



PATTLE DELAMORE PARTNERS LTD

Impact of Per and Poly Fluoroalkyl Substances on Ecosystems

Ministry for the Environment



Impact of Per and Poly Fluoroalkyl Substances on Ecosystems

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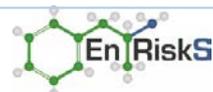
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Executive Summary

General

Per and poly fluoroalkyl substances (PFAS) are a wide range of chemical compounds which have been used in a large number of commercial and industrial products since the 1950s. Recent findings from international research and investigation on PFAS have found that PFAS are highly mobile and persistent in the environment. Due to concerns regarding the persistence, bio-accumulative potential and toxicity of some PFAS compounds, international regulations have begun to phase out some long chain PFAS compounds (most notably PFOS and PFOA).

The Ministry for the Environment (MfE) has engaged Pattle Delamore Partners (PDP) to undertake a literature review of the potential ecological impacts of PFAS in response to a number of site investigations within New Zealand and Australia that have found elevated concentrations of these compounds in surface and groundwater.

The scope of this literature review was to:

- ∴ Peer review globally available research in the realm of [potential] impacts of PFAS compounds on ecosystems.
- ∴ Assess the conclusions of available research and consider their application in a New Zealand context.
- ∴ Outline data gaps and provide recommendations on the scope of research possibilities within New Zealand.

PFAS compounds are persistent and many have a high solubility resulting in dispersal over large distances via water. Consequently, PFAS compounds are wide spread in the aquatic environment. Despite the global distribution of PFAS and active research being undertaken in a number of countries, their fate and transport is still poorly understood, particularly in the aquatic environment. This is because the issues associated with these compounds are complex (in the range of individual compounds as well as the behaviour) and there are many aspects that we still need to understand better. Furthermore, there are only a limited number of published studies relating to PFAS in Australia and none for New Zealand.

Aquatic Environment

For aquatic organisms, documented effects have been reported when organisms are exposed at 1-10 µg/L, where reproductive and developmental effects have been identified in fish fry where the parent fish are exposed. These studies show that there are reproductive and developmental effects (such as infertility, reduced survival of fry and reduced growth).

The main route of uptake of PFAS in aquatic organisms is via contact with water and sediments with some contribution from ingestion of contaminated food; however, the exact mechanisms of uptake are still largely unknown. PFAS tend to accumulate in the body by attaching to proteins. This occurs mainly in blood and organs which accumulate blood (liver and kidneys). While accumulation into muscle occurs to a more limited extent the proportion of muscle in the body can result in significant accumulation of ingested PFAS. Unlike other persistent pollutants, PFAS compounds do not accumulate in fatty tissue. Recent information indicates that different types of PFAS present in more recent formulations of AFFF and other products bind as strongly or more strongly to binding proteins in the blood known to bind the primary PFAS contaminants from historical use. This may mean they bioaccumulate to a similar extent to PFOS or PFOA. Field biomonitoring data does not currently include analysis of these newer PFAS so this report of laboratory assessments cannot currently be validated by field data.

The ability of these types of these compounds to become widely distributed in the aquatic environment and their ability to bio-accumulate in organisms (particularly air breathing organisms) and bio-magnify up the food chain is of concern to apex predators. Sea birds and marine mammals have been shown to accumulate high concentrations of these compounds and, therefore, may be impacted by PFAS discharges into the environment.

Sampling of aquatic organisms near contaminated sites in Australia and New Zealand have shown that they can bio-accumulate very high concentrations of PFOS (up to 20,000 µg/kg) and other long chain PFAS compounds (including PFNA and PFDA).

Testing of marine organisms near PFAS discharges has shown elevated levels of PFAS compounds, particularly among some gastropod species and other invertebrate species. Limited PFAS testing of bivalve species (particularly mussels) near discharges of PFAS contaminated storm water and contaminated sites have only found very low (or non-detected) concentrations indicating that these organisms do not bio-accumulate PFAS compounds strongly. However, further research is needed to confirm this.

The potential impact of PFAS compounds on traditional foods (such as eels, kina, paua and other shellfish species) have not been investigated within New Zealand and there is insufficient information within the literature to understand the potential impacts (if any) that environmental levels of PFAS might have on them. Analysis of tissues from fin fish species within the Waitemata harbour has found very low levels of PFAS compounds in a variety of fish species caught even at control sites.

Terrestrial Environment

The occurrence within the terrestrial environment may be more limited in New Zealand due to the (estimated) relatively small number of PFAS-contaminated sites. The occurrence of PFAS compounds in wild avian species within New Zealand is largely unknown but PFAS concentrations could be elevated in some bird species which live near landfills and Waste Water Treatment Plants (WWTP) as well as some contaminated sites.

For avian species, the primary exposure route is likely to be dietary consumption and, for other terrestrial species, exposure routes are likely to be either direct ingestion of contaminated soil, drinking of contaminated water and/or other dietary exposure.

Ecotoxicological studies of PFOS and PFOA on animals mainly show effects on the liver, gastrointestinal tract, suppression of the immune systems, reproductive organs and on thyroid hormone levels as well as disrupting cell growth in algae.

For other PFAS compounds there are much less toxicological data. Shorter chain PFAS compounds are generally less toxic, and thought to pose an overall lesser environmental risk than PFOS compounds.

Plants

Plant uptake of PFAS compounds is found to increase with increasing soil concentration. However, the factors controlling the uptake of PFAS compounds by plants are very complex and depend on concentration of organic matter, soil pH and concentration of mineral surfaces (i.e. clay content).

Studies on the uptake and toxicity of PFAS compounds in plants indicate that that long chain PFAS compounds (such as PFOS and PFOA) have very low transfer factors and the concentrations of PFHxS, PFOS and PFOA in leaves and fruit of most vegetable species are very low or non-detectable. However, uptake factors are very dependent on soil type and plant species and only a limited number of plant species have been investigated so far. Shorter chain PFAS compounds (i.e. PFBS and PFBA) can be transferred to the above ground parts of plants (i.e. leaves and fruit). However, long chain PFAS compounds largely remain in the roots and storage organs of plants.

There has been very little research on the phytotoxicity of PFAS compounds to plant. Research indicates that significant phytotoxic effects are unlikely to occur at concentrations less than 50 mg/kg, but effects such as decreased shoot weight and height may occur at concentrations greater than 5 mg/kg. Such levels have not been found in most NZ sites.

Impacts of PFAS exposure on New Zealand Ecosystems

There is a paucity of data regarding the concentration of PFAS compounds within the New Zealand environment and in aquatic or terrestrial organisms. There are also limitations on the availability of such data in most environments around the world. Impacts on population dynamics, species distribution, and dispersion, interactions between trophic levels in New Zealand ecosystems (or for ecosystems in other countries) are unclear due to the data limitations and the limited understanding of the mechanisms by which these chemicals cause adverse effects.

For the data available, it is clear that concentration of PFAS compounds within waterways and aquatic organisms at some impacted sites would exceed some toxicity thresholds (particularly for reproductive and development toxicity).

The long-term impact of exposures to low concentrations (as would be expected in typical background areas) is unclear and low-level exposures have not been adequately investigated by researchers. However, there are concerns about the potential long-term impacts on apex predators due to the following factors:

1. Aquatic systems are likely to be the ultimate receiving environment for PFAS compounds.
2. Widespread use of PFAS compounds means they are likely to be present in landfill leachate and WWTP effluents. Landfills and WWTP processes are only likely to transform PFAS compounds into terminal PFAAs so landfills and WWTP effluents are likely to be low level diffuse sources of PFAS contamination into the aquatic environment (and groundwater) over the long term.
3. PFAS have a much longer half-life within the environment than other persistent organic pollutants (i.e. DDT and PCBs).
4. PFAS are only slowly eliminated from some organisms which will allow long term accumulation (some PFAS compounds are very bio-persistent compared to other classes of chemicals).
5. These compounds bioaccumulate within organisms and biomagnify within the food chain, which means that dietary exposure is likely to be an important exposure pathway for some apex species.

Currently, there is insufficient information to determine if current exposure to PFAS is having an adverse effect amongst apex predators in New Zealand. However, evidence exists to indicate that exposure to PFAS compounds can result in reproductive, developmental and immunotoxicity in marine mammals and avian receptors so it is possible that in the future concentrations of these compounds within apex predators may reach levels which could have adverse impacts on the populations of these organisms.

Recommendations

Currently, there is little or no information available on the impact of PFAS on New Zealand ecosystems. Therefore, this study recommends that:

- ∴ A national inventory of PFAS stockpiles, wastes and usage is undertaken to meet the requirements of Article 6 of the Stockholm Convention.
- ∴ Development of additional water quality and biota guidelines for short chain and new PFAS compounds, particularly PFBS, PFNA, ADONA, F35B and GenX.
- ∴ Improved characterisation of the distribution of different classes of PFAS chemicals and precursors in different environmental compartments including soil:porewater:plants:soil biota, groundwater:aquifer solids, dissolved:particulate:sediment:plant:biota in aquatic ecosystems, dissolved:particulate:sewage sludge in WWTPs.
- ∴ Characterisation of the effects and mode of toxicity of PFAS on key native species that are most likely to be exposed.
- ∴ Characterisation of bio-accumulation potential of PFAS in NZ native species.
- ∴ Liaise with Australia and perhaps other countries to develop sediment quality guidelines for PFAS compounds.
- ∴ Make sure that New Zealand is well connected with main international research groups working on PFAS risk characterisation and management.

Glossary of Terms¹

Abiotic A physical or chemical rather than a biological process.

Acidic Having a pH of less than 7.

Acute Exposure Contact with a substance which occurs over a very short period of time (typically 14 days or less).

Absorption The incorporation of a substance in one state into another of a different state (e.g., liquids being absorbed by a solid or gases being absorbed by water). Also defines the process of taking in. For a person or an animal, absorption is the process of a substance getting into the body through the eyes, skin, stomach, intestines, or lungs. See sorption.

Adsorption The adhesion of molecules of gas, liquid, or dissolved solids to a surface. Also see sorption.

AFFF Aqueous film forming foam. A type of firefighting foam which is used to fight class B (flammable liquids such as petrol, aviation fuel, ethanol, etc.).

Alkaline (or basic) Having a pH of greater than 7.

Anion A negatively charged ion.

ANZECC Australia and New Zealand Environment and Conservation Council (see <http://www.waterquality.gov.au/anz-guidelines/guideline-values/default>).

Apex predator A predator at the top of the food chain.

ATSDR Agency for Toxic Substances and Disease Registry (see <https://www.atsdr.cdc.gov/>)

Bio-accumulation The accumulation of a compound within an organism from the uptake of that compound from all possible sources (including water/sediment and dietary exposure).

Bio-accumulation Factor (BAF) is the ratio of a compound within an organism over all source of exposure to that compound. BAF is a result of both bio-concentration and bio-magnification. It takes into account both the exposure from respiratory surface and the dietary exposure.

Bio-concentration The accumulation of a compound within an organism from the uptake of that compound from water.

Bio-concentration Factor (BCF) is the ratio of a compound within an organism over the concentration of that chemical in water.

Bio-availability The fraction (or percentage) of a compound which is taken up by an aquatic organism and reaches the circulation system (i.e. blood). Bio-

¹ Primary sources of definition: EnRisks 2017.

availability assessment requires in-vivo testing (i.e. inside organisms) to determine the absolute amount of a compound which can cause harm to the organism.

Bio-magnification, also known as **bio-amplification** or **biological magnification**, is the accumulation of a substance in the tissues of organisms at successively higher levels in a food chain.

Bio-magnification Factor (BMF) is the ratio of the substances in a predator (mg/kg)/Concentration in the predator's prey (or food) at steady-state (mg/kg).

Trophic Magnification factor (TMF) is the average value of prey to predator magnification over a whole food chain or a part thereof.

Bio-persistent is the tendency for a chemical to remain within an organism, rather than be expelled or metabolised.

Biotic refers to a process relating to or resulting from living organisms. Biotic degradation is the breakdown of substances by a living organisms (usually microbial or fungi).

Cation A positively charged ion.

Chronic Exposure Contact with a substance that occurs over a long time (more than 1 year) (compare with acute exposure and intermediate duration exposure).

Dermal Contact with (touching) the skin (see the route of exposure).

Direct ecotoxicity refers to exposure as a result of organism from contact with contaminated water or soil. Indirect exposure (also called **dietary exposure** or **secondary poisoning**) to exposure as a result of the animal consuming contaminated food.

Dose The amount of a substance to which a person is exposed over some time period. Dose is a measurement of exposure. Dose is often expressed as milligram (amount) per kilogram (a measure of body weight) per day (a measure of time) when people eat or drink contaminated water, food, or soil. In general, the greater the dose, the greater the likelihood of an effect. An "exposure dose" is how much of a substance is encountered in the environment. An "absorbed dose" is the amount of a substance that actually got into the body through the eyes, skin, stomach, intestines, or lungs.

EC50 (median effective concentration) is the concentration of a test substance which is expected to cause a specific toxic effect over a certain time. These toxic effects may relate to growth, reproduction success, avoidance behaviour, immobilisation, etc. For algae the term EbC50 (for algae growth) or ErC50 (algae growth rate) can be used to designate different toxicological endpoints. They are often obtained from acute aquatic toxicity studies. EC5 and EC10 are statistically-derived concentration which, over the specified time period are

expected to cause a specific toxic effect in 5% and 10% of the test organisms. EC5 and EC10 are used instead of LOEC/NOEC values in some guideline derivations.

Exposure Contact with a substance by swallowing, breathing, or touching the skin or eyes. Exposure may be short-term (acute exposure), of intermediate duration, or long-term (chronic exposure).

Exposure pathway The route a substance takes from its source (where it began) to its end point (where it ends), and how people can come into contact with (or get exposed to) it. An exposure pathway has five parts: a source of contamination (such as chemical leakage into the subsurface); an environmental media and transport mechanism (such as movement through groundwater); a point of exposure (such as a private well); a route of exposure (eating, drinking, breathing, or touching), and a receptor population (people potentially or actually exposed). When all five parts are present, the exposure pathway is termed a completed exposure pathway.

Fluorophilic Refers a compound which has an affinity for fluorocarbons. Fluorophilic solutions will increase the solubility of fluorocarbons and fluorophilic surfaces or solids phases will increase the sorption of fluorocarbons.

Fluorotelomer Refers to a tetrafluoro-ethene group which can be joined together to produce straight chain PFAS compounds (in a process called telomerisation) with an even number of carbon atoms.

FSANZ Food Standards Australia New Zealand. Food Standards Australia New Zealand (FSANZ) is a statutory authority in the Australian Government Health portfolio. FSANZ develops food standards for Australia and New Zealand.

Functional Group An atom or group of atoms, acting as a unit, which replaces a hydrogen (or fluorine atom) within the carbon-fluorine chain and thereby changes the chemical characteristics of the molecule (e.g. -COOH, -SO₂, -PO₄, -NH₂).

Guideline Value Guideline value is a concentration in soil, sediment, water, biota or air that is used to identify conditions below which no adverse effects, nuisance or indirect health effects are expected. The derivation of a guideline value utilises relevant studies on animals or humans and relevant factors to account for inter- and intra-species variations and uncertainty factors. Separate guidelines may be identified for protection of human health and the environment. Dependent on the source, guidelines will have different names, such as investigation level, trigger value, ambient guideline etc.

Half-life The time required for a chemical or substances to reduce its concentration to half its initial value. Half-life in this report can refer to **Biological Half-life, Degradation Half-life or Elimination half-life. Biological half-life** is the time it takes to reduce the concentration of PFAS within an

organism to half its initial value. **Degradation Half-life** is the time required to break down a PFSA compound (either into a final PFAA or to an immediate product) to half its initial value. **Elimination half-life** is the time it takes to reduce the concentration of PFAS within the plasma (or blood serum) to half its initial value.

HC5 A term used within the European Union risk assessment process for setting a predicted no effect concentration (PNEC). These are statistical extrapolation to derive a 5th percentile effect concentration (similar to ANZECC 95% ecosystem protection number) using a species sensitive distribution over a sufficient large dataset of ecotoxicity data.

Henry's Law Henry's law states that at a constant temperature the mass of gas dissolved in a given volume of water (i.e. 1 L) is proportional to the partial pressure of the gas. Henry's law constant is an important parameter in predicting chemicals behaviour in the environment. Chemical substances with a low Henry's law constant will tend to remain dissolved in water, whereas a substances with a high Henry's law constant will volatilise from water into the air.

Homologue A series of PFAS compounds that differ by a CF₂ group (i.e. PFHxS is a homologue of PFOS and PFPeS).

Hydrophilic A compound that is polar and attracted to water.

Hydrophobic A compound which is non-polar and is not attracted to water.

Ingestion The act of swallowing something through eating, drinking, or mouthing objects. A hazardous substance can enter the body this way (see the route of exposure).

Inhalation The act of breathing. A hazardous substance can enter the body this way (see the route of exposure).

Immunotoxicity Adverse effects on the functioning of the immune system that results from exposure to a chemical substances or substances. Alteration in the immune system can lead to an increase incidence or severity of diseases, however identifying immunotoxicants is difficult because we currently have an inadequate understanding of how the immune system functions and chemicals can cause a wide range of complicated effects on the immune system.

Ion A negatively or positively charged atom or molecule which has either an excess or shortage of electrons, respectively.

Isomers two or more chemical compounds with the same chemical formula (i.e. PFOS chemical formula is C₈H₁₇O₃S) but a different arrangement of atoms in the molecule and may have different chemical properties.

ITRC Interstate Technology and Regulatory Council (see <https://www.itrcweb.org/>).

K_{oc} organic carbon-water partition co-efficient. Defines the mobility of a substance in soil. A very high value means it is strongly adsorbed onto organic matter and hence does not move throughout the soil. A very low value means it is highly mobile in soil. K_{oc} values for various chemicals range widely; hence it is common practice to report the natural logarithm of the K_{oc} value (log K_{oc}).

LOAEL lowest-observed-adverse-effect-level. The lowest exposure level, at which there are biologically significant increases in frequency or severity of adverse effects between the exposed population and its appropriate control group.

LOEC Lowest observed effects concentration.

Long chain Perfluoroalkyl carboxylic acids (PFCA) with eight carbons or more (seven or more perfluorinated carbons); perfluoroalkyl sulfonates (PFSA) with six or more perfluorinated carbons).

NEPM National Environment Protection Measure. This is a document which details how soil guideline values should be calculated within Australia.

NOAEL No-observed-adverse-effect-level: The highest tested dose of a substance that has been reported to have no harmful (adverse) health effects on people or animals. Some effects may be produced at this level, but they are not considered adverse effects.

NOEC No-observed-adverse-effect-level: Is the concentration in an environmental compartment (water, soil, etc.) which when concentration below this value, an unacceptable effect is unlikely to be observed. It is typically obtained from chronic aquatic toxicity studies and terrestrial toxicity studies. The units of NOEC are mg/L.

Oleophobic A compound that is repelled from oil

PFAS Per- or Poly-fluoroalkyl Substances

PFAA perfluoroalkyl acids. A group of perfluorinated compounds that include perfluoroalkyl carboxylic acid and perfluorosulphonic acids/(sulphonates)

PFCA perfluoroalkyl carboxylic acid

PFBA Perfluorobutanoic Acid

PFBS Perfluorobutanesulfonic Acid

PFPeA Perfluoropentanoic Acid

PFHxA Perfluorohexanoic Acid

PFHxS Perfluorohexanesulfonic Acid

PFHpA Perfluoroheptanoic Acid

PFOA Perfluorooctanoic Acid

PFOS Perfluorooctanesulfonic Acid

PFNA Perfluorononanoic Acid

PFDA Perfluorodecanoic Acid

PFDS Perfluorodecanesulfonic Acid

PFUdA Perfluoroundecanoic Acid

PFDoA Perfluorododecanoic Acid

PFTTrDA Perfluorotridecanoic acid

4:2 FtS 4:2 Fluorotelomer Sulfonic Acid also referred to as 1H.1H.2H.2H-Perfluorohexanesulfonic Acid

6:2 FtS 6:2 Fluorotelomer Sulfonic Acid also referred to as 1H.1H.2H.2H-Perfluorooctanesulfonic Acid

8:2 FtS 8:2 Fluorotelomer Sulfonic Acid also referred to as 1H.1H.2H.2H-Perfluorodecanesulfonic Acid

PFOSA Perfluorooctanesulfonamide.

pH A measure of the acidity or alkalinity of a solution.

pKa The most widely used form of the acid dissociation constant (also known as the acidity constant) which is a quantitative measure of the strength of an acid. This value helps to predict what a molecule will do at a specific pH.

Point of Exposure The place where someone can come into contact with a substance present in the environment (see exposure pathway).

Part per billion (ppb) Denotes one part per 1,000,000,000 parts or one part in 10^9 . Parts-per-billion notation is used to describe very dilute solutions where the element is present at one-billionth of a gram per gram of sample solution. When working with aqueous solutions, it is common to assume that the density of water is 1.00 g/mL. Therefore, it is common to equate 1 kilogram of water with 1 L of water. Consequently, 1 ppb corresponds to 1 $\mu\text{g/L}$. This is equivalent to one drop of water (25 mL) diluted into an Olympic size swimming pool (2500 m^3), or about three seconds out of a century.

Part per trillion (ppt) Denotes one part per 1,000,000,000,000 parts or one part in 10^{12} . Parts-per-billion notation is used to describe very dilute solutions where the element is present at one-billionth of a gram per gram of sample solution. A part per trillion is the equivalent to about three seconds out of every hundred thousand years or one drop of detergent in enough water to fill a string of railroad tank cars ten miles long.

Receptor People or organisms who could come into contact with a hazardous substance (see exposure pathway).

Species Sensitivity Distributions (SSD) is cumulative probability distributions of toxicity values for multiple species. For environmental risk assessment, the chemical concentration that may be used as a hazard level can be extrapolated from a species sensitivity distribution using a specified percentile of the distribution. Typically species sensitivity distributions are calculated using mainly chronic toxicity data to calculate endpoints that will protect 80%, 90%, 95% and 99% of the community. ANZECC freshwater and marine criteria use species sensitivity distributions to calculate trigger values for ecosystem protection.

Sorption Sorption is a physical and chemical process by which one substance becomes attached to another. The term sorption covers both absorption and adsorption.

Short-chain Perfluoroalkyl carboxylic acids (PFCA) with seven carbons or less (six or fewer perfluorinated carbons); perfluoroalkyl sulfonates (PFSA) with five or less perfluorinated carbons).

TRV Toxicity reference value e.g. a Reference Dose (**RfD**), Acceptable Daily Intake (**ADI**), Tolerable Daily Intake (**TDI**), or Provisional Tolerable Weekly Intake (**PTWI**). A guideline toxicity value that incorporates uncertainty or safety factors to identify a safe dose assuming daily lifetime exposure to a substance that is unlikely to cause harm in humans. Toxicity reference values are typically set by international scientific committees such as Joint FAO/WHO Expert Committee on Food Additives (JECFA) or statutory authorities/ government agencies such as European Food Safety Authority (EFSA), Food Safety Australia New Zealand or Agency for Toxic Substances and Disease Registry (ATSDR) or World Health Organization (WHO).

US EPA United States Environmental Protection Agency.

Note on Terms Used in this Report

To ensure consistency within this document and with the majority of scientific literature PDP have adopted the naming convention for PFAS compounds recommended in Buck *et al.*, 2011 and ITRC, 2017.

- ∴ **Anionic form of the Chemical Names:** Many PFAS compounds can have various ionic states (i.e. acids, anions, cations) in this document we will generally refer to the anionic state.
- ∴ **“PFC” is not used:** the term PFAS has replaced the term PFC in most scientific literature and is the terminology being used in current New Zealand and Australian government publications.
- ∴ **“PFAS”, not “PFASs”:** The acronym “PFAS” stands for per and polyfluoroalkyl substances and refers to more than one chemical. Therefore “PFAS” is plural and a small “s” is not needed. When referring to one particular compound, the specific name of that compound will be used instead of PFAS.
- ∴ **Fluoropolymers:** refers to polymers with a carbon only backbone with fluorine directly attached to the carbons. All other fluorine containing polymers are referred to as fluorinated polymers. Fluorinated polymers may or may not be PFAS compounds depending on whether they contain perfluoroalkyl monomers.
- ∴ **Perfluoroalkyl acids (PFAA):** refers to both perfluoroalkyl carboxylic acids (PFCA) and perfluoroalkyl sulfonic acids (PFSA). These compounds are essentially non-degradable and many polyfluoroalkyl substances ultimately degrade into PFAA. PFAA are sometimes referred to as “terminal PFAS” or “terminal degradation products”. The terms “terminal PFAS” or “terminal degradation products” are not used in this report.
- ∴ **Precursor compounds:** refers to polyfluoroalkyl substances that degrade to create PFAA.

Note on Units Used in this Report

The standard units in this report for ground and surface water are mg/L (milligrams per litre or ppm) and $\mu\text{g/L}$ (micrograms per litre or ppb) for most elements analysed at the trace level. In this study, PFAS compounds have also been assessed at the ultra-trace level which is quoted in ng/L (nanograms per litre). Nanograms per litre is equivalent to parts per trillion (ppt or 1 in 1,000,000,000,000). See the glossary above for a comprehensive definition of ppb and ppt.

For soil, the standard units used in this report are mg/kg.

