority 2b determinands are not assigned to supplies when the source of the metal in a tap sample is the consumer's plumbing. Instead, the water is designated as plumbosolvent, Priority 2c. Although the term plumbosolvent refers to lead, plumbosolvent waters are also likely to cause the release of other metals from plumbing materials. Elevated concentrations of metals of health concern caused by poor grade domestic plumbing, fittings or faulty installation are not covered in the DWSNZ.

Waters designated as plumbosolvent do not have to be monitored for heavy metals. However, to reduce the intake of heavy metals by consumers, the DWSNZ require consumers receiving plumbosolvent water to be advised to flush taps briefly before water is drawn for drinking or food preparation purposes (see DWSNZ section 8.2.1.4).

New Zealand's source waters are generally softer, and have lower dissolved solids content than is typical of many overseas waters. These characteristics are often associated with waters having slightly acidic pH levels and moderate to low alkalinities, and give rise to plumbosolvent drinking-waters being widespread in New Zealand. Many untreated bore waters contain carbon dioxide, which also causes corrosion of metallic pipes and fittings. Removal of the carbon dioxide is relatively straightforward and is not a particularly expensive treatment process (see Chapter 12) and should be considered as an appropriate remedial action in supplies where it causes corrosion of consumers' plumbing. Also, drinking-waters prepared by deionisation, distillation and reverse osmosis contain very few minerals so readily dissolve or corrode chemicals from water supply fittings.

Many factors influence the concentration of heavy metals found in a water sample. As well as the materials in contact with the water and the water's chemistry and temperature, other factors include: sample volume; surface area to volume ratio; water scour rate (velocity); standing time of water in the plumbing; and previous use of the sampling point. The combined effects of these factors can result in highly variable metal concentrations being found in a distribution zone. Limited sampling in a distribution zone may not, therefore, find evidence of corrosion despite a water being plumbosolvent.

To avoid plumbosolvent waters being overlooked, and because of the nature of source waters in New Zealand, the assumption is made in the DWSNZ that all drinking-waters are plumbosolvent, in which case, water suppliers are to follow the requirements in section 8.2.1.4 of the DWSNZ. Section 8.3.5(b) of the DWSNZ offers the option of demonstrating that the water supply is not plumbosolvent, and the procedure for this is specified in section 10.3.3 of the Guidelines.

Section 8.2.1.4 of the DWSNZ requires water suppliers servicing more than 500 people to issue a notice every six months. The notice could be a public notice in the local newspapers. A notice should also be included with the rate demand or water invoice, in which case it is recommended that landlords pass the information on to their tenants. A suggested format was sent to water suppliers on 12 December 2006, signed by the Director-General of Health. It said:

Some plumbing fittings have the potential to allow minute traces of metals to accumulate in water standing in the fittings for several hours.

Although the health risk is small, the Ministry of Health recommends that you flush a mugful of water from your drinking-water tap each morning before use to remove any metals that may have dissolved from the plumbing fittings.

We are recommending this simple precaution for all households, including those on public and private water supplies.

In 2014, the Ministry of Health stated that reference to the Director-General of Health should no longer be used on these notices as water suppliers should be taking ownership of their own compliance with the DWSNZ.

The following text may be used or adapted by water suppliers.

DRINKING WATER STANDARDS COMPLIANCE

As part of compliance with the *Drinking-water Standards for New Zealand 2005 (Revised 2008)*, the [insert name of water supplier or council] is legally required to publish the following notice.

DRINKING WATER Public Notice

Some plumbing fittings have the potential to allow minute traces of metals to accumulate in water standing in the fittings for several hours. Although the health risk is small, the Ministry of Health recommends that you flush a mugful of water from your drinking water tap each morning, before use, to remove any metals that may have dissolved from the plumbing fittings. We recommend this simple precaution for all households, including those on public and private water supplies.

[Name]

[Position title, eg, CEO water supply or council]

This notice is placed by [insert name of council or water supplier], in relation to the [insert name of water supply /water supplies in their district – select appropriate text].

Plumbosolvency is also discussed in sections 10.3.2, 10.3.3 and 10.4.2, and in the Aggressiveness datasheet (Appendix 2.4). Corrosion is discussed in section 10.3.4 of the Guidelines.

Flushing taps

Taps, and the fittings connecting them to the internal reticulation system of a house, appear to be the primary sources of the heavy metals lead, nickel and cadmium. The materials used in the remainder of the pipework in the dwelling generally contribute little to the concentrations of these metals in the water. As a result, water that has stood in the taps is likely to contain higher concentrations of lead, nickel and cadmium than water that has stood in the pipes. Where copper pipes are used, the situation is different, and copper is likely to be present in water that has stood in the service pipes from the toby.

Taps and their immediate fittings contain only a small volume of water, generally in the range 50–120 mL. Because these are the main sources of heavy metals in New Zealand's drinking water, a correspondingly small flush of water is all that is required to obtain a flow of water with metal concentrations less than 50 percent of their MAV (Nokes 1999).

There are two situations in which flushing the tap may not reduce the metal concentrations to acceptable levels:

- houses in which the internal plumbing is copper. Plumbosolvent water that has been standing in contact with the copper pipes is likely to contain elevated levels of copper (ie, cuprosolvency). A small flush volume (500 mL) will therefore remove metals dissolved from the tap and immediate fittings, but the subsequent volume of water will contain the copper dissolved from the pipes. A sufficiently long flush will eventually clear water from the house pipes and should result in lower metal concentrations, but flushing this volume may be impracticable in large buildings or dwellings on back sections. A dripping cold tap can often indicate corroding copper systems by the blue stain on baths and basins.

Concerns about copper in these situations are usually less than those for other metals because the MAV for copper is much higher than those of the other corrosion-derived metals. Instances of copper concentrations exceeding 50 percent of its MAV consequently occur less frequently than for other metals. However, there are situations where corrosion of copper tubing has resulted in health effects. Brodlo et al (2005) reported a case in an Australian school where several pupils became ill. Copper concentrations in the range of 6–43 mg/L were found in the initial response sampling. Copper levels fell to 1–3 mg/L after remedial action, with no further illness

- houses supplied by rainwater. In these systems, unless care has been taken with the selection of the roof and guttering materials, all the collected rainwater may contain high concentrations of heavy metals, particularly lead. Flushing the tap may reduce the initial concentration of heavy metals, but the residual metal concentrations present in the rainwater may not be reduced further by flushing because lead could be present in all the water in the holding tank.

10.3 Monitoring programme design

10.3.1 Drinking-water Standards for New Zealand

The DWSNZ prescribe what is required to demonstrate chemical compliance for a community drinking-water supply.

Due to the large number of determinands of health significance covered by the DWSNZ, four Priority Classes have been established to ensure that resources are concentrated on likely problems, see section 3.3 in the DWSNZ and section 1.6.9 of the Guidelines. Only Priority 1 determinands (micro-organisms) and any chemical determinands specified by the Ministry of Health as Priority 2 determinands for a specific drinking-water supply need to be monitored to establish compliance with the DWSNZ. Priority 2 determinands for a supply will be notified directly to the manager of that supply and listed in the *Register of Community Drinking-Water Supplies and Suppliers* published by the Ministry of Health. Priority 2 determinands are discussed in greater detail in section 10.3.2. Supplies and zones with P2s can be found at <http://www.drinkingwater.esr.cri.nz/supplies/priority2determinands.asp>

There are three types of Priority 2 chemical determinands:

- Priority 2a Chemical determinands which could be introduced into the drinking-water supply directly by the treatment chemicals at levels potentially significant to public health (usually greater than 50 percent MAV).
- Priority 2b Chemical and radiological determinands of health significance that have been demonstrated to be in the drinking-water supply at levels potentially significant to public health (usually greater than 50 percent MAV). Cyanotoxins are also Priority 2b determinands but require special attention – see Chapter 9.
- The Priority 2b substances are divided into two further types:
- Type 1 where the concentration is unlikely to vary during distribution
 - Type 2 where the concentration may vary during distribution.
- Priority 2c Chemical determinands of health significance, usually a metal, that may appear in drinking-water, having arisen from consumers' plumbing or fittings. When the concentration of a metal in a non-flushed sample, less its concentration in a flushed sample, is more than 50 percent of the MAV, the metal is assigned Priority 2c.

Chemical compliance for Priority 2a and 2b determinands is assessed on the results of sampling carried out over a 12-month period. For chemicals that have been classed as Priority 2a and 2b determinands, the compliance criteria listed below must be met:

- samples are taken at the required sites and frequency for the determinand in question
- the sampling and analytical techniques comply with the requirements of the DWSNZ
- for determinands which are sampled either weekly or monthly, no samples can transgress the MAV during 12 months of monitoring
- where two or more determinands are present which cause similar toxicological effects, the sum of the ratios of the concentration of each determinand to its respective MAV shall not exceed one for compliance with the DWSNZ.

EXAMPLE, using nitrate and nitrite:

(MAVs: nitrate – 50 mg/L NO₃; nitrite – 3 mg/L NO₂)

if a drinking-water contains:

- 7 mg/L nitrate as N (which = 31 mg/L nitrate as NO₃), plus
 - 0.4 mg/L nitrite as N (which = 1.31 mg/L as nitrite as NO₂), then
 - the sum of the ratios = $31/50 + 1.31/3 = 1.06$ which, being greater than 1, exceeds the condition in the MAV Table, despite the concentrations of the individual chemicals each being less than their respective MAVs.
- the procedure outlined in section 8.4 of the DWSNZ *Chemical Transgressions and Remedial Action* is followed and the results and actions documented.

If the results from 12 successive months' monitoring for a Priority 2a or 2b chemical determinand are all less than 50 percent of the MAV for that determinand it is possible that the determinand in question may be relegated to Priority 3 and compliance monitoring may cease. This decision is at the discretion of the Medical Officer of Health.

The following sections explain the reasons behind the above compliance criteria and illustrate how to set up monitoring programmes and assess chemical compliance according to the DWSNZ. In addition, section 10.3.4 provides information about how and why discretionary monitoring may be carried out.

10.3.2 Priority 2a and 2b chemical determinands

The concept of Priority determinands is in the process of being changed. The DWSNZ (2008) said in section 3:

Priority 2 determinands are divided into four types: Priorities 2a, 2b, 2c and 2d.

- *Priority 2a* determinands are chemical and radiological determinands that could be introduced into the drinking-water supply by the treatment chemicals at levels potentially significant to public health (usually greater than 50 percent of the MAV).
- *Priority 2b* determinands are chemical and radiological determinands of health significance that have been demonstrated to be in the drinking-water supply at levels potentially significant to public health (usually greater than 50 percent of the MAV).

Priority 2b includes chemicals present in the raw water that may not be removed by the treatment process, any disinfection by-products, and determinands introduced into drinking-water from the distribution system other than the consumer's plumbing, or other materials present in the water when sampled under flushed protocols.

Cyanotoxins can develop rapidly in surface waters, and many treatment processes will not remove them. There is no simple relationship between their occurrence and the concentrations of the cyanobacteria that produce them. Because of this, and because they are very toxic, the monitoring requirements differ from those of most other Priority 2b chemical determinands.

- *Priority 2c* determinands are chemical determinands of health significance that may appear in consumers' drinking-water having arisen from their plumbing or fittings.

Plumbosolvent water is a category of drinking-water in which metals of health concern are generally found in the first portion of water collected from the tap but occur at a much lower concentration after flushing the tap; metals in the water after flushing are Priority 2b determinands. Priority 2c determinands are produced by the corrosion of the consumer's tap and associated fittings so that one or more metals (eg, lead, nickel, cadmium or antimony) dissolve or scour into the water. See Guidelines, sections 10.2.6, 10.3.3 and 10.4.2.

Similarly, the copper MAV may be exceeded at the consumer's tap, particularly when water containing free (aggressive) carbon dioxide causes corrosion of copper tubing.

