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Quantitative chemical exposure assessment for water recycling schemes

Stuart J. Khan

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Abbreviations and acronyms

ABS	Australian Bureau of Statistics
ADWG	Australian drinking water guidelines
AES	Atomic emission spectroscopy
BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
COR	Coefficient of reliability
CSF	Cancer slope factor
DALY	Disability adjusted life year
DOC	Dissolved organic carbon
EEWTP	Potomac Estuary Experimental Water Treatment Plant
GAC	granular activated carbon
GC	gas chromatography
HPLC	High performance liquid chromatography
ICP	Inductively coupled plasma
LOAEL	Lowest observed adverse effect level
LOD	Limit of detection
LOR	Limit of reporting
LMH	Litres per square metre per hour
MS	Mass spectrometry
MTBF	Mean time between failures
MTTR	Mean time to repair
NDEA	N-nitrosodiethylamine
NDMA	N-nitrosodimethylamine
NDPA	N-nitrosodipropylamine
NHMRC	National Health and Medical Research Council
NOAEL	No observed adverse effect level
PAC	Powdered activated carbon
PCB	Polychlorinated biphenyls
PDF	Probability distribution function
PFBA	perfluorobutanoic acid
PFPeA	Perfluoropentanoic acid
PFHxA	Perfluorohexanoic acid
PFHxS	Perfluorohexane sulfonate
PFOA	Perfluorooctanoic acid
PFOS	perflluorooctane sulfonate
PMSEIC	Prime Minister’s Science, Engineering and Innovation Council

RfD	Reference dose
STP	Sewage treatment plant
TOC	Total organic carbon
US EPA	United States of America Environment Protection Authority
UV	Ultraviolet
WCRWP	Western Corridor Recycled Water Project
WWTP	Wastewater treatment plant

Units used frequently in this report

g	grams
kg	kilograms (1000 grams)
kL	kilolitres (1000 litres)
L	litres
mg	milligrams (1/1000 gram)
mL	millilitres (1/1000 litre)

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Executive summary

Treated municipal wastewater effluent is increasingly being reused for a variety of beneficial applications in Australian towns and cities. Most applications are for non-potable uses and involve a diverse range of treatment processes and water qualities. Interest in planned indirect potable water recycling has grown rapidly during the past five years. This approach is likely to become an important water management strategy for many Australian cities during the next decade.

Conventionally treated municipal wastewater effluent contains a wide variety of trace chemical contaminants, including heavy metals, synthetic industrial organic chemicals, volatile organics, pesticides or their metabolites, algal toxins, disinfection byproducts, radionuclides, pharmaceuticals, estrogenic and androgenic hormones, antiseptics, perfluorochemicals and nanoparticles. Many of these chemicals are known to be toxic to people after exposure by ingestion, inhalation or dermal adsorption.

The degree of harm that a toxic chemical may impart is a function of the level of exposure to that chemical. It follows, therefore, that risks to people from toxic chemicals are manageable by controlling the level of exposure to people by those chemicals. In order to properly manage exposure, it is necessary to be able to quantify it. This report presents information and techniques that are suitable for the quantitative assessment of exposure to chemicals in water recycling schemes.

Many of the chemicals in municipal wastewater effluent will be significantly reduced in concentration by subsequent advanced treatment processes. However, the initial concentrations and the effectiveness of treatment are highly variable parameters. As such, there is no single, universally-applicable ‘answer’ to the question of what is the concentration of a chemical in fully treated recycled water. Instead, techniques based in the establishment of probability density functions are introduced to more fully describe chemical concentrations and treatment performances in terms of variability and uncertainty.

Furthermore, many chemicals are not measureable above available analytical detection limits in fully treated recycled waters. Therefore, their concentrations must be derived from theoretical calculations. This requires a comprehensive characterisation of the performance of individual unit treatment processes and the use of these performance characterisations to model overall multiple barrier treatment schemes. However, computing sums, multiplications and other transformations on multiple probability density functions is a mathematically challenging task. As an alternative, probabilistic techniques are introduced to facilitate these mathematical manipulations and provide probability-based descriptions of final water quality.

Several exposure scenarios—including oral consumption of (recycled) drinking water, dermal adsorption, accidental ingestion while swimming, and inhalation—are considered as essential components of recycled water exposure determination. Where possible, probabilistic approaches to estimating exposure scenarios are also described.

Finally, this report discusses quantitative approaches to the important issues of hazardous events and system reliability. Risks associated with specific hazardous events are measured in terms of the *likelihood* of the hazardous event occurring and the *consequences* if it does. Therefore, quantification of risks associated with hazardous events requires the quantification of these likelihoods and consequences. Techniques such as critical component analysis will help improve future quantification of the likelihood of hazardous events. The consequences of hazardous events could be quantified in terms of their impact on increased effluent concentrations and increased exposure to hazardous contaminants. However, further work is required to quantitatively relate specific hazardous events to such consequences.

This report alone is not sufficient to be used as a comprehensive manual for quantitative risk assessment. However, it is hoped that it will provide a sufficient overview of the key issues, as well as suitable references to more detailed sources of specific information. The aim is to provide a strong starting point for understanding what can be achieved and what should be required in order to comprehensively assess chemical exposure from water recycling schemes.

1. Introduction

The purpose of this handbook is to provide guidance on some relatively specialised techniques for undertaking a comprehensive exposure assessment for chemical contaminants in recycled waters.

The handbook is intended primarily to assist proponents and operators of water reuse schemes by providing an understanding of some of the techniques available to assess and demonstrate the level of safety provided by an existing or proposed scheme. It should also be of value to regulators who are responsible for approving water reuse projects and determining the means by which safety must be demonstrated in order for scheme proponents to gain approval.

The topic of the handbook is focused squarely on chemical contaminants in water since this is an area of rapidly increasing concern in Australia and other developed countries. It is arguable that Australian water utilities and health regulators have justifiably focused their attentions on pathogenic organisms in wastewater and reclaimed water during the past few decades. While it is undeniable that pathogens still pose the greatest human health risks for most water reuse schemes, risk assessment skills and knowledge for chemical contaminants have apparently not kept pace with those for pathogens.

The need for increased research attention to the assessment of health risks associated with trace contaminants in reclaimed water has been emphasised at least since the mid-1990s [1]. Recently, increased attention to chemical contaminants—largely in response to proposals for indirect potable water recycling—has exposed significant knowledge deficits in this area.

Reusing municipal effluents for secondary applications such as irrigation, industrial processing or augmentation of potable water resources presents new potential scenarios for exposure to any residual chemical constituents. In order to effectively assess any risks associated with residual concentrations of chemicals in recycled water supplies, it is necessary to acquire some knowledge and understanding of the likely levels of exposure to these chemicals by people and the environment.

Risk assessment provides a systematic approach for characterising the nature and magnitude of risks associated with environmental health hazards. It is the process of estimating the potential impact of a chemical, physical, microbiological or psychosocial hazard on a specified human population or ecological system under a specific set of conditions and for a certain timeframe [2].

Formalised requirements for risk assessment for drinking water were introduced in the United States of America (US) with amendments to the US Safe Drinking Water Act in 1974. These amendments required improved estimates of exposure to potential hazards for risk management purposes. In 1983, the US National Research Council published what became known as the ‘red book’ [3], which provided a formalised set of steps to be taken for assessing risks to human health by chemicals from environmental and other sources. These were:

1. Problem Formulation and Hazard Identification—to describe the human health effects derived from any particular hazard (for example, acute toxicity, carcinogenicity)
2. Exposure Assessment—to determine the size and characteristics of the population exposed and the route, amount, and duration of exposure
3. Dose-Response Assessment—to characterise the relationship between the dose exposure and the incidence of identified health impacts

4. Risk Characterisation—to integrate the information from exposure, dose response, and health interventions in order to estimate the magnitude of the public health impact and to evaluate variability and uncertainty.

These steps have evolved into a general framework now used by environmental health agencies throughout the world to assess risks posed by environmental human health hazards, including chemicals and microbial organisms. An Australian version is described in detail in the important document *Environmental Health Risk Assessment: Guidelines for Assessing Human Health Risks from Environmental Hazards* published in 2002 by the EnHealth Council [2].

An objective of this handbook is to provide insight to available practical techniques used in the 'Exposure Assessment' step in relation to any additional exposure to chemical contaminants, specifically those from water recycling systems. The quantitative evaluation of chemical exposure from water recycling systems is an essential component required for any health risk assessment of an existing or proposed water recycling scheme.

1.1 Chemical hazards

By the definition provided in the Australian Drinking Water Guidelines, a *hazard* is 'a biological, chemical, physical or radiological agent that has the potential to cause harm' [4]. The type of harm that a hazard may have the potential to cause is not clearly defined. However, obvious examples include detrimental impacts to human health or the environment. Other types of harm, such as damage to treatment plant equipment, increased treatment costs, or even impacts to reputation, elevated community concerns, or dissatisfaction may also be relevant in some situations.

Chemical hazards in municipal wastewater consist of a wide range of naturally occurring and synthetic, organic and inorganic species. They include industrial chemicals, chemicals used in households, chemicals excreted by people, and chemicals formed during wastewater and drinking-water treatment processes.

Some key classes of chemical hazards include heavy metals, synthetic industrial organic chemicals, volatile organics, pesticides or their metabolites, algal toxins, disinfection byproducts, radionuclides, pharmaceuticals, estrogenic and androgenic hormones, antiseptics, perfluorochemicals and nanoparticles. Each of these classes is briefly discussed in the following paragraphs.

Heavy metals may be present in municipal wastewater as a result of industrial discharges to sewers [5]. The presence of some metals can be related to geologic and soil conditions in the potable water catchment. Some heavy metals such as cadmium, chromium and mercury have been associated with human health concerns.

Depending on the catchment area, and the extent of the trade waste program to control chemicals at the wastewater source, a very wide range of synthetic industrial chemicals are often measurable in urban municipal wastewater. Examples include plasticisers and heat stabilisers, biocides, epoxy resins, bleaching chemicals and byproducts, solvents, degreasers, dyes, chelating agents, polymers, polyaromatic hydrocarbons, polychlorinated biphenyls and phthalates. Many of these chemicals are known to be toxic to a diverse range of organisms including humans.

Volatile organic compounds are widely used as industrial solvents. Many are constituents of petrochemical products, and a number of halogenated compounds may be formed as byproducts of chlorine disinfection. Some volatile organic compounds are suspected to be teratogenic or carcinogenic to humans. Because of their high potential to contaminate

traditional potable water sources and supplies, they are tightly regulated in drinking water. Many of them are environmentally resilient, so careful control will be particularly important for planned indirect potable reuse schemes.

Pesticides may enter municipal wastewater systems by a variety of means, including stormwater influx and illegal direct disposal to sewage systems. Some leftover household pesticides are known to be disposed of into municipal sewers [6]. Additional routes, of unknown significance include washing fruit and vegetables prior to household consumption; insect repellents washed from human skin; flea-rinse shampoos for pets; washing clothes and equipment used for applying pesticides. Pesticides have been designed and used for their detrimental effects on a wide range of biological species.

Algal toxins such as microcyctins, nodularins, cylindrospermopsin and saxitoxins are all produced by freshwater cyanobacteria (blue-green algae) [7–9]. Under suitable conditions, cyanobacteria may grow in untreated or partially-treated wastewaters, producing these and other toxins [10; 11]. Numerous algal toxins have been implicated as having serious impacts on human and animal health by the consumption of contaminated water. Many of these toxins are hepatotoxic and some are neurotoxic.

Disinfection byproducts are formed by reactions between disinfection agents and other constituents of water [12; 13]. High initial concentrations of organic components or ammonia may lead to excessive production of disinfection byproducts. The vast majority of the compounds of concern originate from chlorine-based disinfectants. However, some (such as formaldehyde) can be produced by other oxidising disinfectants such as ozone. Some more recent byproducts of concern include bromate and epoxides (from ozone treatment) and nitrosodimethylamine (NDMA) predominantly from chloramination. Disinfection byproducts have been the source of much public health concern due to their widespread identification in water produced at drinking-water treatment plants.

Radionuclides may enter sewage by natural runoff or as a result of medical or industrial usage. In most parts of the world, radium is a constituent of bedrock and hence a natural contaminant in groundwater. In some cases, radium is removed from drinking water by coagulation, and the concentrated sludge is transferred to sewage systems. Radionuclides are carcinogenic and mutagenic substances.

Pharmaceuticals (and their active metabolites) are excreted to sewage by people as well as direct disposal of unused drugs by households [14]. Since pharmaceuticals are designed to instigate biological responses, their inherent biological activity and the diverse range of compounds identified in sewages (and the environment) have been cause for considerable concern during the past decade [15]. Specific concerns have not been raised for most classes of drugs, but issues regarding potent endocrine disrupting compounds [16], aquatic toxicity [17–21] and the spread of antibacterial resistance [22] may have significant ecological implications. A broad range of pharmaceutically active compounds have been reported in US drinking water as a consequence of unplanned indirect potable reuse [23].

Natural steroidal hormones such as oestradiol, oestrone and testosterone are also excreted to sewage by people. During the last two decades, natural steroidal hormones have been widely implicated in a range of endocrinological abnormalities in aquatic species that are affected by sewage effluent [24–27]. Impacts have been identified by a number of bio-indicators, most commonly elevated production of the protein vitellogenin, which is an essential precursor for egg production in fish [16; 28; 29].

Antiseptics such as triclosan and triclocarban are commonly used in face washes and anti-gum-disease toothpaste. Following trends from the USA, they are increasingly being used in a wider range of household products, including deodorants, antiperspirants, detergents,

dishwashing liquids, cosmetics and anti-microbial creams, lotions, and hand soaps. The presence of triclosan and triclocarban in reclaimed sewage effluent has led to concerns regarding their potential to accumulate in irrigated soils and runoff [30–33].

Perfluorochemicals such as perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluorooctanoic acid (PFOA), perfluorohexane sulfonate (PFHxS), and perflluorooctane sulfonate (PFOS) are persistent and toxic chemicals that have recently emerged as drinking water contaminants of concern. These perfluorochemicals are highly water soluble and are used in the production of water- and stain-resistant products, including cookware and clothing, as well as in fire-fighting foams. They also arise from the breakdown of fluorotelomer alcohols, which are widely used in consumer products such as greaseproof food wrappers and stain-resistant carpet treatments. A range of perfluoronated chemicals have recently been reported in drinking water that was not known to be affected by discharge from a facility that manufactures them [34; 35]. Perfluorinated residues (predominantly PFOA and PFOS) have been reported in the reclaimed effluents from tertiary-treatment wastewater treatment plants at total concentrations of 90–470 nanograms per litre [36].

An important group of emerging environmental contaminants of concern is nanoparticles or nanomaterials [37]. These are commonly defined as particles between about 1 and 100 nanometres in diameter that show properties that are not found in bulk samples of the same material [38]. The toxicological concerns for nanoparticles are related not only to their chemical composition, but also to physical parameters including particle size, shape, surface area, surface chemistry, porosity, aggregation tendency and homogeneity of dispersions [39]. As such, it is increasingly recognised that traditional techniques for toxicological and ecotoxicological evaluation of chemical substances are not well applied to the evaluation of nanoparticles [39–42].

1.2 Chemical risk calculations

The risks associated with chemical contaminants in water are highly variable and depend on the precise chemical species. Some chemicals may be acutely toxic, meaning that they impart toxic effects in a short period of time after a single significant dose. However, most toxic chemicals present chronic health risks, meaning that long periods of exposure to small doses can have a cumulative effect on human health.

Human exposure to trace chemical contaminants from water may cause acute or chronic health effects when present above ‘safe’ concentrations [7; 13; 43–45]. The question, then, is how to quantitatively assess the risks and thus determine the safe levels of exposure for chemicals potentially present in recycled water. Toxicology, the study of adverse effects of chemicals on living organisms, provides a means of addressing this question.

The toxicological evaluation of chemical contaminants is normally undertaken using animal testing, most commonly rodents including mice, rats or hamsters [46–49]. The effects of chronic (lifetime) or subchronic (up to 10 per cent of the lifespan) exposure, rather than acute effects from brief exposure to high doses, are considered to be most applicable for drinking water supplies. In rodents, this corresponds to about two years for chronic exposure and two to thirteen weeks for subchronic exposure experiments. For assessment of developmental effects, studies involving exposure during gestation are relevant. Chemicals may be administered to animals by drinking water, diet or by ‘gavage’, which involves the delivery of a bolus dose dissolved in oil or water through a tube into the stomach. In some cases, it may be appropriate for exposure to be assessed by inhalation, dermal adsorption, or intraperitoneal, intravenous, or intramuscular injection.

Animal toxicological studies for non-carcinogenic effects typically involve examination of mortality rate, body weight, organ weights, microscopic appearance and enzyme activities [50–52]. Among the organs most frequently monitored are the liver and kidney because of their roles in metabolism and excretion of toxic chemicals. Increasing attention is being given to studies of teratogenicity and developmental and reproductive toxicology as are now known to be the developmental stages in which animals are most sensitive to many chemicals [53–56]. For the investigation of carcinogenic effects, a wide variety of organs and tissues are examined for tumours [57]. The incidence of malignant and benign tumours in the experimental group is compared to a background incidence in a control group.

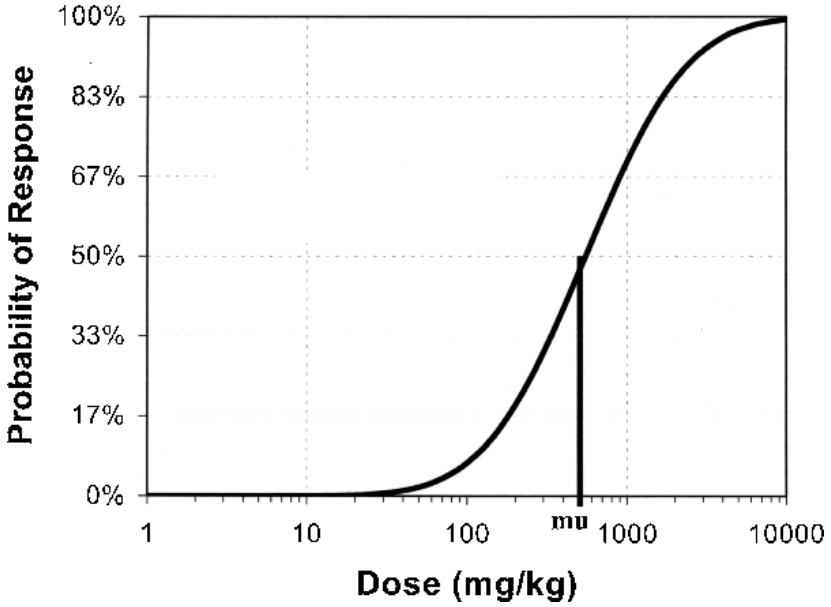
An alternative to animal toxicological studies is the use of *in vitro* bioassays to determine toxic activity of chemicals [58]. Such bioassays may be undertaken using cell cultures, cell components, bacterial strains or other microorganisms [59]. The most widely used example is the Ames test, for which the test substances are specially developed strains of the bacterium *Salmonella typhimurium*: the test is used as a screening test for mutagenicity and other types of genotoxic effects [60–63].

The level of toxicity imparted by specific chemicals is customarily quantified by developing a ‘dose–response’ curve. The dose–response curve defines the relationship between the level of exposure (the dose) of a chemical and incidence of (usually negative) health impacts.

For most toxic effects of chemicals, a clear dose–response relationship exists, with the proportion of responses increasing over a certain dose range. For many toxic effects there is a ‘threshold’ dose, below which no toxic effects are observed [64]. However, for some effects, particularly cancer which occurs through a genotoxic mode of action, it is assumed that exposure to any dose results in some level of risk; thus there is no threshold below which no risk exists [65].

An example of a dose–response curve for a ‘threshold chemical’ is presented in Figure 1. This curve was developed by experiments on animals to determine the relationship between the administered dose of a chemical as a function body weight (milligrams per kilogram [$mg.kg^{-1}$) leading to an established proportion of deaths in the exposed population. From the dose–response curve, it can be observed that a dose in excess of 10,000 $mg.kg^{-1}$ resulted in the death of roughly 100 per cent of the exposed population. Equally, it can be observed that there is exists a dose (about 30 $mg.kg^{-1}$) below which no ‘response’ may be expected. That is, there is an identifiable ‘safe dose’, known as the ‘threshold’ dose.

Figure 1: Example of a dose–response curve for a 'threshold chemical' contaminant

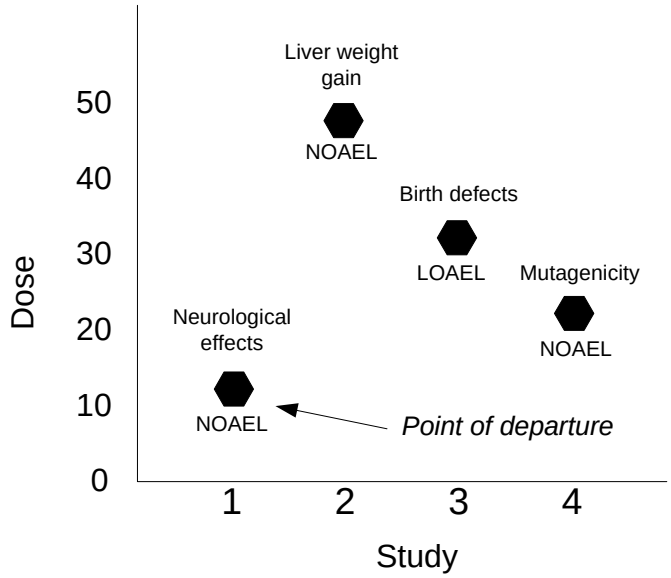


Toxicological investigations for non-carcinogenic ('threshold') studies are usually designed to enable the identification of either the highest dose at which no adverse effects are observed (the No Observed Adverse Effects Level, NOAEL) or else the lowest dose at which adverse effects are observed (the Lowest Observed Adverse Effect Level, LOAEL). NOAELs and LOAELs are conventionally determined in units of milligrams of the substance per kilogram of body mass per day ($mg.kg^{-1}.day^{-1}$).

For non-carcinogenic chemicals, it is common to use the available NOAEL or LOAEL data to derive what is known as a 'Reference Dose' (RfD). The RfD provides a 'safe' level of exposure of the chemicals to humans. It is defined as 'an estimate of exposure … that is likely to be without an appreciable risk of adverse health effects over a lifetime' [66].

The RfD is derived from the lowest relevant NOAEL or LOAEL available from suitably controlled studies. Where numerous suitable studies are available, the lowest dose among the available studies is used as illustrated in Figure 2. In doing this, the 'critical effect' from the 'critical study' is identified. The NOAEL or LOAEL corresponding to the critical effect from the critical study is termed the 'point of departure'.

Figure 2: Identification of point of departure from numerous NOAEL and LOAEL studies



The reference dose is then calculated from the point of departure, after including adjustments to account for sources of variability and uncertainty as shown by Equation 1. Uncertainty factors (sometimes called safety factors) are applied to account for uncertainty derived from incomplete toxicological data bases, the use of subchronic studies to derive chronic effects, the use of a LOAEL in place of a NOAEL, the extrapolation of animal studies to human impacts, and to account for variability amongst the human population. Each of these uncertainty factors are normally applied as a value of either 10 or 3, up to a maximum product of 3000 [64; 66].

Equation 1: Calculation of reference dose (RfD) from Point of Departure (POD) and uncertainty factors (UF)

$$\mathrm{RfD} = \frac{\mathrm{POD\ (NOAEL\ or\ LOAEL)}}{\mathrm{UF}_{\substack{\text{database}\\ \text{incomplete}}} \times \mathrm{UF}_{\substack{\text{subchronic}\\ \text{to chronic}}} \times \mathrm{UF}_{\substack{\text{LOAEL}\\ \text{to NOAEL}}} \times \mathrm{UF}_{\substack{\text{animal}\\ \text{to human}}} \times \mathrm{UF}_{\substack{\text{human}\\ \text{variability}}}}$$

Established RfDs for oral and inhalation exposure routes may be obtained from several sources [67; 68]. Among these is the database, known as the Integrated Risk Information System (or IRIS), which is maintained by the US EPA and is publicly available online [67].

Table 1 presents an example of information sourced from the IRIS site indicating how the RfD for acenaphthene was determined. The information provided indicates that the critical study was a hepatotoxicity study with a NOAEL of 175 mg/kg/day. An uncertainty factor of 3000 was applied, reflecting 10 each for inter- and intraspecies variability, 10 for the use of a subchronic study for chronic reference dose derivation, and 3 for the lack of adequate data in a second species and reproductive/developmental data. From these data, a final RfD of 0.06 mg/kg/day was established.

Table 1: Data used to determine the RfD for acenaphthene [67]

Critical effect		*UF*	*RfD*
Hepatotoxicity	NOAEL: 175 $mg.kg.day^{-1}$	3000	0.06 $mg.kg.day^{-1}$
Mouse Oral Subchronic Study	LOAEL: 350 $mg.kg.day^{-1}$		

Risk assessment for threshold chemicals then is typically undertaken by the calculation of a hazard quotient. The hazard quotient is simply the ratio of an actual (or expected) exposure to a chemical and the RfD as shown in Equation 2.

Equation 2: Calculated hazard quotients (HQ) from ingestion exposure to non-threshold contaminants

$$\text{Hazard Quotient (HQ)} = \frac{\text{Exposure dose } (mg.kg^{-1}.day^{-1})}{\text{RfD } (mg.kg^{-1}.day^{-1})}$$

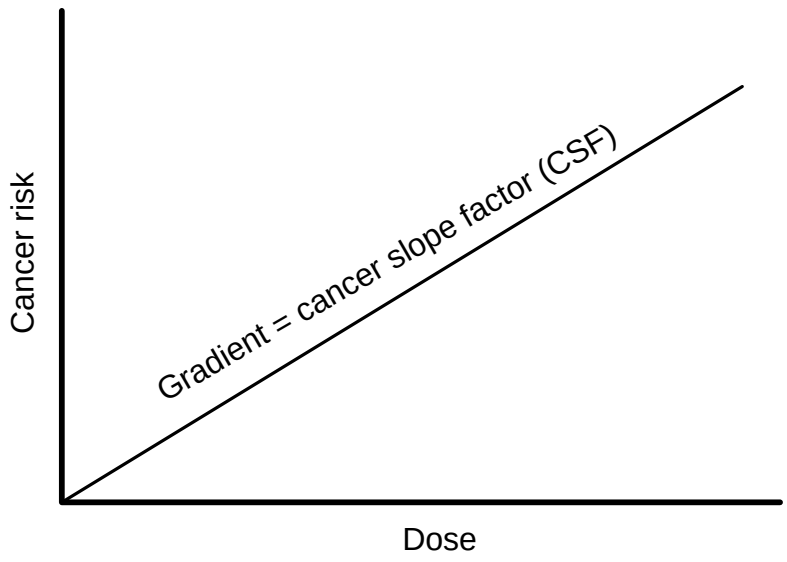
When the calculated HQ is less than 1, the exposure to chemical species is assumed to be at a safe level.

Risk assessments for carcinogenic (and some other) chemicals generally assume that there is no 'threshold level' at which there is no increased risk of detrimental impact [69]. Accordingly, there is assumed to be no 'safe level' of exposure and the calculation of NOAELs, LOAELs and RfDs is not applicable.

Dose–response curves for carcinogenic chemicals are customarily characterised in terms of a 'Cancer Slope Factor' (CSF), in which cancer risk per lifetime daily dose is given in inverse exposure units of $(mg.kg^{-1}.day^{-1})^{-1}$. The carcinogenic risk then is assumed to be linearly proportional to the level of exposure to the chemical, with the CSF defining the gradient of the dose–response relationship as a straight line projecting from zero exposure-zero risk. A sharper gradient, defined by a higher CSF, indicates a more potently carcinogenic chemical leading to increased cancer risk for any identified level of exposure as depicted in Figure 3.

The CSF for a specific carcinogen may be determined from human epidemiological studies or (more commonly) from chronic animal carcinogenicity assays.

Figure 3: Illustration of Cancer Slope Factor (CSF) for carcinogenic chemicals



The CSF is used to calculate the probability of increased cancer incidence over a person's lifetime—the so-called 'excess lifetime cancer risk'. Risks associated with exposure to carcinogenic contaminants may thus be calculated according to Equation 3.

Equation 3: Calculated risk from exposure to carcinogenic contaminants

$$\text{Risk (R)} = \text{CSF (mg.kg}^{-1}\text{.day}^{-1})^{-1} \text{ x Exposure Dose (mg.kg}^{-1}\text{.day}^{-1})$$

Established CSFs for oral and inhalation exposure routes may be obtained from a number of online sources [67; 68]. An example of data used to calculate a CSF for DDT as provided in the IRIS database is presented in Table 2. This includes ten identified published CSFs from six published studies. The final CSF adopted in the IRIS database is the geometric mean of these ten CSF values, 0.34 $(\text{mg.kg}^{-1}\text{.day}^{-1})^{-1}$.

Table 2: CSFs for oral exposure of DDT (mg.kg.day^{-1}) [67]

Species/Strain, Tumour Type	*Male*	*Female*	*Reference*
Mouse/CF-1, Benign	0.8	0.42	Turusov et al. [70]
Mouse/BALB/C, Benign	0.082		Terracini et al. [71]
Mouse/CF-1, Benign, Malignant	0.52	0.81	Thorpe & Walker [72]
Mouse/CF-1, Benign	1.04	0.49	Tomatis & Turusov [73]
Rat/MRC Porton		0.084	Cabral et al. [74]
Rat/Wistar, Benign	0.16	0.27	Rossi et al. [75]

The assumption of the absence of a toxicological threshold for many carcinogenic endpoints (including mutagenicity and genotoxicity) is well entrenched in chemical risk assessment, but is not universally accepted and is increasingly problematic [76]. It is, in fact, likely that there are thresholds for a number of genotoxic effects. Furthermore, the low-dose extrapolation for non-threshold toxicological calculations is often across many orders of magnitude from the effects observed in experimental animals to established tolerable risk levels for humans. This extrapolation introduces significant uncertainties in the determination of acceptable exposure levels. Finally, in cases where non-threshold toxicology is assumed to apply, the appropriateness of the concept of 'tolerable risk' has been subject to ongoing debate. As a result of these limitations and concerns, alternative measures of dose–response are increasingly being developed and adopted [76].

Some trace chemicals are essential nutrients (to humans and other organisms) at low doses, but they impart toxic impacts at higher doses [77]. Examples include essential trace elements such as zinc, selenium, fluorine, molybdenum, chromium and manganese. The dose–response profile for an essential nutrient is generally represented as a U-shaped curve. The left side of the curve represents the improvement in health that occurs as the dose increases from a deficiency state to the level able to support function. The 'valley' of the U-shaped curve represents doses that are fully sufficient to support function, yet low enough to be physiologically processed and excreted without adverse interactions with biological tissues or functions. The right-hand portion of the curve represents a toxicological impact that is manifest at higher exposures to the chemical.

For some chemicals, such as endocrine disrupting chemicals, there is currently a paucity of information regarding the nature of the relationship between low levels of exposure and potential impacts to human health. Accordingly, the satisfactory use of neither the RfD approach nor the CSF approach has been established for the definition of human dose–response relationships for such chemicals. The lack of a defined dose–response relationship for these chemicals renders it currently not possible to establish quantitative descriptors of

risks to people associated with their exposure. In such cases, the use of relative risk assessment can provide a useful alternative as described in Section 1.4.

1.3 Safe concentrations for drinking water contaminants

Safe drinking water concentrations for non-carcinogenic chemicals can be calculated from appropriate NOAEL or LOAEL data and relevant uncertainty factors by applying several assumptions regarding exposure to drinking water. Drinking water guideline values or standards are commonly calculated according to Equation 4 or variations of it [4; 78–80].

Equation 4: Calculation of safe drinking water concentration for non-carcinogenic chemicals

$$\text{Safe Drinking Water Concentration (mg/L)} = \frac{\text{POD (NOAEL or LOAEL) x BW x PF}}{\text{IR x UF}}$$

where:
BW = average body weight of an adult (commonly 70 kilograms)
PF = a proportionality factor to account for the proportion of exposure that may be derived drinking water (typically 1 or 0.1).
IR = the estimated maximum drinking water ingestion rate by an adult (2 litres per day)
UF = one or more uncertainty factors (usually values of 10 or 3 to a maximum product of 3000 [64])

Since it is assumed that there is no 'threshold dose' for most carcinogenic chemicals, the assumption that any level of exposure incorporates some level of risk means that the 'safe' level of exposure must either be defined as zero exposure or else in terms of an identified 'tolerable level of risk'.

On this basis, the US Environmental Protection Agency (US EPA) has set non-enforceable 'maximum contaminant level goals' (MCLGs) for carcinogenic chemicals in drinking water as zero. The enforceable standard, the 'maximum contaminant level' (MCL), is determined as the level that may be achieved with the use of the best available technology, treatment techniques, and other means that the US EPA finds are available, taking cost into consideration.

Some international agencies have identified a tolerable level of risk, usually 10^{-4}, 10^{-5} or 10^{-6}. This the excess lifetime cancer risk as a result of exposure to the chemical. Having defined the tolerable level of risk, a safe drinking water concentration may be calculated according to Equation 5 or variations of it [4; 78–80].

Equation 5: Calculation of safe drinking water concentration for carcinogenic chemicals

$$\text{Safe Drinking Water Concentration (mg/L)} = \frac{\text{Risk level x BW x PF}}{\text{CSF x IR}}$$

where:
Risk Level = tolerable risk level (usually 10^{-4}, 10^{-5} or 10^{-6})
BW = average body weight of an adult (commonly 70 kg)
PF = a proportionality factor to account for the proportion of exposure that may be derived drinking water (typically 1 or 0.1).
IR = the estimated maximum drinking water ingestion rate by an adult (2 L/day)

Established drinking water guidelines and standards are generally limited to 'traditional' drinking water contaminants, known to occur in contaminated surface water from conventional supplies [4; 78]. These include a range of pesticides and industrial chemicals, but not chemicals that are associated with discharges from municipal wastewater effluent. Accordingly, contaminants of concern, such as pharmaceutical residues, personal care

products, household chemicals, and steroidal hormones, are not commonly subject to specific regulation in drinking water. Nonetheless, safe drinking water concentrations of many of these chemicals may potentially be derived based on the same toxicological considerations used for the establishment of current guidelines and standards. For example, suitable toxicological data for determining safe drinking water concentrations have been reported for 26 active pharmaceutical ingredients based on various endpoints [81]. The authors of this study stated that for pharmaceutical substances, the therapeutic effect usually occurs at a dose considerably below those expected to result in toxicity and thus a large proportion of the NOAEL or LOAEL toxicological data used were based on therapeutic effects or minor side-effects such as sensitivity to human intestinal microflora. However, others have reported that for many pharmaceuticals, the most toxic endpoint is not the therapeutic endpoint, but rather it is a side effect, such as carcinogenicity [82]. In the absence of other relevant toxicological data, the Australian Guidelines for Water Recycling have adopted the use of the lowest therapeutic dose in place of a traditional LOAEL [83].

In some cases, however, there is insufficient toxicological data to set a drinking water guideline value by the conventional method. In such situations, the *threshold of toxicological concern* concept can help set an interim guideline while further toxicological information is gathered [84; 85]. This model largely relies on carefully compiled toxicological databases of acute, subchronic and chronic NOAELs from rodent studies to which a safety factor of 100 has been applied for extrapolation to humans. The concept was originally developed to prioritise toxicity testing of food additives and food contact materials, but the methodology can be applied to other occupational and environmental settings, including drinking water contaminants [86; 87]. This approach has been adopted by the *Australian Guidelines for Water Recycling* as a means of identifying conservative upper bounds for safe concentrations of some chemicals as an interim measure until sufficient toxicological data are available [83].

1.4 Relative risk

The techniques described above are aimed at the quantification of human health risks from chemicals in absolute terms according to known dose–response relationships. However, in many cases, absolute quantification of risks is not possible or not practical due to a lack of relevant toxicological data. In such cases, a relative risk assessment approach can be useful.

Relative risk assessment can compare the degree of exposure to a chemical from a new recycled water source to the exposure from a pre-existing water source. Such an approach can be useful for demonstrating reduced or increased risks associated with exposure to a particular contaminant in the absence of quantitative toxicology or infectivity data.

Relative risk assessment was the key approach adopted for a direct potable reuse study undertaken in San Diego during the 1990s [88]. The primary objective of that study was to assess whether a pilot-scale advanced water treatment plant could reliably reduce contaminants of concern to levels such that the health risks posed by an assumed potable use would be no greater than those associated with the present water supply. Over a period of three years, water quality testing was undertaken for a series of pathogenic organisms, potentially toxic chemicals, as well as screening for mutagenicity and bioaccumulation of the chemicals mixtures present in the two water supplies. This results of this research indicated that the advanced water treatment plant could reliably produce water of equal or better quality than that of the present water supply [88].

2. Water Recycling in Australia

Beneficial reuse of treated municipal effluents is a rapidly growing practice in Australia. The increased uptake of 'water reuse' or 'water recycling' has been in response to shifts in environmental and social pressures that have led to changes in what has been considered appropriate practice for the management of urban water resources and natural waterways.

The increased uptake of water reuse in Australia has largely been in response to identified imperatives to find new water resources for Australia's growing cities and to limit pollution caused by the environmental discharge of municipal wastewaters.

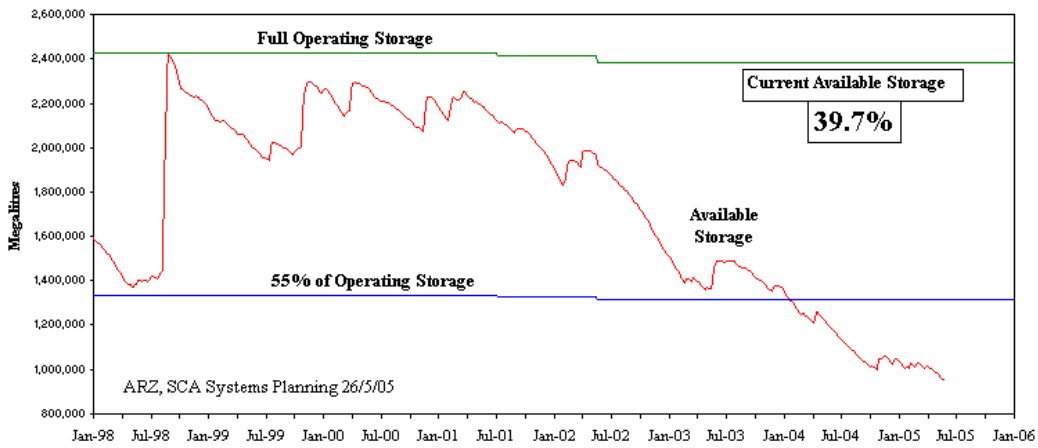
2.1 The imperative to find new water resources

The Australian national population passed 20 million people at the end of 2003, with almost two thirds residing in the six state capital cities [89]. Since then, the growth rate has been around 1.2 per cent each year with continuing disproportionate rates of growth in the capitals.

While Australia's population has continued to grow, the amount of water runoff into some key catchments has been decreasing. Weather patterns in south-eastern Australia were dominated by El Niño conditions for most of the first decade of the twenty-first century. As a result, eastern Australia has experienced its severest drought since the 1930s. Although rainfall has been highly variable during the past century, the CSIRO have forecast a likely general decrease during the next 25 years, particularly during winter and spring [90]. South Western Australia has experienced similarly dry conditions due to significant decreases in rainfall since the mid-1970s [91].

As a result of both population movements and recent droughts, most large cities in Australia have identified the need for new urban water resources. The challenges confronting Australia's largest city, Sydney, in 2005, were starkly demonstrated by trends in the volume of water stored in the cities eleven main dams as shown in Figure 4 [92].

Figure 4: Sydney's stored water supplies Jan 1998 to May 2005 [92]



In May 2002, Sydney's dams had been at 80 per cent capacity; but by May 2005, levels reached record lows of below 40 per cent. Thus if no further action was taken and the current weather patterns continued, it was observed that Sydney could face severe shortages before 2009. Even with subsequent extensive rainfalls, the long-term security of the city's water

supplies would remain uncertain unless significant changes in water management practices were implemented.

On the other side of the continent, Perth's rainfall has dramatically declined during the past thirty years. The effect of this can be seen in lower inflows to Perth's water supply dams. From 1911 to 1974 the average annual inflow to Perth's dams was 338 gigalitres. Between 1975 and 2001 the average dropped to 167 gigalitres—a decrease of almost 50 per cent [93]. Inflows during the first decade of the current century have been even less, resulting in Perth's dams remaining at around 15–40 per cent of capacity during 2002–10 [94].

Perth's dwindling surface water supply is being supplemented by additional use of groundwater, which supplies about half city's water requirements, as well as the introduction of seawater desalination in 2006.

Australia's driest state capital, Adelaide, sources more than 90 per cent of its water from the River Murray, catchments in the Adelaide Hills, and groundwater. All of these resources are under pressure due to decreasing flow rates and water quality in the Murray, over-allocated groundwater extraction exceeding rates of replenishment, and highly variable year-to-year catchments in the Adelaide Hills. In the coming two decades, Adelaide's water supplies are expected to decline by about 20 gigalitres per year as a result of climate change and development in the Adelaide Hills area [95].

The historical response to drought and population growth in Australia has been to increase storage capacity by building new dams on relatively untapped rivers. However, environmental and economic costs, coupled with the long-term inadequacy of many earmarked future dams, have been cause for governments to reconsider plans for their construction. The Victorian Government has put in place policies aimed at deferring the need for a new dam for Melbourne for at least 50 years [96]. The NSW Government has announced an indefinite deferral of a long-planned additional dam for Sydney [97]. In 2009, Queensland Government plans for a new dam to supply drinking water to Brisbane were dramatically overturned by the Federal Government due to significant environmental concerns [98]. It is likely that this will be the future trend for many large dam proposals around Australia as their environmental impacts are increasingly recognised.

In addition to urban water requirements, the volumes and patterns of flow of water in some heavily tapped rivers have been considered inadequate to maintain downstream river health. Important national rivers, such as the River Murray, suffer from quality impairment as over-extraction has caused unnaturally low environmental flow regimes [99]. Problems include rising salinity as well as algal and aquatic weed growth, which can then lead to significant impacts on native fish stocks and water bird habitats, as well as drastically limiting the commercial and recreational uses of the rivers. Australian governments have agreed to pursue the restoration of all over-allocated or overused systems by reverting to environmentally sustainable levels of extraction [100]. The Commonwealth Government *Water Act 2007* was enacted in part 'to make provision for the management of the water resources of the Murray–Darling Basin' [101]. An important objective of that Act is 'to ensure the return to environmentally sustainable levels of extraction for water resources that are over-allocated or overused'.

In 2004 an intergovernmental agreement on a National Water Initiative was established between the Commonwealth of Australia and the governments of all states and territories (The Tasmanian Government joined the Agreement in June 2005 and the Western Australia Government joined in April 2006) [100]. The National Water Initiative provides a framework within which the signatories will operate to address, among other things, urban water shortages. Key actions to be undertaken include the implementation of demand management

practices and the development of innovation and capacity building to create water sensitive Australian cities.

2.2 The imperative to further limit sewage discharge

Marine pollution caused by sewage discharge is recognised as a growing worldwide problem [102]. The 'Coasts and oceans', theme commentary prepared for the 2006 Australia State of the Environment Committee included the following observations [103]:

> *There is growing concern globally about the range of chemicals that enter sewage treatment plants—from human waste or from industrial wastes. These chemicals are not routinely monitored in treatment processes. Sewage discharges of these chemicals and nutrients can be highly significant at local scales because they have a chronic daily delivery concentrated at a point source. For example, although water-industry monitoring found no evidence of sewage impacts in the exposed coastal waters of metropolitan Perth, scientific studies found that Perth's sewage discharge leads to algal blooms, reduction of light penetration by one-third, increase in nitrogen by three to five times natural backgrounds, and more than a doubling of phytoplankton biomass [104]. Furthermore, in NSW waters, it is estimated that 30 to 50 per cent of nitrogen in one species of reef fish is derived from nitrogen discharged in sewage* [105].

The discharges from Australian estuary and ocean outfalls are a cumulating, and often overlooked, burden on marine flora and fauna. Pollutants found in primary and secondary treated effluent include nutrients, suspended solids, organic carbon, pathogens and toxic chemicals. Large volumes of fresh water can also detrimentally alter otherwise saline environments. Furthermore, sewage discharges can carry large quantities of heat to otherwise cooler environments, thereby disrupting local ecosystems.

The discharge of wastewater-borne nutrients supports the growth of plants and phytoplankton in coastal waters. Seagrasses and marine macroalgae have differing requirements for carbon, nitrogen and phosphorus; and variations in their supply may change conditions to favour the growth of one species at the expense of others. The discharge of Adelaide's stormwater and wastewater into Gulf St Vincent is known to contribute to the dieback of seagrasses, which also has consequences for fisheries and other marine environments [95]. There is also strong evidence to link sewage effluent discharges with eutrophication in Moreton Bay off the coast of Brisbane [106]. Since there is no systematic monitoring or reporting of algal blooms in Australia's estuaries and coastal waters, there is no way of knowing if eutrophication is increasing or decreasing as a national problem [103].

The range of toxic chemicals known to persist in primary and secondary treated sewages includes heavy metals, aromatic hydrocarbons and organochlorine compounds. Estrogenic steroid hormones (including estrone, estradiol and the synthetic ethynylestradiol) have been reported in sediments adjacent to an Australian ocean outfall [107]. This suggests that these compounds, associated with particulates in the sewage, aggregate on contact with high ionic strength seawater and accumulate on the seafloor.

Public health may also be at risk from the environmental presence of pathogenic organisms such as bacteria and viruses. Exposure to these organisms in estuarine and coastal waters may occur either through contact recreation or consumption of contaminated seafood. Along some Australian beaches and under certain conditions, beach users risk a range of illnesses such as carditis, conjunctivitis, hepatitis, gastro-intestinal illnesses and skin and wound infections [108]. Comprehensive guidelines have been developed for managing these health risks in recreational water [109]. These guidelines provide control measures for the protection of public heath.

Some Australian cities have highlighted the need to reduce discharges from ocean outfalls and are now actively working to increase the feasibility of ceasing ocean discharge of sewage [96].

2.3 Towards the uptake of water recycling

Throughout most of the last century, engineered water management in Australia comprised dams to collect surface water, uncapped wells to extract groundwater and outfalls to discharge primary or secondary treated effluents. As populations grew, more dams and wells were constructed and ever-increasing volumes of sewage were discharged into the countries' waterways and surrounding seas. In this sense, water was treated as if it were a free resource with unlimited supplies. Little appreciation for the interdependence of all aspects of the water cycle was apparent.

Change began to occur in the later quarter of the twentieth century with the implementation of tighter restrictions on sewage discharges. These restrictions created an impetus to find alternative means of disposing of effluent, particularly for inland sewage treatment plants. Soon many towns and cities began experimenting with small-scale water reuse programs. A national average of 9 per cent of the effluent from sewage treatment plants was being reused by 2001–02 [110]. Of this, around two thirds was used in mining and agricultural industries. Most of the remainder was used to irrigate municipal parks and sports grounds. During this time, most reuse applications involved new uses for water that did not substitute for existing uses from the available water supply sources, but rather added to the overall water usage.

The first decade of the twenty-first century in Australia was characterised by widespread drought coupled with continued population movement to large centres near capital cities. Together, these have led to increasing pressure on fresh water supplies in most large cities and many regional areas. As a result, the focus of improved water management has somewhat shifted from effluent management to the identification of additional resources that could contribute towards conserving or enhancing drinking water supplies.

In 2002 a Federal Parliament Senate Committee was established to conduct an inquiry into Australia's management of urban water [111]. The Committee reported that there were major opportunities for Australia to improve on its performance with regard to water reuse. It observed that, in Australian cities, 'efficient water use is still perceived as an emergency measure to be adopted during drought condition'. It asserted that 'in a country of such limited water resources, this behaviour must be the norm, not the exception'.

Among the recommendations of the Senate Committee was that the 'Commonwealth play a more prominent role in driving the changes needed to manage urban water more sustainably'. The Committee further recommended that 'Australians generally be encouraged and assisted to use less water, recycle more effluent and significantly reduce the impact that urban development and its stormwater collection and transport has on natural systems'.

In 2003, the Prime Minister's Science, Engineering and Innovation Council (PMSEIC) identified possible mechanisms by which Australian cities could make better use of available water resources [112]. The PMSEIC indicated that a mixture of initiatives appropriate to specific circumstances of each city would be required. However, essential criteria for all initiatives would include maintenance of public health, economic viability, environmental sustainability and social acceptance. With these criteria in mind, recycled water was promoted by the PMSEIC as 'a valuable resource that should not be wasted and which can be used in a safe and sustainable manner to reduce pressures on limited drinking water resources'.

The PMSEIC noted the lack of guidance available for the development of risk management systems for recycled water in Australia [112]. It stated that such guidance was essential to

support increased use of recycled water. The PMSEIC recommended fast-tracking the development of national guidelines and that these should adopt the concepts incorporated in the existing framework for management of drinking water quality. This would provide a systematic management approach for the production and use of recycled water.

Australian Guidelines for Water Recycling have now been developed under the auspices of the National Water Quality and Management Strategy. The four key documents are:

- *Australian Guidelines for Water Recycling: Managing Health and Environmental Risks (Phase 1)* (2006)
- *Australian Guidelines for Water Recycling: Managing Health and Environmental Risks (Phase 2): Augmentation of Drinking Water Supplies* (2008)
- *Australian Guidelines for Water Recycling: Managing Health and Environmental Risks (Phase 2): Stormwater Harvesting and Reuse* (2009)
- *Australian Guidelines for Water Recycling: Managing Health and Environmental Risks (Phase 2): Managed Aquifer Recharge* (2009).

These guidelines provide national guidance on best practices for water recycling. They have adopted the innovative risk management framework approach pioneered in the 2004 revision of the Australian Drinking Water Guidelines [4].

2.4 Current practices of municipal water reuse in Australia

In 2004, the Australian Academy of Technological Sciences and Engineering published a comprehensive report detailing current practices of water recycling in Australia [110]. This report identified substantial variations in the relative proportions of available municipal sewage effluent that were reused by the various states and territories in 2001–02. Significantly, much greater rates of water reuse were reported for each overall state than for the respective state capitals. This reflects the greater rates of water recycling in rural towns, particularly those in inland areas. The current principal approaches to water reuse in Australia are summarised in the following sections.

2.4.1 Onsite municipal reuse

In unsewered areas, onsite treatment of sewage is common practice, primarily by the use of aerobic septic systems, which can include sand filtration. In some cases, the effluents from these systems are used for onsite garden or non-edible crop irrigation.

Onsite reuse by the selective capture of greywater sources from laundries and bathrooms is also relatively common. Although greywater treatment systems are available, most reuse involves using temporary and permanent diverters to water gardens with untreated greywater.

Very few houses and offices in Australian cities are capable of treating and reusing black water sources (such as from toilet flushings). Such systems require biological amelioration and disinfection. The few systems in existence operate primarily as experimental or demonstration schemes since they are expensive to install and require careful ongoing management.

2.4.2 Targeted municipal irrigation

Targeted municipal irrigation schemes are among the most common means of water reuse in Australia. In many cases, secondary or tertiary treated effluent is applied to public parks and gardens, golf courses, and playing fields. Such reuse practices are attractive primarily for the generally low levels of treatment required and the need for a relatively small number of distribution pipes to transport the water to the points of use.

An alternative approach has been developed with the introduction of small portable sewer-mining operations. These involve the extraction of untreated sewage from municipal sewer mains. The water is then treated by a small, sometimes mobile, treatment plant (normally using membrane technology) and reused for irrigation. An advantage of portable sewer mining operations is that they may be relocated depending on temporary or seasonal demands.

During 2005–06, Kogarah Council (Sydney) ran a six-month trial of a sewer mining pilot plant at the Beverly Park Golf Course. The treatment system included gross and fine solids separators, a submerged aerated filter, dual media filtration and disinfection by both UV radiation and chlorine dosing. This trial led to the NSW Government giving approval to use of recycled water from this system for irrigation. The project also helped Sydney Water to develop a standard sewer mining agreement as well as a brochure describing how to establish a sewer mining operation in Sydney [113].

Kogarah Council is currently developing a larger version of the sewer mining project, which is to be known as the Beverley Park Water Reclamation Plant. The water from this plant will be used directly for irrigation of the golf course, a nearby sports oval; the water will also be piped or otherwise transported to various council parks. The plant will have a capacity to produce up to 750 kilolitres of irrigation water per day, and it is forecast that the project will reduce potable water use in Kogarah by over 160 megalitres every year.

2.4.3 Industrial reuse

A successful industrial reuse program has operated from the Luggage Point Sewage Treatment Plant (STP) in Brisbane for over a decade. This plant has delivered ten to fifteen megalitres of treated effluent per day to the adjacent BP Amoco oil refinery, where is it used as boiler feed water. In addition to the potable water savings, the construction of this scheme allowed for considerable infrastructure savings by eliminating the need to expand potable water mains capacity. Increased industrial use of recycled water from Luggage Point STP has been facilitated by the Western Corridor Recycled Water Project, involving the construction of a pipeline to Tarong power station, northwest of Brisbane.

Australia is a world pioneer of using recycled water for power station cooling. Pacific Power's Eraring Power Station supplies around 25 per cent of the electricity requirements to NSW and has been using recycled water for well over a decade. Eraring Station is located in the Hunter Valley close to the Dora Creek STP. In the mid-1990s, an agreement was signed to enable Eraring to access more than 5 megalitres of effluent from Dora Creek STP each day. This water is transferred directly to a water reclamation plant at the power station, where it undergoes further treatment by microfiltration and reverse osmosis. Access to recycled water provides a reliable water source for Eraring Power Station. Furthermore, it helps protect the sensitive aquatic environment of Lake Macquarie, which would otherwise be affected by treated effluent discharge.

A large industrial water reuse scheme is operated in Wollongong (NSW), where Sydney Water now provides Bluescope Steel with 20 megalitres of high quality municipal recycled water per day for use in the steel manufacturing plant, comprising more than half of the

plant's total water requirements. Further large-scale agreements for industrial reuse operations have been implemented at Kwinana (Western Australia); these include water for mining, power generation, chemical fertiliser, and petroleum companies.

2.4.4 Agricultural reuse

Recycled water from Adelaide's largest sewage treatment plant (Bolivar STP) has been delivered via the Virginia Pipeline to agricultural areas on the Northern Adelaide Plains and the Barossa Valley since 2000. This scheme supports one of Australia's most valuable produce markets and provides an alternative source of water to the over-utilised local groundwater.

Reclaimed water is transported by an 18-kilometre pipeline to Virginia and then distributed through 120 kilometres of pipeline network to horticultural irrigators. It serves more than 240 irrigators who produce root and salad crops, brassicas (for example, cauliflower, broccoli, cabbage), wine grapes and olives.

However, a major limitation to the quantities of water that can be beneficially reused is the highly seasonal nature of the demand for irrigation water. On average, the Bolivar plant produces about 110 megalitres a day of effluent. During summer, most of this is used by growers at Virginia. However, in winter, when most growers do not need the water, the effluent is discharged to the sea.

If the effluent that is not required during winter could be efficiently stored, the scheme could be significantly expanded to other areas. A research program—funded by a consortium of government and private bodies—is now examining the possibility of storing water in an underground aquifer for seasonal use.

2.4.5 Reticulation for household reuse

A small but growing number of new housing development areas in Australia have incorporated dual reticulation systems for the redistribution of treated sewage back to households. These comprise a dedicated system of pipes, taps and fittings, which must be kept entirely segregated from the potable water supply (Figure 5). The water delivered by dual reticulation schemes may only be used for a limited range of applications such as toilet flushing and garden watering.

The largest dual-reticulation scheme in Australia began operation at Rouse Hill (NSW) in 2001. The scheme is continuing to expand and currently services more than 25,000 properties. The over-riding purpose of the Rouse Hill scheme was to protect the Hawkesbury-Nepean river system from the environmental impact of increasing urban development. More recently, dual-reticulation schemes have been established at Newington (NSW), Mawson Lakes (South Australia), Epping North (Victoria), and Pimpama-Coomera (Queensland).

Dual distribution systems have some specific inherent risks associated with their construction and maintenance, which must be carefully managed to protect consumer safety [114]. Among these is the possibility of incorrectly cross-connecting potable and non-potable water sources [115; 116]. In Australia, for example, fifty cross-connection instances were discovered at Rouse Hill prior to commissioning the scheme in 2001 and at least four cross-connection events attributed to plumbing errors have been documented subsequently [117]. Similar events have also occurred at Newington and Pimpama-Coomera. Such events may have public health implications [118] and risk undermining public confidence in recycled water schemes.

Figure 5: Dual water meters Rouse Hill, Sydney

2.4.6 Streamflow augmentation

Streamflow augmentation is among the most common, but least recognisable forms of water reuse. Effluent discharge into waterways is widespread in Australia, but does not always impart environmental benefits in terms of flow augmentation. However, there are cases where suitably treated discharges may have positive environmental impacts when released to waterways in carefully controlled flow regimes. If managed appropriately, streamflow augmentation can be environmentally beneficial.

Sydney's main drinking water supply is captured by Warragamba Dam on Lake Burragorang. Warragamba Dam retains and allows the diversion of water that would otherwise flow into the Hawkesbury-Nepean river system in western Sydney. However, in order to maintain river health of the Hawkesbury-Nepean, the Sydney Catchment Authority is currently required to release a minimum 12 gigalitres per year from Warragamba Dam.

The NSW Government and Sydney Water Corporation have identified an effective means for preserving much of these environmental releases so that they may be retained as part of Sydney's drinking water supply. The project, known as the 'Replacement Flows Project', involves treating municipal effluent from the St Marys, Penrith and Quakers Hill sewage treatment plants in northwestern Sydney at an advanced water treatment plant located at the St Marys sewage treatment plant. The facility will produce up to 18 gigalitres per year of highly treated recycled water, which will be discharged to the Hawkesbury-Nepean River to replace water that is currently released from Warragamba Dam.

The advanced water treatment plant for the Replacement Flows Project will use ultrafiltration and reverse osmosis membrane treatment followed by chlorination prior to environmental release. In addition to the potable water savings in Lake Burragorang, the Replacement Flows

Project involves an aspect of indirect potable reuse since the North Richmond drinking water treatment plant is located downstream of the Hawkesbury-Nepean discharge point and supplies potable water for the town of North Richmond and surrounding areas. Accordingly, the advanced water treatment processes and associated risk management have been designed with this subsequent water use in mind.

A pilot advanced water treatment plant was constructed and operated at St Marys STP in 2008. This pilot was used to refine the operational parameters of the advanced water treatment processes and confirm the production of high water quality suitable for reuse. Risk assessment activities involved monitoring for chemical and microbial contaminants, as well as challenge testing the treatment system by spiking in high concentrations of selected potential contaminants [119]. Construction of the full-scale plant began in 2008, and highly treated recycled water is expected to flow to the Hawkesbury-Nepean River in 2010.