Note on Bio-concentration Factors/Bio-magnification Factors/Bio-accumulation Factors/Trophic Magnification Factors

In this report Bioconcentration Factors (BCF)/Bio-accumulation Factors (BAF)/bio-magnification factors (BMF)/Trophic Magnification Factors (TMF) are derived from field measurements of PFAS compounds within water/sediment/soil and various biota. There are some limitations associated with using field based measurements to calculate these factors for PFAS compounds, which include:

1. The concentration of PFAS compounds in surface water at contaminated sites can vary significantly over time. This is because PFAS compounds tend to be highly water soluble and therefore during, or soon after rainfall events, significant quantities of PFAS compounds can be released which can then result in changes in surface water concentrations. Therefore, without extensive surface water quality datasets it is difficult to determine the average water concentration that the biota is exposed to over a relevant time period for the organism of interest.
2. Steady state equilibrium between the organism and surface water may not have been reached.
3. Uncertainties in the feeding ecology and the relative importance of dietary exposure to the overall PFAS exposure to the organism. This may be particularly important for predatory species such as freshwater eels where field calculated BCF may significantly overestimate exposure from water.
4. Transformation of precursor compounds within the organisms. PFAS compounds are usually a complex mixture of polyfluorinated precursor compounds and perfluorinated compounds. Data exists which indicates that some precursors (such as fluorotelomers) may be metabolised within organisms.

For more information regarding the use and limitations of field based bio-magnification factors the reader is directed to Franklin (2015) "How reliable are field –derived bio-magnification factors and trophic magnification factors as indicators of bio-accumulation potential? Conclusion from a case study on Per- and Polyfluoroalkyl substances". Integrated Environmental Assessment and Management, 12 (1), pp 6-18.

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Appendices

Appendix A: Tables

1.0 Introduction

1.1 Scope of Project

The Ministry for the Environment (MfE) issued a request for proposal to several different tenderers (including PDP) in mid-2018. As a result of this competitive tender process Pattle Delamore Partners (PDP) was engaged to undertake a literature review of the potential impacts of per- and polyfluoroalkyl substances (PFAS) on ecosystems. The scope of this literature review was to:

- ∴ Peer review globally available research on [potential] impacts of PFAS compounds on ecosystems.
- ∴ Assess the conclusions of the available research and consider their application in a New Zealand context.
- ∴ Outline data gaps and provide recommendations on the scope of research possibilities within New Zealand.

PFAS compounds are emerging contaminants and have been the focus of a considerable amount of research within the last 5 years. Preliminary literature searches undertaken by PDP have identified that there have been over 1,000 scientific papers and conference proceedings published on the topic. Therefore, this literature review is focused mainly on scientific reviews and publications published after 2015 as older papers may no longer contain the most up to date information regarding PFAS compounds. However, PDP has considered some key publications which have been published before 2015 if there have been no newer publications on the particular topic.

1.1.1 Out of Scope

The following have not been considered as part of this report:

- ∴ Cultural impact of PFAS discharges.
- ∴ Human health effects of exposure to PFAS compounds. For more information on the potential health impacts of PFAS compounds the reader is referred to Ministry for the Environment website (<http://www.mfe.govt.nz/land/pfas-and-poly-fluoroalkyl-substances/health>).
- ∴ Trade, and impact on tradable commodities as a result of environmental exposure to PFAS compounds (including meat, eggs and milk). For more information on PFAS in Foods and Food Safety the reader should refer to the Ministry of Primary Industries (MPI) or <https://www.mpi.govt.nz/dmsdocument/31077/loggedIn>.

2.0 Background

2.1 Introduction to PFAS

Per and polyfluorinated alkyl substances (PFAS) are synthetic organo-fluorine compounds which do not occur naturally. They were initially discovered in the 1930's but large-scale production of these compounds began in the 1950s (Concawe, 2016; ITRC, 2017). They have been used in a wide range of commercial, domestic and industrial products as coatings for textiles, paper, cookware products and used in various industrial sectors such as aviation, automotive, electroplating, firefighting and photographic industries due to their unique surface activity properties.

2.1.1 Types of PFAS Compounds

PFAS are a large group of more than 3000 compounds which are, or have been, manufactured for use in commercial products (Wang *et al.*, 2017) (See Table 1). These compounds can either be completely fluorinated (perfluorinated alkyl substances) (i.e. fluorine has replaced all of the hydrogen atoms) or partly fluorinated (polyfluorinated alkyl substances with at least two carbons fully fluorinated). PFAS compounds generally have a carbon chain length (the alkyl part of the compound) of between two to sixteen carbon atoms (C₂-C₁₆) long and can have a variety of functional groups at the end of the carbon chain.

There are many different classes or groups of PFAS but a majority of PFAS produced today fall into seven main classes which include perfluorinated carboxylic acids (PFCAs), perfluorinated sulfonic acids (PFSAs), perfluorinated phosphonic acids (PFPAs), fluorotelomer alcohols (FTOHs), fluorotelomer sulfonic acids (FTSs), polyfluorinated alkyl phosphates (PAPs) and perfluorooctane sulfonamide compounds (PFOSA).

Other types of PFAS compounds have been produced such as fluoropolymers, perfluoropolyethers and side chain fluorinated polymers but there is very little published information regarding fluorinated polymers and PASF in the literature and these compounds have not been discussed in this report.

Table 1: Common Types of PFAS Compounds ¹			
Family	Class	Examples	Common Uses
Perfluoroalkyl acids (PFAA)	Perfluoroalkyl carboxylic acids (PFCA)	PFOA	Surfactant
	Perfluoroalkyl sulfonic acids (PFSA)	PFOS	Surfactant
Polyfluorinated alkyl substances	Fluorotelomers sulfonic acids (FTSA)	8:2 Fluorotelomer sulfonic acid (8:2 FTS)	Surfactant / AFFF
	Fluorotelomer carboxylic acid (FTCA)	6:2 Fluorotelomer carboxylic acid (6:2 FTC)	Intermediate product
	Fluorotelomer alcohols	8:2 Fluorotelomer alcohol (8:2 FTOH)	Use for manufacturing PFCA and PFSA
	Polyfluorinated alkyl phosphates (PAP)	Zonyl	Paper and Food packaging materials
Notes: 1. Modified from ITRC (2017) Naming Conventions and Physical and Chemical Properties of Per- and polyfluoroalkyl Substances (PFAS). Accessed from https://pfas-1.itrcweb.org/wp-content/uploads/2018/03/pfas_fact_sheet_naming_conventions__3_16_18.pdf .			

2.1.1.1 Perfluoroalkyl sulfonic acids (PFSA)

Perfluoroalkyl sulfonic acids (PFSA) are one of the most widely encountered types of PFSA compounds in the environment and this group of compounds is used in a wide range of stain and water resistant products as well as firefighting foams. Perfluoroalkyl sulfonic acids consist of carbon chain lengths varying between two to sixteen carbon atoms with a sulfonic acid (SO₃H) terminal group.

Perfluorooctane sulfonate (PFOS) is one of the most commonly encountered PFSA compounds in the environment and this compound consists of a chain of eight fully fluorinated carbon atoms with a sulfonate group attached to one end. In 2003, 3M phased out production of PFOS and has largely replaced it with PFBS in some of its products (3M, 2002; Concawe, 2016; ITRC, 2017). PFBS consists of a chain of four fully fluorinated carbon atoms with a sulfonate group attached to one end.

2.1.1.2 Perfluoroalkyl carboxylic acids (PFCA)

Perfluoroalkyl carboxylic acids (PFCA) are also among some of the more commonly found types of PFAS compounds in the environment. PFCA, especially PFOA, have been used in stain and water resistant products as well as an

industrial surfactant for a number of industries including carpeting, upholstery, floor waxes, textiles and cookware. PFCA consists of carbon chain lengths varying between two to sixteen carbon atoms with a carboxylic acid (COOH) terminal group.

Perfluorooctanoic acid (PFOA) is a PFCA which consists of a chain of seven fully fluorinated carbon atoms with a carboxylic acid group attached to one end.

2.1.1.3 Perfluoroalkyl phosphonic acids (PFPA)

Perfluoroalkyl phosphonic acids (PFPA) are found in waxes, surface coatings and as a surfactant anti-foaming agent in the textile industry and pesticide production. PFPA consist of carbon chain lengths varying between two to sixteen carbon atoms with a phosphonic acid (PO(OH)₂) terminal group.

Perfluorooctane phosphonic acid (PFOPA) is a PFPA which consists of a chain of eight fully fluorinated carbon atoms with a phosphonic acid group attached to one end.

2.1.1.4 Fluorotelomers

Fluorotelomers are used in fire-fighting foams, grease-resistant food packaging, leather protectants and for stain proofing textiles. There are three main groups of fluorotelomer substances which are the n:2 fluorotelomer alcohols (n:2 FTOHs), n:2 fluorotelomer sulfonic acids (n:2 FTSA) and fluorotelomer carboxylic acids (FTCA). Fluorotelomer alcohols are the raw product for the manufacturing of various surfactants and surface protection products (ITRC, 2018a). They are produced during the telomerisation process (Buck *et al.*, 2011). Fluorotelomers are a major source of PFCA in the environment and are believed to be the major source of PFAS in remote polar regions where they degrade into PFCA (Prevedouros *et al.*, 2006).

Some fluorotelomers and fluorotelomer-based compounds degrade into perfluorinated carboxylic acids such as PFHxA and PFOA.

2.1.1.5 Perfluorooctane sulfonamide compounds and Perfluoroalkyl sulfonamido derivatives

Perfluoroalkane sulfonyl fluorides (C_nF_{2n+1}SO₂F) are precursor compounds used to manufacture PFSA such as PFOS, PFHxS or PFBS plus a variety of other PFAS compounds containing sulfur-nitrogen groups such as N-ethyl perfluoro octane sulphonamide (EtFOSA – pesticide sulfuramid) (Buck *et al.*, 2011).

Perfluorooctane sulfonamide (PFOSA) was an ingredient in Scotchguard and it has also been used to manufacture grease and water repellent food packaging materials.

2.1.1.6 Other PFAS compounds

Since 2002, commercial production of PFSA and PFCA have decreased (Prevedouros *et al.*, 2006; Concawe, 2016; ITRC, 2017; Xiao, 2017). Xiao (2017) undertook a literature survey on the emerging poly- and perfluoroalkyl substances and found that papers published between 2009 and 2017 identified as many as 455 new PFAS which are not detected as part of typical commercial analytical suites available in Australia or New Zealand. These compounds have been found in surface waters, fish, sediments, wastewater, bio-solids, soils, fire-fighting foams, and commercial fluoropolymer surfactants (Xiao, 2017). A large number of novel compounds are found in AFFF fire-fighting foams and Brazen-Hanson *et al.* (2017) estimate that approximately 25% of the PFAS mass in AFFF are unidentified compounds.

F-35B (potassium salt of 6:2 chlorinated polyfluorinated ether sulfonate) and GenX (2,3,3,3-tetrafluoro-2-(1,1,2,2,2,3,3,3,3-heptafluoropropoxy) propanoic acid or HFPO-DA) are two new PFAS compounds which have replaced PFOS and PFOA in some applications (Xiao, 2017). Currently there are major knowledge gaps in regards of the physical and chemistry properties, environmental behaviour, fate and toxicity of these compounds. However, many of the new identified and emerging PFAS compounds appear to be non-volatile and water soluble and, therefore, aquatic environments are likely to be the ultimate sink for these compounds (Xiao, 2017).

2.1.2 Production and Uses

PFAS compounds do not occur naturally. Some PFAS compounds have been manufactured since the 1940s (i.e. PFOA and PFOS) while some types of PFAS compounds (GenX and F35B) have only been manufactured more recently (Prevedouros *et al.*, 2006; Concawe, 2016; ITRC, 2017).

In 1947, the electrochemical fluorination process used to manufacture PFAS was developed and remained the dominant process for producing PFAS compounds until 2002 (Prevedouros *et al.*, 2006; ITRC, 2017). In the 1950s and 1960s PFAS compounds were used in a wide range of products due to the stability and ability to act as a wetting agent by reducing surface tension (Prevedouros *et al.*, 2006). Industrially, PFAS were also used as surfactants, emulsifiers, wetting agents, additives, and coatings (Land *et al.*, 2015). Between the mid-1960s and 2000, PFAS-containing aqueous film forming foams (AFFF) for fire-fighting purposes was produced and based on data from UNEP, PFAS-AFFF was widely used from the 1970s. Anecdotal evidence suggests that Class B AFFF fire-fighting foam was not widely used in New Zealand until 1980s.

In 2002, 3M ceased manufacturing PFAS compounds using the electrochemical fluorination process and telomerisation processes using fluorotelomer iodide

oxidation, fluorotelomer olefin oxidation and fluorotelomer iodide carboxylation (Prevedouros *et al.*, 2006; Concawe, 2016, ITRC, 2017).

By the early 2000s, Europe and Japan made voluntary efforts to phase out production of PFOA and PFOS. Many countries including the USA, Australia, Canada, the UK, the Netherlands, Norway, Germany, and Sweden introduced regulations between 2000 and 2017 aimed at phasing out or reducing the use of PFOS, PFOA, and their precursors (Thalheimer *et al.*, 2017).

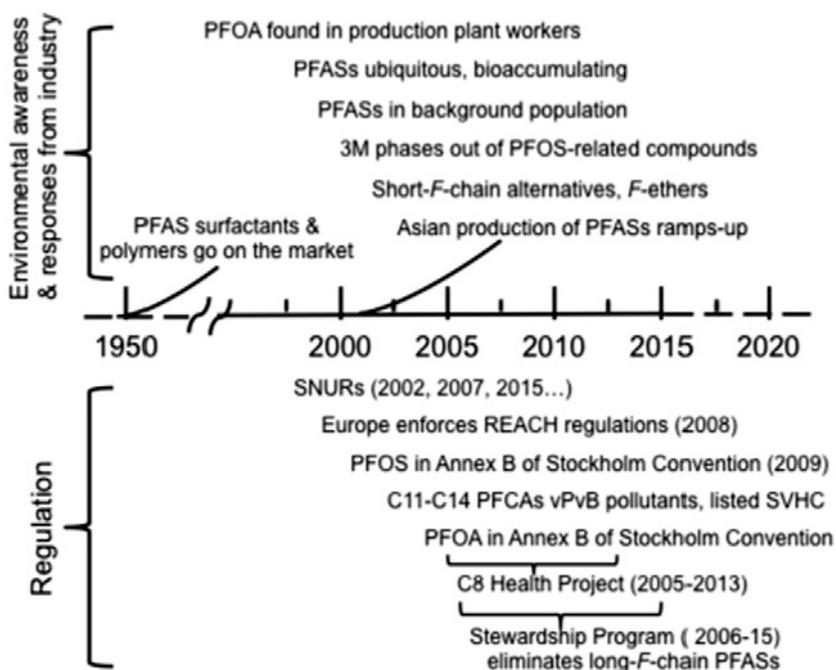


Figure 1: Brief History of PFAS Production and Regulations

The figure above summarises the brief history of PFAS production and the development of associated regulations (adopted from Kraft *et al.*, 2015).

2.2 Fate and Transport

2.2.1 Physicochemical Properties

The primary molecular structure of PFAS consists of fluorine-carbon bonds which accounts for their unique physical and chemical properties, as the fluorine-carbon bond is the strongest chemical bond known. The typical physical and chemical properties of PFAS include:

- ∴ The ability to repel water and oil, and present surfactant characteristics;
- ∴ Resistance to degradation;
- ∴ Resistance to heat;

- ∴ High water solubility; and
- ∴ The ability to stick to surfaces.

Chain length and functional group determine the physical properties of various PFAS such as water solubility, vapour pressure, and sorption onto surfaces.

2.2.1.1 Water Solubility

Water solubility of PFAS varies between different types of PFAS compounds and is dependent on the functional group. Generally shorter chains are more soluble than longer chain PFAS compounds (Concawe, 2016). PFCA and PFAA are usually highly water soluble but some polyfluorinated substances (such as fluorotelomers) are not very soluble.

Octanol/water coefficients (or K_{ow}) have been used to estimate bioaccumulation potential for a number of different persistent organic pollutants. However, PFAS compounds form multiple layers in octanol/water which make determining octanol-water partition coefficients extremely difficult or impossible. Guidance for models used to estimate the fate of chemicals in the environment from the USEPA using physico chemical characteristics indicates that the models generally do not apply to chemicals which can act as surfactants (USEPA EPI Suite available at <https://www.epa.gov/tsca-screening-tools/epi-suite-estimation-program-interface>).

Table A-1 in Appendix A provides a summary of physical properties of some PFAS compounds.

2.2.1.2 Vapour Pressure/Henry's Law Constant Data

There is a lack of essential data regarding vapour pressure and Henry's law constants for many types of PFAS compounds. From the data that is available, there is a significant difference in vapour pressure and Henry's law data (see Table A-1 in Appendix A). Medium and long chain (C6 –C12) PFCA (i.e., PFOA) and PFSA (i.e., PFOS) have a very low vapour pressure and Henry's law constant which mean the loss to the atmosphere and long-range atmospheric transport of these compounds is highly unlikely (Hekster *et al.*, 2003).

2.2.1.3 Sorption

Sorption of PFAS compounds onto solid surfaces such as soil or sediment will impact the mobility of these compounds and the ability of plants to uptake these compounds. Since PFAS includes a wide range of different compounds with varied chemical structures their ability to sorb onto surfaces varies significantly between functional groups. Longer chain and low solubility compounds tend to sorb to surfaces more than the highly water soluble/shorter chain length compounds. Also, anionic or cationic PFAS compounds tend to be more highly sorbed to surfaces than neutral PFAS compounds.

A recent review of the sorption behaviour of a range of PFAS (mainly PFSA and PFCA) concluded no single soil or sediment property could explain their sorption behaviour (Li *et al.*, 2018). Sorption mechanisms of compounds such as Fluorotelomer sulfonates (FtS), Fluorotelomer sulfonamido betaines (FtSaBs) and 6:2 FtSaAM are very complex and their behaviour cannot be predicted (Barzen-Hanson *et al.*, 2017). To better predict the sorption behaviour of PFAS compounds Li *et al.* (2018) found that knowledge of organic carbon content, pH and clay content is needed to predict PFAS sorption behaviour. While sorption processes are complex there appear to be two main sorption mechanisms which control the degree to which PFAA and PFCA compounds are sorbed to surfaces (Concawe, 2016; ATSDR, 2018). These are:

1. Hydrophobic sorption to organic matter, and
2. Electrostatic attraction to charged surfaces.

Little is known regarding the sorption behaviour of zwitterionic and cationic molecules but it is likely that hydrophobic and electrostatic attraction processes will play a part in the sorption of these types of compounds. Recent research into the sorption mechanisms of compounds such as fluorotelomers sulfonates (FtS), fluorotelomers sulfonamido betaines (FtSaB) and fluorotelomer sulfonamido amine (FtSaAm) compounds show these are very complex and their behaviour cannot be predicted by bulk soil properties such as organic carbon, cation exchange capacity and/or pH (Barzen-Hanson *et al.*, 2017). Barzen-Hanson *et al.* (2017) found low K_d values for anionic 6:2 FtS compounds which indicates that this compound will be highly mobile in groundwater. Sorption of fluorotelomers sulfonates such as 6:2 FtS and 8:2 FtS appears to be driven by hydrophobic interactions but Barzen-Hanson *et al.* (2017) notes that multilayer sorption can occur with 6:2 FtS and 6:2FtSaB and fluorophilic interactions may occur between PFAS compounds sorbed to soils and PFAS compounds within the aqueous phase.

Hydrophobic Sorption to Organic Matter

The preference for a compound to be adsorbed onto organic matter is expressed as the organic carbon-water partition coefficient K_{OC} (often reported as $\log K_{OC}$). A high K_{OC} value indicates a compound will strongly sorb on to organic carbon and, therefore, will not move through the soil. A comparison of the $\log K_{OC}$ values of a range of PFAS compounds along with some of the more well-known persistent organic pollutants (POP) is provided in Table 2. In general, it can be seen that most PFAS compounds typically have lower $\log K_{OC}$ values compared to other POP compounds. Consequently, most PFAS will be less strongly sorbed to organic carbon and more mobile in water.

Nevertheless, the amount of organic carbon present in a soil or sediment has been found to influence sorption behaviour of some PFAS compounds, with a

higher organic carbon concentration typically resulting in more sorption of PFAS (Li, *et al.*, 2018; Li, *et al.*, 2019, Milinovic, *et al.*, 2015).

It is important to note however, that studies of PFAS sorption and organic carbon content are not consistent, with some showing a strong positive correlation between sorption and organic carbon content (e.g. Ahrens *et al.*, 2011; Chen *et al.*, 2012; Chen *et al.*, 2013; Higgins and Luthy, 2006; You *et al.*, 2010) and others showing either an inconsistent relationship or no significant relationship (Becker *et al.*, 2008; Pan and You, 2010; Zhu *et al.*, 2014). As stated above, this suggests that organic carbon content alone cannot explain observed variations in sorption. Other factors such as electrostatic attraction and pH also play a significant role in PFAS sorption (Li *et al.*, 2018).

Table 2: Organic carbon-water Partition Co-efficient Values (Log K _{oc}) for Select Persistent Organic Pollutants			
Chemical	Chemical Class	Log K _{oc}	Source
Perfluorobutanoate (PFBA)	Perfluoroalkyl carboxylic acids (PFCA)	1.9	1
Perfluoropentanoate (PFPeA)		1.4	1
Perfluorohexanoate (PFHxA)		1.3	1
Perfluoroheptanoate (PFHpA)		1.6	1
Perfluorooctanoate (PFOA)		1.89 to 2.63	1
Perfluorononanoate (PFNA)		2.36 to 3.69	1
Perfluorodecanoate (PFDA)		2.76 to 2.96	1
Perfluoroundecanoate (PFUnDA)		3.3 to 3.56	1
Perfluorobutane sulfonate (PFBS)	Perfluoroalkyl sulfonic acids (PFSA)	1.2 to 1.79	1
Perfluoroheptane sulfonate (PFHxS)		2.4 to 3.1	1
Perfluorooctane sulfonate (PFOS)		2.4 to 3.7	1
Perfluorodecane sulfonate (PFDS)		3.53 to 3.66	1
Perfluorooctanesulfonamide (PFOSA)	Perfluoroalkane sulfonamide (FASA)	4.10	1
4:2 Fluorotelomer alcohol (4:2 FTOH)	n:2 fluorotelomer alcohol (n:2 FTOH)	0.93	1
6:2 Fluorotelomer alcohol (6:2 FTOH)		2.43	1
8:2 Fluorotelomer alcohol (8:2 FTOH)		4.13	1
10:2 Fluorotelomer alcohol (10:2 FTOH)		6.20	1
2-(N-ethylperfluorooctanesulfonamido) acetic acid (N-EtFOSAA)	Perfluoroalkane sulfonamido acetic acid (FASAA)	3.23 to 3.49	1
2-(N-methylperfluorooctanesulfonamido) acetic acid (N-MeFOSAA)		3.11 to 3.35	1
Aldrin	Organochlorine pesticide (OCP)	7.67	2
Chlordane		3.49 to 6.3	2
Chlordecone		3.38 to 3.42	2
DDT		5.18 to 5.35	2
Dieldrin		6.67	2
Endrin		4.53 to 5.20	2
Heptachlor		4.34	2
Hexabromobiphenyl		Polybrominated biphenyl (PBB)	3.33 to 3.87
Hexachlorobenzene	Organochlorine pesticide (OCP)	3.59 to 6.08	2
Mirex		3.76	2
PCB	Polychlorinated biphenyl (PCB)	4.72 to 7.13	3
Toxaphene	Organochlorine pesticide (OCP)	3 to 5	2
Benzo[a]pyrene	Polycyclic aromatic hydrocarbon (PAH)	6.74	2
Benzo[b]fluoranthene		5.74	2
Benzo[k]fluoranthene		5.74	2
Indenol[1,2,3-c,d]pyrene		6.20	2

Notes:

1. ITRC PFAS Environmental Fate and Transport Fact Sheet, Table 3-1 published in April 2018. Accessed from <https://pfas-1.itrcweb.org/fact-sheets/>.
2. Agency for Toxic Substances and Disease Registry (ATSDR) <https://www.atsdr.cdc.gov/toxprofiledocs/index.html>. Accessed 15/10/2018.
3. Dutch, M., S. Aasen, and E. Long. 2004. PCB Congener Concentrations in Puget Sound Sediments. In T.W. Droscher and D.A. Fraser (eds). Proceedings of the 2003 Georgia Basin/Puget Sound Research Conference.

Electrostatic Attraction to Charge Surfaces

In soil and sediment, mineral surfaces and organic matter provide charged surfaces which can attract PFAS compounds. Under typical environmental conditions, many PFAS compounds exist as negatively charged anions and will, therefore, sorb to positively charged particles such as clay minerals and metal oxides. Soil and sediment usually contain both positively and negatively charged particles. In some instances, the charges of these particles are variable and will change depending on the pH of the surrounding fluid. The pH of the mineral surface is also important. As pH increases, the average charge on the mineral surfaces tends to become less positive. This results in less electrostatic attraction of negatively charged PFAS anions and consequently less sorption.

Sorption of PFAS compounds to soil or sediment is a complex process and is dictated by site-specific conditions including the organic content and mineralogy of the soil/sediment and the pH of the soil/sediment and the surrounding aqueous fluid (Li *et al.*, 2018).