Three types of Priority 2 chemical determinands exist.

- *Priority 2a*: Chemical determinands that could be introduced into the drinking-water supply by chemicals at the treatment plant at levels potentially significant to public health (usually greater than 50 percent of the MAV). Priority 2a does not include disinfection by-products or determinands introduced into the drinking-water from piping or other construction materials.
- *Priority 2b*: Chemical determinands, other than those introduced by the treatment chemicals, that have been demonstrated to be in the drinking-water supply at levels potentially significant to public health (usually greater than 50 percent of the MAV). Priority 2b includes determinands present in the raw water (some or all of which pass through the treatment process), disinfection by-products, cyanotoxins (see section 7) and determinands introduced into the drinking-water from the water supplier's piping or other construction materials.
- *Priority 2c*: Chemical determinands of health significance, usually a metal that may appear in tap water, having arisen from consumers' plumbing or fittings. When the concentration of a metal in a non-flushed sample, less its concentration in a flushed sample, is more than 50 percent of the MAV, the metal is assigned Priority 2c.

Priority 2c determinands arise from a property of the water supply, called 'plumbosolvency' in these standards. The DWSNZ do not cover elevated concentrations of metals of health concern caused by poor grade domestic plumbing, fittings or faulty installation.

- *Priority 2d* relate to micro-organisms.

And in section 8:

8.1.1.1 Compliance criteria for Priority 2a determinands

Compliance can be demonstrated by using the certified analysis of water treatment chemicals and calculating whether any determinands are Priority 2a.

Expand in 10.3.1

8.1.1.2 Compliance criteria for Priority 2b determinands

Priority 2b determinands comprise two types.

- *Type 1*: substances whose concentration is unlikely to vary in the distribution system.
- *Type 2*: substances whose concentration may vary in the distribution system.

The Ministry of Health's Priority 2a and 2b Chemical Determinands Identification Programme (Priority 2 Programme) identifies Priority 2a and 2b chemical determinands in drinking-water supplies serving more than 100 people. Samples are taken under worst-case conditions, and only one test result exceeding 50 percent of a determinand's MAV is sufficient for a recommendation to be made for a Priority 2a or 2b assignment. These two policies are intended to compensate to some degree for the limited number of samples that can be taken from a water supply during its assessment.

The assignment of a Priority 2a or 2b determinand to a water supply does not imply that the Priority 2 programme has determined that the determinand will always exceed 50 percent of its MAV. The purpose of the programme is to identify determinands that may be present at potentially health-significant concentrations. It is the task of the compliance monitoring programme (required for Priority 2a and 2b determinands) undertaken by the water supplier to establish, more reliably than the Priority 2 programme is able, the levels at which the determinand is present in the water. The *Annual Review of Drinking-water Quality in New Zealand* has shown that the results of compliance monitoring in 2003 supported the assignments made through the Priority 2 programme (ie, at least one sample taken exceeded 50 percent of its MAV) in approximately 57 percent of monitored supplies.

Three pieces of information are required as the starting point for the design of a compliance monitoring programme:

- the identity of the determinands that must be monitored
- the site at which samples must be taken
- the frequency with which samples must be taken.

For a particular supply, the Ministry of Health will use all the relevant data available to identify the Priority 2a and 2b chemical determinands that have to be monitored. Water supply owners will be notified of the determinands from Tables 2.2 and 2.3 in the DWSNZ that are classified as Priority 2 for their supply by the Ministry of Health by letter through the District Health Board. The assignments will also be published in the *Register of Community Drinking-Water Supplies in New Zealand*. Compliance monitoring of Priority 2a and 2b determinands must start from the date of notification, not with the date of publication in the *Register*.

For all compliance monitoring, the drinking-water assessor must approve the monitoring programme planned by the supplier. It is also advisable for approval to be obtained if a water supplier wishes to collect data to challenge a Priority 2a or 2b determinand assignment proposed by the Ministry of Health.

To challenge a proposed assignment, a water supplier needs to support their case with monitoring data that have been collected using the same protocols as required for compliance monitoring. The results of tests carried out by the Priority 2 programme can provide the water supplier with an unofficial indication of the likely assignments the Ministry of Health will propose. A copy of the test report should be provided to the water supplier by the district health board about four weeks after the sample is taken. Any determinand identified in this report as exceeding 50 percent of its MAV will be recommended to the Ministry for assignment as a Priority 2a or 2b determinand, unless there are extenuating circumstances. Therefore, if the water supplier considers that the

result from the Priority 2 programme test is not representative of the water quality, or the supplier takes steps to reduce the determinand's concentration, a monitoring programme, approved by the drinking-water assessor, should be carried out to support their challenge to the assignation when it is proposed.

Undertaking this discretionary monitoring, if it shows the target determinand's concentration is less than 50 percent of its MAV in all samples, has the advantage for the water supplier of avoiding publication of the determinand as a P2 determinand for the supply.

The source of the determinand and the likelihood of its concentration changing within the distribution system establish the appropriate sampling locations. Selection of the sampling sites for Priority 2a and 2b determinands should be carried out in accordance with Table 8.1 and Tables A2.1 to A2.4 in the DWSNZ. The sampling location for all Priority 2a determinands is, as set out in Table 8.1 in the DWSNZ, always the finished water leaving the treatment plant.

Table 8.1 in the DWSNZ indicates that samples for monitoring Priority 2b determinands are taken from the water leaving the treatment plant, or from the distribution zone. Sampling from the water leaving the treatment plant is adequate for the Priority 2b, Type 1 determinands because their concentrations are not expected to change during distribution. It is permissible to sample these determinands from the distribution zone, if this is more convenient. Priority 2b, Type 2 determinands, on the other hand, must be taken from the distribution zone because they are likely to change during distribution.

Tables A2.1 to A2.4 can be used to determine whether a determinand is a Priority 2b, Type 1 or Type 2 determinand. The Sampling Location column is subdivided into two sub-columns headed TW – treated water, and DZ – distribution zone. A tick only in the DZ column indicates that the sample must be taken from the distribution zone because the concentration of that determinand may change during distribution (Type 2). Ticks in both columns indicate that samples may be taken either from the water leaving the treatment plant or in the distribution zone because the concentration of the determinand does not change in the distribution system (Type 1).

The last of the three pieces of information needed to design a monitoring programme is the frequency of sampling. The sampling frequency for Priority 2a determinands depends on the determinand in question. All Priority 2a chemical determinands must be monitored at least monthly except for fluoride and chlorine. Fluoride must be monitored at least weekly if the supply is fluoridated,³ and chlorine must also be monitored weekly if it is assigned as a Priority 2a determinand to the treatment plant, that is, if the concentration is likely to exceed 50 percent of the MAV. Note that if chlorine monitoring is being undertaken for bacterial compliance purposes, the frequency of monitoring required will usually be much higher; see Table 4.3a of the DWSNZ for water in the distribution system. Well-managed supplies will carry out process control monitoring at much higher frequencies than these minimum frequencies. If this is done, and the monitoring protocols meet the requirements of the DWSNZ these monitoring results can be used to demonstrate compliance.

³ Water suppliers that fluoridate may wish to refer to NZWWA (2014a and b).

All Priority 2b, Type 1 determinands must be sampled at least monthly. Although the minimum sampling frequency for Priority 2b, Type 2 determinands is monthly, it may be appropriate for additional samples to be taken to provide a better understanding of the range of concentrations of the determinand. Table 8.1 in the DWSNZ does not specifically state where samples from the distribution zone are to be taken, but fixed and random sampling sites may be used.

Fixed sites are of use when trends in the water quality with time are of interest, because other factors that may change with geographical position, such as the composition of distribution system materials, remain fixed. Changes in determinand concentrations may result from changes in source water quality, changes in the treatment processes, or changes water flows through the network.

Random sampling sites may be used in conjunction with fixed sites to gather more information about the way in which a determinand's concentration is influenced by geographical location. This will help establish how representative monitoring from the fixed sites is. Furthermore, when the geographical distribution of possible contamination sources within a reticulation network is unknown, eg, the construction materials used and their whereabouts are uncertain, random sampling will help in determining where these sources may be.

The sampling locations that will provide the most useful information for a Priority 2b, Type 2 determinand will depend on the characteristics of the supply and the determinand in question. Specific rules cannot be set down for many of the determinands. Some of the factors to take into account in selection of sampling locations and frequencies for determinands being monitored in the distribution zone are discussed below.

Once the appropriate sampling area of the distribution zone has been identified for the particular determinand, some sampling should be carried out at fixed sites so water quality trends can be followed. Further sampling at random sites may be useful to investigate:

- the effects of different reticulation materials on water quality
- the spatial and temporal effects on drinking-water quality
- how representative the selected fixed sites are.

Metals

The following discussion will assist in sample site selection for heavy metal monitoring.

- 1 **If the metal is present in the source water (Priority 2b Type 1):** The metal will be carried to all parts of the reticulation system, therefore any sampling location should be acceptable, ie, water leaving the treatment plant, or fixed or random locations in the distribution system can be used.
- 2 **If the metal arises from the reticulation network (Priority 2b Type 2):** Specific sampling locations are needed to ensure that water that has been in contact with the source of the metal is monitored, ie, fixed locations are needed.

- 3 **If the metal is found in water in buildings supplied by the reticulation network (corrosion as the result of aggressive or plumbosolvent water, Priority 2c):** two options arise for assessing the aggressiveness of the water:
- make use of a number of randomly selected buildings, because although some consumers' plumbing may be more likely to leach metals than others, this information is generally not known prior to monitoring, or
 - install standard plumbing fittings that are directly connected to the reticulation network, see section 10.3.3 of these *Guidelines*.

Disinfection by-products

Most disinfection by-products (DBPs) are not formed instantly when a water is disinfected. Slow steps in the process result in continuing formation over a period of days. Formation rates increase with temperature. The concentrations of most DBPs thus increase with time and therefore distance from the treatment plant. They can also increase after rechlorination. In general, maximum DBP concentrations will be found after service reservoirs and at the extremities of the distribution zone, as these situations are where the disinfectant will have been in contact with the water for the longest time. Note however that the haloacetic acids can biodegrade where biological activity is present and disinfectant residual levels are low or non-existent.

Samples taken at the treatment plant, or close to it, will contain the lowest disinfection by-product concentrations in the system, as the reaction time for their formation is very short. Samples taken at these points are unsatisfactory for compliance monitoring purposes.

To obtain valid information on disinfection by-product concentrations from monitoring samples it is also necessary to be certain that the chlorination system has been operational for the previous three or four days, and that satisfactory chlorine residuals have been maintained at the extremities of the zone.

DBP concentrations are related to the composition and concentration of natural organic matter in the raw water, which can be seasonal or variable. A simple technique for predicting when the maximum DBPs may occur is to monitor the raw water for UV absorbance, measured at 254 nm.

The sampling schedule for disinfection by-products must be provided to the DWA before the monitoring starts. This is to ensure that sampling is undertaken randomly with respect to the source water quality and times of good water quality cannot be selected for sampling, thereby reducing the concentrations of by-products found.

A worked example for this type of substance is given for bromodichloromethane further on in this section. See Chapter 15: Treatment Processes, Disinfection, section 15.4 for further discussion about disinfection by-products.

Substances derived from materials within the distribution system

Contaminants, such as heavy metals from pipes, gaskets or fittings, and polycyclic aromatic hydrocarbons (PAH) from coal tar-lined pipes, may be leached into the water as it travels through the reticulation network. In general, longer contact times between the water and reticulation construction materials will lead to an increase the contaminant concentration in the water.

Different construction materials may be present in different parts of the distribution zone. Knowledge of the types of material that are in contact with the water, and their locations, is necessary to evaluate the best sampling locations for specific determinands. In the absence of construction material information, randomly selected sampling locations towards the extremities of the distribution zone provide the best chance of detecting the determinands of concern. At these locations, the water is most likely to contain any available contaminants because of the length of time it has been in the network. Most local authorities should now have a reasonably accurate database describing the materials within their network.