2.4.7 Indirect potable reuse

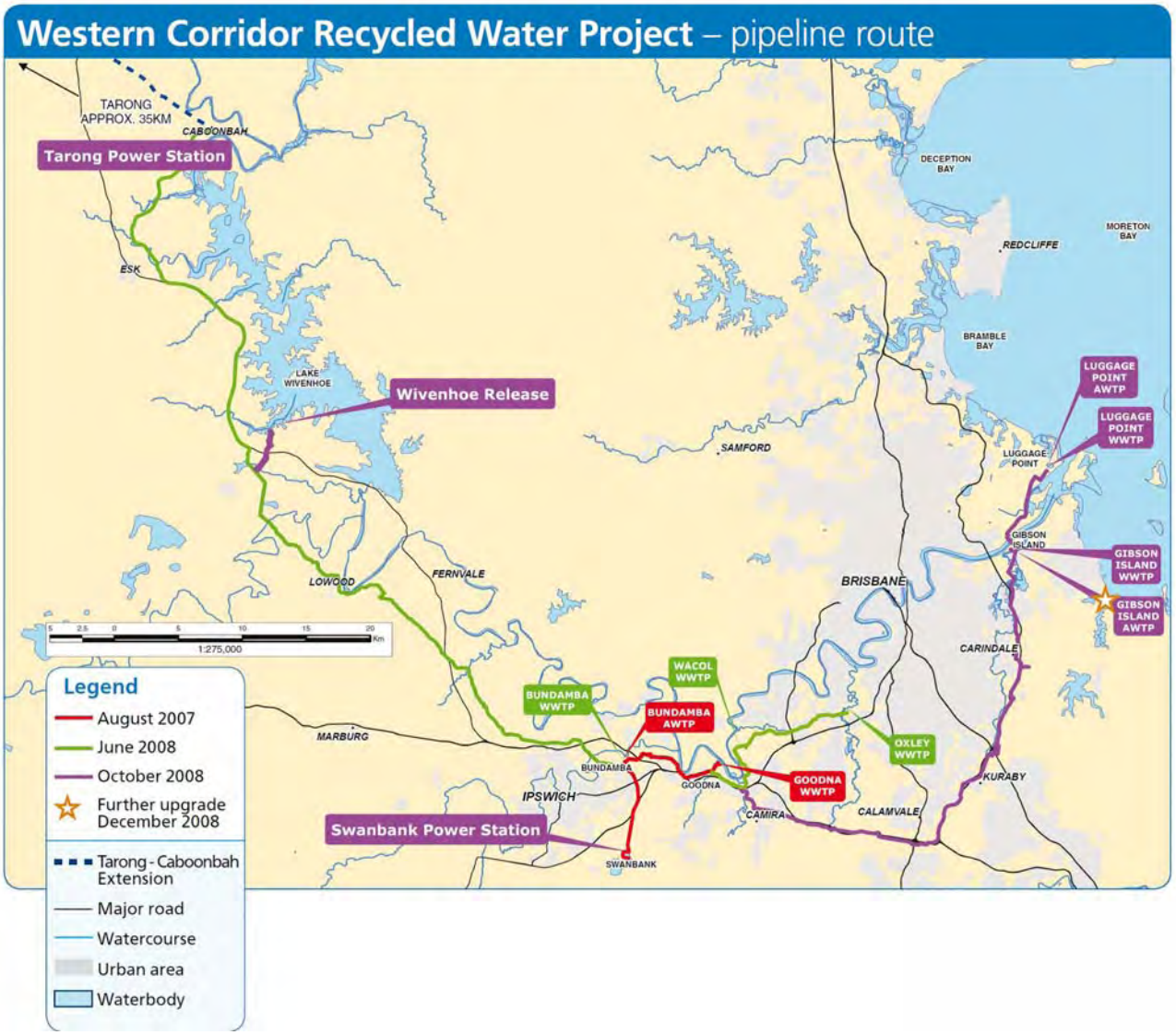
During the past two decades, there have been several planned indirect potable reuse schemes proposed in Australia, which have not eventuated due to strident community opposition. These unsuccessful proposals have generally been in South East Queensland: the cities of Caloundra/Maroochy (planning during 1995 to 1998), Caboolture (1996–97) and Toowoomba (2005–06) were the most prominent examples. More recent proposals for indirect potable reuse in cities such as Goulburn and Canberra were relatively short-lived or have been postponed in part due to a lack of community support.

Despite the earlier difficulties, by 2007 it had become clear to many that a number of Australia's largest cities would need to adopt varying approaches to indirect potable reuse in order to make full use of available water supplies. Major schemes are currently under development in South East Queensland and Perth. However, even these schemes have been associated with controversy from some sections of the community. As a result, the responsible governments appear to have adopted a cautious and slow approach to their full implementation.

South East Queensland

In January 2007, The Queensland Government announced that it would construct a proposed indirect potable reuse scheme that would supplement the potable water supplies of all of South East Queensland, including Brisbane. The scheme is known as the Western Corridor Recycled Water Project (WCRWP) and the major components are illustrated in Figure 6. The WCRWP uses the vast majority of South East Queensland's treated municipal effluent, which was previously discharged into Moreton Bay via the Brisbane River. Municipal effluent is collected from six wastewater treatment plants at Bundamba, Goodna, Oxley, Wacol, Luggage Point and Gibson Island. This is then subjected to advanced water treatment at three new advanced water treatment plants at Bundamba, Luggage Point and Gibson Island.

Figure 6: The Western Corridor Recycled Water Project [120]



Much of the advanced-treated water is now used to supply cooling water to Swanbank and Tarong coal-fired power stations. The remaining water will be used to supply other industrial and agricultural customers and to recharge Brisbane's main drinking water reservoir, Wivenhoe Dam at Logan Inlet. This indirect potable reuse aspect is expected to be initiated once the storage levels in the combined storage at Wivenhoe, Somerset and North Pine Dams drop below 40 per cent of capacity.

All three advanced water treatment plants incorporate treatment by micro- or ultrafilitration, reverse osmosis and advanced oxidation (UV/H_2O_2). The design philosophy of the scheme is in accordance with the 'multiple barriers' approach, incorporating seven largely independent treatment steps operating under a risk management framework.

High-pressure membrane processes such as reverse osmosis generate concentrated waste streams, which must be properly managed [121]. The reverse osmosis concentrate from the Bundamba plant is treated by chemical coagulation and sedimentation for phosphorus removal and with a nitrification/denitrification filter with methanol addition for biological nitrogen removal. It is then discharged to the Brisbane River at the Goodna wastewater treatment plant. The reverse osmosis concentrates from Luggage Point and Gibson Island

are discharged close to the mouth of the Brisbane River, where they are diluted and dispersed into Moreton Bay.

The WCRWP was initially designed to provide around 85 gigalitres per year of purified water. However, wastewater availability is currently limited by current strict water restrictions, so the actual water production is limited to only around 58 gigalitres per year whilst the current demand for the purified water is around 18 gigalitres per year.

Perth

The city of Perth (Western Australia) is located on the Swan Coastal Plain. Approximately 60 cent of drinking water supplies are sourced from groundwater. The unconfined aquifer directly below Perth is known as the Superficial aquifer and is, on average, about 50 metres thick. The Superficial aquifer has two important mounds. These are the Gnangara mound to the north of the city and the smaller Jandakot mound to the south. Below the Superficial aquifer there are several confined aquifers, the largest of which is the Leederville aquifer, which is typically several hundred metres thick, and the Yarragadee aquifer, which in many areas is more than a kilometre thick.

The Leederville aquifer is an important drinking water source for Perth. The Superficial aquifer has also been an important water source for many decades, and it is very common for Perth households to extract water directly from it for garden and lawn watering. The exploitation of this groundwater is rapidly approaching sustainable limits in some areas, causing the watertable to drop markedly.

The organisation that manages Perth's water resources, Water Corporation, have signalled that they see managed aquifer recharge as a means of potentially supplying around 27 gigalitres per year of public drinking water injected via the Gnangara mound by 2015. The source water would be advanced-treated recycled water from an advanced water treatment plant located at the site of the Beenyup wastewater treatment plant. It would then be transported via a (roughly 40 kilometre) pipeline to a nature reserve further north of Perth. At various points *en route*, water would be injected into the confined Leederville aquifer or infiltrated into the Superficial aquifer.

However, before committing to the hundreds of millions of dollars needed to build such a scheme, Water Corporation have elected to begin by the construction of a smaller trial, through which annually 1.5 gigalitres of recycled water is currently injected into the Leederville aquifer at Beenyup. Before injection, the treated effluents are upgraded to indirect potable reuse standard by advanced treatment including microfiltration, reverse osmosis, and UV disinfection. The water is then injected to a depth of around 200 metres. Water Corporation have predicted that this water would then take a minimum of 50 years before reaching drinking-water production bores more than 3 kilometres away.

Water quality is now being closely monitored prior to injection into the aquifer; it is also being monitored through extraction wells as the water moves horizontally away from the Gnangara mound. This monitoring program is intended to be undertaken over a period of three years. As well as demonstrating the technical feasibility, an important aspect of the trial project is to enhance community confidence in potable recycling by managed aquifer recharge.

3. Relevant Australian Guidelines

A variety of national guideline documents have been established and implemented in the Australian water management arena. The risk assessment and risk management frameworks presented in these documents reflect the ongoing international development of scientific understanding of water quality issues, technology, and institutional change.

Each of the documents is distinct in its content and design. The Australian Drinking Water Guidelines focus on the application of a risk management approach, but also include a range of notionally tolerable contaminant concentration limits by which potable water can be judged. The enHealth Council documents provide general frameworks for how chemical risk should be assessed in general terms, as well as details on how the technical risk assessment process might be carried out.

The key guideline documents, with which any successful risk assessment process would need to have some consistency, are described in the following sections.

3.1 Australian/New Zealand Standard: Risk Management

The Australian/New Zealand standard for risk management provides a generic guide, which is applicable to a diverse range of industries and activities, for managing risk [122]. Risk analysis activities, with the key functions of 'identify risks', 'analyse risks' and 'evaluate risks', are embedded within the overall risk management process.

The standard introduces an approach to the risk analysis step that is clearly defined in terms of *likelihoods* and *consequences* of the events that may occur [122]:

> *Risk analysis involves consideration of the sources of risk, their positive and negative consequences and the likelihood that those consequences may occur. Factors that affect consequences and likelihood may be identified. Risk is analysed by combining consequences and their likelihood. In most circumstances existing controls are taken into account.*

The standard states that consequences and likelihood may be estimated using statistical analysis and calculations. Where no reliable or relevant past data are available, subjective estimates may be made which reflect an individual's or group's degree of belief that a particular event or outcome will occur. The standard lists the following examples which maybe used as sources of information for analysing consequences and likelihood [122]:

- past records
- practice and relevant experience
- relevant published literature
- market research
- the results of public consultation
- experiments and prototypes
- economic, engineering or other models
- specialist and expert judgements.

Techniques include:

- structured interviews with experts in the area of interest
- use of multi-disciplinary groups of experts
- individual evaluations using questionnaires
- use of models and simulations.

Where appropriate, the confidence placed on estimates of levels of risk should be included. Assumptions made in the analysis should be clearly stated.

The standard introduces three types of risk analysis as 'qualitative', 'semi-quantitative' and 'quantitative'. It notes that qualitative analysis is often used first to reveal major risk issues and that this may then be followed by more specific or quantitative analysis on the identified major risk issues. The three types of analysis are described as follows [122]:

(a) Qualitative analysis

Qualitative analysis uses words to describe the magnitude of potential consequences and the likelihood that those consequences will occur. These scales can be adapted or adjusted to suit the circumstances, and different descriptions may be used for different risks.

Qualitative analysis may be used:
– as an initial screening activity to identify risks which require more detailed analysis;
– where this kind of analysis is appropriate for decisions; or
– where the numerical data or resources are inadequate for a quantitative analysis.

Qualitative analysis should be informed by factual information and data where available.

(b) Semi-quantitative analysis

In semi-quantitative analysis, qualitative scales such as those described above are given values. The objective is to produce a more expanded ranking scale than is usually achieved in qualitative analysis, not to suggest realistic values for risk such as is attempted in quantitative analysis. However, since the value allocated to each description may not bear an accurate relationship to the actual magnitude of consequences or likelihood, the numbers should only be combined using a formula that recognises the limitations of the kinds of scales used.

Care must be taken with the use of semi-quantitative analysis because the numbers chosen may not properly reflect relativities and this can lead to inconsistent, anomalous or inappropriate outcomes. Semi-quantitative analysis may not differentiate properly between risks, particularly when either consequences or likelihood are extreme.

(c) Quantitative analysis

Quantitative analysis uses numerical values (rather than the descriptive scales used in qualitative and semi-quantitative analysis) for both consequences and likelihood using data from a variety of sources…. The quality of the analysis depends on the accuracy and completeness of the numerical values and the validity of the models used.

Consequences may be determined by modelling the outcomes of an event or set of events, or by extrapolation from experimental studies or past data. Consequences may be expressed in terms of monetary, technical or human impact criteria, or any of the other criteria… In some cases, more than one numerical value is required to specify consequences for different times, places, groups or situations.

The standards state that the uncertainty and variability of both consequences and likelihood should be considered in the analysis and communicated effectively. Furthermore, a sensitivity analysis should be undertaken to test the effect of uncertainty in assumptions and data.

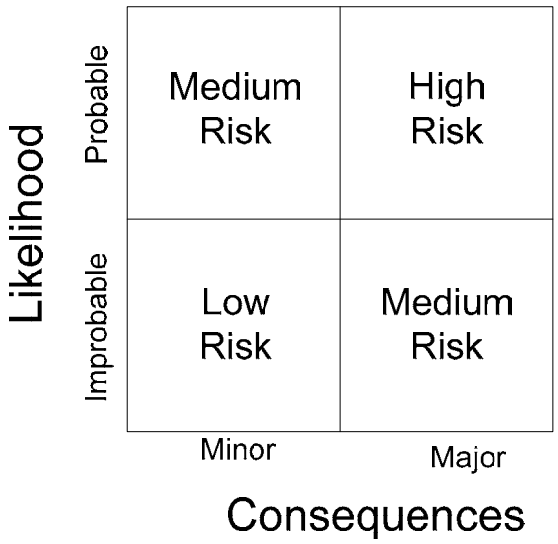
3.2 Risk Management Guidelines (companion to Australian/New Zealand Standard)

Standards Australia and Standards New Zealand have published Risk Management Guidelines as a companion document to the Australian/New Zealand Standard for Risk Management [123]. This is a much more detailed document compared to the Standard for Risk Management and provides a degree of practical information that may be used to implement the Risk Management Standard, including the relevant aspects of risk analysis.

3.2.1 The risk matrix

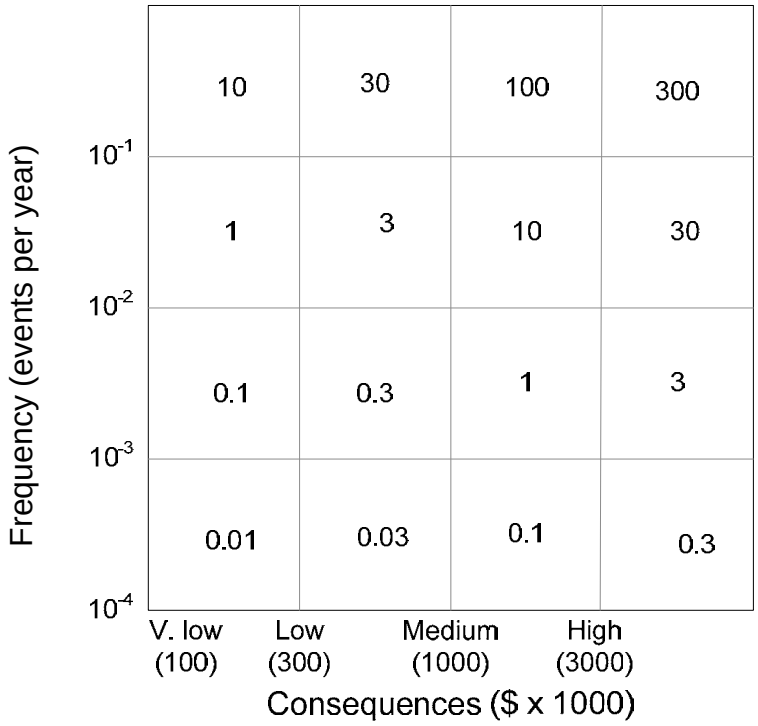
The Risk Management Guidelines introduce the concept of a 'risk matrix' as a graphical technique for relating a given risk to its determining factors, consequence and likelihood. In its simplest form, the risk matrix may be used to derive qualitative risk ratings based on qualitative descriptors of likelihood and consequences (Figure 7). The number of steps or divisions along each axis depend upon the level of detail, the nature of the measures, as well as the context, scope, resources and use for which the output will be used [123]. Although they are qualitative, it remains important to note that the axis scales may not be linear from a conceptual point of view and risk ratings may be dominated by the influence of either likelihood or consequence.

Figure 7: Qualitative risk matrix [123]



A semi-quantitative risk matrix may also be prepared, and similarly, the axis scales for each component may not be linear as illustrated in Figure 8.

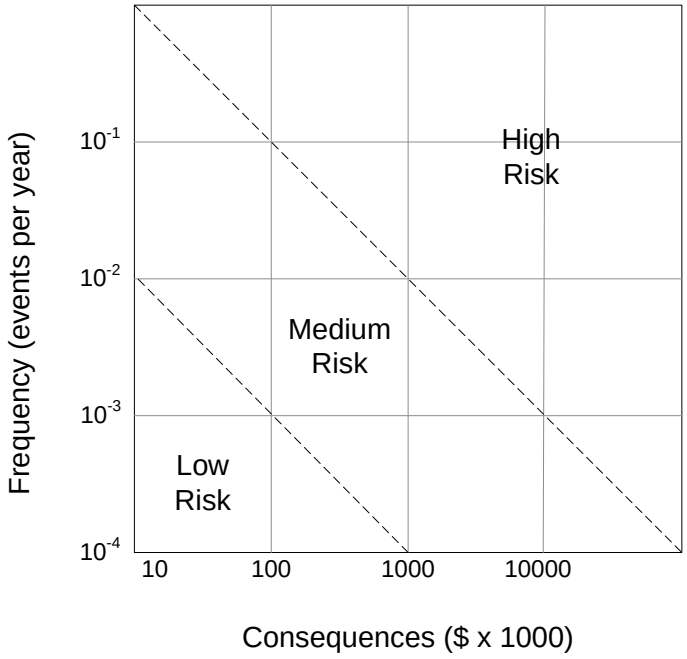
Figure 8: Semi-quantitative risk matrix [123]



A semi-quantitative analysis is undertaken with likelihood and consequence descriptors that relate to quantitative measures. In many such cases, it may also be reasonable to undertake some form of mathematical manipulation to determine risk ratings as shown in Figure 8. However, in cases were ordinal scales (for example, numerical rankings that do not relate to value or quantity), such manipulations that may be undertaken are very limited. On the other hand, the use of ratio scales (for example, measures of a value or effect such as temperature) allow most mathematical operations to be performed, provided suitable units or conversions are applied [123].

If the risk relationship is taken to be the product of the two components, the use of logarithmic scales will allow a constant risk line to be drawn as a straight line as shown in Figure 9.

Figure 9: Semi-quantitative risk matrix showing constant risk lines [123]



Risk matrices may also be applied for quantitative risk analysis, but they usually require more rigorous use and manipulation of the values that represent the likelihood and consequences parameters [123]. The use of any scale other than a form of 'ratio' (with non-arbitrary set points) is usually not valid. The measurement units should always be stated and fully defined when undertaking quantitative analysis.

3.2.2 Consequence and likelihood tables

Consequence and likelihood tables should be used to define ratings scales in order to provide a clear statement of their meaning [123].

Qualitative consequence tables may be developed to assign consequence 'ratings' with numerous consequence criteria such as health and safety, environmental impacts and financial success. In many cases, a very simple descriptive table with a single consequence criterion may be suitable. For example Table 3 shows a simple consequence table with the single criterion of 'ability to achieve objectives'.

Table 3: Simple consequence table [123]

Descriptive	*Definition*
Severe	Most objectives cannot be achieved
Major	Some important objectives cannot be achieved
Moderate	Some objectives affected
Minor	Minor effects that are easily remedied
Negligible	Negligible impact upon objectives

Likelihood tables are analogous to consequence tables and provide definitions to likelihood descriptors. Various scales may be useful, depending on the nature of the risk being considered and the required level of quantitation. Likelihood is essentially a measure of probability, which may, in turn, be considered inversely as a predicted frequency. Accordingly,

Table 4 shows an example likelihood table with a scale defined in terms of an expected frequency of occurrence.

Table 4: Likelihood table defined in terms of expected frequency [123]

Level	*Descriptor*	*Description*	*Indicative frequency (expected to occur)*
A	Almost certain	The event will occur on an annual basis	Once a year or more frequently
B	Likely	The event has occurred several times or more in your career	Once every three years
C	Possible	The event might occur once in your career	Once every ten years
D	Unlikely	The event does occur somewhere from time to time	Once every thirty years
F	Rare	Heard of something like the event occurring elsewhere	Once every 100 years
G	Very rare	Have never heard of this happening	Once in 1000 years
H	Almost incredible	Theoretically possible but not expected to occur	Once in 10,000 years

For some projects, such as those with limited durations, it may be more appropriate to define likelihood in terms of the probability of a particular event occurring at all. An example of such a likelihood table is provided in Table 5.

Table 5: Likelihood table defined in terms of probability [123]

Descriptor	*Description*	*Alternative descriptor*
Probable	Can be expected to occur during the project	Good odds
Possible	Not expected to occur during the project	Low to even odds
Improbable	Conceivable but highly unlikely to occur during the project	Poor odds

The guidelines indicate that 'systems engineering techniques such as fault tree analysis can be used to analyse probabilities in more detail' [123].

3.2.3 Level of risk

The way that the level of risk is described depends upon the type of analysis (qualitative, semi-quantitative, or quantitative) undertaken. Care must be taken with quantitative analyses that involve consequences that may be somewhat intangible such as some environmental or safety effects or reputation.

The guidelines recognise that when selecting specific risks (or hazardous events) for assessment, there are often many choices. For example, a risk analyst could select a typical problem, with low consequence but high probability; or a representative catastrophe, with a high consequence but a low probability, or some intermediate outcome. The guidelines suggest that, in many cases, it is appropriate to focus on events with potentially catastrophic outcomes, as these are the ones that pose the largest threats and are often of greatest concern to managers. However, in some cases it may be important to identify and analyse both 'problems' and 'catastrophes' as separate risks. For example, a frequent but low-impact (or chronic) problem may have large cumulative or long-term effects that are at least as important as those of a rare but high-consequence (or acute) event [123].

Documentation of the risk analysis is important and the guidelines recommend that documentation should include the following [123]:

- key assumptions and limitations
- sources of information used
- explanation of the analysis method, and the definitions of the terms used to specify the likelihood and consequences of each risk
- existing controls and their effectiveness
- description and severity of consequences
- the likelihood of these specific occurrences
- resulting level of risk
- effect of uncertainty.

3.3 enHealth Health Impact Assessment Guidelines

The enHealth *Health Impact Assessment Guidelines* were developed to promote and enhance the incorporation of health impact assessment into environmental planning and impact assessment generally [124]. They provide a framework for development proponents, health authorities and decision-makers to follow in order to achieve this within existing planning structures. The guidelines are framed around the following principles to be addressed when undertaking health impact assessment [124]:

Overall

The Charter of (Environmental Health) Entitlements and Responsibilities for Individuals, Communities, Business and Government will be observed throughout the health impact assessment process.

The Community

Community consultation is a critical and integral part of the health impact assessment process. People and communities are part of the 'environment' and rely on the quality of the environment for their survival and maintenance of good health and wellbeing.

The public has a right to know the actual or potential effects of a proposed activity on their health and their environment, and should be consulted on the management of risks.

- *The community is also a rich source of local information that can only be tapped through its involvement.*
- *The protection and, where possible, the improvement of public health should be fundamental to health impact assessment.*

Scope, relevance and timeliness of the health impact assessment

- *The scope and detail of the health impact assessment should be in proportion to the scale of the potential health impacts of a proposed development. Scoping should identify only those impacts which have significant potential to occur. The level of risk assessment should be in accord with the nature, scale and significance of the actual or potential effects of the proposed activity. Where there is insufficient information or uncertainty about the risks to health, this should be clearly stated.*

- *Both positive and negative health impacts should be considered.*

- *Human health should be safeguarded, i.e. likely health problems should be remedied before they can occur (once they have been identified as a possible concern). The additional financial cost is likely to be less for both industry and governments if action is taken at the design stage.*

Integration of health impact assessment and environmental impact assessment

- *Health impact assessment should be explicitly integrated into the assessment of effects on the environment (i.e. into environment impact assessment) to ensure that any actual or potential impacts or risks to public health are adequately addressed in the development approval process.*

Monitoring and review

- *Where appropriate, monitoring should be carried out to assess whether modification to the proposal has actually been implemented, evaluate the health impact assessment process, and assess the outcomes, i.e. whether anticipated or unanticipated health impacts have occurred.*

- *Environmental and health controls, as conditions in approvals, should be reviewed regularly.*

The enHealth Guidelines provide a framework for the health impact assessment process, which is summarised as a seven-step process [124]:

Step 1 Screening

- *Should the project be subject to health impact assessment?*

Step 2 Scoping

- *What issues must be addressed in the health impact assessment?*

Step 3 Profiling

- *What is the current status of the affected population and the local environment?*

Step 4 Risk assessment

- *What are the risks and benefits?*

- *Who will be affected?*

Step 5 Risk management

- *Can risk be avoided or minimised?*

- *Are better alternatives available?*

- *How can benefits and risks be evaluated and compared?*

- *How can differing perceptions of cost and benefit, nature and magnitude be mediated?*

- *Will predictions of future health risk be robust enough to withstand legal and public scrutiny?*

Step 6 Implementation and decision-making

- *Does the assessment provide sufficient, valid and reliable information for decision-making?*

- *Is there a conflict to be resolved?*
- *How will conditions be enforced?*
- *How and by whom will impacts be monitored?*
- *How will post-project management be resourced?*

Step 7 Monitoring, environmental and health auditing, post-project evaluation

- *Is the project complying with its conditions?*
- *How well is the environment and health impact assessment process as a whole achieving its aims of protecting the environment and health?*

Further details on each of the above steps and how they should be addressed are included within the guideline document [124].

3.4 enHealth Environmental Health Risk Assessment Guidelines

The enHealth *Environmental Health Risk Assessment Guidelines* [2] are a companion document to the enHealth Health Impact Assessment Guidelines. They provide a more detailed and more specific framework for the health assessment of risks from environmental hazards such as toxic chemicals and infectious substances.

A number of key principles have been developed and promoted by the enHealth Council for environmental health risk characterisation. These principles are to be applied generally to all forms of environmental health risk assessment, including the assessment of risks from water recycling schemes.

The key principles as identified by the enHealth Council [2] are:

- *Actions should always adequately protect public health and the environment, putting these responsibilities before all other considerations.*
- *Risk assessments should be transparent. The nature and use of default values and methods, assumptions and policy judgements in the risk assessment should be clearly identified. Conclusions drawn from the evidence should be separated from policy judgements.*
- *Risk characterisations should include a summary of the key issues and conclusions of each of the other components of the risk assessment, as well as describing the likelihood of adverse health effects. The summary should include a description of the overall strengths and limitations (including uncertainties) of the assessment and conclusions.*
- *Risk characterisations (and risk assessments) should be consistent in general format, but recognise the unique characteristics of each specific situation.*
- *Health risk assessment must be undertaken with an appreciation that the health risk assessment is often part of a larger assessment that encompasses ecological risk assessment.*
- *To protect public health and the environment an appropriate degree of conservatism must be adopted to guard against uncertainties.*

- *Ensure that comparisons have been made against environmental health criteria that have been endorsed by the relevant Commonwealth, State or Territory environmental health agencies.*

- *Where there are no Environmental Health Criteria for a particular agent refer to the administrative authority at the relevant Commonwealth, State or Territory level.*

- *Ensure that human health risk assessments are undertaken, where necessary, according to methods in this document [2], or its revisions as published from time to time*

- *When deriving environmental health criteria use toxicological data or exposure criteria from agencies or organisations relevant to the State or Territory (e.g. local or Commonwealth health agencies such as NHMRC, or the enHealth Council) or to which Australia is party (e.g. World Health Organization).*

- *Ensure that human health risk assessments are undertaken using national toxicological assessments (e.g. NHMRC) or WHO assessments or, where neither has been made, methods agreed to by the administrative authority for contaminated sites at the relevant Commonwealth, State or Territory level.*

- *The risk assessor's knowledge of the peer-reviewed scientific literature relevant to risk assessment and the practical aspects of risk assessment should be up-to-date.*

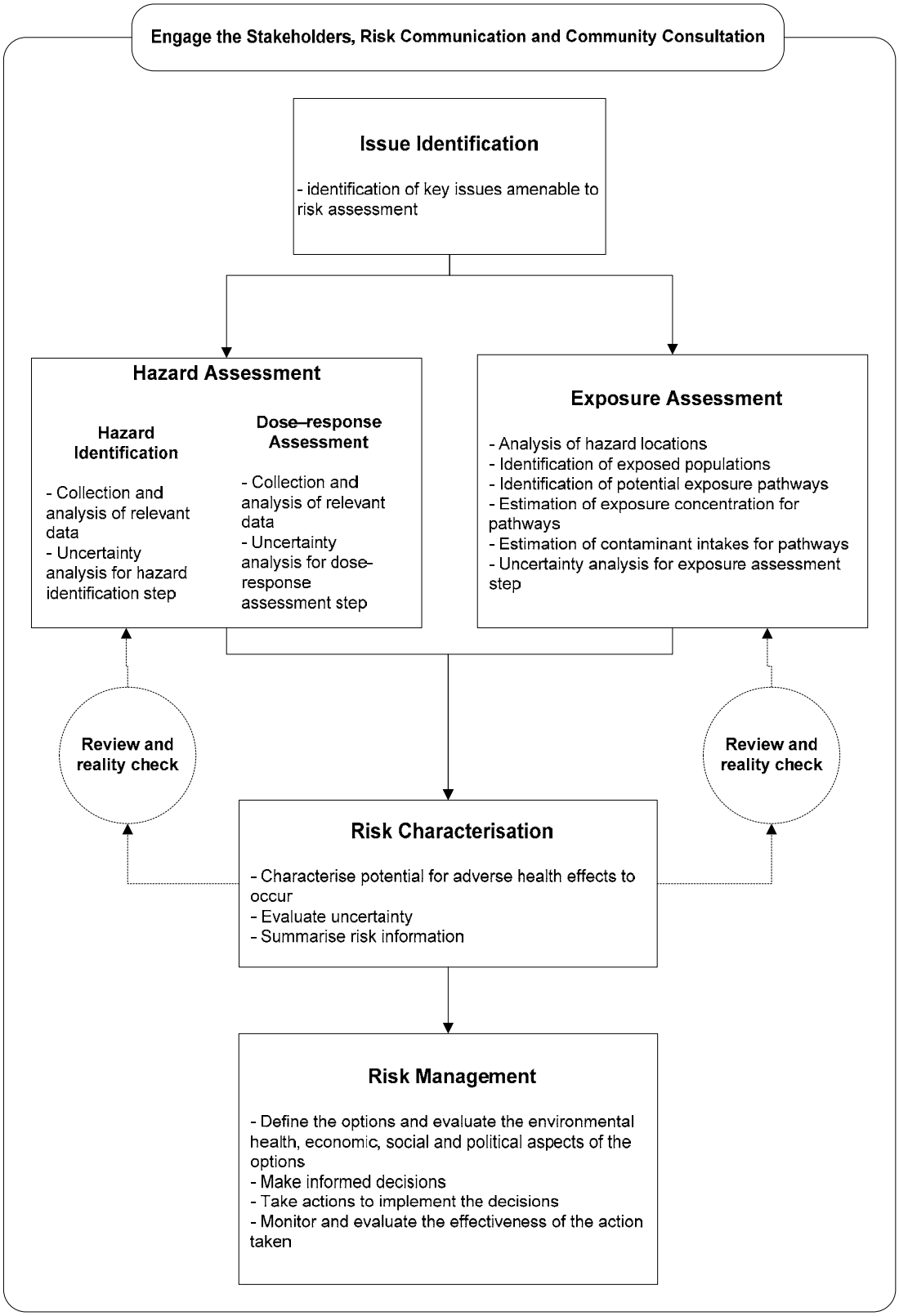
- *Variations in risk assessments as a result of particular statutory requirements, resource limitations, and other specific factors should be explained as part of the risk characterisation. For example, a reason will be required to explain why certain elements are incomplete.*

The enHealth Council guidelines provide a model for risk assessment that involves five stages [2]. It was developed following a review and modification of various national and international models. The five stages are:

- issue identification
- hazard identification
- dose–response assessment
- exposure assessment for the relevant population
- risk characterisation.

These five stages are closely linked and highly dependent on the preceding stages. The model is illustrated in Figure 10 [2].

Figure 10: Risk Assessment Model [2]



The enHealth Council guidelines provide a detailed description of approaches that can be taken for modelling exposures of hazards, including the use of both point estimates and the types of probabilistic determinations described in further detail in the current document [2].

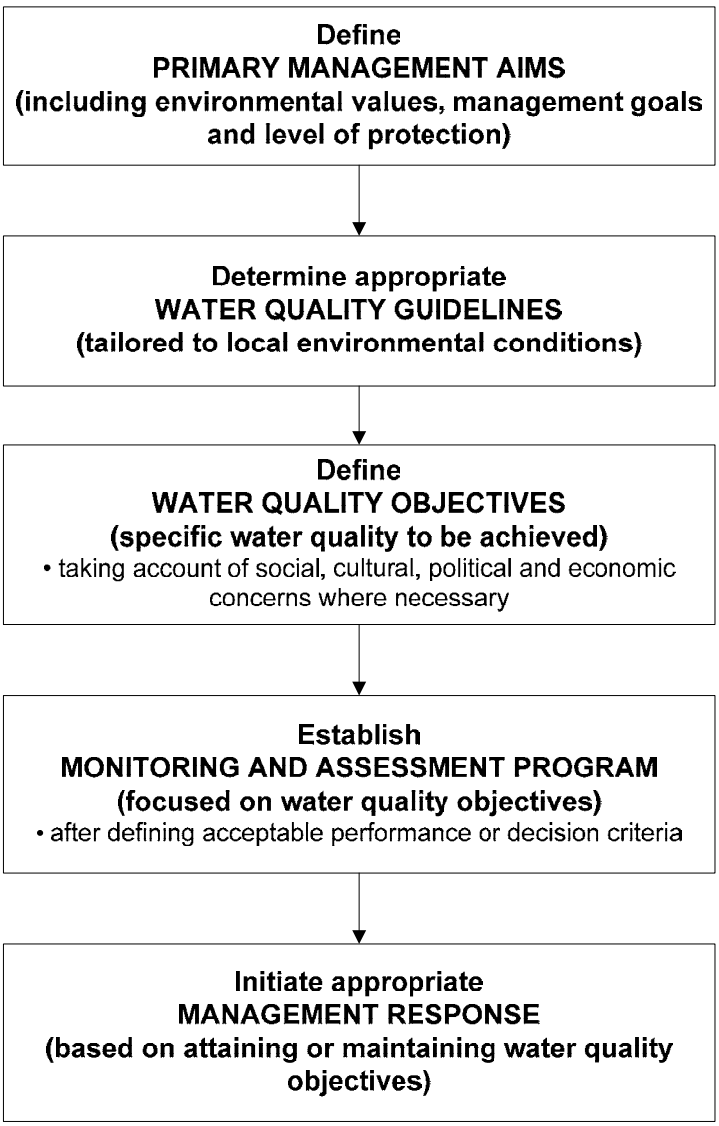
3.5 Australian and New Zealand Guidelines for Fresh and Marine Water Quality

The *Australian and New Zealand Guidelines for Fresh and Marine Water Quality* are a pivotal document of Australia's National Water Quality Management Strategy [125]. They 'provide an authoritative guide for setting water quality objectives required to sustain current, or likely future, environmental values [uses] for natural and semi-natural water resources in Australia and New Zealand'.

Many non-potable water recycling applications have the potential to detrimentally affect the water quality of environmental waterbodies and other uses of water covered by these guidelines. The guidelines address the protection of water quality for aquatic ecosystems, primary industries (irrigation and general water uses, stock drinking water, aquaculture and human consumers of aquatic foods), recreation and aesthetics, drinking water, and industrial water. As such, they provide guidance on how water that may be used for a variety of applications (or affect aquatic ecosystems) should be handled in a way that includes the identification and proper management of associated risks.

These guidelines provide a series of steps that may be taken in order to implement a broad national management strategy at a local level. These steps are outlined in Figure 11 [125].

Figure 11: Management framework for applying the *Australian and New Zealand Guidelines for Fresh and Marine Water Quality* [125]



3.6 Australian Drinking Water Guidelines

The *Australian Drinking Water Guidelines* (ADWG) introduce a framework for management of drinking water quality [4]. A key component of the framework is system analysis and management, which involves understanding the entire water supply system, the hazards and events that can compromise drinking water quality, and the preventive measures and operational control necessary for assuring safe and reliable drinking water.

The ADWG provide the following key definitions for a water quality risk management context:

- *A **hazard** is a biological, chemical, physical or radiological agent that has the potential to cause harm.*
- *A **hazardous event** is an incident or situation that can lead to the presence of a hazard (what can happen and how).*

- ***Risk*** *is the likelihood of identified hazards causing harm in exposed populations in a specified timeframe, including the severity of the consequences.*

The ADWG accept that realistic expectations for hazard identification and risk assessment are important and that rarely will enough knowledge be available to complete a detailed quantitative risk assessment. Instead, the guidelines have adopted a risk prioritisation process, adapting the risk matrix approach presented in the risk management guidelines published by Standards Australia & Standards New Zealand [123]. A likely outcome of such risk assessments is the identification of specific areas where further information and research is required.

Guideline concentration values are provided for a large number of organic and inorganic chemicals. These represent concentrations that, based on present knowledge, do not result in any significant risk to the health of the consumer over a lifetime of consumption.

Guideline values for chemical substances were derived using human data where available, or in most cases, by using animal data accompanied by appropriate safety factors for extrapolation to humans.

For substances for which a toxicity threshold exists, guideline values were generally calculated using Equation 4 (see page 10). Guideline values for chemicals for non-threshold chemicals (such as carcinogens) were generally based on a calculation that estimated an additional lifetime risk of one fatal cancer per one per million people (risk = 10^{-6}) in accordance with Equation 5 (page 10).

In these calculations, it was assumed that the average weight of an Australian adult is 70 kilograms, and where there is a specific need to protect young children, the average weight of a child at two years of age was assumed to be 13 kilograms.

For chemicals that are used commercially or industrially, it was assumed, in the absence of other information, that water contributes 10 per cent of intake. For compounds that are not used commercially or industrially, a higher proportion of intake (usually 20 per cent but sometimes 80 per cent or 100 per cent) was assumed to come from drinking water.

The amount of water consumed by an adult each day was assumed to be two litres. If the guideline value is based on the weight of a child, 1 litre per day was assumed.

Safety factors generally applied include:

- a factor of 10 for variations between animals of the same species (because some animals within a species may be more sensitive to the effects of a chemical than the group tested)
- a factor of 10 for variations between species (because the animal species tested may be less sensitive than humans, and in many cases human sensitivity is unknown)
- a factor of 10 if data from a subchronic study are used in the absence of reliable data from chronic studies (this factor can be less if chronic studies are available and indicate that no other effects occur, or that other effects are mild)
- a factor of up to 10 if the guideline point of departure was based on a LOAEL rather than a NOAEL.

3.7 Australian Guidelines for Water Recycling—Phase 1

Phase 1 of the *Australian Guidelines for Water Recycling* was published in 2006 by the National Resource Management Ministerial Council and the Environment Protection and Heritage Council [126]. Phase 1 does not cover the development or management of potable water recycling schemes: it provides guidance on managing the health and environmental risks associated with the use of recycled water for:

- residential garden watering, car washing, toilet flushing and clothes washing
- irrigation for urban recreational and open space, and agriculture and horticulture
- fire protection and fire fighting systems
- industrial uses, including cooling water
- greywater treated on-site (including in high rise apartments and office blocks) for use for garden watering, car washing, toilet flushing and clothes washing.

These guidelines are notable for the risk management framework that they provide, rather than simply relying on end-product (recycled water) quality testing as the basis for managing water recycling schemes. The risk management framework used is based on the framework detailed in the ADWG [4].

The guidelines consider management of risks to human health and environmental health. For human health, the main focus is on microbial hazards, although chemicals must also be considered. For the environment, chemical hazards are considered to pose a greater risk than microbial hazards, and thus these are the main focus.

3.7.1 Assessment of the recycled water system

Assessment of the recycled water system must be carried out before strategies to prevent and control hazards are planned and implemented. The aim of the assessment is to provide a detailed understanding of the entire recycled water supply system, from source to end use or receiving environment. The hazards, sources and events (including treatment failure) that can compromise recycled water quality are to be characterised and preventive measures needed to effectively control hazards and prevent adverse impacts on humans and the environment identified. Recycled water system analysis then requires the following steps, which are detailed in the guidelines [126]:

Source of recycled water, intended uses, receiving environments and routes of exposure

- *Identify source of water.*
- *Identify intended uses, routes of exposure, receiving environments, endpoints and effects.*
- *Consider inadvertent or unauthorised uses.*

Recycled water system analysis

- *Assemble pertinent information and document key characteristics of the recycled water system*
- *Assemble a team with appropriate knowledge and expertise*
- *Construct a flow diagram of the recycled water system*

- *Periodically review the recycled water system analysis.*

Assessment of water quality data

- *Assemble historical data about sewage, greywater or stormwater quality, as well as data from treatment plants and of recycled water supplied to users; identify gaps and assess reliability of data.*

- *Assess data (using tools such as control charts and trends analysis), to identify trends and potential problems.*

Hazard identification and risk assessment

- *Define the approach to hazard identification and risk assessment, considering both public and ecological health.*

- *Periodically review and update the hazard identification and risk assessment to incorporate any changes.*

- *Identify and document hazards and hazardous events for each component of the recycled water system.*

- *Estimate the level of risk for each identified hazard or hazardous event.*

- *Consider inadvertent and unauthorised use or discharge.*

- *Determine significant risks and document priorities for risk management.*

- *Evaluate the major sources of uncertainty associated with each hazard and hazardous event and consider actions to reduce uncertainty.*

Examples of potential hazardous events that could be considered are provides in the guidelines and reproduced here in Table 6 [126]. A further comprehensive database of potential hazardous events for drinking water supply systems has been developed by the European Commission research project 'TECHNEAU' and is publicly available [127].

The level of risk for each hazardous event can be estimated by identifying the likelihood (Table 7) that it will happen and the severity of the consequences (Table 8) if it does. Guidelines and criteria developed for specific combinations of source water and end use should be referred to when estimating risk. Using a suitable risk matrix, the likelihood and consequences can then be combined to provide a qualitative estimation of risk (Table 9). Risks that are judged to be very high will generally be the focus of critical control points.

Table 6: Examples of potential hazardous events [126]

Stormwater catchments	
• Chemical use in catchment areas (e.g. use of fertilisers and agricultural pesticides) • Sewage overflows and septic system discharges • Entry of livestock waste • Climatic and seasonal variations (e.g. heavy rainfall, drought) Industrial discharges	• Major fires (fire-fighting chemicals), natural disasters, sabotage • Accidental spills or discharge • Leaching from existing or historical waste-disposal (e.g. landfill) or mining sites, and contaminated sites and hazardous wastes • Road washing
Sewer systems	
• Discharges of domestic and household chemicals • Discharges of toxic material • Infiltration of stormwater • Infiltration of saline groundwater to sewer	• Trade-waste discharges, including accidental and illegal discharges • Infiltration of waste from contaminated sites or waste disposal sites (e.g. landfill)
Water reuse and drinking water treatment systems	
• Chemical dosing failures • Disinfection malfunctions • Equipment malfunctions • Failure of alarms and monitoring equipment • Formation of disinfection byproducts • Inadequate: – backup for key processes – equipment or unit processes – filter operation and backwash recycling – mixing of treatment chemicals and coagulants	• Poor reliability of processes • Power failures • Sabotage and natural disasters • Significant flow variations through water treatment systems • Use of unapproved or contaminated water treatment chemicals and materials • Failure of staff to respond appropriately to alarms or fluctuations in treatment processes
Receiving waters (reservoirs, rivers and streams)	
• Short circuiting • Forest fires and natural disasters • Climatic and seasonal variations (e.g. heavy rainfall, drought) • Cyanobacterial blooms • Livestock access • Inadequate buffer zones and vegetation	• Inadequate storage (e.g. during winter or other times of low recycled water usage) • Leakage from storage to groundwater • Birds and vermin • Accidental spillage from public roads • Sabotage
Distribution systems	
• Cross-connections with lower quality water or storages holding industrial chemicals • Inadequate repair and maintenance, inadequate system flushing and reservoir cleaning • Inappropriate materials and coatings or material failure	• Biofilms, sloughing and resuspension or regrowth • Formation of disinfection byproducts • Pipe bursts or leaks • Sabotage and natural disasters
Users of drinking water	
• Leaching of metals from piping and fittings • Unauthorized plumbing work leading to cross-connections to lower quality water	• Inadequate auditing and inspection of internal plumbing systems • Use of inappropriate plumbing and construction materials

Table 7: Qualitative measures of likelihood [126]

Level	*Descriptor*	*Example description*
A	Rare	May occur only in exceptional circumstances. May occur once in 100 years
B	Unlikely	Could occur within 20 years or in unusual circumstances
C	Possible	Might occur or should be expected to occur within a 5- to 10-year period
D	Likely	Will probably occur within a 1- to 5-year period
E	Almost certain	Is expected to occur with a probability of multiple occurrences within a year.

Table 8: Qualitative measures of consequence or impact [126]

Level	*Descriptor*	*Example description*
1	Insignificant	Insignificant impact or not detectable
2	Minor	Health—Minor impact for small population Environment—Potentially harmful to local ecosystem with local impacts contained to on-site
3	Moderate	Health—Minor impact for large population Environment—Potentially harmful to regional ecosystem with local impacts primarily contained onsite
4	Major	Health—Major impact for small population Environment—Potentially lethal to local ecosystem; predominantly local, but potential for offsite impacts
5	Catastrophic	Health—Major impacts for large population Environment—Potentially lethal to regional ecosystem or threatened species; widespread on-site and offsite impacts

Table 9: Qualitative risk estimation [126]

Consequences

Likelihood

	1-Insignificant	*2-Minor*	*3-Moderate*	*4-Major*	*5-Catastrophic*
A Rare	Low	Low	Low	High	High
B Unlikely	Low	Low	Moderate	High	Very high
C Possible	Low	Moderate	High	Very high	Very high
D Likely	Low	Moderate	High	Very high	Very high
E Almost Certain	Low	Moderate	High	Very high	Very high

3.7.2 Managing heath risks in recycled water

In addition to the risk-matrix analysis of hazardous events, the guidelines promote a quantitative assessment of health-based risks (with a strong focus on risks from pathogens).

In managing risks from pathogens to human health, the guidelines use disability adjusted life years (DALYs) to convert the likelihood of infection or illness into burdens of disease, setting a tolerable risk as 10^{-6} DALYs per person per year. The tolerable risk is then used to set health-based targets that, if met, will ensure that the risk remains below 10^{-6} DALYs per person per year.

In considering exposure, both intended and unintended uses need to be considered. Unintended uses can be deliberate (for example, filling a swimming pool with recycled water) or accidental (for example, mistakenly cross-connecting water supplies). Similarly, in characterising risk, both maximum risk (risk in the absence of preventive measures) and residual risk (risk that remains after consideration of existing preventive measures) need to be taken into account.

Examples of exposure volumes and frequencies of exposures per person are provided in the guidelines and reproduced in Table 10. It is stated that these values could be used as defaults where specific or local information is not available. In general, the volumes provided are considered to be conservative.

Table 10: Intended uses and associated exposures for recycled water [126]

Activity	Route of exposure	Volume (mL)	Frequency (yr^{-1})	Comments
Garden irrigation	Ingestion of sprays	0.1	90	Garden watering estimated to typically occur every second day during dry months (half year). Exposure to aerosols occurs during watering.
Garden irrigation	Routine ingestion	1	90	Routine exposure results from indirect ingestion via contact with plants, lawns, etc.
	Accidental ingestion	100	1	Infrequent event.
Municipal irrigation	Ingestion	1	50	Frequencies moderate as most people use municipal areas sparingly (estimate 1/2–3 weeks). People are unlikely to be directly exposed to large amounts of spray and therefore exposure is from indirect ingestion via contact with lawns, etc. Likely to be higher when used to irrigate facilities such as sports grounds and golf courses (estimate 1/week).
Food crop consumption (home grown)	Ingestion	5 (lettuce)	7	100 g of lettuce leaves hold 10.8 mL water and cucumbers 0.4 mL at worst case (immediately post watering). A serve of lettuce (40 g) might hold 5 mL of recycled water and other produce might hold up to 1 mL per serve. Calculated frequencies are based on Australian Bureau of Statistics (ABS) data.
		1 (other raw produce)	50	
Food crop consumption (commercial)	Ingestion	5 (lettuce)	70	100 g of lettuce leaves hold 10.8 mL water and cucumbers 0.4 mL at worst case (immediately post watering). A serve of lettuce (40 g) might hold 5 mL of recycled water and other produce might hold up to 1 mL per serve. Calculated frequencies are based on ABS data.
		1 (other raw produce)	140	
Toilet flushing	Ingestion of sprays	0.01	1100	Frequency based on three uses of home toilet per day. Aerosol volumes are less than those produced by garden irrigation.
Washing machine use	Ingestion of sprays	0.01	100	Assumes one member of household exposed. Calculated frequency based on ABS data. Aerosol volumes are less than those produced by garden irrigation (machines usually closed during operation).
Fire fighting	Ingestion of water and sprays	20	50	Median ingestion for firefighters estimated at 20 mL per fire with a maximum number of fires fought within area served by recycled water of 50 per year.
Cross-connection of dual reticulation systems with drinking water mains	Ingestion	1000/day	1/1000 houses	Total consumption is assumed to be 2 litres per day, of which 1 litre is consumed cold. Affected individuals may consume water 365 days per year. A conservative estimate of 1/1000 houses has been considered.

mL = millilitres; g = gram

The process used to assess environmental risks is to first identify water sources, uses, users and routes of exposure. Following this, the recycled water system and water quality data are assessed; and finally, hazards are identified and the overall risk assessed.

In managing risks to the environment, environmental guideline values are used; these guideline values are related to impacts on specific endpoints or receptors within the environment. Examples of endpoints include specific grasses, native tree species or soil types in the area where the recycled water is to be used.

As with health risks, assessing risks to the environment involves considering both maximum and residual risk. However, in the case of the environment, there is also an initial screening-level risk assessment, which might involve, for example, comparing hazard concentrations in the recycled water with known guideline values for specific applications.

3.8 Australian Guidelines for Water Recycling – Phase 2

Phase 2 of the *Australian Guidelines for Water Recycling* consists of three modules that specifically address stormwater reuse [128], managed aquifer recharge [129], and augmentation of drinking water supplies [83]. The module for the augmentation of drinking water supplies, in particular, provides risk management guidance for chemical and pathogenic contaminants in addition to that which was provided in the Phase 1 guidelines.

Consistent with the Phase 1 guidelines, the Phase 2 guidelines use DALYs as a measure of risk associated with pathogenic organisms and apply a tolerable risk of 10^{-6} DALYs per person per year. The approach adopted for chemicals is based on that of the ADWG where the tolerable risk is implemented through the development of corresponding guideline values. For chemicals with threshold toxicities, the guideline values generally correspond to identified NOAELs or LOAELs with applied uncertainty factors. For non-threshold toxicity chemicals, such as carcinogens, guideline values are based on the 1×10^{-6} cancer risk following lifetime consumption (defined as 70 years).

Chemical guideline values are tabulated in the guidelines along with maximum concentrations of the chemicals that have been reported from studies of secondary or tertiary treated sewage effluent. The data were compiled from a range of Australian and international datasets. However the guidelines note that the table should not be taken as exhaustive and that detailed assessment of individual systems—including surveys of industrial, agricultural, domestic and urban inputs—should be undertaken to identify potential chemical hazards that could affect source water quality. In most cases, this assessment will need to be supported by extensive monitoring of the source water quality.

The health-related guideline values for chemicals have been acquired or derived from various sources as described in Appendix A of the Phase 2 guidelines. Where possible, guideline values were acquired from existing guidelines and standards, with the ADWG being the primary source. Where no existing guideline values could be identified, guidelines were developed from available health, toxicological or structural information.

Guidelines for dioxins, furans and polychlorinated biphenyls (PCBs) were developed using National Health and Medical Research Council (NHMRC) recommended tolerable intakes that account for the combined total exposure for multiple chemicals. Using toxicity equivalency factors as evaluated by the World Health Organisation [130], a total concentration guideline value of 0.016 nanograms per litre toxicity equivalents was determined for this group of chemicals.

Guideline values for human pharmaceuticals were derived from lowest daily therapeutic doses divided by uncertainty factors of 1000–10,000. Guidelines for pharmaceuticals used for agricultural or veterinary purposes were developed from acceptable daily intake (ADI) values established by a range of international food and health agencies.

Where neither existing guidelines, nor relevant toxicological data for developing guidelines was available, a quantitative structure–activity relationship approach was used as method for determining thresholds of toxicological concern.

The guidelines note that an extensive range of parameters can be used to represent a risk. They acknowledge that is not physically or economically feasible to test for all parameters, nor is it necessary. The list of guideline values is not intended to be regarded as a mandatory set of parameters to be included in monitoring programs. However, key characteristics that must be considered for system performance verification include:

- microbial indicator organisms
- health-related chemicals, including:
  - those identified in the ADWG
  - key organic chemicals of concern (for example, NDMA)
  - indicators or index chemicals for organic chemicals (for example, contraceptive hormones)
- biological activity.

The choice of specific parameters must be informed by hazard identification and risk assessment. These, in turn, should be informed by consideration of source water quality, potential agricultural and industrial inputs, treatment processes, chemicals and byproducts, and receiving water quality.

4. Analysis of Chemical Constituents

In order to assess exposure to chemical constituents from a (recycled) water supply, it is generally necessary to undertake some analytical measurement of a contaminant's presence and concentration range. There are several approaches that can achieve this, including direct chemical measurement, measurement of bulk water quality parameters, or the use of bioassays to measure chemical activity that may be indicative of the presence and concentration of a specific group of chemicals.

Numerous decades of water quality monitoring have provided a good (though always improving) understanding of which chemicals are likely to be present in drinking water (from traditional sources) at significant enough concentrations to present an elevated level of risk. However, drinking water suppliers have much less experience in dealing with the diversity of chemicals that may be present in municipal effluent.

Methods involving direct chemical measurements are limited in that they will identify only the chemicals that are specifically targeted. This can only ever be a small subset of the all the chemicals that may be present. Bulk parameters provide a more inclusive measurement, but they tend to provide limited characterisation of the range of chemicals present and thus limited information regarding risk. Toxicological testing can provide quantitative information regarding water quality in terms that may be directly relevant to risk assessment. However, without targeted identification of specific chemical contaminants, few clues are available regarding the source of the contamination or effective steps that may be taken to reduce it. A range of approaches involving bulk parameter monitoring, targeted chemical analysis and direct toxicity testing are described in the following sections.

Figure 12: Sample collection from a reverse osmosis module.

4.1 Bulk parameter monitoring

A number of bulk water quality parameters are commonly monitored as a measure of overall chemical water quality for wastewater and/or potable water supplies. These include biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), conductivity, colour and UV absorbance [131–134]. These measurements may be undertaken in order to meet water quality compliance requirements or to demonstrate the effective performance of water treatment operations.

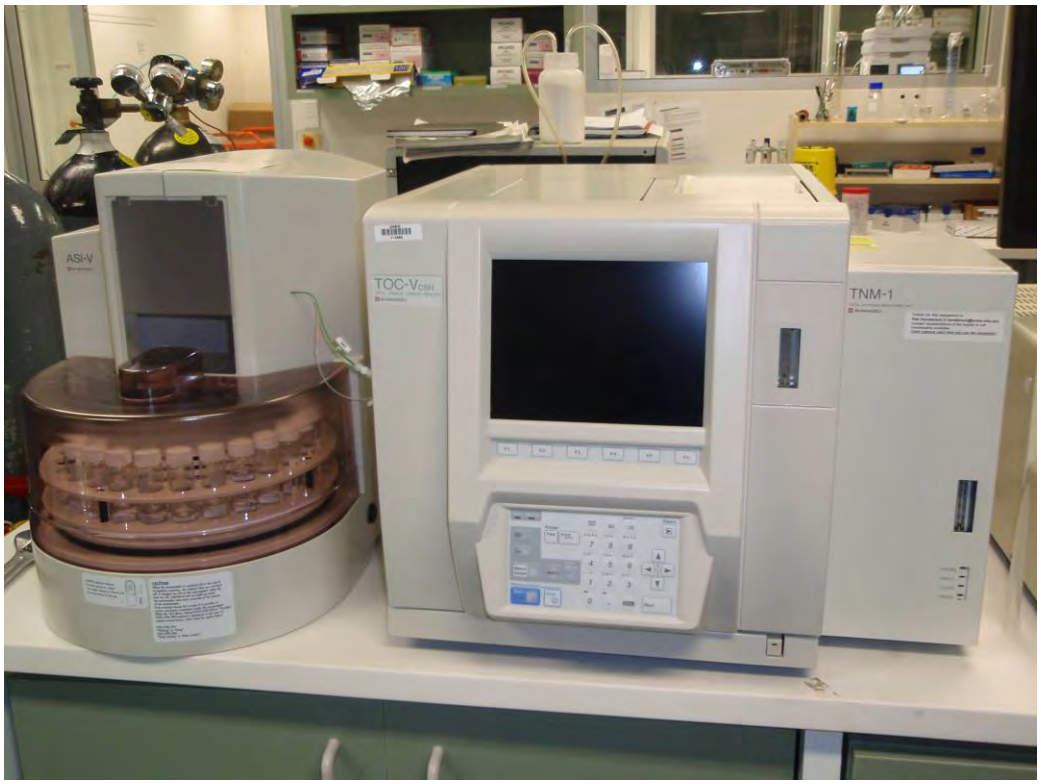
4.1.1 Total organic carbon and dissolved organic carbon

As the term suggests, TOC is used to measure the total concentration of organic carbon in solution (Figure 13). An alternative measurement is of dissolved organic carbon (DOC), which is achieved by filtering the water to remove any suspended matter prior to analysis. TOC or DOC measurement is of vital importance to the operation of water and wastewater treatment plants [135; 136].

Wastewaters may contain very high levels of organic compounds (TOC > 100 milligrams per litre), while drinking water TOCs tend to range from less than 100 micrograms per litre to more than 10 milligrams per litre. In addition to the potentially toxic chemicals that may be part of the measured TOC, organic constituents are known to react with disinfectants to produce potentially toxic and carcinogenic compounds. An increasing number of regulations and methodologies have begun to rely upon TOC analysis as a surrogate measure for disinfectant byproduct formation potential [137].

To determine the total quantity of organic carbon, the organic molecules must be degraded and converted to a single molecular species that can be quantitatively measured. To achieve this, TOC methods use high temperatures, catalysts, and oxygen, or lower temperatures ($<100^{O}C$) with UV irradiation and/or chemical oxidants to convert organic carbon to carbon dioxide (CO_2) [138; 139]. The CO_2 may then be purged from the sample, dried, and quantitatively measured. The measurement of CO_2 is typically undertaken by infrared absorbance or by the use of a coulometric titrator. Alternatively, it can be separated from the aqueous sample by means of a CO_2-selective membrane into a high-purity water solution in which a corresponding measured increase in conductivity is related to the quantity of CO_2 passing the membrane.

Figure 13: Total organic carbon analyser



4.1.2 Organic nitrogen and total nitrogen

Nitrogen occurs in water and wastewater in many forms including nitrate, nitrite, ammonia and organic nitrogen. Organic nitrogen is defined functionally as organically bound nitrogen in the trinegative oxidation state. As such, it does not include all organic nitrogen compounds, but does include proteins and peptides, nucleic acids, urea and numerous synthetic organic materials. Total organic nitrogen concentrations in raw sewage may be as high as 20 mg/L [134].

Organic nitrogen is most commonly determined by the ‘kjeldahl method’, which involves conversion of nitrogen in the trinegative oxidation state to ammonia and subsequent ammonia analysis. Thus organic nitrogen and ammonia may be determined together and are commonly referred to as ‘kjeldahl nitrogen’. Kjeldahl nitrogen methods do not account for nitrogen in the form of azide, azine, azo, hydrazone, nitrate, nitrite, nitrile, nitro, nitroso, oxime, or semi-carbazone [134].

Total oxidised nitrogen is the sum of nitrate and nitrite nitrogen. Nitrite is an intermediate oxidation state of nitrogen, formed during the oxidation of ammonia to nitrate, as well as by the reduction of nitrate. Such oxidation and reduction processes may occur in wastewater treatment plants, either unintentionally or as a result of carefully engineered nitrification and denitrification processes.

Total nitrogen can be determined by oxidative digestion of all digestible nitrogen forms to nitrate, followed by measurement of nitrate concentration. Alkaline persulfate oxidation, either alone or with the aid of UV radiation is commonly used to effect the digestion process [134]. The residual nitrate is most commonly measured by reduction to nitrite by cadmium and then further reaction to form a diazonium ion. The diazonium ion is subsequently used to form a pink dye that absorbs radiation at 540 nanometres in an amount that is proportional to the total nitrogen concentration.