2.2.2 PFAS Transformations in the Environment

Chemical transformations relate to chemical reactions that change the structure of one compound or molecule into another, either by abiotic or biotic processes. In general, there is little or no evidence that PFASs and PFCAs, such as PFOS and PFOA, are broken down by natural biological or chemical processes (Giesy *et al.*, 2010; Lui and Avendano, 2013).

Polyfluorinated compounds can transform in the environment to form other, more persistent PFAS compounds. These PFAS are less stable compounds that have the potential to undergo abiotic or biotic transformation and degrade to form the persistent long-chain PFASs or PFCAs.

There is a growing weight of evidence showing that these compounds can degrade through both biotic and abiotic processes to form stable PFASs and PFCAs, such as PFOS, PFHxS, and PFOA (Liu and Avendano, 2013; Anderson *et al.*, 2016). For example, many studies have shown that the fluorotelomer alcohol 8:2 FTOH can transform to PFOA under certain environmental conditions (see Parsons *et al.*, 2008 and references therein). Some intermediate compounds may be more toxic than the parent compound or the terminal PFAS compounds (an example of this is that 6:2FTSA is more toxic than its parent compound 6:2FTS or the terminal PFAS compound PFOS or PFOA (Buck, 2018)). This could mean that the potential ecological impacts of discharges of firefighting foams (particularly newer foams based on C6 or C8 fluorotelomer compounds) may be underestimated by analysing for the traditional 28 PFAS compounds.

A recent investigation at U.S. Air Force sites where AFFF was used for firefighting appears to indicate that up to 40% of the PFOS and 36% of the PFHxS observed

had formed in situ from these precursor compounds (Anderson *et al.*, 2016). Although the exact mechanism of this in situ transformation was not investigated, the authors suggest it was due to bio-transformation of precursor compounds such as fluorotelomer sulfonates (Anderson *et al.*, 2016). It should be noted, however, that while these precursor compounds are commonly present in AFFFs, the study did not analyse for these specific compounds. While the results of this study are limited by the fact that the authors did not undertake the analysis of a wide range of PFAS compounds (including precursor compounds) monitoring data for several AFFF contaminated sites within New Zealand do indicate that some precursor compounds are being transformed into PFCA.

Butt *et al.*, 2014 undertook a literature review of various bio-transformation pathways via various microbial systems or within rodents. This literature review concluded that 6:2 fluorotelomer alcohol (6:2 FTOH) can be degraded into shorter chain perfluoroalkyl carboxylic acids such as (PFHxA, PFPeA, and PFBA) as well as fluorotelomer carboxylates 5:3 FTCA and 4:3 FTCA. The biotic transformation of 6:2FTOH is quite fast with the soil half-life being approximately 1.3 to 1.6 days (Butt *et al.*, 2014). The proposed degradation pathways undergo multiple transformations forming a wide number of immediate products including a number of fluorotelomer ketones and aldehydes (Butt *et al.*, 2014). 8:2 FTOH is transformed into PFOA and to a lesser extent PFNA (Butt *et al.*, 2014).

Wang *et al.* (2011) undertook an investigation of the aerobic biotransformation of 6:2 fluorotelomer sulfonate (6:2 FTS) in activated sludge of a WWTP. This work showed that it breakdowns into shorter chain perfluoroalkyl carboxylic acids such as (PFHxA, PFPeA, and PFBA) as well as fluorotelomer carboxylates 5:3 FTCA and 4:3 FTCA. Weiner, *et al.* 2013) postulated that the initial step in the degradation of 6:2 FTS is the formation of 6:2 FTOH.

Less research has been undertaken on the breakdown of Perfluoroalkane sulphonamide compounds. Avendano and Liu (2015) found that the bio-transformation of EtFOSE (N-ethyl perfluorooctane sulphonamide ethanol (EtFOSE) and EtFOSA (N-ethyl perfluorooctane sulphonamide also known as sulfuramid) in semi-closed soil microsoms over a period of 182 days. This study showed that these compounds degrade into PFOS as well as other persistent sulphonamide derivatives similar to those which are detected in bio-solids and landfill leachates.

A list of polyfluorinated compounds which may degrade into perfluoroalkyl carboxylic acids (PFCA) is provided in the OECD (2007) monograph *Lists of PFOS, PFAS, PFOA, PFCA, Related Compounds and Chemicals that may degrade to PFCA* (as revised in 2007). This document identifies fluoroalcohol, fluoroammonium, fluoroamine, fluoroester, fluoroethers, fluoro iodide, fluorophosphates,

fluoroalkyl silicate, fluoro siloxane, fluoro thiol, and fluoro urethane as compounds which have the potential to degrade into perfluorocarboxylic acids.

2.3 Environmental Concerns with PFAS Compounds

A number of PFAS compounds are persistent (P) in the environment, bio-accumulative (B) and toxic (T), meaning they fulfil the PBT-criteria for the European Chemicals Regulation (REACH) and the Stockholm Convention for Persistent Organic Pollutants.

At environmentally expected pH values, many PFAS compounds are present as anions; consequently, they are highly water soluble and can be transported over long distances via groundwater and surface water (Prevedorous *et al.*, 2006; Xiao *et al.*, 2015; Hu *et al.*, 2016; ATSDR, 2018). Surface water contamination from point source discharges of PFAS has been shown to extend for many 10's of kilometres (e.g., Awad *et al.*, 2011; Kwadijk *et al.*, 2014). Similarly, in groundwater, PFAS plumes extending for 10's of kilometres from source areas have been observed in some locations (e.g., Oakey (AECOM, 2018) and Williamtown (AECOM, 2017)), indicating that PFAS compounds can be highly mobile in some groundwater aquifers. This is of particular concern for areas where most drinking water is sourced from aquifers. In the United States, a recent report documented PFAS contamination in the drinking water of communities in 33 states (Hu *et al.*, 2016). In New Zealand, there have been recent concerns regarding the presence of PFAS in groundwater and surface water at and in the vicinity of a number of current and former fire training areas.

As discussed in Section 2.2.1.3, short chain PFAS compounds are not significantly sorbed onto sediment (Chen *et al.*, 2016), and although longer chain PFAS compounds can be sorbed onto sediment, the low concentration of suspended solids often found in the marine and some freshwater environments means that most PFAS are predominantly transported in the dissolved phase and are, therefore, available for bio-accumulation (Ahrens *et al.*, 2011). Consequently, many PFAS are ubiquitous in the environment and are found to bio-accumulate in birds, fish and mammals (including livestock) (ITRC, 2018b; Liu *et al.*, 2018).

Although some of the polyfluorinated compounds do not fit the PBT-criteria (partly because there is insufficient information to undertake a full PBT assessment), biotic and abiotic transformations of these precursor compounds may result in the formation of stable per-fluorinated end products which do meet the PBT-criteria.

3.0 Australian and New Zealand Data

3.1 Australian data

Detailed studies of a large number of Department of Defence bases have been undertaken in Australia. Consultants for the Department of Defence have put together summary figures of the available data to October 2018 (Andrew Mitchell, personal communication). These figures have used all the available data from on the bases and in off-site areas around bases for which results have been reported at this time. These summary Figures 2 and 3 are provided below.

The Figure 2 looks at PFOS levels in a wide variety of flora and fauna. The figure includes the 90th percentile concentration for the dataset for each organism type as well as the percent of samples that reported detectable PFOS in tissues.

For mammals, birds, reptiles, fish, amphibians, crustacea and eggs, more than 80% of samples that have been taken around Australia, in the vicinity of Defence bases, have detectable levels of PFOS. The 90th percentile concentrations for these organism types range from 10s to 1000s µg/kg of PFOS. For terrestrial invertebrates, PFOS has been detected in approximately 70% of samples with concentrations up to 100s µg/kg. For aquatic invertebrates and leafy plants, PFOS has been detected in approximately 50% of samples with concentrations up to 80 µg/kg. For other types of plants including edible and inedible ones, PFOS was detected in 3 to 35% of samples. Concentrations were in the 1 to 10 µg/kg range.

The second figure (i.e Figure 3) looks at the range of PFAS that have been detected in flora and fauna. The data reported in this figure includes the 99th and 95th percentile within the dataset and the frequency of detection for each of the PFAS included in the standard analytical suite for these investigations.

PFOS has been detected in more than 60% of the more than 4000 biota samples collected and analysed to date with concentrations up to almost 6000 µg/kg. The next most frequently detected PFAS was PFHxS with a frequency of detection of around 30% and concentrations up to around 300 µg/kg. The fluorotelomers and some of the precursor chemicals were not detected or rarely detected. PFHpS, PFOA, PFDA, PFUnDA, PFDoDA were detected in around 10% of samples with concentrations up to around 10 µg/kg.

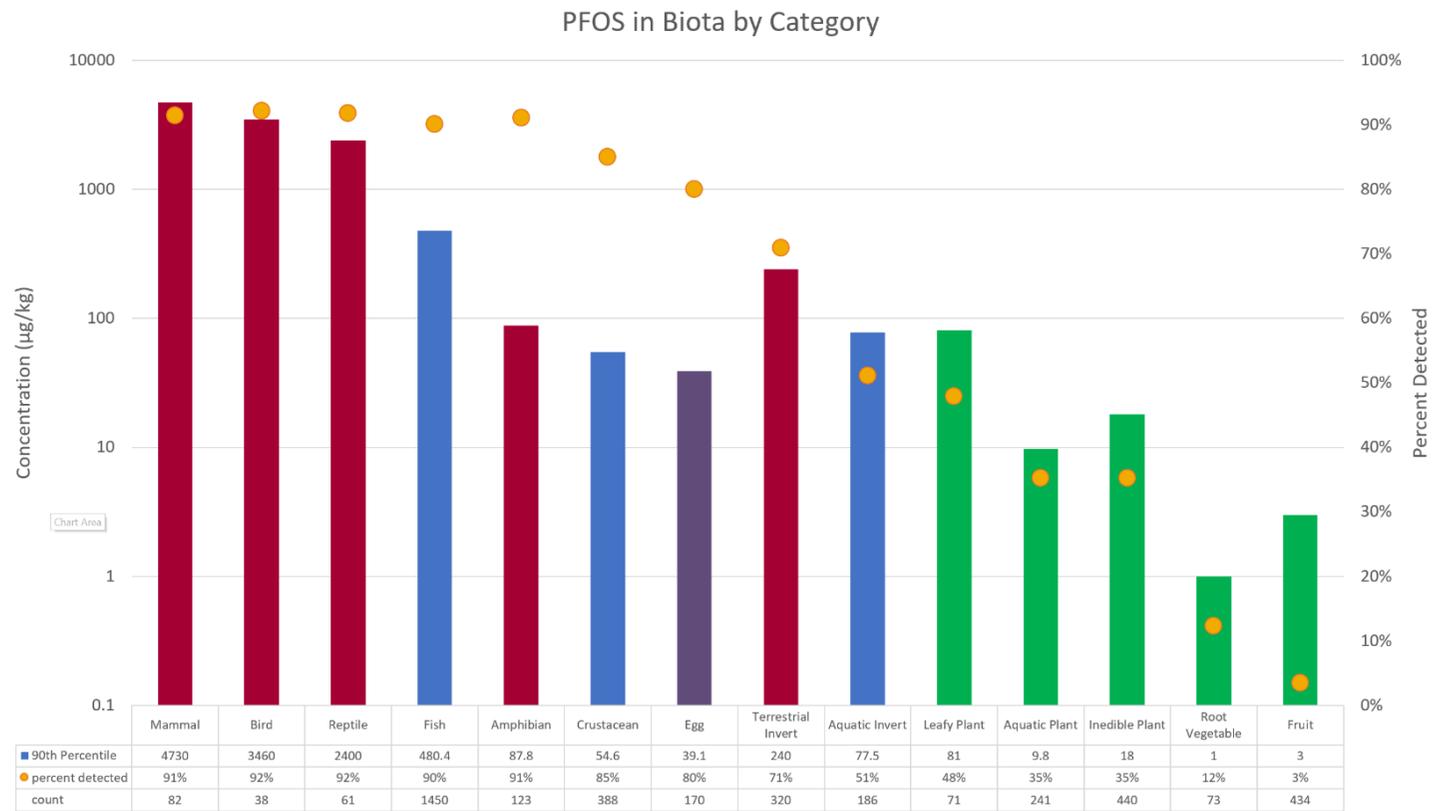


Figure 2: PFOS Concentration Detected in Biota near Australian Defence Forces Base

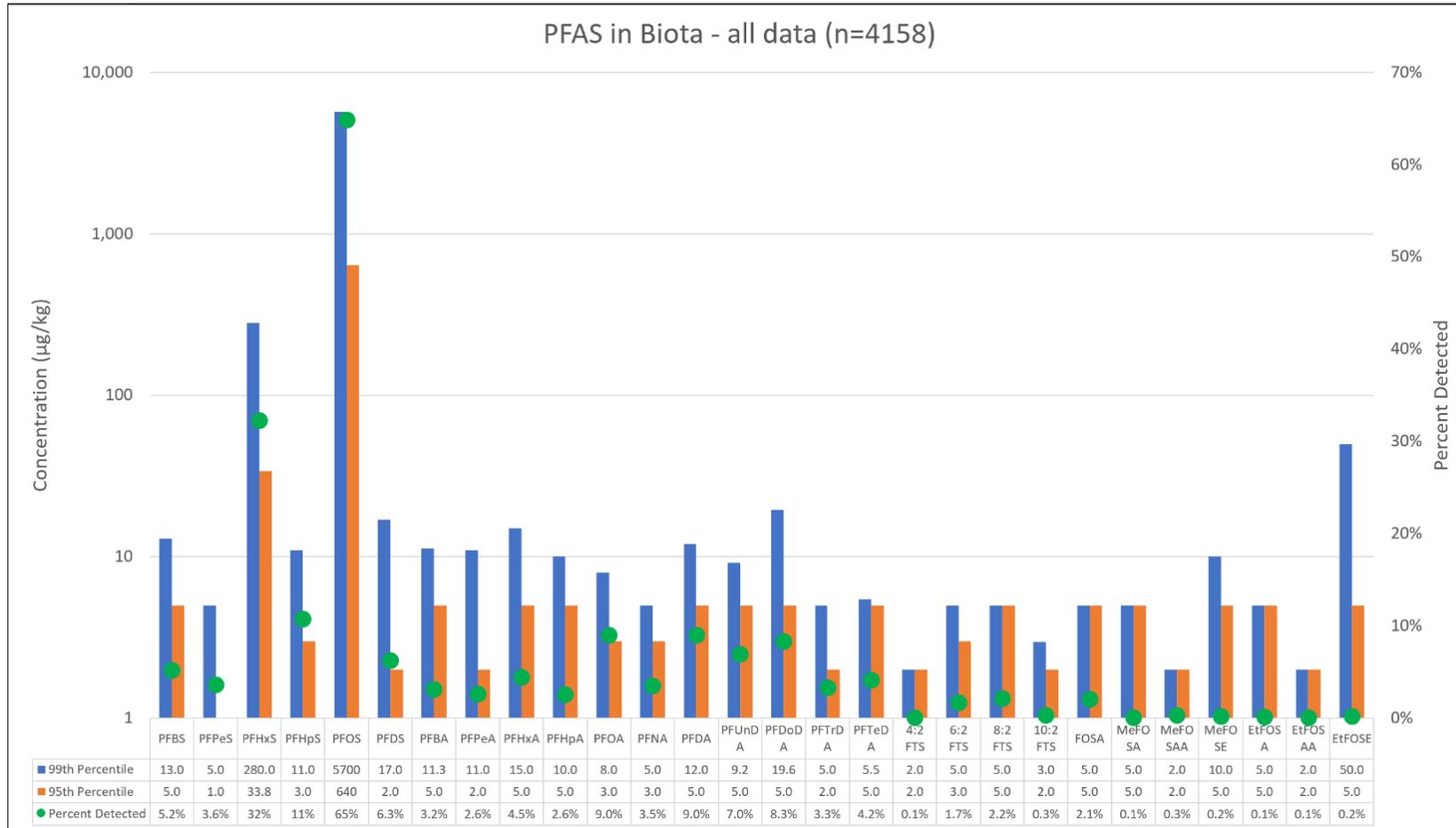


Figure 3: PFAS in Biota – near Australian Defence Force Base

3.2 New Zealand Data

There are no published studies on the concentration or effects of PFAS on New Zealand species. What little data there is on PFAS in New Zealand aquatic ecosystems is contained within unpublished consultant's reports.

Tables 3 and 4 summarise the data from a number of different investigations throughout New Zealand. BCFs have been calculated where possible. Field-based bio-concentration factors (BCF)/bio-magnification factors (BMF) are highly variable for the same species which may indicate that measured water concentrations were not representative of exposure or that dietary exposure or metabolism of precursor compounds may have been important exposure pathways.

In line with results from Australian defence force bases, PFOS and PFHxS are detected at the highest concentrations of all the PFAS analysed. A number of species analysed, particularly various bullies species and short finned eels, have very high BCF/BMF under certain conditions. Accumulation of PFOS has also been observed in some watercress plants that have been analysed from contaminated waterways.

Tissue samples from marine organisms collected near contaminated sites, or near discharge points of contaminated water have been analysed. These studies are very limited in terms of number of animals tested and number of species tested. However, the data does indicate that some gastropod species can have elevated concentration of PFOS compounds within their tissue. The limited amount of testing to date indicates that bivalve species only poorly accumulate PFAS compounds.

Testing of various fin-fish species has also revealed that very low concentrations of PFOS was detected in a number of species collected from several different locations within the Waitemata harbour including at control sites which have been located far away from known discharges.

Table 3: NZ Biota Sampling Results - Per- and Poly-Fluoroalkyl Substances (PFAS) - Freshwater Fish ^{1,2}

Sample Results ⁴	Tissue Residues				Bio-concentration Factor ³			
	Species							
	Carp (<i>Cyprinus spp.</i>)	Shortfin Eels (<i>Anguilla australis</i>)	Longfin Eel (<i>Anguilla dieffenbachii</i>) ⁵	Bully (<i>Giomorphus cotidanus</i>)	Carp (<i>Cyprinus spp.</i>)	Shortfin Eels (<i>Anguilla australis</i>)	Longfin Eel (<i>Anguilla dieffenbachii</i>) ⁵	Bully (<i>Giomorphus cotidanus</i>)
PFSA Compounds								
PFBS	<LOR	<LOR	<LOR	<LOR	NC	NC	NC	NC
Sum of Total PFHxS+PFOS ^{6,7}	23 - 81	19 – 400+	30	13 - 17	NC	9 - 727	40	23 - 591
PFNS	<LOR	<LOR -20	<LOR	<LOR	NC	NC – 12,500	NC	NC
PFCA Compounds								
PFBA	<LOR	<LOR - 0.56	<LOR	<LOR	NC	NC	NC	NC
PFHxA	<LOR	0.25 - 0.45	<LOR	<LOR	NC	1 - NC	NC	NC
PFOA	<LOR	0.37 - 0.69	0.35	<LOR	NC	9 - 69	4	NC
PFNA	0.31 - 0.96	<LOR - 4.3	0.5	<LOR - 0.4	NC	NC -123	25	NC - 20
<p>Notes:</p> <ol style="list-style-type: none"> All values in µg/L. Results are shown as a range of minimum and maximum concentrations. Bio-concentration Factor calculated by dividing tissue residue concentrations by surface water concentrations at the same locations. Only selected compounds. Result is from one sample only. Total PFOS is calculated by summing monoethyl, dimethyl and linear isomers. Where an isomer is below the detection limit it is not added to the summation. This is following the method in the reported lab results. Summations are made by adding compounds Total PFOS (7), Total PFHxS (3) together. Where one compound is below detection, it is not included in the summation. 								
<LOR		Less than the Limit of Reporting						
NC		Not Calculated due to results less than the limit of reporting in fish and / or surface water samples.						

Table 4: NZ Biota Sampling Results – Per and Poly Fluoroalkyl Substance (PFAS) – Marine Species ^{1,2}

Sample Results ³	Tissue Residues											
	Yellowbelly Flounder (<i>Rhombosolea leporine</i>)	Yellow-eyed Mullet (<i>Aldrichetta forsteri</i>) ⁴	Parore (<i>Girella tricuspidata</i>)	Mud Crab (<i>Helice crassa</i>)	Oyster (<i>Crassostrea gigas</i>)	Green-lipped Mussel (<i>Perna canaliculus</i>)	Hornshell (<i>Zeacumantus lutulentus</i>)	Harbour Top Shell (<i>Diloma subrostrata</i>)	Mud Whelk (<i>Cominella glandiformis</i>)	Cockle (<i>Austrovenus stutchburyi</i>)	Mud Snail (<i>Potamopyrgus spp.</i>)	Cats Eye (<i>Lunella smaragda</i>)
PFSA Compounds												
PFBS	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	0.47 - 0.62
Sum of Total PFHxS+PFOS ^{5,6}	<LOR - 7.7	0.75	1.2 - 1.8	<LOR - 8.5	<LOR - 0.4	<LOR	<LOR - 300	<LOR - 4.3	<LOR - 12	<LOR - 0.31	0.54 - 0.6	0.67 - 68
PFNS	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR
PFCA Compounds												
PFBA	<LOR	<LOR	<LOR	<LOR - 1.1	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR
PFHxA	<LOR	<LOR	<LOR	<LOR - 0.46	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR - 0.43
PFOA	<LOR - 0.33	<LOR	<LOR	<LOR - 0.99	<LOR	<LOR	<LOR - 10	<LOR	<LOR	<LOR	<LOR	<LOR - 1.1
PFNA	<LOR - 0.38	<LOR	<LOR	<LOR - 0.27	<LOR	<LOR	<LOR - 1.2	<LOR	<LOR	<LOR	<LOR	<LOR - 0.53

Notes:

1. All values in µg/kg.
2. Results are shown as a range of minimum and maximum concentrations.
3. Only selected compounds are shown.
4. Result is from one sample only.
5. Total PFOS is calculated by summing monoethyl, dimethyl and linear isomers. Where an isomer is below the detection limit it is not added to the summation. This is following the method in the reported lab results.
6. Summations are made by adding compounds Total PFOS (7), Total PFHxS (3) together. Where one compound is below detection, it is not included in the summation.

<LOR	Less than the Limit of Reporting
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4.0 Aquatic Ecology

4.1 Introduction

This section of the literature review includes a summary of the available ecotoxicity data for aquatic organisms and the water quality guidelines for PFAS compounds that have been derived from these data and discussion of the data limitations.

Ambient background concentrations of PFAS are unknown in New Zealand but several contaminated sites investigations within NZ have reported PFOS concentrations in unimpacted rural surface waters of less than 0.1 ng/L. Vedagiri *et al.* (2018) undertook a literature review of various published reports from North America and found that the background concentration of PFOS in freshwater bodies ranged from 0.8 ng/L to 138 ng/L. Saito *et al.* (2004) found PFOA concentrations as low as 0.1 ng/L in remote surface waters in Japan but PFOA concentrations near cities were generally between 2 to 10 ng/L. It is likely that background concentrations of PFOS compounds in New Zealand rural and urban areas ranges between the pg/L to low ng/L.

For aquatic organisms, multigenerational studies have documented effects when organisms are exposed to 1-10 µg/L of PFOS. In these cases, reproductive and developmental effects have been identified in fish fry where the parent fish are exposed (Ankley *et al.*, 2005; Du *et al.*, 2009; Han and Fang, 2010; Ji *et al.*, 2008; Keiter *et al.*, 2012; Wang *et al.*, 2011). When used in conjunction with all other aquatic toxicity data in a species sensitivity distribution, the extrapolation of these results has resulted in a very low guideline level for the draft ANZECC freshwater 99% protection level (ANZECC, 2015a and 2015b).

Bio-accumulation and bio-magnification of PFAS compounds has been observed in a number of different species and different ecosystems around the world, with apex predators tending to have the highest concentrations of PFAS compounds (Ahrens and Bundschuh, 2014). A number of studies have indicated that both PFOA and PFOS compounds are accumulated more strongly in the livers of aquatic organisms and that longer chain PFAS compounds are more strongly accumulated than shorter chain compounds (Gruber *et al.*, 2007; Fujii *et al.*, 2018; Sanganyado *et al.*, 2018; Shi *et al.*, 2018). New Zealand data have shown that PFAS can bio-accumulate within aquatic organisms to very high levels (see Tables 3 and 4). A number of different species tested in New Zealand have shown that aquatic organisms have the ability to bio-accumulate PFAS compounds. This raises concerns that PFAS compounds could be bio-magnifying up the food chain and could pose a risk to apex predators such as eels, sea birds and marine mammals.

Very limited testing of some marine species has been undertaken within New Zealand. Marine gastropods appear to bio-magnify PFAS compounds more strongly than bivalve species but it is difficult to make a direct comparison as the two different taxa have not been collected at all sampling sites.

There is limited data regarding the potential for PFAS to cause immunotoxicity in exposed organisms (DeWitt *et al.*, 2012). However, there is some data which suggests that environmental exposures can result in immunosuppression and increases the susceptibility of marine organisms (particularly marine mammals) to infectious diseases (Fair *et al.*, 2013). Information on the impacts of PFAS exposure on aquatic flora is very limited but studies suggest that aquatic flora are less sensitive receptors than aquatic fauna. However, New Zealand data does show that watercress does have the ability to accumulate long chain PFAS compounds such as PFOS and it may be possible for watercress to accumulate concentrations of PFAS that could pose a risk to higher organisms or even human consumers.