See Chapter 16: Distribution System, section 16.2.6 for a discussion on permeation and leaching of chemicals (usually organic) from and into pipes.

Substances that precipitate and deposit within the distribution system

These include some metals, such as manganese, that may have been in a soluble form in the source water but are slowly oxidised following treatment. The oxidised form is insoluble, and in parts of the distribution system where the water flow is low, compounds of these metals may settle to form deposits within the pipes. Lime leaching from concrete lining of pipes may increase the pH of the water at the pipe-water interface, facilitating or accelerating chemical reactions. Chemicals added during water treatment may disturb the chemical equilibria in treated water. This can result in post-treatment precipitation in the distribution zone. In volcanic areas of the North Island, source water may be supersaturated with silica compounds that precipitate in the distribution.

The concentrations of these substances may vary both with time and geographical position. Their concentrations may drop in parts of the distribution system when there is the opportunity for them to settle. At other times, and in different locations, their concentration may increase due to deposits in the pipes being disturbed by increased or reversed flows.

Samples from the distribution system close to the treatment plant will provide information about the likely maximum concentrations of the substance to which consumers will be routinely exposed. If deposition of contaminants is occurring throughout the distribution system the concentrations may be lower for consumers at the far ends of the distribution. Occasionally however, when the deposits are disturbed, significantly higher concentrations than those found close to the treatment plant may arise in the water. These episodes will be hard to monitor because of their random nature, and are unlikely to fit neatly into a planned monitoring programme. Consumer complaints of black, or coloured, water may prove to be the best guide to where and

when samples for this type of substance should be collected. The purpose of compliance monitoring is not to determine the cause of such problems; the water supplier may have to undertake a separate programme to provide this information. See Chapter 18: Aesthetic Considerations for further discussion about dirty water.

Substances that are consumed as they pass through the distribution

The most common examples of this type of substance are the disinfectants, eg, chlorine. In most instances, chlorine will be monitored as part of the bacterial compliance programme, in which case the residuals present at the extremities of the reticulation are of importance. It is also possible for chlorine to be a Priority 2a determinand if it is being dosed heavily. Excesses may perhaps arise through poor dosing control, or because the poor condition of a distribution system requires high chlorine doses to maintain a satisfactory chlorine residual throughout. Where a high concentration of the disinfectant is a concern, samples should be taken from the water leaving the treatment plant.

Rechlorination may be needed in large distribution systems to ensure adequate residuals in all parts of the distribution system. In supplies where this is done, other sampling locations, in addition to those near the treatment plant, will need to be selected.

The example of chlorine is discussed more fully in a worked example later in this section.

Other substances that may be consumed in the distribution system include dissolved oxygen and nitrate (by bacteria in biofilms or corrosion build-up), and carbon dioxide (in corrosion processes).

Substances derived from the dissolution of plumbing materials in dwellings

The main class of substances in this category are the heavy metals. Copper may come from copper pipes. Taps and fittings are the source of the other metals, mostly lead and nickel. Sampling for corrosion-derived metals is discussed in sections 10.3.3 and 10.4.2, but note that metals from these sources are an indication of the aggressiveness or plumbosolvency of the water, and do not lead to the assignment of Priority 2a or 2b determinands.

Worked examples for planning a monitoring programme

The following worked examples demonstrate how information in the DWSNZ can be used to design monitoring programmes. The heading for each example states the sources of the determinand considered in that particular example rather than considering all possible sources for that determinand. Some determinands can be both Priority 2a and 2b depending on the situation.

- 1 **Acrylamide** (introduced with polyacrylamide water treatment chemicals): If acrylamide is present because of water treatment processes (Priority 2a), samples should be taken from the water leaving the treatment plant on a monthly basis.

Note that the requirement to monitor acrylamide monthly as a Priority determinand can be avoided if it can be shown by calculation that the maximum level of acrylamide in the finished water leaving the plant **cannot** exceed 50 percent of the MAV by virtue of the maximum dose rate used and the verified contaminant level in the polyacrylamide product.

- 2 **Arsenic** (source water contaminant): Arsenic is a Priority 2b Type 1 determinand because its concentration is not expected to change within the distribution zone. Table A2.1 in the DWSNZ indicates that samples for arsenic could be collected either from water leaving the treatment plant or from water in the distribution system. Where the plant feeds more than one distribution zone, monitoring would be minimised by taking one sample from the water leaving the plant rather than in each distribution zone.
- 3 **Fluoride** (dosed into the supply during treatment): The acceptable concentration range for intentionally added fluoride is 0.7–1.0 mg/L as F. The MAV for fluoride is 1.5 mg/L, and as a result, fluoridation of a supply places fluoride in the Priority 2a class. Table 8.1 in the DWSNZ requires a weekly minimum sampling frequency for fluoride with samples being taken from the water leaving the plant. This sampling frequency may be superseded by the requirements for controlling fluoride when dosed for oral health purposes; a drinking-water assessor will be able to advise on the requirements.
- 4 **Chlorine** (intentionally added during treatment): Chlorine is added to water as a treatment chemical for disinfection purposes. The two aspects to the monitoring requirements for chlorine are:
 - 1 microbiological requirements that the chlorine residual in the reticulated water is sufficient to achieve adequate inactivation of micro-organisms
 - 2 chemical compliance requirements that the concentration in the water does not exceed the MAV of 5 mg/L as chlorine.

In terms of its classification for chemical monitoring, chlorine is a Priority 2a determinand (because it is added during treatment), and it is required to be tested in the water leaving the treatment plant. Its high reactivity with other components in the water and material coating the distribution pipework results in a continuous drop in the chlorine concentration as the water passes through the reticulation network. Sampling at the treatment plant therefore provides a measure of the highest concentration to which consumers may be exposed (those living closest to the treatment plant).

Table 8.1 (DWSNZ) notes that the sampling frequency for chlorine monitoring must be at least weekly.

It is important that the monitoring requirements for chlorine as a Priority 2a determinand are not confused with those for microbiological monitoring. Chlorine monitoring for microbiological purposes must either occur at the treatment plant at the frequency given in section 4.3 (DWSNZ) or in the distribution system at the frequencies specified in section 4.4.

- 5 **Bromodichloromethane** (disinfection by-product): Bromodichloromethane is a disinfection by-product produced from the reaction of chlorine with bromide and natural organic matter in water. The reactions producing bromodichloromethane will continue in finished water after it has left the treatment plant, and as a result this substance is classified as a Priority 2b, Type 2 determinand. Tables A2.2b and 8.1 in the DWSNZ show that the determinand must be monitored in the distribution system, and that monthly sampling is required.

Like all disinfection by-products, the concentration of bromodichloromethane is likely to vary with changes in the various factors influencing its formation, such as the amount of organic matter in the water. Where possible more than the minimum of 12 monthly samples should be taken to establish better the range of concentrations that may appear in the treated water. Monthly sampling for disinfection by-products is a bare minimum if a good indication of their variability is to be gained. These additional samples may be taken from randomly selected locations, and their number should increase with the size of the distribution zone.

The monitoring programme should provide information on the maximum bromodichloromethane concentration being supplied to consumers. Maximum concentrations are likely to be present in sections of the distribution system where the water is oldest, therefore fixed monitoring sites should be positioned at the extremities of the distribution system. Sampling sites can be located at in other parts of the distribution zone if the water supplier wants information about the range of concentrations present in the zone, but it is the sites at the extremities that are required for compliance monitoring.

Change in status of a Priority 2 chemical

A determinand assigned P2 status can be reassigned a P3 status after sufficient satisfactory monitoring results. However, some further monitoring will be required to confirm that the change in concentration is permanent. See Chapter 1 (section 1.6.9), and the *Priority 2 and Priority 3 Chemical Determinands Identification Guide* produced by ESR for the Ministry in 2015, for discussion about monitoring chemicals that were once P2 but subsequently reassigned as P3.

10.3.3 Plumbosolvent water

Plumbosolvent water is called Priority 2c. Several factors can influence the concentrations of metals in water samples. These include the:

- time the water has been in contact with plumbing materials
- temperature of the water
- composition, quality, condition and age of the plumbing materials
- metal surface to water volume ratio
- volume of water recently drawn from the tap
- volume of water in the sample

- velocity of the water as it scoured the pipe/fittings
- chemistry of the water. This may include pH, the carbon dioxide content and whether this has been absorbed by passage through concrete-lined mains, and in some situations, high chloride or sulphate concentrations.

Because of this range of factors, the collection of samples from random locations throughout a distribution system makes reliable assessment of plumbosolvency difficult. As a result, the DWSNZ assumes all water supplies are plumbosolvent; see section 8.2.1.4 of the DWSNZ and section 10.2.6 of these *Guidelines* for subsequent requirements.

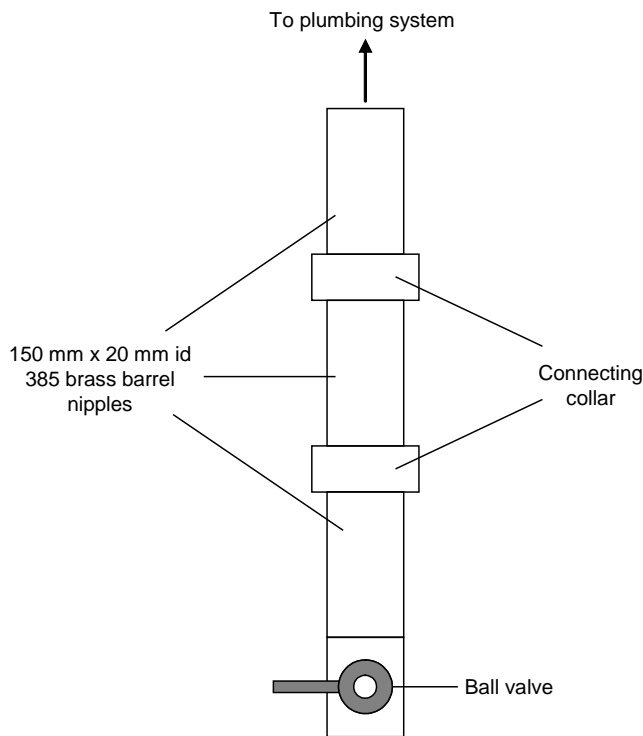
Section 8.3.5 of the DWSNZ offers a procedure for demonstrating that a water supply is not plumbosolvent. To reduce variability in results arising from differences in materials at the sampling point, this procedure requires the use of a standard plumbing fitting, fitted directly to the distribution system at a suitable central location, preferably protected, as follows.

Preparation and use of the standard plumbing fitting

A The sampling procedure is as follows.

- 1 Water that has been standing in the fitting is flushed from it by about 20 L of water being run through it or whatever volume the supplier thinks is necessary to draw fresh water free of corrosion products into the fitting. The 20 L of water is discarded.
- 2 A sample of no more than 150 mL is then taken to allow the lead concentration to be measured in water that has not been standing in the fitting (the flushed sample).
- 3 The water is then allowed to stand in the fitting for a minimum of 12 hours, preferably overnight (see point 3 under the description of the fitting below).
- 4 After the standing time, a sample of no more than 150 mL is taken directly, that is, without flushing the fitting (the unflushed sample).
- 5 The samples are collected and preserved in the manner required by the referee analysis method for lead used by the analytical laboratory or any alternative method (which must be calibrated against the referee method) used by the laboratory.
- 6 The information the water supplier provides at the end of the testing period is:
 - the lead concentration measured in each sample
 - the date and time at which the tap was flushed in preparation for the test (step 1)
 - the date and time at which the sample was taken (step 3)
 - the signatures of the people, or person, responsible for steps 1 and 3.