4.1.3 Biochemical oxygen demand (BOD)

BOD is used as a standardised measure of the relative oxygen requirements of wastewater, effluent and polluted water. The widest application is in evaluation of the BOD removal efficiency of secondary biological treatment systems such as activated sludge treatment or trickling filters.

The BOD test involves the measurement of dissolved molecular oxygen utilised during a specified incubation period for the biochemical degradation of organic material as well as the oxygen used to oxidise inorganic material such as reduced sulphides and ferrous iron. BOD may also measure the consumption of oxygen used to oxidise reduced forms of nitrogen unless their oxidation is prevented by an inhibitor.

The most common application of the BOD test involves an incubation period of five days (BOD_5). Accordingly, the use of BOD for rapid or online monitoring of water quality is severely limited. Furthermore, BOD testing relies on the measurement of residual oxygen, which is often present at lower concentrations than the solution BOD. Therefore samples often need to be diluted prior to measurement thus further limiting the sensitivity of the technique. The typical analytical detection limit for BOD is around 2 milligrams per litre, which is significantly greater than would normally be expected for high quality recycled waters.

4.1.4 Chemical oxygen demand (COD)

COD is a measure of the amount of a specified oxidant that reacts with the constituents of a water sample under controlled conditions. It is often used as a measurement of pollutants in wastewater and natural waters.

Both organic and inorganic components of a solution may be oxidised during COD measurement. However, in most cases, the organic component predominates and is of greatest interest. The quantity of the oxidant consumed is expressed in terms of its oxygen equivalence. The most commonly used oxidant for COD measurement is the dichromate ion ($Cr_2O_7^{2-}$), which is reduced to the chromic ion (Cr^{3+}) during the measurement.

Like BOD, COD is generally not useful for high quality recycled water compliance monitoring since normal concentrations are well below available analytical detection limits.

4.1.5 Conductivity

Conductivity is a measure of the ability of the water solution to carry an electric current. The ability to do so depends on the presence of dissolved ions. The conductivity measurement is a function of the total concentration of ions, their valence (charge), their mobility, and the temperature of the solution. Of these, the parameter most subject to change during advanced water treatment processes is total ion concentration. As such, conductivity is used as a surrogate measure of total inorganic ion concentration. Solution conductivity is sometimes reported in units of microohms per centimetre ($\mu\Omega$/cm) or equivalently in microsiemens per centimetre (μS/cm).

4.1.6 Ultraviolet (UV) absorbance

The use of UV absorbance for monitoring wastewater treatment processes has been widely researched and is rapidly growing in application [140–145]. Bench-scale UV-visible spectrophotometers are well established and commonly available in many water quality laboratories (Figure 14).

For UV measurements, absorbance of incident radiation causes the excitation of loosely-held electrons within double and triple bonds of organic molecules. UV absorbance is a measure of the absorbance (A) of such radiation at a specified wavelength according to the Beer-Lambert Law:

$$A = \alpha Lc = Log_{10} (I_0/I_1)$$

Where α = absorption coefficient, L = absorbance path length, c= concentration of absorbing species, I_0 = intensity of the incident radiation, and I = intensity of the radiation remaining after transmission through the test sample.

It can be inferred from the Beer-Lambert Law that the level of absorbance (A) at a specified wavelength is directly proportional to the concentration of the absorbing species in solution. Accordingly, UV absorbance provides a surrogate measure of the total concentration of dissolved chemicals with UV-absorbing molecular characteristics. UV absorbance of water is most commonly undertaken at a wavelength of 254 nanometres (so called UV_{254}), which provides a surrogate measure of the concentration of organic chemicals containing aromatic (benzene-like) and other unsaturated functional groups.

Figure 14: UV-Visible spectrophotometer

A more appropriate parameter that is used for assessing the relative degree if aromaticity of dissolved organic carbon is the specific UV absorbance ($SUVA_{254}$), which is the ratio between UV_{254} and DOC. The $SUVA_{254}$ measure is widely used as a surrogate parameter to quantify the disinfection formation potential of natural organic matter [146; 147].

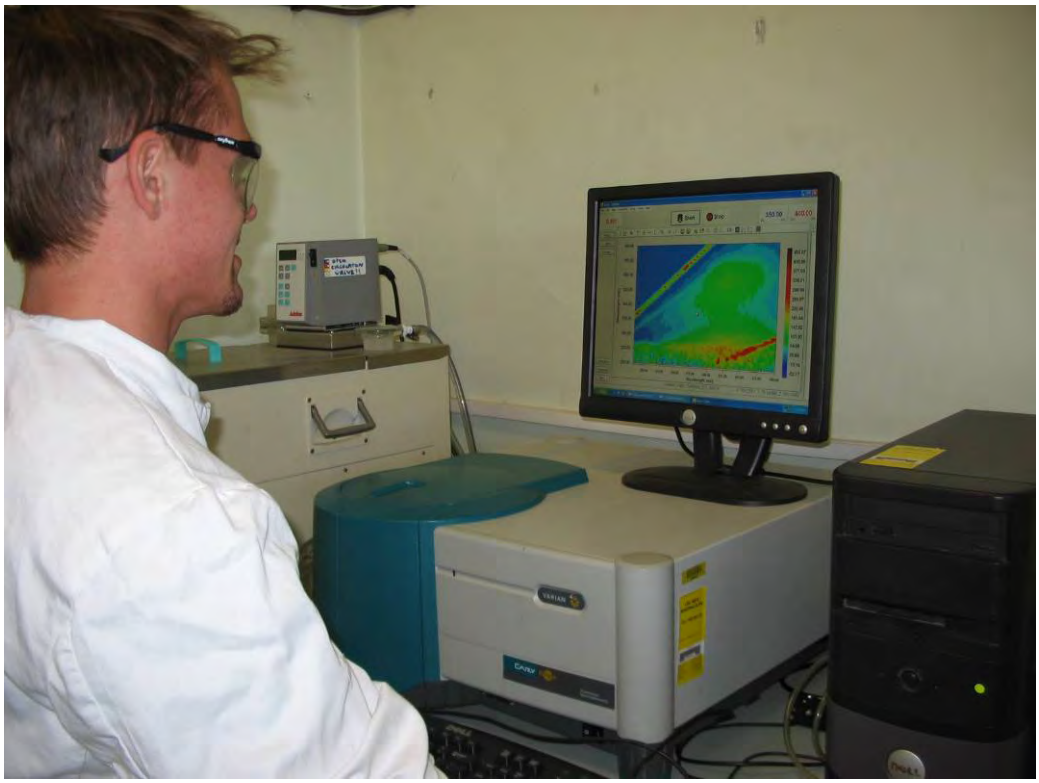
4.1.7 Fluorescence

The use of fluorescence spectroscopy for monitoring wastewater treatment processes is still an emerging area of research, but one that shows considerable promise as a sensitive and

powerful application [148–152]. The potential use of fluorescence as a monitoring tool of specific application to recycled water has been proposed by Henderson et al. [153].

Traditionally, fluorescence measurements have been presented as emission spectra following irradiation at a fixed excitation wavelength. Further developments have allowed synchronous fluorescence scanning, which is the measurement of emission spectra at an offset of the emission wavelength minus the excitation wavelength (Δλ), with typical offsets of 20–60 nanometres [149; 154; 155]. Recent technological advances have allowed the rapid detection (less than 1 minute) of 3-dimensional excitation-emission matrices [153; 156] (Figure 15). Each such matrix is a composite of emission scans from a single sample recorded at incrementing excitation wavelengths and arranged in a grid (excitation x emission x intensity). Hence, large amounts of data are collected from each sample, facilitating the application of a wide range of powerful statistical analyses.

Figure 15: Fluorescence excitation-emission matrix spectrophotometer



4.2 Trace chemical analysis

Monitoring of specific trace chemicals in water is commonly undertaken with two distinct aims:

1. to confirm safe levels of specific chemical species according to previously established toxicological or ecological implications
2. to enable a broader assessment of water quality or treatment process performance on the basis of the presence or removal of established specific ‘indicator chemicals’.

Trace chemical analysis is routinely undertaken to assess or demonstrate the meeting of compliance objectives for wastewater quality or dinking water quality. In most jurisdictions, wastewater and drinking water quality is assessed by the measured presence of a series of inorganic and organic species, including a range of disinfection byproducts, metal ions, pesticides and industrial organic chemicals.

Figure 16: Sampling ports at an Australian advanced water treatment plant

4.2.1 Organic chemicals

Trace organic chemicals—such as pesticides, pharmaceuticals and industrial chemicals—must generally be monitored by advanced instrumental techniques. For many organic chemicals such as pesticides and industrial chemicals, relevant concentrations in drinking water, in terms of health significance, are commonly in the microgram per litre or nanogram per litre range. To achieve suitably low analytical detection limits, it is therefore usually necessary to undertake analysis by initial sample concentration followed by highly sensitive and highly selective instrumental techniques.

Many standard methods incorporate liquid–liquid extraction techniques using solvents such as hexane, chloroform, dichloromethane or diethyl ether for the extraction of organic substances from water. However, since the 1990s, there has been a rapid shift away from solvent extraction methods towards methods requiring lower volumes of organic solvents.

Solid phase extraction, using cartridges (‘SPE tubes’) or disks, is an increasingly popular alternative and the majority of newly developed techniques for trace organics extraction rely upon it. Solid phase extraction of water samples typically involves passing a volume of water (up to a litre) through an adsorbent solid phase with the aim of retaining the organic analytes on the surface of the solid phase. The analytes are subsequently washed from the solid phase using a small volume (up to 10 millilitres) of solvent such as methanol or acetone.

Some emerging extraction techniques are moving towards the use of only extremely small volumes of organic solvents or none at all. Examples include solid-phase microextraction, single-drop microextraction, hollow-fibre liquid-phase microextraction, and subcritical water extraction [157].

Following extraction, there are numerous approaches to selective measurement of organic chemical species. The most universal of these rely upon chromatographic separation and then detection. Chromatographic separation is most commonly undertaken by gas chromatography (GC) or high performance liquid chromatography (HPLC). The choice between the two normally depends on physical properties of the analytes, including volatility, thermal stability and suitability for appropriate chemical derivatisations.

After chromatographic separation, detection can be undertaken by a wide range of detectors, including UV/Vis spectrometers, fluorescence spectrometers, electron caption detectors, flame ionisation detectors, and mass spectral (MS) detectors.

MS detectors themselves are quite variable with appropriate selection to be made on the basis of analyte properties, matrix properties and necessary detection limit. In general, MS detectors may be operated in 'scan' mode or, more selectively, in selected ion monitoring mode. Considerably greater selectivity (and hence sensitivity) can normally be achieved with tandem mass spectral methods (MS–MS) including HPLC/MS–MS (Figure 17) and GC/MS–MS (Figure 18).

Figure 17: Trace quantitative analysis of organic contaminants by HPLC/MS–MS

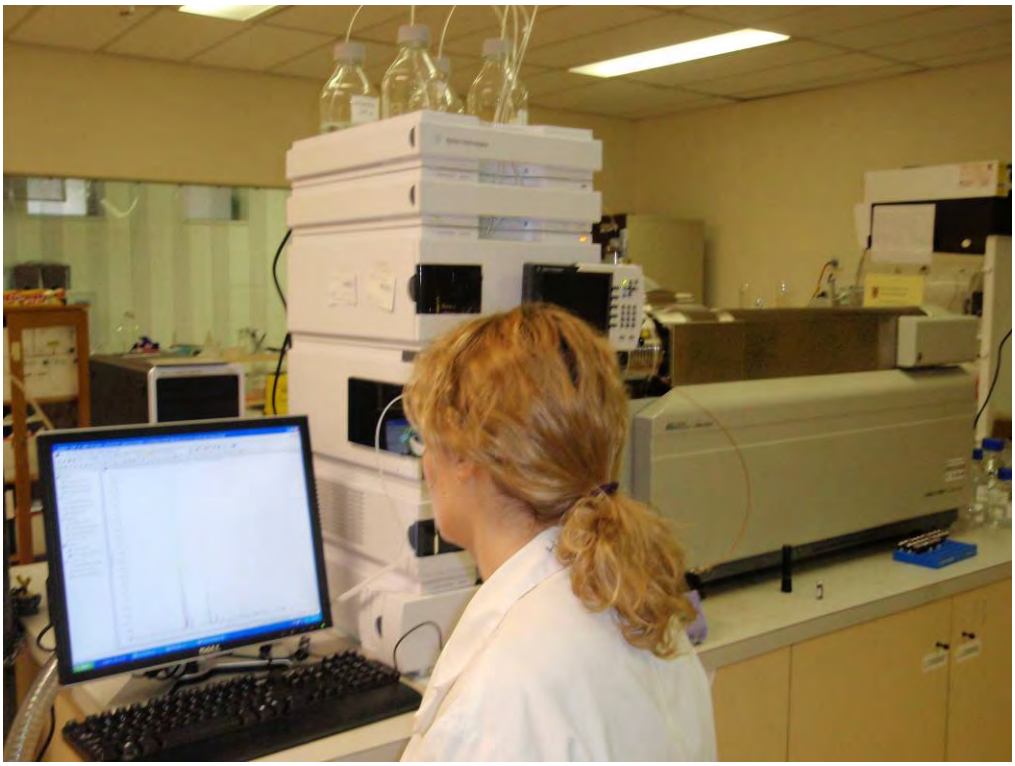
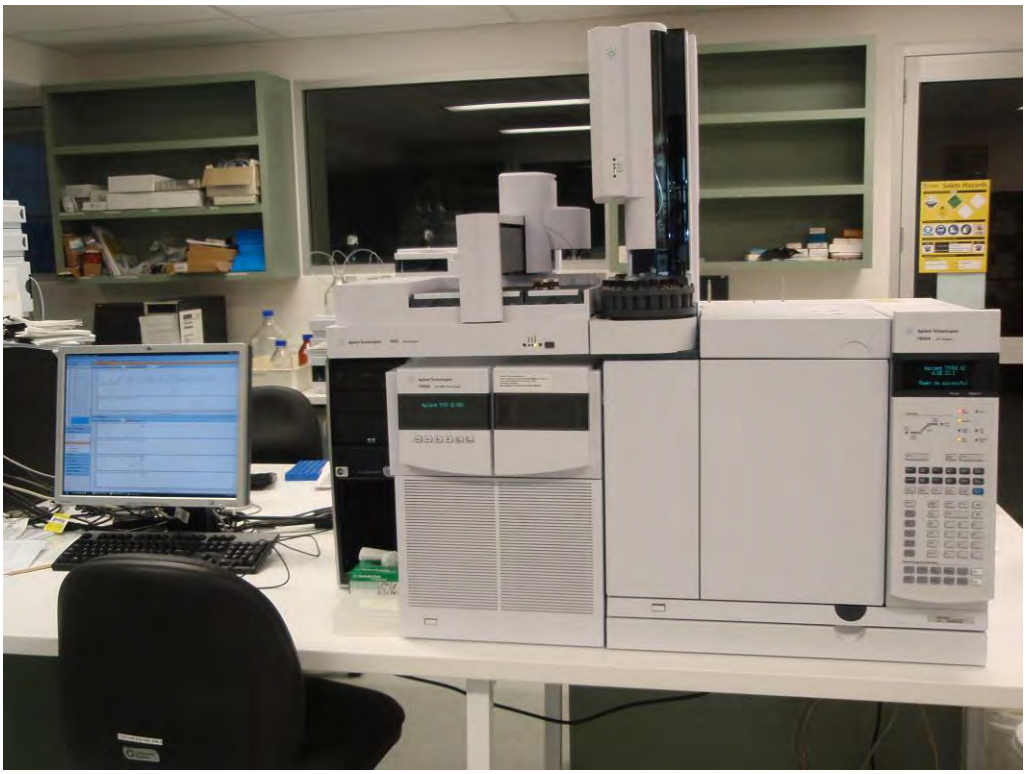


Figure 18: Trace quantitative analysis of organic contaminants by GC/MS–MS



4.2.2 Inorganic chemicals

Trace elements including metal ions can be simply measured by graphite furnace atomic absorption spectrometry following suitable pre-treatment. More sensitive methods include Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP–AES) (Figure 19) and, more recently, Inductively Coupled Plasma – Mass Spectrometry (ICP–MS). Colourimetric methods also exist, but they are less sensitive and suffer from interference.

Figure 19: ICP–AES for trace metals analysis

The presence of radionuclides can initially be identified relatively simply by gross alpha and gross beta measurements. The metallic radionuclides can be further identified by means of ICP–MS. Radon, as a noble gas is more difficult to identify in water and is most commonly measured in the air phase. Radionuclides can also be more broadly identified by the energy of the emitted radiation and half-life. Gamma-emitting radionuclides can be identified by gamma spectrometry.

Nitrogen analysis is complicated by the fact that it may be found in water in numerous forms and oxidation states, including nitrate, nitrite, ammonia and organically bound nitrogen (see organic nitrogen and total nitrogen, page 46). Along with nitrogen gas (N_2), the various forms are biochemically interconvertable. A number of methods exist for nitrite and nitrate, but ion chromatography is the most reliable for complex samples. Ammonia may be measured by titrimetric methods, an ammonia-selective electrode or by colourimetric analysis. An alternative approach to the selective analysis of ionic substances such as nitrite and nitrate anions is by the use of an ion chromatograph as pictured in Figure 20.

Important forms of phosphorous in wastewater can include orthophosphates, condensed phosphates and organically bound phosphates. Analysis generally involves conversion of the phosphorus form of interest to dissolved orthophosphate and then colourimetric determination.

Figure 20: Ion chromatograph for analysis of ionic substances such as nitrite and nitrate

4.3 Toxicity testing

Many scientists have suggested that direct toxicological testing assessment of recycled water may be the most effective way to ensure the water's chemical safety [158]. Toxicological testing involves collecting whole water samples and subjecting these to tests for a range of toxicological end-points. Toxicological endpoints may include testing for mutagenic activity, carcinogenic activity, hormonal activity such as estrogenicity, or various forms of acute toxicity. Such testing will generally require at least a pilot-scale advanced water treatment plant to be constructed in order to provide relevant samples for testing. Alternatively, it may be possible in some cases to undertake testing at existing water treatment facilities, as long as a case can be made that the source water quality and treatment process performance are comparable.

Even if the operators of a water recycling system could identify all of the organic chemical components in the specific municipal effluent, there would be scant toxicological data available for most of them and thus little basis for assigning risks. Recent Australian water recycling guidelines have partially addressed this data gap by the use of structurally-related 'thresholds of toxicological concern' [159].

Other important limitations of chemical species monitoring are that the full additive toxicity of a large number of chemicals, each present at very low concentrations, may not be identified unless each of the individual species is analysed for and determined to be present at concentrations greater than analytical detection limits. Finally, there is some concern that the toxicity of complex mixtures is poorly understood and, in some cases, may amount to more (or less) than simply additive impacts from the summation of each of the contributing chemical species. Toxicity testing provides a means of addressing these concerns.

4.3.1 *In vivo* toxicity testing

The most comprehensive approach to toxicity testing is considered to be live animal testing with organisms such as rats, mice and fish. One particular outbred line of mice has been used extensively for carcinogenesis experiments. These strains are known as SENCAR mice, which is derived from SENsitivity to CARcinogenisis. SENCAR mice are used to test for the presence of carcinogens and/or promoter agents to induce carcinogenesis. Other live-animal testing may include monitoring for subchronic toxicity (leading to death or other end-point indicators) or fetotoxicity. Fish biomonitoring may also be employed to test for effects of bioaccumulating chemicals as well as a range of toxic endpoints.

A comprehensive, two-year heath-effects study in Denver, Colorado used rats to investigate chronic toxicity and oncogenicity effects of reclaimed water [160]. These tests were conducted using 150-fold and 500-fold reclaimed water concentrates. Denver's current drinking water was used as a negative control since it is derived from a relatively protected source. Seventy male and 70 female Fischer 344 rats were supplied with concentrates of one of three kinds of water. These were drinking water, reverse osmosis – treated reclaimed water or ultrafiltration-treated reclaimed water. An additional 70 male and 70 female rats were supplied with distilled water and served as a control group. A further 15 males and 15 females served as the sentinel group.

The parameters evaluated in this study included clinical observations, survival rate, growth, food and water consumption, haematology, clinical chemistry, urinalysis, organ weights, gross autopsy and histopathological examination of all lesions, major tissues and organs. The incidence and types of clinical signs were comparable in all groups of the same sex. There were numerous statistically significant differences between control and treated groups in weekly measurements of body weight, food consumption, and water consumption, but all of these were minor and not consistent with treatment groups throughout the study. Therefore the differences were not considered to be treatment related.

There was a decrease in survival rates in some of the male treatment groups. The toxicological significance of this finding was not known since there was no similar decrease in survival in the female treatment groups. Furthermore, there was no decrease in survival rates in any male or female treatment group in a parallel mouse study.

Clinical pathology, gross pathology, and microscopic pathology conducted at weeks 26 and 65 and at the end of the study (week 104) did not reveal any findings that could be considered to be treatment related. The variety, frequency and severity of spontaneously occurring incidental lesions and neoplasms were within the anticipated range for the age and strain of rat. There was a higher incidence of thyroid 'C' cell adenoma in a group of male rats fed conventional drinking water concentrates. However, this higher incidence was reported to have been well within the historical range anticipated for this type of neoplasm.

The authors resolved that the administration of reclaimed water treated by reverse osmosis or ultrafiltration, or Denver's present drinking water at up to 500 times their normal concentration to rats over an extended period of their life expectancy, did not result in any demonstrable toxicological or carcinogenic effects. On the basis of this study as well as the parallel chronic mouse study and a two-generation reproductive study, it was concluded that the application of ultrafiltration/reverse osmosis treatment process to a secondary treated effluent can produce water that may be safely added to a water supply used as a source of drinking water for public consumption.

Fish biomonitoring experiments were undertaken to assess a pilot potable recycling plant in San Diego, California (the San Diego AQUA III plant). The aim was to provide information on chronic exposure to trace contaminants that accumulate in tissue but are not known to be

identified by genetic toxicity screening bioassays [161]. Juvenile Fathead Minnows (*Pimephales promelas*) were exposed to AQUA III plant effluent, drinking source water or laboratory-control water in flow-through aquaria. The biomonitoring measurements were survival and growth, swimming performance, and trace amounts of 68 base/neutral/acid extractable organics, 27 pesticides, and 27 inorganic chemicals found in fish tissues after exposure.

Survival of fish in the three water sources during 28-day experiments ranged from 94 to 99 per cent. With longer exposures, survival over the 180-day experiment continued to be 93–99 per cent in the laboratory-control water but fell to 82 per cent in AQUA III plant effluent and approximately 50 per cent in the raw drinking-water source. High mortality observed in the raw drinking-water source occurred in the first five days after the fish were transferred, and the survival rate in remaining fish over the second 90-day period was still only 65 per cent. This higher mortality could not be explained by chlorination upstream or other wastewater treatment plant records. Mortality in the AQUA III plant effluent was gradual, but still occurred mostly within the first 90 days of the 180-day exposure period. During the second 90-day period, the survival rate in the AQUA III plant effluent was 96 per cent.

There were no significant differences in weight or standard length attributable to water source after the 28-day exposure. However, after 90 days weight and standard length of AQUA III plant and raw drinking-water source fish were statistically different. Fish from the AQUA III plant effluent at both 90 and 180 days had significantly lower mean weight and standard length than those from the raw drinking-water source.

In seven comparisons of AQUA III plant effluent fish to laboratory control water fish, mean critical swimming speed was higher in AQUA III plant effluent fish in three trials, lower in three and essentially the same in one. Slightly higher critical swimming speed was seen in fish from raw drinking water compared to laboratory control water in six of the seven comparisons.

The authors of the biomonitoring study postulated that the underlying reasons for better growth, and probably as a consequence, better swimming performance of fish grown in the raw drinking water source may be related to ionic composition [161]. They point out that fish are known to thrive better in water containing an abundance of calcium, magnesium and other minerals. Effluent from the AQUA III plant did not contain as much of these and other trace elements as the raw drinking-water source because of the use of reverse osmosis treatment that generally removes more than 95 per cent of monovalent and divalent cations from the feed water. Also, this effluent contained no zooplankton and algae that were common in the raw drinking water.

The vast majority of the chemicals analysed in fish tissue were below analytical detection limits in samples. AQUA III plant effluent and raw drinking-water samples were not readily distinguishable in terms of bioaccumulation of organic chemical contaminants other than higher pesticide levels in fish from the raw drinking water. Concentrations of certain inorganic analytes were statistically different between the two sources. Higher lithium in the fish from AQUA III plant effluent was reported to be associated with added lithium introduced to the AQUA III plant during spiking experiments conducted in conjunction with the microbiology component of the health study. However, nickel accumulation in the tissue of fish from AQUA III plant effluent was presumed to be a result of original source water (sewage effluent) quality.

Fish studies were also undertaken in Singapore as a component of the NEWater Study [162]. The purpose was to assess long-term chronic toxicity as well as the estrogenic potential (reproductive and developmental). The orange-red strain of the Japanese Medaka Fish (*Oryzias latipes*) was selected for the study due to the availability of an extensive biological database for this species.

The fish testing was conducted over a 12-month period with two generations of fish. The NEWater tests were initially undertaken during 2001, and both generations showed no evidence of carcinogenic or estrogenic effects from exposure to NEWater. However, the fish study was to be repeated owing to design deficiencies of the aquarium system, fish husbandry issues, and weaknesses in the study protocol [162]. The repeated fish study was completed in 2003 and confirmed the findings of no estrogenic or carcinogenic effects [163].

A more recent study undertaken in Orange County California has demonstrated the use of live fish for a long-term online flow-through bioassay used to evaluate recycled water quality [164]. The approach that was used in this study included monitoring for the effects of endocrine-disrupting, tissue-altering, and carcinogenic compounds.

4.3.2 *In vitro* toxicity testing

In vitro toxicity tests are tests performed at the molecular or cellular level in the laboratory. Examples of molecular endpoints include binding to specific biological receptors or induction of particular biomolecular pathways, while cellular events could include cell death, maturation or growth. *In vitro* assays can be based on human cells, thus eliminating the inter-species predicament of *in vivo* testing. *In vitro* tests can also detect biological effects at much lower, environmentally-relevant concentrations, often below detection limits of chemical analysis and *in vivo* testing [165]. There are of course also limitations to *in vitro* bioassays, in particular the lack of metabolism and transport mechanisms that may modulate toxicity in whole organisms.

In vitro assays were developed for screening purposes and there is still much debate about their ability to predict whole-organism effects [158]. Nevertheless, *in vitro* bioassays are well-suited to monitoring of water quality, as they are significantly faster and cheaper than *in vivo* exposures, are amenable to high-throughput screening, and allow the generation of relatively rapid toxicology data without the need for ethically and financially expensive whole-animal experimentation [166].

In recent years, there has been a move towards standardising the various *in vitro* techniques available, with the creation of the European Centre for the Validation of Alternative Methods in 1991 and the US National Toxicology Program Interagency Centre for the Evaluation of Alternative Toxicological Methods in 1998. These two programs have generated thoroughly validated alternative methods using *in vitro* toxicity tests for some toxic endpoints.

Chemicals can be considered depending on their potential for subsequent effects in exposed humans and wildlife, and *in vitro* toxicity tests exist for a variety these endpoints [167]:

- Cytotoxic chemicals are acutely toxic, causing rapid cell death. Cytotoxicity can be caused by a wide range of chemicals in drinking water, in particular disinfection byproducts and cyanobacterial toxins. Some *in vitro* assays used to measure cytotoxicity include the Microdot and the Microtox assays.
- Immunotoxic chemicals cause an adverse effect on the immune system. These effects can include immunosuppression (reducing the efficacy of the immune system), immunostimulation (abnormal overstimulation of the immune system), hypersensitivity (such as allergic reactions) and autoimmunity (a condition where the immune system targets the organism's own cells and tissue). A range of chemicals have been linked to immunotoxicity in exposed humans, including PCBs, dioxins and organochlorine pesticides. Lymphotoxicity tests, cytokine expression tests, and genetically-engineered cell lines are examples of *in vitro* assays used to determine immunotoxicity.

- Genotoxic and mutagenic chemicals cause damage or modification to DNA, which may lead to formation of malignant tumours and cancer. It has been estimated that about 20 per cent of the approximately 80,000 chemicals in commerce are mutagens [168]. In water, mutagenic/genotoxic chemicals include heavy metals, polyaromatic hydrocarbons (PAHs), PCBs, pesticides and aromatic amines. Some *in vitro* assays to measure genotoxicity/mutagenicity include the Ames test, the SOS/umu test, the Comet assay and the gammaH2AX test.
- Neurotoxic chemicals cause damage to the nervous system or the brain. Nervous system damage can result in fatigue, confusion, irritability and other behavioural changes, as well as brain degeneration (encephalopathy). Neurotoxic chemicals in water include cyanobacterial toxins, heavy metals, organophosphorous pesticides, PCBs and halogenated aromatic hydrocarbons. Some examples of *in vitro* assays to measure neurotoxicity include the human neuroblastoma viability and neurite extension assays and acetyl cholinesterase enzyme activity assays.
- Teratogenic, fetogenic and embryogenic chemicals negatively impact the development of the developing foetus. Estimating development toxicity *in vitro* is more challenging. While *in vitro* bioassays for developmental effects can be based on embryonic stem cells [169], social and scientific debate persists over the use of stem cells and currently limits their application in Australia. As a result, these endpoints can currently be estimated by *in vivo* techniques only.
- Endocrine disrupting compounds are chemicals that can mimic the action of natural hormones and interfere with the endocrine system of exposed biological organisms. There is a wide range of suspected endocrine disrupters, including natural steroids (products of animal and human excretion), industrial plasticisers such as nonylphenol and bisphenol A, phthalates, pesticides such as dieldrin, DDT metabolites and atrazine, and some specific pharmaceuticals. Endocrine effects can be measured *in vitro* in assays such as the cancer cell proliferation assay, genetically-engineered cell lines, and competitive receptor binding assays.

Each type of bioassay has its advantages and limitations, and no single assay can provide a complete assessment of the biological activity of a sample. Therefore a battery of bioassays is required to rigorously assess the biological-effects potential of a sample. There is no doubt, however, that *in vitro* bioassays can be used as an effects-based assessment of water quality. Several studies have used *in vitro* toxicity testing to measure pollutants in Australian sewage water [170; 171]; and a similar approach could be used to monitor recycled water quality, particularly as a screen and prioritisation tool for subsequent chemical analysis.

A five-year toxicological study was initiated in 1978 at the Montebello Forebay Groundwater Replenishment Project, which is an indirect potable reuse scheme located within the Central Groundwater Basin in Los Angeles County [172]. At the time of the study, recycled water comprised around 16 per cent of the total inflow to the groundwater basin. The toxicological study sought to detect, isolate, characterise, and if possible, trace the origins of any previously unidentified carcinogens in the recycled water sources (three STP effluents) and well waters.

The Ames test and *Salmonella* tester strains (TA98 and TA100) were used to screen for mutagenic organics in 10,000 to 20,000-fold concentrates of reclaimed water prior to groundwater replenishment, stormwater, imported water, and also in chlorinated and unchlorinated groundwaters [172]. Some mutagenic activity was detected in 43 of the 56 organic concentrates tested, including at least one from each source. The level of mutagenic activity was (in decreasing order):

Storm runoff > dry weather runoff > reclaimed water > ground water > imported surface water

Most of the mutagenic activity appeared to be derived from chlorination processes. No relationship was observed between the estimated proportion of reclaimed water in the various wells and strength of mutagenic responses. Attempts were made to identify specific chemical species that may be responsible for the observed mutagenicity in groundwater samples; however, these efforts were not conclusively successful.

Based on the results of the Health Effects Study [172] and recommendations of the State of California Scientific Advisory Panel [173], authorisation was given in 1987 by the Regional Water Quality Control Board to increase the annual quantity of recycled water used for replenishment. The water reclamation requirements for the project were revised again to allow for even greater recharge volumes and up to 50 per cent reclaimed water in any one year providing that the running three year total did not exceed 35 per cent reclaimed water. The Los Angeles County Sanitation District continues to divert tertiary quality wastewater and captured stormwater into the groundwater recharge basins in the Montebello Forebay. This water contributes to the groundwater supply in Los Angeles County.

In the 1980s, the Potomac Estuary Experimental Water Treatment Plant (EEWTP) was constructed adjacent to a conventional sewage treatment plant on the Potomac Estuary in Washington DC. The US Army Corps of Engineers undertook a research program to determine the feasibility of using the EEWTP to produce potable water as a potential source for the city [174].

Based on potential future water use plans, an influent mix of 50 per cent estuary water and 50 per cent nitrified secondary effluent was selected for further treatment at the EEWTP. The blended water was treated by a series of processes that are generally considered to be conventional drinking-water treatment processes (such as flocculation, sedimentation and disinfection) as well as some additional processes including filtration and granular activated carbon adsorption. Advanced water treatment processes that would nowadays be considered for planned potable recycling (such as reverse osmosis or advanced oxidation) were emerging technologies at this time and not included in trials at the EEWTP. Three overall treatment trains were tested and these were compared to current water supplies from three local conventional drinking-water treatment plants.

Two short-term *in vitro* toxicology tests were selected to characterise the produced and conventional waters. These tests were undertaken with concentrated (150-fold) organic extracts used in the Ames *Salmonella* / microsome test, and a mammalian cell transformation test. Results showed low levels of mutagenic activity in the Ames test with the EEWPT-produced water exhibiting less activity than the three conventional drinking-water plants. The cell transformation test showed a small number of positive samples with no difference between the EEWPT water and the conventional drinking water.

Within the limits of the analytical techniques used and the influent water quality conditions observed, it was concluded that the process combinations monitored at the EEWPT were technically feasible for producing a water acceptable for human consumption from a 50 per cent blend of treated effluent [174]. However, it is important to note that a National Research Council review panel did not support this conclusion on the basis of the limited toxicological tests that were conducted [175]. This outcome was to have a significant impact in the USA in ensuring more thorough assessment of future trials in order to more comprehensively establish safety.

A health effects study was undertaken to compare the San Diego AQUA III plant effluent with the city's present raw water supply [88; 176; 177]. The study included screening for mutagenicity and bioaccumulation of the chemical mixtures present in the conventional water produced by the proposed indirect potable reuse scheme. Genetic toxicity and carcinogenicity testing were undertaken in a short-term study using four separate bioassay systems. These

were the Ames Assay, Micronucleus Test, 6-Thioguanine Resistance Assay, and Cellular Transformation Assay. The data from these bioassays of organic extracts indicate that the AQUA III plant effluent exhibited less genotoxic or mutagenic activity than the low levels observed in the raw drinking-water source.

A pilot advanced water treatment plant was operated in Tampa, Florida from 1987 to 1989 [178]. This was known at the Tampa Water Resource Recovery Project. The project was originally operated using chlorine as the final disinfectant, but this was replaced with ozone since the results of Ames testing indicated that ozone-disinfected product waters were less mutagenic. For similar reasons, the treatment train using granular activated carbon was selected for toxicological testing based on preliminary screening using the Ames assay.

The performance of the Tampa Water Resource Recovery Project was assessed in comparison Tampa's current water supply. Concentrated extracts of these water sources were used to prepare doses for toxicological testing at up to 1000 times the potential human exposure of a 70-kilogram person consuming two litres of water per day. Eight different toxicological tests were conducted to assess potential genotoxicity (Ames and sister chromatid assays), carcinogenicity (strain A lung adenoma and SENCAR mice initiation-promotion studies), fetotoxicity (teratology in rats and reproductive effects in mice), and subchronic toxicity (90-day gavage studies in mice and rats). The results were reported to be uniformly negative for the Tampa project product water [179].

4.3.3 Practicalities and ethics of toxicity testing

An obvious advantage of toxicological testing is that it is not necessary to know which chemicals may be responsible for a specific toxicity in order to measure it. Furthermore, depending on the specific mechanisms of the applied assay, full additive or synergistic effects of unknown chemicals can be accounted for.

However toxicity testing also has a number of limitations that must be recognised. One is that no matter how complex a bioassay system (or organism) may be, it will never be identical to a human being; and thus some uncertainty will remain in terms of extrapolation of results to public health implications. A further complication is that bioassays are sometimes prone to 'false positives' due to other sub-optimal conditions for organism survival (for example, temperature, oxygen availability, nutrient deficiency, salinity). For this reason, careful interpretation of results is necessary and in some cases it may be difficult to convince a sceptical public that assay results indicate a satisfactory water quality.

An ideal approach would be to screen water samples with *in vitro* toxicity tests for a wide range of potential human health endpoints [167]. Samples resulting in positive biological response *in vitro* would be forwarded to a thorough targeted chemical analysis to determine the causative chemical(s). If no clear link between chemical and bioassay data could be established, then a full toxicity identification evaluation may be necessary, where the sample is fractionated and then re-analysed in both bioassay and chemical method to identify the class of the causative chemical(s). This process is repeated until the exact nature of the chemical(s) can be determined. This conclusion is then confirmed by creating artificial samples spiked with the causative chemical to ascertain that it will elicit the expected response in the bioassay.

For ethical reasons, live animal testing should only be considered where a strong case can be made that such testing has a reasonable likelihood of leading to significantly beneficial public health outcomes. If animal experiments are regarded as the only way (or most reliable way) of establishing the safety of a water supply, and thus of ensuring the safety of a large population, suitable guidelines such as those published by the NHMRC should be consulted [180]. Furthermore, the Australian Code for the Responsible Conduct of Research guides

institutions and researchers in responsible research practices [181]. Most universities and other research organisations will also have internal ethics codes that should be adhered to.

In general terms, experiments should be conducted so that the animals are kept in conditions that suit their species-needs. Furthermore, the experiments should be terminated, and the animals painlessly killed, as soon as abnormal responses appear. The use of death, or something near to death, as an endpoint in toxicity experiments is unlikely to be defensible.

5. Chemical Removal by Advanced Water Treatment Processes

Exposure to chemical hazards in water recycling systems is managed by the effective operation of advanced water treatment processes and, in some cases, by onsite management and usage controls.

In order to properly assess the effectiveness of advanced water treatment processes for a diverse range of potential chemical contaminants, it is essential to have some understanding of the fundamental (molecular-scale) processes occurring. This understanding provides important insight into which chemicals may be anticipated to be well (or else poorly) removed by various processes and, thus, which chemicals might be monitored for useful indicative behaviour that may be related to the removal of other chemical contaminants.

This section provides an overview of the fundamental processes leading to removal of trace chemical contaminants during some common advanced water treatment processes including some biological treatment processes, managed aquifer recharge, reverse osmosis, adsorptive treatment processes and advanced oxidation processes.

5.1 Biological treatment processes

Biological wastewater treatment processes rely upon microorganisms that utilise the dissolved and colloidal organic material as a food source. These microorganisms derive energy and cellular material from the degradation of the organic matter. During this process, the microorganisms grow and reproduce, and are subsequently separated from the wastewater.

Biological wastewater treatment processes can be aerobic (requiring oxygen) or anaerobic (requiring an absence of oxygen). These processes are variously effective for the removal of BOD, suspended solids, ammonia, heavy metals and synthetic organic chemicals.

Some forms of biological wastewater treatment are so well established that they are classified as ‘conventional wastewater treatment processes’, rather than advanced water treatment processes. Accordingly, those such as activated sludge treatment processes and conventional trickling filters are not discussed here. However, some other forms of biological treatment such as membrane bioreactors and biological activated carbon processes are increasingly being adopted for some types of water recycling applications.

Biological activated carbon filters are a form of fixed film reactor. The activated carbon surface aids physical adsorption of trace chemical substances (see Section 5.4), while biological films (‘biofilms’) encouraged to grow on the surface facilitate degradation processes.

Biofilms are composed of microorganism cells, slimy extracellular material and sometimes particulate material that has become attached to the film. The organisms associated with a biofilm may belong to a wide range of species, predominantly bacterial. Biofilms are highly efficient at extracting nutrients from the passing solution, but the exact mechanisms mediating this uptake are not well understood.

Membrane bioreactors are the amalgamation of a suspended growth biological reactor and a membrane filtration device into a single unit process. The membrane unit can be configured external to the bioreactor, or can be immersed in the bioreactor.

In the case of an external-membrane system, the bioreactor mixed liquor is pumped around an external recirculation loop containing a membrane unit, from which permeate is discharged and the retentate returned to the reactor tank. In this case, the transmembrane pressure and crossflow velocity, which define the operation of the membrane, are generated from a pump.

Immersed membrane systems differ from external systems in that there is no recirculation loop, as the separation occurs within the bioreactor itself. Under these circumstances, the transmembrane pressure is commonly derived from the hydraulic head of the water above the membrane. Membrane fouling control is achieved by a scour at the membrane surface. The energy is derived from the aeration process with the movement of bubbles close to the membrane surface generating the necessary liquid shear velocity.

The coupling of a membrane separation process to a bioreactor offers a number of advantages over conventional biological wastewater treatment systems, including process intensification and improved water quality. The membrane permeate is free from suspended solids and macro-colloidal material, with typical water qualities of than 5 milligrams per litre of suspended solids and turbidity of less than 1 nepholometric turbidity unit. Sludge age (solids retention time) and hydraulic retention time are independent of each other, thus membrane bioreactors can be operated at short hydraulic retention times and long solids retention times without washout of biomass in the effluent, which is a common constraint for activated sludge systems.

In most biological systems, various species of bacteria are primarily responsible for primary reduction of chemical contaminants. However, grazing organisms are also important for maintaining a balanced microbial system. Important roles of various types of organisms include the following [182]:

- Bacteria
  - conversion of soluble and particulate organic compounds into biomass and gaseous products (CO_2 and CH_4)
  - conversion of ammonia to nitrate (nitrification)
  - conversion of nitrate to nitrogen gas (denitrification)
  - conversion of soluble phosphate to insoluble intracellular phosphate (thus permitting removal from dissolved liquid phase)
- Protozoa
  - consumption of particulate organics (including bacteria)
  - an important role in the removal of suspended solids
- Fungi
  - may assist bacteria in the removal of organics in fixed film reactors
- Algae
  - have a role in nutrient uptake in specialised tertiary treatment systems
- Others
  - larger biological species such as rotifers, nematode worms and insect larvae may contribute to the consumption of particulate organic matter, especially in fixed film reactors.

5.2 Managed aquifer recharge

It is well known from the hydrologic cycle that the qualities of many surface waters are improved as they pass through soils and permeate down to groundwater aquifers. Various approaches to the use of natural or engineered systems have been developed to take advantage of this phenomenon for water treatment. Managed aquifer recharge is the infiltration or forced injection of water (including surface water, treated wastewater or urban stormwater) into an aquifer under controlled conditions with the intention of storage or treatment of the water [183; 184]. Various diverse applications of managed aquifer recharge include river bank filtration, aquifer recharge and recovery, subsurface groundwater treatment and soil-aquifer treatment. If properly designed and operated, these systems can provide a comprehensive, sustainable treatment of multiple contaminants present in water sources.

A diverse range of mechanisms contribute to the overall improvement of water quality during managed aquifer recharge processes. During infiltration and movement through the soil and aquifer sediments, the aqueous solution is subjected to a combination of physical, chemical and biological processes including the following [184–187]:

- filtration
- solution–precipitation
- ion exchange
- sorption–desorption
- complexation
- redox reactions
- microbial degradation
- dilution.

Several studies have been undertaken to characterise the performance of managed aquifer recharge systems in removing pathogens, precursors to disinfection byproducts (primarily TOC), nutrients, and selected trace organic chemicals from treated municipal effluents [188–193]. Many of these studies indicate that several factors affect the quality of the recovered water, including the initial effluent quality, spreading basin characteristics, subsurface conditions, the degree of blending with native groundwater, and operational conditions. Although some of these factors can be influenced by engineering design, others are dependent upon the individual site and local hydrogeological conditions.

Biological activity has been shown to be most significant in the infiltration zone of spreading basins [194]. The accumulation of microbial populations also increases the adsorption capacity of the first sediment layer. Biological decay is assumed to regenerate the adsorption sites. The diversity of microorganism and surface structures present enhance the natural attenuation of degradable pollutants and the accumulation of adsorbable persistent substances [195].

Under suitable conditions, managed aquifer recharge systems have demonstrated high removal efficiencies for some endocrine disrupting compounds, including steroidal hormones [187; 196; 197] as well as alkylphenol polyethoxylates and nonylphenol [187; 198]. Furthermore, many pharmaceutically active compounds and nitrosamines are amenable to biodegradation during managed aquifer recharge treatment [192; 199].

However, managed aquifer recharge has exhibited some limitations in removing certain organic contaminants. Examples include antiepileptic drugs (such as carbamazepine,

primidone), some blood-lipid regulators (such as clofibric acid), antibiotics (such as sulfamethoxazole), x-ray contrast media, chlorinated flame retardants (TCEP, TCPP) and trihalomethane disinfection byproducts (such as chloroform) [192; 199–203]. In these cases, partial reduction in concentration was achieved only under certain redox conditions and through dilution with local groundwater.

Geochemical processes may also change the composition of the recharged water during subsurface transport and storage. For example the presence of pyrite or sediment-bound organic matter in anaerobic aquifers has been shown lead to the reduction of nitrate concentrations [204]. However, these or other reducing agents will be successively depleted, and the aerobic zone surrounding the injection well will grow over time. Under this scenario, nitrate removal is not an enduring process. Hence, geochemical modelling of aquifer processes has been recommended in order to determine the longevity of specific facets of aquifer treatment [184].

The interactions of aquifers with chemical constituents in recharged water has been categorised into three types [205]:

- sustainable hazard removal—includes pathogen inactivation and biodegradation of some organic contaminants during the residence time of the recharged water in the soil or aquifer within an attenuation zone of finite size
- ineffective hazard removal—some hazards must be removed prior to recharge since they are either not removed (for example, salinity) or removal is unsustainable (for example, adsorption of any metals or organics that are not subsequently biodegraded, or excessive nutrients or suspended solids)
- new hazards introduced by aquifer interaction—in some aquifers some hazards may be introduced to the recharged water including mobilised metals, hydrogen sulphide, salinity, sodicity, hardness or radionuclides. There is a need to change the quality of recharge water to avoid these (for example, change acidity-alkalinity, oxidation-reduction status, or reduce nutrients).

5.3 Reverse osmosis

The first reverse osmosis membranes were developed in the 1950s for seawater desalination applications. The membranes were relatively rigid and thus self-supporting. They were produced by precipitation of soluble cellulose acetate polymer in a non-solvent (referred to as a liquid–solid phase inversion process). By the mid-1970s, the membranes were made by a polycondensation process in which polyamide is deposited as a thin film on a porous substrate. Cellulose acetate membranes were first used in advanced water treatment plants in 1976 at California's 'Water Factory 21'. However, by the late 1990s, thin film composite membranes had become the industry standard for both seawater desalination, wastewater recycling and industrial water treatment.

Thin film composite membranes have been designed with chemical functional groups attached to the membrane surface to facilitate electrostatic repulsion of susceptible chemicals in the feed water. Such functional groups include sulfonic acid and carboxylic acid groups, which are negatively charged under normal pH conditions (typically pH 6–8). Solutes that are also negatively charged (including many pharmaceuticals and endocrine disrupters) can be efficiently rejected by such membranes [206].

Membrane rejection of chemical contaminants is ultimately determined by complex interactions of electrostatic and other physical forces acting between a specific solute (chemical contaminant), the solution (water and other solutes present), and the membrane

itself. The nature of these forces is dependent on numerous physical properties of the solute, solution and membrane.

A systematic approach has been proposed for estimating the removal efficiency for organic contaminants by reverse osmosis based on molecular properties of the organic contaminants [207]. This system was derived from a comprehensive review of published studies reporting variable rejection behaviour of a wide range of organic solutes by various commercially available membranes. The important molecular factors determining rejection are presented in Figure 21. These include:

- molecular size—the size of a molecule is often approximated by reference to its molecular weight, but can be more accurately described in terms of its molecular diameter and molecular width
- electrostatic properties—the electrical charge of a molecule is related to how acidic it is. This is commonly described by an acid dissociation constant and its relationship to the overall acidity of the water
- polarity or hydrophobicity—the 'polarity' of a molecule determines whether it is generally very soluble in water or would prefer to partition to non-water phases. Molecules that tend to partition away from water are said to be 'hydrophobic'. The degree of hydrophobicity is commonly described by an 'octanol-water partitioning coefficient' (log K_{ow}).

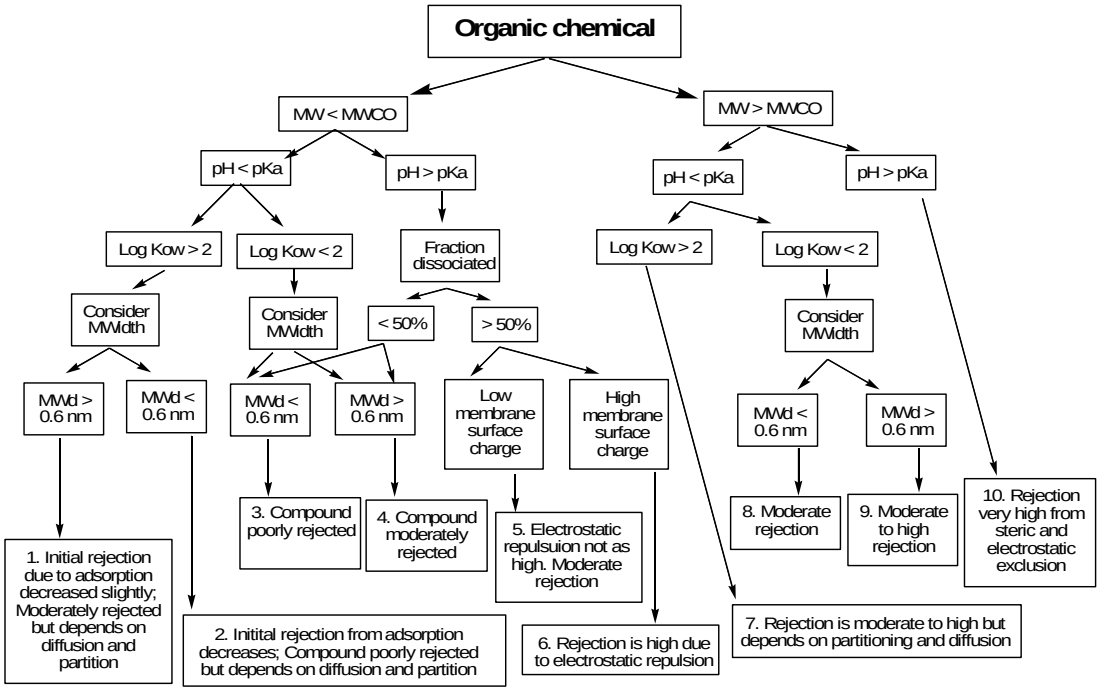
The three mechanisms a molecule may be rejected by the reverse osmosis membrane are size exclusions (or sieving), electrostatic repulsion and hydrophobic adsorption.

The most fundamental of the rejection mechanisms is size exclusion. This is a sieving process for which molecular size or geometry prevents large molecules from passing through the dense molecular structure presented by the active surface of the membrane. Size exclusion is believed to be the dominant retention mechanism for relatively large organic molecules such as surfactants, hormones, most pharmaceuticals, proteins and other molecules with a molecular weight greater than 200 atomic mass units (measured in grams per mole) by reverse osmosis membranes [208; 209]. However, commercial membranes vary in terms of their ability to reject molecules by size exclusion. Their ability to do so is often described by the membrane's molecular weight cut-off. This is the manufacturer's rating of the ability of the membrane to reject an uncharged dextran (sugar) based on molecular weight. Membranes with a low cut-off are commonly referred to as 'tight' membranes compared to those with a higher cut-off, referred to as 'loose' membranes.

Experiments with looser membranes (nanofiltration, ultrafiltration and microfiltration), have revealed that, under some conditions, some chemicals are prevented from permeating the membrane due largely to adsorption onto the membrane surface [208; 210]. This adsorption is believed to be due to hydrophobic interactions between relatively non-polar solutes and membranes. Such adsorptive removal may be less reliable than removal based purely on size exclusion since variations in solution pH lead to variations in hydrophobicity, which in turn may result in variable ability of some molecules to partition through the membrane polymer [211].

An example of how the rejection diagram in Figure 21 may be used to describe the removal efficiency for organic molecules that are commonly found in wastewater is presented in Table 11. The predictions derived from the rejection diagram were determined assuming the use of a high surface-charge reverse osmosis membrane with a molecular weight cut-off of 100 at pH 7. These predictions are qualitatively consistent with recent findings from groundwater treatment and water recycling plants where molecules such as monochloramine, NDMA and 1,4-dioxane are poorly removed by reverse osmosis membranes.

Figure 21: Rejection diagram for organic micropollutants during membrane treatment based on solute and membrane properties [207]



MW=molecular weight, pKa= acid dissociation constant, Log K_{ow} = logarithm of octanol-water partitioning coefficient, MWd=molecular width, MWCO=molecular weight cut-off

Table 11: Predicted reverse osmosis rejection categories of some organic chemicals based on molecular properties. Rejection category is described in Figure 21

Organic chemical	*MW*	*pKa*	*log K_{ow}*	*MWd > 0.6 nm*	*Rejection category*
1,2-Dichloroethane	98.96	nil	1.48	n	3
1,4-Dioxane	88.10	nil	-0.27	n	3
2-Naphthol	144.17	9.57	2.73	n	7
Acetic acid	60.05	4.79	-0.29	n	6
Acetylsalicyclic acid	180.16	3.48	1.19	n	10
Acrylonitrile	53.06	nil	0.25	n	3
Aldrin	364.92	nil	6.5	n	7
Benzene	78.11	nil	2.13	n	2
Bromoform	252.73	nil	2.42	n	7
Caffeine	194.19	12.61	-0.081	y	9
Carbamazepine	236.27	13.94	2.673	n	7
Carbon Tetrachloride	153.82	nil	2.83	n	7
Chloroform	119.38	nil	1.97	n	8
Clofibric acid	214.65	3.18	2.724	n	10
Dichloroacetic acid	128.94	1.37	0.54	n	10
Dichloromethane	84.93	nil	1.25	n	3
Dichlorprop	235.06	3.03	2.945	n	10
Diclofenac	296.15	4.18	3.284	n	10
Dieldrin	380.91	nil	5.4	n	7
Estradiol	272.39	10.27	4.01	n	7
Estrone	270.37	10.25	3.13	n	7
Ethinylestradiol	296.41	10.2	3.67	n	7
Fenofibrate	360.83	nil	4.804	n	7
Gemfibrozil	250.33	4.75	4.387	y	10
Glucose	180.16	12.45	-3.17	n	8
Glutaric acid	132	4.33	-1.04	n	10
Ibuprofen	206.28	4.41	3.722	n	10
Ketoprofen	254.28	4.23	2.814	n	10
Mecoprop	214.65	3.18	2.835	n	10
Monochloramine	51.48	nil	-1.19	n	3
Naphthalene	128.2	nil	3.3	n	7
Naproxen	230.26	4.4	2.998	n	10
NDMA	74.08	nil	0.57	n	3
Nonylphenol	220.36	10.14	5.76	n	7
Octylphenol	206.33	10.15	5.5	n	7
Phenacetine	179.22	nil	1.626	n	8
Primidone	218.25	12.26	-0.844	n	8
Propyphenazone	230.31	2.37	1.737	n	10
Salicylic acid	138.12	3.01	2.061	n	10
Sucrose	342.3	12.81	-3.85	n	8
Testosterone	288.42	nil	3.48	n	7
Trichloracetic acid	163.39	1.1	1.67	n	10
Trichloroethylene	131.39	nil	2.42	n	7
Tris(2-chloroethyl)-phosphate	285.49	nil	0.48	n	8
Tris(2-chloroisopropyl)-phosphate	327.57	nil	1.53	y	9
Urea	60.06	13.9	-2.11	n	3

The final concentration of organic molecules in the reverse osmosis permeate is highly dependant on the configuration of the membrane, the type of membrane, the membrane surface charge and the MWCO. Other important factors that contribute to rejection include the

type of spacer material used to form the membrane feed channels and the system operating conditions including flux, pH and membrane recovery. All these factors determine the concentration of the molecules at the surface of the membrane and the subsequent transport or rejection of the molecules across the membrane based on the physical–chemical properties described in Figure 21. For this reason, rejection data determined in simple laboratory-scale experiments should be interpreted cautiously before drawing conclusions on full-scale plant performance because the conditions under which the membranes operate will be different.

During normal operation, membranes are prone to fouling by the build-up of precipitated chemicals or, in the case of indirect potable reuse, by the growth of microbial biomass [212–214]. Fouling can lead to significant changes in membrane surface properties and thus in the way in which they interact with water and solutes. In many cases, fouling is regarded as a hindrance since it decreases membrane porosity and thus requires elevated pressures to maintain operational flux. However, recent investigations reveal that fouling can also lead to improved rejection of many solutes [209; 215; 216]. This observation is believed to be due to increased negative surface charge leading to increased electrostatic rejection of ionic species; along with simultaneously increased adsorptive capacity for non-ionic solutes [215]. Most previous studies reporting relationships between physical–chemical properties of solutes and membrane interactions have been conducted using unfouled 'virgin' membranes, and thus their conclusions are unlikely to be quantitatively extendable to full-scale systems subjected to long-term operation [208; 217–219]. Indeed, Bellona et al. [207] used data generated with non-fouled membranes in the development of the guide for predicting the relative removal efficiencies. Furthermore, recent research has indicated that gradual reaction of membrane materials with chlorine residuals in water can alter the membrane permeability [220]. Consequently this guide should be used cautiously for predicting chemical behaviour in real treatment systems.

5.4 Activated carbon adsorption

Among the most well-established processes for advanced trace organic chemical removal is adsorption to activated carbon. This is a form of carbon usually derived from charcoal. The term 'activated' refers to the way the carbon has been prepared to enhance its ability to physically 'adsorb' chemicals to its surface. Adsorption is the accumulation of a dissolved chemical (solute) onto a solid surface.

An important property of activated carbon is its extremely high surface area. One gram (about a teaspoon full) of activated carbon can have a surface area of 400–2000 square metres. By comparison, a tennis court is about 260 square metres. A microscopic view of activated carbon reveals a complex web structure intermingled with trapped smaller particles. There are many interstices, which provide excellent conditions for adsorption of suitable chemicals.

The most common applications of activated carbon for water treatment are known as GAC and powdered activated carbon (PAC). These terms refer to the physical form (particle size) in which the activated carbon is applied. Smaller particle sizes in PAC tend to have higher surface areas while large particle sizes (GAC) tend to be more easily separated from the water subsequent to treatment. PAC is often used by direct addition to water with mixing and then separated by gravity or filtration (or both). Alternatively, GAC is more commonly used as filtration media with the water being percolated through it.

The effectiveness of PAC and GAC to adsorb a particular chemical can generally be predicted based on how 'hydrophilic' or 'hydrophobic' the chemical is. These terms refer to the tendency of a chemical to partition preferentially into aqueous phases (hydrophilic) or non-aqueous phases (hydrophobic). PAC and GAC are effective for the removal of a diverse

range of hydrophobic organic compounds as well as well as some relatively hydrophobic inorganic compounds such as nitrogen, sulphides and heavy metals. More hydrophilic compounds, such as small carboxylic acids and alcohols, are relatively poorly removed by activated carbon adsorption [221].

The parameter most commonly used to describe how well a substance can be adsorbed to activated carbon is the Freundlich capacity factor [222]. The Freundlich capacity factor is determined experimentally by testing various ratios of chemical concentration and activated carbon masses in otherwise clean waters under controlled conditions. A high Freundlich capacity factor indicates that the chemical is very effectively adsorbed, while a low Freundlich capacity factor indicates the chemical is poorly adsorbed.

The range of Freundlich capacity factors for potential water contaminants is extremely wide. For example, polychlorinated biphenyls have Freundlich capacity factors greater than 10^4 (mg/g)(L/mg)$^{1/n}$ while NDMA has a Freundlich capacity factor of around 10^{-4} (mg/g)(L/mg)$^{1/n}$. Because of this wide variation, the Freundlich capacity factor must be determined for each specific compound [221]. As a further complication, mixtures of compounds in a raw water source will affect the adsorptive capacity for each compound by competitive adsorption.