Eels particularly seem to be able to accumulate elevated concentration of PFAS compounds (particularly PFOS). In Australia and New Zealand, PFOS concentrations in fish tissue of up to 20,000 µg/kg have been measured. Similar results have been seen overseas as well; Couderc *et al.*, (2015) found European eels from the Loire estuary in France contained between 130-1293 µg/kg and on average PFOS concentrations were 75% higher than the EU EQS (Environmental Quality Standard) for biota of 9.1 µg/kg. Dungen *et al.*, (2016) also found levels of PFAS compounds in marketable eels from polluted rivers in the Netherlands which resulted in higher body burdens of PFAS compounds than the lower exposed group.

Overall, the limited data available indicates that environmental exposure of aquatic organisms to PFAS compounds at concentrations over 1-10 µg/L may have adverse impacts (particularly decreased reproductive success), but the sensitivity of aquatic organisms to PFAS compounds is very species specific and can vary over 5 orders of magnitude.

The following sections provide more information on the occurrence, toxicity, immunotoxicity and bio-accumulation potential of PFAS compounds in freshwater and marine water species.

4.1.1 Occurrence of PFAS in Aquatic Environment

PFAS chemicals are ubiquitous in the aquatic environment. They are persistent, bio-accumulative and some studies have shown them to be toxic. They have been reported to be present in surface waters, groundwaters, and aquatic biota.

Prevedourous *et al.* (2006) concluded that the oceans are the ultimate environmental sink for PFCA (such as PFOA) and the majority of the PFCA that have been historically released have ended up in the world's seas. This is due to

the fact that PFCA do not undergo metabolic or environmental bio-degradation, they are water soluble and they have very long environmental residence times.

A number of studies have reported elevated PFAS concentrations in freshwater (Saito *et al.*, 2004; Prevedourous *et al.*, 2006; Rumsby *et al.*, 2009; Awad *et al.*, 2011; Oliaei *et al.*, 2013; Pan *et al.* 2014; Anderson *et al.*, 2016; Liu *et al.*, 2018; Taylor *et al.*, 2018). Saito *et al.* (2004) found PFOA concentrations as low as 0.1 ng/L in remote surface waters in Japan but PFOA concentrations near cities were generally between 2 to 10 ng/L. Measurement of PFAS concentrations in surface waters in several locations around New Zealand has found PFOS concentrations between 5,000 -10,000 ng/L near fire fighting training facilities. At control sites upstream of these facilities and at sites several kilometres downstream PFOS concentrations were less than 0.1 ng/L (PDP, unpublished data). PFOA concentrations in New Zealand surface waters have tended to be even lower.

4.2 Freshwater Ecology

Discharges from contaminated sites (such as fire training areas and airports) as well as wastewater treatment plants have impacted on water quality in a number of freshwater bodies around the world (Rayne and Forest, 2009; Rumsby *et al.*, 2009; Muller *et al.*, 2009; Pan and You, 2010; Awad *et al.*, 2011; Oliaei *et al.*, 2013; Ahrens and Brundschun, 2014; Kwadijk *et al.*, 2014; Pan *et al.*, 2014; Ahrens, *et al.* 2015; Liu *et al.*, 2015; Anderson *et al.*, 2016; Taylor *et al.*, 2018). The Swedish Environmental Research Institute (2015) found that firefighting training areas can cause locally elevated concentrations of PFOS in fish near large airports. This has also been observed at a number of airports and rural fire fighting facilities with fire training areas in Australia and New Zealand.

This section of the report summarises the potential for exposure to PFAS compounds to impact on freshwater fauna and flora.

4.2.1 Fauna

4.2.1.1 Bio-accumulation

Ahrens and Bundschuh have presented a summary of the potential impacts of PFAS on aquatic systems including bio-accumulation (Ahrens and Bundschuh 2014). They note that these chemicals bio-accumulate. Average concentrations range from 0.1 to 10 µg/kg ww for invertebrates, from 1 to 100 µg/kg ww for fish, from 1 to 100 µg/kg ww for reptiles, from 1 to 500 µg/kg ww for birds and 5 to 10,000 µg/kg ww for mammals. Some of the higher values in birds and mammals were found in samples of liver. The review notes that these chemicals accumulate in blood in animals by binding to proteins which is different to most other persistent chemicals which accumulate in lipid. PFOS accumulates more readily than PFOA. Also, branched isomers are more readily excreted than linear isomers, so they accumulate less (Ahrens and Bundschuh, 2014).

Babut *et al.* (2017) investigated the uptake of PFAS in fish and other aquatic species in the Rhone River, France. Composite samples of aquatic plants and benthic invertebrates were collected as well as samples of three fish species (*Barbus barbus*, *Gobio gobio* and *Rutilus rutilus*). The researchers also looked at the stomach contents of the fish to assist with dietary makeup for use in determining bio-magnification factors. Aquatic plants contained between 4 and 7 µg/kg ww for the sum of PFAS detected with PFNA, PFUnDA and PFTriDA detected at the highest levels. For the benthic invertebrates, concentrations ranged from 6 to 350 µg/kg ww for the sum of all PFAS detected with PFUnDA, PFTriDA, PFOS, FOSA and 6:2 FTS detected in 100% of samples and PFNA, PFDA, PFDoDA, PFTeDA, and PFHxS detected in more than 80% of samples. PFAS concentrations in the fish species ranged from 100-300 µg/kg ww for *Rutilus rutilus*, 200-300 µg/kg ww for *Gobio gobio* and 200 to 800 µg/kg ww for *Barbus barbus*. Bio-magnification factors significantly greater than 1 were calculated for PFNA, PFDA, PFUnDA, PFDoDA, PFTriDA, PFHxS, FOSA, PFOS and PFDS for at least one of the species. These bio-magnification factors were calculated assuming dietary exposure only (as is relevant for bio-magnification). But that does mean that uptake from water was not included in the considerations (Babut *et al.*, 2017).

Taylor *et al.* (2018) investigated bio-accumulation of PFOS in fish collected in two estuaries in Australia. For fish collected in Port Stephens, levels of PFOS in all species showed a clear trend of decreasing concentrations with distance from the likely source. For fish collected in the Hunter River, only some species showed such a trend. These results indicate that fish caught more than 10 km away from the presumed source may still contain concentrations that are above recommended guidelines for seafood to be consumed by people (Taylor *et al.*, 2018).

Falk *et al.* (2015) studied the uptake and elimination of PFBS, PFHxS, PFOS, PFOA and PFNA in rainbow trout when the fish were exposed via their diet. The fish were fed with food containing these PFAS chemicals for 28 days and then PFAS free food for the next 28 days. The presence of the chemicals was assessed in muscle, liver, kidneys, gills, blood, skin and the carcass. Up to 15% of the total amount of PFOS to which the fish were exposed ended up in the whole fish. For PFOA, the total amount taken up was 0.6%. The majority of the chemicals were found in the livers. Sulfonates were taken up more readily and took longer to clear from the body than the carboxylic acids. The concentration of PFOS in muscle tissue reached 50 µg/kg at day 28 (Falk *et al.*, 2015).

Ulhaq *et al.* (2015) also investigated uptake and elimination of PFOA in zebrafish. Exposure occurred via the water in which the fish lived. Fish were exposed to 10 µg/L of radiolabelled PFOA for 40 days followed by 80 days in clean water for elimination. Fish were sampled regularly through the study and analysed for PFOA. Steady state concentration was reached at 20-30 days at 300 µg/kg. The

study found that PFOA was present in oocytes at the end of the exposure period indicating the potential for transfer of the chemical from the parent to the eggs and the resulting exposure of embryos during development. Additional experiments were undertaken with a range of exposure concentrations. These indicated that the higher the exposure concentration, the higher the bio-concentration factor in a linear fashion. The kinetics of elimination appears to follow a two-step process with an initial fast elimination phase followed by a second slower elimination phase (Ulhaq *et al.*, 2015).

4.2.1.2 Distribution in Tissue

There are a number of studies on the distribution of PFOS and PFOA in fish and marine mammal tissues (Gruber *et al.*, 2007; Fujii *et al.*, 2018; Sanganyado *et al.*, 2018; Shi *et al.*, 2018). Both PFOA and PFOS are significantly more elevated in liver and blood serum than muscle tissue. No literature was identified regarding tissue distribution in other aquatic organisms.

4.2.1.3 Toxicity

Ecotoxicity data for various types of aquatic organisms have been collated in a number of reviews including ANZECC, 2015a, 2015b; Environment Canada, 2018; RIVM, 2010; Verbruggen *et al.* 2017. These data are summarised in Tables A-2 and A-3 in Appendix A.

The available ecotoxicology data indicates that of the different species studied (which include zooplankton, algae, plants, insects, invertebrates, fish and frogs), the most sensitive species/studies are the following:

- ∴ European damselfly (*Enallagma cyathigerum*) (Bots *et al.*, 2010; Environment Canada 2015): NOEC of <10 µg/L (for larvae emergence);
- ∴ Freshwater midge (invertebrate) (*Chironomus tentans*) (MacDonald *et al.*, 2004): NOEC <2.3 µg/L (with most sensitive effect being total emergence); and
- ∴ Multi-generation fish studies (species including Japanese medaka (*Oryzias latipes*), zebrafish (*Danio rerio*), Swordtail (*Xiphophorus helleri*) and fathead minnow (*Pimephales promelas*)) (Ankley *et al.*, 2005; Du *et al.*, 2009; Han and Fang 2010; Ji *et al.*, 2008; Huang, *et al.*, 2010; Keiter *et al.*, 2012; Wang *et al.*, 2011): NOEC in the range 0.6 to 10 µg/L (with survival, growth and fertility the most sensitive endpoints).

These studies show that there are reproductive and developmental effects in aquatic species at low concentrations of PFOS in water, with the lowest NOEC of approximately 0.6 µg/L. When used in conjunction with all other aquatic toxicity data in a species sensitivity distribution, this results in extrapolation of these results to give a very low level for the draft ANZECC freshwater 99% protection level.

ANZECC Water Quality Guidelines

Draft fact sheets for PFOS and PFOA prepared for the Australian and New Zealand Guidelines for Fresh and Marine Water Quality review the available data for the ecotoxicity of these chemicals. These guidelines have used a species sensitivity distribution using chronic data to generate a guideline value. The data included in the distributions are provided in Table A-2 and Table A-3.

For PFOS, this review was undertaken in 2015, so there were additional studies reviewed that were not covered in the RIVM (Netherlands National Institute for Public Health and the Environment) review discussed below. The additional studies showed effects at much lower concentrations for some organisms (fish and insects) than were used in the RIVM review. These data were fitted to a species sensitivity distribution to allow the calculation of the concentration likely to affect 5% of species (i.e., HC5). The concentration protective of 95% of species was determined to be 0.13 µg/L. The concentration protective of 99% of species was determined to be 0.00023 µg/L. This very low value for the extreme end of the tail of the species distribution is in part because of the large concentrations required to affect algae compared to those that affect fish. Limitations in the data for the low end of the species sensitivity distribution also affect the statistical calculations (ANZECC, 2015a, 2015b).

Further refinement of the evaluation of the data available for PFOS has been undertaken since 2015. Revised draft guidelines have been developed based on separating the data for aquatic plant species from the data for aquatic animal species. These data were separated because it was considered the distribution was bimodal – i.e. the mechanism for effects on plants was quite different and much less sensitive than for animals and including the plant data in the calculations had the potential to not give appropriate protection to the most sensitive animal species.

It is important to note that the guidelines from 2015 and the refined ones being discussed currently all remain as draft. No values are considered final at this time (late 2018).

Another issue to consider is the basis of the approach used in the ANZECC guidelines. As with many similar methodologies for the development of water quality guidelines internationally, it is considered that using a species sensitivity distribution to estimate a concentration that should not affect more than 5% of species is appropriately protective for chemicals that are not particularly long lived in the environment (i.e. 95% protection). For chemicals that are more long lived, it has been difficult to determine the best approach to generate water quality guidelines. ANZECC chose to use the same toxicity data as used to determine a 95% protection value but to use a more conservative statistic – the 99% value – to give a higher level of protection. This approach is not based on

any understanding of how a chemical might bioaccumulate or how much it might bioaccumulate.

The guidance in the ANZECC document notes that, for any bioaccumulative compound, field measurements of tissue concentrations are the preferred approach for managing secondary poisoning etc. The next best approach is using the 99% protection value instead of the 95% protection value to screen water data. It has been common practice to just use the 99% protection value to screen most such chemicals. Given the highly bioaccumulative nature of PFAS and that they accumulate in blood and other protein rich tissues compared to the lipid stores where most other bioaccumulative chemicals are stored, it is appropriate to take note of the guidance in the ANZECC guidelines – that field measurements are the appropriate way to address secondary poisoning.

In regard to PFOA, this data was fitted to a species sensitivity distribution to allow the calculation of the concentration likely to affect 5% of species (i.e. HC5). The concentration protective of 95% of species was determined to be 220 µg/L. The concentration protective of 99% of species was determined to be 19 µg/L. There were fewer issues with the statistical evaluation of this data so the difference between the 95% and 99% protection values is more like that normally seen for other bio-accumulating chemicals (ANZECC, 2015a, 2015b).

Dutch Water Quality Guidelines

The data used in the RIVM review show that the ecotoxicity of PFOS varies across 5 orders of magnitude varying from values around 2 µg/L to almost 300,000 µg/L depending on species (RIVM, 2010).

The data were considered to generally fulfil the requirements for use to develop a species sensitivity distribution. However, some of the more sensitive species only had lowest observed effect concentrations (LOEC), not no observed effect concentrations (NOEC). This means that fitting a species sensitivity distribution to this data is not reliable for the lower end of the distribution – the most important end for determining a water quality guideline. The Dutch authorities then determined that this method could not be used, and instead they used an assessment or uncertainty factor of 100 with the lowest LOEC to give a water quality guideline of 0.023 µg/L for freshwater. This value is approximately 10 fold lower than the ANZECC guideline for PFOS discussed above (RIVM 2010).

Verbruggen *et al.*, (2017) proposed a similar approach to develop a guideline for PFOA. Verbruggen *et al.*, 2017 derived water quality guidelines for PFOA using both assessment factors and species sensitivity distributions as had been done previously for PFOS. For freshwater, a guideline of 1200 µg/L was determined for PFOA using assessment factors and the combined dataset for fresh and marine species and 4400 µg/L using just the data for freshwater species. A species sensitivity distribution was also derived. It yielded an HC5 of 54000 µg/L which

gives a guideline value of 5400 µg/L using a standard uncertainty factor of 10. When the marine and freshwater data were combined, the guideline value becomes 2800 µg/L. The difference between all of these values is not large. The recommended value for implementation was 2800 µg/L for freshwater species. These values are all maximum acceptable concentrations (Verbruggen *et al.*, 2017).

These authors also derived an annual average guideline using the species sensitive for chronic exposures. This is the value that is more in line with how water quality guidelines are calculated in Australia/New Zealand. There were limited data so only the assessment factor approach could be used. For freshwater, the annual average guideline is 30 µg/L based on the NOEC from the fish microcosm experiment and an assessment/uncertainty factor of 10. This value is similar to the proposed 95% protection Australia/New Zealand value. In addition, a value in water protective for secondary poisoning in higher trophic organisms was calculated at 0.99 µg/L (Verbruggen *et al.*, 2017).

Canadian Water Quality Guidelines

Environment Canada reviewed the available literature for the ecotoxicity of PFOS and determined a guideline value of 6.8 µg/L for direct ecotoxicity (i.e. toxicity to the organisms exposed to the water). They did not undertake such a review for PFOA. They also did not determine a water quality guideline based on protecting higher organisms from secondary poisoning. Instead, they determined tissue concentrations in fish and other food items protective for higher organisms that could be affected by secondary poisoning (i.e., excess uptake through diet) (Environment Canada 2018).

The aquatic toxicity data used in determining the water quality guideline were chronic values that ranged from 10 to 53,000 µg/L. They used the data to generate a species sensitivity distribution from which they determined the concentration that could affect 5% of species (i.e. HC5). Unlike the European approach (i.e. RIVM) where the HC5 was divided by a standard uncertainty factor of 100 to get a guideline value, Environment Canada used the HC5 value directly as the guideline value. If Environment Canada had taken the same approach as the Europeans – using an assessment factor of 100 – they would have determined a guideline for the protection of direct aquatic toxicity of 0.1 µg/L which is similar to the value determined by the Europeans – 0.023 µg/L and the value determined by ANZECC – 0.13 µg/L (Environment Canada 2018).

Other Reviews and Studies

CONCAWE (2016) has also prepared a review of the ecotoxicity of PFOS and PFOA. For PFOS, ecotoxicity for various aquatic organisms ranged from 2 to 283,000 µg/L. This is the same range as used by RIVM. The review notes that the lack of robust longer-term studies is a significant limitation on developing an

appropriate water quality guideline, given the persistence of this chemical. For PFOA, no European guideline was available at the time of this review, but the limited information about the ecotoxicity of PFOA indicated that it was less toxic than PFOS to aquatic organisms (Concawe, 2016).

UNEP prepared a risk profile for PFOA in 2016. The profile noted that generally, ecotoxicity for aquatic organisms was low using standard tests such as US EPA and OECD test protocols. However, adverse developmental and reproductive effects in multi-generation experiments were reported in fish and there was toxicity to algae and other organisms observed in non-standard tests. Other studies showed estrogenic effects, impacts on reproduction, liver toxicity and inflammation. While standard tests are useful for most chemicals, those that are extremely persistent and bio-accumulative tend to be better assessed using non-standard tests specifically targeting potential modes of action. The profile noted that PFOA meets the technical requirements for listing as a persistent organic pollutant under the Stockholm Treaty (UNEP, 2016).

UNEP prepared a risk profile for PFOS in 2006. The profile noted that the lowest LC50 value for fish was 4700 µg/L and NOEC was 300 µg/L. For aquatic invertebrates, the lowest LC/EC50 value was 3600 µg/L and NOEC was 250 µg/L. For algae, the most sensitive result (EC50) was 48000 µg/L with a NOEC of 5300 µg/L. The profile noted that a non-standard study on *Chironomus tentans* (Midge) gave a much lower NOEC of 49 µg/L based on growth and survival. The profile noted that PFOS meets the technical requirements for listing as a persistent organic pollutant under the Stockholm Treaty and it has been listed on the Treaty (UNEP, 2006).

Valsecchi *et al.* (2017) undertook a review of the literature to develop water quality guidelines for PFOA, PFBA, PFPeA, PFHxA and PFBS (Valsecchi *et al.*, 2017). In accordance with European guidance, data was collated and evaluated. In regard to direct toxicity the following guidelines were developed:

- ∴ PFOA – a short term guideline of 2,220 µg/L for fresh water and 450 µg/L for marine waters and an annual average (long term) guideline of 30 µg/L for freshwater and 3 µg/L for marine waters.
- ∴ PFBA – a short term guideline of 1,100 µg/L for fresh water and 110 µg/L for marine waters and an annual average (long term) guideline of 110 µg/L for freshwater and 11 µg/L for marine waters.
- ∴ PFPeA – a short term guideline of 3,180 µg/L for fresh water and 318 µg/L for marine waters and an annual average (long term) guideline of 32 µg/L for freshwater and 3.2 µg/L for marine waters.
- ∴ PFBS - a short term guideline of 3,720 µg/L for fresh water and 372 µg/L for marine waters and an annual average (long term) guideline of 372 µg/L for freshwater and 37 µg/L for marine waters.

- ∴ PFHxA -insufficient data was available to derive a guideline (Valsecchi *et al.*, 2017).

In addition, for PFOA, water quality guidelines based on protection for secondary poisoning, rather than just direct toxicity, were derived. As is the case for the RIVM reviews described above, these values are much lower than those derived for protection from direct toxicity. The values in this review are 0.1 µg/L for freshwater and 0.02 µg/L for marine waters (Valsecchi *et al.*, 2017).

A number of other reviews are available which provide summaries of the same data as has already been discussed above (Ahrens and Bundschuh 2014; Beach *et al.*, 2006; Ding and Peijnenburg 2013; Giesy *et al.*, 2010; McCarthy *et al.*, 2017).

All of the government agencies discussed above and the reviews by individual research teams identified similar ecotoxicity, and concluded that standard ecotoxicity tests do not adequately characterise the potential for these chemicals to cause impacts; and that multi-generation effects or reproduction/development effects are the most sensitive effects driving the development of water quality guidelines for these chemicals.

The effects seen in the F1 generation (first set of offspring) in multi-generation fish tests may be related to the bio-accumulation of these chemicals in the parents including in the eggs. This could mean exposure of the embryos to PFAS during development is much higher than would occur when the chemicals are just in the water in which a fish might be swimming (or an egg may be developing) so the effects are more about the level of internal exposure, rather than due to genetic changes in the parents that are passed onto the next generation. It does indicate that the highly bio-accumulative nature of these chemicals is a critical aspect and that the standard ecotoxicity tests are not designed to cover this aspect well.

This is not the first chemical group for which this shortcoming has been identified. During the investigation of the potential ecological impacts of dioxin-like chemicals, it was noted that if fish were kept in clean water for some time (weeks to months) after they had been exposed in a short term acute test or other type of fish tests, they died. Fish are not normally retained in the laboratory after such a test, so it took some time to identify this phenomenon. It was linked to the accumulation of the dioxin-like chemicals in the fish (Gatehouse, 2004).

Toxicity of PFAS compounds to marine mammals is less well understood because there are very few published studies on marine mammals. This is because research is difficult to undertake on marine mammals due to regulatory issues as well as the costs to undertake such studies (Fair and Houde, 2018). Fair and Houde (2018) raised concerns regarding the potential impacts that PFAS may have on marine mammals because of:

1. The toxicological properties of PFAS compounds and the ability to impact on development, reproduction, immune system as well as systematic toxicity, especially during critical stages of development, and
2. The high concentration of PFAS compounds found in marine mammals.

4.2.1.3.1 Immunotoxicity

There is limited information about the potential immunotoxicity of PFAS on aquatic species. Also, there is limited understanding of the immune systems of most aquatic organisms.

One study has reported some effects of environmental PFAS exposure on the immune systems of some aquatic organisms, with effects reported at serum levels around the same levels commonly reported in the environment (DeWitt *et al.*, 2012). Levels of PFOS in serum in a range of aquatic fish and reptile species were of the order of 0.006 to almost 500 ng/mL ($\mu\text{g/L}$). The species with the highest concentration was an eel species. Concentrations were in whole blood for the fish species and in plasma for the reptile species (DeWitt *et al.*, 2012). Given that this study was based on serum concentrations of PFOS, it is difficult to discuss in the context of normal ecotoxicity tests.

4.2.2 Flora

Ecotoxicity data for various types of aquatic plants have been collated in a number of reviews including (CRC CARE, 2017; Environment Canada, 2018; RIVM, 2010; Pi *et al.*, 2017; Verbruggen *et al.*, 2017). This data is summarised in Tables A-4-6 in Appendix A.

Most PFAS are not particularly toxic to plant species. The water quality guidelines for these chemicals are driven by fish and insect data.

4.2.2.1 Uptake and distribution in Tissues

There is very little information regarding the uptake and distribution of PFAS compounds in aquatic plants. However, it is likely to be similar to terrestrial plants (see Section 4.3.2). Pi *et al.* (2017) found that all PFAS compounds are readily accumulated by aquatic macrophytes. Shorter chain length PFAS (PFBS, PFPeA and PFHxA) had higher translocation factors to leaf tissue than longer chain length PFAS compounds. Pi *et al.* (2017) also found that bio-concentration factors for free-floating macrophytes were substantially lower compared to submerged species, especially for long chain length PFAS compounds.

4.2.2.2 Bio-accumulation Potential

Babut *et al.* (2017) investigated the uptake of PFAS in fish and other aquatic species in the Rhone River, France. Composite samples of aquatic plants and benthic invertebrates were collected as well as samples of three fish species

(*Barbus barbus*, *Gobio gobio* and *Rutilus rutilus*). Aquatic plants contained between 4 and 7 µg/kg ww for the sum of PFAS detected with PFNA, PFUnDA and PFTriDA detected at the highest levels. For the benthic invertebrates, concentrations ranged from 6 to 350 µg/kg ww for the sum of all PFAS detected with PFUnDA, PFTriDA, PFOS, FOSA and 6:2 FTS detected in 100% of samples and PFNA, PFDA, PFDoDA, PFTeDA and PFHxS detected in more than 80% of samples (Babut *et al.*, 2017).

4.3 Marine Ecosystems

4.3.1 Fauna

Uptake of PFAS into marine organisms has been documented in numerous studies and reviews such as (Fernandes *et al.* 2018; Giesy and Kannan 2001; RIVM 2010; Rüdél *et al.* 2011). These chemicals are known to accumulate, particularly in higher trophic organisms that consume marine species but are air breathing.

Routti *et al.* (2011) have reported on the concentrations of PFAS in Weddell Seal. Plasma was taken from 10 lactating seals from McMurdo Sound. PFUnDA (C11) was detected in all samples ranging from 0.08 to 0.23 ng/mL (µg/L). PFOS (C8), PFHxA (C6) and PFTriDA (C13) were detected in some samples. No other PFAS were detected in these plasma samples. The samples were collected during a much larger study investigating the health and nutrition of these animals. Other Antarctic species have also been assessed for PFAS contamination in other studies. PFOS has been detected in elephant seals (blood), Antarctic fur seals (muscle, liver), Adelie penguins (eggs), Gentoo penguins (eggs, muscle), South Polar skua (egg, blood) and white chinned petrel (muscle). The highest concentration in any of these species was 3.6 ng/mL in the muscle of the Antarctic fur seal (Routti *et al.*, 2015).