Figure 10.1: Standard fitting for testing plumbosolvency



B The standard plumbing fitting specification is as follows.

- 1 The brass selected for the fitting to be used is the AS/NZS 1567 C38500 alloy. This has a relatively high lead content (2.5–4.5 percent) and has been used in the manufacture of some parts of taps. The fitting is a low internal volume ball valve connected to the plumbing system by a mounting nipple of 385 brass (AS1567) having a 20 mm ID and a total internal volume of not less than 140 mL. This arrangement can be achieved by either:
 - a 450 mm length of threaded 20 mm ID 385 brass nipping tube
 - 3 x 150 mm x 20 mm ID 385 brass barrel nipples coupled together (see Figure 10.1).
- 2 The part of the fitting of importance to the test is the mounting nipple. Proof, such as a statement from the manufacturer, that it is composed of 385 alloy should be obtained.
- 3 The fitting is to be mounted inside a building, or otherwise protected against changes in temperature, to minimise temperature drops overnight.
- 4 The fitting should not be mounted close to other taps. This is to avoid the use of other taps disturbing the water standing in the mounting nipple. If this is not possible, the water should stand overnight, when water use is minimal.

C Assessment of non-plumbosolvency

For a non-plumbosolvent water to be identified, monthly pairs of samples must be collected for 12 months. Each pair consists of a sample taken without the sampling point being flushed, and the second after an extensive flush (20 L, or more if necessary). Comparison of the lead concentration in these two samples provides information about its source. An increased difference in the lead concentration points to dissolution of lead from the standard plumbing fitting. If

the difference in the lead concentration between the two samples in any flushed-unflushed sample pair taken during the 12-month monitoring period does not exceed 50 percent of the lead MAV, the water is designated as non-plumbosolvent. Section 10.4.2 covers sampling procedures in more detail.

Sampling arrangements for water supplies with more than one source water need to be discussed with the DWA.

10.3.4 Discretionary monitoring

Sections 10.3.2 and 10.3.3 discuss the monitoring of chemical determinands required to demonstrate compliance with the DWSNZ. The water supplier may also wish to obtain information on determinands of aesthetic importance because of consumer complaints, or to collect further data on determinands of health significance. Many industries need to have information about the composition of the water supply. Non-obligatory sampling of this nature is referred to as discretionary monitoring and will often include determinands that can be assigned to the Priority 3 or 4 classes.

Chemical determinands are classified as Priority 3, by default, until assessed as Priority 2 in the process of preparing the Water Safety Plan. Where a water supplier considers that a determinand may be occurring at health significant levels in the supply, but the determinand has not been classified as Priority 2, they should undertake discretionary monitoring to be more certain of the safety of the water being supplied to their consumers. Discretionary monitoring should also be undertaken where assessment by the Priority 2 Programme has resulted in a determinand being classified as Priority 3, but factors influencing the concentration of the determinand have changed since the assessment; see *Priority 2 and Priority 3 Chemical Determinands Identification Guide* produced by ESR for the Ministry in 2015.

The water supplier needs to identify the purpose of a discretionary monitoring programme so that it can be designed appropriately; this will provide a guide to determining sampling locations and frequencies. For example, a sampling programme with the aim of establishing the typical concentration range of a determinand may take samples at random locations on a regular basis. On the other hand, monitoring to establish the cause of consumer complaints should take samples at places where the problem has been found to occur and at times when it occurs.

Discretionary monitoring should be carried out for routine process control, and it may be required to investigate the cause of consumer complaints or troubleshooting water quality problems. Process control monitoring is discussed in Chapter 17. The following discussion deals with consumer complaints and troubleshooting. Aesthetic considerations are also discussed in Chapter 18.

The geographical distribution of consumer complaints is likely to act as a good guide for monitoring locations within the distribution system. Some further factors that should be considered when selecting monitoring sites for aesthetic determinands (those contained in Table A2.1 in the DWSNZ) are discussed below; refer also to Chapter 18: Aesthetic Determinands.

Corrosion

Corrosion is the deterioration of a substance (eg, water supply asset) or its properties because of a reaction with its aqueous environment. Waters that give rise to corrosion are usually called corrosive. In some instances they may also be termed plumbosolvent, as is done in the DWSNZ (see also section 10.2.6 and Datasheets 2.4: Aesthetic determinands, Aggressiveness).

The build-up of corrosion products in the distribution system or plumbing can shield bacteria from free available chlorine, give rise to coloured water, and can also reduce flow or increase pumping costs.

Not all 'corrosion processes' are electrochemical: designers must be aware that water flowing through copper tube piping systems must not exceed 3 metres per second. When this occurs there is a high risk that the internal bore of the piping system will be eroded by high flow and velocity scouring, see section 10.3.2 in WHO (2006).

DWI (2010) discusses blue water, mainly in new copper pipes in large buildings. They state that blue water is usually caused by unsuitable plumbing, for example, when excess flux or the wrong type of flux is used to join pipes and fittings. Another risk factor is when water is left to stagnate in the newly installed pipes following pressure testing and before occupation of the property. Most recorded cases relate to large public buildings or new housing estates. Blue water is not known to occur when work is undertaken by qualified plumbers and water company approved contractors who will use only approved materials and procedures.

It is known that blue water is less likely to occur if:

- minimum quantities of flux are used
- new pipes are immediately flushed very thoroughly
- water is not left to stand or get warm for long periods in new pipes
- the installation is drained down when it is not put into immediate use.

The phenomenon of corrosion is complex, and many factors affect the rate and extent to which it occurs. Some of the more readily measurable determinands that may have a bearing on the extent of corrosion occurring within a distribution system include temperature, pH, total dissolved solids, calcium, chloride, sulphate, dissolved oxygen, free available chlorine, carbon dioxide, and alkalinity.

In the past stainless steel has been used in an attempt to overcome problems arising from corrosion of copper and galvanised steel pipes, not always with an adequate understanding of the types of stainless steel available and where it can be useful. WRF (2015b) presents guidelines for the use of stainless steel in the water industry.

In the DWSNZ, the designation of a water as plumbosolvent is based on the consequences of corrosion, ie, the appearance of metals in the water that exhibit health effects. However, the **Langelier Saturation Index** (LSI) is often used as a guide to the general corrosivity of a water. The Index should be used as a guide only, and care is required in the interpretation of the results. It can be calculated from measurements of pH, alkalinity, calcium, conductivity (or dissolved solids), and temperature using Table 10.1.

Table 10.1: Data for calculating the Langelier Index

A. Total solids		B. Temperature	
mg/L	Index value	°C	Index value
50–300	0.1	0–1	2.6
400–1000	0.2	2–6	2.5
		7–9	2.4
		10–13	2.3
		14–17	2.2
		18–21	2.1
		22–27	2.0
		28–31	1.9
		32–37+	1.8
C. Calcium hardness (or calcium expressed as calcium carbonate)		D. Methyl-orange alkalinity expressed as calcium carbonate	
mg/L CaCO ₃	Index value	mg/L CaCO ₃	Index value
10–11	0.6	10–11	1.0
12–13	0.7	12–13	1.1
14–17	0.8	14–17	1.2
18–22	0.9	18–22	1.3
23–27	1.0	23–27	1.4
28–34	1.1	28–35	1.5
35–43	1.2	36–44	1.6
44–55	1.3	45–55	1.7
56–69	1.4	56–69	1.8
70–87	1.5	70–88	1.9
88–110	1.6	89–110	2.0
111–138	1.7	111–139	2.1
139–174	1.8	140–176	2.2
175–220	1.9	177–220	2.3

Table 10.1 can be used to estimate whether water will tend to deposit or dissolve calcium carbonate, by substituting the various index values into the following equation:

$$\text{Langelier Saturation Index} = \text{pH} - (\text{A} + \text{B}) + \text{C} + \text{D} - 9.3$$

The water will tend to deposit calcium carbonate if the LSI is positive and dissolve it if the LSI is negative. To avoid the unwanted effects of a strongly negative or strongly positive index, an LSI value in the range –0.5 to 0.0 is often considered desirable. For a more detailed discussion, see Chapter 17 of AWWA (1990). Many workers have attempted to refine the index, giving rise to slightly different results. An online calculator can be accessed at

<http://www.awwa.org/Resources/RTWCorrosivityCalc.cfm?navItemNumber=1576>

Many of New Zealand's drinking-waters are soft, with a low alkalinity, so the LSI will be well in excess of -2. Dosing lime into these waters to lower the LSI to < -0.5 often results in water with a $\text{pH} > 9$. This has a negative impact on some disinfection processes, and may cause aesthetic problems. Lime can be added to water without raising the pH excessively by also dosing carbon dioxide into the water.

The excellent publication by Health Canada (2009) states:

Corrosion indices should not be used to assess the effectiveness of corrosion control programs, as they provide only an indication of the tendency of calcium carbonate to dissolve or precipitate. They were traditionally used to assess whether the distributed water was aggressive towards metals and to control for corrosion. These corrosion indices were based on the premise that a thin layer of calcium carbonate on the surface of a metallic pipe controlled corrosion. Accordingly, a number of semi-empirical and empirical relationships, such as the Langelier Index, the Ryzner Index, the Aggressiveness Index, the Momentary Excess and the Calcium Carbonate Precipitation Potential, were developed to assess the calcium carbonate–bicarbonate equilibrium. However, a deposit of calcium carbonate does not form an adherent protective film on the metal surface. In light of significant empirical evidence contradicting the presumed connection between corrosion and the most common of the corrosion indices, the Langelier Index, the American Water Works Association Research Foundation recommended that the use of corrosion indices for corrosion control practices be abandoned.

The water entering the distribution system should be non-corrosive. A common cause of metallic corrosion and concrete dissolution is the presence of aggressive carbon dioxide, most commonly in groundwaters. Aggressive carbon dioxide is that portion of the free carbon dioxide not required to maintain the carbonate/bicarbonate equilibrium. Its concentration can be calculated using the nomographs in Standard Methods for the Examination of Water and Wastewater (APHA, AWWA, WEF), (4500- CO_2 , 22nd edition, 2012). A high level of carbon dioxide can strip copper from brass and some bronzes and can dissolve copper tubing. The effects of high concentrations of carbon dioxide can become apparent within a few months of commissioning a new bore water supply; it has been known to 'dissolve' pumps inside a year. A blue stain on porcelain beneath taps is a sure sign of copper corrosion. Carbon dioxide also assists in the removal of the galvanising from coated steel, initially causing quite high levels of zinc in the drinking-water, and when the coating has gone, quite high concentrations of iron.

A common form of brass corrosion is dezincification, which occurs particularly with the cheaper duplex brasses. Turner (1961) observed a relationship (Figure 10.2) between chloride and temporary hardness levels that indicated the likelihood of dezincification. Dezincification of brass fittings such as Ajax valves can interfere quite seriously with the operation of hot water cylinders, such as causing the cylinder to leak or even (rarely) rupture. Fittings are available now that are fairly resistant to dezincification.

Monitoring of metals to investigate their origin is discussed under *Metals* below, and in sections 10.2.6 and 10.3.2.

Where the source water of a supply is known to be corrosive, and treatment processes are in place to reduce the corrosiveness, process control monitoring in the treatment plant should be in place to check that water with an acceptable chemistry is being produced.

As an alternative to the Langelier Saturation Index AWWA (1990) recommends in Chapter 17 that the Larsen Ratio (LR) for waters in ferrous materials should be less than 5, where:

$$\text{LR} = \frac{\text{chloride} + 2 \times \text{sulphate}}{\text{bicarbonate}}$$

The selection of fittings used in buildings is not covered by the Health Act so generally falls outside the water supplier's control. It is covered by the Building Code. All building work in New Zealand must comply with the Building Code, even if it doesn't require a building consent. This ensures buildings are safe, healthy and durable for everyone who may use them. The Building Code clause that covers lead leaching into the potable (drinking) water is G12 Water Supplies. New building work must comply with the Building Code.