PAC has been shown to be highly effective for the removal of a wide range of pharmaceuticals, endocrine disruptors and pesticides from relatively clean water sources [223; 224]. A recent Southern Nevada Water Authority study provides a useful illustrative example [224]. For this research, raw drinking water supplies were collected and high concentrations of 62 different chemicals were spiked into them. These waters were then treated by a number of laboratory-scale water treatment processes including PAC. Addition of 5 milligrams per litre of PAC with a four-hour contact time removed different compounds by between 10 per cent to greater than 98 per cent. Higher PAC dosages improved the removal of most compounds. This study confirmed that the removal effectiveness for specific chemicals could be reasonably well predicted based on their hydropobicity.

GAC has also been shown to be effective for the removal for some important organic chemical contaminants in water. For example, GAC filtration has been shown to be an effective method for removing a range of pharmaceuticals from drinking water including carbamazepine, diclofenac, clofibric acid, bezafibrate and primidone [225].

5.5 Advanced oxidation processes

Oxidative processes may be used to degrade (or transform) organic constituents of wastewaters that prove to be both biologically recalcitrant and poorly retained by membranes or activated carbon. Strong chemical oxidants—such as ozone [226], potassium permanganate [227; 228] and chlorine [229; 230]—have been shown to be effective for the degradation or transformation of chemical contaminants in water.

Oxidative degradation can occur either by direct reaction with the applied oxidant, or via the production of highly reactive secondary species—most commonly hydroxyl radicals ($^{\cdot}OH$). The hydroxyl radical is one of the most powerful oxidants known. With sufficient doses, organic chemicals may be completely mineralised, that is, converted to carbon dioxide and other inorganic forms.

Ultraviolet (UV) light can also be used to degrade organic chemicals in water (though this is not an oxidation process) [231; 232]. Furthermore, UV light is commonly used to promote the formation of hydroxyl radicals. This can be achieved by a number of methods, including photocatalysis with titanium dioxide (TiO_2) [233; 234] or by direct reaction of hydrogen peroxide (H_2O_2) [235–237].

Processes that promote the enhanced formation of hydroxyl radicals are generally referred to as advanced oxidation processes. Most commonly, advanced oxidation processes for water treatment are achieved by the addition of hydrogen peroxide to ozone or UV contact chambers. The key chemical reactions for the production of hydroxyl radicals using hydrogen peroxide are:

Ozone/H_2O_2: $H_2O_2 + 2O_3 \rightarrow 2^{\bullet}OH + 3O_2$

UV/H_2O_2: H_2O_2 + UV (200–280 nm) $\rightarrow 2^{\bullet}OH$

Furthermore, ozone applied to wastewater effluents has been shown to rapidly decompose with associated $^{\bullet}OH$ generation, particularly at elevated pH [238]. This effect means that ozonation of wastewater can be assessed as an advanced oxidation process, even without the addition of peroxide.

Both molecular ozone (O_3) [226] and UV light [235] by themselves can be used to degrade chemical contaminants to some degree. However, without the enhanced generation of hydroxyl radicals, molecular ozone or UV light alone are relatively specific in the chemical groups that they attack. Conversely, oxidation of organic chemicals by hydroxyl radicals is non-specific, and all organics are ultimately susceptible if sufficient dose is applied [239].

At the low concentration of compounds found in water treated by reverse osmosis, the oxidation of these compounds follows first-order kinetics. UV doses required for NDMA destruction (1,000 millijoules per square centimetre) are approximately an order of magnitude higher than those for virus removal [240]. The electrical energy required for this oxidation is expressed in EE/O units, defined as the electrical energy input per unit volume per log order of reduction [221]. Based on currently available technology, the required EE/O value for NDMA is in the order of 21–265 kWh/10^3m^3/log order with a 5–6 mg/L dose of H_2O_2 [241]. However, in the case of NDMA treatment after reverse osmosis, the addition of H_2O_2 is considered to be somewhat redundant since UV light alone is highly effective [240; 242].

Advanced oxidation processes widen the range of organic chemicals that may be oxidised as well as significantly increase the reaction rates [226]. Once generated, hydroxyl radicals can attack organic molecules by a number of mechanisms including radical addition, hydrogen abstraction, electron transfer and radical combination. Under suitable conditions, the reaction of hydroxyl radicals with organic compounds may proceed to complete oxidation to produce water, carbon dioxide and salts. This process is known as mineralisation.

In an ozone advanced oxidation process, oxidative degradation of organic chemicals can occur either by direct reaction with molecular ozone or via the formed hydroxyl radicals [243]. The relative dominance of the actual oxidative pathway will depend on the ratio of molecular ozone and hydroxyl radicals, and the corresponding reaction kinetics [226; 244].

The overall extent of oxidation for any advanced oxidation process is dependant on the contact time and the concentration of scavengers in the water (ie non-target oxidisable species). Typically, DOC and carbonate/bicarbonate are the most important scavengers in drinking waters. High concentrations of DOC and carbonate/bicarbonate can render mineralisation of micropollutants quite inefficient and very costly [226]. However, pre-treatment processes such as GAC or reverse osmosis significantly reduce DOC concentrations, thus enhancing oxidation efficiency.

Direct UV photolysis of some endocrine disrupting chemicals such as bisphenol A, estradiol and ethinylestradiol has been investigated using both monochromatic (254 nanometre) low-pressure UV lamps, and polychromatic medium-pressure UV lamps [235]. This study revealed that, without enhanced hydroxyl radical formation, medium-pressure lamps are

required for effective degradation of these contaminants. However, in all cases, endocrine disrupters were even more effectively degraded using UV/H_2O_2 advanced oxidation than by direct UV photolysis.

Similarly, oxidation of contaminants in secondary treated effluent by direct application of molecular ozone is an effective process for some contaminants. For example, many pharmaceuticals and estrogenic hormones can be oxidised to more than 90–99 per cent using typical ozone treatment doses [224; 245–247]. Typical doses depend on the initial water quality, but they are normally calculated to achieve a set product of ozone concentration and exposure time (CT). However, advanced oxidation utilising hydrogen peroxide is a more effective process for an even wider range of these target species [226; 248; 249].

Advanced oxidation is often relied upon to degrade chemicals that may not be well removed by reverse osmosis. Two important examples are NDMA [250] and 1,4-dioxane [251].

There are many possible sources of NDMA in treated effluent, including contamination of source wastewater by industrial discharges [240]. However, an important possible source for indirect potable reuse water is its formation during chloramination processes used for membrane biofouling control [252]. Effective removal of NDMA can be achieved by UV photolysis with a typical dose of 1000 milliJoules per square centimetre [240; 250; 253]. Low pressure UV lamps emitting mainly monochromatic light at 254 nanometres, medium-pressure lamps emitting polychromatic light and pulsed UV systems have all been used for NDMA removal [240; 250].

The chemical 1,4-dioxane is mainly used as an industrial solvent and as a solvent stabilising agent [251]. It is also present in many household surfactants and some fraction of these products ultimately ends up in wastewater treatment plant influent. 1,4-dioxane is efficiently mineralised by advanced oxidation with UV/H_2O_2 [254; 255]. Advanced oxidation with ozone/H_2O_2 can also be used to degrade 1,4-dioxane [256].

Investigations on some active pharmaceuticals such as the contraceptive hormone, ethynylestradiol [257], and the anti-epileptic drug, carbamazepine [258], have shown that even partial oxidation is sufficient to reduce pharmacological activity of these agents.

6. Probability Density Functions (PDFs)

Exposure to chemical contaminants from water recycling schemes may be quantitatively determined through calculations used to model such factors as source water quality and the effectiveness of various water treatment processes. This concept is discussed in detail in Chapter 8. All such calculations and models require numerical input variables. For example, the input variable for source water concentration of a particular chemical may be simply assumed, calculated from other factors (for example, use of the chemical in the catchment) or measured directly.

Modelled variables may be classified as either 'stochastic' or 'deterministic'. Stochastic variables are those for which the 'value' or 'outcome' may not be precisely determined or predicted since it involves a degree of variability or randomness. Deterministic variables are those for which the precisely known value will lead to ('determine') a specific outcome.

Many of the variables used for calculating chemical exposure are characteristically stochastic variables. Examples include source water concentrations of chemicals, and treatment performance for fractional removal of specific chemical species by unit treatment processes. The stochastic nature of these variables arises from both inherent *variability* (for example, the source water concentration of a chemical changes with time) and *uncertainty* (for example, uncertainty introduced by limitations in analytical precision).

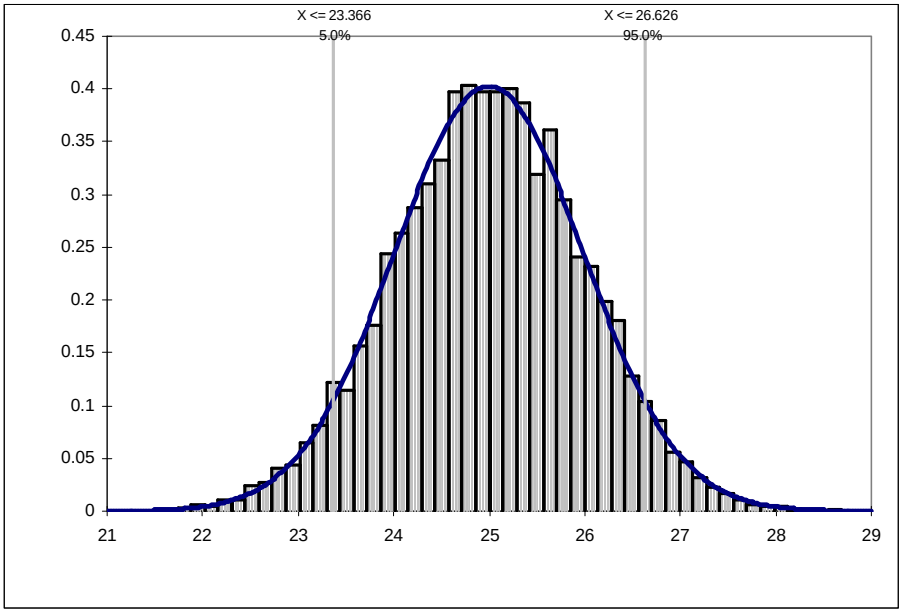
A useful way of dealing with a stochastic variable in mathematical models is by describing it, not as a 'point value', but as a distribution of values. A probability density function (PDF) is a mathematical function that represents a distribution in terms of the probability or frequency of occurrence of specific values within the distribution. The PDF can be conceptualised as a 'smoothed out' version of a histogram of occurrences of a range of values. If sufficient values of a continuous random variable are sampled, producing a histogram depicting relative frequencies of output ranges, then this histogram will resemble the random variable's probability density.

A brief introduction to some important distributional forms is given here since these are used throughout the following sections and chapters of this book.

6.1 Normal distribution

Among the best-known and widely used distributional forms is the *normal distribution*, which is used to describe symmetric continuous data. The normal distribution is also known as the Gaussian distribution, after Carl Friedrich Gauss, who used them to study the motion of objects orbiting the sun. It is defined in terms of two parameters, the mean (μ) and variance (standard deviation squared, σ^2). An example of a normal distribution (mean = 25, standard deviation = 1) showing a histogram of sampled values overlayed with a fitted PDF is presented in Figure 22.

Figure 22: Normal distribution with mean = 25 and standard deviation = 1



Many distributional forms may be described mathematically in terms of a central tendency and the occurrence of variances from that central tendency. This is the case for the normal distribution, characterised by the familiar bell-shaped curve. The general characteristics of the normal distribution and the functions required to determine summary statistics are presented in Table 12.

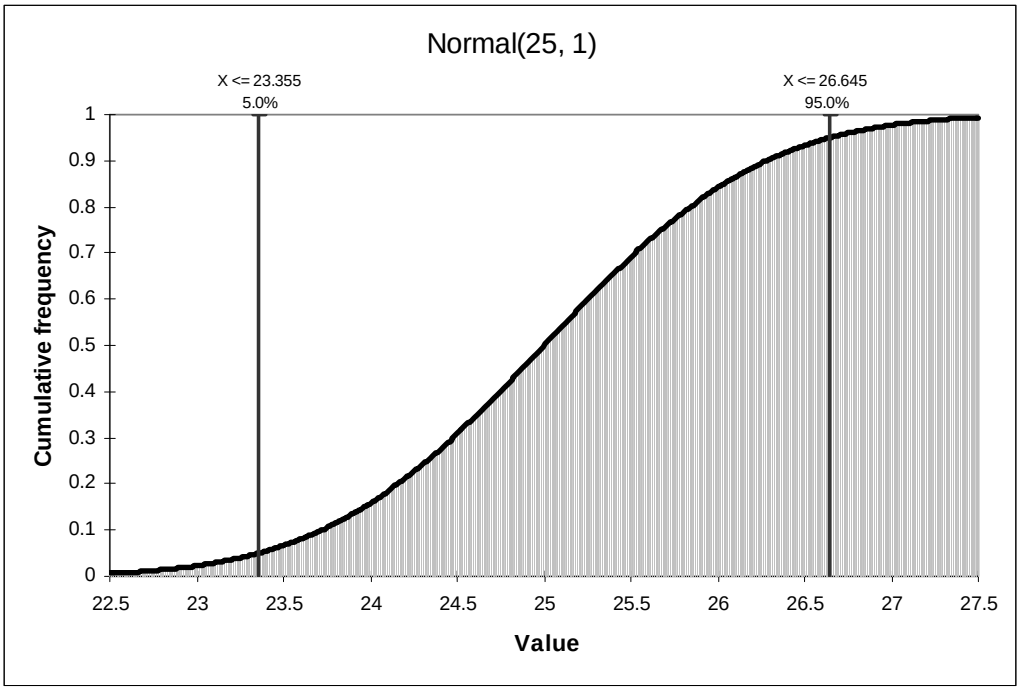
Table 12: Characteristics and their determination for normal distributions

Characteristic	*Determination*
Parameters	μ (continuous location parameter) σ (continuous scale parameter), $\sigma > 0$
Domain	$-\infty < x < +\infty$ (continuous)
PDF	$f(x) = \frac{1}{\sqrt{2\pi\sigma}} e^{-\frac{1}{2}(\frac{x-\mu}{\sigma})^2}$
Mean	μ
Standard deviation	σ
Variance	σ^2
Skewness	0
Kurtosis	3
Mode	μ

The normal distribution is widely applied in modelling quantitative phenomena in natural sciences. While the mechanisms underlying these phenomena are often unknown, the use of the normal distribution can often be theoretically justified by assuming that many small, independent effects are additively contributing to each observation.

An alternative form of any PDF is the cumulative density function. The cumulative density function, evaluated at a number x, is the probability of the event that a random variable X with that distribution is less than or equal to x. Figure 23 shows the cumulative density function corresponding to the same normal distribution represented in Figure 22.

Figure 23: Normal distribution with mean = 25 and standard deviation = 1, presented as a cumulative density function

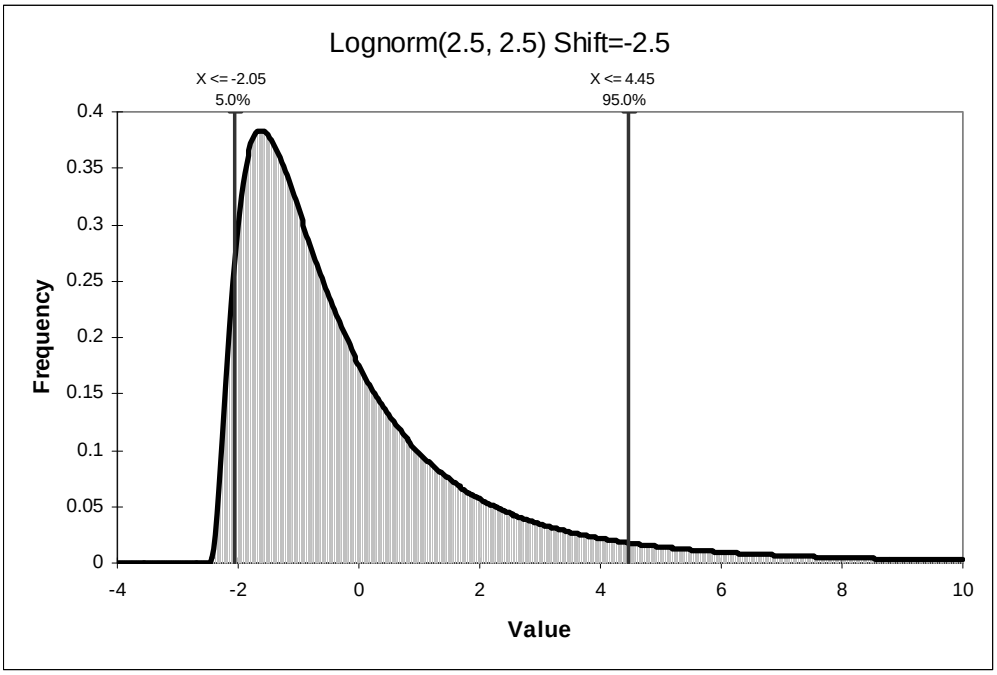


In addition to the normal distribution, there are many alternative distributions that can suitably describe frequency data for various phenomena. Some of these are used to characterise water quality variables and to make estimates and inferences.

6.2 Lognormal distribution

The lognormal distribution is used for right-skewed continuous data, as is common with many water quality variables—including both microorganisms and some chemical contaminants. Like the normal distribution, the asymmetrical lognormal distribution may be characterised by just two parameters—in this case, the mean and standard deviation of the logarithms of the transformed variable ($y = \ln(x)$). It can also be described by a third parameter, known as the 'shift', to accommodate a shift along the x-axis without changing the distribution's shape. An example of the lognormal distribution is presented in Figure 24.

Figure 24: An example of a lognormal distribution (format 1)



Two different formats of the lognormal distribution are used by many statistical texts and computer software applications. These two formats, described here as lognormal (format 1) and lognormal (format 2) are summarised in Table 13 and Table 14, respectively.

The distributions of both format 1 and format 2 are defined in terms of two parameters—mean and standard deviation—but the actual values of these parameters depend on which of the two formats was applied. In some cases (but not always!), these parameters are referred to as the ‘logmean’ and ‘log standard deviation’ when format 2 has been applied.

While either lognormal format can be equally well applied to describe a particular data set or distribution, the actual format applied in some reference papers is often not clearly indicated. Thus care must be taken to apply the correct format when using the mean and standard deviation quoted from the literature. In some cases, whether a quoted mean value refers to a ‘mean’ or a ‘logmean’, can be inferred by inspection of the original source data (when available).

Table 13: Characteristics and their determination for lognormal distributions (format 1)

Characteristic	*Determination*
Parameters	μ (continuous parameter), μ > 0 σ (continuous parameter), σ > 0
Domain	$0 \le x < +\infty$ (continuous)
PDF	$f(x) = \frac{1}{x\sqrt{2\pi\sigma'}} e^{-\frac{1}{2}(\frac{\ln x - \mu'}{\sigma'})^2}$ with $\mu' \equiv \ln\left[\frac{\mu^2}{\sqrt{\sigma^2+\mu^2}}\right]$ and $\sigma' \equiv \sqrt{\ln\left[1+\left(\frac{\sigma}{\mu}\right)^2\right]}$
Mean	μ
Variance	σ^2
Skewness	$\left(\frac{\sigma}{\mu}\right)^3 + 3\left(\frac{\sigma}{\mu}\right)$
Kurtosis	$\omega^4 + 2\omega^3 + 3\omega^2 - 3$ with $\omega \equiv 1 + \left(\frac{\sigma}{\mu}\right)^2$
Mode	$\frac{\mu^4}{(\sigma^2+\mu^2)^{3/2}}$

Table 14: Characteristics and their determination for lognormal distributions (format 2)

Characteristic	*Determination*
Parameters	μ (continuous parameter) σ (continuous parameter), σ > 0
Domain	$0 \le x < +\infty$ (continuous)
PDF	$f(x) = \frac{1}{x\sqrt{2\pi\sigma}} e^{-\frac{1}{2}(\frac{\ln x - \mu}{\sigma})^2}$
Mean	$e^{\mu + \sigma^2/2}$
Variance	$e^{2\mu}\omega(\omega - 1)$ with $\omega \equiv e^{\sigma^2}$
Skewness	$(\omega + 2)\sqrt{\omega - 1}$ with $\omega \equiv e^{\sigma^2}$
Kurtosis	$\omega^4 + 2\omega^3 + 3\omega^2 - 3$ with $\omega \equiv e^{\sigma^2}$
Mode	$e^{\mu - \sigma^2}$

6.3 Uniform distribution

The uniform distribution as illustrated in Figure 25 is used to describe data where all values occur with equal probability or frequency. It is occasionally used in quantitative risk assessment to investigate the significance of a variable for which the actual distribution is unknown, but presumed to be relatively restricted to within the two defining boundary values.

The general characteristics of the uniform distribution and the functions required to determine summary statistics are presented in Table 15.

Figure 25: An example of a uniform distribution

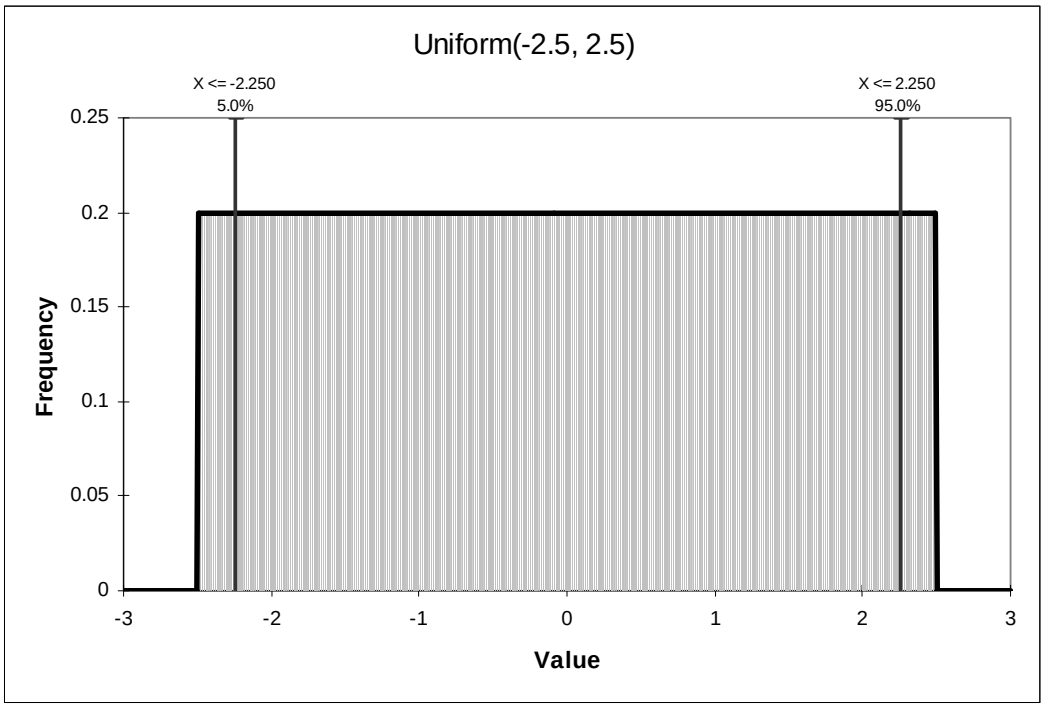


Table 15: Characteristics and their determination for uniform distributions

Characteristic	*Determination*
Parameters	min (continuous boundary parameter) min < max max (continuous boundary parameter)
Domain	$\min \le x \le \max$ (continuous)
PDF	$f(x) = \dfrac{1}{\max - \min}$
Mean	$\dfrac{\max - \min}{2}$
Variance	$\dfrac{(\max - \min)^2}{12}$
Skewness	0
Kurtosis	1.8
Mode	*Not uniquely defined*

6.4 Weibull distribution

An important application of the Weibull distribution is in modelling lifespans and it is used in mechanical engineering to model 'lifespans' of mechanical components before they fail. This is discussed in some detail later in Section 10.1 (page 160). A representation of a Weibull distribution is presented in Figure 26. The general characteristics of the Weibull distribution and the functions required to determine summary statistics are presented in Table 16.

The Weibull distribution may be described in terms of two parameters—the shape parameter (α) and the scale parameter (β). A shift parameter is also sometimes included to accommodate a shift along the x-axis. When α<1, the Weibull distribution has a failure rate that decreases with time (leading to a large number of 'early life failures). When α=1, the distribution has a constant failure rate indicative of random failures. When α>1, the distribution has a failure rate that increases with time (leading to substantial 'wear-out failures').

Figure 26: An example of a Weibull distribution

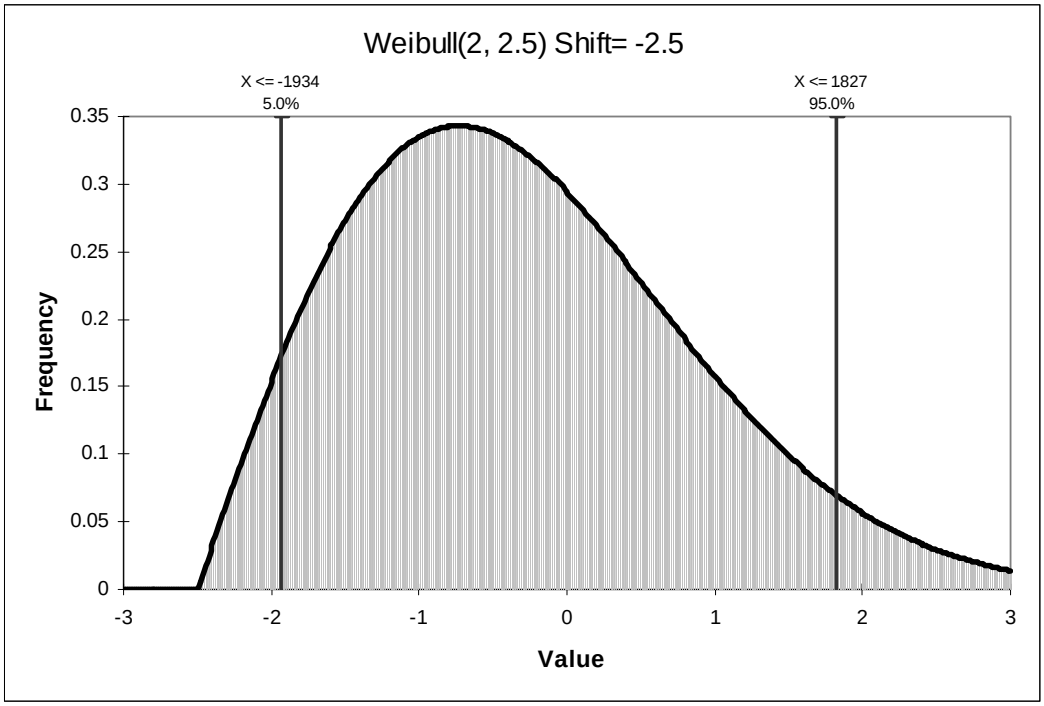


Table 16: Characteristics and their determination for Weibull distributions

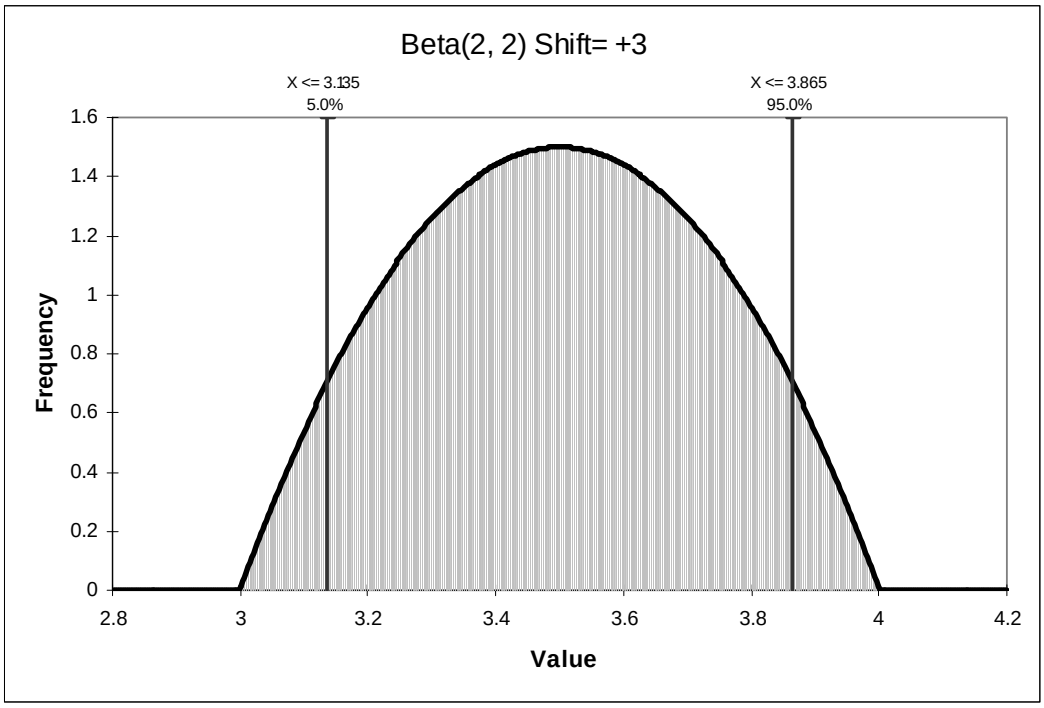
Characteristic	*Determination*
Parameters	α (continuous shape parameter) $\alpha > 0$ β (continuous scale parameter) $\beta > 0$
Domain	$0 \le x < +\infty$ (continuous)
PDF	$f(x) = \frac{\alpha . x^{\alpha-1}}{\beta^{\alpha}} e^{-(x/\beta)^{\alpha}}$
Mean	$\beta . \Gamma\left(1+\frac{1}{\alpha}\right)$ where Γ is the *Gamma Function*.
Variance	$\beta^2\left[\Gamma\left(1+\frac{2}{\alpha}\right)-\Gamma^2\left(1+\frac{1}{\alpha}\right)\right]$ where Γ is the *Gamma Function*.
Skewness	$\frac{\Gamma\left(1+\frac{3}{\alpha}\right)-3\Gamma\left(1+\frac{2}{\alpha}\right)\Gamma\left(1+\frac{1}{\alpha}\right)+2\Gamma^3\left(1+\frac{1}{\alpha}\right)}{\left[\Gamma\left(1+\frac{2}{\alpha}\right)-\Gamma^2\left(1+\frac{1}{\alpha}\right)\right]^2}$
Kurtosis	$\frac{\Gamma\left(1+\frac{4}{\alpha}\right)-4\Gamma\left(1+\frac{3}{\alpha}\right)\Gamma\left(1+\frac{1}{\alpha}\right)+6\Gamma\left(1+\frac{2}{\alpha}\right)\Gamma^2\left(1+\frac{1}{\alpha}\right)-3\Gamma^4\left(1+\frac{1}{\alpha}\right)}{\left[\Gamma\left(1+\frac{2}{\alpha}\right)-\Gamma^2\left(1+\frac{1}{\alpha}\right)\right]^2}$
Mode	$\beta\left(1-\frac{1}{\alpha}\right)^{1/\alpha}$ for $\alpha > 1$, 0 for $\alpha \le 1$

6.5 Other distributional forms

A wide variety of other distributional forms are available and used in various statistical applications. Two that are applied in some aspects of risk assessment include the beta distribution and the binomial distribution. Since they will not be used in the current document, they are not described here in detail. However, a brief description and illustrative example is provided to indicate the general characteristics.

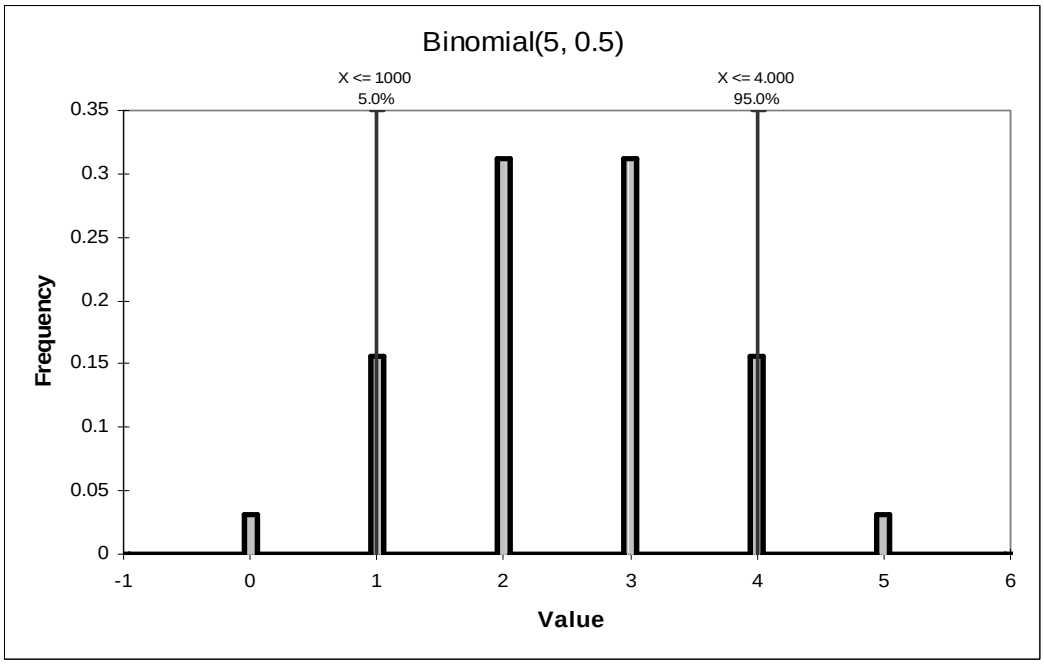
The beta distribution as depicted in Figure 27 can take a variety of shapes and is commonly used in Bayesian analyses. The beta distribution is characterised by two parameters (α and β) and is commonly used to derive the 'beta-Poisson' dose response model used in quantitative human health risk analysis.

Figure 27: An example of a beta distribution



The binomial distribution presented in Figure 28 is an example of a discrete distribution in which only discrete (non-continuous) values are allowed. The binomial distribution is used for discrete dichotomous data, where each sampling event can result in only one of two outcomes (for example, valve opens or valve does not open). The distribution of such outcomes in random samples is always binomial, provided the probability of a result is the same for each trial. The binomial distribution can be described in terms of two parameters being the number of trials and the probability of a particular outcome (such as pass, exceed) for each trial.

Figure 28: An example of a binomial distribution

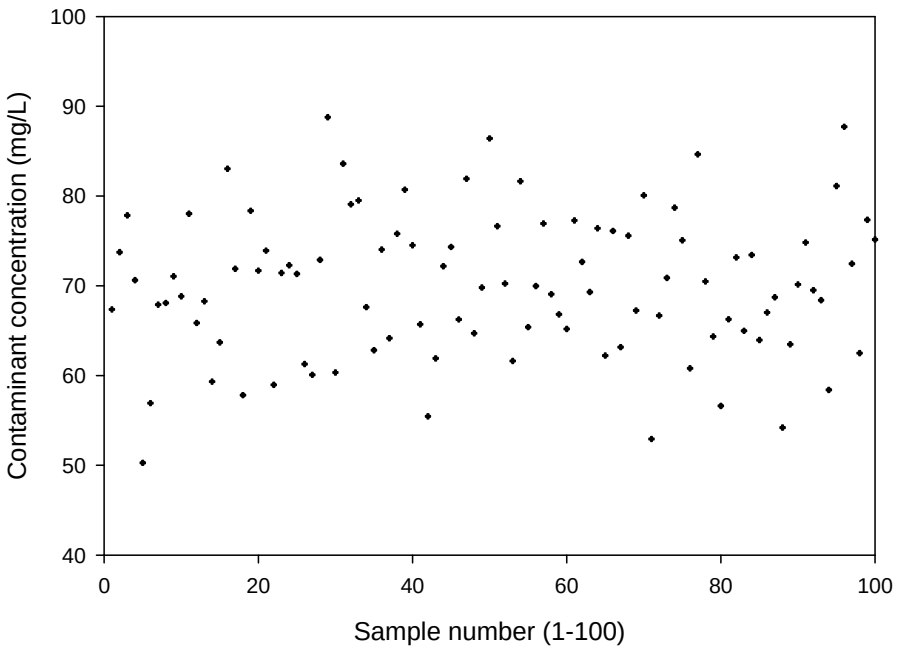


6.6 Probability plots

Probability plots may be used to accurately present measured distributions of stochastic variables. Probability plots display the quantiles, or percentiles (which are equivalent to the quantitles multiplied by 100) of the distribution of sample data.

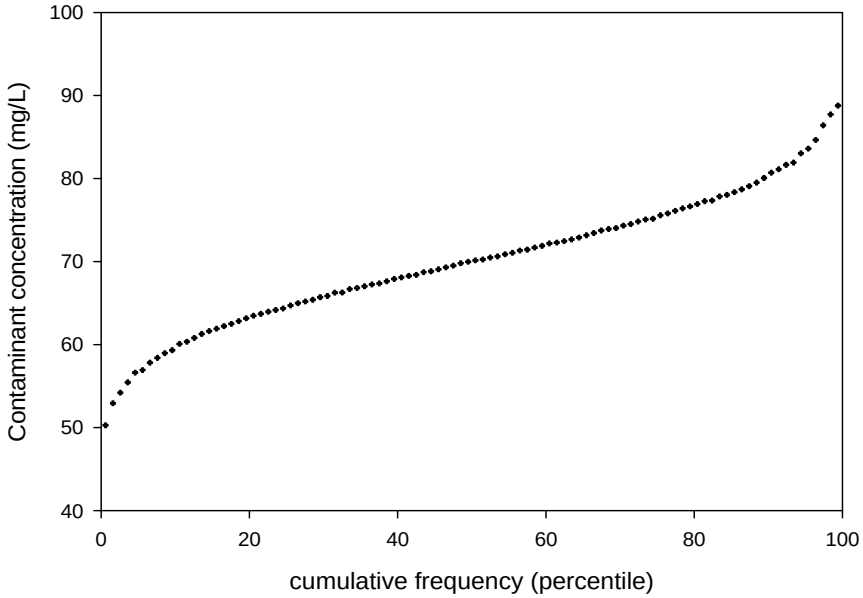
In order to illustrate the use of probability plots, first consider the scatter plot presented in Figure 29. This shows a hypothetical distribution of a water quality contaminant obtained by 100 individual samples. The vertical axis shows the contaminant concentration (mg/L) and the horizontal axis shows the sample number (1–100). It can be observed that the data range is approximately 50–90 mg/L.

Figure 29: Scatter plot for 100 sample measurements of hypothetical chemical contaminant (normal distribution)



A cumulative frequency plot for the same sampled water quality data is presented in Figure 30. The vertical axis is unchanged, showing the values of the contaminant concentration for each of the data points. The horizontal axis shows the cumulative frequency in percentiles, plotted on a linear scale. The value corresponding to any data point can be interpreted as the percentage of data points that are less than or equal to the corresponding concentration. In this case, it can be observed that the 20th percentile is around 63 mg/L, the median (50th percentile) is around 70 mg/L, and the 80th percentile is just below 80 mg/L.

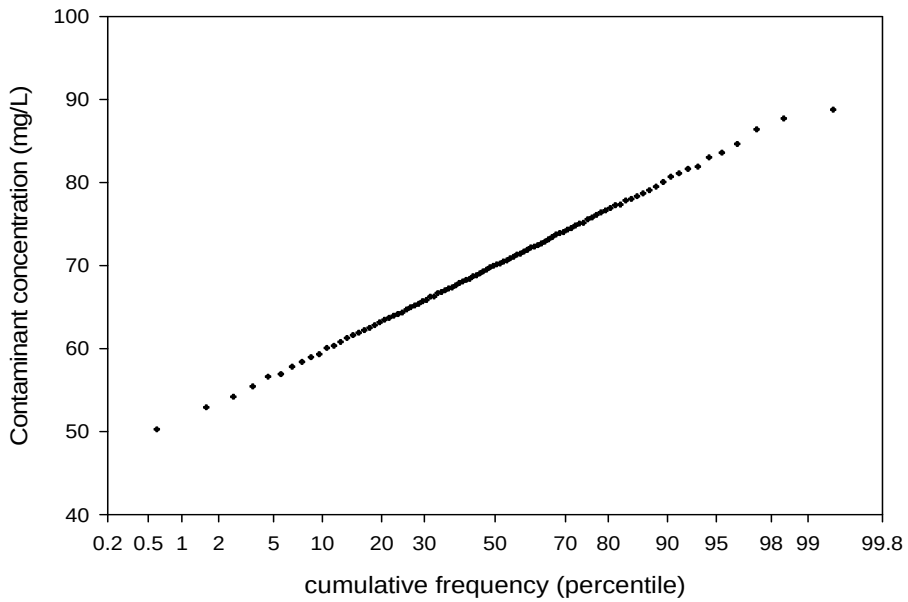
Figure 30: Cumulative frequency plot for hypothetical chemical contaminant (linear scale)



The curved shape of cumulative frequency presented in Figure 30 appears to be characteristic of a normal distribution. To test whether these data are in fact normally distributed, a simple approach is to change the scale of the horizontal axis from a liner scale to what is commonly known as a 'probability scale'. The probability scale realigns the data in terms of evenly spaced quantiles of a standard normal distribution. This is related to the number of standard deviations that any data point is from the mean value.

The probability-scaled chart is commonly referred to as a 'probability plot' as shown in Figure 31. If the data are truly normally distributed, then the probability plot will present the data in a straight line. Outliers and deviations from normality can be clearly observed as deviations from the straight line. Values corresponding to the 5th and 95th percentile may be relatively accurately read from Figure 31 (approximately 55 and 85 mg/L, respectively).

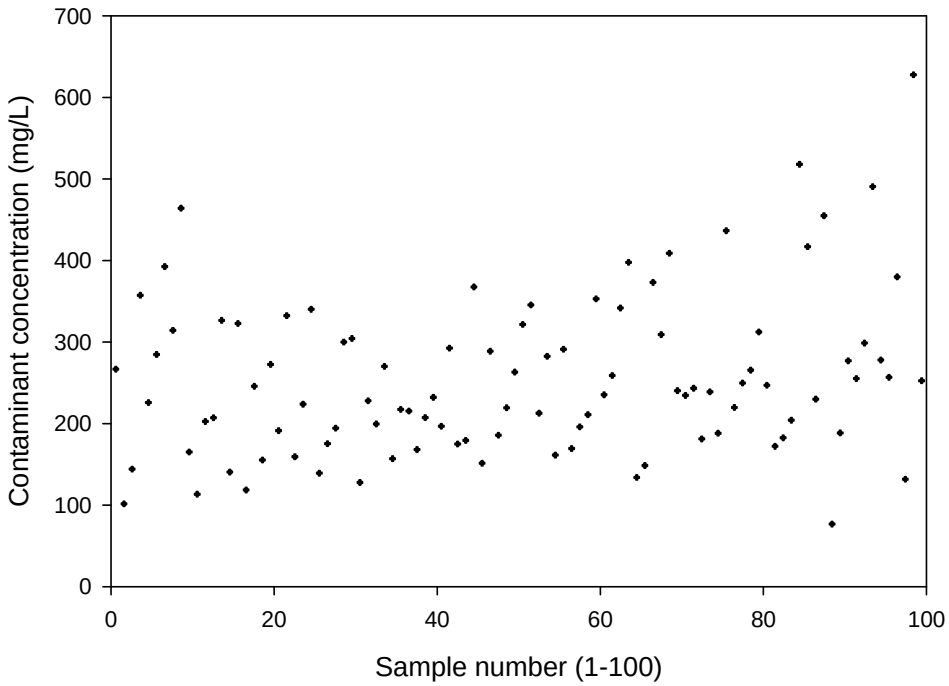
Figure 31: Probability plot for hypothetical chemical contaminant (probability scale)



The probability scale shown in Figure 31 specifically applies to a normal distribution. However, the general concept of scaling to evenly spaced quantiles can be applied to other distributional forms. This may be achieved by plotting data on specially scaled 'probability paper' or with the assistance of specialised statistical software packages.

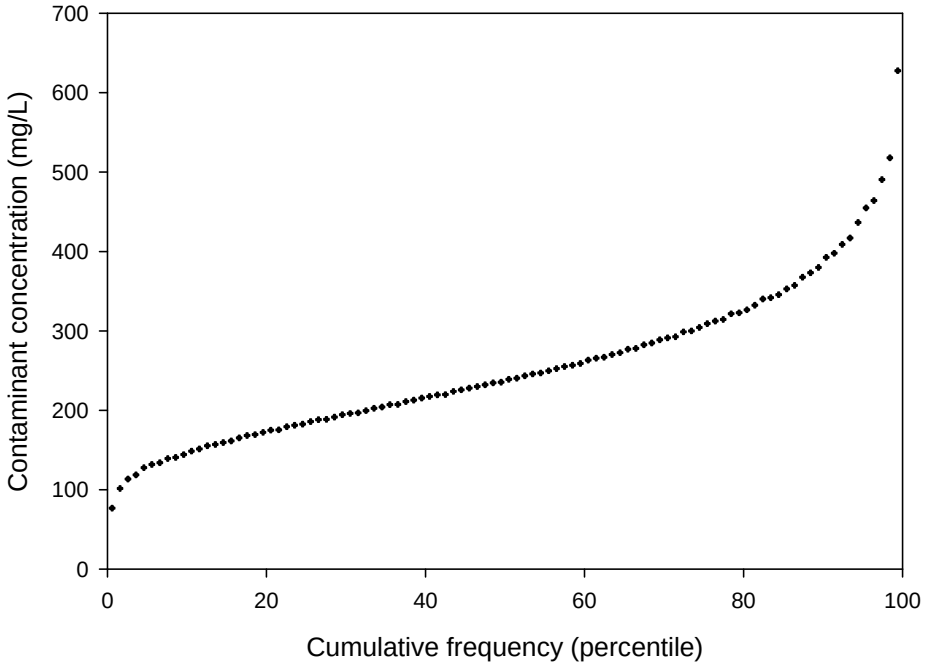
The lognormal distribution may simply be tested using a normal probability scale and plotting the logarithms of the data values (in this example, contaminant concentration) or by rescaling the vertical axis to a log scale. An example is shown for a lognormal data series in Figure 32.

Figure 32: Scatter plot for 100 sample measurements of hypothetical chemical contaminant (lognormal distribution)



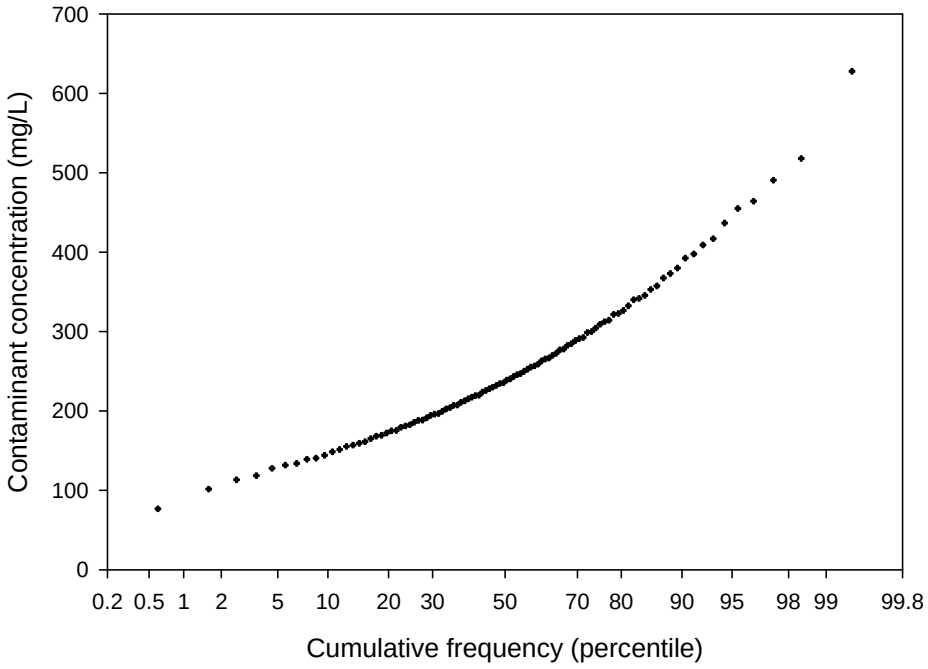
Plotted on two linear scales, the cumulative frequency (Figure 33) for this dataset appears to provide a similar shaped curve to that obtained by a normal distribution (for example, Figure 30).

Figure 33: Cumulative frequency plot for hypothetical chemical contaminant (lognormal distribution, linear scale)



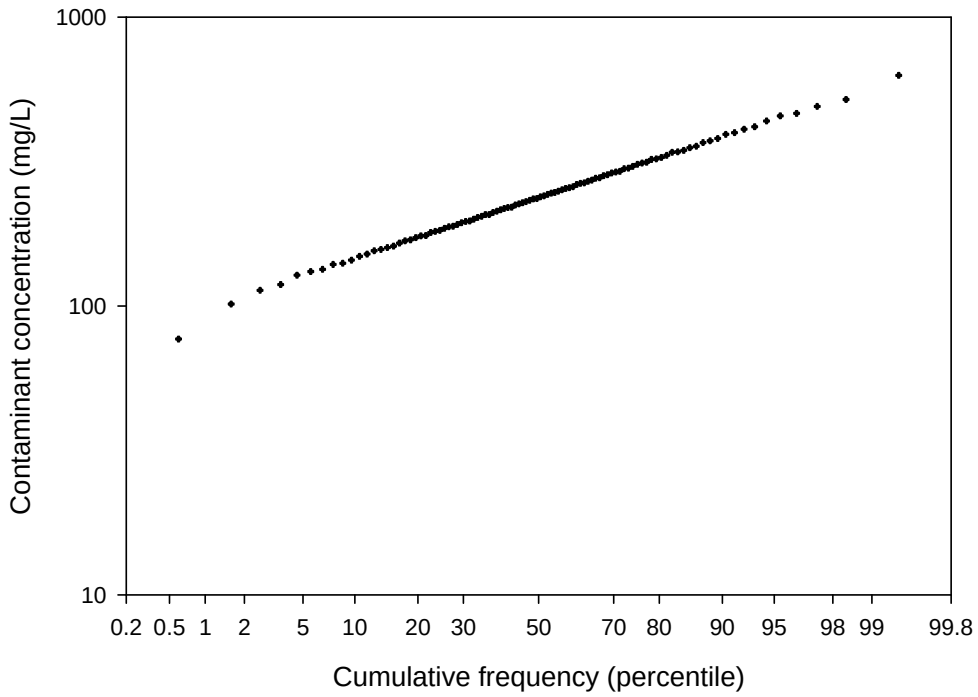
However, a true visual test for normality is achieved by plotting the cumulative frequency (x-axis) on a normal probability scale as shown in Figure 34. In this case, the curve obtained does not resemble a straight line, and no straight line can be satisfactorily fitted across the entire sampled distribution (even with the removal of any extreme outliers).

Figure 34: Probability plot for hypothetical chemical contaminant (lognormal distribution, probability scale)



Replotting the data values (y-axis) on a log scale (or simply plotting their log values) provides a test of lognormality as shown in Figure 35. In this case a straight line is obtained, indicating that the data set are approximately lognormally distributed and thus may be fitted to a lognormal PDF.

Figure 35: Lognormal probability plot for hypothetical chemical contaminant (lognormal distribution, probability scale)



6.6.1 Procedure for developing probability plots

Probability plots can be developed by following a relatively simple general procedure. After acquiring the data, the first step is sort it from the lowest value to the highest value. The sorted data values are then ranked from 1 to n, where n is the sample size of the data set. The smallest value is then assigned a rank i=1, while the largest received a rank i=n.

The data themselves are plotted along one axis (in the preceding examples this is the vertical axis). The other axis is the 'plotting position' (p), which is a function of the rank i and sample size n. A number of different formulae for assigning the plotting position have been proposed and used [259; 260]. The most applicable formula for normal distributions (and transformed lognormal distributions) is known as the Blom formula as presented in Equation 6 [261].

Equation 6: Blom formula for assigning plotting positions

$$p_i = \frac{i - 0.375}{n + 0.25}$$

A very similar alternative to the Blom formula is known as the Cunnane formula [260], which has been adopted in some water resources texts and presented in Equation 7 [259].

Equation 7: Cunnane formula for assigning plotting positions

$$p_i = \frac{i - 0.4}{n + 0.2}$$

To plot the data in terms of percentiles (as opposed to fractiles), it is necessary to multiply the value of the plotting position by 100. The example provided in Table 17 shows how plotting

positions may be assigned to measured concentrations of chloroform in the feed, permeate and concentrate streams of a reverse osmosis treatment process. In this case, 13 data points were available for all three streams, and thus the same 13 plotting positions (p_i) were used for all three streams. However in many cases, different number of data points may be available for different streams. That is, *n* is variable, and thus the plotting positions would need to be calculated for each stream.

Table 17: Example of assignment of plotting positions to chloroform concentration data during reverse osmosis treatment

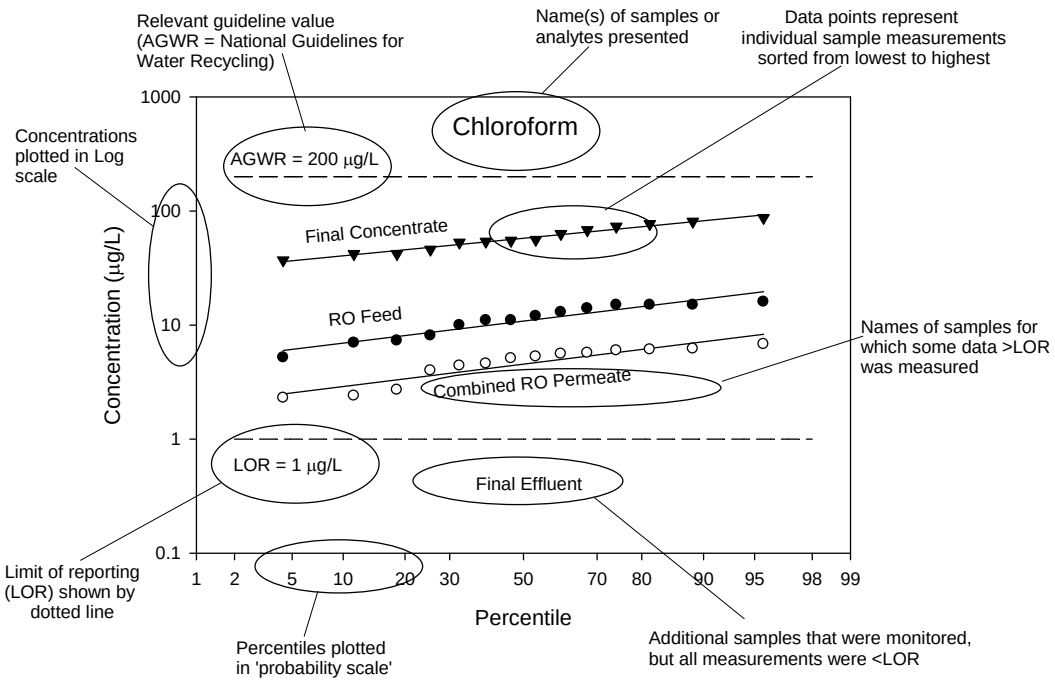
i	p_i x 100	RO Feed (μg/L)	RO Permeate (μg/L)	RO Concentrate (μg/L)
1	4.4	5.2	4.2	37
2	11.4	7.0	4.5	42
3	18.4	7.3	4.5	42
4	25.4	8.1	6.4	46
5	32.5	10.0	6.8	53
6	39.5	11.0	7.8	54
7	46.5	11.0	7.9	55
8	53.5	12.0	8.2	56
9	60.5	13.0	8.4	63
10	67.5	14.0	8.6	68
11	74.6	15.0	8.7	73
12	81.6	15.0	9.1	77
13	88.6	15.0	9.3	81
14	95.6	16.0	11.0	87

Normal quantiles for a given plotting position may be obtained from most statistics text books. Alternatively, probability plotting paper may be used as described above to rescale the linear scale for quantiles of the standard distribution into the non-linear scale of plotting positions. However, the simplest approach is to use a statistical computer software package to rescale the linear cumulative frequency axis to ‘probability scale’.

For lognormally distributed data, the vertical axis must either be plotted as the log values of the data points, or else rescaled from a linear scale to a log scale. This again may be achieved by plotting on specialised log paper or with the aid of statistical or chart-drawing software.

Figure 36 provides an example of a lognormal probability plot developed for the removal of chloroform by a three stage reverse osmosis treatment processes. This chart was prepared using the data and plotting positions shown in Table 17.

Figure 36: Example of a lognormal probability plot for removal of chloroform by reverse osmosis (RO) treatment



Fitted probability plots are shown for chloroform concentrations measured in the reverse osmosis feed water, final (stage 3) concentrate and combined (stages 1–3) permeate. While some permeate data points are greater than some of the feed data points, the overall trend of decreasing concentration from reverse osmosis feed to permeate is clear. This is further emphasised by the clearly increased concentration of the final concentrate. In this example, the overall recovery of feed water into the permeate was approximately 85 per cent. Therefore, the volume of final concentrate is roughly 15 per cent of the reverse osmosis feed.

The example provided in Figure 36 also shows how references to other relevant concentrations such as the limit of reporting (LOR) and relevant guideline values (or water quality standards) can be clearly indicated as dotted lines on the chart.

6.7 Fitting PDFs to data

The selection of appropriate PDFs for all stochastic variables is a key step for many applications of quantitative risk assessment [262]. In a probabilistic risk analysis, the selection of PDFs for the most uncertain contributing parameters will strongly influence the distribution of resulting risk determination [263].

In most cases, only a limited number of model input assumptions and parameters will have a significant impact on the final determined variability and/or uncertainty. For some assumptions and parameters, equivalent final predicted PDFs may be derived even when some stochastic variables are treated as single point values (deterministic variables). Recognising this, it is considered good practice to undertake preliminary sensitivity analyses or numerical experiments to identify model inputs, parameters and exposure pathways that make significant contributions to the assessment endpoint and its overall variability and/or uncertainty [262; 264]. Identifying important pathways and parameters where assumptions about distributional form contribute significantly to overall uncertainty may aid in focusing data gathering efforts. On the other hand, it is important to avoid premature or unjustified elimination of pathways or parameters from full probabilistic treatment. Any pathway or

parameter that is eliminated from full probabilistic treatment should be identified and the reasons for its elimination clearly justified.

To aid in the judicious selection and parameterisation of a PDF, an evaluation must be made regarding what data are available and whether this information are suitable for this purpose. Knowledge regarding the nature of the parameter being modelled should be used to inform the choice of input distribution. For example, in counting nuclear radiation, a Poisson distribution is usually selected since the nuclear decay process is known to be governed by events following Poisson statistics. In selecting a distributional form, the US EPA [262] has recommended that a series of questions including (but not limited to) the following should be asked:

- Is there any mechanistic basis for choosing a distributional family?
- Is the shape of the distribution likely to be dictated by physical or biological properties or other mechanisms?
- Is the variable discrete or continuous?
- What are the bounds of the variable?
- Is the distribution skewed or symmetric?
- If the distribution is thought to be skewed, in which direction?
- What other aspects of the shape of the distribution are known?

According to the *Central Limit Theorem*, normal and lognormal distributions may often be inferred by the structure of the variations in a stochastic variable. If the variability of a quantity may be assumed to be derived from a sum of contributions with many variations but each with a defined mean and variance, the distribution of the sum is asymptotically normal. However, if the variability arises from the product of many factors, each with a variability defined by a mean and variance, the resulting distribution is asymptotically lognormal.

The exponential distribution may be appropriate if the stochastic variable represents a process akin to inter-arrival time of events that occur at a constant rate. A gamma distribution may be a reasonable candidate if the random variable of interest was the sum of independent exponential random variables [262].