4.3.1.1 Bio-accumulation

Bio-accumulation of PFAS compounds is very species specific and depends on chain length and functional group of the PFAS compounds.

The review by RIVM notes that trophic magnification up the food chain has been investigated a number of times. For gill breathing organisms, bio-concentration occurs for these chemicals and at times magnification has been identified. For air breathing organisms, the magnification aspect of bio-accumulation (i.e. from diet) is more obvious. Magnification factors of between 2 and 20 have been identified in various studies reviewed by RIVM. Some of the magnification factors for PFOS that have been measured are the highest magnification factors ever reported for any chemical (RIVM, 2010).

A summary of bio-accumulation/bio-magnification factors is presented in Table A-4 in Appendix A. Published bio-accumulation factors range from less than 1

(for shorter chain compounds) to greater than 500 for some longer chain compounds.

4.3.1.2 Toxicity

PFAS are anions under environmental conditions which means toxicity could be different between freshwater and marine organisms as differences in salinity can affect a range of characteristics including solubility and uptake of a chemical. The data available does not indicate that there are significant differences but the dataset for marine organisms is limited.

Ecotoxicity data for various types of marine organisms have been collated in a number of reviews including (CRC CARE, 2017; Environment Canada, 2018; RIVM, 2010; Verbruggen *et al.*, 2017). These data are summarised in Tables A-1 and A-2 in Appendix A.

4.3.1.2.1 Immunotoxicity

There is limited information about the potential immunotoxicity of PFAS on marine aquatic species. Also, there is limited understanding of the immune systems of these types of organisms. Most studies have been undertaken on freshwater species and are discussed in Section 4.2.1.3.1.

One study has reported some effects of environmental PFAS exposure on the immune systems of some marine aquatic organisms (DeWitt *et al.*, 2012). Concentrations of PFOS in aquatic mammals in plasma ranged up to 3000 ng/mL (DeWitt *et al.*, 2012). It has been noted the infectious disease outbreaks in aquatic mammals have been observed (DeWitt *et al.*, 2012), however, it is not possible to link these disease outbreaks conclusively to chemical exposure.

The potential for immunotoxicity was observed in Green Mussels (*Perna viridis*) by Liu and Gin (2018). Liu and Gin (2018) monitored the response of several immunological bio-markers to assess the immune fitness of green mussel as a result of exposure to several PFAS compounds (PFOS, PFOA, PFNA and PFDA). This study found a significant decrease in bio-marker response to concentrations of PFAS compounds greater than 100 µg/L; and a 50% decrease in bio-marker response at concentrations greater than 1,000 µg/L. Liu and Gin (2018) concluded that exposure to PFAS compounds can inhibit Green mussel immune mechanisms and increase the susceptibility of the organism to diseases.

A study undertaken by Kannan *et al.* (2006) found significantly higher concentrations of PFAS compounds in sea otters that died of infectious disease than in sea otters that died of other causes. While correlation does not prove causation, the study indicates that further research is needed on the potential immunotoxicity of PFAS on marine mammals. Fair *et al.*, (2013) found that chronic PFAS exposure in Charleston Harbour dolphins resulted in immunological changes which could potentially make the dolphins more susceptible to diseases.

Impacts on a sensitive marker for immunotoxicity were reported in terrestrial species at serum concentrations around 100 to 1000 ng/mL (see Section 6.2.4.3). These concentrations overlap with the measured serum concentrations in the aquatic species, so it is possible that there may be impacts on the immune systems of wildlife due to exposure to these chemicals.

4.3.2 Flora

Ecotoxicity data for various types of marine aquatic plants have been collated in a number of reviews including (CRC CARE, 2017; Environment Canada 2018; RIVM 2010; Verbruggen *et al.*, 2017). These data are summarised in Tables 5 and 6.

Table 5: Ecotoxicity Data for Marine Plants for PFOS ¹	
Taxonomic Group	NOEC/EC10 (µg/L)
Algae	
<i>Skeletonema costatum</i> (Diatom)	3,200
<i>Isochrysis galbana</i> (Other algae)	12,200
Notes:	
1. Data obtained from CRC CARE 2017; Environment Canada 2018; RIVM 2010; Verbruggen <i>et al.</i> , 2017	

Table 6: Ecotoxicity Data for Marine Plants for PFOA ¹	
Taxonomic Group	NOEC/EC10 (µg/L)
Algae/Cyanobacteria	
<i>Skeletonema marinoi</i> (Diatom)	74,000
<i>Chlorella vulgaris</i> (Green algae)	195,000
<i>Geitlerinema amphibium</i> (Cyanobacteria)	50,000
<i>Isochrysis galbana</i> (Other algae)	42,000
Notes:	
1. Data obtained from CRC CARE 2017; Environment Canada 2018; RIVM 2010; Verbruggen <i>et al.</i> , 2017	

4.4 Marine Guidelines

There are no current ANZECC marine water quality guidelines for ecosystem protection. The National Environmental Management Plan for PFAS (NEMP PFAS) recommends that freshwater guidelines are used as an interim measure.

4.5 Key points of impacts of PFAS compounds on aquatic organisms

- ∴ PFAS compounds are widely distributed in the aquatic environment as the aquatic environment is a key sink for these compounds.
- ∴ Background concentrations of PFOS in surface waters reported in literature range between sub ng/L levels to several hundred ng/L concentrations. PFOS concentrations near impacted sites can exceed several hundred µg/L.
- ∴ Studies show that there are reproductive and development effects in aquatic species at low concentrations of PFOS in water, with the lowest NOEL around 0.6 µg/L (600 ng/L).
- ∴ Longer chain PFAS compounds are more toxic to aquatic organisms than shorter chain compounds.
- ∴ There is evidence that some PFAS are potential immunotoxins. Serum levels in some wild organisms exceed concentration ranges associated with immunological changes in laboratory studies.
- ∴ PFAS compounds can bio-accumulate in freshwater and marine species. Longer chain PFAS compounds are more strongly bio-accumulated than short chain compounds.
- ∴ Apex predators may be at risk from secondary poisoning due to the ability of some PFAS compounds to bio-magnify up the food chain, and their bio-persistence.

4.6 Ecological guidelines for aquatic organisms

There are no New Zealand ecological guidelines for PFAS compounds and there are relatively few international guideline values for aquatic organisms.

Currently, the Heads of Australian Environment Protection Agencies have proposed to adopt draft ANZECC water quality guidelines for PFOA and PFOS in freshwater in the interim (NEMP, 2018) and suggests the use of the freshwater guidelines for marine waters.

Valsecchi *et al.* (2017) derived environmental quality standards from a variety of protection objectives and ecotoxicological studies for PFAS. Guidelines for the protection of predators from secondary poisoning were derived only for PFOA and PFBS.

A summary of various ecological guidelines is presented in Table 7.

Table 7: Ecological Guidelines for aquatic organisms

Reference	Scenario	PFBA	PFOA	PFPeA	PFHxA	PFBS	PFOS
ANZECC (draft 2018)	95% ecosystem protection (direct toxicity)	-	220	-	-	-	0.13
RIVM (2010) Verbruggen <i>et al.</i> , 2017	Surface water (protection for direct toxicity – 95% protection)	-	30	-	-	-	0.023 (fw) 0.0046 (marine)
Valsecchi <i>et al.</i> (2017)	AA-QS _{fw,eco} Pelagic community	110	30	32	-	372	-
Valsecchi <i>et al.</i> (2017)	AA-QS _{sw,eco} Pelagic community	11	3	3.2	-	37	-
Valsecchi <i>et al.</i> (2017)	QS _{sed,fw} Benthic community	NR	-	NR	-	NR	-
Valsecchi <i>et al.</i> (2017)	QS _{sed,sw} Benthic community	NR	-		-	NR	-
Valsecchi <i>et al.</i> (2017)	QS _{biota,secpois} Predators (secondary poisoning)	0.9	NR	NR	-	-	-

Notes:

- All values are in µg/kg.
- '-' Insufficient data.
- 'NR' Not required.
- fw = freshwater; sw = salt water (Marine, coastal and transitional waters).

5.0 Sediment

5.1 Partitioning of PFAS compounds to Sediment/Soil

Due to the ionic and surface active nature of these compounds under environmental conditions, the methodologies available to predict partitioning do not work well (McCarthy *et al.*, 2017). This makes normal approaches to developing sediment quality guidelines not applicable.

More research is needed on the way PFAS partitions to solids before this gap can be filled. Some work is being undertaken in Australia on how these chemicals partition to soil which may assist in understanding some aspects of partitioning to sediment (Li *et al.*, 2018).

Valsecchi *et al.* (2017) reviewed the need for sediment quality guidelines for PFOA, PFBA, PFPeA, PFHxA and PFBS for the Italian government (Valsecchi *et al.*, 2017). They did not identify the availability of any ecotoxicity data for sediment dwelling organisms. They evaluated the potential of developing guidelines based on water quality guidelines and partitioning coefficients (Kow or Koc). Their review identified the lack of robust information for these partitioning coefficients and recommended that no sediment guidelines be derived for these chemicals at the time of the review (Valsecchi *et al.*, 2017).

5.2 Toxicity to Sediment Dwelling Organisms

There are currently no data available for ecotoxicity tests using benthic organisms.

6.0 Terrestrial Ecosystems

6.1 Introduction

There has been significantly less research undertaken on PFAS in terrestrial ecosystems than there has been on aquatic ecosystems. This is common for many chemicals. Most of the studies of terrestrial fauna have focused on the bio-magnification and bio-accumulation of PFOS in food chains (D'Hollander *et al.*, 2012). Studies of PFOS concentrations in arctic ecosystems (Kelly *et al.*, 2009; Latala, *et al.* 2009; Tartu *et al.*, 2017; and Dietz *et al.*, 2018) have found the highest concentrations of PFOS occur in apex predators such as polar bears. However, arctic food chains may not be a suitable comparison for New Zealand's ecological settings as they have been exposed to the emissions of volatile precursors, leading to a higher exposure to odd-carbon number homologues (Bossi *et al.*, 2015), rather than the C6/C8 homologues that are more commonly seen in New Zealand.

Vedagiri *et al.* 2018 estimated that the background concentration of PFOS in North American soils ranged from 0.018 to 2.55 µg/kg. These concentrations are two to three orders of magnitude below US EPA soil Regional Screening Levels for human health protection and well below observed effect concentrations in toxicity studies on terrestrial organisms reviewed within this report.

Limited research has been undertaken of effects and toxicity of PFAS on soil invertebrates (Sinderman *et al.*, 2002; Yaun *et al.*, 2017). These studies show that earthworm exposure to soil with highly elevated concentrations (greater than 100 mg/kg) of PFOS or PFOA can lead to weight loss, neuronal development and mortality. It is, however, unlikely that most sites would have PFOS concentration in soils at these levels.

The elimination of PFAS from terrestrial organisms is species dependent and some PFAS chemicals are very bio-persistent. Generally, with respect to the biological half-life of PFAS in terrestrial ecosystems:

- ∴ PFSA (i.e. PFOS) is longer than PFCA (i.e. PFOA).
- ∴ Straight chain compounds are more bio-persistent than branched chain compounds.
- ∴ Bio-persistence increases with chain length for PFCA (i.e. PFNA is more bio-persistent than PFHxA).
- ∴ Is often shorter for females than males.

However, it should be noted that the bio-persistence of PFAS compounds is highly species dependent.

PFOS is the most frequently detected PFAS in wildlife and is generally the most dominant PFAS species in most animals (Butt *et al.*, 2010). PFOS compounds are generally more toxic to wildlife than PFOA (NGWA, 2017). Both PFOS and PFOA have been linked to a wide range of adverse effects including hepatic, developmental toxicity as well as suppression of the immune system (NGWA, 2017). PFOS and PFOA can move from tissues in parents to the next generation (i.e. crosses the placenta in mammals and moves into eggs for fish, reptiles, amphibians and birds) thereby exposing early life stages to these compounds (Wang *et al.*, 2011; DEPA, 2015; Yang *et al.*, 2016; Grønnestad *et al.*, 2017). In the study by Ji *et al.* (2008) on Japanese medaka (a fish species) it was hypothesised that the effects seen in early life stages when parent fish were exposed were due to a higher level of exposure during development from the concentrations present in the eggs compared to the amount the eggs and fry could be exposed to directly from the water were they to develop within water from parents who had not been exposed. Therefore, there are significant concerns about the potential for these compounds to harm early life stages.

There is very limited information on the developmental toxicity of PFAS compounds. There is some information which suggests that exposure to long chain PFSA (such as PFNA and PFDeA) may cause some adverse developmental effects including decreased postnatal survival, delays in eye opening and decreased body weight amongst baby rats (Wolf *et al.*, 2010).

No studies were identified which indicated reproductive toxicity on wild terrestrial fauna as a result of PFAS exposure.

Limited data regarding phytotoxicity indicates exposure to PFOS may cause a reduction in shoot height/weight at concentrations greater than 10 mg/kg (Brignole *et al.*, 2003). Some studies found evidence of decreased germination rates and survival of seedlings at concentrations greater than 51 mg/kg. Overall, plant species seem to be less sensitive to the effects of PFAS compounds compared to aquatic and terrestrial fauna. Studies indicate that transfer factors from soil to plants are low (Kordel and Herrchen, 2008; Stahl *et al.*, 2013; Schner *et al.*, 2018). Short chain carboxylic acids have the highest potential to accumulate in the edible parts of plants, while longer chain PFAS compounds remain in the roots and storage organs of plants (Stahl *et al.*, 2009, 2013; Lechner & Knapp, 2011; Yoo *et al.*, 2011; Felizeter *et al.*, 2012, 2014; Krippner *et al.*, 2014; and Wan *et al.*, 2018).

The following sections provide more information on the occurrence, toxicity, immunotoxicity and bio-accumulation potential of PFAS compounds in terrestrial flora and fauna as well as avian species.

6.2 Terrestrial Fauna

6.2.1 Occurrence

There is no information on the occurrence of PFAS in New Zealand terrestrial fauna. However, the exposure of terrestrial fauna to PFAS compounds is likely to be limited to the vicinity of a relatively small number of contaminated sites and perhaps near locations where land disposal of municipal solid waste has occurred². Exposure of terrestrial biota to PFAS compounds may occur some distance downgradient of contaminated sites if impacted surface or groundwater is used for either irrigation purposes or animal drinking water.

6.2.2 Distribution in Tissue

Unlike other persistent organic pollutants (POPs), PFAS compounds are not concentrated in the fatty tissue of animals (Lau *et al.*, 2007). PFAS concentrations are generally highest in the liver, then present in decreasing

² This is based on multiple field observations in Australia and New Zealand around contaminated sites, the physicochemical properties of PFAS compounds in soils (see Section 2.2.1.3) and low transfer factor to plants (see Section 6.3.1).

concentrations in blood serum, kidney and then muscles. Contrary to other persistent organic pollutants PFAS compounds do not accumulate in fatty tissues (Lau *et al.*, 2007).

6.2.3 Bio-accumulation

There is limited information of the bio-accumulation potential of PFAS in terrestrial organisms and most of the available data appears limited to mammal species such as rabbits, pigs and cows (Numata *et al.*, 2014; Tarazona *et al.*, 2016; Vestergren *et al.*, 2013). There is considerable variation in the published field-derived BMF or TMF and there are very few laboratory-based studies to compare to the field-based studies. A summary of the BMF and TMF values are presented in Tables A-3-A-4 of Appendix A.

The bio-accumulation potential of PFAA in terrestrial organisms is generally higher than aquatic species (Concawe, 2016). As PFAA are highly water-soluble, aquatic organisms can excrete PFAAs via their gills but because of the low volatility of PFAA terrestrial organisms cannot effectively excrete PFAAs via their lungs. For most terrestrial organisms, PFAS compounds are mostly eliminated via urine rather than faeces (Concawe, 2016).

A recent study looking at the accumulation and effects of PFAA on earthworms found that PFAA can be detected in earthworms when they live in soil containing PFAS compounds as low as 0.1 µg/kg (Karnjanapiboonwong *et al.*, 2018). Zhu and Kannan (2019) found that longer chain PFCA (i.e. PFUnDA and PFDoDA) were accumulated in earthworms more readily than shorter chain PFCA. This trend was also found by Brauning *et al.*, (2019) in soils from two firefighting training grounds in Australia (see Table 8).

PFAA	Soil A (Sand with 2.9% Organic Content)	Soil B (fine grained Sand with 0.5% Organic Content)	Soil C (clayey Sand with 1.1 % organic content)
PFBA	16±0.9	0.4±0.2	2.3±1
PFPeA	1.4±0.5	0.3±0.1	>3
PFHxA	0.3±0.1	1±0	0.9±0.3
PFHpA	0.2±0	0.1±0	
PFOA	0.8±0.1	0.7±0.1	1.1±0.8
PFNA	1±0.3	2±0.6	
PFDA	1.6±0.1	3.6±0.8	>2.3

Table 8: BAF for PFAA into earthworms (from Brauning *et al.*, 2018)

PFAA	Soil A (Sand with 2.9% Organic Content)	Soil B (fine grained Sand with 0.5% Organic Content)	Soil C (clayey Sand with 1.1 % organic content)
PFUnA	4.2±0.7	9±1.7	>2
PFDoA	9±1.1	23±6	>2.8
PFBS	5.2	4.7±1.3	>49
PFHxS	6.1	6±2.6	31±10
PFOS	5±2.1	8±3.5	10±1

Notes:

1. Bio-accumulation Factors are in g_{soil}/g_{worm} .
2. Error is calculated from standard deviation from three samples.

Perfluorononanoic acid (PFNA) was the most strongly accumulating PFSA compound within the study and bio-accumulation potential decreased with decreased carbon chain length (i.e. PFNA > PFHxS > PFHpA > PFBS) (Karnjanapiboonwong *et al.*, 2018).

The elimination of PFAS from terrestrial organisms is species dependent and some PFAS chemicals are very bio-persistent (see Table 9). In general, with respect to the biological half-life of PFAS:

- ∴ PFSA (i.e. PFOS) is longer than PFCA (i.e. PFOA).
- ∴ Straight chain compounds are more bio-persistent than branched chain compounds.
- ∴ Bio-persistence increases with chain length for PFCA (i.e. PFNA is more bio-persistent than PFHxA).
- ∴ Is often shorter for females than males.

There are species differences in the elimination half-life of PFOS; the half-life is 100 days in rats, 200 days in monkeys, and 5.4 years in humans (OCED, 2002) (See Table 9).

Species	Elimination Half-life	Source
Mice	731-1,027 hours	ATSDR, 2018
Rats	179-1,968 hours	ATSDR, 2018
Cows	38.7 days	Vestergren <i>et al.</i> , 2013
Rabbits	88 days	Tarazona <i>et al.</i> , 2016
Monkey	110 days	Chang <i>et al.</i> , 2012
Monkey	170 days	Seacat <i>et al.</i> , 2002
Chickens	230 days	Tarazona <i>et al.</i> , 2015
Pigs	634 days	Numata <i>et al.</i> , 2014
Humans	5.4 years	ATSDR, 2018

6.2.4 Toxicity

While there have been a number of toxicity studies undertaken on animals to use in extrapolating to estimate human toxicity, there has been little testing undertaken on other terrestrial organisms or using studies outside of the laboratory setting. In most animal species tested, PFOS was much more toxic than PFOA.

Toxicity testing on rodents has raised concerns about potential developmental, neuroendocrine system, reproductive and systematic effects of PFOS (Cui *et al.*, 2009). Changes in liver weight and spleen have been seen during a number of laboratory studies on animals including mice, monkeys, and rats for PFOA, PFHxS and PFOS (ATSDR, 2018). The ATSDR review of the effects of PFAS exposure in laboratory animals concluded the primary effects observed were liver toxicity, developmental toxicity, and immune system toxicity.

Overall, the toxicity and bio-accumulation potential of short-chain PFAS compounds (C6 or less) in mammals is considered to be lower than long chain analogs (Lan *et al.*, 2018). Liu *et al.* (2017) undertook an ecotoxicity evaluation of PFBS (the potassium salt of PFBS) and compared it to the ecotoxicity of PFOS. PFBS did not show any acute or chronic effects to terrestrial animals (earthworms) at concentrations up to 1,000 mg/kg (dw) for the two endpoints examined (mortality and abnormalities) (Liu *et al.*, 2017). Karnjanapiboonwong *et al.* (2018) found no mortality effects except for PFBS at 1,000 µg/kg (i.e. 1 mg/kg) and all PFASs at 100,000 µg/kg (i.e. 100 mg/kg) which is lower than observed by Liu *et al.* (2017).

There have been a limited number of laboratory studies focused on the toxicity of PFAS compounds to invertebrates species, namely Odonata (Dragonflies and Damselflies) (Van Gossum *et al.*, 2009), Diptera (Flies) (Van Gossum *et al.*, 2010) and Bumble bee (*Bombus terrestris*) (Mommaerts *et al.*, 2011). These studies have found a reduction in off-spring and reproductive capacity. Van Gossum *et al.* (2010) found evidence of intergenerational effects on the offspring of the fly species (*Drosophila hydei*) when the parental flies were exposed to 50 ng/mL of PFOS.

Some pesticides have used PFOS and N-Ethyl Perfluorooctanesulfonamide compounds as active ingredients (such as LiPFOS) to control wasps (US EPA, 1999) and to control leaf-cutting ants (sulfluramid) (Nascimento *et al.*, 2018). Therefore, it is highly likely that some PFAS compounds are highly toxic to insects and bee species.

6.2.4.1 Developmental Toxicity

There are very few studies on the developmental toxicity in wildlife. However, laboratory studies undertaken on animals to assess the potential for developmental toxicity have found evidence that PFOS and PFOA may exhibit developmental toxicity on some mammalian species. PFOA and PFOS have induced developmental effects in rodents (ATSDR, 2018). Laboratory tests exposing mice to PFDeA (Harris and Birnbaum, 1989) and PFNA (Wolf *et al.*, 2010) resulted in a number of adverse developmental effects including decreases in postnatal survival, delays in eye opening, and decreases in pup body weight gain.

6.2.4.2 Reproductive Toxicity

No studies were identified which indicated reproductive toxicity on wild terrestrial fauna as a result of PFAS exposure. Laboratory studies have been undertaken on a number of animals, usually at doses (greater than 10 mg/kg/day) which are much higher than typical environmental exposures. However, multi-generation studies of rats do not provide indications of reproductive toxicity (ATSDR, 2018).

Decreases in testosterone levels and sperm count have been observed in mice administered with PFOS for 21 days (Wan *et al.*, 2011).

A 2-generational reproduction study undertaken by Butenhoff *et al.* (2004b) did not find any evidence of effects on estrous cycling, sperm number and quality or fertility in rats with doses up to 30 mg/kg/day of PFOA. Histological alteration has not been observed in monkeys or rats with PFOA exposures up to 100 mg/kg/day (ATSDR, 2018).

Overall, the reproductive system does not seem to be a sensitive target of PFOA, PFHxS or PFOS toxicity in laboratory studies of animals (mainly mammals),

although exposure to very high concentrations of PFOS did result in changes in testosterone and estradiol levels in some laboratory animals (ATSDR, 2018).

6.2.4.3 Immunotoxicity

No research was identified on the immunotoxicity of PFAS compounds on wild species. However, a number of laboratory trials have been undertaken on animals. Monkey toxicological trials undertaken in the 1970s show immunotoxicity and other adverse effects to PFOA (Goldenthal *et al.*, 1978 cited in Grandjean, 2018). Immune systems effects have also been observed in PFOA and PFOS exposed mice (ATSDR, 2018).

Impacts on a sensitive marker for immunotoxicity were reported in mice and chickens at serum concentrations around 100 to 1000 ng/mL (ATSDR, 2018). These concentrations overlap with the measured serum concentrations in the aquatic species, so it is possible that there may be impacts on the immune systems of wildlife due to exposure to these chemicals.

6.3 Key points of impacts of PFAS compounds on terrestrial fauna

- ∴ PFOS is more toxic than PFOA to terrestrial organisms.
- ∴ Both PFOS and PFOA have been linked to a wide range of adverse effects including hepatic, developmental toxicity as well as suppression of the immune system.
- ∴ Shorter chain PFAS compounds are less toxic than longer chain PFAS compounds.

6.4 Terrestrial Flora

There has been very limited research on the impacts of PFAS on terrestrial flora with much of the research being focused on plant uptake factors and the distribution of PFAS. Most of the research has focused on uptake in food crops and the potential hazards to human consumers.

6.4.1 Uptake and Distribution in Tissues

There have been relatively few long-term investigations on the uptake of PFAS substances from soil. Stahl *et al.* (2013) undertook a five-year long lysimeter experiment to study the behaviour of PFAS in soil and the potential for uptake into plants. This study found that short-chain compounds and PFOA were leached more readily from soil than PFOS. Approximately 3% of the PFOA was leached from soil over the 5-year experiment but only 0.013% of the PFOS was lost via leaching. The study showed that for wheat, rye, bailey, and canola PFAS concentrations were higher in the straw than seeds. Overall, during this experiment approximately 0.001% of the mass of applied PFOA was taken up by plants and about 0.004% of the applied PFOS was taken up by plants (Stahl *et al.*, 2013).

Research undertaken by Kordel and Herrchen (2008) indicates that plants have relatively low uptake rates (transfer factors) for both PFOS and PFOA (see Table 10 below), but elevated concentrations of PFAS can be found in edible plant material. This study corroborates the finding of Stahl *et al.* (2013) and Scher *et al.* (2018).