- G12.3.1 Water intended for human consumption, food preparation, utensil washing or oral hygiene must be potable.
- G12.3.2 A potable water supply system shall be –
 - (a) protected from contamination; and
 - (b) installed in a manner which avoids the likelihood of contamination within the system and the water main; and
 - (c) installed using components that will not contaminate the water.

There have been several instances in New Zealand and Australia where substandard fittings have been imported; the Master Plumbers may be able to assist with enquiries.

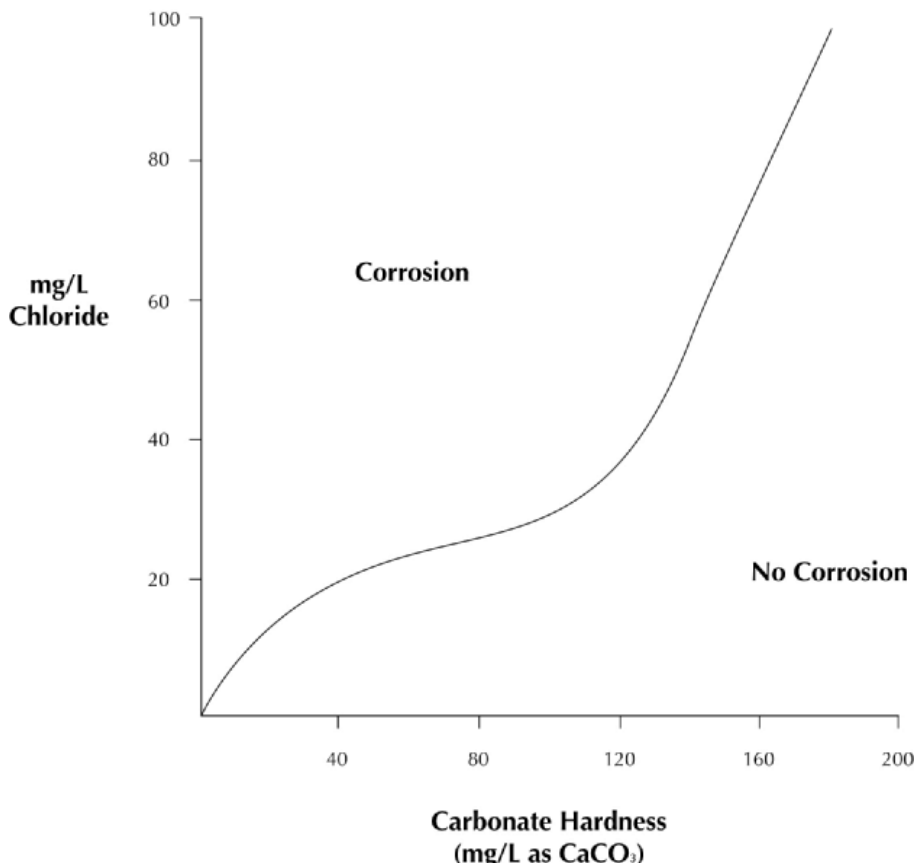
Scaling/deposit formation

Scale formation occurs most frequently from calcium carbonate or, occasionally, calcium sulphate precipitation. Silica deposition can also arise in some cases, particularly in the volcanic regions of the North Island. The tendency for a water to precipitate calcium carbonate can be estimated using the Langelier Saturation Index, which requires measurement of pH, alkalinity, calcium, conductivity and temperature. See the discussion above. Magnesium salts can precipitate out at very high pH, say over 10.

To help in interpreting results from samples taken in the reticulation, water leaving the treatment plant must be sampled. Signs of precipitation may not be evident directly after the plant, but the chemistry of the water may be such that reactions with reticulation materials in the distribution system produce water with a tendency to deposit calcium carbonate. In the event of complaints being received, monitoring sites will need to be selected in the distribution zone to determine whether the problem is spread throughout the whole system, or whether it is localised to a particular section.

Where the source water of a supply is known to be hard (high calcium which may lead to scale formation) and treatment processes are in place to reduce the hardness, process control monitoring in the treatment plant should be in place to ensure that scale-forming water is not leaving the plant.

Figure 10.2: Influence of water composition on meringue dezincification



Metals

Metals in drinking-water can cause taste and staining problems. Staining problems are usually associated with iron, copper and manganese. Taste problems are usually due to iron, copper, manganese or zinc. The metals that usually appear at the highest concentrations are iron, copper and zinc. Iron and zinc may arise from iron pipes or galvanised or brass fittings in the distribution system. Copper is more likely to arise from the corrosion of the consumer's own plumbing, although both iron and zinc may also appear in water from the dissolution of materials on the consumer's property.

When investigating the appearance of metals in drinking-water, information about the metal concentrations in the source water, after treatment, and in the water at consumers' taps is required. Samples taken from the water leaving the treatment plant establish the background levels of metals in water entering the distribution system. Where metals, such as iron or manganese, need to be removed by treatment, samples taken following treatment will show the effectiveness of the treatment process.

Metal concentrations measured in the first volume of water drawn from a consumer's tap arise from metals in the water supplied to the consumer and corrosion of the consumer's plumbing fittings. The difference between the metal concentration in unflushed water and that in a sample taken after a substantial volume of water has been flushed from the tap shows the contribution to the metal concentration made by the tap (and nearby fittings). This is discussed in section 10.2.6 and further in section 10.3.3.

High metals concentrations in water supplied to consumers, if not present in the water leaving the treatment plant, may result from corrosion of materials within the reticulation network, or the mobilisation (by sporadic high water velocities) of metals that have been gradually deposited in parts of the network over time. Consumer complaints may be helpful in locating suitable sites to understand the origins of these metals.

High dissolved solids

High levels of dissolved solids in water can lead to scaling, taste, and enhanced corrosion. High levels of calcium have already been considered under Scaling. Anions and cations that often appear at elevated concentrations in water include bicarbonate, chloride, sodium and sulphate, although only the last three have been given guideline values in the DWSNZ.

Silica can reach high concentrations in groundwater and can cause problems in some boilers.

Some treatment processes may affect the concentrations of these ions during treatment. Ion-exchange softening resins in the sodium form for removing high calcium concentrations will release high levels of sodium back into the water in exchange for the calcium removed. Although changes in the concentrations of the ions may occur as the result of treatment, their concentrations will not change during distribution. A single monitoring point where the water leaves the treatment plant will therefore be adequate for programmes designed to monitor these ions. Once it is established that the treatment processes do not significantly affect the concentrations of the ions, and that seawater intruded bores are not subject to tidal influence, the monitoring frequency need not be very high.

Treatment chemical residuals

The carryover of chemical residuals from treatment processes is a major concern for some treatment plants. Process control monitoring is the primary tool by which these residuals should be controlled. The most frequently encountered residual chemical (apart from the chlorine residual) is aluminium, which is added for coagulation purposes and which appears as either soluble aluminium, or pin flocs that have passed through the filters. Manganese (from the use of potassium permanganate) and iron (from the use of iron-based coagulants) are other possible residual substances that will be clearly evident to consumers.

The metal residuals (aluminium, iron and manganese) are best monitored at a series of locations throughout the distribution zone, because of the possibility of their concentrations changing due to precipitation and deposition. For example, aluminium may be predominantly in soluble form leaving the treatment plant, but floc formation can recur in the distribution system. Precipitation of the residual metals in the distribution system may result in the extremities typically having lower concentrations than areas of the distribution zone near the treatment plant, unless these extremities are dead-end mains. Deposits that develop in the distribution system may, from time-to-time, be disturbed by changes in water flow (the use of fire hydrants for example) and the concentrations of the metals in regions of the distribution downstream may be subjected to very high concentrations of these determinands. Regular or random monitoring will only record elevated levels of the metals caused by the disturbance of deposits by chance.

10.4 Sampling procedures and techniques

10.4.1 Chemical determinands

Monitoring programmes usually provide information on the quality of water at a particular point and at a particular time. Obtaining reliable information about the water quality relies on accurate analysis, and upon the sample being taken in a way that will provide the information needed for answering the question the monitoring intends to address.

Chapter 17: Monitoring, Water Treatment and Drinking-water discusses sampling in a general manner, and section 17.2 discusses factors influencing the day of the week for sample collection.

The two most important factors in ensuring that the composition of the water reaching the laboratory is as close as possible to that of the water when the sample was taken are correct sampling and correct preservation. Standard analytical methods provide details on sampling and preservation requirements in addition to analytical detail. The necessary sampling and preservation requirements for a determinand should therefore be obtained from the analytical method chosen. Tables A2.1–A2.4 in the DWSNZ list referee methods and some sampling information. Other analytical methods may be acceptable, see section 10.5.

Although analytical methods state the specific sampling and preservation requirements, there are good sampling practices that are generally applicable. These are discussed below.

i) Correct sampling

Correct containers are essential. The testing laboratory usually provides the containers, but at the beginning of the programme, and at any time when a new laboratory is used, a check should be made to determine what the laboratory's requirements are. The Referee Methods specify the container-type and preservative needed, but laboratories do have their own ways of meeting these requirements in terms of the volume of sample they require for each determinand.

Containers must be made of the correct material. As a rule, samples for organic determinand testing must be collected in glass bottles. Plastic containers are satisfactory to collect samples for inorganic substances and physical determinands except for chlorine, chloramines and mercury; which require glass containers.

The container must also be properly prepared, eg, acid washed, solvent rinsed. The details for each determinand will be specified in the method of analysis chosen. It must not be assumed that a sterile container prepared for microbiological sampling is satisfactory for chemical sampling, or vice versa. Sampling personnel must be made aware that the correct sample bottle must be used if valid test results are to be obtained.

Care is required when samples are taken with regard to air gaps above the sample. For chemical samples, fill all containers to eliminate air gaps. (This precaution is not necessary for all determinands, but by doing it as a matter of course sampling personnel do not have to remember the determinands for which it is important and those for which it is not.)

Leaving an air gap above the water allows volatile chemical components to move from the water into the air space, which alters the concentration of the substance in the water. This will happen with small, volatile organic compounds (ie, the trihalomethanes, and other halogenated hydrocarbons, and also carbon dioxide) whose escape from the water may significantly alter its pH.

The top of the sampling container must be removed without touching the inside of the top or the top rim of the bottle. The top should then be placed upside down in a place where it cannot be contaminated while the bottle is being filled.

Care must be taken when filling containers to avoid the loss of any preservative used. Chemical sampling containers holding preservative must not be rinsed. Bottle rinsing should not be necessary for any chemical sample, although unpreserved chemical sample containers can be refilled if necessary. Overflowing the container is permissible when the bottle contains no preservative.

After filling the container, screw the top on firmly to avoid loss of sample during transit to the laboratory.

The following notes provide advice on sampling from taps and from raw water sources.

- a) **Sampling from a tap:** Except when sampling for metals arising from corrosion (eg, lead, copper or zinc), which is discussed in section 10.4.2, 10–20 L of water should be flushed from the sampling point before collecting the sample.

- b) **Sampling from a stream, river or lake:** Loss of preservative from pre-preserved containers can be a problem when trying to obtain chemical samples from a body of water. To overcome this difficulty, use a clean, unpreserved container to fill the pre-preserved sampling bottle. Hold the unpreserved bottle by the base, facing the top of the bottle upstream. Lower the bottle to a depth of at least 30 cm. In a lake the bottle should be lowered into the water and moved slowly forward in a scooping motion to ensure that water uncontaminated by the sampler is drawn into it. Completely fill the bottle by tilting it to allow the air to escape. Fill the pre-preserved bottle from the unpreserved bottle.
- c) **Sampling from a bore:** If not in constant use, the bore should be purged for a minimum of three bore volumes to give a representative sample of source water. The sample tap should be upstream of any treatment or storage facilities.