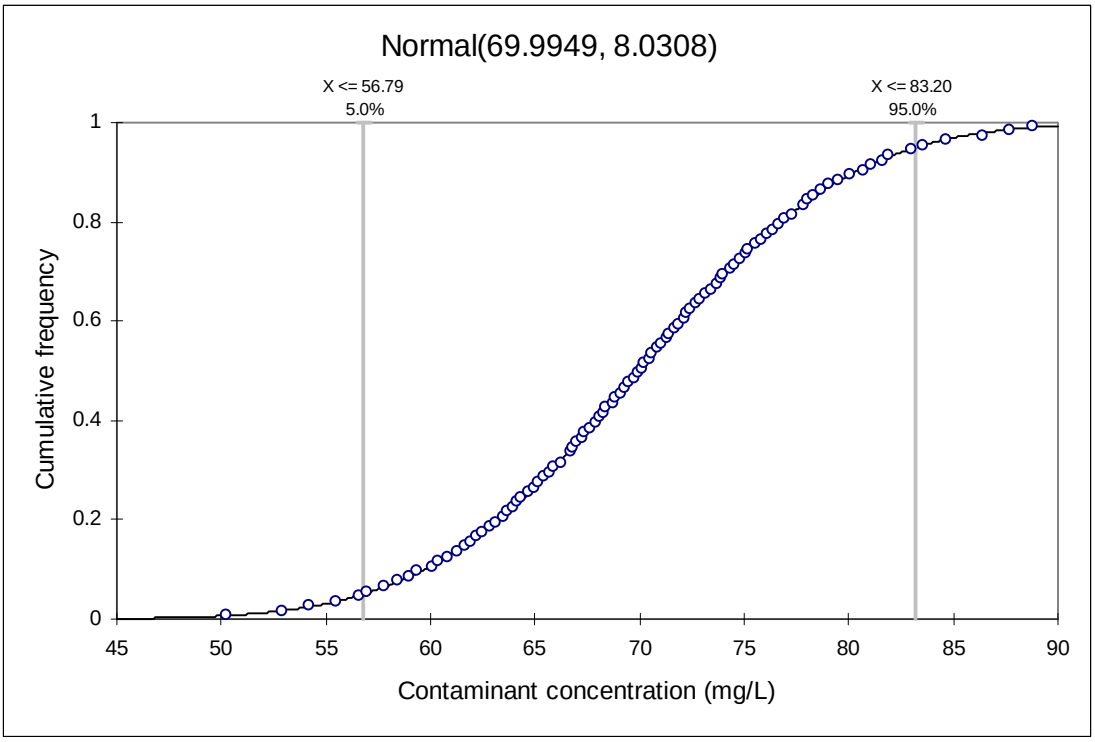
In situations where the underlying nature of a distribution is unknown or only approximately known, there are a number of considerations and techniques available for assessing and selecting appropriate PDFs and associated parameters [263]. However caution should be exercised since it has been shown that the PDF shape may significantly influence model outputs for some situations [265]. Where uncertain distributions have been applied for significant parameters, it is important to test the sensitivity of the model findings and conclusions to changes in the modelled distributional shape.

Numerous commercial software packages are available for fitting sampled data to distributions and for testing the veracity of the fit. Examples presented here were fitted using @Risk [266] since this software is also suitable for the Monte Carlo simulations described in Chapter 8.

There are a number of ways in which distribution-fitting software can be used to fit sampled data. However, a reliable technique that will later be useful for its application to censored data sets (Section 6.9) is to fit the data as a cumulative distribution. This requires, initially, the calculation of plotting positions (p) as described in Section 6.6.1. Once the data values are paired with their corresponding plotting positions (p_i), they may be used to describe the sampled distribution in order for this to be fitted to a standardised cumulative density function.

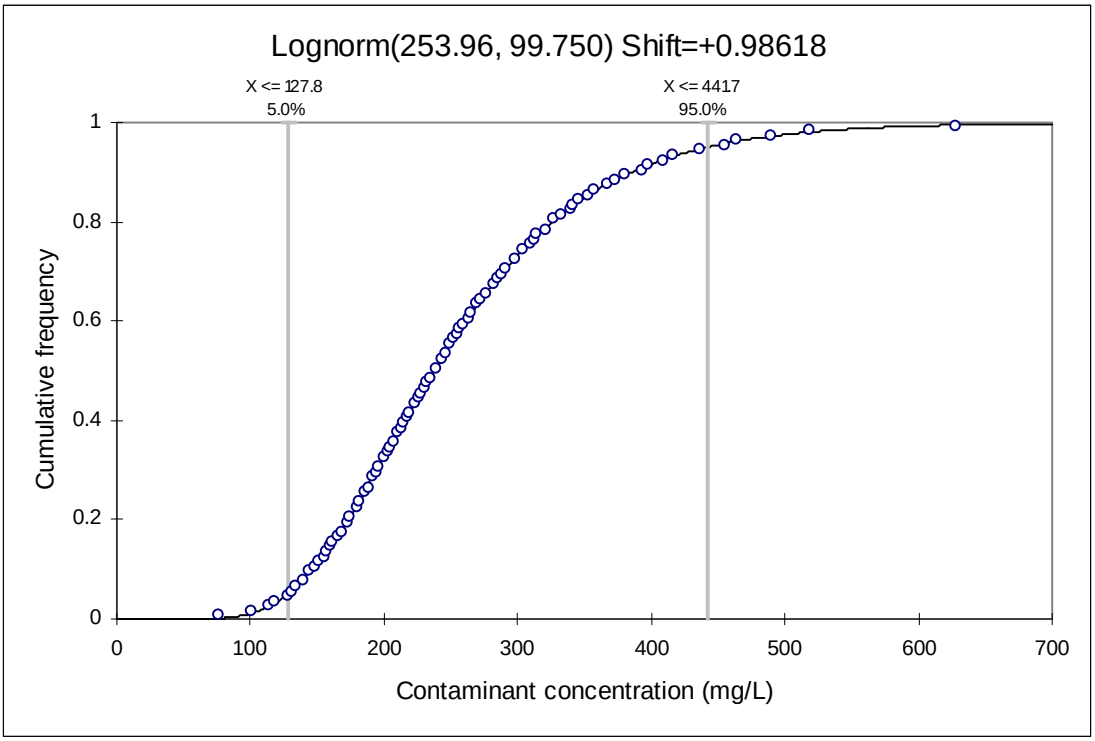
The normally distributed data previously presented in Figure 29 to Figure 31 has been fitted to a cumulative density function using @Risk with the final fit shown by the curved line in Figure 37. The suitability of the fit can be visually inferred by the close match between the sampled data points and the curved fit line. Once the data have been fitted to a suitable curve, summary statistics describing the fitted distribution can be obtained. In this case, the data were fitted to a normal distribution described by a mean of 69.99 mg/L and standard deviation of 8.0 mg/L.

Figure 37: Cumulative density function fitted to normally distributed data



In environmental and water quality sampling, data are generally more commonly fitted to a lognormal distribution. Using appropriate software, this can be achieved as simply as was described for a normal distribution. To demonstrate the outcome of such a fitting procedure, Figure 38 shows the lognormally distributed data previously presented in Figures 32–35 fitted to a cumulative density function using @Risk. Summary statistics of the fitted curve including the mean (253.96 mg/L) and standard deviation (99.75 mg/L) can be obtained.

Figure 38: Cumulative density function fitted to lognormally distributed data



A literature review has previously been reported, comparing distributions used in published probabilistic assessments for the parameters of body weight, food consumption, soil ingestion rates, breathing rates, and fluid intake [267]. This study revealed that even where extensive, well-collected data exist, investigators used a variety of different distributional shapes to approximate these data. Where such data do not exist, investigators have collected their own data, often leading to substantial disparity in parameter estimates and subsequent choice of distribution. The authors concluded that more attention should be paid to the data underlying distributional choices, including greater emphasis on sensitivity analyses and quantifying the impact of assumptions.

It has been observed that the absence of a standard approach for developing input exposure factor PDFs can result in probabilistic risk assessments that are inconsistent and difficult to review by regulatory agencies [268]. Accordingly, a two-step approach has been proposed, involving the development of archetypal distributions for an identified list of subpopulations [268].

When obtaining data to develop input PDFs, the basic tenets of statistically significant sampling should be followed. For example, environmental sampling should be undertaken at appropriate spatial or temporal scales using an appropriate stratified random sampling methodology. If possible, multi-staged sampling should be used to evaluate the degree of statistical power and uncertainty in the data. Particular attention should be given to the quality of information at the tails of the distribution, which is often not as well defined as the central values.

When sufficient data regarding a particular parameter is unavailable, it can sometimes be possible to develop a PDF using surrogate data if they can be appropriately justified. In such circumstances, it is important to pay careful attention to any potential biases that may exist in the surrogate data and their implications for the representativeness of the fitted PDFs. Where possible, some site, contaminant or case specific data should be acquired to help justify the use of the PDF based on surrogate data.

An analysis of PDF characteristics has illustrated that arithmetic mean is a more appropriate measure of central tendency than geometric mean for microbial concentration with respect to repeated samples of daily exposure [269]. This is despite frequent characterisation of microbial density by the geometric mean, since the microbial distributions may be lognormal or skewed in nature.

For situations involving a limited number of data observations, some additional degree of uncertainty will generally be imposed by the selection of the PDF to be fitted to the data [270]. Probability bounds analysis has been introduced as a method of investigating the full extent of uncertainty in risk assessment models, including the selection of input distributions [270; 271].

6.8 Goodness of fit

Once a PDF has been selected, it is appropriate to test the 'goodness of fit' of the distribution with known data. Goodness-of-fit tests are formal statistical tests of the hypothesis that the set of sampled observations are an independent sample from the assumed distribution.

To undertake goodness-of-fit tests, graphical tests such as the plotting of histograms, the Probit or the Logit plot for normal or lognormal distributions may be used. Alternatively, numerical methods such as the chi-squared test, the Kolmogorov-Smirnov test and the Anderson-Darling test can be used. For each of these, a numerical value is calculated relating the data to the fit statistics, and in each case, the smaller the value, the better the fit. Each of these numerical tests offers variable advantages and disadvantages and a careful decision should be made when considering which of them (or other available tests) to use.

The chi-squared test is the best-known goodness-of-fit statistic. It is calculated by partitioning the x-axis domain into several discrete 'bins'. The chi-squared statistic is then given by Equation 8.

Equation 8: The chi-squared test for goodness-of-fit

$$\chi^2 = \sum_{i=1}^{K} \frac{(N_i - E_i)^2}{E_i}$$

Where:

K = the number of bins

N_i = the observed number of samples in the ith bin

E_i = the expected number of samples in the ith bin.

A weakness of the chi-squared test is that there are no universally accepted guidelines for selecting the number and location of bins. In some situations, it is possible to reach different conclusions for the same data depending on the selection of bins. Some software packages are able to reduce this arbitrariness by adjusting bin sizes based on the fitted distribution with an aim to making each bin contain an equal amount of probability (for example, smaller bins around the mean and larger bins around the tails).

The Kolmogorov-Smirnov and Anderson-Darling tests do not require binning and thus are less arbitrary than the chi-squared test. However, the Kolmogorov-Smirnov focuses on the middle of the distribution, and thus does not detect tail discrepancies very well. The Anderson-Darling test more effectively highlights differences between the tails of the fitted distribution and the input data. Decisions regarding the most appropriate tests to use to assess goodness-of-fit should be made with consideration of the relative significance of the strength and limitations of the particular test.

When testing for normality or lognormality, more powerful tests include Lilliefor's test, the Shapiro-Wilks test (for sample size less than 50) and the D'Agostino test (for sample size greater than 50). The latter two are considered to be the tests of choice for normality and lognormality [262].

Despite the power of complex distribution fitting techniques, and even despite apparent excellent results of goodness-of-fit tests, caution should always prevail where limited or incomplete data are available. Depending on the proportion of available data and the patterns of 'missingness', significant bias may arise from some common approaches to handling missing data [272]. Goodness-of-fit tests are considered to have low discriminatory power and are generally best used for rejecting poor distribution fits, rather than for identifying good fits [262].

Graphical methods can provide clear and intuitive indications of goodness-of-fit. Among the most common of graphical methods is the frequency comparison, which compares a histogram of the experimental data with the PDF of the fitted data (see Figure 22). Probability plots compare the observed cumulative density function with the fitted cumulative density function.

Probability–probability (P–P) plots and quantile–quantile (Q–Q) plots are also commonly used and easily accessible by many statistical software packages. P–P plots compare the observed probability with the fitted probability, and Q–Q plots compare the *i*th quantile of the data against the *i*th quantile of the fitted distribution. P–P plots tend to emphasise differences in the middle of the predicted and observed cumulative distributions, while Q–Q plots tend to emphasise differences at the tails.

6.9 Censored data

A common difficulty encountered in investigations of many water contaminants is that a substantial portion of the analysed samples are below limits of detection (LODs) or limits of reporting (LORs) established by analytical laboratories.

The LOD refers to the lowest concentration of a contaminant that can be reliably detected above a blank sample. LORs are typically slightly higher than LODs and are used as a means of incorporating a safety factor to account for variable sample matrices, variable detection performance, increased confidence in contaminant identification (reduced false positives) and increased confidence in quantitation.

While data returned as 'less than limit of detection' (<LOD) or 'less than limit of reporting' (<LOR) are clearly known to be below a particular value (as defined by the LOD or LOR), their precise values remain unknown. As such, they are examples of what is commonly called 'censored data'. Censored data can present considerable difficulties when there is a need to fit PDFs, graphically present data, or estimate summary statistics [273].

Simply ignoring censored data and using only the fraction of the data that is above the LOR distorts the relationship between the sampled data and the underlying true distribution of values. Accordingly this practice inevitably leads to biases in fitting a PDF and in summary statistics such as means and standard deviations.

In some cases, it may be tempting to record <LOR data points as 'zero' since that may be the direct (mis)interpretation of an analytical instrument reading. However, the true value is generally not known (and not knowable) to be zero, since analytical instruments have minimum values greater than zero at which they are able to reliably detect the presence of contaminants. As such, the true value may—for all the analyst can tell—be anywhere between zero and the analytical detection limit. Assigning all such data points a value of zero

introduces a negative bias to fitted PDFs and many calculated summary statistics such as means.

Substituting data deemed to be <LOR with the value of the LOR is similarly as flawed as substituting data with zero. This approach introduces positive biases to fitted distributions and calculated summary statistics. While it may, in some cases, be considered to be a useful approach of introducing worst-case scenarios, it undermines many of the efforts that may be used to accurately describe and account for the stochastic nature of water quality parameters.

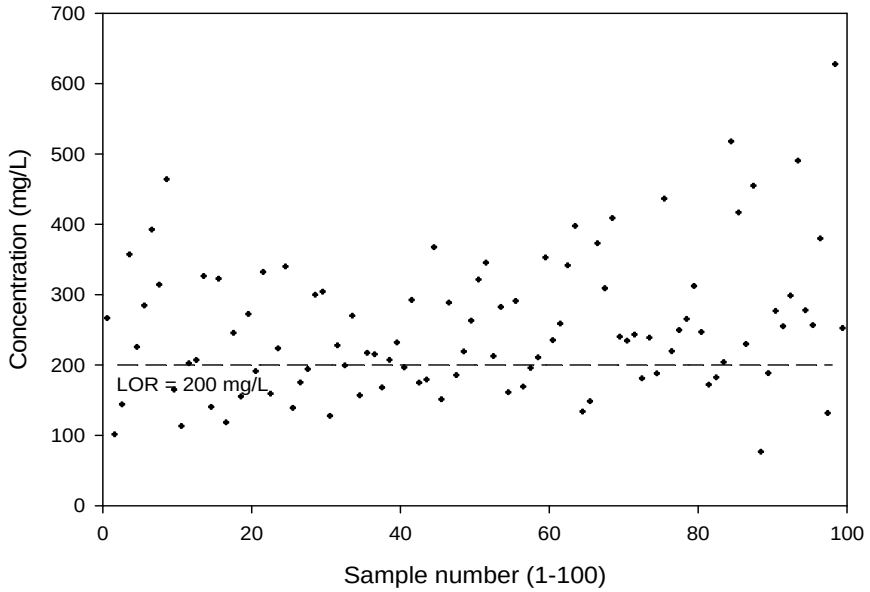
The most common method in environmental studies for dealing with data <LOR is to substitute the value for one-half of the LOR [274]. However, this is approach is not considered to be a reasonable method for interpreting censored data since it too can provide a poor representation of the true data distribution leading to inaccurate summary statistics that may have significant regulatory consequences [274]. This approach can introduce a signal that was not actually present in the original data, or obscure a signal that was actually there.

The most statistically appropriate procedures for managing censored data combine the values above the LOR with the information contained in the proportion of data below the LOR. A number of such suitable techniques, of varying complexity and suitability for various datasets, are available for managing censored data [273–275]. Rigorous techniques are available for estimating distributional parameters for censored trace level water quality data [276] and for estimation of descriptive summary statistics for censored water quality data [277]. However, the problem can be approached quite simply using modern statistical software packages.

As described in Section 6.7, there are several steps and important considerations that should be followed when fitting any type of data to a PDF or a cumulative density function. After carefully considering the basis for selecting any particular distributional form, it is appropriate to visually inspect the linearity (or lack thereof) of a cumulative frequency plot for anticipated normal or lognormal data (see Figure 31 and Figure 35 respectively). This can be achieved for censored data sets by following the same procedure as for non-censored sets.

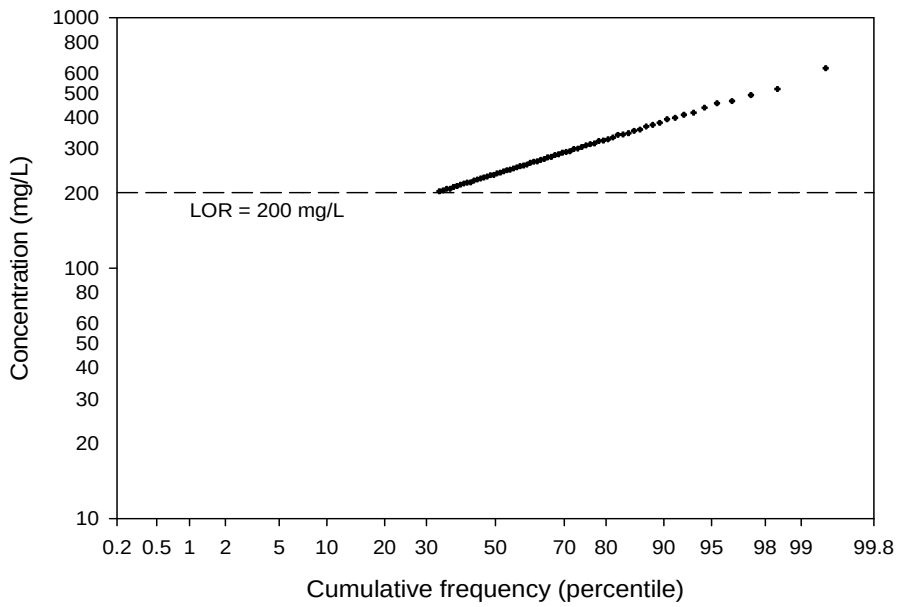
Consider the lognormally distributed data from Figure 32, but in this case assume a LOR of 200 mg/L as shown in Figure 39. In this case all of the samples with a value of less than 200 mg/L would be reported as <LOR or <200 mg/L, and the precise values would remain unknown. This would leave us with two key pieces of information. First, we would have the remaining data above 200 mg/L, for which we could examine the distribution. Secondly, we would know the proportion of the samples that are <200 mg/L. From these two pieces of information, we can often make a reasonable estimation of the overall distribution as shown the in following examples.

Figure 39: Scatter plot for 100 sample measurements of hypothetical chemical contaminant (lognormal distribution); LOR=200 mg/L



In this example, 33 of 100 sample measurements would have been returned with the result <200 mg/L and the remaining 67 points have been reported with values greater than 200 mg/L. Accordingly, values may be assigned to the 34th, 35th, 36th, etc percentiles. The plotting positions of these percentiles may be calculated and plotted as described in Section 6.6.1. The result in this case is presented in Figure 40.

Figure 40: Censored probability plot for hypothetical chemical contaminant; LOR = 200 mg/L

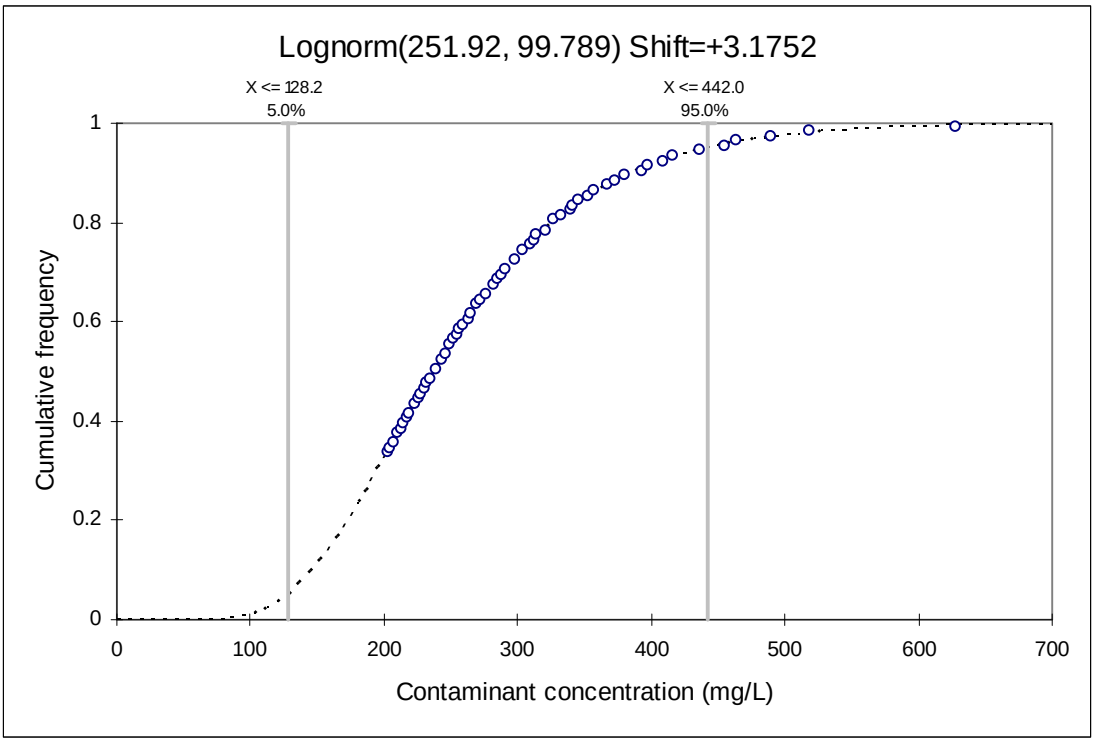


Once the validity of a distributional form has been established, it is possible to use the available data values, paired with their corresponding plotting positions (p_i), to describe the

sampled distribution in order for this to be fitted to a standardised cumulative density function (as described in Section 6.7 for non-censored data sets).

The result of fitting this sampled data to a lognormal distribution after censoring all data <200 mg/L is presented in Figure 41. The data points indicate the sampled data, while the curved dotted line indicates the fitted distribution.

Figure 41: Fitted lognormal distribution to data censored by LOR = 200 mg/L



For the purposes of comparison, the same data have been fitted to a lognormal distribution assuming a LOR=300 mg/L (Figure 42) and LOR=400 mg/L (Figure 43). By visual inspection, it is apparent that relatively good matches to the PDF developed from the non-censored data set (Figure 38) are achieved in each case. Nonetheless, the greater the proportion of censored data, the less reliable will be the match of the fitted PDF to the dataset.

Figure 42: Fitted lognormal distribution to data censored by LOR = 300 mg/L

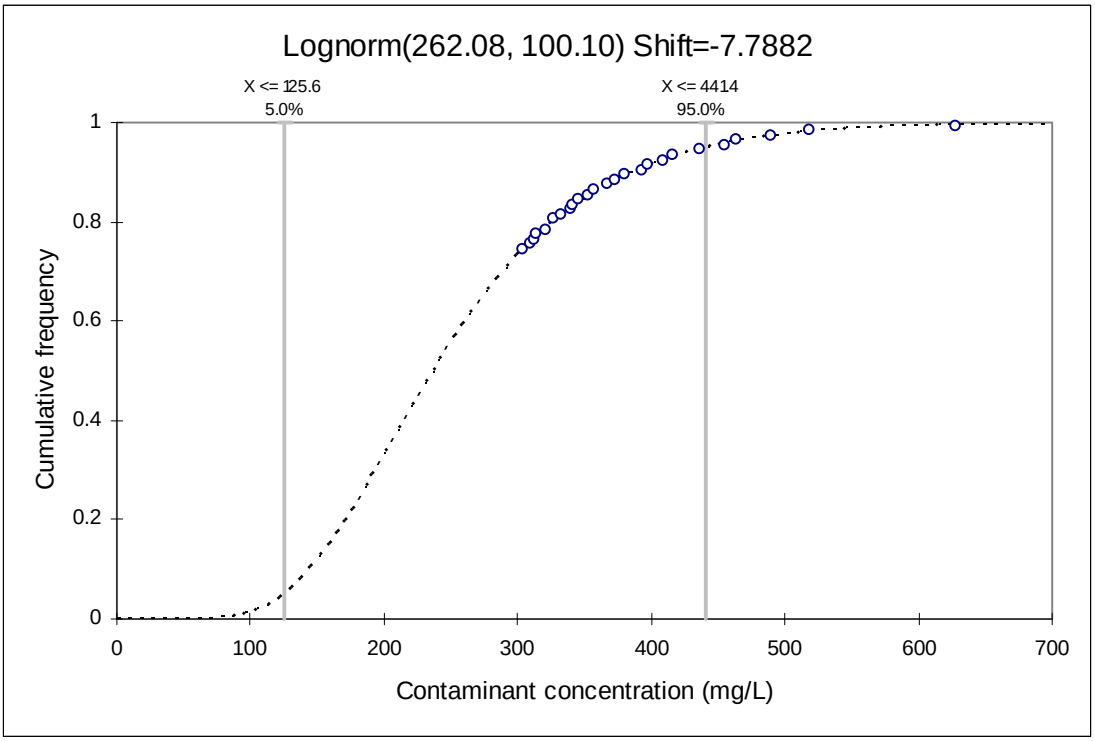
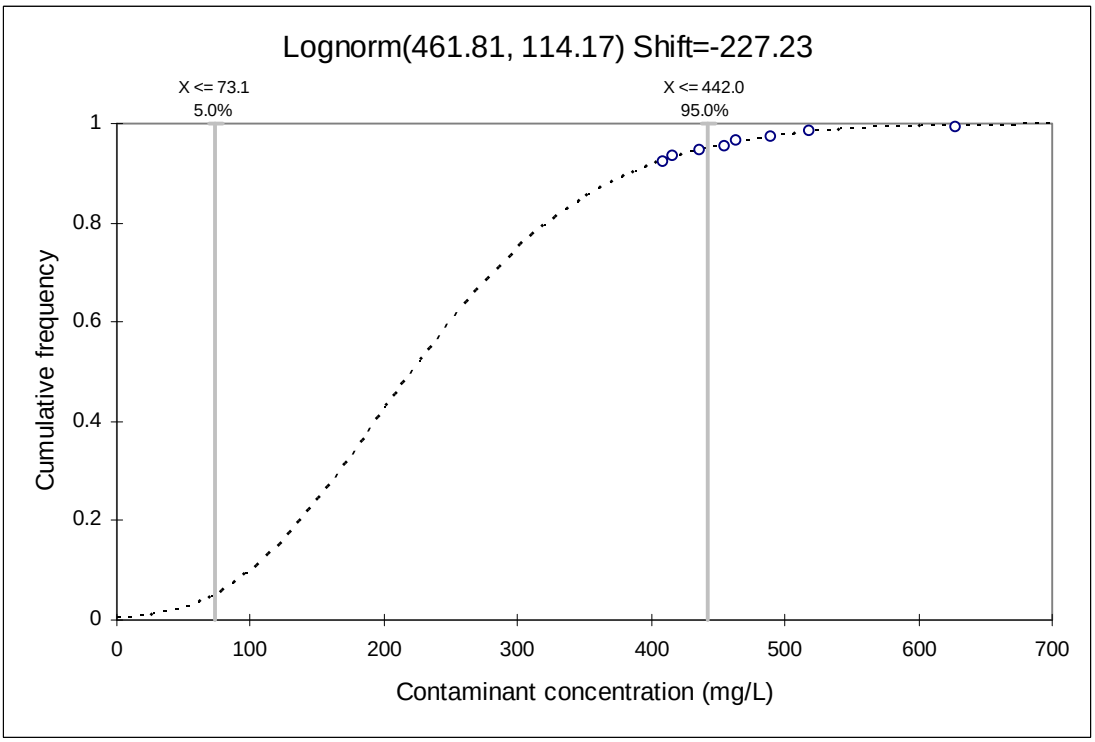


Figure 43: Fitted lognormal distribution to data censored by LOR = 400 mg/L



Censored water quality data can be very effectively presented as a lognormal probability plot as described in Section 6.6.1. For example, consider the data presented Table 18. This shows sorted values and assigned plotting position for the removal of the pharmaceutical

‘gemfibrozil’ during reverse osmosis treatment. In this case, the final reverse osmosis concentrate was well above the limit of reporting (LOR = 5 nanograms per litre) and none of the data are censored. The reverse osmosis permeates were consistently less than the limit of reporting, and thus are fully censored, and the LOR must be used for all calculations. However, the reverse osmosis feed concentration is an example of partially censored data.

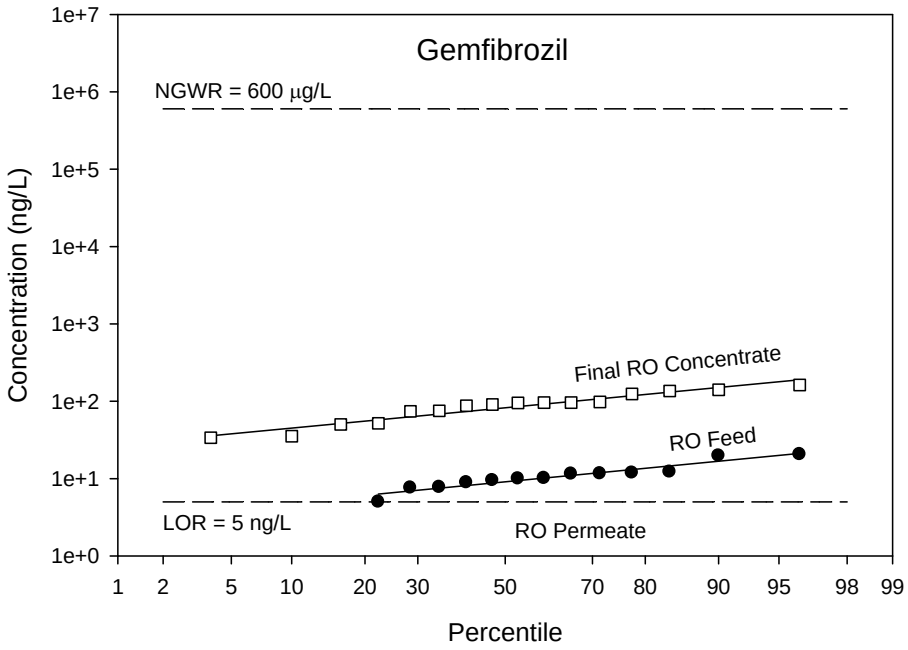
Table 18: Example of assignment of plotting positions to chloroform concentration data during reverse osmosis treatment

i	p_i *x 100*	*Feed (ng/L)*	*Permeate (ng/L)*	*Concentrate (ng/L)*
1	3.8	<5	<5	34
2	10.0	<5	<5	35
3	16.2	<5	<5	50
4	22.3	5.0	<5	52
5	28.5	7.6	<5	74
6	34.6	7.8	<5	75
7	40.8	8.9	<5	87
8	46.9	9.5	<5	91
9	53.1	10.0	<5	95
10	59.2	10.1	<5	96
11	65.4	11.5	<5	96
12	71.5	11.6	<5	98
13	77.7	11.9	<5	124
14	83.8	12.2	<5	135
15	90.0	19.7	<5	140
16	96.2	20.6	<5	162

Shaded entries show censored data points; ng/L = nanograms per litre

The lognormal probability plot shown in Figure 44 presents the data from Table 18. For the partially censored data of the reverse osmosis feed concentration, a reasonable assumption may be made regarding the overall concentration distribution. While 20 per cent of the data were determined to be <LOR, the remaining 80 per cent may be visually observed to be a reasonable fit to the lognormal distribution represented by the straight line plotted on the curve.

Figure 44: Lognormal probability plot for reverse osmosis treatment of gemfibrozil



Censored probability plots such as the one provided in Figure 44 can be prepared by following the same process as described in Section 6.6.1. The only difference is that, in this case, only a proportion of the data (the non-censored data) and their corresponding plotting positions are plotted. However, the full number of data points (including the censored data) must be used for determining the values of *i* and *n* for the calculation of the p_i.

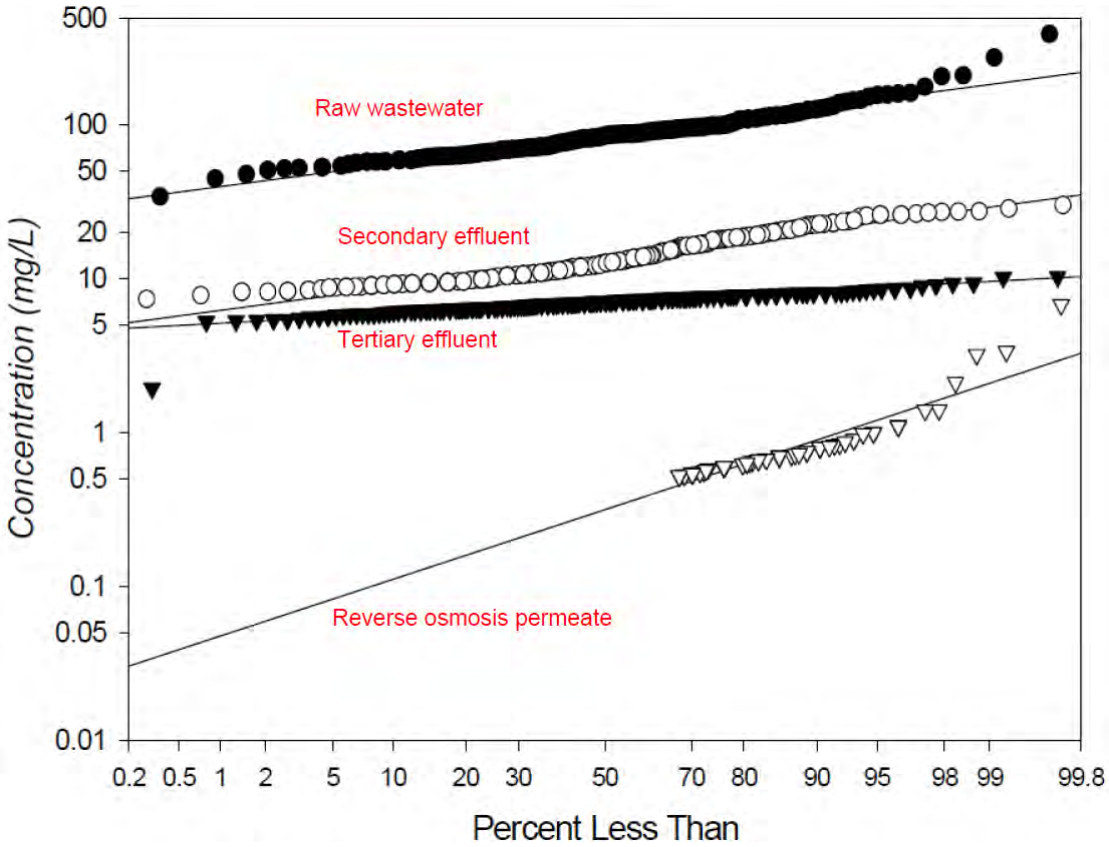
7. Treatment Process Performance Assessment

The evaluation of treatment variability under normal plant operation may be achieved by summarising observed water quality using basic statistical tools associated with frequency analysis (such as means, standard deviations).

The overall system variability may be characterised by estimating the cumulative probability distributions associated with individual contaminants at key treatment units throughout the facility. These probability distributions allow the estimation of probability that treatment goals would be exceeded.

The assumption of a lognormal distribution for contaminant variability has previously been recommended [278]. Water quality variability may then be characterised by the construction of lognormal cumulative probability plots, such as those shown for total organic carbon (TOC) in Figure 45 [278]. The TOC data presented in this figure include raw wastewater, secondary effluent, tertiary effluent, and reverse osmosis effluent from the City of San Diego's pilot scale 'Aqua III' advanced water treatment plant from October 1994 through September 1995.

Figure 45: Lognormal probability plot for TOC after various treatment processes [278]

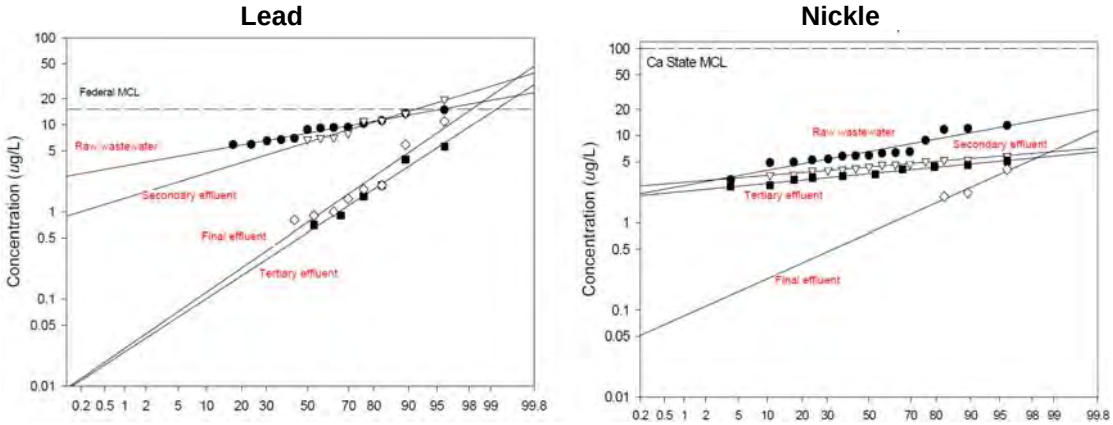


As can be observed from Figure 45, TOC levels in raw wastewater could be expected to range between 30 and 500 mg/L, secondary effluent 7–20 mg/L, and tertiary effluent 2–7 mg/L. Seventy per cent of the data for reverse osmosis effluent were reported to be below detectable limits (0.5 mg/L) and 99 per cent were below 1 mg/L. The reverse osmosis effluent data demonstrate the use of this kind of analysis to estimate the distribution of

treatment plant performance when a large percentage of data are below detection limits. This procedure allows for the estimation of summary statistics such as mean and standard deviation for largely censored data (see Section 6.9).

The Aqua III plant performance was also assessed in terms of physical parameters, nitrogen compounds, anions, trace and major metals, organic compounds and bacterial indicators. Parametric time series analysis was conducted to identify and investigate trends and periodicity that may have occurred within the collected data at the specific sampling sites. Lognormal probability plots were created for all constituents with sufficient detected data. For example, the lognormal probability plots for lead and nickel concentrations in raw wastewater, secondary effluent, tertiary effluent, and final effluent are shown in Figure 46 [279].

Figure 46: Lognormal probability plots of lead and nickel at the Aqua III advanced water treatment plant [279]



The geometric mean values for both lead and nickel for all unit processes were shown to be well below the corresponding maximum contaminant levels (MCLs). Furthermore, the lognormal probability plots demonstrated that the probability that the final plant effluent will exceed the maximum contaminant level was approximately 0.03 for lead and was estimated through extrapolation to be 0.00001 for nickel.

As a stochastic variable, the final produced water quality from a water recycling scheme may be defined in terms of a PDF. The final water quality PDF will be a function of a number of other variables, most obviously source water quality to the advanced water treatment plant and the treatment performance of advanced water treatment plant processes. Accordingly, the expected PDF for final water quality may be derived from PDFs of source water quality and treatment performance. The techniques used for achieving this are described in Chapter 8. However, it is first necessary to develop PDFs for source water quality and unit operation treatment performance.

7.1 Source water quality assessment

Source water quality can be assessed from newly acquired or pre-existing water quality data. In many cases, pre-existing data is preferable since it may have been obtained over a significant period of time and thus includes large number of data points representing a broad array of conditions. An example is presented in Figure 47, which was prepared from aluminium concentration monitored in the final effluent of an Australian sewage treatment plant. In this case, 54 samples were recorded for environmental compliance monitoring during 2000–04. The historical collection of these data provided an excellent resource for a quantitative chemical risk assessment for a water recycling scheme that was proposed a number of years later.

Figure 47: Aluminium concentrations in tertiary treated effluent 2000–04

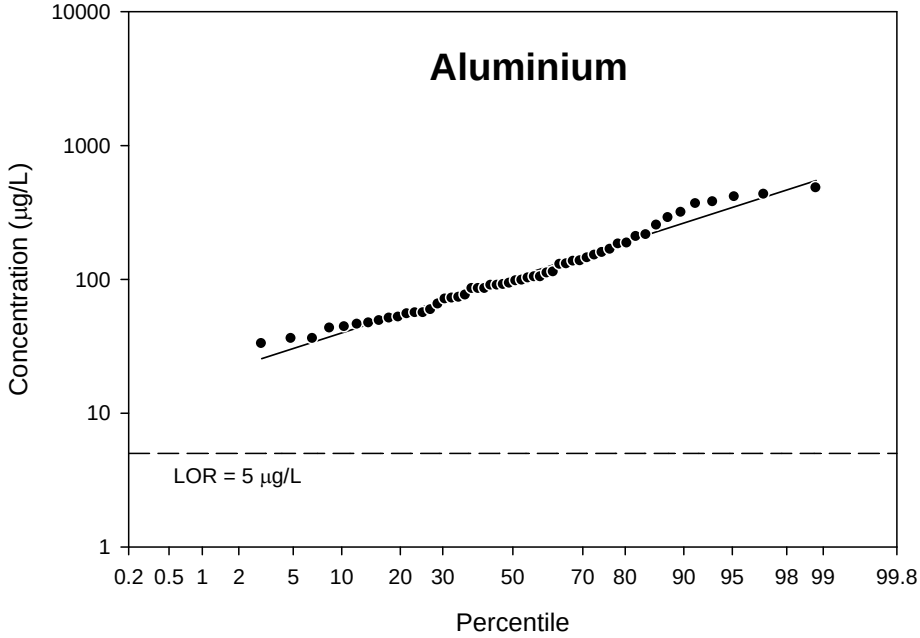
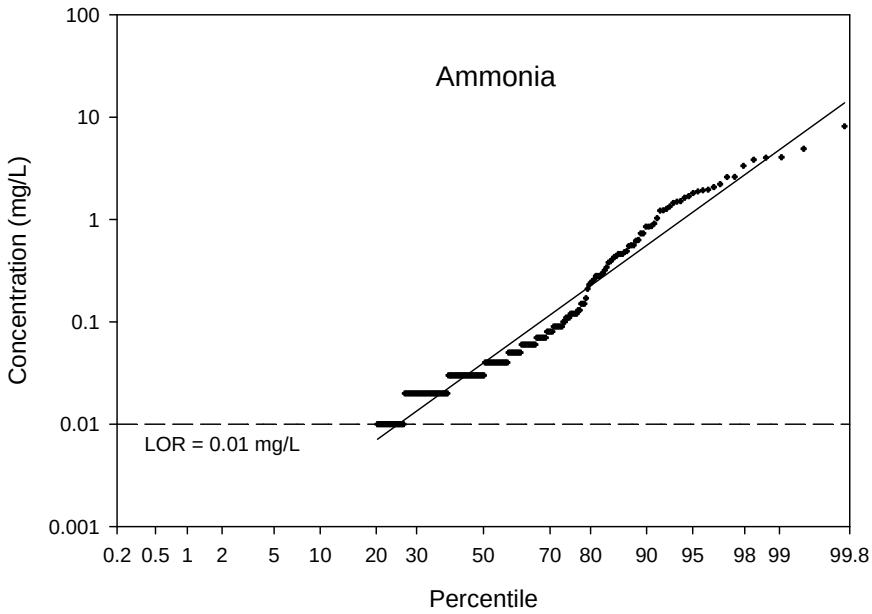


Figure 48 shows a similar collection of historical data from effluent discharge compliance monitoring for ammonia during 2000–04. In this case the level of reporting (LOR) was 0.1 mg/L, which led to 55 of the total of 274 data points being censored. Nonetheless, it is apparent that a reasonable lognormal distribution could be fitted to the available data.

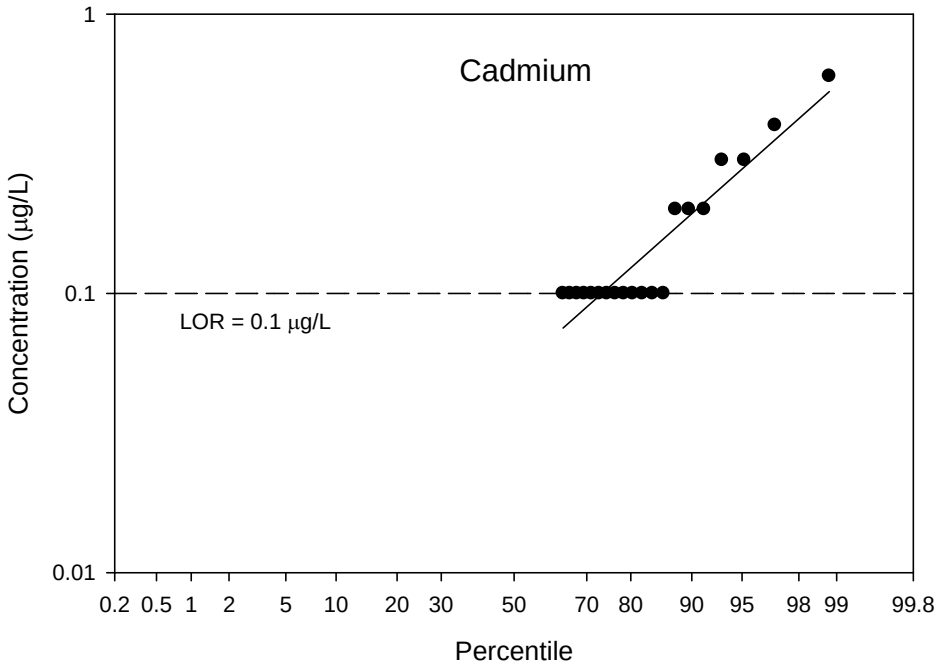
Figure 48: Ammonia concentrations in tertiary treated effluent 2000–04



It can also be seen from Figure 48 that the data resolution is 0.01 mg/L. That is, samples are recorded as intervals of <0.010 mg/L, 0.010 mg/L, 0.020 mg/L, 0.030 mg/L, 0.040 mg/L, 0.050 mg/L. However, this of course does not mean that the underlying distribution occurs in these discrete intervals. On the contrary, it can be assumed to be continuous like all other water contaminants. Accordingly, when judging the suitability of the fitted distribution, the stepwise nature of the plotted data should be ignored.

The characteristics described for the fitted ammonia distribution are further emphasised in the fitted distribution for historical cadmium concentration presented in Figure 49. In this case, 54 measurements were taken and 35 reported as <LOR. A significant number of samples were reported as being precisely on the LOR (0.1 μg/L), leading to the long horizontal arrangement of data points observed in the lognormal probability plot. In this case, the reporting resolution was also 0.1 μg/L, leading again to the step-wise appearance of the data. Nonetheless, the available imperfect data appear to provide a reasonable indication of an overall lognormal distribution.

Figure 49: Cadmium concentrations in tertiary treated effluent 2000–04

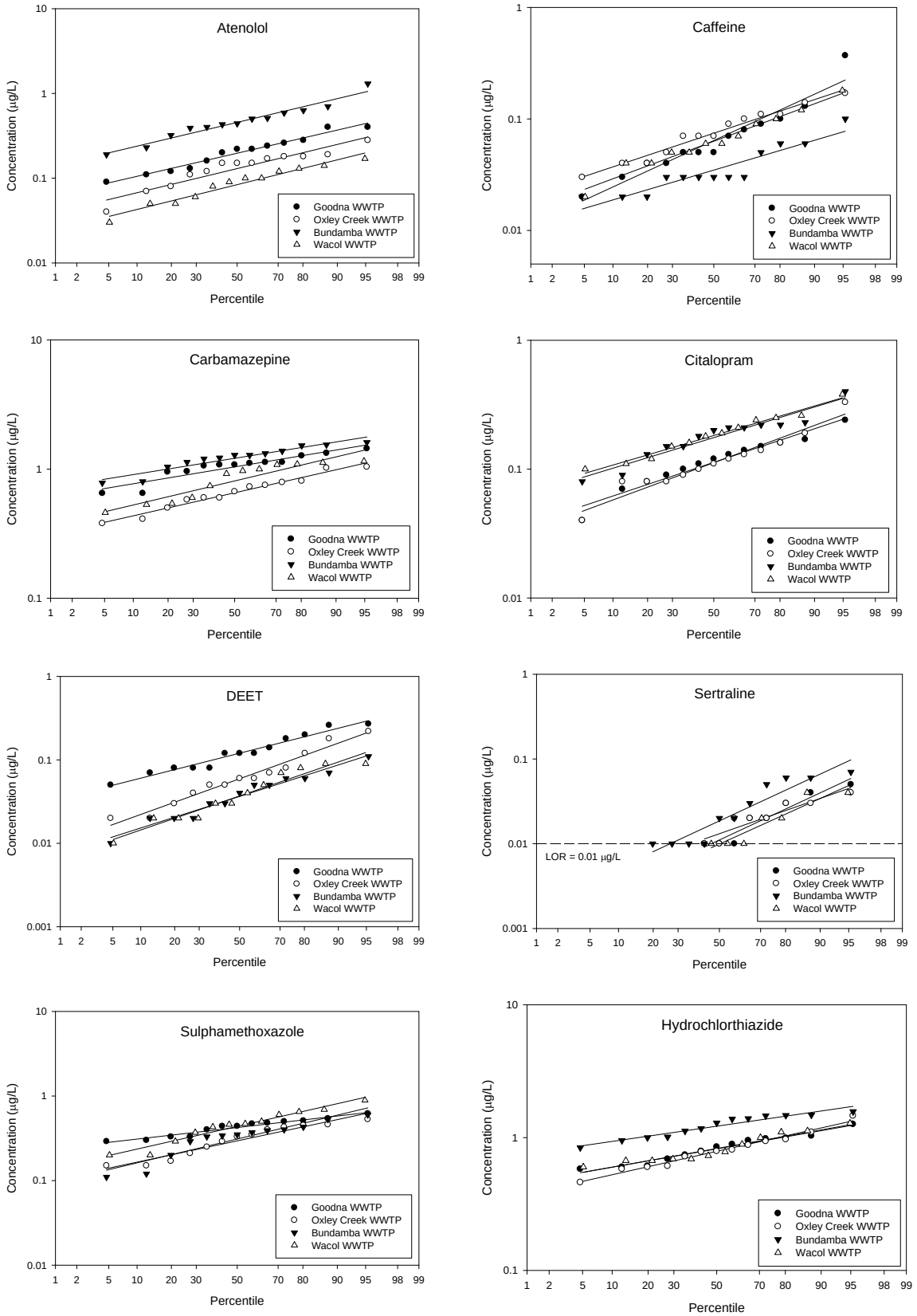


Long-term monitoring data tend not to be so readily available for many trace chemicals. This is partially due to the fact that significant attention to some contaminants, such as pharmaceuticals and personal care products, has only recently emerged.

Where extensive historical data are not available, it may be necessary to undertake more intensive medium or short-term occurrence surveys to ascertain an approximate concentration distribution for contaminants of interest in advanced water treatment plant source waters.

Intensive sampling of effluent from four wastewater treatment plants has been undertaken by the operators of the Bundamba advanced water treatment plant in South East Queensland [280]. Monitoring data for a range of pharmaceuticals and personal care products, over a period of approximately 13 months (July 2008 to August 2009) was supplied for the preparation of Figure 50 [280]. These data include the final effluents of the four wastewater treatment plants (Goodna, Oxley Creek, Bundamba and Wacol) that variably supply feed waters to the Bundamba advanced water treatment plant (see Figure 6). The figures are provided here as an indication of the type of data that may be collected in order to establish lognormal distributions. Monitoring also included a large number of additional pharmaceuticals, which are not shown here.

Figure 50: Lognormal probability plots for selected trace contaminants in four wastewater treatment plants (WWTP), July 08 to August 2009 [280].



7.2 Advanced treatment process performance

In addition to source water quality, it is necessary to characterise the removal of source-water contaminants during unit treatment processes at the advanced water treatment plant. Treatment performance can be characterised by observed performance, challenge testing, or by modelling of fundamental process variables. Using appropriate data for each treatment step can greatly reduce uncertainty in treatment assessment [281].

Intensive sampling of reverse osmosis feeds and reverse osmosis effluents has been undertaken by the operators of the Bundamba advanced water treatment plant in South East Queensland [280]. Monitoring data for a range of bulk parameters and inorganic species, during a period of approximately 14 months (August 2008 to October 2009), were supplied by WaterSecure to for the preparation of Figure 51 and Figure 52 [280]. These figures are provided as an indication of the type of data that may be collected in order to establish lognormal distributions for unit process operations. Monitoring also included a large number of additional trace chemical species, which are not shown here.

The variable reverse osmosis rejection performance that is apparent between the parameters shown in Figure 51 and Figure 52 is consistent with previously reported trends (see Section 5.3). For example, excellent reverse osmosis rejection is observed for many of the anionic and cationic species, while less significant reverse osmosis rejection is observed for ammonia and NDMA. As is consistent with previous reports, rejection of boron at ambient pH appears insignificant. Further treatment (for example, advanced oxidation and chlorination) is required to ensure the guideline targets (indicated by the ‘std’ dotted line) are met for ammonia and NDMA prior to reservoir augmentation.

Figure 51: Concentrations of chemical constituents in reverse osmosis feed and permeate August 2008 to October 2009 (Part 1) [280]

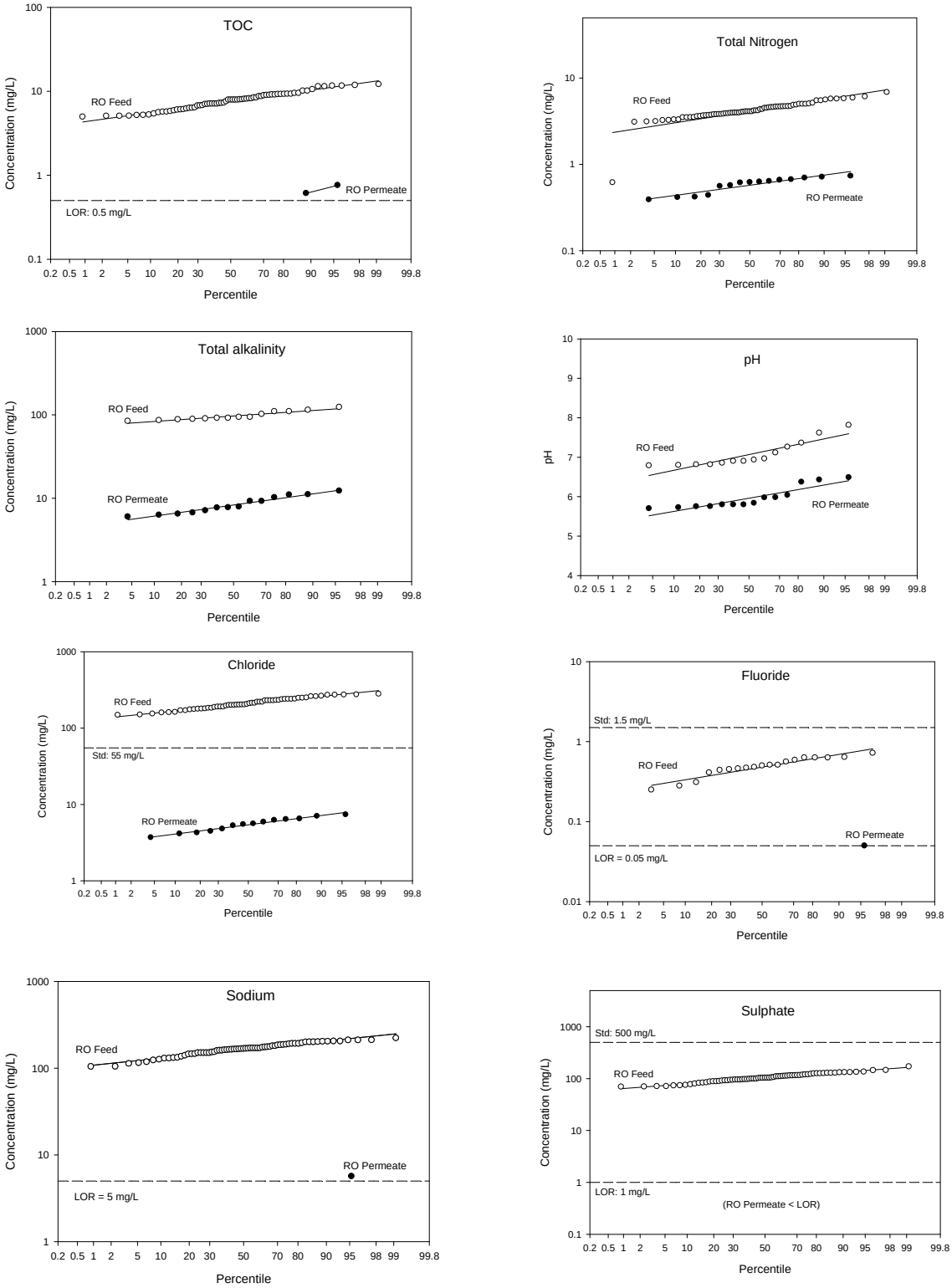
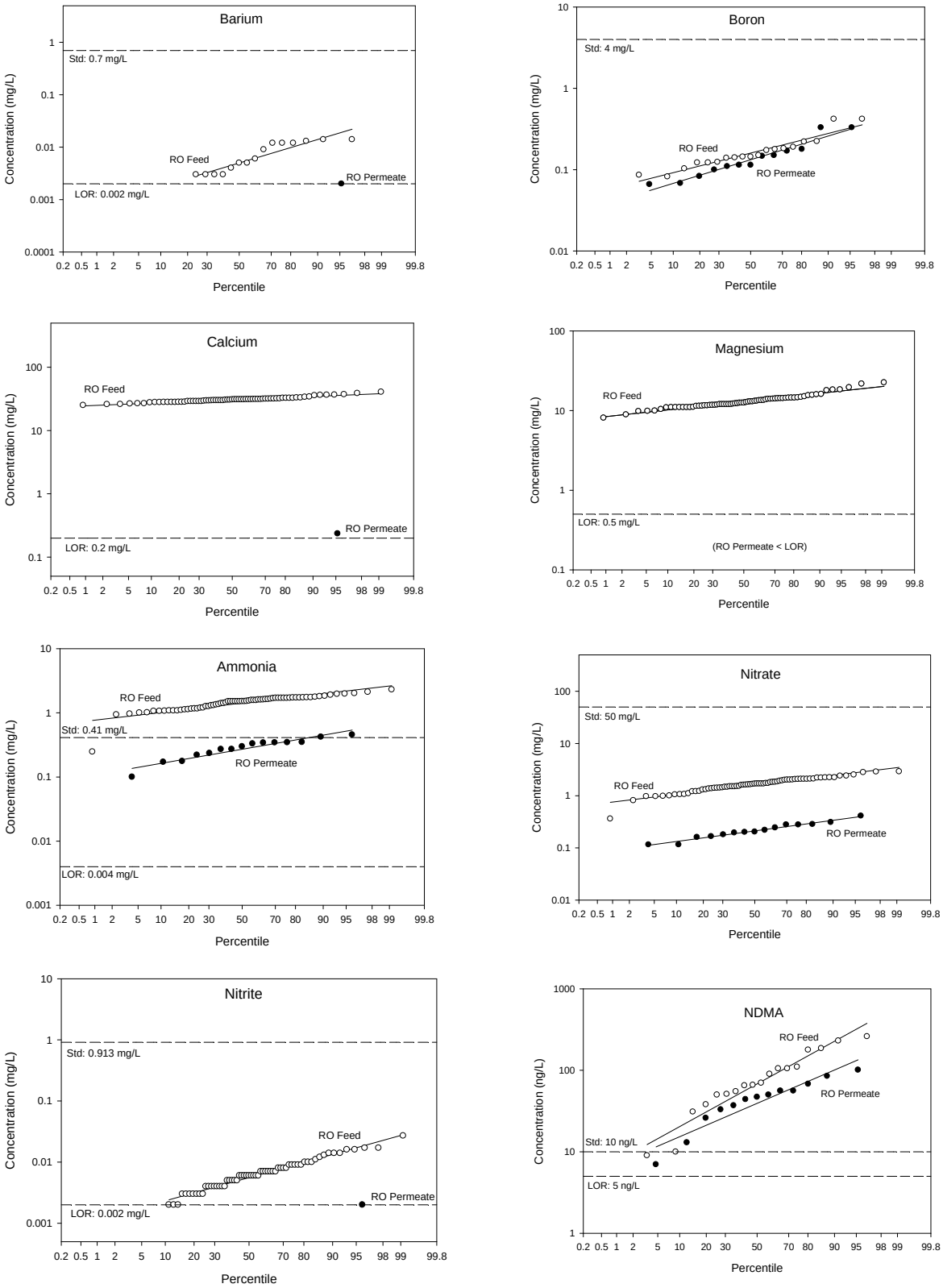


Figure 52: Concentrations of chemical constituents in reverse osmosis feed and permeate August 2008 to October 2009 (Part 2) [280]



7.3 Indicator chemicals and surrogate parameters

An important task in designing a monitoring program for a water treatment system is to determine which parameters should be monitored. One approach is to identify key contaminants of concern from a toxicological point of view. For some specific chemicals, there may be a valid justification for doing this. However, as noted in Chapter 4, this approach can never be sufficiently comprehensive to ensure sufficiently low concentrations of all potential toxic contaminants. Toxicity testing may help to address this limitation, but toxicity also suffers from some significant practical limitations, including the resources and time required to undertake testing, as well as an inability to test the very large number of potentially toxic end-points that are targeted by various chemicals.