Table 10: PFOA and PFOS in Plant Material and Soil-Edible Transfer Factors (Kordel <i>et al.</i>, 2008)				
	PFOA		PFOS	
	Concentration (µg/kg dry weight)	Transfer factor	Concentration (µg/kg dry weight)	Transfer factor
Wheat Grain	0.49	0.021	0.10	0.004
Wheat Grain	1.12	0.014	0.031	0.001
Wheat Grain	42.92	0.147	4.30	0.001
Maize	0.47	0.021	0.53	0.022
Maize	1.56	0.020	14.41	0.031
Maize	6.36	0.022	93.89	0.028
Ryegrass	9.51	0.417	1.02	0.043
Ryegrass	37.04	0.480	26.41	0.057
Ryegrass	254.46	0.872	435.24	0.130
<i>Notes:</i>				
Plants watered with uncontaminated water				
Plants watered with moderately contaminated water				
Plants watered with highly contaminated water				

Some studies have shown that vegetables or grains which have been grown on agricultural lands that were irrigated with PFAS contaminated water can accumulate these compounds (Stahl *et al.*, 2009; Lechner *et al.*, 2011). Scher *et al.* (2018) undertook a study on the translocation potential of PFAS compounds into plants from domestic gardens with a history of irrigating soil with PFAS contaminated drinking water. This study found that PFBA, PFOA, and PFOS were detected in all of the residential gardens tested and PFOS was present in soil at a much higher concentration than other PFAS compounds. However, it found that short-chain PFAS compounds (such as PFBA and to a lesser extent PFPeA) had a

greater uptake potential by plants than longer chain PFAS and short chain sulfonates. Several other studies (Stahl *et al.*, 2009, 2013; Lechner and Knapp, 2011; Yoo *et al.*, 2011; Felizeter *et al.*, 2012, 2014; Krippner *et al.*, 2014; Gobelius *et al.*, 2017; Wan *et al.*, 2018 and Brauning *et al.*, 2018) have also found the above trend as well as concluding that long-chain PFAS compounds largely remain in the roots and storage organs of plants and short chain PFAS compounds transfer to and accumulate within the above-ground parts of plant (i.e., leaves and fruit). It is, however, expected that tuber type vegetables (such as potatoes and carrots) will have a higher potential to accumulate long chain PFAS compounds than above ground vegetables (i.e., cucumbers) and fruit (Lechner and Knapp, 2011).

Overall, short chain carboxylic acids compounds have the highest potential to accumulate in the edible parts of plants (Scher *et al.*, 2018, Ghisi *et al.*, 2019) due to their higher mobility in soil and higher translocation factors from soil to plants.

A summary of various transfer factors in various species of plants are presented in Tables A-5 and A-6 in Appendix A.

6.4.2 Phytotoxicity

There has been very little research associated with toxicity of these compounds to plants. Some studies have found a reduction in seedling germination and growth associated with high concentrations of PFOS in soil (Kordel and Herrchen, 2008). Brignole *et al.* (2003) undertook a study of PFOS phytotoxicity of onion, ryegrass, alfalfa, flax, lettuce, soybean and tomato, and the relative sensitivity and endpoints are summarized in Table 11.

Common name (<i>Latin name</i>)	Relative Sensitivity EC₂₅ (mg/kg)	End Point
Lettuce (<i>Lactuca sativa</i>)	6.79	Height
Ryegrass (<i>Lolium perenne</i>)	7.51	Shoot weight
Tomato (<i>Lycopersicon esculentum</i>)	11.7	Shoot weight
Onion (<i>Allium cepa</i>)	12.9	Shoot weight
Alfalfa (<i>Medicago sativa</i>)	53.3	Shoot weight
Flax (<i>Linum usitatissimum</i>)	81.6	Shoot weight
Soybean (<i>Glycine max</i>)	160	Shoot weight

Notes:

1. Data from Brignole *et al.*, 2003

Apart from a reduction in shoot height and shoot weight Brignole *et al.* (2003) did not find any other evidence of phytotoxicity over the period of the test for soils containing up to 1,000 mg/kg of PFOS.

Zhang *et al.* (2011) undertook a study to determine the potential effects of PFOS exposure to Chinese cabbage. During the 15 day trial, Zhang *et al.* (2011) found that PFOS inhibited the germination rate of seeds, growth processes and survival of Chinese cabbages at concentrations greater than 51 mg/L. However, research undertaken by Li (2009) found that PFOS had no observed effects on germination of lettuce, pakchoi, and cucumber at concentrations up to 200 mg/L. However, effects on root elongation were observed in lettuces and pakchoi when exposed to PFOS concentrations of 99 to 130 mg/L. Li (2009) study also found that PFOS was more toxic to plants than PFOA.

Currently, there is little information regarding the phytotoxicity of short-chain PFAA (Wen *et al.*, 2017). However, Liu *et al.* (2018) did undertake some phytotoxicity testing of PFBS (the potassium salt of PFBS). Lui *et al.* (2018) examined the seedling emergence and seedling growth of tomato (*Lycopersion escaeatum*), cucumber (*Cucumis sativus*), wheat (*Triticum aestivum*) and rice (*Oryza sativa*) to exposure of up to 1,000 mg/kg (dw) of PFBS. This study found that seedling emergence and growth appeared to be inhibited by exposure to PFBS with wheat being the most sensitive plant species. Overall PFBS has a similar level of toxicity to terrestrial plants as PFOS (Lui *et al.*, 2018).

6.5 Key points of impacts of PFAS compounds on terrestrial flora

- ∴ Plants are less sensitive to PFAS toxicity than aquatic or terrestrial fauna.
- ∴ Uptake factors of PFAS compounds are relatively low (generally less than 1).
- ∴ Short chain PFAS have a greater uptake potential than long chain PFAS compounds.
- ∴ Long chain PFAS compounds largely remain in the roots and storage organs of plants.
- ∴ Short chain PFAS compounds can be transferred to the above ground parts of plants (i.e. leaves and fruit).
- ∴ Significant phytotoxic effects are unlikely to occur at concentrations less than 50 mg/kg.

6.6 Ecological Guidelines for Soil

There are no New Zealand ecological guidelines for PFAS compounds, and there are relatively few international guideline values. A summary of various ecological guidelines to protection terrestrial ecosystems is presented in Table 12.

Table 12: Ecological Guidelines for Soil

Reference	Scenario	PFOS	PFOA
NEMP (2018)	Residential	0.01 mg/kg	-
RIVM (2011)	MTR _{lower}	10 µg/kg	-
RIVM (2011)	VR	0.1 µg/kg	-

6.7 Avian Fauna

6.7.1 Introduction

PFAS has been detected in the tissues of wild birds, or their eggs, including in North America, Europe, Asia, Australia and Greenland (Ahrens *et al.*, 2011b; Rüdél *et al.*, 2011; Thompson *et al.*, 2011; Environment Canada, 2013; Swedish Environmental Research Institute, 2015; Sedlak *et al.*, 2017; Su *et al.*, 2017; Barghi *et al.*, 2018). The substances have also been found in birds and eggs in remote locations such as the North Pacific and Arctic Oceans (Giesy and Kannan, 2001; Gewurtz *et al.*, 2013).

Bird species with terrestrial or aquatic diets are affected, with PFAS detected in a range of species including (but not limited to) owls, falcons, doves, kestrels, vultures, gulls, terns, ducks, ibis, pelicans, and albatross (Giesy and Kannan, 2001; Verreault *et al.*, 2005; Olivero-Verbel *et al.*, 2006; Thompson *et al.*, 2011; Bertolero *et al.*, 2015; Swedish Environmental Research Institute, 2015; Barghi *et al.*, 2018; Vorkamp *et al.*, 2018). PFOS concentrations in predatory birds are likely to be higher than in non-predatory species.

The majority of published research into PFAS in wild bird populations (such as those studies above) have focussed on assessing trends in concentrations of the contaminants in the organisms not necessarily the toxicity. There have, however, been some investigations that have found PFAS in wild bird eggs at levels close to, or greater than environmental guidelines (e.g. Environment Canada, 2013). Environment Canada (2013) found that the concentration of PFOS in gull eggs increased near polluted urban areas and the highest PFOS in starling eggs were found in starling nesting near landfills. An Environment Canada (2013) study found bird eggs near landfills and wastewater treatment plant have elevated concentrations of PFOS. Therefore, avian wildlife nesting near these sites may have higher PFOS concentrations within eggs near these types of sites. Environment Canada (2013) found that the concentration of PFOS within gull and starling eggs commonly exceeded draft FEQG for the protection of wildlife consumers. This indicates that, while the concentrations of PFOS observed in the eggs are unlikely to pose a risk to the birds themselves, they may pose a risk to apex predators.

Furthermore, among laboratory experiments (usually conducted on chickens), immunological, developmental and neurological effects have been observed at doses that are similar to those found in environmental samples (Peden-Adams *et al.*, 2009).

6.7.2 Uptake and Distribution in Tissue

PFAS are known to accumulate in protein-rich tissues; however, detailed studies on the uptake and distribution of PFAS in different bird tissues are limited. In studies on pelicans, gulls, and guillemots, the highest concentrations were found in blood plasma, liver, and eggs, with PFOS generally found at higher levels than other PFAS (Verreault *et al.*, 2005; Olivero-Verbel *et al.*, 2006; Holmström and Berger, 2008; Gebbink and Letcher, 2012).

6.7.3 Bio-accumulation

PFAS are known to bio-accumulate, particularly in protein-rich tissues such as eggs, liver, and blood. High trophic level animals (i.e., predators), including birds, have been found with higher concentrations of PFOS in their tissues than is contained in their food sources (Giesy and Kannan, 2001), indicating the bio-magnification of PFAS up the food chain. There is evidence of potentially harmful concentrations of PFOS in some wild predatory birds (Barghi *et al.*, 2018). Baragh *et al.* (2018) found that PFAS was higher in predator birds than non-predator birds. PFOS concentrations in most of the predatory birds exceeded threshold values for adverse health effects (Baragh *et al.*, 2018).

Birds that feed in aquatic environments may be at particular risk because PFAS are highly soluble in water and are known to bio-accumulate in fish and benthic (sediment dwelling) invertebrates (Rüdel *et al.*, 2011; Larson, Conder and Arblaster, 2018). Rates of bio-accumulation vary considerably between organisms (Concawe, 2016), therefore, understanding the ecological risks to birds associated with different exposure pathways remains difficult.

6.7.3.1 Toxicity

There have been a handful of laboratory studies assessing the toxicity of PFAS to birdlife, but only for PFOS and PFOA. Of those studies, most have tested the effects of directly injecting PFOS or PFOA into developing eggs (Molina *et al.*, 2006; O'Brien *et al.*, 2009; Peden-Adams *et al.*, 2009; Nordén, Berger and Engwall, 2016). Only one study to date has examined various doses given to adult birds (Newsted *et al.*, 2005). Therefore, PFOS is currently the only PFAS for which dietary intake avian toxicity reference values (TRV) are available that are robust enough for use in ecological risk assessments for avian wildlife (Larson, Conder and Arblaster, 2018).

Environment and Climate Change Canada (2018) cites a number of studies which indicate that exposure to PFOS results in increased liver weight in mallards and

northern bobwhite quail as well as causing hepatocellular adenomas in the liver in test species. Other toxic effects that Environment and Climate Change Canada (2018) notes are hypothyroidism in northern bobwhite quails.

6.7.3.2 Developmental Toxicity

Conflicting results have been reported in studies of the developmental toxicity of PFAS in birds. For example, Molina *et al.* (2006) injected domestic chicken eggs with PFOS, and while some embryo death occurred at high doses, no effect was noted on body or organ weights for surviving birds. This is in contrast to findings that included increased spleen and liver weights, and increased brain and wing asymmetry, in chicken hatchlings after exposure during incubation (Peden-Adams *et al.*, 2009).

Only one study has assessed the developmental toxicity of PFAS when administered in bird feed (Newsted *et al.*, 2005). High doses of PFOS fed to mallards and quail in the laboratory caused mortality in both species. For lower doses, no treatment-related mortality was observed. However, there was an increase in liver weight for quail, but no accompanying adverse effects were recorded. The results were used to develop a range of avian TRVs for a generic high-trophic level (i.e., predatory) species (see Table 13).

Table 13: PFOS Toxicity Reference Values and Predicted No Effect Concentrations for a Generic Trophic Level IV Predator						
	Male			Female		
	LOAEL	TRV	PNEC	LOAEL	TRV	PNEC
ADI (mg PFOS kg ⁻¹ body weight day ⁻¹)	0.77	0.021	0.013	0.77	0.021	0.013
liver (µg PFOS g ⁻¹ wet weight)	88	2.4	1.5	4.9	0.14	0.08
serum (µg PFOS mL ⁻¹)	141	3.9	2.4	8.7	0.24	0.15
egg yolk (µg PFOS mL ⁻¹)	-	-	-	62	1.7	1.0
Notes:						
1. Table adapted from (Newsted <i>et al.</i> , 2005).						

6.7.3.3 Reproductive Toxicity

No studies identifying the reproductive toxicity of PFAS to birds were identified in this literature survey.

6.7.3.4 Immunotoxicity

Immunological effects, in particular, an increased normal immune response in the absence of any infection, was detected in chicken hatchlings that were exposed to PFOS injected into eggs (Peden-Adams *et al.*, 2009). Because such effects occurred even at low doses, close to those found in the blood of wild birds, this indicates that the transfer of PFOS from mother to egg may be a risk to birdlife in the environment.

7.0 Impacts of PFAS exposure on New Zealand Ecosystems

Sections 4 and 6 outline the reported effects of PFAS when aquatic and terrestrial ecosystems are exposed. The data presented in Section 3.0 indicates that some aquatic organisms are likely to be exposed to concentrations of PFAS which will result in adverse effects (particularly reproductive and developmental outcomes). While PFAS compounds are an emerging contaminant from a regulatory point of view, it is likely that PFAS compounds have been discharged from some sites for 20 to 50 years. Therefore, the ecosystems around some of these sites probably have already been impacted if environmental levels were sufficiently high to cause effects. However, no studies have been undertaken to determine if the ecosystems have been impacted and it would be difficult to attribute any changes in the ecosystems around these sites to a single chemical or group of chemicals like PFAS. Organisms at these locations have been exposed to multiple chemicals and environmental stressors (i.e. changes in habitat, water temperature, flow, dissolved oxygen and suspended sediment).

There is a paucity of data with respect to the concentration of PFAS compounds within the New Zealand environment and in aquatic or terrestrial organisms. There are also limitations on the availability of such data in most environments around the world. Impacts on population dynamics, species distribution, dispersion, interactions between trophic levels on New Zealand ecosystems (or for ecosystems in other countries) are unclear due to the data limitations and the limited understanding of the mechanisms by which these chemicals cause adverse effects.

Overseas data suggests that typical background concentrations of PFAS compounds range from low pg/L to ng/L (Vedagiri *et al.*, 2018). It is difficult to get a good understanding of “typical background” concentrations in water, air or soil given the nature of these chemicals. Concentrations will be highly variable over short distances and over short time periods due to their water solubility, mechanisms by which they leave source areas and the surfactant characteristics which make fate and transport difficult to predict.

The long-term impact of exposures to low concentrations (as would be expected in typical background areas) is unclear and low-level exposures have not been

adequately investigated by researchers. However, there are concerns about the potential long-term impacts on apex predators due to the following factors:

1. Aquatic systems are likely to be the ultimate receiving environment for PFAS compounds.
2. Widespread use of PFAS compounds means they are likely to be present in landfill leachate and WWTP effluents. Landfills and WWTP processes will transform PFAS compounds into terminal PFAAs so landfills and WWTP effluents are likely to be low level diffuse sources of PFAS contamination into the aquatic environment (and groundwater) over the long term.
3. PFAS have a much longer half-life within the environment than other persistent organic pollutants (i.e. DDT and PCBs).
4. PFAS are only slowly eliminated from some organisms which will allow long term accumulation (some PFAS compounds are very bio-persistent compared to other classes of chemicals).
5. These compounds bioaccumulate within organisms and biomagnify within the food chain, which means that dietary exposure is likely to be an important exposure pathway for some apex species.

Currently, there is insufficient information to determine if current exposure to PFAS is having an adverse effect amongst apex predators. However, evidence exists to indicate that exposure to PFAS compounds can result in reproductive, developmental and immunotoxicity in marine mammals and avian receptors, so it is possible that in the future concentrations of these compounds within apex predators may reach levels which could have adverse impacts on the population of these organisms.

Another potential area of concern is birds (particularly fish eating birds and raptors) near contaminated sites, landfills and WWTP outfalls. Currently, there is no information about PFAS concentrations within the eggs of these species in New Zealand but, based on overseas data, it is likely that they will be more highly exposed than other avian species.

The impact on plants and terrestrial organisms is likely to be limited to the immediate area around highly contaminated sites. Other than a reduction in shoot height and growth rate, most studies have not observed any toxicological effects of exposure to PFOS at concentration below 1,000 mg/kg. Typical soil concentration of PFAS compounds published within literature (i.e. AECOM, 2017; Ahrens, *et al.*, 2015; Braunig, *et al.* 2019, Filipovic *et al.*, 2015; Houtz, *et al.*, 2013 and Karrman, *et al.*, 2011) at fire training areas have been found to be much lower than 1000 mg/kg so phyto-toxicity is unlikely.

The low translocation potential of PFAS compounds into edible portions of plants means that there is a lower potential for secondary poisoning to consumers of plant species.

8.0 Gaps in Knowledge

Based upon the literature review undertaken as part of this project, there are a number of areas where there is not enough information to understand the potential impact of PFAS compounds, particularly within the New Zealand ecosystem. However, gaps in knowledge of the environmental fate and ecological impacts that a chemical may have in the environment are not uncommon. In environmental investigations undertaken in Australia and New Zealand, PFBS, PFHxS, PFOS, PFOA and PFNA are the most commonly detected PFAS compounds and, therefore, any research should focus initially on these compounds. Further, for the PFAS compounds listed above we do see some evidence of effects in some studies at low environmental levels. On this basis, it is considered that priority should be given to the further study of these compounds.

Specific areas where there are gaps in knowledge include:

- ∴ The quality and quantity of ecotoxicological data available. There is a particular shortage of amphipod and insect data as well as intergenerational effects of freshwater and marine species.
- ∴ Additional research is required on the ecotoxicological properties of short chain perfluoroalkyl carboxylic acids, and perfluorobutane sulfonate, as these compounds are being detected.
- ∴ Toxicological and environmental fate data on short chain PFAS compounds and next-generation PFAS compounds (particularly ADONA, F35B, and GenX), this includes within the New Zealand environment.
- ∴ Insufficient data on sediment-dwelling organisms which results in the inability to develop reliable risk-based sediment quality guidelines.
- ∴ Insufficient data on the potential impacts of PFAS in birds and bird eggs around WWTP and landfills.

In addition, and more specifically, for New Zealand:

- ∴ There is a complete lack of any toxicological data for NZ species.
- ∴ There is insufficient data on PFAS presence in, and effects on, marine mammals within NZ coastal waters.
- ∴ There is insufficient data on the impact of PFAS compounds on apex level predators within the New Zealand ecosystem. In particular there is no information on the concentration and potential effects on shorebirds.

9.0 Recommendations for Future Research

There are significant knowledge gaps in the behaviour, environmental fate and toxicity of all PFAS compounds. However, it is beyond New Zealand resources alone to address all of these issues and it will require international effort over many years to gather sufficient data.

PDP suggests that the key aspects requiring more research (in order of decreasing priority) may be the New Zealand specific points detailed in Section 8, then more robust multi-generational studies, and then data on the next generation of PFAS compounds.

Some specific areas of research/work which could be undertaken include:

- ∴ Develop a national inventory of PFAS stockpiles, wastes and usage to meet the requirements of Article 6 of the Stockholm Convention.
- ∴ Characterisation of the effects and mode of toxicity of PFAS on key native species that are most likely to be exposed.
- ∴ Characterisation of bio-accumulation potential of PFAS in New Zealand native species.
- ∴ Development of additional water quality and biota guidelines for short chain and new PFAS compounds, particularly PFBS, PFNA, ADONA, F35B and GenX.
- ∴ Improved characterisation of the distribution of PFBS, PFHxS, PFOS, PFOA, PFNA, ADONA, F35B and GenX in different environmental compartments including:
 - Connections between soil:porewater:plants: soil biota for terrestrial environments,
 - Connections between groundwater:aquifer for solids,
 - Connections between dissolved:particulate:sediment:plant:biota in aquatic ecosystems,
 - Connections between dissolved:particulate:sewage for sludge in WWTPs.
- ∴ Liaise with Australia and perhaps other countries to develop sediment quality guidelines for PFAS compounds.
- ∴ Make sure that New Zealand is well connected with the main international research groups working on PFAS risk characterisation and management.

The potential impact of PFAS compounds on traditional foods (such as eels, kina, paua and other shellfish species) has not been investigated within New Zealand and there is insufficient information within the literature to understand the

potential impacts (if any) that discharges might have on them. Research specific to these impacts is considered likely to be of interest to mana whenua.

10.0 Conclusions

Despite the global distribution of PFAS, the fate and transport, particularly in the marine environment, is poorly understood. Furthermore, there are only a limited number of studies relating to PFAS in Australasia.

PFAS are persistent, and many have a high water solubility resulting in dispersal over vast distances via water. Consequently, PFAS are ubiquitous in the aquatic environment but its occurrence within the terrestrial environment may be more limited in New Zealand due to the (estimated) relatively small number of PFAS-contaminated sites. The presence of PFAS in avian species within New Zealand is mostly unknown but PFAS concentrations may be elevated in some bird species which live near landfills and WWTPs, as well as some contaminated sites.

The main route of uptake of PFAS in aquatic organisms is via contact with water and sediment with some contribution from ingestion of contaminated food; however, the exact mechanisms of absorption are still mostly unknown. PFAS tend to accumulate in the body by attaching to proteins. This occurs mainly in blood and organs which accumulate blood (liver and kidneys). While accumulation into muscle occurs to a more limited extent the proportion of muscle in the body can result in significant accumulation of ingested PFAS in the body. Unlike other persistent pollutants, PFAS compounds do not accumulate in fatty tissue.

For avian species, the primary exposure route is likely to be dietary consumption and for terrestrial species it is expected that exposure routes are likely to be either direct ingestion of contaminated soil, drinking of contaminated water and/or other dietary exposure.

Plants species appear to be less sensitive to PFAS toxicity than aquatic or terrestrial fauna. Shorter chain PFAS have a greater uptake potential than long chain PFAS compounds. Long chain PFAS compounds largely remain in the roots and storage organs of plants, whilst shorter chain PFAS compounds can be transferred to the above ground parts of plants (i.e. leaves and fruit).

Ecotoxicological studies of PFOS and PFOA on animals mainly show effects on the liver, gastrointestinal tract, suppression of the immune systems, reproductive organs and on thyroid hormone levels as well as disrupting cell growth in algae.

For other PFAS compounds, there is much less toxicological data. Shorter chain PFAS compounds are generally less toxic and thought to pose an overall lesser environmental risk than PFOS compounds.

In environmental investigations undertaken in Australian and New Zealand PFBS, PFHxS, PFOS, PFOA and PFNA are the most commonly detected PFAS compounds.

Currently, there is little or no information available on the impact of PFAS on the New Zealand ecosystem, but limited sampling of freshwater and marine fauna has found low levels of PFAS compounds in a variety of fish species caught even at control sites; and that freshwater and marine organisms can bio-accumulate long chain PFAS compounds. The ability of these compounds to be transported in water and the fact they can bio-accumulate and be bio-persistent in some organisms' means there is the potential for PFAS compounds to accumulate in apex predators within the New Zealand environment.