The timing of the sampling is a very important consideration. With determinands for which preservation is available, it is desirable to minimise the time between sampling and analysis. For determinands that cannot be preserved or measured in the field, a rapid return to the laboratory and minimal delay before analysis may be crucial. Sampling personnel must therefore dispatch samples as soon as possible after sampling, and the analytical laboratory should be contacted before sampling to ensure that the scheduled arrival of the samples will permit urgent analyses to be undertaken. The arrival of samples late on a Friday afternoon may make it impossible for the laboratory to carry out urgent tests.

The timing of sampling also needs to be coordinated with the operation of the treatment plant. Sampling should be carried out when all treatments are in operation. This is especially important with regard to disinfection, which may degrade the chemical quality of the water, eg, sampling when disinfection is offline may result in atypical concentrations of disinfection by-products.

It is necessary to ensure that the results reported for a particular sampling location and date are for the water taken at that time and from that location. The following minimum information should be recorded on the sampling container:

- a) the name and code of the community
- b) the name and code of the source, treatment plant, or distribution zone sampled
- c) date of sampling.

The codes referred to in a) and b) are the Ministry of Health code tabulated in the *Register of Community Drinking-water Supplies in New Zealand*.

Sampling for metals

When sampling for metals, particularly in plumbing systems, the sample volume needs to be kept small (100–150 mL), and the extent of flushing must suit the purpose for taking the sample.

The small sample volume is necessary to ensure that the sample taken is drawn from the location of interest, and that it is not unduly affected by water from other locations, which may contain different metal concentrations. For example, if information about metal concentrations derived from a tap is needed, this information can be obtained from a small volume of the first flush water. The metal concentration found in a large

sample (eg, 1 litre) may be different from that at the point of interest, because it would contain water from further through the plumbing system where the metal concentration may be different.

The extent of flushing is important for similar reasons. The amount of water drawn from the tap before the sample is taken will influence the location from which the collected water originates: the greater the flushing, the farther away is the actual sampling location. As metals can arise from sampling points, when data on reticulated water quality are required, adequate flushing (usually more than 20 litres) is needed to avoid misleading results. Record the sampling (ie, flushing) technique used.

Sample sites and containers

It can be important to collect samples from specified parts of the water supply when monitoring P2 determinands. The type of container can be important too. Advice appears in the Appendix to this chapter.

ii) Correct preservation

For a large number of the determinands referred to in the DWSNZ, some form of preservation is required to avoid changes in their concentration after sampling. Others do not require preservation because they are physically stable, unreactive, or will not undergo microbiological conversion, while others cannot be preserved (eg, pH).

For the latter group, the delay between sampling and analysis must be kept to a minimum. Some substances in this group can be returned to the laboratory, so long as it is done rapidly. For others, although the analytical procedures in the field are less accurate than their laboratory counterparts, the field measurement can provide an approximate result of the determinand concentration before it is able to change. When samples are being transported to the laboratory, deterioration of some samples can be minimised by chilling or freezing; disinfection by-products fall into this class.

Some laboratories may despatch their sampling containers with preservatives already in them. This overcomes the difficulty of having to add a measured quantity of preservative in the field, but care must be taken to ensure that the container is not overflowed, and the preservative lost during sampling.

Preservatives are used to achieve conservation of a determinand's concentration in a number of ways, including:

- inhibition of adsorption of the determinand on the walls of the container. Acid is used to preserve metal samples to avoid this
- inhibition of microbiological conversion of the determinand. Mercuric chloride and acid preservation are used for some determinands to avoid microbiological conversion
- reduction of losses by volatilisation. Samples for ammonia are acidified to form the non-volatile ammonium ion, and samples for cyanide are preserved with caustic soda to avoid the loss of volatile hydrogen cyanide

- quenching reactions producing or removing the determinand. Disinfection by-products will continue to be formed after sample collection, if the disinfectant is not quenched, usually with a reducing agent, such as ascorbic acid, at the time of sampling.

10.4.2 Plumbosolvent water

It is assumed in the DWSNZ that all waters are plumbosolvent unless the water supplier can show otherwise. The only sampling the water supplier is required to do, if they wish to demonstrate that their water is not plumbosolvent, is that from a standard plumbing fitting. This option is offered in section 8.3.5 of the DWSNZ. Plumbosolvency is discussed also in sections 10.2.6, 10.3.2 and 10.3.3, as well as in the aggressiveness datasheet in the appendices.

The standard plumbing fitting protocol described in section 10.3.3 is designed to minimise variability in the plumbosolvency assessment by controlling a number of variables that may influence the results:

- The sample volume:** As discussed in section 10.4.1, the volume of the sample can have a strong effect on the concentration of the metal measured in the sample. A maximum sample volume of 150 mL is permitted by the DWSNZ when assessing plumbosolvency. This volume ensures the water collected is only that from the standard plumbing fitting and that there is very little influence from materials beyond the fitting that were in contact with the water.
- The contact time with the standard plumbing fitting:** A minimum contact time of 12 hours is required. This is intended to reflect the typical overnight standing time for water in the plumbing system.
- The composition of the fitting:** The brass selected for the fitting is AS 1567 C38500 alloy. This alloy has a relatively high lead content (ca 2.5–4.5 percent) and has been used in the manufacture of some parts of taps in the past. The standard fitting dimensions have been selected to provide a sample of approximately 140 mL volume that has been in contact with C38500 alloy only.

It is not the intention of the design to reflect the best composition of new taps made from low-lead alloy. The percentage of plumbing fittings in use that are composed of low lead brass will increase with time, but fittings with high lead content are still present. To protect those consumers with high-lead fittings, the plumbosolvency of water is therefore assessed with respect to the ability of the water to dissolve lead from high-lead brass.

Because lead is the corrosion-derived metal of greatest health concern, it is the degree to which lead is leached from the fitting that is used as the measure of the metal dissolving property of the water. To simplify the interpretation of results and reduce analytical costs, no other metals need to be tested using the standard plumbing fitting.

- d) **Flushing before use:** The state of the brass surface used in the standard plumbing fitting will influence the rate at which the metal is dissolved from it, and therefore the concentration of metal in the water. To reduce the variability in the nature of the surface, repeated flushing for a week before using the fitting is required. This can be done by filling the fitting, allowing it to stand for three to four hours, running the water to waste, refilling, and repeating the process. The fitting can be allowed to stand overnight, and should be flushed and refilled in the morning.
- e) **Direct connection to the distribution system:** This eliminates any uncertainties related to the composition and length of service pipe or tubing from the street to the tap, and any doubt about the age of the water if tested in high-rise buildings. Using a distribution system site instead of the water treatment plant will allow any effects from, for example, concrete lining of pipes, to be taken into account; a central site will also be more representative of the water being drunk.
- f) **Interpretation:** The water supply is non-plumbosolvent if the lead concentration in the unflushed sample, less that in the flushed sample, is less than 50 percent of the MAV, in monthly tests over a 12-month period.

Some water supplies may not cause lead to leach from fittings, yet may cause other metals, for example copper, to exceed the MAV due to corrosion of the water service. Section 8.4 of the DWSNZ discusses remedial actions when a MAV is exceeded.

10.5 Analytical details

10.5.1 Chemical determinands

The use of reliable modern instrumentation for analysis of samples should allow good analytical results to be obtained when samples can be returned to the laboratory for analysis. This should cover most chemical determinands that are required to be tested for chemical compliance. An appropriate analytical technique (see below) and laboratory (see section 10.5.2) are required.

Some comments on the methods of analysis are made in the datasheets. *Standard Methods for the Examination of Water and Wastewater* 22nd edition (APHA 2012) and manuals covering USEPA methods provide details of suitable methods of analysis. In most instances a number of suitable analytical methods for each determinand are provided in *Standard Methods*. The method of choice will depend upon such factors as cost, whether the measurements have to be made in the field, the availability of instrumentation, time lines, other determinands to be measured (multi-determinand methods may be of value), whether the determinand is to be reported as total, soluble etc, and the required sensitivity and accuracy.

Chapter 17: Monitoring Water Treatment and Drinking-water, section 17.2: Sampling; section 17.3: Monitoring for process control; section 17.4: Continuous monitoring for compliance; and section 17.5: Testing, go into this topic in more detail. This section concentrates more on chemical compliance issues. Section 18.6 discusses the analytical details for aesthetic determinands.

The discussion that follows is intended to inform those without analytical training of some aspects of testing that are important, or that are not explicitly noted in method procedures. Rather than discuss each determinand separately, the tests are grouped according to the type of measurement method used.

Field/treatment plant analyses

There are times when it is necessary for water analyses to be carried out in the field. Chlorine measurement is a good example. The high reactivity of chlorine can result in its concentration changing considerably between sampling and analysis for most waters; field measurements are therefore preferable to laboratory measurement, so long as the field measurements are reliable. Having reliable information on the chlorine residual in a water is very important, and because of this a more detailed discussion on chlorine measurement methods is provided in Chapter 15.

Another example is fluoride and pH. It is possible to measure pH and the fluoride concentration online, and this is often done to control dosage. If the monitoring system is standardised satisfactorily, these process control results can be used for compliance as well.

The detailed procedures for field analyses will be set out either in the analytical reference book from which they are taken, or in the manufacturers' instructions if a commercial test kit or on line method is being used.

Section 3.1.1 of the DWSNZ states that the DWA must assess the competence of the analyst for commonly performed treatment plant or distribution system analyses (field tests).

The pH test

The pH test is discussed in the chemical chapter because although it is an operational requirement in the DWSNZ, strictly speaking, it is a measure of the concentration of hydrogen ions. There is a datasheet for pH in the aesthetic determinands section.

Standardising the pH meter should be done at at least two pH values. This fixes one pH point and sets the slope. The first standardisation point is at or near pH 7, and the second standardisation point could be near pH 4 or pH 9–10, depending on whether the pH level of the water is typically slightly acidic or alkaline. The third pH buffer should be checked at monthly intervals. Two-point standardisation needs to be carried out daily, or each time if the electrode is not used daily; a standardisation once every week or so is insufficient. Online pH meters should be standardised following the manufacturer's instructions, or as above, whichever is the more frequent. See Appendix A2.5 in the DWSNZ.

Certified buffers can be obtained from laboratory suppliers, otherwise an analytical laboratory accredited for pH testing should be requested to prepare the necessary buffers. Buffer solutions deteriorate as a result of microbial growths so working buffers should be stored appropriately, ie, in the dark in a cool place but not in the refrigerator. Buffers should be dated when received, and should not be used after the expiry date. New buffers should be checked against the old. Details of buffer checks should be recorded.

The electrode must be treated with care and not allowed to dry out. It should be stored in tap water, or preferably a KCl solution. Buffer solutions are quite 'strong' so storing the electrode in a buffer solution can give rise to memory effects when testing water samples. Some electrodes require filling solutions to be replaced regularly. Follow the manufacturer's instructions.

The pH reading from an electrode will not come immediately to the final value and there will be a delay before a reliable reading can be obtained. Although the response of the electrode is rapid in high ionic strength solutions, such as buffers, in natural waters that contain very little dissolved matter, the response is very much slower. Ensure that the buffer has been thoroughly rinsed off the electrode before testing water samples. Meters being used for potable water require special thin glass electrodes to work properly on unbuffered waters. Robust electrodes are not suitable.

The performance of a pH electrode can degrade with age or through lack of maintenance. The drop in performance, unless extreme, is not obvious when using buffers of high ionic strength such as most of the commercial buffers used for electrode standardisation. The effect that this electrode deterioration has on the accuracy of a reading is much more marked in solutions of low ionic strength. Hence, although an electrode may appear to give satisfactory results in the high ionic strength buffers used to check the electrode's standardisation, the pH reading of the electrode in a natural water may be significantly in error. If the time taken for the electrode to equilibrate in a drinking-water sample becomes excessive, the electrode may need attention (see supplier's information sheet) or replacement.