An alternative (or additional) approach for chemical monitoring program is to aim to confirm that the water treatment processes are operating correctly and performing sufficiently to produce water of an acceptable quality. This approach implies that there is some known relationship between the observed performance of a water treatment process and the produced water quality. Accordingly, there is a need to validate such assumptions where they are made.

One approach that has recently been validated in concept is the use of indicator compounds and surrogate measures to assess and monitor water treatment process performance [282].

In this context, an *indicator compound* is an individual chemical, occurring at a quantifiable level, which represents certain physicochemical and/or biodegradable characteristics of a larger group of trace constituents. The representative characteristics must be relevant to the transport and fate of the indicator compound, as well as the larger represented group of constituents, providing a conservative assessment of removal.

A *surrogate parameter* is a quantifiable change of a bulk parameter that can serve as a performance measure of individual unit processes or operations regarding their removal of trace compounds.

The ultimate advantage of the ‘indicators and surrogates’ approach is that it requires only a limited set of analytes to be measured in order to assess and monitor treatment processes for an assumed much larger group of chemicals. Thus the tailored employment of appropriate surrogates and indicator compounds within predefined boundary conditions results in a monitoring regime aimed at obtaining information that provide certainty in proper treatment performance at minimal costs.

Physicochemical properties (for example, molecular size, pK_a, log K_{ow}, volatility, and dipole moment) often determine the fate and transport of a compound during various treatment processes such as high-pressure membranes [207]. Thus, the judicious selection of multiple indicators, representing a broad range of properties, enables the assessment to account for compounds that may not be currently identified (‘unknowns’), as well as new compounds synthesised and entering the environment in the future (for example, new pharmaceuticals), provided they fall within the range of the properties covered by the indicators.

The underlying assumption is that absence or removal of an indicator compound during a treatment process would also ensure absence or removal of other compounds with comparable physicochemical properties. The most sensitive compounds to assess the performance of a specific treatment process will be those that are partially removed under normal operating conditions. Thus a system failure will be indicated by poor removal of the

indicator compound while normal operating conditions will be indicated by partial or complete compound removal.

Predetermined changes of surrogate parameters can be used to define and assure normal operating conditions of a treatment process. Proper removal is ensured as long as the treatment process of interest is operating according to its technical specifications. It is therefore necessary to define, for each treatment process, the operating conditions under which proper removal is to be expected [282].

Potential indicator compounds and surrogate parameters have been identified for a range of conventional and advanced water treatment processes [282]. These treatment processes have then been characterised by key removal mechanisms, such as biodegradation (managed aquifer recharge), chemical oxidation (ozonation, advanced oxidation, chlorination and chloramination), photolysis (low pressure UV radiation), adsorption (granular activated carbon treatment), or physical separation (nanofiltration and reverse osmosis). The potential indicator compounds were then grouped into four removal categories:

- Good Removal (>90 per cent)
- Intermediate Removal 1 (90 per cent < x <50 per cent)
- Intermediate Removal 2 (50 per cent < x <25 per cent)
- Poor Removal (<25 per cent).

This classification of indicators into removal categories for individual treatment processes was dependant upon the physicochemical and biodegradable properties of the compounds. Whether the proposed degree of removal is achieved will depend upon the operational conditions of the treatment process (for example, water matrix, oxidant contact time, membrane flux). Therefore, along with this classification, relevant boundary conditions were defined for each type of treatment.

Surrogate parameters are often not strongly correlated with the removal of indicator compounds occurring at concentrations in the order of nanograms per litre [282]. However, partial or complete change of carefully selected surrogate parameter removal can demonstrate the proper performance of a unit operation or treatment train. Some surrogate parameters are also sufficiently sensitive to indicate the beginnings of performance deficiencies, which may or may not be resulting in a diminished removal of contaminants of toxicological concern. Thus to fully assess the performance of unit operations, a combination of appropriate surrogate parameters and indicator compounds should be used.

Performance assessment of individual unit processes comprising an overall treatment train are distinguished into two phases: *validation monitoring* during piloting or commissioning; and compliance monitoring during full-scale operation (defined as *operational and verification monitoring*). The individual steps followed in tailoring such a monitoring program are outlined in Table 19.

Table 19: Application of the surrogate/indicator framework to an overall treatment train [282]

	Surrogate parameters	*Indicator compounds*
Validation Monitoring: Piloting or commissioning		
Step 1	Define and verify operational boundary conditions for each unit process comprising the overall treatment train after operating the system assuring steady-state conditions. Do operational boundary conditions meet design criteria within an acceptable range? If yes, proceed to step 2. If not, determine cause for deviation.	Baseline Monitoring: Conduct occurrence study to confirm presence of viable indicator compounds in the feedwater of each unit process.
Step 2	Quantify surrogate, e.g. conductivity, rejection of overall system. Is conductivity rejection within previously observed range and does it meet performance specification of manufacturer? If yes, proceed to step 3. If not, determine cause for deviation, for example by quantifying conductivity rejection of individual vessels.	Identify 5–10 suitable indicator compounds for spiking study (challenge test).
Step 3	Validation Monitoring: Quantify removal differential of viable surrogate parameter: $\Delta X_i = (X_{i,in}-X_{i,out})/X_{i,in}$	Validation Monitoring: Conduct spiking study with select indicator compounds (5–10) to determine the removal differentials under pre-determined operating conditions: $\Delta Y_i = (Y_{i,in}-Y_{i,out})/Y_{i,in}$
Step 4	Select viable surrogate and operational parameters for each unit process	Select 3-6 indicator compounds from categories classified as 'Good removal'
Compliance Monitoring: Full-scale operation		
Step 5	Confirm operational boundary conditions of full-scale operation and removal differential ΔX_i for selected surrogate and operational parameters	
Step 6	Operational Monitoring: Monitor differential ΔX_i of select surrogate and operational parameters for each unit process or/and the overall treatment train on a regular basis (daily, weekly)	Verification Monitoring: Monitor differential ΔY_i of selected indicator compounds for each unit process and the overall treatment train regularly, but less frequently (semi-annually, annually).

Piloting of a treatment process or treatment train allows both validation that operational parameters are within technical specifications and quantification of the removal (differential) of surrogate parameters (X_i) within these conditions ($\Delta X_i = (X_{i,in}-X_{i,out})/X_{i,in}$). In parallel, an occurrence study can be undertaken to confirm the presence of viable indicator compounds in source waters to the advanced water treatment plant.

During piloting of the treatment process, challenge tests may be conducted with selected indicator compounds (Y_i) spiked at elevated concentrations to determine their removal differential ΔY_i under normal operating conditions.

The meaningful use of all of these measures requires that suitable process boundary conditions regarding plant design and operation are maintained. For example, for a reverse osmosis process, both at pilot- and full-scale, these boundary conditions might be defined as a source water quality equivalent to UF-treated secondary effluent, pH adjusted to 6.3–6.7, addition of scale inhibitors, and operation at a recovery of 80 to 85 per cent, and a permeate flux of approximately 20 $L.m^{-2}.h^{-1}$.

Sensitive surrogate parameters identified for various treatment types are presented in Table 20 [282].

Table 20: Sensitive surrogate parameters identified for different treatment categories [282]

Mechanism	*Treatment process*	*Surrogate for performance assessment*
Biodegradation	Managed aquifer recharge	BDOC; ΔDOC; ΔUVA; ΔTOX; Δammonia; Δnitrate
	Riverbank filtration	SFLUOR; SUVA; 3-D fluorescence
	Membrane bioreactor	ΔTOC; ΔUVA
Chemical oxidation	Ozone	ΔUVA; Δcolour; 3-D fluorescence; Δformate; Δassimilable organic carbon (ΔAOC); integral contact time (CT)
	AOP (ozone/H_2O_2; ozone/UV; UV/H_2O_2)	ΔUVA; Δcolour; 3-D fluorescence; Δformate; Δoxalate; Δaldehyde; ΔAOC;
	Chlorination	Integral contact time (CT)
	Chloramination	Not a viable process to remove wastewater-derived organic contaminants
UV disinfection	Low-pressure UV	Not a viable process to remove wastewater-derived organic contaminants
Adsorption	PAC	ΔUVA; 3-D fluorescence
	GAC	ΔUVA; 3-D fluorescence; ΔTOC
Physical separation	Reverse osmosis	Δconductivity; Δboron
	Nanofiltration	Δcalcium; Δmagnesium

AOP = Advanced oxidation process; BDOC = biodegradable dissolved organic carbon; TOX = total organic halide.

Indicator chemicals characterised for managed aquifer recharge systems are presented in Table 21. Most managed aquifer recharge operations are characterised by percolation of water through a vadose zone followed by additional attenuation processes occurring in the saturated zone of the underlying aquifer. The primary removal mechanisms during managed aquifer recharge for target contaminants include adsorption to soil grains or soil organic matter, as well as biodegradation under oxic and anoxic redox conditions (see Section 5.2).

The operational boundary conditions for the categorisation presented in Table 21 are a TOC concentration of less than 10 mg/L in the recycled water prior to spreading, a travel time in the subsurface of approximately four weeks, redox regimens that transition from oxic to anoxic between the point of spreading and abstraction, low organic carbon soil, and no dilution with native groundwater during the four-week travel time.

Table 21: Treatment removal categories for indicator compounds of managed aquifer recharge systems [282]

Good Removal (>90%):
Acetaminophen, Acetyl cedrene[b], Atenolol[c], Atorvastatin (*o*-hydroxy)[b], Atorvastatin (*p*-hydroxy)[b], Atorvastatin[b], Benzyl acetate[c], Benzyl salicylate[d], Bisphenol A, Bucinal[d], Butylated hydroxyanisole, Caffeine, DEET, Dichlorprop, Diclofenac, EDTA, Erythromycin–H_2O, Estriol, Estrone, Fluoxetine, Galaxolide[b], Gemfibrozil, Hexyl salicylate[d], Hexylcinnamaldehyde[b], Hydrocodone, Ibuprofen, Indolebutyric acid[c], Iopromide, Isobornyl acetate[b], Isobutylparaben[d], Ketoprofen, Mecoprop, Methyl dihydrojasmonate[c], Methyl ionine[d], Methyl salicylate[c], Metoprolol, Musk ketone[b], Musk xylene[b], Naproxen, NDMA, Nonylphenol, OTNE[b], Phenylphenol[d], Propranolol, Propylparaben[c], Salicylic acid, Simvastatin hydroxy acid[d], Sulfamethoxazole, Terpineol[b], Tonalide[b], Triclobarban[b], Triclosan, Trimethoprim
Intermediate Removal (50–90%):
Meprobamate
Intermediate Removal (25–50%):
Chloroform
Poor Removal (< 25%):
Carbamazepine, Dilantin, Primidone, TCEP, TCPP, TDCPP

[b] Removal estimate is based upon log D being > 3.0 (pH 7); [c]Removal is estimated as fast biodegradation on the basis of a BioWin prediction; [d]Removal estimate is based upon log D being > 3.0 (pH 7) and upon fast biodegradation on the basis of a BioWin prediction.

Indicator chemicals characterised for membrane bioreactor treatment are presented in Table 22. Membrane bioreactor treatment processes are characterised by the optimisation of aerobic (and sometimes anaerobic) biodegradation conditions, with a high biomass concentration and abundant supply of oxygen and nutrients. The primary removal mechanisms during membrane bioreactor treatment for target contaminants include adsorption to biomass and biodegradation under oxic or anoxic redox conditions. The operational boundary conditions of the categorisation presented in Table 22 include a primary effluent of TOC concentration 40 to 60 mg/L; a sludge retention time of 15 days, and a mixed liquor suspended solids of around 3500 mg/L.

Table 22: Removal of indicator compounds during membrane bioreactor treatment [282]

Good Removal (>90%):
Acetaminophen, Benzophenone, Bisphenol A, Butylated hydroxyanisole, Caffeine, Enalapril, Erythromycin–H_2O, Gemfibrozil, Ibuprofen, Indolebutyric acid, Isobutylparaben, Mecoprop, Menthol, Naproxen, Norfluoxetine, Oxybenzone, Phenacetine, Phenoxyethanol, Phenylphenol (o-), Propylparaben, Salicylic acid, Simvastatin, Triclosan, Vanillin
Intermediate Removal (50–90%):
Atenolol, Atorvastatin, Atorvastatin (o-hydroxy), Atorvastatin (p-hydroxy), DEET, NDMA, Simvastatin hydroxy acid, Trimethoprim
Intermediate Removal (25–50%):
EDTA (total), Fluoxetine, Sulfamethoxazole, TCEP, TCPP
Poor Removal (<25%):
Carbamazepine, Dilantin, Meprobamate

Indicator chemicals characterised for ozone treatment are presented in Table 23. The predominant removal mechanism is chemical oxidation. Ozone reacts with organic compounds through either the direct reaction with molecular ozone or through the formation of free radicals, including the hydroxyl radical (HO•). The categorisation presented in Table 23 assumed the operational boundary conditions of a tertiary treated wastewater with TOC less than 10 mg/L and an ozone exposure greater than 26 mg min/L. This represents an upper

margin of typical recycled water ozonation. Thus, the reported actual efficiencies may be expected to be lower under lower dose conditions.

Table 23: Treatment removal categories for indicator compounds of systems using ozone [282]

Good Removal (>90%):
Acetaminophen, Acetyl cedrene[h,i], Atenolol, Atorvastatin, Atorvastatin (*o*-hydroxy)[d], Atorvastatin (*p*-hydroxy)[d], Benzyl acetate[f], Benzyl salicylate[b], Bisphenol A, Bucinal[f], Butylated hydroxyanisole, Caffeine, Carbamazepine, Ciprofloxacin[c,j], DEET, Dichlorprop[e], Diclofenac, Dilantin, EDTA, Erythromycin–H_2O, Estriol, Estrone, Fluoxetine, Galaxolide, Gemfibrozil, Hexyl salicylate[b], Hexylcinnamaldehyde[f], Hydrocodone, Ibuprofen, Isobutylparaben, Ketoprofen, Mecoprop[e], Methyl ionine[h,i], Methyl salicylate[b], Metoprolol, Naproxen, Nonylphenol, Norfluoxetine[e,f], Ofloxacin[j], OTNE[h,], Phenylphenol[b], Primidone, Propranolol, Propylparaben, Salicylic acid[b], Simvastatin hydroxy acid[h,i], Sulfamethoxazole, Terpineol[h,i], Tonalide, Triclocarban, Triclosan, Trimethoprim
Intermediate Removal (50–90%):
Iopromide, Indolebutyric acid, Isobornyl acetate[h,i], Meprobamate, Methyl dihydrojasmonate[h,i]
Intermediate Removal (25–50%):
NDMA, Musk ketone, Musk xylene
Poor Removal (<25%):
Chloroform, TCEP, TCPP[g], TDCPP[g]

[b] Hydroxy aromatic (activating); [c]Amino aromatic (activating); [d]Acylamino aromatic (activating); [e]Alkoxy aromatic (activating); [f]Alkyl aromatic (activating); [g]Aliphatic (halogens); [h]Aliphatic ketone/hydroxyl/ester; [i]Cycloalkane/cycloalkene; [j]Aromatic with heterocyclic ring (nitrogen containing).

Indicator chemicals characterised for advanced oxidation processes are presented in Table 24. Advanced oxidation processes are used to promote the formation of hydroxyl radicals (HO•) for the non-selective degradation of organic compounds (see Section 5.5). Examples of these processes include ozone/hydrogen peroxide, UV/hydrogen peroxide, and UV/ozone. The categories presented in Table 24 were derived specifically from the investigation of ozone/hydrogen peroxide systems; however, similar removal efficiencies have been reported for UV/hydrogen peroxide advanced oxidation processes [235; 283; 284]. The operational boundary conditions of Table 24 include reverse osmosis-treated feedwater; 7 mg/L of ozone, 3.5 mg/L of H_2O_2; and a two-minute contact time.

Table 24: Treatment removal categories for indicator compounds of advanced oxidation processes [282]

Good Removal (>90%):
Acetaminophen, Acetyl cedrene, Atenolol, Atorvastatin, Atorvastatin (*o*-hydroxy), Atorvastatin (*p*-hydroxy), Benzyl acetate, Benzyl salicylate, Bucinal, Butylated hydroxyanisole, Caffeine, Carbamazepine, Ciprofloxacin, DEET, Dichlorprop, Diclofenac, Dilantin, EDTA, Erythromycin–H_2O, Estriol, Estrone, Fluoxetine, Galaxolide, Gemfibrozil, Hexyl salicylate, Hexylcinnamaldehyde, Hydrocodone, Ibuprofen , Indolebutyric acid , Isobornyl acetate , Isobutylparaben , Ketoprofen , Mecoprop , Meprobamate , Methyl dihydrojasmonate , Methyl ionine , Methyl salicylate , Metoprolol , Naproxen, Nonylphenol, Norfluoxetine, Ofloxacin, OTNE, Phenylphenol, Primidone, Propranolol, Propylparaben, Salicylic acid, Simvastatin hydroxy acid, Sulfamethoxazole, Terpineol, Tonalide, Triclocarban, Triclosan, Trimethoprim
Intermediate Removal (50–90%):
NDMA, Iopromide
Intermediate Removal (25–50%):
Musk ketone, Musk xylene
Poor Removal (<25%):
Chloroform, TCEP, TCPP, TDCPP

Indicator chemicals characterised for chloramination processes are presented in Table 25. Chloramines are relatively week oxidants compared to ozone and advanced oxidation processes. Thus the expected removal efficiency of chloramines for organic indicator compounds is relatively poor, and most identified indicator compounds are expected to exhibit removal of less than 25 per cent. Accordingly, chloramination is not considered to be a significant barrier in removing wastewater-derived trace organic compounds in water recycling schemes.

The operational boundary conditions for Table 25 include secondary/tertiary-treated wastewater; 0.75–1 hour of contact time; and 2.5–4.5 mg/L of residual chloramine.

Table 25 Removal of indicator compounds during chloramination operations [282]

Good Removal (>90%):
Butylated hydroxyanisole
Intermediate Removal (50–90%):
Vanillin, Triclosan
Intermediate Removal (25–50%):
Bisphenol A
Poor Removal (<25%):
Benzophenone, Caffeine, DEET, Diclofenac, EDTA, Gemfibrozil, Ibuprofen, Indolebutyric acid, Naproxen, NDMA, Primidone, Salicylic acid, TCEP, TCPP, TDCPP, Triclocarban

Indicator chemicals characterised for chlorination processes are presented in Table 26. Oxidation and substitution are the main reaction mechanisms observed during chlorination of trace organic compounds. The operational boundary conditions for the categorisation presented in Table 26 include 1 mg of Cl per mg of C; 24-hour contact time; and pH 8.

Table 26: Treatment removal categories for indicator compounds of chlorine systems [282]

Good Removal (>90%):
Acetaminophen, Atorvastatin (*o*-hydroxy)[d], Atorvastatin (*p*-hydroxy)[d], Atorvastatin[d], Benzyl salicylate[b], Bisphenol A, Butylated hydroxyanisole[b], Ciprofloxacin, Diclofenac, Erythromycin–H_2O, Estriol, Estrone, Hexyl salicylate[b], Hydrocodone, Isobutylparaben[b], Methyl salicylate[b], Naproxen, Nonylphenol, Phenylphenol[b], Propranolol[e,k], Propylparaben[b], Salicylic acid[b], Sulfamethoxazole, Triclocarban[d], Triclosan, Trimethoprim
Intermediate Removal (50–90%):
Gemfibrozil, Musk ketone
Intermediate Removal (25–50%):
Galaxolide, Ibuprofen, Tonalide[f,k]
Poor Removal (<25%):
Acetyl cedrene[h,i], Atenolol, Benzyl acetate[f], Bucinal[f], Caffeine, Carbamazepine, Chloroform, DEET, Dichlorprop[e], Dilantin, EDTA, Fluoxetine, Hexylcinnamaldehyde[f], Indolebutyric acid[j], Iopromide, Isobornyl acetate[h,i], Ketoprofen, Mecoprop[e], Meprobamate, Methyl dihydrojasmonate[h,i], Methyl ionine[h,i], Metoprolol, Musk xylene, NDMA, Norfluoxetine, Ofloxacin, OTNE[h,i], Primidone[j], Simvastatin hydroxy acid[h,i], TCEP, TCPP[g], TDCPP[g], Terpineol[h,i]

[b] Hydroxy aromatic (activating); [c]Amino aromatic (activating); [d]Acylamino aromatic (activating); [e]Alkoxy aromatic (activating); [f]Alkyl aromatic (activating); [g]Aliphatic (halogens); [h]Aliphatic ketone/hydroxyl/ester; [i]Cycloalkane/cycloalkene; [j]Aromatic with heterocyclic ring (nitrogen containing); [k]Activating group in meta position.

Indicator chemicals characterised for ultraviolet (UV) disinfection processes are presented in Table 27. The operational boundary conditions for the categorisation presented in Table 27 include tertiary-treated wastewater; low-pressure UV at 30–40 millijoules per square centimetre.

Table 27: Removal of indicator compounds during full-scale UV operation [282]

Good Removal (>90%):
Intermediate Removal (50–90%):
Diclofenac
Intermediate Removal (25–50%):
Carbamazepine, Fluoxetine, Sulfamethoxazole
Poor Removal (< 25%):
17β-Estradiol, Bisphenol A, Butylated hydroxyanisole, Caffeine, DEET, Dichloroprop, Dilantin, EDTA (total), Erythromycin–H_2O, Estrone, Gemfibrozil, Hydrocodone, Ibuprofen, Indolebutyric acid, Mecoprop, Meprobamate, Naproxen, NDMA, Salicylic acid, TCEP, TCPP, TDCPP, Triclosan, Trimethoprim, Vanillin

Indicator chemicals characterised for PAC systems are presented in Table 28. The operational boundary conditions for the categorisation presented in Table 28 include feedwater quality DOC of less than 4 mg/L; 5 mg/L of PAC (Calgon WPM and Anticarb 800); four hour CT.

Table 28: Treatment removal categories of indicator compounds of PAC systems [282]

Good Removal (> 90%):
Acetyl cedrene[c], Benzyl salicylate[c], Bucinal[c], Fluoxetine[b], Hexyl salicylate[c], Hexylcinnamaldehyde[c], Methyl ionine[c], Nonylphenol[c], Norfluoxetine, OTNE[c], Simvastatin hydroxy acid[c], Tonalide[c], Triclocarban[c], Triclosan[b]
Intermediate Removal (50–90%):
Acetaminophen[b], Benzyl acetate[d], Bisphenol A[d], Butylated hydroxyanisole[d], Caffeine[b], Carbamazepine[b], Chloroform[d], DEET[b], Dilantin[b], Erythromycin–H_2O[b], Estriol[b], Estrone[b], Galaxolide[b], Hydrocodone[b], Isobornyl acetate[d], Isobutylparaben[d], Methyl dihydrojasmonate[d], Methyl salicylate[d], Musk ketone[b], Musk xylene[d], Naproxen[b], Phenylphenol[d], Propranolol[f], Propylparaben[d], TCEP[b], TCPP[d], TDCPP[d], Terpineol[d], Trimethoprim[b]
Intermediate Removal (25–50%):
Atenolol[g], Atorvastatin (*o*-hydroxy)[h], Atorvastatin (*p*-hydroxy)[h], Atorvastatin[h], Diclofenac[b], Gemfibrozil[b], Indolebutyric acid[h], Iopromide[b], Ketoprofen[h], Meprobamate[b], Metoprolol[g], NDMA[e], Primidone[e], Sulfamethoxazole[b]
Poor Removal (< 25%):
Ciprofloxacin[i], Dichlorprop[i], EDTA[i], Ibuprofen[b], Mecoprop[i], Ofloxacin[i], Salicylic acid[i]

[b] [224]; [c]Removal estimate is based upon log D > 4 (pH 7); uncharged; [d]Removal estimate is based upon log D = 0–4 (pH 7); uncharged; [e]Removal estimate is based upon log D < 0 (pH 7); uncharged; [f]Removal estimate is based upon log D = 0–1.5 (pH 7); protonated base; [g]Removal estimate is based upon log D < 0 (pH 7); protonated base; [h]Removal estimate is based upon log D = 0–2.5 (pH 7); deprotonated acid; [i]Removal estimate is based upon log D < 0 (pH 7); deprotonated acid.

Indicator chemicals characterised for GAC processes are presented in Table 29. The operational boundary conditions for the categorisation presented in Table 29 include a DOC concentration of less than 3 mg/L; GAC Norit HD4000 (at bed volume (BV) = 55,000) and Norit Superdarco (at BV = 90,000); and an empty bed CT (EBCT) = 7.5 minutes.

Table 29: Treatment removal categories of indicator compounds of GAC systems [282]

Good Removal (>90%):
Acetyl cedrene[c], Benzyl salicylate[c], Bisphenol A[c], Bucinal[c], Butylated hydroxyanisole[c], Estrone[b], Fluoxetine[b], Galaxolide[c], Hexyl salicylate[c], Hexylcinnamaldehyde[c], Isobornyl acetate[c], Isobutylparaben[c], Methyl ionine[c], Musk ketone[c], Musk xylene[c], Nonylphenol[c], Norfluoxetine, OTNE[c], Simvastatin hydroxy acid[c], Terpineol[c], Tonalide[c], Triclocarban[c], Triclosan[b]
Intermediate Removal (50–90%):
Acetaminophen[b], Caffeine[b], Carbamazepine[b], Erythromycin–H_2O[b], Estriol[b], Hydrocodone[b], Methyl dihydrojasmonate[d], Methyl salicylate[d], Naproxen[b], Phenylphenol[d], Propranolol[g], Propylparaben[d], Trimethoprim[b]
Intermediate Removal (25–50%):
Atenolol[h], Atorvastatin (*o*-hydroxy)[i], Atorvastatin (*p*-hydroxy)[i], Atorvastatin[i], Benzyl acetate[e], Chloroform[e], DEET[b], Diclofenac[b], Dilantin[b], Gemfibrozil[b], Ibuprofen[b], Indolebutyric acid[i], Ketoprofen[i], Metoprolol[h], TCPP[e], TDCPP[e]
Poor Removal (< 25%):
Ciprofloxacin[f], Dichlorprop[f], EDTA[f], Iopromide[b], Mecoprop[f], Meprobamate[b], NDMA[f], Ofloxacin[f], Primidone[f], Salicylic acid[f], Sulfamethoxazole[b], TCEP[b]

[b][285]; [c]Removal estimate is based upon log D > 3 (pH 7); uncharged; [d]Removal estimate is based upon log D = 2–3 (pH 7); uncharged.; [e]Removal estimate is based upon log D = 0–2 (pH 7); uncharged; [f]Removal estimate is based upon log D < 0 (pH 7); uncharged or deprotonated acid.; [g]Removal estimate is based upon log D = 0–1.5 (pH 7); protonated base; [h]Removal estimate is based upon log D < 0 (pH 7); protonated base; [i] Removal estimate is based upon log D = 0–2.5 (pH 7); deprotonated acid.

Indicator chemicals characterised for reverse osmosis processes are presented in Table 30. The vast majority of indicator chemicals are efficiently rejected by reverse osmosis membranes exceeding 90 per cent removal [282; 285]. Compounds that are non-ionic (neutral) and small can exhibit a partial removal, as observed for nitrosamines such as NDMA

or 1,4-dioxane [207]. Indicator chemicals that are small but exhibit hydrophobic properties can adsorb to the polymeric structure of thin-film composite membranes and partition through the active layer of the membrane into the permeate. For example, one compound meeting these properties is chloroform, which usually exhibits only moderate removal during reverse osmosis treatment [286]. The highly efficient rejection of wastewater-derived contaminants by reverse osmosis membranes limits the number of available indicator compounds representing intermediate removal to a few. None of the indicator compounds considered in this study exhibited poor removal (< 25 per cent).

The operational boundary conditions for the categorisation presented in Table 30 include recovery: 80 per cent; permeate flux: approximately 20 litres per square metre per hour (LMH); pH = 6.5.

Table 30: Treatment removal categories for indicator compounds of reverse osmosis systems [282]

Good Removal (> 90%):
Acetaminophen, Acetyl cedrene[b], Atenolol, Atorvastatin, Atorvastatin (*o*-hydroxy), Atorvastatin (*p*-hydroxy), Benzyl acetate[b], Benzyl salicylate[b], Bisphenol A, Bucinal[b], Butylated hydroxyanisole[b], Caffeine, Carbamazepine, Ciprofloxacin[b], DEET, Dichlorprop, Diclofenac, Dilantin, EDTA, Erythromycin–H_2O, Estriol, Estrone, Fluoxetine, Galaxolide, Gemfibrozil, Hexyl salicylate[b], Hexylcinnam-aldehyde[b], Hydrocodone, Ibuprofen, Indolebutyric acid[b], Iopromide, Isobornyl acetate[b], Isobutylparaben[b], Ketoprofen, Mecoprop, Meprobamate, Methyl dihydrojasmonate[b], Methyl ionine[b], Methyl salicylate[b], Metoprolol, Musk ketone, Musk xylene[b], Naproxen, Nonylphenol, Norfluoxetine, OTNE, Phenylphenol[b], Primidone, Propranolol, Propylparaben[b], Salicylic acid, Simvastatin hydroxy acid, Sulfamethoxazole, TCEP, TCPP, TDCPP, Terpineol[b], Tonalide[b], Triclocarban[b], Triclosan, Trimethoprim
Intermediate Removal (50–90%):
Intermediate Removal (25–50%):
Chloroform, NDMA
Poor Removal (< 25%):

[b]Removal estimate is based upon molecular weight being > 150 grams per mole.

Indicator chemicals characterised for nanofiltration processes are presented in Table 31. The operational boundary conditions for the categorisation presented in Table 31 include an NF-4040 membrane; recovery: 85%; permeate flux: approximately 20 LMH; pH 6.5

Table 31: Treatment removal categories of indicator compounds during nanofiltration operation [282]

Good Removal (> 90%):   Atrazine, 17β-Estradiol, Carbamazepine, Clofibric acid, DEET, Dichlorprop, Diclofenac, Dilantin, Erythromycin–H_2O, Estrone, Fenofibrate, Gemfibrozil, Hydrocodone, Ibuprofen, Ketoprofen, Mecoprop, Meprobamate, Naproxen, Primidone, Salicylic acid, Sulfamethoxazole, TCEP, TCPP, TDCPP, Trimethoprim
Intermediate Removal (50–90%):   Bisphenol A, Caffeine
Intermediate Removal (25–50%):   Phenacetine
Poor Removal (< 25%):   Chloroform, Acetaminophen

7.4 Challenge testing

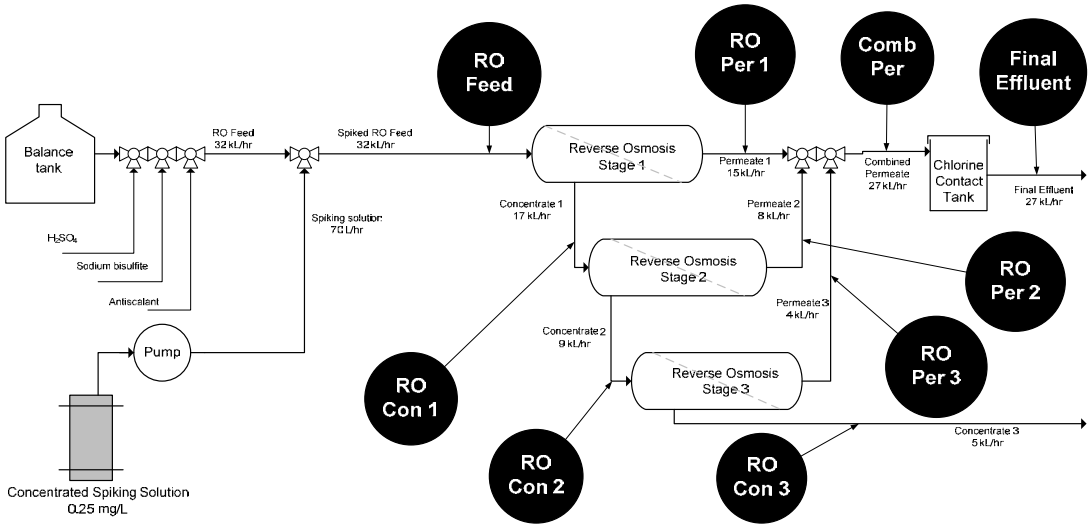
In cases where ambient concentrations of suitable indicator compounds are not reliably sufficient to confirm effective removal, challenge testing can be a useful technique for characterising performance.

The objective of challenge testing is to validate the performance of a unit treatment operation for removing trace organic constituents. The example described in this section refers primarily to challenge testing of a reverse osmosis process; however, the concept can equally well be applied other processes such as advanced oxidation of activated carbon adsorption.

Typically, the test requires elevating the concentration for the select target compounds in the reverse osmosis feed to levels approximately two orders of magnitude above the available analytical detection limits for a period of approximately 90 minutes. During this time, samples of the elevated feed water after the high-pressure pump, permeates and concentrates of each stage, and the combined permeate are collected. Two sets of samples should be collected for analysis after 60 and 90 minutes from initiating the spike. This is to confirm that concentration-dependant removal processes such adsorption to the reverse osmosis membrane have reached an equilibrium.

As a useful protocol, a one litre stock solution is prepared containing 30 mg/L of each of the selected indicator compounds in water. The one litre stock solution is then diluted into a 120-litre plastic drum to give a final challenge test solution concentration of approximately 0.25 mg/L. This solution is then pumped into the reverse osmosis feed line at a flow rate of approximately 70 litres per hour as depicted in Figure 53. These figures relate to a small advanced water treatment plant with a reverse osmosis feed flow rate of 32 kilolitres per hour. Appropriate concentrations and pump flow rates should be determined for individual specific circumstances.

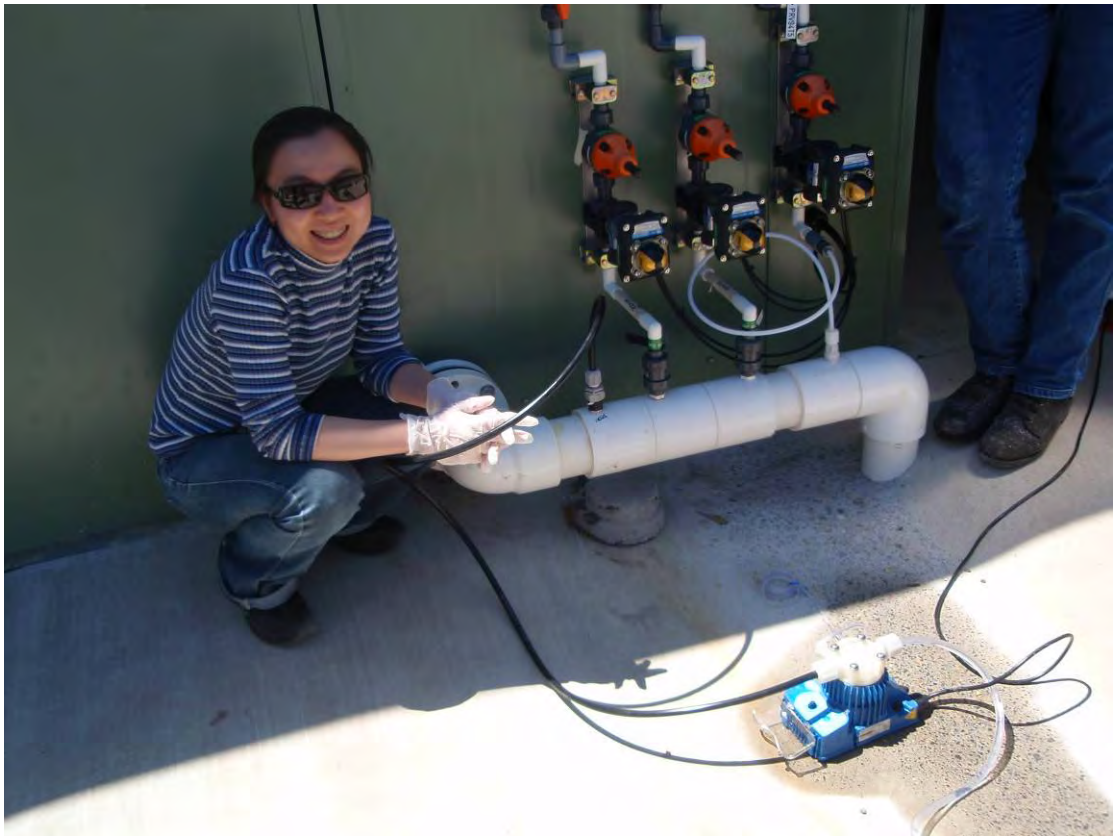
Figure 53 Illustrative challenge testing protocol



RO = reverse osmosis

Prior to and during the challenge tests, online pH, temperature, permeate flux, recovery and conductivity measurements are recorded. The challenge test is executed only after confirming that the system is achieving an expected conductivity rejection range and is operating within the identified operational boundary conditions (for example, recovery: approximately 80 per cent; permeate flux: approximately 20 LMH; pH 6.5).

Figure 54: Point of infusion of challenge testing solution into the reverse osmosis feed line



For each indicator compound, rejection is calculated and can be compared to the removal categories reported for indicator compounds for reverse osmosis systems (see Section 7.3).

Observed removal percentage similar or larger than the expected removal percentage indicates that proper performance of the reverse osmosis system may be assumed.

An example of a reverse osmosis challenge testing result is presented for three N-Nitrosamine compounds, NDMA (Figure 55), NDEA (Figure 56) and NDPA (Figure 57). These figures present the elevated concentrations from the nine sampling locations identified in Figure 53. Three samples were collected at 60 minutes after initiating the spike and another three at 90 minutes after initiating the spike.

In these experiments, overall removals may be estimated by subtracting the mean combined permeate concentration from the mean feed concentration.

A more detailed investigation of the removal pattern may be achieved by fitting PDFs to the concentration data and using these to derive PDFs for the removal efficiency. Probabilistic techniques such as those described in Chapter 8 are generally required. The outcomes of such a process are presented in for NDMA, NDEA and NDPA in Section 8.5.1.

Figure 55: Lognormal probability plot for NDMA in reverse osmosis (RO) challenge testing experiment

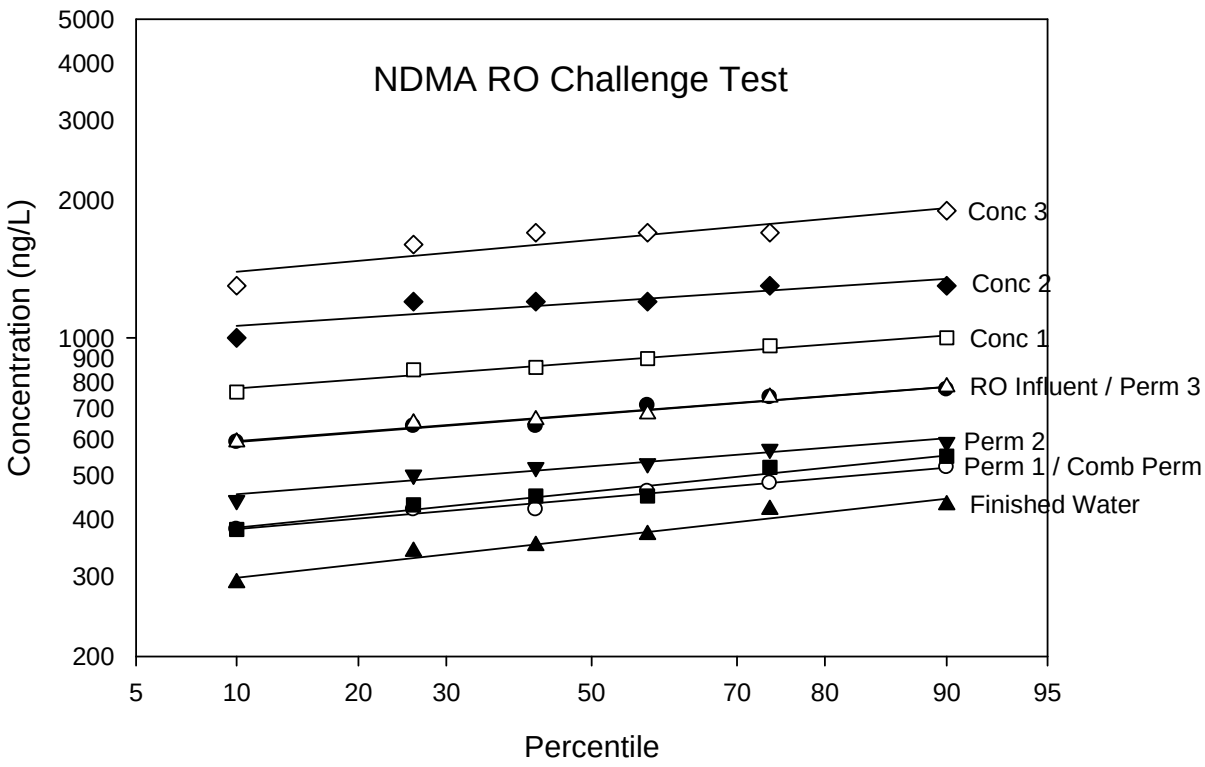


Figure 56: Lognormal probability plot for NDEA in reverse osmosis (RO) challenge testing experiment

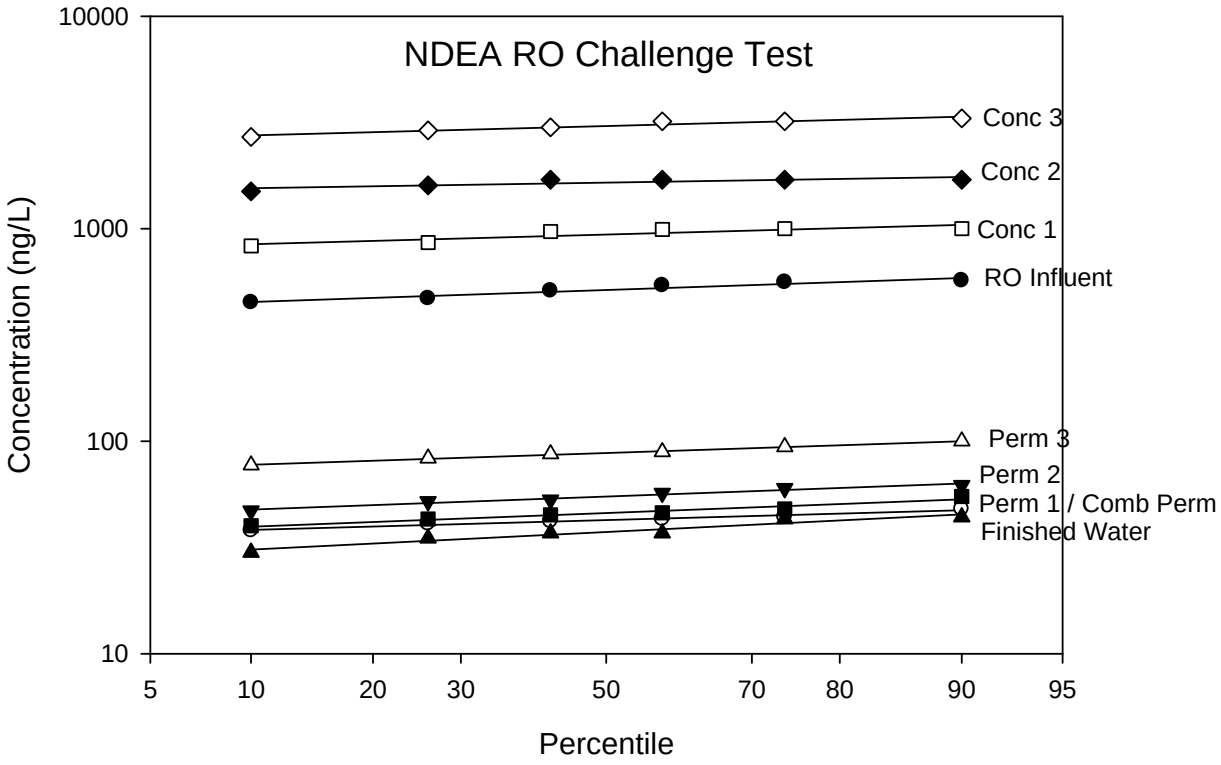
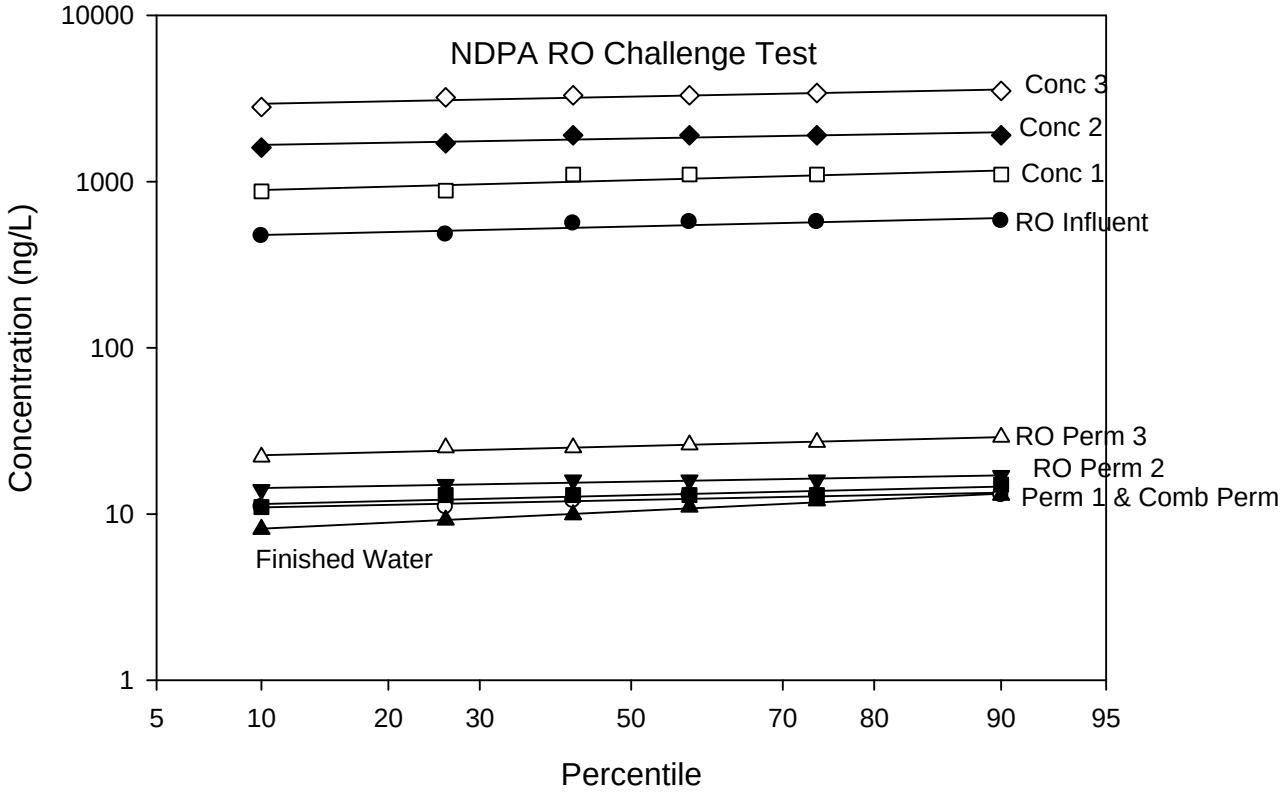


Figure 57: Lognormal probability plot for NDPA in reverse osmosis (RO) challenge testing experiment



8. Probabilistic Assessment

Computing sums, multiplications and other transformations on multiple PDFs is a mathematically challenging task that is, in some cases, impossible. For this, probabilistic techniques can provide a powerful alternative approach. Probabilistic techniques have been used for many decades for such diverse applications as nuclear physics and future stock option valuations [287]. Monte Carlo simulation is currently the most widely used method for probabilistic health risk assessment [288; 289].

As a result of the large number of stochastic variables involved, chemical exposure assessment is particularly suited to probabilistic analysis and a diverse range of applications have been reported during the past two decades [288; 290].

Conventional deterministic approaches to risk assessment tend to rely on multiple conservative assumptions, which are adopted to compensate for the lack of knowledge regarding uncertainty. When such conservative assumptions are compounded over a multi-step calculation, the effect is often that the calculated risk outcomes are comparable with maximum values resulting from a probabilistic approach [291–293]. This leads to a risk focus on situations with extreme and very low probabilities of occurrence.

Probabilistic risk assessment relies on the incorporation of numerous stochastic variables to compute a final distributional outcome or prediction. In light of their increasing application, the US EPA have developed guidelines for probabilistic environmental risk assessments [262]. Recent examples of such risk assessment have considered exposures to chemical contaminants from sources including food [293–297], water [298–300], soil [301] and air [302; 303].

For many modelled variables, the stochastic nature is derived from two distinct factors: variability and uncertainty (see Section 8.4). In many cases, it is desirable to separate—as much as possible—the consideration and reporting of these two factors. Such assessments are known as two-dimensional Monte Carlo methods [288; 304; 305].

Not every risk assessment requires or warrants a probabilistic assessment. Indeed, six different levels of analytical sophistication in the treatment of uncertainties in risk analysis have been identified by Paté-Cornell [306]. These are summarised as:

Level 0: Hazard detection and failure modes identification

Level 1: ‘Worst case approach’

Level 2: Quasi-worst case and plausible upper bounds

Level 3: Best estimates and central values

Level 4: Probabilistic risk assessment, single risk curve

Level 5: Probabilistic risk analysis, multiple risk curves.

A useful approach is to undertake a tiered evaluation whereby some risks are deemed to be within acceptably safe limits without the need for intensive scrutiny [306]. Further efforts and resources may then be allocated only to those risks that require such additional efforts in order to establish that safe levels may be met or to demonstrate that further controls are needed.

The first tier of a tiered risk assessment would normally consist of a very conservative risk evaluation requiring minimal data. Variables that might otherwise be considered stochastically are assigned conservative point-values on the basis of on worst-case assumptions. Examples

include zero environmental degradation of a chemical in the environment or zero inactivation of a pathogen during water treatment. Hazards that are shown to be at safe levels under 'tier 1 conditions' would require no further evaluation. Hazards that are not demonstrably safe under tier 1 conditions are then further subjected to a second tier assessment, which can require significantly more data and more complex analysis. A probabilistic analysis may be helpful in such circumstances since this approach involves carrying full PDFs through multiple calculations, thus avoiding the need for compounding conservative assumptions.

With some refinement, probabilistic assessment can be applied to most existing calculations and models for environmental exposure. For example, a Monte Carlo module has been incorporated into a steady state nonequilibrium level III fugacity model in order to account for variability in degradation half-lives and observe the effects that this variability has on the model outputs [307]. Similarly, a probabilistic shell has been applied to existing deterministic wastewater treatment plant performance models [308–311].

Probabilistic models may be constructed from most deterministic risk calculations simply by replacing single-value variables with PDFs. The existing mathematical transformations (such as multiplications or additions) will still apply.

The underlying calculations for probabilistic models are commonly constructed using spreadsheet software such as Microsoft Excel. Commercial software packages are then available to facilitate the assignment of PDFs and Monte Carlo sampling. Two common probabilistic software packages are @Risk [266] and Crystal Ball [312].

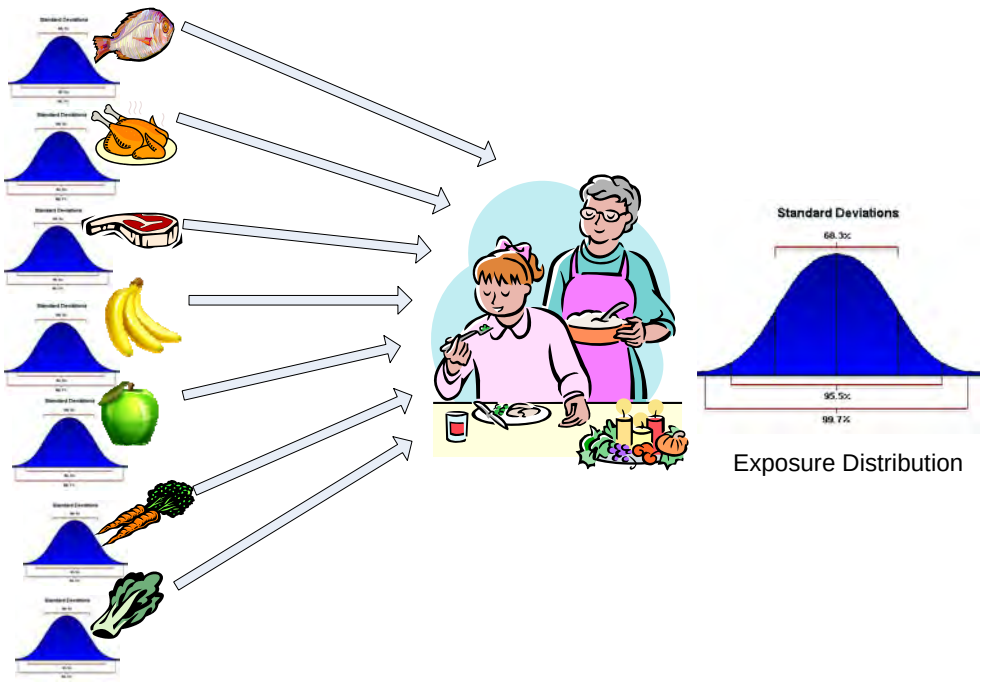
8.1 Summing PDFs in parallel

In some cases, exposure may be computed as a sum of numerous individual exposure pathways. For example, human exposure to dioxins has been determined as the sum of exposures from numerous sources, including dairy products, meat, fish and vegetables [295]. Similarly, exposure of children to lead has been determined as the sum of exposures from air, food, water, soils and dust [301]. Dietary exposure to dithiocarbamate has been determined as the sum of exposures from 26 different individual food types [293].

Alternatively, exposure to trihalomethanes from water may be from the sum of various exposure routes including oral ingestion, inhalation and dermal absorption [300].

Probabilistic analysis of any of these situations will involve the summing of parallel PDFs as illustrated in Figure 58.

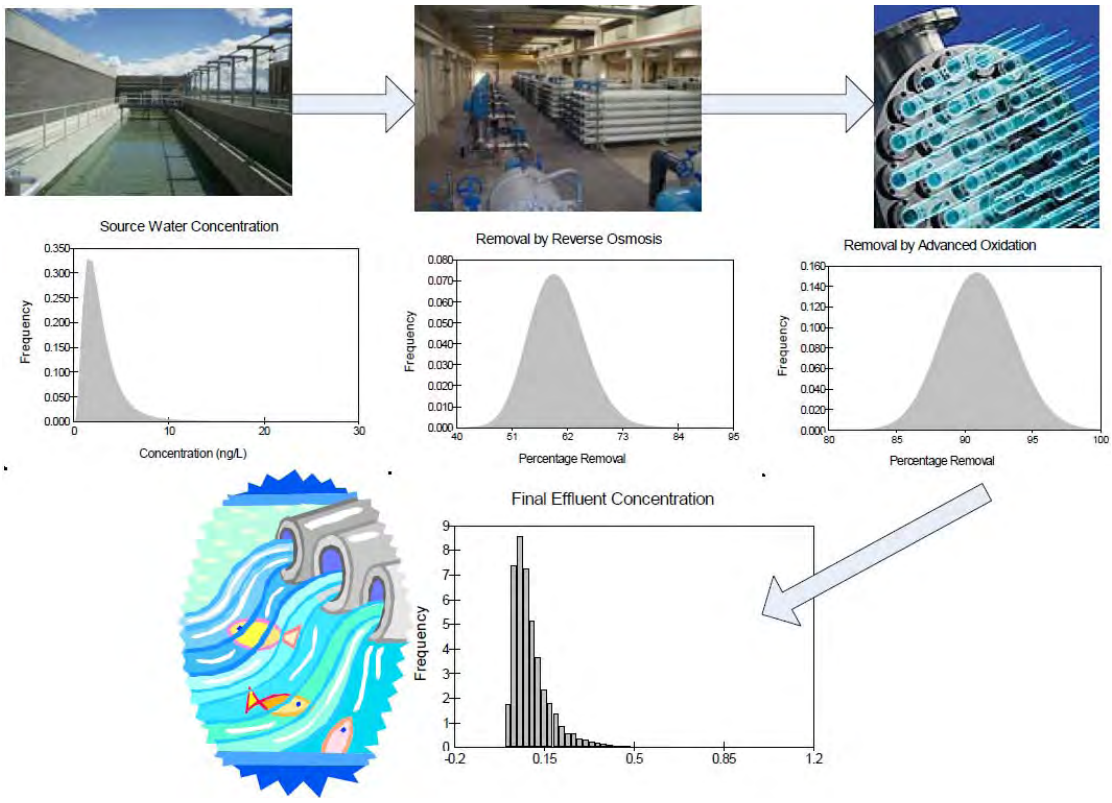
Figure 58: Illustration of PDFs in parallel (such as multiple dietary sources of a chemical contaminant)



8.2 Multiplying PDFs in series

In some cases, exposure may be determined in terms of sequential factors such as exposure to a chemical from a raw drinking water source after multiple treatment processes, each with variable capability to reduce the concentration of the chemical. A probability density function can be used to describe the variability in source water concentration of the chemical; subsequent PDFs then describe the variable percentage (or fractional) removal of the chemical by various treatment processes such as reverse osmosis and advanced oxidation. These PDFs can then be used to derive a simulated PDF for final effluent concentration as illustrated in Figure 59.

Figure 59: Illustration of PDFs in series (such as exposure to a contaminant after multiple barrier treatment processes)



The approach of assessing sequential unit water treatment operations and combining the PDFs by probabilistic techniques was used very effectively in the assessment of a pilot-scale advanced water treatment plant in San Diego [313]. In that study, PDFs were generated for plant influent water quality and sequential treatment performance of four types of treatment processes (microfiltration, ultrafiltration, reverse osmosis, and chlorine disinfection). These PDFs were generated by a combination of challenge tests and theoretical considerations. A key advantage of this process was that it allowed for the mathematical estimation of the entire treatment train performance. This estimation would not have been possible simply by end-point sampling since final effluents consistently yielded non-detectable results.

8.3 Monte Carlo and Latin Hypercube sampling

There are two main sampling types that may be used for randomly sampling distributions for probabilistic analysis. These are known as Monte Carlo sampling and Latin Hypercube sampling. These sampling types differ in how they draw samples from across the range of a PDF.

Monte Carlo sampling refers to the traditional technique for undertaking random sampling from a PDF. Monte Carlo sampling techniques are entirely random, and any given sample may be drawn from anywhere within the range of the input PDF. Samples, of course, are more likely to be drawn from areas of the PDF that have higher probabilities of occurrence. With sufficient iterations, Monte Carlo sampling ‘recreates’ the input PDF through sampling it. However, for a small number of iterations, significant clustering can occur and large areas of the PDF may be missed. This clustering can be problematic when a PDF includes low probability outcomes, and this could have a major effect on the results. This problem has led to the development of stratified sampling techniques such as Latin Hypercube sampling [314].