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Data on Physicochemical and Toxicological Properties of PFAS compounds

Table A-1: Physicochemical Properties									
Name	Acronym	CAS Registry Number	Molecular Formula	Molecular Weight (g/mol)	Water Solubility ^b (20-20°C) (g/L)	Vapor Pressure ^b (Pa)	Henry Coefficient [Pa·m ³ ·mol ⁻¹]	log Kow ^b [-]	log KOC [L/kg]
Perfluoroalkyl Carboxylates / Perfluoroalkyl Carboxylic Acids	PFCAs								
Perfluorobutanoic Acid	PFBA	375-22-4	F(CF ₂) ₃ COOH	214.04	Miscible	1307	--	2.82	1.9*
Perfluoropentanoic Acid	PFPeA	2706-90-3	F(CF ₂) ₄ COOH	264.05	112.6	1057	--	3.43	1.4*
Perfluorohexanoic Acid	PFHxA	307-24-4	F(CF ₂) ₅ COOH	314.05	21.7	457	--	4.06	1.3*
Perfluoroheptanoic Acid	PFHpA	375-85-9	F(CF ₂) ₆ COOH	364.06	4.2	158	--	4.67	1.6*
Perfluorooctanoic Acid	PFOA	335-67-1	F(CF ₂) ₇ COOH	414.07	3.4 - 9.5	4 - 1300	0.04 - 0.09	5.30	1.89 – 2.63*
Perfluorononanoic Acid	PFNA	375-95-1	F(CF ₂) ₈ COOH	464.08	9.50	1.3	--	5.92	2.36 – 3.69*
Perfluorodecanoic Acid	PFDA	335-76-2	F(CF ₂) ₉ COOH	514.09	9.50	0.2	--	6.50	2.76 – 2.96*
Perfluoroundecanoic Acid	PFUnA	2058-94-8	F(CF ₂) ₁₀ COOH	564.09	0.004	0.1	--	7.15	3.30
Perfluorododecanoic Acid	PFDoA	307-55-1	F(CF ₂) ₁₁ COOH	614.10	0.0007	0.01	--	7.77	--
Perfluorotridecanoic Acid	PFTrdA	72629-94-8	F(CF ₂) ₁₂ COOH	664.11	0.0002	0.3	--	8.25	--
Perfluorotetradecanoic Acid	PFTeDA	376-06-7	F(CF ₂) ₁₃ COOH	714.12	0.00003	0.1	--	8.90	--
Perfluoropentadecanoic Acid	PFPeDA	141074-63-7	F(CF ₂) ₁₄ COOH	764.12	--	--	--	--	--
Pentadecafluorooctanoic Acid Ammonium Salt (Ammonium Pentadecafluorooctanoate)	APFO	3825-26-1	C ₈ H ₄ NF ₁₅ NO ₂	445.11	14.2	0.01	--	--	--
Perfluoroalkyl Sulfonates / Perfluoroalkyl Sulfonic Acids	PFSAs								
Perfluorobutane Sulfonate	PFBS	375-73-5	F(CF ₂) ₄ SO ₃ H	300.10	46.2 - 56.6	631	--	3.90	1.2 – 1.79*
Perfluorohexane Sulfonate	PFHxS	432-50-8	F(CF ₂) ₆ SO ₃ H	400.11	2.3	58.9	--	5.17	2.4 – 3.1*
Perfluoroheptane Sulfonate	PFHpS	357-92-8	F(CF ₂) ₇ SO ₃ H	450.12	--	--	--	--	--
Perfluorooctane Sulfonate	PFOS	1763-23-1	F(CF ₂) ₈ SO ₃ H	500.13	0.52 - 0.57	6.7	<2e-6 to 3e-4	6.43	2.4 – 3.7*
Perfluorodecane Sulfonate	PFDS	333-77-3	F(CF ₂) ₁₀ SO ₃ H	600.14	0.002	0.71	--	7.66	3.53 – 3.66*

Table A-1: Physicochemical Properties									
Name	Acronym	CAS Registry Number	Molecular Formula	Molecular Weight (g/mol)	Water Solubility ^b (20-20°C) (g/L)	Vapor Pressure ^b (Pa)	Henry Coefficient [Pa·m ³ ·mol ⁻¹]	log Kow ^b [-]	log KOC [L/kg]
Perfluoroalkyl Phosphonic Acids	PFPA								
Perfluorobutyl Phosphonic Acid	PFBPA	52299-24-8	F(CF ₂) ₄ P(O)(OH) ₂	350.02	14259.1	0.18	--	2.19	--
Perfluorohexyl Phosphonic Acid	PFHxPA	40143-76-8	F(CF ₂) ₆ P(O)(OH) ₂	400.03	515.3	0.04	--	3.48	--
Perfluorooctyl Phosphonic Acid	PFOPA	40143-78-0	F(CF ₂) ₈ P(O)(OH) ₂	500.05	24.5	0.01	--	4.73	--
Perfluorodecyl Phosphonic Acid	PFDDPA	52299-26-0	F(CF ₂) ₁₀ P(O)(OH) ₂	600.06	0.5	0.0002	--	5.98	--
Perfluorooctane Sulfonamide and Derivatives									
Perfluorooctane Sulfonamide	PFOSA	754-91-6	F(CF ₂) ₈ SO ₂ NH ₂	499.14	-	--	--	-	2.5 - 2.62
Perfluorooctane Sulfonamidoethanol	FOSE	10116-92-4	F(CF ₂) ₈ SO ₂ NH(CH ₂) ₂ O H	543.19	0.0009	0.00	--	5.78	--
N-Methyl-Perfluorooctane Sulfonamide	N-MeFOSA	31506-32-8	F(CF ₂) ₈ SO ₂ NHCH ₃	513.17	0.0002	0.30	--	6.07	3.14
N-Ethyl-Perfluorooctane Sulfonamide	N-EtFOSA	4151-50-2	F(CF ₂) ₈ SO ₂ NHCH ₂ CH ₃	527.20	0.0001	0.12	--	6.71	3.23
N-Methyl-Perfluorooctane Sulfonamidoethanol	N-MeFOSE	24448-09-7	F(CF ₂) ₈ SO ₂ N(CH ₃)(CH ₂) ₂ O H	557.22	0.0003	0.0004	--	6.00	--
N-Ethyl-Perfluorooctane Sulfonamidoethanol	N-EtFOSE	1691-99-2	F(CF ₂) ₈ SO ₂ N(CH ₂ CH ₃)(CH ₂) ₂ O H	571.25	0.0001	0.002	--	6.52	--
Fluorotelomer sulfonic acids	FTSs								
1H, 1H, 2H, 2H-Perfluorobutanesulfonic Acid	H4-PFBS (2:2 FTS)	149246-63-9	F(CF ₂) ₂ CH ₂ CH ₂ SO ₃ H	228.13	-	-	--	--	--
1H, 1H, 2H, 2H-Perfluorohexanesulfonic Acid	H4-PFHxS (4:2 FTS)	757124-72-4	F(CF ₂) ₄ CH ₂ CH ₂ SO ₃ H	328.15	27.9	0.33	--	3.21	--
1H, 1H, 2H, 2H-Perfluorooctanesulfonic Acid	H4-PFOS (6:2 FTS)	27619-97-2	F(CF ₂) ₆ CH ₂ CH ₂ SO ₃ H	428.17	1.3	0.11	5726	4.44	--
1H, 1H, 2H, 2H-Perfluorodecanesulfonic Acid	H4-PFDeS (8:2 FTS)	39108-34-4	F(CF ₂) ₈ CH ₂ CH ₂ SO ₃ H	528.18	0.06	0.01	5039	5.66	0.01
1H, 1H, 2H, 2H-Perfluoroundecanesulfonic Acid	H4-PFUdS (10:2 FTS)	120226-60-0	F(CF ₂) ₁₀ CH ₂ CH ₂ SO ₃ H	628.20	0.002	0.001	7776	6.91	--
1H, 1H, 2H, 2H-Perfluorotetradecanesulfonic Acid	H4-PFTeS (12:2 FTS)	149246-64-0	F(CF ₂) ₁₂ CH ₂ CH ₂ SO ₃ H	728.21	0.0002	0.001	--	7.94	--

Table A-1: Physicochemical Properties									
Name	Acronym	CAS Registry Number	Molecular Formula	Molecular Weight (g/mol)	Water Solubility ^b (20-20°C) (g/L)	Vapor Pressure ^b (Pa)	Henry Coefficient [Pa·m ³ ·mol ⁻¹]	log Kow ^b [-]	log KOC [L/kg]
Fluorotelomer Alcohols	FTOHs								
Perfluormethylethanol 2:2	2:2 FTOH	54949-74-5	F(CF ₂) ₂ CH ₂ CH ₂ O H	164.08	--	--	--	--	--
Perfluorethylethanol 4:2	4:2 FTOH	2043-47-2	F(CF ₂) ₄ CH ₂ CH ₂ O H	264.09	0.98	214	--	0.93	0.93*
Perfluorhexylethanol 6:2	6:2 FTOH	647-42-7	F(CF ₂) ₆ CH ₂ CH ₂ O H	364.11	0.02	18.2	--	2.43	2.43*
Perfluorocylethanol 8:2	8:2 FTOH	865-86-1	F(CF ₂) ₈ CH ₂ CH ₂ OH	464.12	0.0001	3.98	--	3.84	4.13*
Perfluordecylethanol 10:2	10:2 FTOH	678-39-8	F(CF ₂) ₁₀ CH ₂ CH ₂ OH	564.14	0.00001	0.20	--	6.20	6.2*
Perfluordodecylethanol 12:2	12:2 FTOH	39239-77-5	F(CF ₂) ₁₂ CH ₂ CH ₂ OH	664.15	--	--	--	--	--
Polyfluorinated Alkyl Phosphates	PAPs								
Monoester	monoPAP								
4:2 Fluortelomerphosphatemonoester	4:2 monoPAP	150065-76-2	F(CF ₂) ₄ CH ₂ CH ₂ OP(O) (OH) ₂	344.07	11.9	0.000	--	--	--
6:2 Fluortelomerphosphatemonoester	6:2 monoPap	57678-01-0	F(CF ₂) ₆ CH ₂ CH ₂ OP(O) (OH) ₂	444.09	2.6	0.000	--	--	--
8:2 Fluortelomerphosphatemonoester	8:2 monoPAP	57678-03-2	F(CF ₂) ₈ CH ₂ CH ₂ OP(O)(OH) ₂	544.10	0.16	0.000	--	--	--
10:2 Fluortelomerphosphatemonoester	10:2 monoPAP	57678-05-4	F(CF ₂) ₁₀ CH ₂ CH ₂ OP(O) (OH) ₂	644.12	0.01	0.000	--	--	--
12:2 Fluortelomerphosphatemonoester	12:2 monoPAP	57678-07-6	F(CF ₂) ₁₂ CH ₂ CH ₂ OP(O) (OH) ₂	744.13	0.0003	0.000	--	--	--
Diester	diPAP								
4:2 Fluortelomerphosphatediester	4:2 diPAP	135098-69-0	F(CF ₂) ₄ CH ₂ CH ₂ OP(OH)OCH ₂ CH ₂ -	590.15	0.0004	0.000	--	--	--
6:2 Fluortelomerphosphatediester	6:2 diPAP	57677-95-9	F(CF ₂) ₆ CH ₂ CH ₂ OP(OH)OCH ₂ CH ₂ -	790.18	8.E-07	0.000	--	--	--
8:2 Fluortelomerphosphatediester	8:2 diPAP	678-41-1	F(CF ₂) ₈ CH ₂ CH ₂ OP(OH)OCH ₂ CH ₂ -	990.21	5.E-10	0.000	--	--	--
10:2 Fluortelomerphosphatediester	10:2 diPAP	1895-26-7	F(CF ₂) ₁₀ CH ₂ CH ₂ OP(OH)OCH ₂ CH ₂ -	1190.24	2.E-12	0.000	--	--	--
12:2 Fluortelomerphosphatediester	12:2 diPAP	57677-99-3	F(CF ₂) ₁₂ CH ₂ CH ₂ OP(OH)OCH ₂ CH ₂ -	1390.27	3.E-15	0.000	--	--	--
Polytetrafluoroethylene (Teflon)	PTFE	9002-84-0	(CF ₂) ₂ n	--	--	--	--	--	--

Notes:

1. Table modified from CONCAWE and supplemented with data from ASTR
2. "*" Indicates that data has been collected from the Interstate Technology Regulatory Council PFAS Environmental Fate and Transport fact sheet.

Table A-2: Aquatic Ectotoxicity of Flora			
Taxonomic Group	Environment	Organism	Master reference
Algae & aquatic plants (mg.l ⁻¹) (PFOS)	Freshwater	Selenastrum capricornutum/96h EC50: 71mg/l and 126mg/l	Environment Agency, 2004
		Selenastrum capricornutum/96h EC50: 48.2mg/l *	Environment Agency, 2008
		Navicula pelliculosa / 96 h EC50: 283 mg/l	OECD, 2002 in RIVM, 2010
		Navicula pelliculosa / 96h growth rate IC ₅₀ : 305mg/l NOEC: 206mg/l	OECD, 2002
		Navicula pelliculosa / 96 h NOEC: 44mg/l	Environment Agency, 2004; OECD, 2002 in RIVM 2010
		Navicula pelliculosa NOEC/EC10: 191mg/l	ANZECC, 2015a; RIVM, 2010
		Navicula pelliculosa NOEC/EC10: 62.3 mg/l	ANZECC, 2015a; RIVM, 2010
		Chlorella vulgaris/96h EC50: 81.6 mg/l	Environment Agency, 2004; Boudreau <i>et al.</i> , 2003b in RIVM, 2010
		Chlorella vulgaris / 96h cell density IC ₅₀ : 81.6mg/l NOEC: 8.2mg/l	Bourdrea <i>et al.</i> , 2003
		Chlorella vulgaris / 96h Chlorophyll (a) IC ₅₀ : 88.1mg/l NOEC: 9.6mg/l	Bourdrea <i>et al.</i> , 2003
		Chlorella vulgaris / 96h EC10: 8.2mg/l	Environment Agency, 2008; Boudreau <i>et al.</i> , 2003b in RIVM, 2010
		Chlorella vulgaris LC50/EC50: 82 mg/l	ANZECC, 2015a; RIVM, 2010
		Anabaena flos-aquae / 96h EC50: 176 mg/l	Environment Agency, 2004; OECD, 2002 in RIVM, 2010
		Anabaena flos-aquae / 96h growth rate IC ₅₀ : 176mg/l	OECD, 2002
		Anabaena flos-aquae NOEC: 94 mg/l	ANZECC, 2015a; RIVM, 2010
		Anabaena flos-aqua /96h NOEC: 44mg/l	OECD, 2002 in RIVM, 2010
		Anabaena flos-aqua NOEC/EC10: 82mg/l	ANZECC, 2015a; RIVM, 2010
		Lemna gibba / 7d EC50: 31.1mg/l	Environment Agency, 2004; Boudreau <i>et al.</i> , 2003b in RIVM, 2010
		Lemna gibba/7d NOEC: 15.1mg/l	Environment Agency, 2004
		Lemna gibba/42d EC10: 0.2mg/l **	Environment Agency, 2008
		Lemna gibba/7d EC10: 6.6mg/l	Environment Agency, 2008; Boudreau <i>et al.</i> , 2003b in RIVM, 2010
		Pseudokirchneriella subcapitata / 72h cell density IC ₅₀ : 70 mg/l NOEC: 70 mg/l	OECD, 2002
		Pseudokirchneriella subcapitata / 72h area under curve IC ₅₀ : 74 mg/l NOEC: 70 mg/l	OECD, 2002
		Pseudokirchneriella subcapitata / 72h growth rate IC ₅₀ : 120 mg/l NOEC: 70 mg/l	OECD, 2002
		Pseudokirchneriella subcapitata / 96h cell density IC ₅₀ : 71 mg/l NOEC: 44 mg/l	OECD, 2002
		Pseudokirchneriella subcapitata / 96h area under curve IC ₅₀ : 71 mg/l NOEC: 44 mg/l	OECD, 2002
		Pseudokirchneriella subcapitata / 96h growth rate IC ₅₀ : 126mg/l NOEC: 44 mg/l	OECD, 2002
		Pseudokirchneriella subcapitata NOEC/EC10: 53mg/l	ANZECC, 2015a; RIVM, 2010
		Pseudokirchneriella subcapitata LC50/EC50: 120 mg/l	ANZECC, 2015a; RIVM, 2010
		Pseudokirchneriella subcapitata / 72 h EC50: 120 mg/l	OECD, 2002 in RIVM, 2010

Table A-2: Aquatic Ectotoxicity of Flora			
Taxonomic Group	Environment	Organism	Master reference
		Scenedesmus obliquus / 72h fluorescence IC ₅₀ : 77.8 mg/l	Liu <i>et al.</i> , 2008
		Scenedesmus obliquus / 72h optical density IC ₅₀ : 99.9 mg/l	Liu <i>et al.</i> , 2008
		Scenedesmus obliquus NOEC/EC10: 51 mg/l	ANZECC, 2015a; RIVM, 2010
		Selenastrum capricornutum / 96h cell density IC ₅₀ : 48.2mg/l NOEC: 5.3mg/l	Bourdrea <i>et al.</i> , 2003
		Selenastrum capricornutum / 96h Chlorophyll (a) IC ₅₀ : 59.2mg/l NOEC: 16.6mg/l	Bourdrea <i>et al.</i> , 2003
		Selenastrum capricornutum/96h EC10: 5.3mg/l *	Environment Agency, 2008
		Rhaphidocelis subcapitata /96h EC10: 53mg/l	OECD, 2002 in RIVM, 2010
		Myriophyllum sibiricum NOEC/EC10: 0.1 mg/l	ANZECC, 2015a; RIVM, 2010
		Myriophyllum sibiricum NOEC/EC10: 0.56 mg/l	ANZECC, 2015a; RIVM, 2010
		Myriophyllum sibiricum NOEC/EC10: 3.3 mg/l	ANZECC, 2015a; RIVM, 2010
		Myriophyllum sibiricum / 42 d NOEC: 0.092mg/l	Hanson <i>et al.</i> , 2005 in RIVM, 2010
		Myriophyllum spicatum / 42 d NOEC: 3.2mg/l	Hanson <i>et al.</i> , 2005 in RIVM, 2010
		Daphnia magna / 21-day EC ₅₀ 11 (28-day repro)	OECD, 2002
		Daphnia magna / 21/28 d NOEC: 7.0 mg/l (geomean of 4 values)	Boudreau <i>et al.</i> , 2003b; OECD, 2002 and Ji <i>et al.</i> , 2008 in RIVM, 2010
		Moina macrocopa / 7 d EC10: 0.40mg/l	Ji <i>et al.</i> , 2008 in RIVM 2010
		Chironomus tentans / 10d NOEC: 0.049mg	Environment Agency, 2008
		Chironomus tentans / 36d NOEC: 0.049mg <0032mg/l LOEC with 32% effect	MacDonald <i>et al.</i> , 2004 in RIVM, 2010
		Chironomus tentans / 36d NOEC: <0.00mg LOEC 0.002mg/l	MacDonald <i>et al.</i> , 2004 in RIVM, 2010
		Enallagma cyathigerum / 120 d NOEC: <0.01mg/l LOEC with 18% effect	Bots <i>et al.</i> , 2010 in RIVM, 2010
		Marine	Skeletonema costatum /96h NOEC : >3.2mg/l
Skeletonema costatum/96 h EC50 : >3.2mg/l	Environment Agency, 2004		
Algae & aquatic plants (mg.l ⁻¹) (PFOA)	Freshwater	Chlamydomonas reinhardtii LC50/EC50: 51.9 mg/l	ANZECC 2015b; Verbruggen <i>et al.</i> 2017
		Chlorella vulgaris LC50/EC50: 97.4 mg/l	ANZECC 2015b; Verbruggen <i>et al.</i> 2017
		Pseudokirchneriella Subcapitata NOEC/EC10: 125 mg/l	ANZECC 2015b; Verbruggen <i>et al.</i> 2017
		Pseudokirchneriella Subcapitata LC50/EC50: >100 mg/l	ANZECC 2015b; Verbruggen <i>et al.</i> 2017
		Scenedesmus obliquus NOEC/EC10: 8.8 mg/l	ANZECC 2015b; Verbruggen <i>et al.</i> , 2017

Table A-2: Aquatic Ectotoxicity of Flora			
Taxonomic Group	Environment	Organism	Master reference
		Scenedesmus obliquus LC50/EC50: 44 mg/l	ANZECC 2015b; Verbruggen <i>et al.</i> , 2017
		Scenedesmus quadricauda LC50/EC50: 270 mg/l	ANZECC 2015b; Verbruggen <i>et al.</i> , 2017
		Selanstrum capricornutum NOEC/EC10: 5.3 mg/l	ANZECC 2015b; Verbruggen <i>et al.</i> , 2017
		Chlorella vulgaris NOEC/EC10: 8.2 mg/l	ANZECC 2015b; Verbruggen <i>et al.</i> , 2017
		Scenedesmus obliquus NOEC/EC10: 51 mg/l	ANZECC 2015b; Verbruggen <i>et al.</i> , 2017
		Navicula pelliculosa NOEC/EC10: 62.3 mg/l	ANZECC 2015b; Verbruggen <i>et al.</i> , 2017
		Anabaena flos-aqua NOEC/EC10: 49 mg/l	ANZECC 2015b; Verbruggen <i>et al.</i> , 2017
		Anabaena flos-aqua LC50/EC50: 40 mg/l	ANZECC 2015b; Verbruggen <i>et al.</i> , 2017
		Anabaena flos-aqua NOEC/EC10: 14.46 mg/l	ANZECC 2015b; Verbruggen <i>et al.</i> , 2017
		Anabaena flos-aqua NOEC/EC10: 82 mg/l	ANZECC 2015b; Verbruggen <i>et al.</i> , 2017
		Geitlerinema amphibium LC50/EC50: 247 mg/l	ANZECC 2015b; Verbruggen <i>et al.</i> , 2017
		Myriophyllum sibiricum NOEC/EC10: 7.9 mg/l	ANZECC 2015b; Verbruggen <i>et al.</i> , 2017
		Myriophyllum spicatum NOEC/EC10: 5.7 mg/l	ANZECC 2015b; Verbruggen <i>et al.</i> , 2017
Algae & aquatic plants (mg.l ⁻¹) (Other PFAS)	Freshwater	Selanstrum capricornutum (PFBS) LC50/EC50: >2347 mg/l	Danish Ministry of the Environment, 2015
		Pseudokirchneriella subcapitata (PFBA) LC50/EC50: 261 mg/l	Danish Ministry of the Environment, 2015
		Pseudokirchneriella subcapitata (PFPeA) LC50/EC50: 817 mg/l	Danish Ministry of the Environment, 2015
		Pseudokirchneriella subcapitata (PFHxA) LC50/EC50: >1000 mg/l	Danish Ministry of the Environment, 2015
		Geitlerinema amphibium (PFHxA) LC50/EC50: 998 mg/l	Danish Ministry of the Environment, 2015
		Scenedesmus subspicatus (PFHxA) LC50/EC50: 86 mg/l	Danish Ministry of the Environment, 2015
		Lemna gibba (4:2 FTCA) LC50/EC50: 9.39 mg/l	Danish Ministry of the Environment, 2015
		Lemna gibba (4:2 FTCA) LC50/EC50: 6.6 mg/l	Danish Ministry of the Environment, 2015
		Lemna gibba (4:2 FTUCA) LC50/EC50: 6.64 mg/l	Danish Ministry of the Environment, 2015
		Lemna gibba (4:2 FTUCA) LC50/EC50: 9.4 mg/l	Danish Ministry of the Environment, 2015
		Pseudokirchneriella subcapitata (5:3 acid) LC50/EC50: 22.5 mg/l	Danish Ministry of the Environment, 2015
		Lemna gibba (6:2 FTCA) LC50/EC50: 1.29 mg/l	Danish Ministry of the Environment, 2015
Lemna gibba (6:2 FTCA) LC50/EC50: 1.3 mg/l	Danish Ministry of the Environment, 2015		

Table A-2: Aquatic Ectotoxicity of Flora			
Taxonomic Group	Environment	Organism	Master reference
		Pseudokirchneriella subcapitata (6:2 FTCA) LC50/EC50: 47.9 mg/l	Danish Ministry of the Environment, 2015
		Lemna gibba (6:2 FTUCA) LC50/EC50: 5.02 mg/l	Danish Ministry of the Environment, 2015
		Lemna gibba (6:2 FTUCA) LC50/EC50: 10.4 mg/l	Danish Ministry of the Environment, 2015
		Pseudokirchneriella subcapitata (6:2 FTUCA) LC50/EC50: 28.5 mg/l	Danish Ministry of the Environment, 2015
		Pseudokirchneriella subcapitata (6:2 FTOH) LC50/EC50: 4.52 mg/l	Danish Ministry of the Environment, 2015
		Pseudokirchneriella subcapitata (6:2 FTOH): NOEC 0.62 mg/l	Danish Ministry of the Environment, 2015
		Pseudokirchneriella subcapitata (5H 4:1 FTOH) LC50/EC50: 1125 mg/l	Danish Ministry of the Environment, 2015
		Pseudokirchneriella subcapitata (6:2 FTAC) NOEC: 0.022 mg/l	Danish Ministry of the Environment, 2015
		Pseudokirchneriella subcapitata (C4 acrylate) NOEC: 0.34 mg/l	Danish Ministry of the Environment, 2015
<p>Notes:</p> <ol style="list-style-type: none"> * Noted that this study should be considered with care as it is based on nominal concentrations and the study duration is longer than the recommended test duration. ** This value was generated in a static system with nominal concentrations and therefore the data should be treated with care. *** This study was conducted in a static system with nominal test concentrations and should therefore be treated with care. Table modified from CONCAWE report and supplemented with data from ANZECC, 2015a; RIVM, 2010, ANZECC, 2015b; Verbruggen et al. 2017 and Danish Ministry of the Environment, 2015. 			