Checks on the performance of an electrode can be performed by using a low ionic strength 'natural water' buffer prepared in the following way: Dissolve 0.084 ± 0.001 g of sodium bicarbonate, and 0.15 ± 0.01 g of potassium bromide in 1000 ± 0.5 mL of distilled water. (Discard as soon as signs of microbiological growth become evident.) This solution needs to be saturated thoroughly with air before it is used to check the electrode performance. This can be done by bubbling air through the solution, or by repeated vigorous shaking with air in a large container, renewing the air between each shaking. At 15°C the pH of this buffer should be between 8.1 and 8.2. The electrode performance is satisfactory if the pH reading from this buffer, after previously standardising the electrode using an acid buffer, lies between 8.0 and 8.3.

Fluoride: Ion selective electrode (ISE)

Fluoride measurements can be made by electrode, and some larger treatment plants may have them in use online, but because their operation is more complex than a pH probe they are more often used in laboratories.

One of the pitfalls in the use of ISE meters is the unwarranted impression of accuracy they give because of their digital display. The ease with which results can be read from the unit often result in the user thinking that the result from the meter is reliable, and the need for careful standardisation of the instrument is forgotten. The results from an ISE are only reliable if the unit has been properly standardised, and the electrode is in good condition.

Aluminium can interfere with the fluoride analysis; this can be overcome by adding CDTA to the buffer. The electrode must be treated with care and not allowed to dry out. It should be stored in distilled water, or preferably an acidic buffer. Some electrodes require filling solutions to be replaced regularly. Follow the manufacturers' instructions.

Free available chlorine

(a) Titration

Free and total available chlorine can be measured in the field by titration using the DPD/FAS titration method (APHA 4500-Cl F) although this is not very practical. APHA 4500-Cl F requires the ferrous ammonium sulphate to be standardised against potassium dichromate. If the ferrous ammonium sulphate has at least a 99 percent assay, the potassium dichromate standardisation step can be omitted. Also, it is possible to purchase a certified chemical solution, eg, 0.10 N, but note that the ferrous ammonium sulphate titrant has a life of only one month once opened. Ferrous ethylenediamine sulphate is also acceptable. See Chapter 18: Aesthetic Considerations, section 18.6, for a more extensive discussion about titrations.

If the amperometric titrator is used for compliance testing, follow the manufacturer's instructions; if they are not explicit regarding standardisation, use APHA 4500-Cl D and/or E which involves preparing and standardising a solution of phenylarsine oxide. The titrator must be standardised at least quarterly.

(b) Comparator

Free available chlorine (FAC) can be measured using portable equipment such as a comparator or Nessleriser for compliance purposes. This involves visual colour matching so the analyst and equipment must check out satisfactorily against APHA 4500-Cl F or a calibrated portable colorimeter. See Chapter 18: Aesthetic Considerations, section 18.6, for a more extensive discussion.

(c) Colorimetry

FAC can be measured in the field using a portable spectrophotometer. These instruments should be standardised at least six-monthly using the DPD/FAS titration method (APHA 4500-Cl F), see (a) Titration above. Where an instrument comes with the calibration set by the factory, it should still be sent to an accredited laboratory⁴ to determine how the reading of the instrument calibrates against the DPD/FAS method. The portable spectrophotometer must be verified to be within specification using the manufacturer's verification device, at least weekly. If it is outside specification the spectrophotometer is to be returned to the supplier for recalibration.

⁴ There are at least three laboratories accredited for this in New Zealand.

Colorimetric methods can also be used for several anions such as nitrite and nitrite, but are usually not sensitive enough for testing metals for compliance with the DWSNZ.

(d) Online monitoring

The online FAC monitor must be calibrated against either the portable spectrophotometer or amperometric titrator at least quarterly, or more often if required by the manufacturer. The calibration checks should be carried out at least in duplicate.

Referee methods

Originally, the column headed Referee Method in Tables A2.1–A2.4 of the 2005/08 DWSNZ were intended to serve as the reference method for that determinand, so that in the event of contention over an analytical result for a particular water, the result obtained by a recognised laboratory using the Referee Method would be considered to be the correct value for the purposes of determining compliance. Alternative methods could have been used for compliance testing if they had been calibrated satisfactorily against the referee method.

Referee methods first appeared in the DWSNZ in 1995 when there were several laboratories testing water samples in New Zealand, not all accredited by IANZ. Infrequent revisions of the DWSNZ mean that the concept of referee methods is too difficult to implement for chemical compliance. The procedure for the approval of new test(s) used for drinking-water sample compliance was altered in December 2010; see <http://www.health.govt.nz/publication/ministry-health-procedure-approval-new-test-methods-bacteriological-compliance-testing-drinking>.

The selection of appropriate test methods is not a function of the DWSNZ, it is part of the laboratory accreditation process. The next DWSNZ will not include referee methods for bacterial compliance testing either.

Chapter 17: Monitoring, Water Treatment and Drinking-water, section 17.5 discusses referee methods, standards and traceability from the laboratory perspective.

10.5.2 Laboratory competency

10.5.2.1 *The Register of Recognised Laboratories for Drinking-water Supplies*

For the results of monitoring programmes to be reliable, not only must a satisfactory analytical method of measurement be used, but also the laboratory performing the analysis must be competent in the use of the method. A list of water testing laboratories considered qualified to carry out this work is maintained in the Ministry of Health's *Register of Recognised Laboratories for Drinking-water Supplies*. See also Chapter 1: Introduction, section 1.6.14.

See Chapter 17 for more detail.

10.5.3 Interpretation of analytical data

The concentration of a determinand in a water sample cannot be measured exactly. Each analytical measurement contains some uncertainty that should be known to the laboratory as the result of its quality control procedures. Refer to Chapter 17 (on Monitoring), section 17.6 for a discussion on how to comparing a test result against a MAV or operational requirement.

10.6 Records and assessment of compliance

Section 13 of the DWSNZ lists the information to be recorded in order for a drinking-water supply to be assessed for compliance. The following example illustrates the information to be collected in order to assess compliance for a supply that contains Priority 2 chemical determinands. Comments included to explain the example that do not necessarily have to be provided are written in small italics.

10.6.1 Example: Records and assessment of chemical compliance for Bogus community drinking-water supply

Comment: The community of Bogus has two distribution zones, Upperbogus and Lowerbogus. These two distribution zones receive water from the Bogus treatment plant. Lowerbogus is situated in the immediate vicinity of the treatment plant whereas Upperbogus is a small satellite settlement two km from the outskirts of the Lowerbogus distribution zone.

Records

Records for the Bogus community drinking-water supply for the period 1 January 2006 to 31 December 2006.

Names and codes for supply

Name of the community, distribution zones, plant and sources that the information relates to. This information should be extracted from the Register of Community Drinking-Water Supplies in New Zealand including the register codes. If the supply is not listed in the Register then the Ministry of Health should be contacted to obtain the necessary codes.

Community:	BOG001	Bogus
Zone:	BOG001UP	Upperbogus
	BOG001LO	Lowerbogus
Plant:	TP00999	Bogus
Source:	G01531	Bogus Bore
Source:	S01223	Bogus River

Treatment processes in operation at Bogus treatment plant

On 1 January 2006	Coagulation/flocculation using alum, sedimentation, dual media filtration, pH adjustment with lime and chlorination.
On 24 April 2006	Adjusted coagulation pH to improve removal of natural organics.
On 21 September 2006	Added activated carbon to control taste and odour problems due to algae in river source.
On 14 December 2006	Stopped adding activated carbon.

Priority 2 chemical determinands

All Priority 2 chemical determinands identified for Bogus must be monitored according to the Standards for chemical compliance.

Priority 2 chemical determinands for Bogus community water supply published in the *Register of Community Drinking-Water Supplies in New Zealand* (and as notified to the supply manager):

- Upperbogus Distribution Zone (BOG001UP): arsenic, bromodichloromethane
- Lowerbogus Distribution Zone (BOG001LO): arsenic.

Monitoring programmes, results and actions taken

Monitoring of arsenic for chemical compliance

Because arsenic is a Priority 2b, Type 1 chemical determinand whose concentration should not change during distribution, it can be monitored in the water leaving the treatment plant or in the distribution zone (Table A3.1 in the DWSNZ). Therefore, the samples for arsenic were collected from the water leaving the treatment plant to prevent having to monitor the Upper- and Lowerbogus distribution zones separately. Samples were collected monthly. The MAV for arsenic is 0.01 mg/L.

Date sample collected	Sampling site	Result (mg/L)
12 January 2006	Tap in Bogus plant	0.007
17 February 2006	Tap in Bogus plant	0.005
10 March 2006	Tap in Bogus plant	0.004
15 April 2006	Tap in Bogus plant	0.003
12 May 2006	Tap in Bogus plant	0.007
14 June 2006	Tap in Bogus Plant	0.006
13 July 2006	Tap in Bogus Plant	0.005
14 August 2006	Tap in Bogus Plant	0.005
11 September 2006	Tap in Bogus Plant	0.004
13 October 2006	Tap in Bogus Plant	0.003
14 November 2006	Tap in Bogus Plant	0.004
14 December 2006	Tap in Bogus Plant	0.005

The laboratory that analysed for arsenic was Excellent Laboratory of Bogus, which is on the list of recognised laboratories held by the Ministry of Health. The method used was furnace atomic absorption spectrometry.

The MAV for arsenic was not transgressed, and therefore no corrective action was taken.

Discretionary monitoring of arsenic

The two sources used for the Bogus supply were monitored for arsenic to determine the source of the arsenic to the supply. The river was found to be the source of the arsenic (0.023 mg/L on 10 March 2006 and 0.027 mg/L on 13 July 2006). On the same dates the bore water contained <0.002 mg/L arsenic. At present the (name of supply authority) is carrying out a feasibility study to see whether it would be possible to rely exclusively, or at least predominantly on the bore source.

Monitoring of Bromodichloromethane in Upperbogus Distribution Zone for Chemical Compliance

Bromodichloromethane is a Priority 2b, Type 2 chemical determinand that should be sampled from the distribution zone for compliance purposes (Table A3.2b in the DWSNZ). It is a disinfection by-product and the fixed site that has been used to collect samples is located in Stevens Street, a cul-de-sac near at the end of the distribution system. The concentrations of bromodichloromethane are expected to be higher in Stevens Street than near the treatment plant. Samples were sometimes also collected at Matthews Road, in the centre of town and Queen Street, located near the treatment plant, to be able to compare these results with those taken at Stevens Road. Samples have to be collected monthly. The MAV for bromodichloromethane is 0.07 mg/L.

Date sample collected	Sampling site	Result (mg/L)
12 January 2006	27 Stevens Street	0.043
	14 Matthews Road	0.020
	7 Queen Street	0.012
17 February 2006	27 Stevens Street	0.052
	14 Matthews Road	0.023
	7 Queen Street	0.013
10 March 2006	27 Stevens Street	0.056
14 April 2006	27 Stevens Street	0.078
	14 Matthews Road	0.029
	7 Queen Street	0.018
20 April 2006	27 Stevens Street	0.080
27 April 2006	27 Stevens Street	0.020
3 May 2006	27 Stevens Street	0.022
	14 Matthews Road	0.012
	7 Queen Street	0.005
12 May 2006	27 Stevens Street	0.020
14 June 2006	27 Stevens Street	0.023
13 July 2006	27 Stevens Street	0.020
14 August 2006	27 Stevens Street	0.015
11 September 2006	27 Stevens Street	0.018
13 October 2006	27 Stevens Street	0.020
14 November 2006	27 Stevens Street	0.022
14 December 2006	27 Stevens Street	0.012

On 14 April 2006 the sample for bromodichloromethane transgressed its MAV of 0.07 mg/L. This was not the first time the (name of supply authority) has had trouble with bromodichloromethane and confirmed the results which resulted in it being a Priority 2 determinand for Bogus. We increased the monitoring frequency as required in the transgression section (8.4) of the DWSNZ and investigated the options available to us to reduce the level of bromodichloromethane in the Upperbogus distribution zone. In late April 2006 we adjusted the coagulation pH to improve the removal of natural organic matter and subsequent monitoring has shown that this was successful. We continued monitoring at a weekly frequency until we had three clear results and then we returned to monthly monitoring.