Latin Hypercube sampling was designed to accurately recreate the input PDF through sampling in fewer iterations compared with Monte Carlo sampling. To achieve this, Latin Hypercube sampling applies stratification to the input PDF. This stratification divides the cumulative distribution curve into equal intervals on the cumulative probability scale (0 to 1). A sample is then randomly taken from each interval or 'stratification' of the input distribution. Thus sampling is forced to recreate the input PDF. Because of the ability to more adequately represent a PDF with fewer iterations, Latin Hypercube sampling is generally preferred over random Monte Carlo simulation [314; 315]. In some cases, correlated sampling techniques are also of value [316].

8.4 Distinguishing variability and uncertainty

The concepts of variability and uncertainty are distinct [262]. Variability refers to observed differences attributable to true heterogeneity or diversity in a population or parameter. Uncertainty refers to a lack of knowledge about specific factors, parameters, or models [270; 306; 317–319].

As an example, variability exists in human dietary habits, thus there is variability in exposure to specific contaminants from particular food types [297]. This variability is not reducible by further measurement or study (although it may be better characterised). Quantitative characterisations of this exposure parameter would also be subject to uncertainty which may be derived from the sampling uncertainties, distributional uncertainties or uncertainties associated with other processes such as the effect of cooking prior to consumption. Uncertainty is sometimes reducible through further investigation.

Variability and uncertainty may often be accounted for separately, allowing the final presentation of probabilistic results to retain the distinction between them [297]. Separating variability and uncertainty is sometimes considered necessary to provide greater accountability and transparency [262]. Furthermore, distinguishing uncertainty from variability can help to identify parameters for which it could be worthwhile to collect additional data [318]. Nonetheless, it has been emphasised that variability and uncertainty are often confounded and it is not always appropriate to give special significance to distinguishing between the two [320].

There are a number of methodological approaches that may be adopted for distinguishing variability and uncertainty in a probabilistic analysis. The US EPA has recommended that when deciding on methods for evaluating uncertainty and variability, the following issues should be considered [262]:

- Variability depends on the averaging time, averaging space, or other dimensions in which the data are aggregated.
- Standard data analysis tends to understate uncertainty by focusing solely on random error within a data set. Conversely, standard data analysis tends to overstate variability by implicitly including measurement errors.
- Various types of model errors can represent important sources of uncertainty. Alternative conceptual or mathematical models are a potentially important source of uncertainty. A major threat to the accuracy of a variability analysis is a lack of representativeness of the data.

Distinguishing variability and uncertainty allows for the presentation of final risk determinations as plots that concisely summarise the probabilistic results, retaining the distinction between variability and uncertainty [305].

Sensitivity analysis to risk assessment models with two-dimensional probabilistic frameworks that distinguish between variability and uncertainty has been demonstrated using analysis of variance (ANOVA) methods [321].

Since probabilistic techniques rely on random sampling, they are themselves imprecise. Thus care should be taken to minimise and characterise any additional uncertainty that may be introduced as a result in insufficient sampling. Depending on the algebraic structure of the model and the nature of the PDFs used to characterise input parameters, some outputs may stabilise after relatively few sampling iterations. That is, the shape and character of the output PDF, as well as the mean and variance values, are not significantly changed as a consequence of further sampling. On the other hand, some model outputs may take longer to stabilise. As a general rule, simulations should be undertaken using more samples than assumed to be necessary, and repeated numerous times to confirm stability and repeatability [262]. If possible, is recommended to use software that allows for Latin Hypercube sampling to help stabilise the tails of the outputs as quickly as possible [264].

In practice, there are limits to the degree to which all sources of uncertainty may be quantitatively characterised. However, efforts should be made to identify all significant sources of uncertainty and to clearly disclose what sources are quantitatively represented in the model outcomes as well as those that are not.

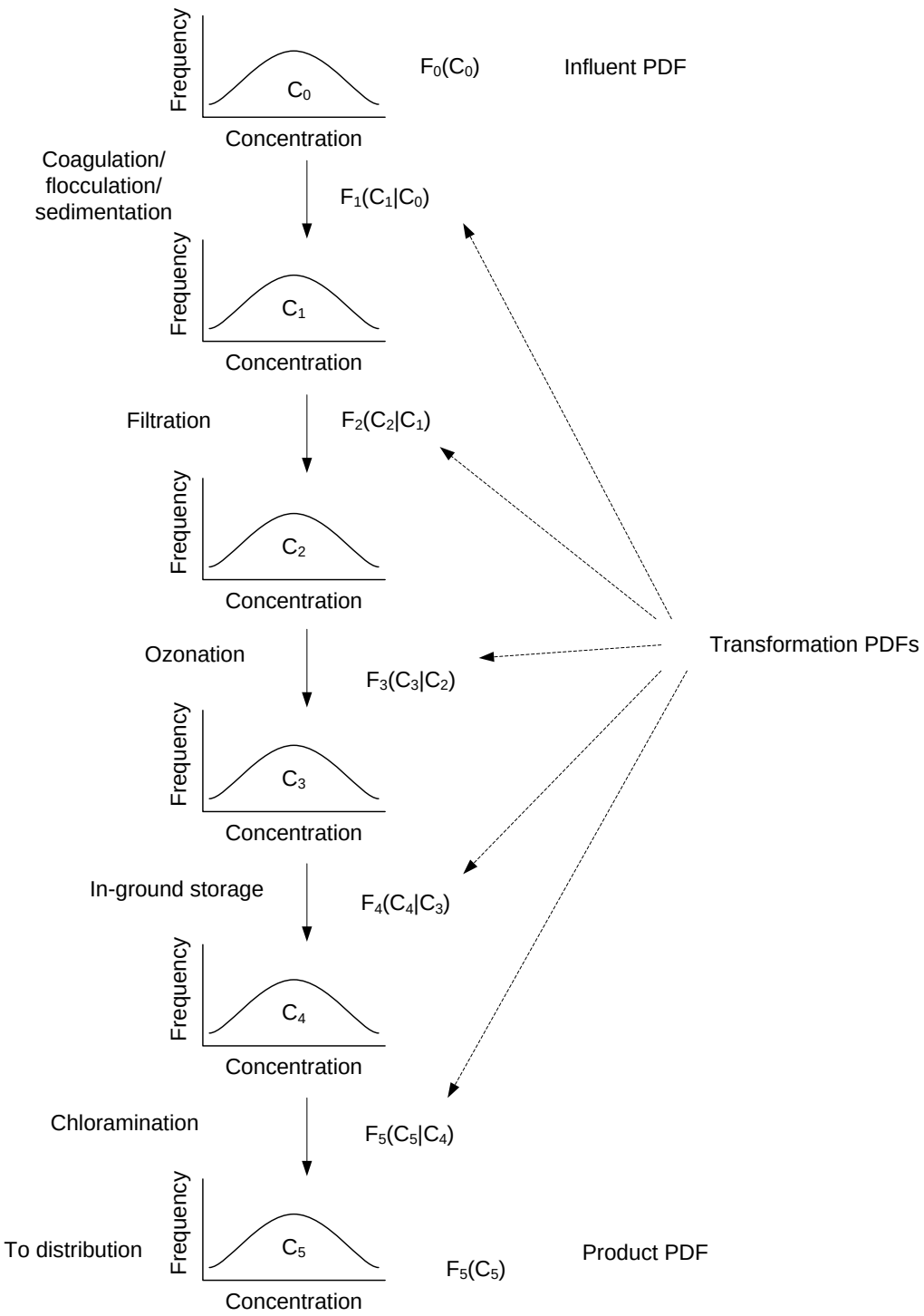
Sampling-based methods for uncertainty and sensitivity analysis have been comprehensively reviewed [322], covering the following topics:

- definition of PDFs to characterise epistemic uncertainty in analysis inputs
- generation of samples from uncertain analysis inputs
- propagation of sampled inputs through an analysis
- presentation of uncertainty analysis results
- determination of sensitivity analysis results.

8.5 Probabilistic assessment of water treatment unit operations

The idea of assessing multiple barrier water treatment process performance as a series of unit process performance PDFs has been promoted for at least a decade [313; 323–325]. The concept may be generally depicted as in Figure 60 [324].

Figure 60: Conceptual diagram of multiple barrier process train and treatability distributions [324].



Concentrations of a particular contaminant at each stage of the multiple barrier treatment process are represented as $C_0 \ldots C_5$ [324]. The connection between subsequent concentrations is described as a conditional PDF. For example, $F_3(C_3|C_2)$ is the probability density of the contaminant concentration following ozonation (C_3) given the concentration in the influent to ozonation reactor (C_2). In the simplest of circumstances, the processes may be assumed to behave in a linear (first order) fashion, and the distribution may then be determined simply in terms of a ratio of effluent:influent. However, the conditional framework provides a more general approach allowing for more complex treatment process removal

functions. Individual conditional PDFs may even be dependant on other descriptors of the system such as hydraulic flow rates.

Formally, the PDF of the product concentrations may be evaluated as a multiple integral, which can be expressed as follows [324]:

$$f_5(C_5) = \iiiint f_0(C_0)F_1F_2F_3F_4dC_0dC_1dC_2dC_3dC_4$$

Analytical evaluation of this integral may not be possible in many cases and would most generally be determined by probabilistic (Monte Carlo) simulation.

The cumulative removal (and inactivation) of coliphage has been estimated for five potential treatment systems considered for implementation at proposed advanced water treatment plant in San Diego, California [313]. These estimates were obtained through a series of Monte Carlo simulations where, for each trial, the simulation model generated an influent concentration from a wastewater treatment plant (WWTP) and appropriate removals for each unit process. Using these values, the resultant effluent concentration was computed along with a cumulative removal for each of the entire treatment trains as follows:

- WWTP effluent → ultrafiltration → reverse osmosis → chlorination
- WWTP effluent → ultrafiltration → reverse osmosis → ozonation
- WWTP effluent → microfiltration → reverse osmosis → ozonation
- WWTP effluent → microfiltration → reverse osmosis → chlorination
- WWTP effluent → ultrafiltration → reverse osmosis → ozonation → chlorination

All of the treatment trains investigated removed significant quantities of coliphage. It was also noted that the method used is sensitive enough to account for relatively small differences between treatment systems. The predicted median log removals of the above treatment trains varied between 13.6 and 21.6 logs. Based on influent data generated from routine monitoring and the predicted treatment train removal rates, the median predicted effluent coliphage concentrations ranged from 8.5×10^{-11} to 8.0×10^{-19} plaque forming units (pfu) per 100 millilitres [313].

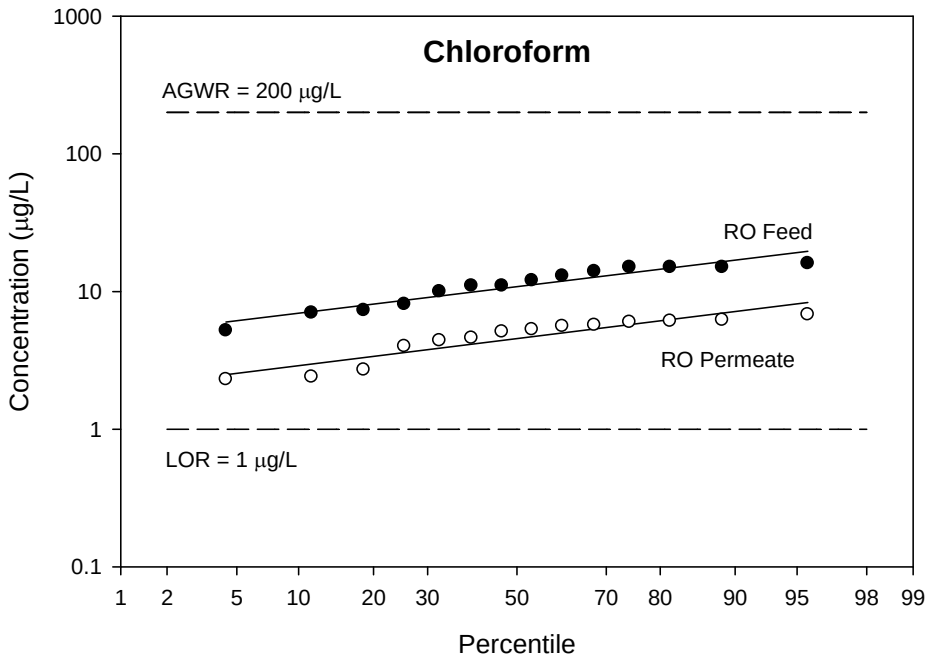
Approaches to determining conditional PDFs for numerous individual water treatment operations have been described and some examples are summarised in the following sections.

8.5.1 Reverse osmosis

Probabilistic characterisation of reverse osmosis treatment performance for a pilot-scale advanced water treatment plant in Sydney, Australia, has been recently reported [326]. The reverse osmosis process was operated at a recovery of 83–85 per cent and flux of 17–20 LMH using a Hydranautics ESPA2 membrane. Some illustrative results are presented here for two trihalomethanes (chloroform and bromoform) and three N-nitrosamines (NDMA, NDEA and NDPA). These are all disinfection byproducts formed by the variable operation of chlorination disinfection processes.

A lognormal probability plot for ambient chloroform concentrations observed in reverse osmosis feed permeate over 14 sampling periods is presented in Figure 61.

Figure 61 Lognormal probability plot for chloroform during reverse osmosis treatment



As presented in Figure 61, chloroform levels were in the range 5–16 micrograms per litre in the reverse osmosis feed. Reverse osmosis was partially effective in removing chloroform, resulting in a probable permeate concentration of 2–7 micrograms per litre.

This chloroform concentration dataset was then used to fit full lognormal (format 1) PDFs as shown in Figure 62 and Figure 63 using @Risk software [266]. Three parameters are required to reproduce these PDFs for reverse osmosis feed (μ = 41772, σ = 4.0019, shift= -41760) and reverse osmosis permeate (μ = 6585.9, σ = 1.4894, shift = -6580.9).

Figure 62: Chloroform concentration in reverse osmosis feed

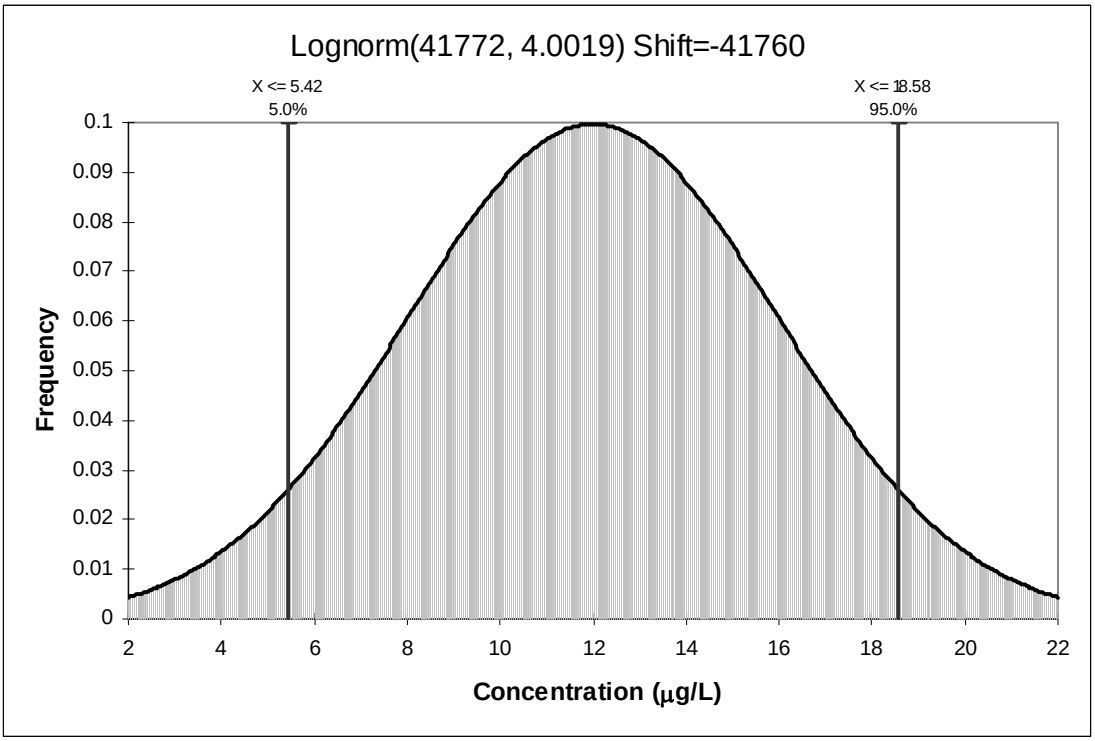
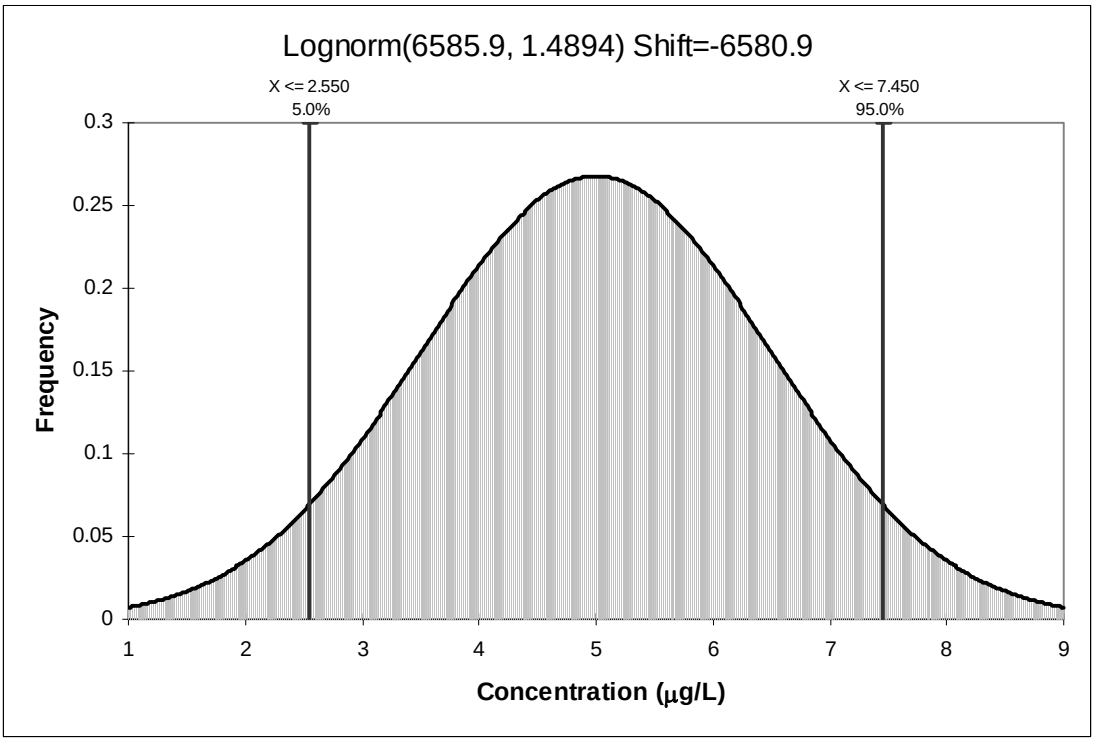


Figure 63: Chloroform concentration in reverse osmosis permeate



These PDFs were then used to simulate a PDF for percentage reverse osmosis rejection by Equation 9.

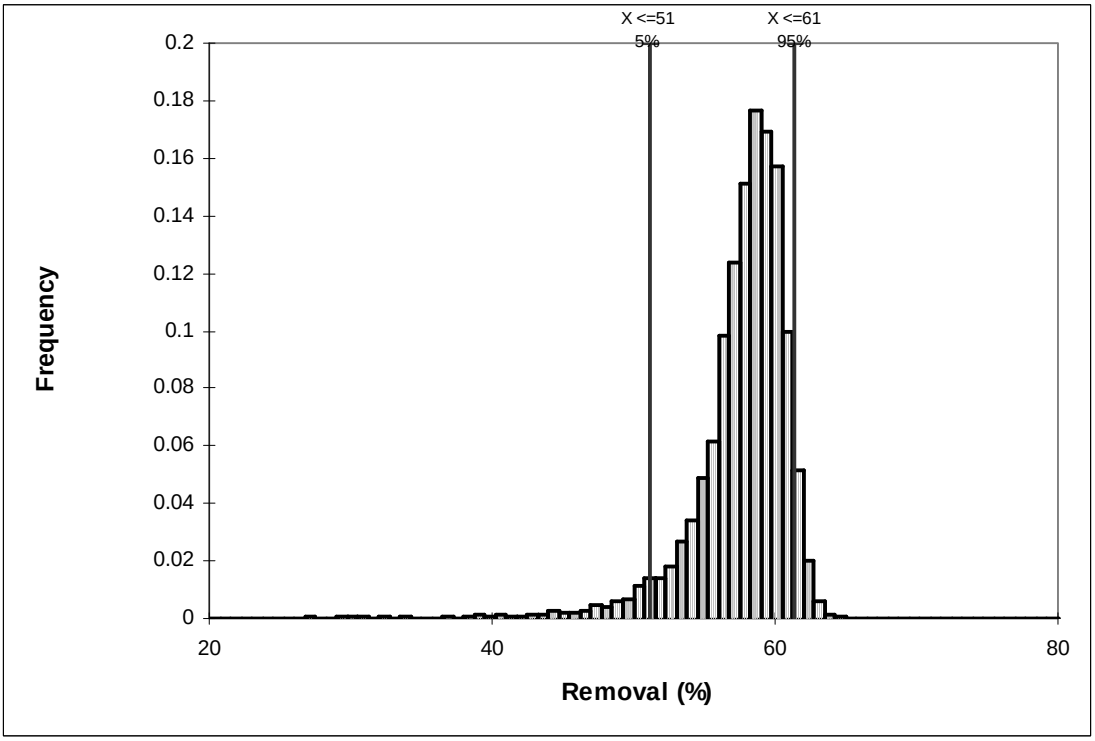
Equation 9: Calculation for Monte Carlo simulation of reverse osmosis rejection

$$PDF_{\text{RO Rejection(\%)}} = \frac{PDF_{\text{RO Feed}} - PDF_{\text{RO Permeate}}}{PDF_{\text{RO Feed}}} \times 100$$

The probabilistic simulation was undertaken using Latin Hypercube sampling with 10,000 sampling iterations. A correlation co-efficient of 0.99 was assumed between sampling of the reverse osmosis feed and permeate PDFs. That is, it was assumed that very low reverse osmosis feed concentrations directly corresponded to very low reverse osmosis permeate concentrations and likewise for high concentrations.

Figure 64 shows the simulated PDF for percentage chloroform removal during reverse osmosis treatment. The 5th and 95th percentiles are 51 per cent and 61 per cent respectively. The mean removal (not indicated in the figure) is 57 per cent.

Figure 64 Simulated PDF of chloroform removal (%) from ultrafiltration influent to reverse osmosis permeate



In some cases, chemicals may not be measurable in reverse osmosis permeates since their concentrations are below analytical limits of reporting. Nonetheless, the concentrating nature of reverse osmosis filtration can often result in these chemicals being of such elevated concentrations in reverse osmosis concentrates that they may be measured there. By measuring the concentrations in subsequent reverse osmosis stage concentrates, it is possible to derive an understanding of the degree and nature of rejection by reverse osmosis processes (as a function of reverse osmosis feed concentration). Using this approach, it is possible then to back-calculate feed concentrations and, subsequently, permeate concentrations. An example where such an approach can provide useful information is

provided in Figure 65 showing bromoform concentrations in the advanced water treatment plant.

Figure 65: Lognormal probability plots for bromoform in reverse osmosis feed and Stage 1, 2 and 3 reverse osmosis concentrates

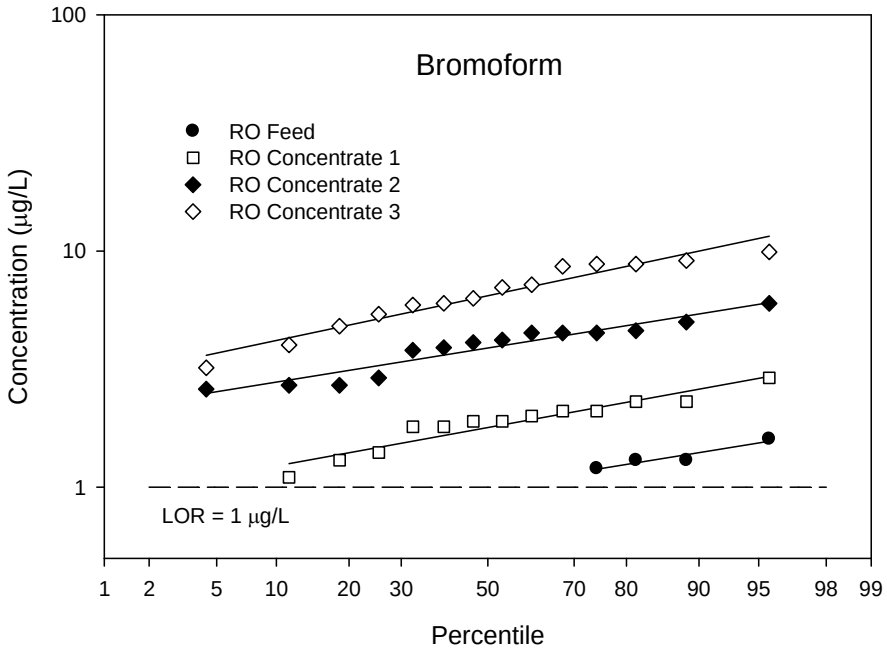


Figure 65 shows the measurable concentration data for bromoform in the three-stage reverse osmosis treatment process. All reverse osmosis permeate measurements were below the analytical limit of reporting (LOR = 1 microgram per litre). Only four out of 14 data points were measurable for bromoform in the reverse osmosis feed. However, at least 13 of 14 data points were measurable in the Stage 1, Stage 2 and Stage 3 concentrates. By fitting PDFs to these data, it was possible to derive a PDF for bromoform rejection by Stage 2 and Stage 3 reverse osmosis. This information allowed an estimation of rejection PDF by Stage 1 reverse osmosis and hence back-calculation of the initial reverse osmosis feed PDF. The combination of reverse osmosis feed PDF and reverse osmosis rejection PDFs then allowed the determination of individual and combined permeate concentration PDFs.

Due to the nature of the treatment processes in the conventional wastewater treatment plant, concentrations of N-nitrosamines such as N-nitrosodimethylamine (NDMA) were generally found to be below the available analytical detection limit (5 nanograms per litre). Therefore, in order to develop PDFs for N-nitrosamine reverse osmosis rejection, it was necessary to undertake challenge testing. This involved spiking the feedwater to the reverse osmosis process with high concentrations (~500 nanograms per litre) of nitrosamines and monitoring the corresponding permeate (and concentrate) concentrations. From these challenge testing experiments, it was possible to derive PDFs for the percentage removal of N-nitrosodimethylamine (NDMA) (Figure 66), N-nitrosodiethylamine (NDEA) (Figure 67) and N-nitrosodipropylamine (NDPA) (Figure 68) by the reverse osmosis process. Lognormal probability plots for these data were presented earlier in Figure 55 to Figure 57.

Figure 66: Simulated PDF of NDMA removal by reverse osmosis

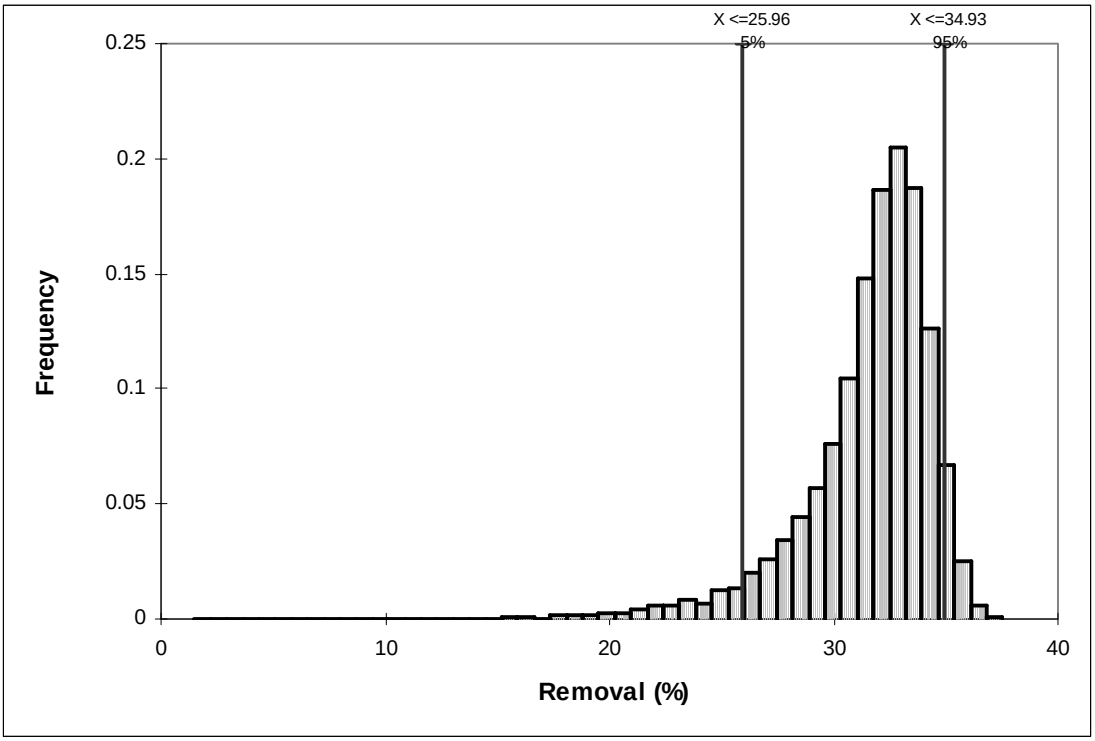


Figure 67: Simulated PDF of NDEA removal by reverse osmosis

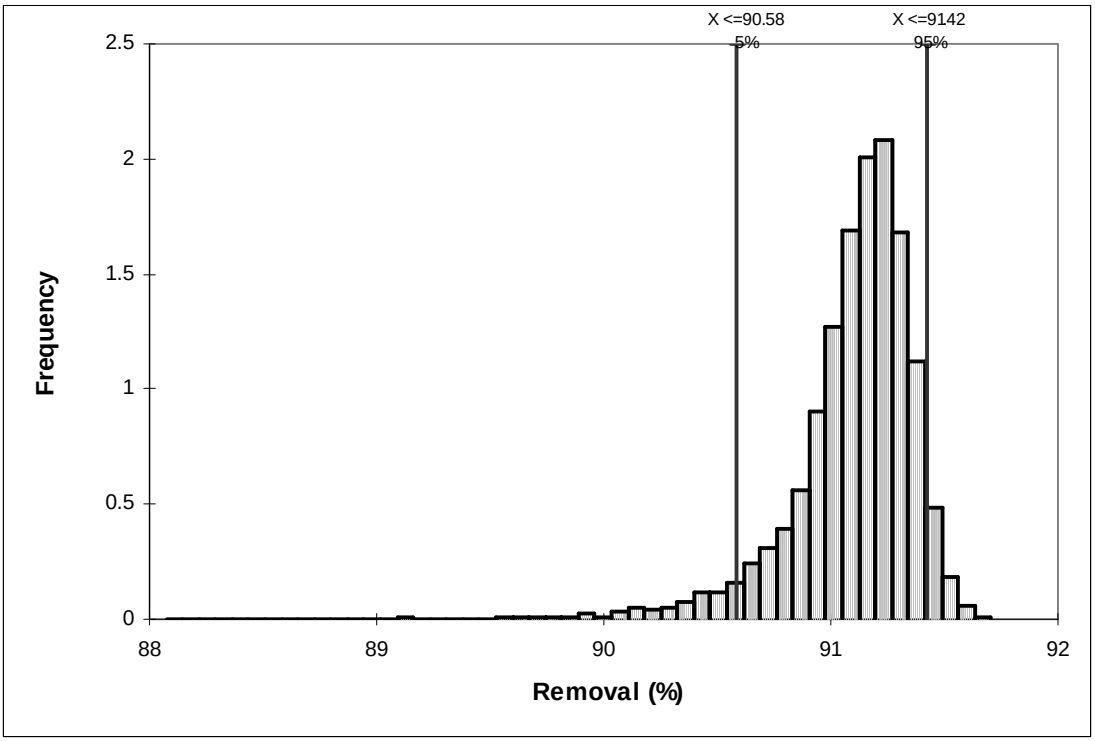
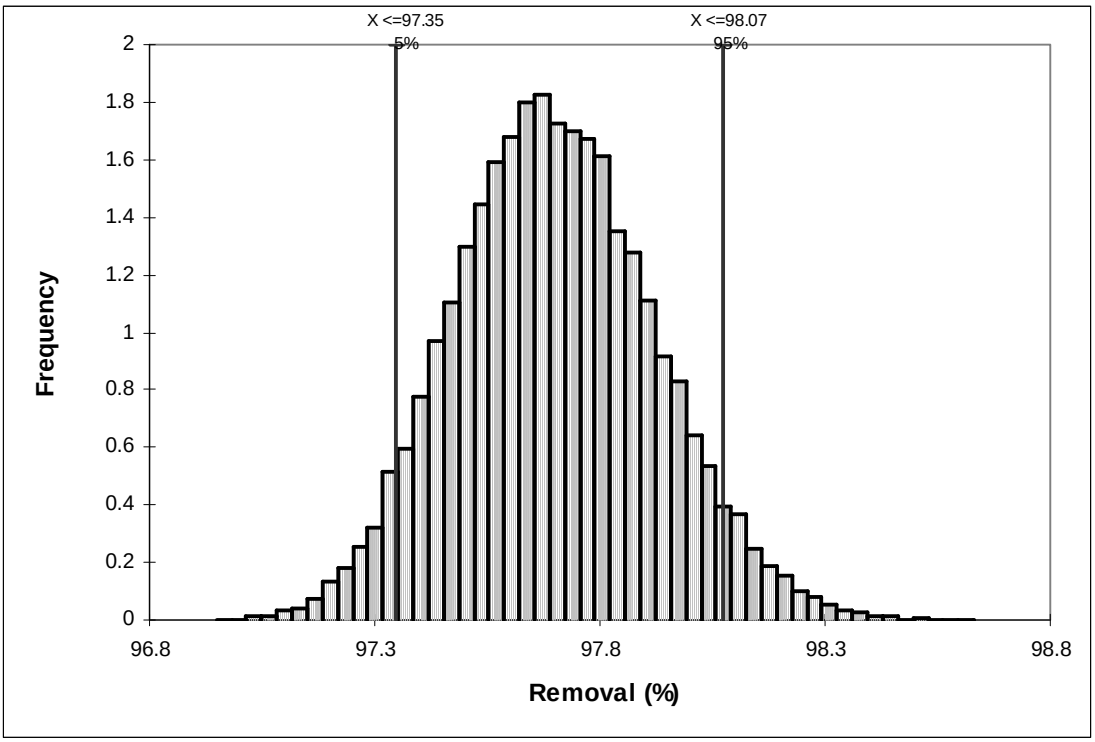


Figure 68: Simulated PDF of NDPA removal by reverse osmosis



The observed reverse osmosis rejections indicate that NDMA was not only relatively poorly removed, but that the removal was highly variable, with 5th and 95th percentile values of 26 per cent and 35 per cent, respectively. NDEA was both more effectively and more consistently rejected by the reverse osmosis membrane, with 5th and 95th percentile values both around 91 per cent. This trend was further followed by NDPA, with 5th and 95th percentile values of 97 per cent and 98 per cent. Undertaking this membrane challenge testing, and the subsequent development of PDFs for reverse osmosis removal, allows the estimation of human exposure to this series of toxic chemicals which would not otherwise be analytically measureable.

The PDFs presented here are simulated, and while they may be fitted to a standard distributional form (such as a lognormal distribution), they are unlikely to conform perfectly to a simple standard distribution. However, the general features of these PDFs can be statistically summarised as presented in Table 1.

Table 32: Statistical summaries of N-nitrosamine reverse osmosis rejection PDFs

PDF parameter	***NDMA***	***NDEA***	***NDPA***
Mean	31.56	91.10	97.70
Std Dev	2.99	0.28	0.22
Variance	8.94	0.08	0.05
Skewness	-2.06	-2.37	0.18
Kurtosis	11.02	17.07	3.02

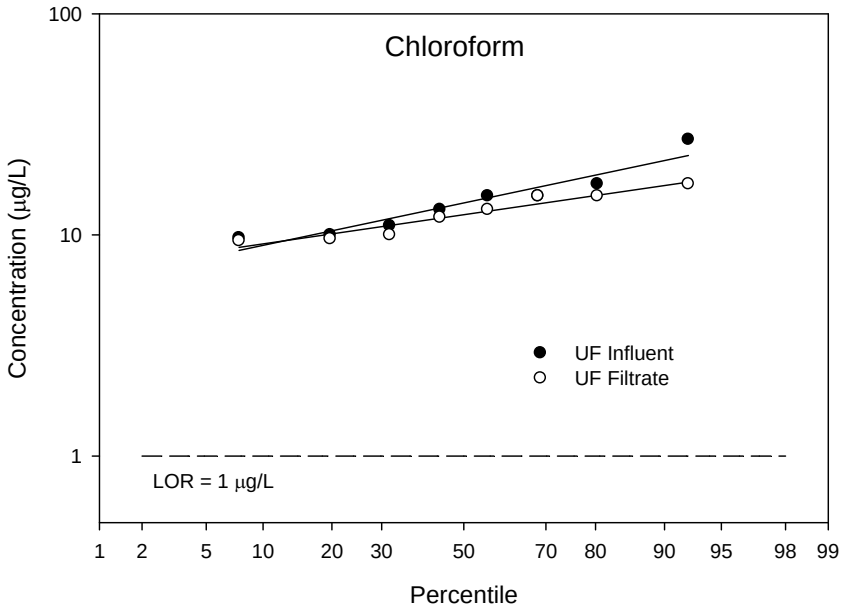
Probabilistic analysis of challenge testing with coliphage on a number of reverse osmosis membranes has been reported from a pilot-scale plant for a proposed indirect potable reuse scheme in San Diego [313]. Weibull PDFs were fitted for maximum likelihood estimate removals for 'Fluid Systems HR' and 'Dow Filmtec' reverse osmosis membranes, with scale and shape parameters equal to (3.16, 10) and (5.65, 9.3), respectively. Maximum likelihood

estimates for a Hydranautics and Fluid Systems Ultra Low Pressure reverse osmosis units were fitted to Gamma PDFs with scale and shape parameters equal to (0.0744, 63.48) and (0.07, 50.0), respectively.

8.5.2 Microfiltration and ultrafiltration

Probabilistic characterisation of ultrafiltration treatment performance for the removal of some trace chemical contaminants was undertaken at a pilot-scale advanced water treatment plant in Sydney, Australia [326]. Lognormal probability plots for ultrafiltration influent and ultrafiltration filtrate are presented in Figure 69.

Figure 69: Lognormal probability plot for ultrafiltration treatment of chloroform



Chloroform levels in the ultrafiltration influent water from this plant could be expected to be in the range of 10–30 micrograms per litre, and negligible reduction was observed during ultrafiltration.

These chloroform concentration data were then used to fit full lognormal (format 1) PDFs as shown in Figure 70 and Figure 71 using @Risk software [266]. Three parameters are required to reproduce these PDFs for the ultrafiltration feed (μ = 8.0598, σ = 6.8537, shift = 7.0497) and the ultrafiltration filtrate (μ = 26.163, σ = 3.4712, shift = -13.468).

Figure 70: Chloroform concentration in ultrafiltration influent

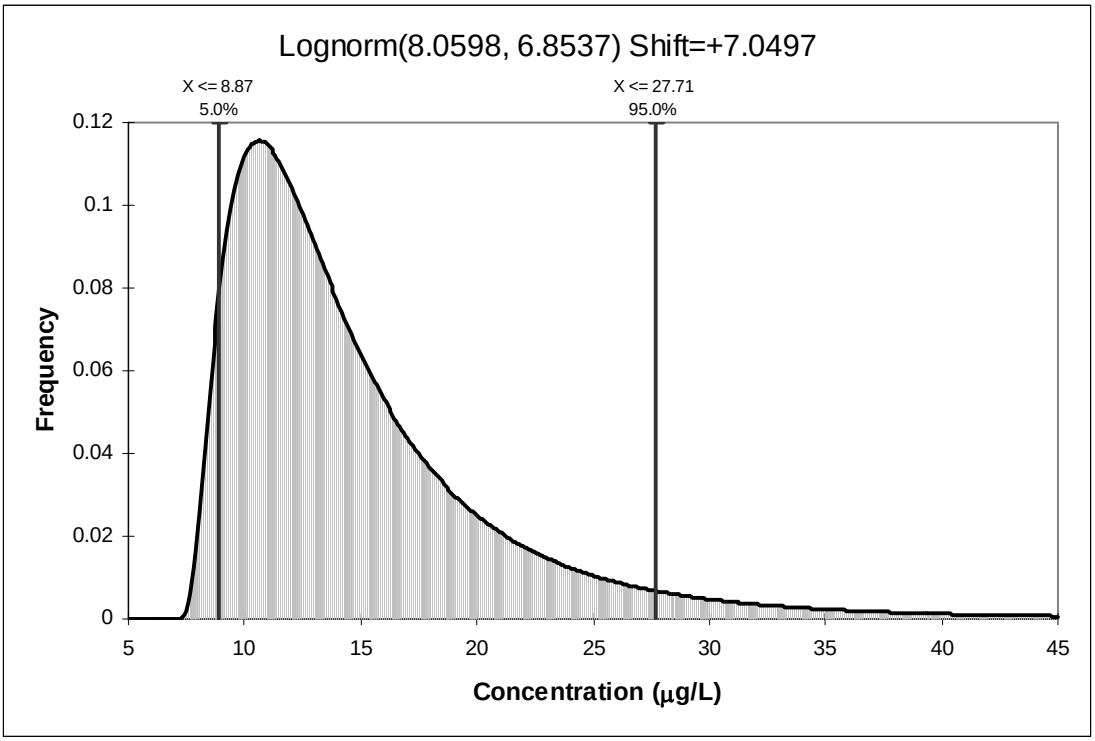
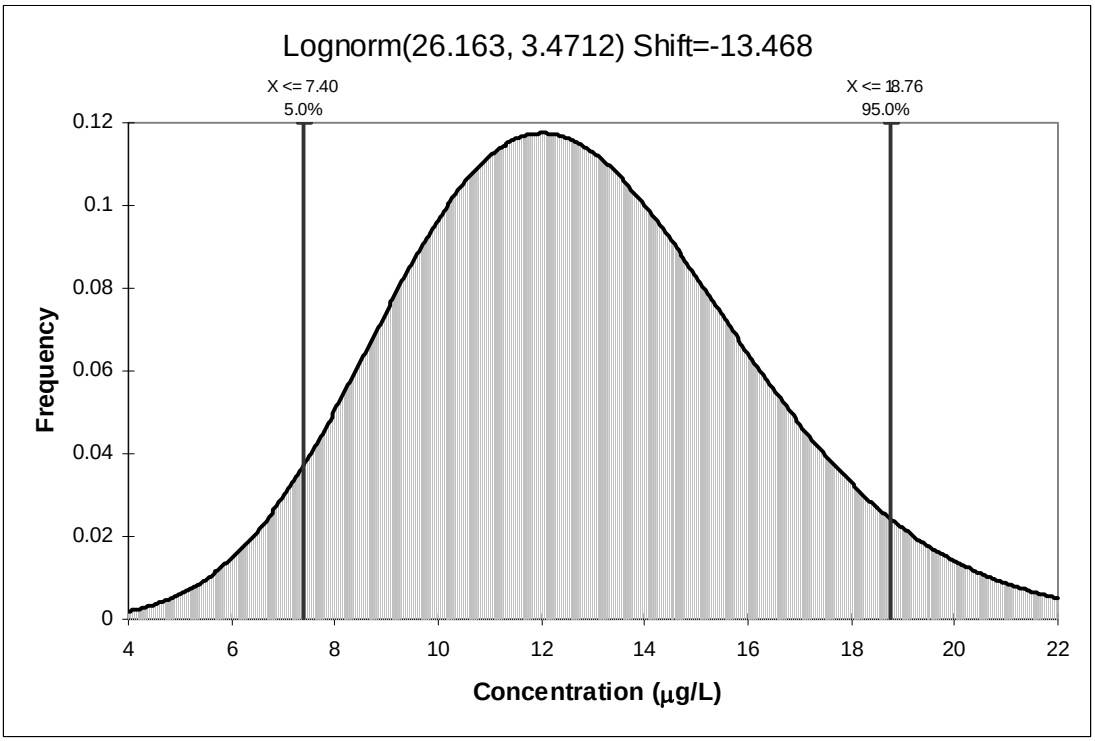


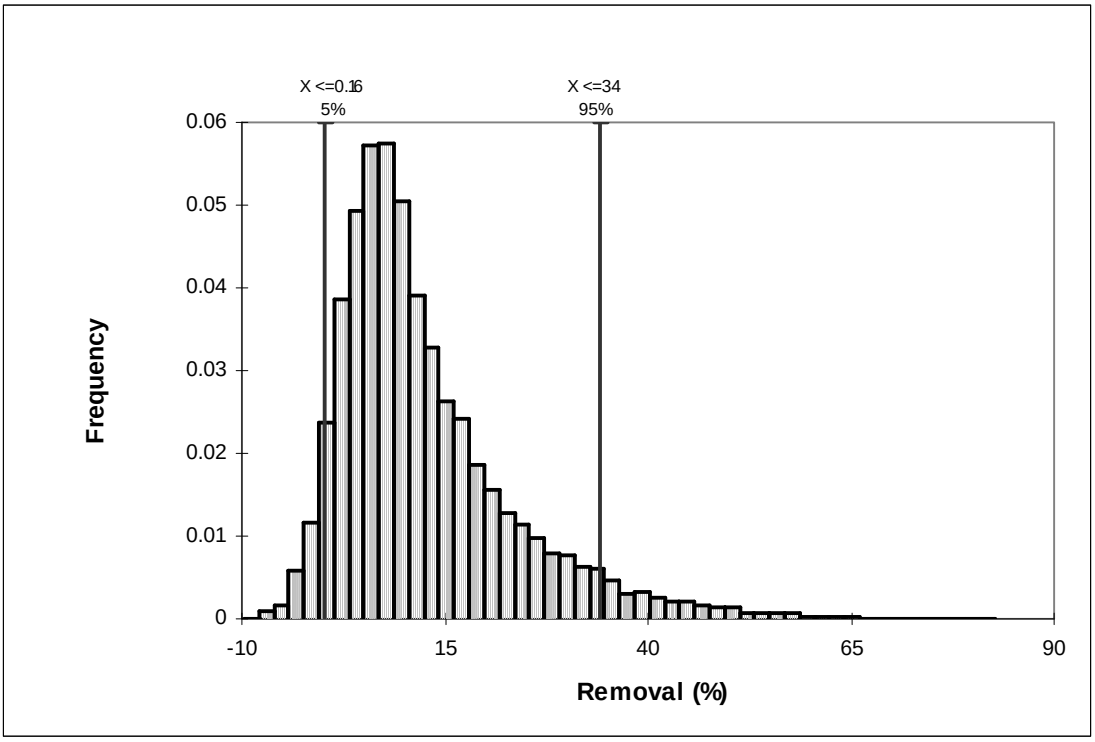
Figure 71: Chloroform concentration in ultrafiltration filtrate



The fitted lognormal PDFs for chloroform concentrations in ultrafiltration influent and filtrate were used to derive a simulated PDF for percentage removal of chloroform during ultrafiltration treatment (Figure 72). In this case Latin Hypercube sampling was used with 10,000 iterations. A sampling correlation of 0.99 was used between the ultrafiltration influent

and filtrate PDFs. Note that this technique does not provide any insights regarding the actual removal mechanism. It is therefore not implied that any observed removal was achieved by mechanisms such as size exclusion. Other removal mechanisms, such as adsorption or volatility, may be responsible for the small differences between the ultrafiltration influent and filtrate PDFs. Alternatively, it is possible that the small differences observed between these two input PDFs are simply the result of analytical uncertainty. An increased number of data samples would help to distinguish between such analytical uncertainty and real concentration differences.

Figure 72: Simulated PDF for percentage removal of chloroform during ultrafiltration treatment



MS-2 bacteriophage has been employed as a model virus for treatment process challenge studies since it is not a human pathogen and is an RNA virus of similar size and shape to poliovirus and hepatitis A virus. Furthermore, large numbers of MS-2 bacteriophage can be grown in a laboratory. Challenge studies using MS-2 bacteriophage have previously been reported for microfiltration and ultrafiltration processes at a pilot-scale advanced water treatment plant [313]. These were used to develop cumulative probability plots for microfiltration and ultrafiltration performance during the MS-2 seeding studies.

A PDF for microfiltration performance for coliphage removal was reported based on the relationship between transmembrane pressure and coliphage removal [313]. The relationship itself was not treated stochastically, but the transmembrane pressure applied in the calculation was. The transmembrane pressure was based on nine months of monitored data and fitted to a gamma PDF with scale and shape parameters equal to (1.19, 10.583), respectively.

A challenge testing study involving an ultrafiltration unit process has been reported with challenging on six separate occasions [313]. It was reported that the ultrafiltration membrane used during the first three events was compromised due to broken fibres. Accordingly, the results from the first three tests were modelled separately to the latter three, which were conducted on an intact membrane unit. Maximum likelihood estimate removals for coliphage

through the compromised membrane unit were determined and fitted to a lognormal (format 1) distribution with mean 3.83 log removal and standard deviation 1.3 log removal.

8.5.3 Flocculation and settling

A method has been proposed for predicting the distribution of suspended solids concentrations in a water treatment plant effluent following flocculation and sedimentation processes [327]. The predicted final suspended solids distribution is determined as a function of PDFs for influent suspended solids, temperature, floc particle specific gravity, sedimentation basin performance index, flocculation unit velocity gradient and surface over flow rate [327].

Probabilistic modelling of the removal of permanganate index (COD_{Mn}) as a surrogate parameter for natural organic matter removal during drinking water treatment processes has been described [328]. In this study, the simulation results of a probabilistic model were used to assess the performance risk of a range of water treatment plants in China for compliance with COD_{Mn} regulation subject to various source water quality and operational conditions.

8.5.4 Ozone disinfection

An early attempt to develop PDFs for coliphage removal was reported from a study undertaken in San Diego [313]. In that study, seeding experiments were undertaken at four different disinfection dosages (CTs) ranging from 0.3 to 1.7 mg/L.minute. However, because endpoints were never reached in the ozone effluent samples, it was not possible to generate the maximum likelihood estimates required to characterise performance.

An alternative approach was more recently reported in which ozone disinfection of *Campylobacter* was modelled based on operational parameters including ozone concentrations, contact time and temperature [281].

Modelling of operational conditions has been developed further for the quantification of inactivation of *Cryptosporidium parvum* oocysts for an ozone reactor treating lake water [329]. This approach was based on stochastic sampling from PDFs of ozone exposure and lethal ozone dose. The ozone exposure PDF was computed with a tank in series model derived from tracer data and measurements of flow, ozone concentration and ozone decay. The PDF of lethal ozone doses was computed with a delayed Chick–Watson model that was calibrated using a large number of inactivation studies. Parameter uncertainty was propagated with Monte Carlo simulation. This study demonstrated that the lethal dose model PDF was responsible for over 90 per cent of the output variance.

8.5.5 Chlorination

Chlorine inactivation of pathogens has been incorporated in stochastic modelling by the use of pre-established functions to relate inactivation to the disinfection dosages [313]. In this case, a uniform PDF was established for disinfection dosages between 5 and 500 mg/L.minute and this was used to derive a PDF corresponding to the specific inactivation function. A forecast chlorination inactivation of coliphage based on 5000 sampling trials was developed in this study.

The chemical transformation of particulate and dissolved organic matter during chlorine disinfection has also been modelled assuming that it is subject to chlorination to form disinfectant byproducts [328], based on a previously published disinfectant byproduct formation model [330].

The model for predicting chlorine disinfection of *Klebsiella oxytoca* in a beverage industrial process has been described based on input PDFs of influent contamination levels, chlorine concentration and residence time in the chlorination tanks [331]. Chlorine disinfection kinetics were determined in laboratory experiments and applied to the industrial process. The final probabilistic simulation model was validated in a pilot plant for a six month period and the linear relationship between the predicted and observed probability of Klebsiella-detection was characterised with a determination coefficient of $R^2 = 0.905$.

8.5.6 Sand filters

The efficiency of slow sand filters for removing total coliforms from secondary treated effluent has been subjected to a detailed probabilistic assessment [332]. Stochastic parameters included influent concentrations, filtration rate, sand bed depth and sand grain size. Normal and lognormal distributions of the removal efficiency were considered, but the final results were best fitted to a 'Type III extreme value distribution'. This analysis was able to demonstrate that slow sand filter average removal efficiency was not significantly affected by the sand grain size, as well as indicating optimal values for flow rates and sand bed depths. The risk of exceeding the imposed reuse standard for unrestricted irrigation (100 total coliforms per 100 millilitres) was determined to be approximately 50 per cent, at the 95 per cent confidence level, thus implying that additional treatment processes would be required to reliably meet the standard.

The treatment efficacy for reducing *Campylobacter* concentrations by a drinking water treatment plant including rapid and slow sand filtration steps has also been assessed using a stochastic Monte Carlo model [281]. Modelling of permanganate index (COD_{Mn}) as a surrogate parameter for removal of natural organic matter during filtration processes has also been described using probabilistic techniques [328].

8.5.7 Activated sludge

Stochastic performance analysis of activated sludge processes has been an area of research interest for more than 30 years [333–335]. These analyses were generally aimed at the optimal production of high quality effluent at minimum cost. To do this, techniques were required for engineers to estimate the expected final water quality and its variations.

Traditional performance criteria such as biochemical oxygen demand (BOD) and suspended solids have been shown to commonly be fittable to lognormal distributions [335]. This is consistent with theoretical considerations of the central limit theorem. That is, when an observed variable (for example, BOD) may be viewed as the product of numerous similarly distributed variables (for example, influent characteristics, plant operational conditions), the sum of logarithm of these variables will be approximately normally distributed. Most kinetic models for the activated sludge process result in multiplicative expressions for effluent BOD [335].

The use of probabilistic assessment of activated sludge systems has been introduced, with the aim of providing a more efficient approach to the currently somewhat manual trial and error method of model calibration used in activated sludge modelling practice [336]. The Monte Carlo calibrated model was validated at a domestic wastewater treatment plant in the Netherlands using three months of dynamic oxygen, ammonia and nitrate sensor data. The calibrated model was shown to provide statistically accurate and valid predictions for these parameters. The authors did not propose that this approach may also useful for quantitative exposure assessment; however, the analysis of key parameters could be expected to be useful for such an investigation.

A similar methodology has been described for the design and upgrade of wastewater treatment systems by applying a probabilistic shell to existing deterministic wastewater treatment plant performance models [308–311].

8.6 Probabilistic hazard characterisation including dose-response assessment

International regulatory agencies have generally confined probabilistic analysis for human health assessments to the exposure variables. However, a recent technical panel has recommended that the US EPA 'further evaluate approaches such as probabilistic analysis for characterising variability and uncertainty in toxicity reference values' [66].

The deterministic risk assessment methods that are currently used yield human limit values or margins of safety without quantitative measurements of uncertainty [289; 337]. However, the use of probabilistic methods in hazard characterisation, including dose–response assessment, is now an active area of research and regulatory attention in both human health and ecological risk assessments [288].

Numerous probabilistic approaches have been proposed for the derivation of reference doses (RfDs) for non-cancer toxic chemicals [337–343]. RfDs are typically reported as single numbers, although it is widely acknowledged that there are significant uncertainties inherent in their derivation (see Section 1.2). The probabilistic approach takes account of the major sources of this uncertainty to express the human population threshold as a PDF. Particular attention has been paid to sources of uncertainty and variability including the use of adult and child toxicokinetic intraspecies uncertainty factors [344] and estimations of exposure duration [345]. A probabilistic approach for RfD derivation has been demonstrated for some chemicals including trichloroethylene [346] and ethylene oxide [347].

A few recent studies have also examined the feasibility of using probabilistic uncertainty assessment for cancer-risk chemicals [343; 348; 349].

Toxic equivalency factors for a range of dioxins, furans and PCPs have been developed by the World Health Organization. These were derived from a range of relative potency estimates obtained from *in vivo* and *in vitro* studies. For most congeners, the range of relative potency values spans several orders of magnitude, and the degree of conservatism varies widely among the congeners. The use of relative potencies as data PDFs, rather than point estimates, to derive toxic equivalency factors has been investigated [350–352]. This approach permits a more informed evaluation of the variability and uncertainty in the attendant risk estimates. Furthermore, it provides a method to ensure a uniform degree of conservatism in the toxic equivalency factor values.

Probabilistic consideration of variability and uncertainty in microbial hazard characterisation has also been described [353; 354].

8.7 Probabilistic combination of exposure assessment and hazard characterisation

The final stage of risk analysis is the combination of the exposure assessment with hazard characterisation (including dose–response assessment) to produce what is generally referred to as the 'risk characterisation' [289]. Important roles of the characterisation are to interpret and summarise risk information in a meaningful way. This would normally require some discussion of the uncertainties inherent in the key exposure parameters and the dose-response assessment, model assumptions, and analytical limitations.

Williams and Paustenbach have provided a comprehensive review and discussion of approaches that may be taken for risk characterisation, including examples of qualifying information that may often be used to provide additional value to chemical risk assessment reports [289]. Although probabilistic methods have gained attention in hazard characterisation, and they are increasingly used in exposure assessment, full use of the available probabilistic information in risk characterisation is less common [355]. Usually, after probabilistic exposure assessment or hazard characterisation, percentiles from the obtained distributions are used as point estimates in risk characterisation. In this way, all information on variability and uncertainty is lost [289].

An alternative approach is to integrate the entire PDFs from probabilistic exposure assessment and hazard characterisation into one risk characterisation plot. This approach has been illustrated with a practical example, deriving a final risk characterisation plot containing two key pieces of information [355]:

- the confidence that may be held in concluding there is no risk
- the fraction of the population that this conclusion applies to.

This information leads to a better-informed conclusion regarding the risk of a hazard; and it is a powerful communication tool regarding overall risk.

A detailed framework has been proposed for integrated probabilistic risk assessment where exposure assessment and hazard characterisation are both included in a probabilistic way [305]. The aim is to specify the probability that a random individual from a defined population will have an exposure sufficient to cause a particular health effect of a defined magnitude. Uncertainties involved in the overall risk assessment (regarding both exposure and effect assessment) are quantified using Monte Carlo and bootstrap methods, resulting in an uncertainty distribution for any statistic of interest, such as the probability of critical exposure.

A human health risk assessment was reported for exposure to DEET, triclosan and acetaminophen by trace concentrations in drinking water [356]. This is a useful illustrative example of bringing exposure and dose–response data together.

8.8 Expert elicitation and fuzzy logic

When attempting to model the behaviour of environmental processes, analyses often suffer from a lack of data or imperfect knowledge about processes. This can impede rigorous probabilistic study. As a result, the direct application of environmental risk analysis using Monte-Carlo simulation methods may lead to two potential shortcomings [357]:

- inaccurate risk assessment outcomes as a result of poorly defined PDFs for input parameters
- inaccurate risk assessment outcomes as a result of assumptions that input parameters are independent of one another when often they are not.

An approach that may assist to overcome data deficiencies in some circumstances is the use of rigorous expert elicitation [306; 358; 359]. A number of studies have applied this method as a tool for assessing quantitative risks. For example, expert elicitation has been used in:

- chemical risk assessment and its associated uncertainty [360–363],
- components of risk assessment such as hazard assessment and dose-response evaluation [364; 365]
- exposure assessment [366–370].

One approach to dealing with uncertainties derived from randomness and incompleteness is known as ‘fuzzy set technique’ or ‘fuzzy logic’. Fuzzy logic uses membership functions and linguistic parameters to express areas of uncertainty, lack of information or vagueness [357].

If uncertainty in a risk analysis is not due to randomness or if the available information is in the form of an expert judgment or subjective interpretations of system parameters or imprecisely defined boundaries of parameters, then probabilistic analysis might not be sufficient to represent the true nature of uncertainty. In such cases, fuzzy set theory can be used to incorporate uncertainty into the computational models [371; 372]. This approach enables the analyst to use other types of information (that is, other than statistical data) such as expert knowledge in health risk assessment studies. The probability bounds method is a particular application of fuzzy methods that is well suited to demonstrating the full extent of uncertainty [373].

In contrast to the development of PDFs, fuzzy logic membership functions express the *possibility* of an outcome rather than the *likelihood* of an outcome. In a probabilistic approach, uncertainty is modelled by expressing the determined probability that an event either occurs or does not. But with fuzzy logic, uncertainty is modelled as the degree of membership in the set that defines an outcome [374].

Fuzzy logic may be used to define a degree of membership of an element in a set by means of a membership function. For classical or ‘crisp’ sets, the membership function takes one of only two values: 0 (non-membership) and 1 (membership). In fuzzy logic sets, the membership function can take any value in the interval [0,1]. The value 0 represents complete non-membership, the value 1 represents complete membership, and values in between are used to represent partial membership [375; 376]. Thus fuzzy sets have the capability to express gradual transitions from membership to non-membership and *vice versa*.

Fuzzy logic set theory provides a way to use imprecise, uncertain information generated by human judgments (and other sources) in a structured way. Fuzzy logic also can merge different kinds of parameters such as environmental and health, and quantitative and qualitative.

The key to fuzzy logic inference compared with traditional mathematical models lies in the fact that relationships between inputs and outputs are not determined by complex equations, but by a set of logical rules, reflecting an expert’s knowledge.

However, fuzzy logic has at least has two limitations. Firstly, it relies heavily on subjective inputs; and secondly, it can fail to capture the ranges of values in complex data sets and the correlations among the parameters.

Since some aspects of a risk assessment are more amenable to probabilistic determinations then others, fuzzy logic set theory has been used in combination with probabilistic methods to generate hybrid approaches for risk-assessment studies [377–380]. Kentel and Aral [372] demonstrated the use of a hybrid approach for risk assessment with a case study considering chemical contaminants in tap water as the source of contaminants in a human exposure model. The tap water concentration of the contaminant and cancer potency factors for ingestion, inhalation and dermal contact were treated as fuzzy variables while the remaining model parameters were assessed using PDFs.

As an alternative to two-dimensional probabilistic analysis, a two-dimensional Fuzzy Monte Carlo Analysis (2D FMCA) has been proposed [381]. In this approach, instead of describing the parameters of PDFs used in defining the variables of the risk equation as random variables, they are described as fuzzy numbers. The data requirements for the fuzzy variables are considered to be comparatively less or easier to obtain compared to probabilistic analysis.

The membership functions of the parameters of the random variables are formed using imprecise, vague information or expert judgement. Thus, it was suggested that application of the 2D FMCA approach to risk assessment problems instead of various one-dimensional probabilistic approaches may be more realistic for some cases and may provide sufficient information for making decisions.

The application of the fuzzy set theory in propagating uncertainties in health risk assessment is relatively new, and well established procedures to evaluate acceptability of fuzzy risk with respect to a clear numerical guideline do not exist [382]. One proposed method involves the use of the possibility and the necessity measures in decision making [378; 379]. This approach has been furthered with the introduction of a new measure, the risk tolerance measure, which combines the possibility and the necessity measures into a single measure to evaluate the acceptability of the fuzzy risk [382]. Another alternative approach involves 'defuzzifying' the fuzzy risk in order to compare it with the numerical standard [382; 383].

8.9 Presentation of probabilistic analysis results

The results of probabilistic analyses should be presented along with a complete and thorough description of the model parameters, construction and equations [262; 289]. This would include all formulae used to estimate exposure point concentrations, exposure doses, toxic potencies, hazard indices, or incremental life-time cancer risks [264]. The key presentation objectives should be transparency and reproducibility. Accordingly, sufficient description should be provided such to allow independent model duplication and verification.

Detailed information on the modelled input PDFs should be included. This information should identify whether each PDF represents largely inherent variability or largely uncertainty, or some combination of the two. To the extent that it is possible, the input PDFs should be specified such that they capture both the variability and uncertainty and permit these two components to be analysed separately [264].

Presenting data as both a PDF plot and cumulative distribution frequency plot is useful since these provide different, but equally important insights. A PDF plot displays the relative probability of values allowing visual identification of the most likely values, the shape of the distribution (such as skewness, kurtosis), and small changes in probability density. A cumulative distribution frequency plot provides a clear indication of fractiles (including the median), probability intervals (including confidence intervals), stochastic dominance, and differences between mixed, continuous and discrete distributions. It has been recommended that the associated PDF and cumulative distribution frequency plots should be provided together using identical horizontal scales [262].

It is also recommended that numerical data be presented in tabular form showing key summary statistics such as the following [264].

- the mean
- the standard deviation
- the minimum (if one exists)
- the 5th percentile
- the median
- the 95th percentile
- the maximum (if one exists).

The outcomes of numerical and graphical goodness-of-fit tests should be included for fitted input data as well as any output data for which attempts have been made to fit it to a specific distribution [264].

Probabilistic sensitivity analysis for all of the key inputs contributing to a derived PDF should be undertaken and the outcomes displayed in a way as to distinguish the effects of variability from uncertainty. It is recommended that the outcomes of sensitivity analyses be represented in graphical form [264].

Covariance among input variables can significantly affect the analysis output. Accordingly, any dependencies or correlations among input data should be identified and discussed. If it is considered possible that one or more moderate or strong correlations may exist, but no data are available to estimate them, it is recommended to display and discuss the results of a correlation sensitivity analysis [264].

In circumstances where traditional deterministic (point) estimates are commonly used, it is helpful to also calculate these using established protocols. The outcome point estimates may then be indicated graphically on the PDF generated by probabilistic analysis [264] or the two approaches may be compared in more detail [292].

9. Exposure Scenarios

Many well-established exposure calculations are available for estimating the intake rate of chemical substances assuming a variety of exposure scenarios. The equations used for these calculations may vary somewhat in their construction and terminology as adopted by various international agencies, guidelines and texts. However, generically, they tend to be conceptually consistent with many of the equations provided by the National Research Council's 'Red Book' in 1983 [3] and adopted in US EPA risk assessment guidance for human health evaluation in 1989 [80]. It is these versions of some of the now standard calculations that are presented in the following sections.

Exposure scenarios that may be relevant to some recycled water applications include use as a drinking water source (intentionally or not), recreational use (swimming), and edible crop irrigation. Each of these may involve various oral, inhalation or dermal adsorption exposure pathways. Some of the most important of these scenarios and pathways are described in the following sections.

The specific inclusion of various exposure scenarios or pathways is not intended to suggest that these are the most important for any particular recycled water application. In some cases, many of the discussed scenarios and pathways may be insignificant or irrelevant, while others that have not been included here may be significant. In each case, it is essential to consider the likely scenarios and pathways for any recycled water application (issue identification) and then to give careful consideration to all of the potentially important scenarios.

This section ends with a brief discussion of fugacity modelling—a technique that may be used to estimate potential concentrations of chemicals in various environmental compartments based on a real or hypothetical recycled water application. The estimated intake rate is expressed in units of mg/kg/day (or $mg.kg^{-1}.day^{-1}$).

9.1 Risk-based exposure calculations

The calculation of risks (for non-threshold chemicals) and hazard quotients (for threshold chemicals) requires the determination of 'exposure', usually as a function of water, soil or air concentration and other parameters describing the level of contact. Exposure may be calculated, depending on the identified exposure scenario.

9.1.1 Oral exposure by drinking water

In the case of using the final treated recycled water as a potable water supply, exposure would be typically determined as defined in Equation 10 [80]. This equation considers oral exposure only and does not account for potential inhalation or dermal exposure of chemicals in drinking water.

Equation 10: Calculation of exposure to chemicals in drinking water [80]

$$\text{Intake } (mg.kg^{-1}.day^{-1}) = \frac{CW \times IR \times EF \times ED}{BW \times AT}$$

CW = Chemical concentration in water (mg/L)
IR = Ingestion rate (L/day)
EF = Exposure frequency (days/year)
ED = Exposure duration (years)
BW = Body weight (kilograms)
AT = Averaging time (period over which exposure is averaged, days)

The default deterministic values of the terms in Equation 10 as proposed by the US EPA are as follows:

IR: The US EPA commonly uses the default average ingestion rate assumption of 2 litres per day for adults (and 1 litre per day for children). These figures are assumed to be upper-percentile values across the general population, and data provided in the US EPA Exposure Factors Handbook generally supports this [320; 384]. However, assessors are encouraged to use more specific values that most accurately reflect the exposed population (in terms of age, etc). Many such values are available in table form for simple look-up [320; 384].

EF: The exposure frequency refers to the number of days per year that a person is expected to be exposed to the water source (and partake in the assumed average ingestion rate). For residents it is normally assumed to be 365 days per year.

ED: The exposure duration is the number of years that a person is assumed to be exposed to the particular contamination source. Lifetime exposure is conventionally assumed to be 70 years. However, the 1997 Exposure Factors Handbook recommends the use of 75 years to reflect the (US) average life expectancy of the general population [384]. Suggested adjustments are also provided for sex and race. Based on US data, time spent living at a single residence is commonly assumed to be 30 years (based on an upper-bound limit). The median time at a single residence is assumed to be nine years [384]. If relevant local (and current) data are available, they should be preferentially used.

BW: Body weight is commonly assumed to be 70 kilograms for an adult, which is an average value used by the US EPA (71.8 kilograms is the actual mean value [384]). However, in many circumstances it may be more appropriate to use age-specific values, which are available from the US EPA Exposure Factors Handbook [320; 384].

AT: The averaging time is generally assumed to be a pathway specific period for non-carcinogenic effects (ie. ED x 365 days/year) and lifetime for carcinogenic effects (that is: 70 years x 365 days/year).

9.1.2 Dermal adsorption

Some exposure scenarios including showering, bathing and swimming may require the estimation of a dermally adsorbed dose (DAD) of chemical contaminants in the water. The dermally adsorbed dose may be calculated using Equation 11 [385].

Equation 11: Calculated risk from dermal exposures to carcinogenic contaminants in water [385].

$$\mathrm{DAD}\ (\mathrm{mg.kg^{-1}.day^{-1}}) = \frac{\mathrm{DA_{event}} \times \mathrm{EV} \times \mathrm{ED} \times \mathrm{EF} \times \mathrm{SA}}{\mathrm{BW} \times \mathrm{AT}}$$

DA_{event} = Adsorbed dose per event (mg/cm^2/event)
EV = Event frequency (events/day)
ED = Exposure duration (years)
EF = Exposure frequency (days/year)
SA = Skin surface area available for contact (cm^2)
BW = Body weight (kilograms)
AT = Averaging Time (days)

The default deterministic values for many of the terms in Equation 11 are the same as those described above for Equation 10.

The remaining values are as briefly described below:

DA_{event}: The assumed adsorbed dose per event is chemical-specific and can be estimated from calculations and data provided by the US EPA [385]. It is a function of a calculated chemical-specific dermal permeability co-efficient- K_p ($cm.hr^{-1}$) and event duration- t_{event} (hours per event).

EV: The event frequency is the assumed number of days per year that the exposure scenario is encountered. Recommended values for central tendency and reasonable maximum exposure scenarios are provided in Table 33.

SA: Skin surface area available for contact is typically assumed to be 18,000 cm^2 for adults and 6600 cm^2 for children [385].

Table 33: Recommended dermal exposure values for central tendency and reasonable maximum exposure residential scenarios—water contact [385].

Exposure Parameters	*Central tendency scenarios*				*Reasonable maximum exposure scenarios*			
	Showering/ bathing		*Swimming*		*Showering/ bathing*		*Swimming*	
Cw (mg/cm^3)	Site-specific							
EV (events/day)	1		Site-specific		1		Site-specific	
EF (days/year)	350		Site-specific		350		Site-specific	
t_{event} (hours/event)	Adult	Child	Adult	Child	Adult	Child	Adult	Child
	0.25	0.33	Site-specific		0.58	1.0	Site-specific	
ED (years)	9	6	9	6	30	6	30	6
SA (cm^2)	18000	6600	18000	6600	18000	6600	18000	6600
K_p (cm/hr)	Chemical-specific							

9.1.3 Accidental ingestion while swimming

Recreational use of water for swimming may involve accidental ingestion of small quantities of water. Calculation of exposure to chemicals by ingestion of water while swimming is presented in Equation 12 [80].

Equation 12: Calculation of exposure to chemicals by ingestion of water while swimming [80]

$$\text{Intake } (mg.kg^{-1}.day^{-1}) = \frac{CW \times CR \times ET \times EF \times ED}{BW \times AT}$$

CW = Chemical concentration in water (mg/L)
CR = Contact rate (equivalent to ingestion rate) (L/hour)
ET = Exposure time (hours/event)
EF = Exposure frequency (days/year)
ED = Exposure duration (years)
BW = Body weight (kilograms)
AT = Averaging time (period over which exposure is averaged, days)

CR: The contact rate (assumed ingestion rate) from recreational swimming has been assessed based on a 2006 study on recreational activities in a swimming pool [386]. The draft 2009 update to the US EPA Exposure Factors Handbook recommends a mean water ingestion rate of 49 millilitres per hour for children under 18 years of age and 21 millilitres per hour for adults [320]. Because the data are limited, the upper-percentile water ingestion rates

for swimming activities are based on the maximum values observed in the study: 205 millilitres per hour for children and 71 millilitres per hour for adults.

ET and EF: The exposure time refers to the (average) amount of time spent per swimming event, while exposure frequency is the number of days per year that a person is assumed to partake in a (relevant) swimming event. In many cases these may be scenario-specific, but representative data are available from the US EPA [320].

9.1.4 Inhalation of volatile chemicals

In some exposure scenarios for some chemicals, inhalation exposure of volatile chemical contaminants may be relevant. Inhalation exposure is typically calculated according to Equation 13 or equivalent [80].

Equation 13: Inhalation of airborne (vapour phase) chemicals [320]

$$\text{Intake (mg.kg}^{-1}\text{.day}^{-1}) = \frac{\text{CA x IR x ET x EF x ED}}{\text{BW x AT}}$$

CA = Chemical concentration in air (mg/m^3)
IR = Inhalation rate (m^3/hour)
ET = Exposure time (hrs/day)
EF = Exposure frequency (days/year)
ED = Exposure duration (years)
BW = Body weight (kilograms)
AT = Averaging time (period over which exposure is averaged, days)

The default deterministic values for many of the terms in Equation 13 are the same as those described above for Equation 10. The remaining values are as briefly described below:

CA: The chemical concentration in air is a site-specific or modelled value, depending on the volatility (Henry's Law coefficient) of chemical and environmental conditions.

IR: The established adult inhalation rate defaults are a mean value of 20 cubic metres per day and an upper-bound value of 30 cubic metres per day. An all-age group showering rate of 0.6 cubic metres per day has been widely used [80]. A wide range of more specific inhalation rate values are available from the US EPA Exposure Factors Handbook [320; 384].

ET: The exposure time requires scenario-specific values (dependent on duration of exposure-related activities). A median of seven minutes and an upper percentile of 12 minutes for showering have been widely used [80].

EF: The exposure frequency is a pathway-specific value (dependent on frequency of showering or other exposure-related activities). Default values for many relevant activities and scenarios are available from the US EPA Exposure Factors Handbook [320; 384].

9.1.5 Other exposure pathways

In some cases additional exposure pathways may be relevant including ingestion or dermal exposure of contaminated soil, ingestion of contaminated food. Additional guidance and default values for each of these pathways are available [80; 267; 320; 384].

9.2 Probabilistic exposure scenarios

Water contaminant exposure scenarios, such as potable water consumption or accidental ingestion of non-potable water are inherently variable parameters and thus they are highly suited to analysis as stochastic variables. Stochastic and probabilistic treatment of water

exposure scenarios have been applied in an increasing number of published investigations [356; 387; 388].

The US EPA has stated that accounting for variability and uncertainty is fundamental to exposure assessment and risk analysis [320]. Recent publications have emphasised that characterising and communicating uncertainty and variability should be done throughout all components of the risk assessment process [319; 320]. Proper characterisation of variability and uncertainty in exposure scenarios will also support effective communication of risk estimates to risk managers and the public [320].

The implementation of probabilistic assessment for a range of potential recycled water exposure scenarios are described in the following sections. Since exposure is most commonly normalised to body weight (units of $mg.kg^{-1}.day^{-1}$), fitted PDFs of body weight are often useful for probabilistic analysis and suitable data can be obtained from the US EPA Exposure Factors Handbook [320; 384].

9.2.1 Potable water consumption

The distribution of water intakes is usually, but not always, lognormal [384].

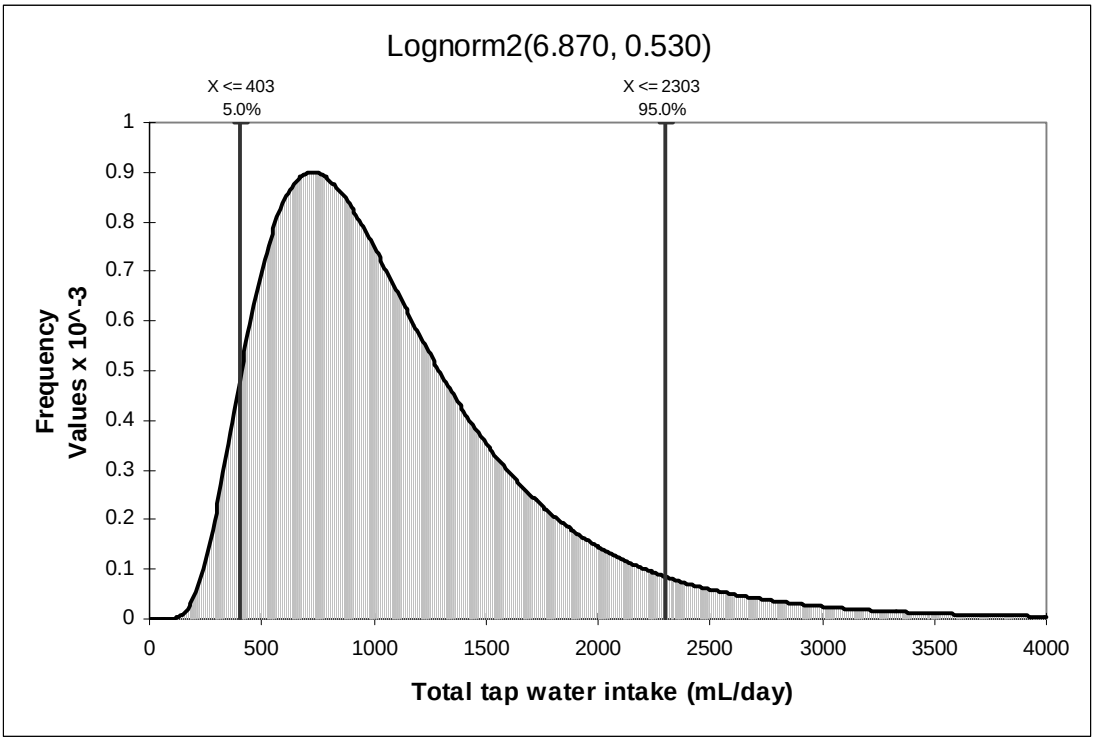
Stochastic parameters were provided for potable water consumption in the 1997 edition of the US EPA Exposure Factors Handbook [384]. Among the studies cited in that document was a paper published by Roseberry and Burmaster in 1992 describing lognormal distributions fit to data obtained from a US survey (of 26,446 individuals) for both total water intake and tap water intake for children and adults in a variety of age groups [389]. Note that in this case, lognormal (format 2) is used.

Table 34: Best-fit lognormal (format 2) distributions for total tap water intake [384; 389].

Group	μ	σ	R^2
0 < age < 1	5.587	0.615	0.970
1 ≤ age < 11	6.429	0.498	0.984
11 ≤ age < 20	6.667	0.535	0.986
20 ≤ age < 65	7.023	0.489	0.956
65 ≤ age	7.088	0.476	0.978
All ages	6.870	0.530	0.978
Simulated balanced population	6.864	0.575	0.995

The summary statistics from Table 34 can be used directly to calculate quantiles (percentiles) and averages for total tap water intake [384; 389]. For example, the median (50th percentile) is given by $\exp(\mu)$ and the mean is given by $\exp(\mu + 0.5.\sigma^2)$ (see Table 14). Alternatively, the summary statistics may be used directly to define the full distribution for a probabilistic analysis. An example is provided in Figure 73 for the lognormal distribution for total tap water intake for all ages.

Figure 73: Lognormal distribution for total tap water intake (all ages)



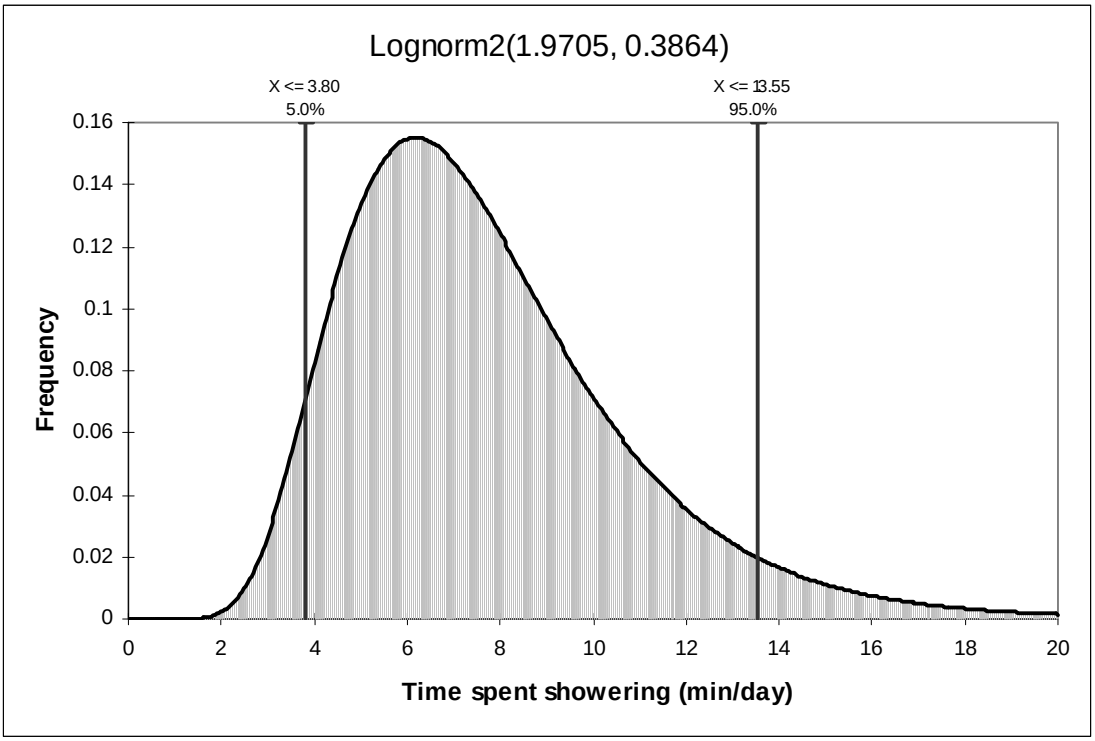
The 'simulated balanced population' of intakes listed in Table 34 are not recommended for current use since it corrects the 1978 original data only for differences in the age structure of the US population between 1978 and 1988 [384]. More recent US drinking water data is presented in the external review draft of the 2009 update of the US EPA's exposure factors handbook [320]. Summary statistics are unfortunately not provided; however, in many cases a suitable number of fractiles are (including 10th, 25th, 50th, 75th, 90th, 95th and 99th percentiles). These data can effectively be used to fit a lognormal cumulative distribution function with the aid of software such as @Risk. However, it is noted by the US EPA that the data on which the Roseberry and Burmaster (1992) distributions were based includes rates that, in general, are similar to those provided in the current key study (which includes data from 1994–1996 and 1998) [320].

A more sophisticated approach to probabilistic description of water consumption can include a more broad consideration of age groups, factors such as pregnancy, and quantities of tap water consumed as a component of prepared foods [387]. Lognormal distributions for total water intake and tap water intake by pregnant and lactating women in the United States have been reported [390].

9.2.2 Showering

Showering is an exposure scenario that can include both dermal adsorption and inhalation of some chemical constituents in water. Time spent showering was investigated as part of a comprehensive study of domestic water use involving 3000 households in Perth, Western Australia for a 2-week period during the year July 1981 to June 1982 [391]. The showering data from this survey has been recast as a lognormal (format 2) distribution suitable for probabilistic analysis, with μ = 1.9705 and σ = 0.3864 [392] as represented in Figure 74.

Figure 74: Lognormal distribution for time spent showering



A further important parameter for dermal adsorption exposure scenarios (including showering as well as swimming) is skin area. A lognormal distribution for skin area as a function of body weight has been previously reported with the following mean and standard deviation parameters [393]:

$$\mu_{\text{skin area}} = 0.6821 \times \mu_{\text{body weight}} - 2.2781$$

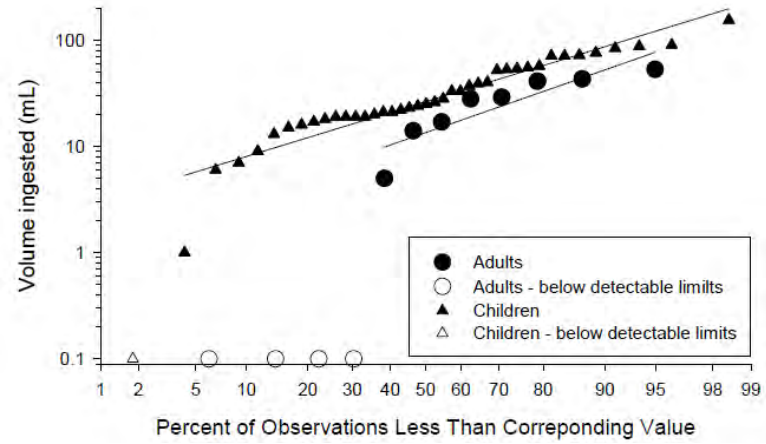
$$\sigma_{\text{skin area}} = 0.6821\ \sigma_{\text{body weight}}$$

Lognormal distributions fitted to percentiles of body weight for males and females as a function of age from six months to 74 years are also available in the literature [394].

9.2.3 Recreational swimming

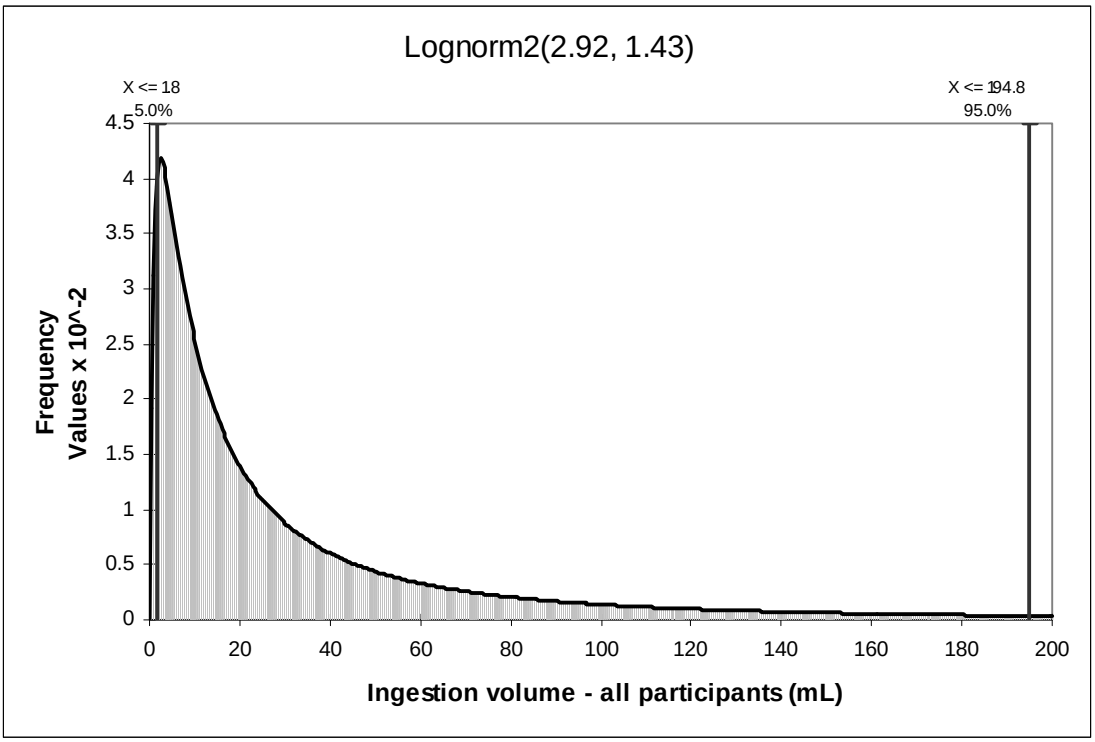
For recreational exposure, it has previously been assumed that individuals are exposed to reclaimed water through accidental ingestion while participating in recreational activities in undiluted reclaimed water [395]. The key data used to characterise the volume of water ingested during recreational activities was taken from a previously published report of water ingestion during swimming activities in a pool [386]. Raw data from that investigation was acquired and fit to statistical distributions as depicted in Figure 75 using the method of maximum likelihood [395].

Figure 75: Ingestion volumes during recreation activities [386] fit to a lognormal distribution [395]



The resultant lognormal (format 2) distribution was determined with μ = 2.92 and σ = 1.43 based on all subjects in the study is presented in Figure 76.

Figure 76: Lognormal (format 2) distribution of ingestion volume of recreational water



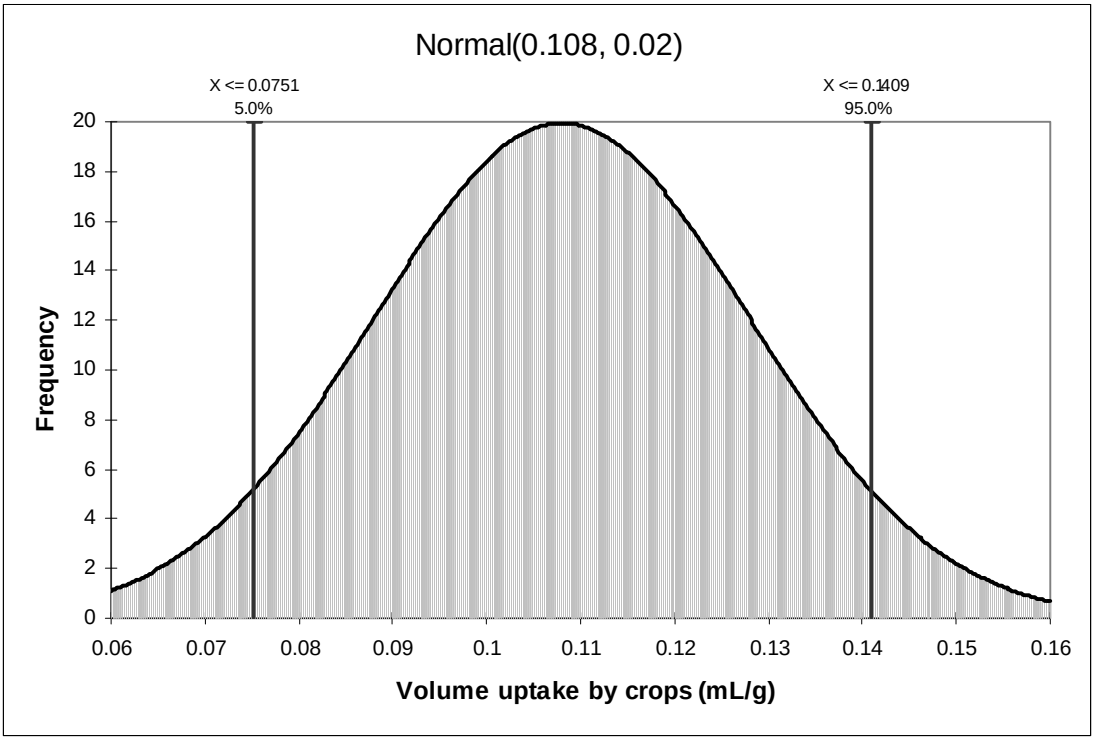
9.2.4 Crop irrigation

For exposure to recycled water by crop irrigation it has previously been assumed that the ingestion of reclaimed water is the product of three distributions: consumption of crops irrigated with reclaimed water (grams per kilogram-day [g/kg-day]), body mass (kilograms), and volume uptake (millilitres per gram) [396].

In a microbial risk assessment study, crop consumption was based on lettuce since this was assumed to be a higher exposure scenario relative to other vegetables [395; 397]. The

consumption value for lettuce was a point estimate of 0.205 g/kg-day [397]. Body mass was estimated by a lognormal (format 1) distribution with μ = 61.429 and σ = 13.362 kg [384]. Volume uptake was estimated as a normal distribution with μ = 0.108 and σ = 0.02 millilitres per gram [396] (Figure 77).

Figure 77: Volume uptake of recycled water by irrigated crops



9.3 Fugacity modelling

In many situations, environmental concentrations of specific chemical contaminants are unknown and, in some cases, unmeasurable. One example is when a risk assessment is to be undertaken for a proposed development that is not yet in place or operational. In this case, the assessment is to be undertaken for a hypothetical scenario and direct environmental sampling is obviously not possible. In such situations, environmental modelling techniques can be useful.

In the absence of comprehensive quantitative analytical data, modelling techniques can provide useful estimations of overall fate and behaviour of individual chemical components. Although such techniques are limited by the availability of high-quality site-specific characterisation data, they represent valuable tools for the broad evaluation of the distribution and removal of chemicals in the environment.

One well-established approach to environmental modelling of chemical fate in known as fugacity modelling. Fugacity modelling techniques can be used to model the multimedia environmental fate of chemical contaminants in water used for a variety of applications. A series of fugacity models of variable complexity have been developed since the 1980s [398–402].These models use physical-chemical properties, reactivity, transport characteristics and the extent of production (or release) of the modelled chemical in the environment to produce a comprehensive picture of environmental behaviour.

Fugacity models rely on defined environmental compartments such as air, water and soil. By equating the fugacity of a chemical in each of the compartments, an environmental distribution is calculated. Variable removal processes such as advection or degradation provide determinations of final concentrations among the defined compartments.

Fugacity (*f*) can be described as the 'escaping tendency' of a chemical from a phase or compartment. It has units of pressure and can be related to concentration (C) by the use of a fugacity capacity constant (Z), with units of $mol.m^{-3}.atm^{-1}$, as shown in Equation 14.

Equation 14: Relationship of chemical concentration and fugacity by fugacity capacity constant

$$C = Zf$$

Z is a function of temperature, pressure, the nature of the substance, and the medium in which the substance is present. Its concentration dependence is usually slight at high dilutions. A system is assumed to be at equilibrium where *f* is equal for all phases.

Established methods are available for calculating fugacity capacity constants (Z) for a solute in a system component medium (air, water, biomass) [398].

The rates of transport and transformation processes are given by the relationship presented in Equation 15, where D is the fugacity rate parameter.

Equation 15: Rate of transport and transformation processes as a function of fugacity and fugacity rate parameter

$$\text{rate } (mol.h^{-1}) = Df$$

Three types of D values are assigned. These are for flow, degradation and volatilisation. Degradation D values can be determined for chemical transformation reactions, biotransformation and photolysis.

Once the fugacity rate parameters are calculated, steady-state mass balance equations can be derived and solved for the fugacities. The various concentrations and rates are calculated and the overall mass balance of the system is assembled.

In a well-defined situation, fugacity models can be used to estimate prevailing concentrations under steady-state and unsteady-state conditions. The fugacity concept has been applied by many research groups internationally to a variety of chemicals and environmental conditions [403–411]. An illustration of how fugacity modelling may be used to predict the fate of organic chemicals in water reuse applications is available [412]. Fugacity modelling has also been used to model and predict the fate of trace chemical contaminants during secondary waste water treatment plant processes [413; 414].

10. Hazardous Events and System Reliability

Quantitative health risk assessments for water recycling schemes tend to focus on the estimation of chemical and pathogen concentrations expected when a scheme is operating under normal performance conditions. However, few assessments effectively account for the issues of treatment plant reliability and associated water quality variability. Although the technology exists to provide extremely high quality water under normal conditions, in some circumstances, the risks to public health are determined by the performance reliability of the system.

For contaminants for which environmental or health impacts are predominantly associated with long-term exposure (such as carcinogens), occasional short-term events may be relatively unimportant since the effect depends upon the long-term average dose. However, for contaminants with health effects associated with acute exposures (such as pathogens or acute chemical toxins), individual events resulting in short-term increases in exposure may be highly significant [324].

The vast majority of observed waterborne disease outbreaks in developed countries during the past few decades have been associated with 'hazardous events' such as unusual weather patterns, plumbing errors or treatment failures [415; 416].

A comprehensive review of published case studies of waterborne disease outbreaks in developed countries revealed that factors contributing to outbreak failures included the following [415; 417]:

- wastewater contamination
- inadequate knowledge of source water hazards
- inadequate disinfection
- extreme weather (for example, heavy precipitation and runoff)
- filtration failures
- cross-connections and distribution failures
- livestock or wildlife faecal contamination
- plant maintenance or treatment process changes.

In practically all of the reviewed outbreaks, more than one mechanism was involved and vulnerable conditions had often been in place for years, if not decades [417]. The authors conclude that in hindsight, all of these outbreaks were preventable, often with even a modest level of foresight and care.

'Consequences' of hazardous events may be evaluated in terms of change in chemical concentrations and exposures that may be the result of a specific hazardous event occurring. For example, changes in chemical exposure can be assessed for a wet weather situation leading to an increased hydraulic flow (or bypass) through a wastewater treatment plant and thus reduced treatment performance and final water quality.

Techniques for quantitatively assessing the likelihoods of specific hazardous events could be investigated including the use of historical data such as weather patterns and frequencies of power failures or plumbing errors. An alternative approach is by the use of available

mechanical reliability measures such as Critical Component Analysis methodology [88; 278; 279; 418].

Reliability of a system has been defined as 'the ability to perform the specific requirements free from failure' or 'the probability of adequate performance for at least a specified period of time under specified conditions' [335]. A treatment plant (or process) is completely reliable if there is no failure in process performance (for example, water quality performance violations). Failure of a treatment process has been defined by Equation 16 as when the required effluent water quality is exceeded [335].

Equation 16: Definition of water treatment process failure [335]

$$\text{Failure} = \text{effluent concentration} > \text{effluent requirements}$$

Because of the numerous uncertainties underlying the design and operation of unit water treatment processes, there is some risk of failure that is inevitable. This risk should be recognised and it is considered that water treatment plants ought to be designed on the basis of an acceptable measure of risk. In a technical definition, the essential concept of reliability is 'probability of success' or 'probability of adequate performance'; that is, the proportion of the time that effluent concentration meets the requirements as determined by Equation 17.

Equation 17: Definition of reliability for water treatment process performance [335]

$$\text{Reliability} = 1 - P(\text{failure}) = 1 - P(\text{effluent conc.} > \text{requirements})$$

The probability of failure is extremely sensitive to the PDF of effluent concentration. Thus, to develop a reliability model, the distribution of effluent concentration should be modelled first. If the PDF of effluent concentration can be determined, then the reliability of the treatment process can be computed. If an expression can be found that gives the fraction of the time that a given concentration has been exceeded in the past, the future performance of the plant can be predicted provided process variables remain the same.

A treatment process with 99 per cent reliability is expected to have between three to four violations in one year (3.65 failure days in 365 days). If a treatment process is designed to allow no more than one violation per year, its reliability should be at least 99.7 per cent.

Because of variations in effluent quality performance, a treatment process should be designed to produce an average effluent concentration below the required water quality standards. The question that must be considered is, what mean value (m_x) guarantees an effluent concentration consistently less than the standard within a certain reliability? To answer this, the coefficient of reliability (COR) has been introduced to relate mean constituent values (that is, design values) to the standard that must be achieved (X_s) on a probability basis (Equation 18).

Equation 18: Determination of mean effluent design value based on a fixed standard and COR [335]

$$m_X = (\text{COR})X_S$$

For a lognormally distributed parameter (which quality contaminants often are), the expression given in Equation 19 has been derived [335].

Equation 19: Determination of COR for a lognormally distributed water quality parameter [335]

$$COR = m_X/X_S = (V^2_X + 1)^{1/2} \exp(-Z_{1-\alpha}[\ln(V^2_X + 1)]^{1/2})$$

Where: α = the probability of failure ($X<X_S$), Z = a percentile derived from the cumulative probability P(1-α), V_X = the co-efficient of variation of X.

The co-efficient of variation (V_X) is a function of the mean and standard deviation of the data (X) and thus may be determined when there is sufficient data to determine these. Table 35 provides an illustration of COR as a function of V_X and reliability based on a true lognormal distribution [335].

Table 35: COR as a function of V_X and reliability based on a true log-normal distribution [335]

Reliability:	*50%*	*80%*	*90%*	*92%*	*95%*	*98%*	*99%*	*99.9%*
V_X								
0.3	1.04	0.81	0.71	0.69	0.64	0.57	0.53	0.42
0.4	1.08	0.78	0.66	0.63	0.57	0.49	0.44	0.33
0.5	1.12	0.75	0.61	0.58	0.51	0.42	0.37	0.26
0.6	1.17	0.73	0.57	0.54	0.47	0.37	0.32	0.21
0.7	1.22	0.72	0.54	0.50	0.43	0.33	0.28	0.17
0.8	1.28	0.71	0.52	0.48	0.40	0.30	0.25	0.15
0.9	1.35	0.70	0.50	0.46	0.38	0.28	0.22	0.12
1.0	1.41	0.70	0.49	0.44	0.36	0.26	0.20	0.11
1.2	1.56	0.70	0.46	0.41	0.33	0.22	0.17	0.08
1.5	1.80	0.72	0.45	0.39	0.30	0.19	0.14	0.06

The COR was originally proposed to aid activated sludge treatment plant design. However, it may equally provide a useful measure as a back-calculation to describe an achieved reliability based on observed process performance. For the initially proposed application, the following example was provided to describe the implications of Table 35 [335]:

> To have 95 per cent reliability that effluent BOD concentration is equal or less than a certain standard X_S, when V_X for the plant is estimated to be 0.70, the plant should be designed for the mean value equal to or less than 0.43 X_S. (If X_S = 30 mg/L; then average BOD = 0.43 x 30 = 12.9 mg/L or less. Similarly, for a less stringent standard of X_S = 40 mg/L; average BOD = 0.43 x 40 = 17.2 mg/L or less).

The actual operational COR can be calculated based on observed performance data by the relationship presented in Equation 20.

Equation 20: Determination of operational COR based on performance data

$$COR_{(data)} = 1/(Z_{1-\alpha}.V_X + 1)$$

where the percentile Z is calculated from the data.

It was proposed (three decades ago) that the coefficient of reliability may be a useful parameter by which to set water treatment design standards [335]. Similarly, it may be a useful measure to define treatment process reliability for risk assessment applications.

10.1 Critical component analysis

A critical component analysis can be carried out by creating a list of all components in a facility and then categorising the components by treatment unit, component and subcomponent [278]. Data are collected for all planned and unplanned maintenance events.

These data are aggregated and then used to compute performance statistics for treatment units and for individual components in the treatment system. The performance statistics describe the expected time between failures for treatment units, the overall mean time between failures of components, and the fraction of time that a unit or component was operating, either including or excluding preventative maintenance. Examples of the type of data that may be accumulated are presented in Table 36 [278].

Table 36: Plant performance statistics for mechanical reliability [278]

Treatment unit	*Number of maintenance events*[1]	*Number of unplanned events*[2]	*ETBF (days)*[3]	*Operating availability*[4]
Headworks	16	13	26	0.9953
Primary	36	28	41	0.9985
Secondary	82	40	9	0.9757
Tertiary	30	27	13	0.9994
UV	1	1	212	0.9991
RO	55	35	10	0.9990

[1]Number of times repairs were made including scheduled maintenance on components within the given unit.
[2]Number of times repairs were made due to component failure with the unit.
[3]Expected time between failure somewhere in the unit process, based on chi-squared distribution.
[4]Fraction of the study period that all components in the unit were operating.

The data in Table 36 indicate that there were a number of planned and unplanned maintenance events on each unit process. The expected time between failures within the unit processes varied between nine and 212 days. The operating availability, defined as the fraction of the study period that all components in the unit were operating for each of the treatment units was greater than 0.97. The authors of this study concluded that all treatment units were operational more than 97 per cent of the time and that neither component maintenance nor failure caused a significant interruption in the operation of the overall plant [278].

This type of analysis provides a foundation from which an assessment of the inherent reliability of a treatment system may be made. For example, if it can be demonstrated that a treatment facility is operational nearly 100 per cent of the time on a long-term basis, plant performance data (as described in earlier chapters) may be used to evaluate the probability that the effluent will meet a specified set of criteria. Otherwise, it may be necessary to investigate if and how component failures impact treatment plant effluent quality.

The mechanical reliability of an advanced water treatment plant in San Diego was undertaken by determination of the inherent availability and the operating availability [279]. The inherent availability was used as a measure of the fraction of time that the component or treatment unit could be expected to be operational excluding preventative maintenance downtime. The operating availability was used to describe the fraction of the time in which the component or unit was operating.

A statistical analysis was undertaken on the 11 treatment units and the 295 plant components in the water treatment plant. A summary of the statistical parameters rating mechanical reliability indicated mechanical availability (operating and inherent availability) greater than 99 per cent, and that failures within the facility did not affect the overall mechanical reliability of the treatment units.

To investigate the relationship between plant failures and effluent quality, bacteriological indicator organism monitoring results were correlated to plant component failures. The results indicated that there was no observable association between any specific maintenance procedure or plant failure and the occurrence of indicator organisms concentrations above the detection limit.

The established engineering parameters Mean Time Between Failures (MTBF, a function of reliability), and Mean Time to Repair (MTTR, a function of availability) may be used to calculate the operational availability (A_o, the probability that an item is in an operable state at any time) as shown in Equation 21.

Equation 21: Determination of operational availability from MTBF and MTTR

$$A_o = \frac{MTBF}{MTBF + MTTR}$$

Reliability of machinery can be derived through parametric models to serve as population models for failure times arising from a wide range of products and failure mechanisms. Weibull statistics (see Section 6.4, page 78) provide a life distribution model, which has been useful in many engineering applications to derive failure rates [419–421]. The two-parameter Weibull distribution function has been used to derive a reliability function R(t) given by the cumulative form of the Weibull distribution presented in Equation 22.

Equation 22: Reliability function R(t) from the cumulative form of the Weibull distribution

$$R(t) = \int_t^{\infty} f(x)dx = e^{-(x/\beta)^{\alpha}} \qquad t \geq 0,\ \alpha > 0,\ \beta > 0$$

Where α is the Weibull shape parameter, β is the scale parameter, and t is the time of operation.

The scale parameter β has the same units as t and the shape parameter α is a dimensionless quantity. When α=1, representing a constant failure rate, the reliability model is simplified to the form presented in Equation 23.

Equation 23: Reliability function R(t) for a constant failure rate (α=1)

$$R(t) = e^{-\lambda.t} \quad \text{with the failure rate } (\lambda), \quad \lambda(t) = \frac{1}{\beta} = \frac{1}{MTBF}$$

For assessments of maintainability, the random variable is time-to-repair, in the same manner as time-to-failure is the random variable in reliability. For a system in which the repair times follow the Weibull distribution, the maintainability M(t) and MTTR are given by Equation 24.

Equation 24 Maintainability M(t) and MTTR for systems following Weibull distribution

$$M(t) = 1 - e^{[-t/\beta]^{\alpha}} \qquad MTTR = \beta.\Gamma\left[1 + \frac{1}{\alpha}\right]$$

To calculate the maintainability or MTTR of an item, the time required to perform each anticipated repair task is multiplied by the relative frequency with which that task is performed (for example, number of times per year). At the system level, MTTR for a total system is calculated by summing the product of the MTTR's of the replaceable items and their corresponding failure rates; the result is then divided into the sum of all replaceable items' failure rates.

For a water treatment plant, the reliability assessment may be derived through the components and Weibull distribution parameters. The two Weibull parameters, the shape parameter and the scale parameter for key components of a typical advanced water treatment plant are shown in Table 37 [422].

Table 37: Weibull distribution parameters for the advanced water treatment plant components [422]

Item	***Weibull shape parameter (α)***			***Weibull scale parameter (β)*** *(characteristic life hours)*		
	Low	*Typical*	*High*	*Low*	*Typical*	*High*
1. Pre-chlorination						
Cylinders, hydraulic	1	2	3.8	9000000	900000	200000000
Diaphragm, rubber,	0.5	1.1	1.4	50000	60000	300000
gasket, hydraulics	0.5	1.1	1.4	700000	75000	3300000
Valves, recip comp.	0.5	1.4	4	3000	40000	80000
Diaphragm couplings	0.5	2	4	125000	300000	600000
Motors, AC	0.5	1.2	3	1000	100000	200000
Transmitters	0.5	1	2	100000	150000	1100000
Flow instrumentation	0.5	1	3	100000	125000	10000000
Electro-mechanical parts	0.5	1	3	13000	25000	1000000
2. Pre-screening						
Ball bearing	0.7	1.3	3.5	14000	40000	250000
Sleeve bearing	0.7	1	3	10000	50000	143000
Bolts	0.5	3	10	125000	300000	100000000
Couplings, gear	0.8	2.5	4	25000	75000	1250000
gasket, hydraulics	0.5	1.1	1.4	700000	75000	3300000
Gears	0.5	2	6	33000	75000	500000
Joints, mechanical	0.5	1.2	6	1400000	150000	10000000
Nuts	0.5	1.1	1.4	14000	50000	500000
Pins	0.5	1.4	5	17000	20000	170000
Springs	0.5	1.1	3	14000	50000	5000000
Motors, AC	0.5	1.2	3	1000	100000	200000
Controllers, pneumatic	0.5	1.1	2	1000	25000	1000000
Control valves	0.5	1	2	14000	100000	333
Motorised valves	0.5	1.1	3	17000	25000	1000000
Transmitters	0.5	1	2	100000	150000	1100000
Temperature indicators	0.5	1	2	140000	150000	3300000
Flow instrumentation	0.5	1	3	100000	125000	10000000
Electro-mechanical parts	0.5	1	3	13000	25000	1000000
Pressure vessels	0.5	1.5	6	1250000	2000000	33000000
Filters, strainers	0.5	1	3	5000000	5000000	200000000
Check valves	0.5	1	3	100000	100000	1250000
Relief valves	0.5	1	3	100000	100000	1000000
3.Microfiltration / reverse osmosis						
Ball bearing	0.7	1.3	3.5	14000	40000	250000
Roller bearing	0.7	1.3	3.5	9000	50000	125000
Sleeve bearing	0.7	1	3	10000	50000	143000
Belts, drive	0.5	1.2	2.8	9000	30000	91000
Bellows, hydraulic	0.5	1.3	3	14000	50000	100000
Bolts	0.5	3	10	125000	300000	100000000
Clutches, friction	0.5	1.4	3	67000	100000	500000
Clutches, magnetic	0.8	1	1.6	100000	150000	333000

Item	***Weibull shape parameter (α)***			***Weibull scale parameter (β)*** *(characteristic life hours)*		
	Low	*Typical*	*High*	*Low*	*Typical*	*High*
Couplings	0.8	2	6	25000	75000	333000
Couplings, gear	0.8	2.5	4	25000	75000	1250000
Cylinders, hydraulic	1	2	3.8	9000000	900000	200000000
Diaphragm, metal	0.5	3	6	50000	65000	500000
Diaphragm, rubber,	0.5	1.1	1.4	50000	60000	300000
Gasket, hydraulics	0.5	1.1	1.4	700000	75000	3300000
Filter, oil	0.5	1.1	1.4	20000	25000	125000
Gears	0.5	2	6	33000	75000	500000
Impellers, pumps	0.5	2.5	6	125000	150000	1400000
Joints, mechanical	0.5	1.2	6	1400000	150000	10000000
Knife edged, fulcrum	0.5	1	6	1700000	2000000	16700000
Liner, recip. comp.cyl	0.5	1.8	3	20000	50000	300000
Nuts	0.5	1.1	1.4	14000	50000	500000
O-rings elastomeric	0.5	1.1	1.4	5000	20000	33000
Packings, recip.comp.rod	0.5	1.1	1.4	5000	20000	33000
Pins	0.5	1.4	5	17000	20000	170000
Pivots	0.5	1.4	5	300000	50000	1400000
Pumps, lubricators	0.5	1.1	1.4	13000	400000	125000
Seals, mechanical	0.8	1.4	4	3000	50000	50000
Shafts, cent.pumps	0.8	1.2	3	50000	25000	300000
Springs	0.5	1.1	3	14000	50000	5000000
Vibration mounts	0.5	1.1	2.2	17000	25000	200000
Wear rings, cent. Pumps	0.5	1.1	4	10000	50000	90000
Valves, recip comp.	0.5	1.4	4	3000	40000	80000
Circuit breakers	0.5	1.5	3	67000	100000	1400000
Compressors, centrifugal	0.5	1.9	3	20000	60000	120000
Compressor blades	0.5	2.5	3	400000	800000	1500000
Compressor vanes	0.5	3	4	500000	1000000	2000000
Diaphragm couplings	0.5	2	4	125000	300000	600000
Motors, AC	0.5	1.2	3	1000	100000	200000
Pumps centrifugal	0.5	1.2	3	1000	35000	125000
Transformers	0.5	1.1	3	14000	200000	14200000
Controllers, pneumatic	0.5	1.1	2	1000	25000	1000000
Controllers, solid state	0.5	0.7	1.1	20000	100000	200
Control valves	0.5	1	2	14000	100000	333
Motorised valves	0.5	1.1	3	17000	25000	1000000
Solenoid valves	0.5	1.1	3	50000	75000	1000000
Transducers	0.5	1	3	11000	20000	90000
Transmitters	0.5	1	2	100000	150000	1100000
Temperature indicators	0.5	1	2	140000	150000	3300000
Pressure indicators	0.5	1.2	3	110000	125000	3300000
Flow instrumentation	0.5	1	3	100000	125000	10000000
Level instrumentation	0.5	1	3	14000	25000	500000
Electro-mechanical parts	0.5	1	3	13000	25000	1000000

Item	***Weibull shape parameter (α)***			***Weibull scale parameter (β)*** *(characteristic life hours)*		
	Low	*Typical*	*High*	*Low*	*Typical*	*High*
Pressure vessels	0.5	1.5	6	1250000	2000000	33000000
Filters, strainers	0.5	1	3	5000000	5000000	200000000
Check valves	0.5	1	3	100000	100000	1250000
Relief valves	0.5	1	3	100000	100000	1000000
Coolants	0.5	1.1	2	11000	15000	33000
Lubricants	0.5	1.1	3	11000	15000	40000
Lube oils, mineral	0.5	1.1	3	3000	10000	25000
Lube oils, synthetic	0.5	1.1	3	33000	50000	250000
Greases	0.5	1.1	3	7000	10000	33000
4. H_2O_2 addition						
Cylinders, hydraulic	1	2	3.8	9000000	900000	200000000
Diaphragm, rubber,	0.5	1.1	1.4	50000	60000	300000
Gasket, hydraulics	0.5	1.1	1.4	700000	75000	3300000
Valves, recip comp.	0.5	1.4	4	3000	40000	80000
Diaphragm couplings	0.5	2	4	125000	300000	600000
Motors, AC	0.5	1.2	3	1000	100000	200000
Transmitters	0.5	1	2	100000	150000	1100000
Flow instrumentation	0.5	1	3	100000	125000	10000000
Electro-mechanical parts	0.5	1	3	13000	25000	1000000
5. UV-irradiation						
Sleeve bearing	0.7	1	3	10000	50000	143000
O-rings elastomeric	0.5	1.1	1.4	5000	20000	33000
Controllers, pneumatic	0.5	1.1	2	1000	25000	1000000
Control valves	0.5	1	2	14000	100000	333
Transmitters	0.5	1	2	100000	150000	1100000
Temperature indicators	0.5	1	2	140000	150000	3300000
Flow instrumentation	0.5	1	3	100000	125000	10000000
Pressure vessels	0.5	1.5	6	1250000	2000000	33000000
Check valves	0.5	1	3	100000	100000	1250000
Relief valves	0.5	1	3	100000	100000	1000000

Process reliability for a water recycling scheme may be engineered through reliability assessments made using Weibull distribution databases for each of the stages that employs mechanical equipment [422]. Historical MTTR for each component should be tracked and updated through corrective maintenance work orders. The MTBF and MTTR values analysed should be a part of the asset replacement strategy.

Failure events can be defined in terms of both failure to meet treatment quality objectives and failure to meet treatment capacity objectives. For example, if a chlorine dosing plant in the disinfection process fails, treatment quality objective will not be met. Similarly, if a UV lamp fails in a UV disinfection reactor, the treatment system will not provide the necessary log reduction removal for viruses. However, in each case, it is possible for the plant to continue to meet the treatment capacity objective because the failure of the dosing pump or UV lamp does not impact the hydraulic capacity of the process.

11. Epilogue

Water reuse for non-potable applications is an important and well-established component of water management for practically all Australian towns and cities. Water recycling for potable reuse is rapidly emerging as a large-scale solution to dwindling water resources in some Australian cities.

As the uses of highly treated reclaimed wastewaters have developed to involve increasing human exposure and contact, increased attention to the degree of exposure to chemical contaminants in recycled water is essential. A high degree of confidence that public health is fully protected requires a sophisticated understanding of the levels of exposure to potentially hazardous substances and the risks associated with that exposure.

Quantitative chemical exposure assessment for water recycling schemes presents a significant challenge for many utilities, regulators and consultants. It requires an amalgamation of technical knowledge and sophisticated techniques from a diverse selection of fields, including chemistry, toxicology, statistics, risk analysis and mechanical engineering.

This text has presented an overview of some of the more advanced approaches that have been implemented or proposed for the assessment of water recycling schemes internationally. It is intentionally cutting-edge in that many of the techniques described are not routinely used in the Australian water industry and general levels of familiarity with some of them are low. However, all of the methods described have been selected on the basis that they may realistically be adopted where appropriate investments are made in up-skilling.

Many of the techniques described are relatively data-intensive. However, the acquisition of some quantity of data is always necessary in order to have a reasonable characterisation of process performance and water quality. In many cases, existing data is suitable for use in probabilistic exposure assessment. Furthermore, as these techniques are increasingly adopted, it is envisaged that more widely-applicable data will be published in a format that is immediately usable by others.

Like any rapidly developing field, the methods used for quantitative exposure assessment for water recycling schemes will evolve and improve with time. New ideas will emerge allowing an ever-improved understanding of water treatment processes and their effectiveness. Thus it is the job of the dedicated risk assessor to remain open to new developments and opportunities to gain new insights and knowledge.

Many of the techniques described in this document are primarily focused on quantifying exposure to chemicals within the bounds of *normal* operation (as variable as that may be) of an advanced water treatment plant or water recycling scheme. However, all relevant contemporary Australian guideline documents have a clear focus on the issue of *hazardous events*. That is, understanding what might go wrong, what the *likelihood* of it going wrong is, and what the *consequences* of it going wrong are. In many cases, these factors are much more difficult to quantify than the variability of during normal operation.

In time, it is hoped that the types of risk matrices presented in Chapter 3 will be applicable to water recycling schemes in a fully quantitative way. In order to achieve this, it is first necessary to be fully quantifying each of the two axes of the matrix: likelihood and consequences. Techniques such as the critical component analysis described in Chapter 10 will assist in the future improved quantification of hazardous event likelihood. Consequences of hazardous events could be quantified in terms of their impact on increased effluent concentrations and increased exposure to hazardous contaminants. However, a considerable

amount of work is still required to quantitatively relate specific hazardous events to such consequences.

It is notable that many of the key concepts presented in this document were initially proposed for application to advanced water treatment plants and water recycling schemes more than a decade ago. Yet few comprehensive case studies are apparently available. Part of the reason for this may be the lack of a clear guidance document bringing the necessary diverse sources of information together.

This report alone is not sufficient to be used as a comprehensive manual for quantitative risk assessment. However, it is hoped that it will provide a sufficient overview of the key issues, as well as suitable references to more detailed sources of specific information, as to provide a strong starting point for understanding what can be achieved and what should be required in order to comprehensively assess chemical exposure from water recycling schemes.

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