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Assessment of results

- A The results for arsenic in the Upperbogus and Lowerbogus distribution zones are all less than the MAV for arsenic of 0.01 mg/L. Therefore arsenic complies with the DWSNZ. Some results exceeded 50 percent MAV for arsenic (0.005 mg/L) so arsenic will remain a Priority 2 determinand and it will be necessary to continue to monitor for arsenic in this supply.
- B The concentration of bromodichloromethane exceeded the MAV of 0.07 mg/L in two samples. Corrective action remedied the situation, but for the period of 1 January 2006–31 December 2006, the supply did not comply for bromodichloromethane and therefore failed chemical compliance. The supply will need to continue to be monitored for bromodichloromethane. However, the action taken appears to have resulted in a concentration of bromodichloromethane of less than 50 percent MAV (ie, 0.035 mg/L). If these results continue for 12 successive months then bromodichloromethane can be relegated to Priority 3 by agreement with the public health agency for the Upperbogus distribution zone and will no longer need to be monitored monthly.

10.7 Response to transgressions

Refer to Appendix A1.2 in DWSNZ, and to Chapter 17 (on Monitoring), section 17.6 for a discussion on how to compare a test result against a MAV or operational requirement.

Figure 8.1 and section 8.4 of the DWSNZ provide greater flexibility with regard to what remedial actions a water supplier should take in the event of a chemical MAV transgression, than is allowed with respect to the transgression of a microbiological MAV. When a chemical transgression has occurred the water supplier is required to take appropriate action, and to inform the DWA of the cause of the transgression as soon as this is known.

Water suppliers should discuss their intended remedial action, once it has been determined, with the DWA to ensure that it is mutually regarded as being appropriate. A record must be kept of monitoring results, the actions taken and the outcomes of these actions.

The primary reasons for allowing the greater flexibility in dealing with chemical transgressions are:

- 1 chemical MAVs are almost always set to take account of chronic effects, therefore the need for a rapid response, as is required for the appearance of microbial contaminants in the water, does not exist (unless a chemical spill or similar event has resulted in a concentration that may have acute health effects)
- 2 remedial actions required to overcome chemical transgressions may require more time and resources to implement that may often be the case for microbial contamination.

The following factors, and possibly others, will influence the nature of the remedial action considered appropriate under the particular circumstances of each supply:

- a) **The cause of the transgression and the options for improving water quality:** The cause of the transgression must be determined so that possible remedial actions can be identified.
- b) **Timeframes associated with the possible remedial actions:** Once the possible remedial actions have been identified, the action that best meets the needs of the situation should be selected. In making this selection consideration has to be given to the protection of public health, and availability of resources. In judging whether a remedial action is satisfactory, the timeframe for implementation required by the nature of the remedial action needs to be taken into account.
- c) **Availability of resources and cost of possible remedial actions:** When remedial actions can be taken easily these should be implemented as soon as practicable. Improved control over an existing process, as discussed in the previous section, is an example of this type of action. After any necessary assistance has been sought, this action can be taken within a few weeks.

Actions that can be implemented quickly may not, however, achieve an adequate reduction in the determinand of concern. Under these circumstances, major capital expenditure may be required to achieve improved water quality. It is unreasonable to expect this type of remedial action to be implemented in a few weeks; time will be needed to accommodate it within budgets and for construction, or installation, to be carried out.

Remedial actions that will take time to implement can be considered as appropriate if they are introduced into the Improvements Schedule of the WSP.

- d) **Frequency at which transgressions occur:** While remedial actions requiring substantial resources might be considered if transgressions are occurring frequently, it may not be possible to justify them where infrequent transgressions that do not greatly exceed the MAV are encountered. In these cases, discussion between the supplier and the DWA is important so that action that meets public health needs and the resource limitations of the supplier can be identified.

There may be instances in which a MAV is transgressed regularly, but no effective remedial actions are available to the water supplier to reduce the concentration of the determinand in the water supply. Nitrate in groundwater may be an example of this. The source of the nitrate is likely to be linked to present, or past, activities in the catchment, over which the water supplier may have no control. In looking for appropriate remedial action, actions that protect public health without improving the water quality should not be overlooked.

Continuing with the example of nitrate, as bottle-fed infants are the primary concern, the public health risk could be greatly reduced by making certain mothers of newborn infants are made aware of the need to prepare milk from bottled water. Water supplies where nitrate exceeds the short-term MAV will need a process for advising parents of newborn children that they will need to use a different water for a few months if the baby is bottle fed. This information could be disseminated by the water supplier through organisations such as the Plunket Society, maternity hospitals, midwives and doctors. It may need to be sent out at regular intervals. The procedure should be described in the WSP.

Water suppliers' WSPs must also document planned responses to events other than failing to satisfy the criteria in the DWSNZ that will obviously lead to a chemical transgression or non-compliance. These should be rare in New Zealand, and will tend to be supply-specific. The most likely cause will be spills of wastewater or other contaminants upstream of the intake. This will require a good knowledge of the catchment activities and what substances are transported, used or stored upstream.

The USEPA (2008) has developed a manual to provide guidance to water suppliers on identifying TTHM and HAA5 peaks and conducting operational evaluations to determine the cause(s) of and reduce such peaks.

Appendix: Sampling requirements

These tables were in the 1995, 2000, 2005 and 2008 DWSNZ. They have been transferred to the Guidelines without the Referee Methods. The DWSNZ now state that laboratories can use the test methods for which they have accreditation.

The choice of sample containers is explained in texts such as "Standard Methods" (APHA, AWWA, WEF). Laboratories may specify alternative sample containers if appropriate.

The tables in the Appendix indicate which sampling site(s) are appropriate for each determinand. A tick in the distribution zone (DZ) column indicates the sample must be taken from only the distribution zone. Ticks in both the water leaving the treatment plant (TW) and DZ columns indicate the determinands may be sampled from the drinking-water at the treatment plant or in the distribution zone. The sampling location (distribution zone or treatment plant) will be identified when the Priority 2b assignment is made.

Note: Abbreviations used in the tables are explained in Table A10.6

Table A10.1: Inorganic determinands: sampling requirements

Name	Sampling location		Container
	TW	DZ	
antimony		✓	P(A), G(A)
arsenic	✓	✓	P(A), G(A)
barium	✓	✓	P(A), G(A)
boron	✓	✓	P
bromate		✓	P
cadmium		✓	P(A), G(A)
chlorate	✓	✓	P
chlorine		✓	G
chlorite		✓	P
chromium		✓	P(A), G(A)
copper		✓	P(A), G(A)
cyanide	✓	✓	P
cyanogen chloride		✓	G(S)
fluoride	✓	✓	P
lead		✓	P(A), G(A)
manganese		✓	P(A), G(A)
mercury	✓	✓	G(A)
molybdenum	✓	✓	P(A), G(A)
monochloramine		✓	G
nickel		✓	P(A), G(A)
nitrate		✓	P, G
nitrite		✓	P, G
selenium	✓	✓	P(A), G(A)
uranium	✓	✓	P(A)

Table A10.2: Cyanotoxins: sampling requirements

Name	Sampling location		Container
	TW	DZ	
anatoxin-a	✓	✓	G(S) P(S)
anatoxin-a(S)	✓	✓	G(S) P(S)
cylindrospermopsin	✓	✓	G(S) P(S)
homoanatoxin-a	✓	✓	G(S) P(S)
microcystins (expressed as MC-LR toxicity equivalents)	✓	✓	G(S) P(S)
nodularin	✓	✓	G(S) P(S)
saxitoxins (as STX-eq)	✓	✓	G(S) P(S)

Table A10.3: Organic determinands: sampling requirements

Name	Sampling location		Container
	TW	DZ	
acrylamide	✓	✓	G(S)
benzene	✓	✓	G(S)
benzo[a]pyrene		✓	G(S)
bromodichloromethane		✓	G(S)
bromoform		✓	G(S)
carbon tetrachloride		✓	G(S)
chloroform		✓	G(S)
di(2-ethylhexyl)phthalate		✓	G(S)
dibromoacetonitrile		✓	G(S)
dibromochloromethane		✓	G(S)
dichloroacetic acid		✓	G(S)
dichloroacetonitrile		✓	G(S)
1,2-dichlorobenzene		✓	G(S)
1,4-dichlorobenzene	✓	✓	G(S)
1,2-dichloroethane		✓	G(S)
1,2-dichloroethene (cis/trans)	✓	✓	G(S)
dichloromethane		✓	G(S)
1,4-dioxane	✓	✓	G(S)
EDTA	✓	✓	G(S) P(S)
epichlorohydrin	✓	✓	G(S)
ethylbenzene	✓	✓	G(S)
hexachlorobutadiene	✓	✓	G(S)
monochloroacetic acid		✓	G(S) P(S)
nitrilotriacetic acid	✓	✓	G(S)
styrene	✓	✓	G(S)
tetrachloroethene		✓	G(S)
toluene		✓	G(S)
trichloroacetic acid		✓	G(S)
trichloroethene		✓	G(S)
2,4,6-trichlorophenol		✓	G(S)
vinyl chloride		✓	G(S)
xylenes		✓	G(S)

Table A10.4: Pesticides: sampling requirements

Name	Sampling location		Container
	TW	DZ	
alachlor	✓	✓	G
aldicarb	✓	✓	G
aldrin/dieldrin	✓	✓	G
atrazine	✓	✓	G
azinphos-methyl	✓	✓	G
bromacil	✓	✓	G
carbofuran	✓	✓	G
chlordane	✓	✓	G
chlorotoluron	✓	✓	G
chlorpyrifos	✓	✓	G
cyanazine	✓	✓	G
2,4-D	✓	✓	G
2,4-DB	✓	✓	G
DDT + isomers	✓	✓	G
1,2-dibromo-3- chloropropane	✓	✓	G
1,2 dibromoethane	✓	✓	G
1,2-dichloropropane	✓	✓	G
1,3-dichloropropene	✓	✓	G
dichlorprop	✓	✓	G
dimethoate	✓	✓	G
diuron	✓	✓	G
endrin	✓	✓	G
fenoprop	✓	✓	G
hexazinone	✓	✓	G
isoproturon	✓	✓	G
lindane	✓	✓	G
MCPA	✓	✓	G
mecoprop	✓	✓	G
metalaxyl	✓	✓	G
methoxychlor	✓	✓	G
metolachlor	✓	✓	G
metribuzin	✓	✓	G
molinate	✓	✓	G
oryxalin	✓	✓	G
oxadiazon	✓	✓	G
pendimethalin	✓	✓	G
pentachlorophenol	✓	✓	G
picloram	✓	✓	G

Name	Sampling location		Container
	TW	DZ	
pirimiphos methyl	✓	✓	G
primisulphuron methyl	✓	✓	G
procymidone	✓	✓	G
propazine	✓	✓	G
pyriproxifen	✓	✓	G
simazine	✓	✓	G
2,4,5-T	✓	✓	G
terbacil	✓	✓	G
terbuthylazine	✓	✓	G
thiabendazole	✓	✓	G
triclopyr	✓	✓	G
trifluralin	✓	✓	G
1080	✓	✓	G

Table A10.5: Radiological determinands: sampling requirements

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Table A10.6: Abbreviations used in Tables A10.1–A10.4

Sample sites	
DZ	distribution zone
TW	water leaving the treatment plant
Containers	
(A)	acid washed
G	glass
P	plastic
(S)	solvent washed

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