Table A-3: Aquatic Ectotoxicity of Fauna			
Taxonomic Group	Environment	Organism	Master reference
Invertebrates (mg.l ⁻¹) (PFOS)	Freshwater	Daphnia magna / 48 h EC50 : 27 mg/l	Environment Agency,2004
		Daphnia magna / 48 h EC50: 4 mg/l **	Environment Agency,2008
		Daphnia magna / 48 h EC50: 48 mg/l (geometric mean of 6 values)	OECD, 2002; Boudreau <i>et al.</i> , 2003b; Ji <i>et al</i> 2008; and Li, 2009 in RIVM, 2010
		Daphnia magna / 48 h static acute toxicity test IC ₅₀ : 61 mg/l NOEC: 33mg/l	OECD, 2002
		Daphnia magna / 48 h Effect of Potassium Perfluorooctanesulfon-ate on Survival IC ₅₀ : 27 mg/l	OECD, 2002
		Daphnia magna / 48 h acute toxicity of PFOS IC ₅₀ : 58 mg/l	OECD, 2002
		Daphnia magna / 48 h Acute Toxicity to Daphnia, Daphnia magna. FC-94-X (Li salt of PFOS) IC ₅₀ : 210 mg/l NOEC: 100mg/l	OECD, 2002
		Daphnia magna / 48 h Acute toxicity of P3025 developmental material to Daphnia magna IC ₅₀ : 4.0mg/l NOEC: 2.2mg/l	OECD, 2002
		Daphnia magna / 48 h IC ₅₀ : 63 mg/l NOEC: 20mg/l	Li, 2009
		Daphnia magna / 48 h IC ₅₀ : 37.36 mg/l	Ji <i>et al.</i> , 2008
		Daphnia magna / 48 h LC ₅₀ : 130mg/l IC ₅₀ : 67.2 mg/l NOEC: 33.1;0.8	Boudreau <i>et al.</i> , 2003
		Daphnia magna / 21-day EC ₅₀ : 110mg/l	Boudreau <i>et al.</i> , 2003
		Daphnia magna / 21-day EC ₅₀ : 9.1mg/l	Li, 2010
		Daphnia magna / 21d Semi-Static Life-Cycle Toxicity Test with the Cladoceran (Daphnia magna) 21-day EC ₅₀ : 12 (repro)	OECD, 2002
		Daphnia magna / 21 d NOEC : 12 mg/l	Environment Agency,2004
		Daphnia magna/28d NOEC: 7mg/l ***	Environment Agency,2004
		Daphnia magna/21d NOEC: 5.3mg/l **	Environment Agency,2004
		Daphnia magna / 21/28 d NOEC: 7.0 mg/l (geomean of 4 values)	Boudreau <i>et al.</i> , 2003b; OECD, 2002 and Ji <i>et al.</i> , 2008 in RIVM, 2010
		Daphnia pulicaria / 48 h EC50: 124 mg/l	Boudreau <i>et al.</i> , 2003b in RIVM, 2010
		Daphnia pulicaria / 48 h LC ₅₀ : 169mg/l IC ₅₀ : 134 mg/l NOEC: 46.9mg/l; 0.8mg/l	Boudreau <i>et al.</i> , 2003
		Moina macrocopa / 48 h EC50: 18 mg/l	Ji <i>et al.</i> , 2008 in RIVM, 2010
		Moina macrocopa / 7 d EC10: 0.40mg/l	Ji <i>et al.</i> , 2008 in RIVM, 2010
		Neocaridina denticulate / 96 h EC50: 9.3 mg/l	Li, 2009 in RIVM, 2010
		Neocaridina denticulate / 24 hr Lethal EC ₅₀ /LC ₅₀ : >200 mg/l	Li, 2009
		Neocaridina denticulate / 48 hr Lethal EC ₅₀ /LC ₅₀ : 57 mg/l	Li, 2009
		Neocaridina denticulate / 72 hr Lethal EC ₅₀ /LC ₅₀ : 20 mg/l	Li, 2009
		Neocaridina denticulate / 96 hr Lethal EC ₅₀ /LC ₅₀ : 10 mg/l	Li, 2009
		Dugesia japonica / 96 hr LC50: 18 mg/l (geometric mean of two values)	Li, 2008 and Li, 2009 in RIVM, 2010
		Dugesia japonica / 24 hr Lethal EC ₅₀ /LC ₅₀ : 34 mg/l	Li, 2009

Table A-3: Aquatic Ectotoxicity of Fauna			
Taxonomic Group	Environment	Organism	Master reference
		Dugesia japonica / 48 hr Lethal EC ₅₀ /LC ₅₀ : 27 mg/l	Li, 2009
		Dugesia japonica / 72 hr Lethal EC ₅₀ /LC ₅₀ : 26 mg/l	Li, 2009
		Dugesia japonica / 96 hr Lethal EC ₅₀ /LC ₅₀ : 23 mg/l	Li, 2009
		Physa acuta / 96 hr LC ₅₀ : 165 mg/l	Li, 2009 in RIVM, 2010
		Physa acuta / 24 hr Lethal EC ₅₀ /LC ₅₀ : 271 mg/l	Li, 2009
		Physa acuta / 48 hr Lethal EC ₅₀ /LC ₅₀ : 233 mg/l	Li, 2009
		Physa acuta / 72 hr Lethal EC ₅₀ /LC ₅₀ : 208 mg/l	Li, 2009
		Physa acuta / 96 hr Lethal EC ₅₀ /LC ₅₀ : 178 mg/l	Li, 2009
		Unio complamatus / 96 hr LC ₅₀ : 59 mg/l	Environment Agency, 2004; OECD, 2002 in RIVM, 2010
		Chironomus tentans / 10-day Survival EC ₅₀ /LC ₅₀ : >0.15mg/l	MacDonald <i>et al.</i> , 2004
		Chironomus tentans / 10-day Growth EC ₅₀ /LC ₅₀ : 0.087 mg/l	MacDonald <i>et al.</i> , 2004
		Chironomus tentans / 20-day Survival EC ₅₀ /LC ₅₀ : 0.092 mg/l	MacDonald <i>et al.</i> , 2004
		Chironomus tentans / 20-day Growth EC ₅₀ /LC ₅₀ : 0.093 mg/l	MacDonald <i>et al.</i> , 2004
		Chironomus tentans / 20-day emergence EC ₅₀ /LC ₅₀ : 0.094 mg/l	MacDonald <i>et al.</i> , 2004
		Chironomus tentans / 10d NOEC: 0.049mg	Environment Agency, 2008
		Chironomus tentans / 36d NOEC: 0.049mg <0032mg/l LOEC with 32% effect	MacDonald <i>et al.</i> , 2004 in RIVM, 2010
		Chironomus tentans / 36d NOEC: <0.00mg LOEC 0.002mg/l	MacDonald <i>et al.</i> , 2004 in RIVM, 2010
		Enallagma cyathigerum / 120 d NOEC: <0.01mg/l LOEC with 18% effect	Bots <i>et al.</i> , 2010 in RIVM, 2010
	Marine	Mysid shrimp (Americamysis bahia) / 96 h EC ₅₀ : 3.6mg/l	Environment Agency,2004; OECD, 2002 in RIVM, 2010
	Marine	Mysid shrimp (Americamysis bahia) NOEC/EC10: 0.25 mg/l	CRC CARE, 2017; Environment Canada, 2018; RIVM, 2010; Verbruggen <i>et al.</i> , 2017
	Marine	Brine shrimp (Artemia spp.) / 48hr LC50: 8.9 mg/l	Environment Agency, 2004
	Marine	Artemia spp. / 48 hr LC50: 8.3 mg/l	OECD, 2002 in RIVM, 2010
	Marine	Artemia NOEC/EC10: 0.92 mg/l	CRC CARE, 2017; Environment Canada 2018; RIVM 2010; Verbruggen <i>et al.</i> , 2017
	Marine	Crassostrea virginica (Eastern oyster) 96hr EC50 >3.0mg/l (Shell deposition)	Wildlife international (2000) referenced in OECD, 2002
	Marine	Crassostrea virginica (Eastern oyster) NOEC/EC10: 1.9mg/l	CRC CARE, 2017; Environment Canada, 2018; RIVM, 2010; Verbruggen <i>et al.</i> , 2017
	Marine	Mysidopsis bahia / 35 d NOEC : 0.25mg/l	Environment Agency, 2004; OECD, 2002 in RIVM, 2010
	Marine	Glyptocidaris crenularis NOEC/EC10: 0.1 mg/l	CRC CARE 2017; Environment Canada 2018; RIVM, 2010; Verbruggen <i>et al.</i> , 2017

Table A-3: Aquatic Ectotoxicity of Fauna			
Taxonomic Group	Environment	Organism	Master reference
		Mysidopsis bahia NOEC/EC10 : 0.36 mg/l	CRC CARE, 2017; Environment Canada, 2018; RIVM, 2010; Verbruggen <i>et al.</i> , 2017
		Tigriopus japonicas (growth) NOEC/EC10 : 0.5 mg/l	CRC CARE, 2017; Environment Canada, 2018; RIVM, 2010; Verbruggen <i>et al.</i> , 2017
		Tigriopus japonicas (reproduction) NOEC/EC10 : 0.1 mg/l	CRC CARE, 2017; Environment Canada, 2018; RIVM, 2010; Verbruggen <i>et al.</i> , 2017
Invertebrates (mg.l ⁻¹) (Other PFAS)	Freshwater	Daphnia magna (PFBS) LC50/EC50: 2180 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017
		Daphnia magna (PFBS) NOEC: 502 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017
		Daphnia magna (PFBA) LC50/EC50: >100 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017
		Daphnia magna (PFBA) NOEC: 239 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017
		Daphnia magna (PFPeA) LC50/EC50: >112 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017
		Daphnia magna (PFHxA) LC50/EC50: >96.5 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017
		Daphnia magna (4:2 FTCA) LC50/EC50: >100 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017
		Daphnia magna (4:2FTUCA) LC50/EC50: >100 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017
		Daphnia magna (6:2 FTCA) LC50/EC50: >97.5 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017
		Daphnia magna (6:2FTUCA) LC50/EC50: 29.6 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017
		Daphnia magna (6:2 FTOH) LC50/EC50: 7.84 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017
		Daphnia magna (6:2 FTOH) LC50/EC50: 21.6 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017
		Daphnia magna (6:2 FTAC) LC50/EC50: >0.141 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017
		Chironomus tentans (4:2 FTCA) LC50/EC50: >100 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017
		Chironomus tentans (5:3 acid) LC50/EC50: >103 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017
		Chironomus tentans (6:2 FTCA) LC50/EC50: 63.1 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017
		Chironomus tentans(6:2 FTCA) LC50/EC50: 75.2 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017
Chironomus tentans (6:2 FTUCA)LC50/EC50: >100 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017		
Invertebrates (mg.l ⁻¹) (PFOA)	Freshwater	Daphnia magna NOEC/EC10: 7 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017
		Daphnia magna LC50/EC50: 305 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017
		Daphnia magna NOEC/EC10: 11.18 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017
		Chydorus sphaericus LC50/EC50: 103 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017

Table A-3: Aquatic Ectotoxicity of Fauna				
Taxonomic Group	Environment	Organism	Master reference	
	Freshwater	Macrobrachium nipponense LC50/EC50: 201 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017	
		Moina macrocopa NOEC/EC10: 3 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017	
		Moina macrocopa NOEC/EC10: 3.125 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017	
		Moina macrocopa LC50/EC50: 367 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017	
		Neocaridina denticulate LC50/EC50: 454 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017	
		Brachionus calyciflorus NOEC/EC10: 4 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017	
		Brachionus calyciflorus LC50/EC50: 150 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017	
		Brachionus calyciflorus NOEC/EC10: 0.25 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017	
		Chironomus tentans NOEC/EC10: 100 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017	
		Chironomus plumosus LC50/EC50: 402 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017	
		Dugesia japonica LC50/EC50: 392 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017	
		Lampsilis siliquoidea LC50/EC50: >500 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017	
		Ligumia recta LC50/EC50: >500 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017	
		Cipangopaludina cathayensis LC50/EC50: 740 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017	
		Physa acuta LC50/EC50: 672mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017	
		Limnodrilus hottmeisteri LC50/EC50: 568 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017	
		Marine	Perna viridis NOEC/EC10 119 mg/l	CRC CARE, 2017; Environment Canada, 2018; RIVM, 2010; Verbruggen <i>et al.</i> 2017
			Paracentrotus lividus NOEC/EC10 31 mg/l	CRC CARE, 2017; Environment Canada, 2018; RIVM 2010; Verbruggen <i>et al.</i> 2017
	Siriella armata NOEC/EC10 2.6 mg/l		CRC CARE, 2017; Environment Canada, 2018; RIVM, 2010; Verbruggen <i>et al.</i> 2017	
	Siriella armata NOEC/EC10 1.6 mg/l		CRC CARE, 2017; Environment Canada, 2018; RIVM 2010; Verbruggen <i>et al.</i> 2017	
Siriella armata NOEC/EC10 0.64 mg/l	CRC CARE, 2017; Environment Canada, 2018; RIVM, 2010; Verbruggen <i>et al.</i> , 2017			
Fish (mg.l ⁻¹) (PFOA)	Freshwater	Carassius auratus LC50/EC50: 606 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017	
	Marine	Cyprinus carpio LC50/EC50: >55 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017	
		Pseudorasbora parva NOEC/EC10: 12 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017	

Table A-3: Aquatic Ectotoxicity of Fauna			
Taxonomic Group	Environment	Organism	Master reference
		Pseudorasbora parva LC50/EC50: 365 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017
		Danio rerio NOEC/EC10: >33 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017
		Gobiocypris rarus NOEC/EC10: >33 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017
		Oncorhynchus mykiss NOEC/EC10: 40 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017
		Oncorhynchus mykiss LC50/EC50: 750 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017
		Oncorhynchus mykiss NOEC/EC10: 40 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017
		Oryzias latipes NOEC/EC10: 10 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017
		Oryzias latipes NOEC/EC10:10 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017
		Salmo salar NOEC/EC10: 0.1 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017
		Psetta maxima NOEC/EC10: 3.9 mg/l	CRC CARE, 2017; Environment Canada, 2018; RIVM, 2010; Verbruggen <i>et al.</i> , 2017
Fish (mg.l ⁻¹) (Other PFAS)	Freshwater	Danio rerio (PFBS) LC50/EC50: 450 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017
		Danio rerio (PFBA) LC50/EC50: 2200 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017
		Danio rerio (6:2 FTOH) LOEC 0.03 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017
		Danio rerio (6:2 FTOH) LOEC 0.3 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017
		Danio rerio (4:2 FT olefin)NOEC 1.86 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017
		Lepomis macrochirus(PFBS) LC50/EC50: 1938 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017
		Pimephales promelas (PFBS) LC50/EC50: 6452 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017
		Pimephales promelas (PFPeA) LC50/EC50:32 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017
		Pimephales promelas (6:2 FTOH) LC50/EC50:4.84 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017
		Oncorhynchus mykiss (PFHxA) LC50/EC50: 99.2 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017
		Oncorhynchus mykiss (PFHxA) NOEC 10.1 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017
Oryzias latipes (6:2 FTAC) LC50/EC50:0.306 mg/l	ANZECC, 2015b; Verbruggen <i>et al.</i> , 2017		
Fish (mg.l ⁻¹) (PFOS)	Freshwater	Fathead minnow (Pimephales promelas / 42d NOEC : 0.3mg/l	Environment Agency, 2004
		Fathead minnow (Pimephales promelas /96 h EC50 : 4.7mg/l ***	Environment Agency, 2004
		Fathead minnow (Pimephales promelas/96h LC50: 9.5mg/l	Concawe (2016) citing Environment Agency, 2008
		Fathead minnow (Pimephales promelas) / 21d NOEC: 0.028mg/l	Environment Agency, 2004

Table A-3: Aquatic Ectotoxicity of Fauna			
Taxonomic Group	Environment	Organism	Master reference
		Pimephales promelas / 96 h LC50: 6.6 mg/l (geometric mean of two values)	OECD, 2002 in RIVM, 2010
		Bluegill sunfish (Lepomis macrochirus) / 96 h LC50: 6.9 mg/l	Environment Agency, 2004
		Lepomis macrochirus / 96 h LC50: 6.4 mg/l	OECD, 2002 in RIVM, 2010
		Oncorhynchus mykiss / 96h LC50: 7.8mg/l	Environment Agency, 2008
		Oncorhynchus mykiss / 96 h LC50: 13 mg/l (geometric mean of two values)	OECD, 2002 in RIVM, 2010
		Oryzias latipes / 14 d NOEC:	Concawe (2016) citing Environment Agency, 2008 Ankley <i>et al.</i> , 2005 in RIVM, 2010
		Bluegill sunfish (Lepomis macrochirus) / 62d NOEC:	Ji <i>et al.</i> , 2008 in RIVM, 2010
	Marine	Cyprinodon variegatus NOEC/EC10: 1.5 mg/l	CRC CARE, 2017; Environment Canada, 2018; RIVM 2010; Verbruggen <i>et al.</i> , 2017
		Oryzias melastigma (embryo development) NOEC/EC10: 1 mg/l	CRC CARE, 2017; Environment Canada, 2018; RIVM, 2010; Verbruggen <i>et al.</i> , 2017
		Oryzias melastigma (growth) NOEC/EC10: 4 mg/l	CRC CARE, 2017; Environment Canada, 2018; RIVM, 2010; Verbruggen <i>et al.</i> , 2017
		Sheepshead minnow (Cyprinodon variegatus) / 96hr EC50 : >15mg/l	Environment Agency, 2004
		Oncorhynchus mykiss / 96h LC50: 13.7mg/l	Environment Agency, 2004; OECD, 2002 in RIVM, 2010
		Psetta maxima NOEC/EC10: 0.02 mg/l	CRC CARE, 2017; Environment Canada, 2018; RIVM, 2010; Verbruggen <i>et al.</i> , 2017
		Amphibians (mg.l ⁻¹) (PFOS)	Freshwater
Rana pipiens / 1-week lethal LC50/EC50: >12.5 mg/l	Ankley <i>et al.</i> , 2004		
Rana pipiens / 2-week lethal LC50/EC50: 11.0 mg/l	Ankley <i>et al.</i> , 2004		
Rana pipiens / 3-week lethal LC50/EC50: 7.71 mg/l	Ankley <i>et al.</i> , 2004		
Rana pipiens / 4-week lethal LC50/EC50: 6.59 mg/l	Ankley <i>et al.</i> , 2004		
Rana pipiens / 5-week lethal LC50/EC50: 6.21 mg/l	Ankley <i>et al.</i> , 2004		

Notes:

- * Noted that this study should be considered with care as it is based on nominal concentrations and the study duration is longer than the recommended test duration.
- ** This value was generated in a static system with nominal concentrations and therefore the data should be treated with care.
- *** This study was conducted in a static system with nominal test concentrations and should therefore be treated with care.
- Table modified from CONCAWE report and supplement data from ANZECC, 2015b; Verbruggen *et al.*, 2017 and CRC CARE 2017; Environment Canada 2018; RIVM 2010; Verbruggen *et al.*, 2017.

Table A-4: Bio-accumulation Factors						
Report	Compound	BMF	TMF	TL adjustment	Prey (known or assumed) or diet → Predator	Comments
Kannan <i>et al.</i> (2002)	PFOS	18		No	Feed mixture of river carp and marine fishes (whole) → mink liver	Study conducted on adult ranch mink fed with 10, 20 and 40 % of river carp incorporated in their usual diet of marine fishes. BMF reported as the mean value derived from the three experiments.
Martin <i>et al.</i> (2004)	PFOA	0.41		No	3 forage fishes (whole) → lake trout (whole)	Study conducted on a Lake Ontario freshwater food web. The BMF (reported in the paper as the “bio-accumulation factor, BAF”) is defined on a diet-weighted basis for the 3 prey species (rainbow smelt, slimy sculpin and alewife). No TL adjustment was made.
	PFNA	2.3		No		
	PFDA	2.7		No		
	PFUnDA	3.4		No		
	PFDODA	1.6		No		
	PFTTrDA	2.5		No		
	PFOS	> 2.3		No		
	FOSA	2.9		No	1 crustacean (whole) → 2 forage fishes (whole) → lake trout (whole) (2 crustaceans and 3 forage fishes for FOSA)	The TMF is derived from a plot of the logarithm of the whole-organism concentration of the PFAS in various organisms versus TL, with the latter deduced from $\delta^{15}\text{N}$ measurements reported in the literature and with plankton being assigned TL = 1. Observations on benthic organisms (one crustacean and one forage fish species) were excluded from the TMF calculation, except for FOSA. The TLs covered ranged from 3.6 to 4.9 (3.3 to 4.9 for FOSA). The TMF values reported as (1.0) refer to non-significant regressions.
	PFOA		0.58			
	PFNA		(1.0)			
	PFDA		3.67			
	PFUnDA		4.71			
	PFDODA		(1.0)			
	PFTTrDA		2.45			
PFTeDA		(1.0)				
PFOS		5.88				
FOSA		0.51				
Tomy <i>et al.</i> (2004)	PFOS	4.6		2	Clam (whole) → walrus (liver)	Study conducted on eastern Arctic marine food webs, including seabirds. Samples taken at various locations between 1996 and 2002.
	PFOA	1.6		2	Cod (whole) → narwhal (liver)	
	PFOS	7.2		2		Cod (whole) → beluga (liver)
	EtFOSA	0.1		2		
	PFOA	2.7		2	Cod (whole) → beluga (liver)	
	PFOS	8.4		2		
	EtFOSA	0.04		2	Redfish (liver) → beluga (liver)	
	PFOA	0.8		2		
	PFOS	4.0		2	Cod (whole) → black-legged kittiwake (liver)	
	PFOS	5.1		2		
	PFOA	0.6	(1.0)	2	Cod (whole) → glaucous gull (liver)	The TMF for PFOS is derived from a plot of the logarithm of the concentration of the PFAS in various organisms versus trophic TL. Species considered for this regression are: zooplankton, clam, shrimp and cod (all whole-organism based concentrations), as well as redfish, walrus, narwhal, beluga, black-legged kittiwake and glaucous gull (all liver concentrations). For PFOA and EtFOSA, no significant correlation with TL was observed, as indicated by TMF = (1.0).
	PFOS	9.0		2		
	PFOA	0.04		2	Zooplankton (whole) → cod (whole)	
	PFOS	0.4		2		
EtFOSA	238	(1.0)	2	See “Comments” column		
PFOS			3.1			

Table A-4: Bio-accumulation Factors							
Report	Compound	BMF	TMF	TL adjustment	Prey (known or assumed) or diet → Predator	Comments	
Kannan <i>et al.</i> (2005)	PFOS	2-4		No	Benthic algae (whole) → round goby (whole)	Study conducted on food webs in the North American Great Lakes area (freshwater aquatic species + mink and bald eagle). The BMF values, defined as the ratio of predator concentrations to prey concentrations, for assumed predator-prey relationships, are rough estimates. First, the prey considered did not necessarily constitute the sole or predominant diet of the corresponding predator (see the paper for details of the diet of each predator). Second, the organisms were not necessarily sampled in the same year.	
	PFOS	2-4		No	Crayfish (whole) → round goby (whole)		
	PFOS	10-20		No	Round goby (whole) → Chinook salmon (liver)		
	PFOS	5-10		No	Chinook salmon (liver) → mink (liver)		
	PFOS	5-10		No	Chinook salmon (liver) → bald eagle (liver)		
Houde <i>et al.</i> (2006)	PFDODA	89		No	Sarasota Bay location: zooplankton → striped mullet	Study conducted on marine food webs at two locations off the US East Coast: Sarasota Bay (FL) and Charleston (SC). All concentrations are expressed on a whole-body basis. In the case of dolphins, the whole-body concentrations were estimated by the authors from the concentrations in plasma and various tissues.	
	PFOS	23		No			
	FOSA	2.5		No			
	PFDODA	2.5		No	Sarasota Bay location: zooplankton → pigfish		
	PFHxS	9.1		No			
	PFOS	12		No			
	PFDODA	156		No	Sarasota Bay location: zooplankton → sheephead		The BMFs are defined as the ratio of predator concentrations to prey concentrations, for assumed predator-prey relationships, with no adjustment for TL difference. When several fish species potentially constituted the prey for seatrout or dolphin, no attempt was made to calculate the BMFs on the basis of weighted-mean prey concentrations.
	PFOS	14		No			
	FOSA	2.5		No			
	PFDODA	2.5		No	Sarasota Bay location: zooplankton → pinfish		
	PFHxS	10		No			
	PFOS	19		No			
	PFDODA	35		No	Sarasota Bay location: striped mullet → seatrout	The term “dolphin (whole)” means that the equivalent whole-body PFAS concentration in dolphins was calculated from the corresponding levels in the organs, tissues and plasma sampled, knowing the weights of these organs and tissues and the volume of plasma, as well as the weight of the whole dolphin.	
	PFOS	35		No			
	FOSA	2.5		No			
	PFDODA	0.4		No	Sarasota Bay location: striped mullet → seatrout		
	PFOS	1.5		No			
	FOSA	1.0		No			
	PFDODA	14		No	Sarasota Bay location: pigfish → seatrout		When several fish species potentially constituted the prey for seatrout or dolphin, no attempt was made to calculate the BMFs on the basis of weighted-mean prey concentrations.
	PFOS	2.8		No			
	PFDODA	0.2		No			
	PFOS	2.6		No	Sarasota Bay location: sheephead → seatrout		
	FOSA	1.0		No			
	PFDODA	14		No			
	PFOS	1.8		No	Sarasota Bay location: pinfish → seatrout		
	PFDODA	0.1		No			
PFOS	9.6		No				
FOSA	5.2		No	Sarasota Bay location: striped mullet → dolphin			
PFDODA	2.0		No				
PFHxS	2.0		No				
PFOS	18		No	Sarasota Bay location: pigfish → dolphin			
PFDODA	0.0		No				
PFOS	16		No				
FOSA	5.2		No	Sarasota Bay location: sheephead → dolphin			

Table A-4: Bio-accumulation Factors						
Report	Compound	BMF	TMF	TL adjustment	Prey (known or assumed) or diet → Predator	Comments
	PFDoDA	2.0		No	Sarasota Bay location: pinfish → dolphin	
	PFHxS	1.8		No		
	PFOS	11		No		
	PFDoDA	0.1		No	Sarasota Bay location: seatrout → dolphin	
	PFOS	6.2		No		
	FOSA	5.2		No		
	PFOA	7.2		No	Charleston location: pinfish → seatrout	
	PFNA	1.5		No		
	PFDA	3.7		No		
	PFUnDA	0.9		No		
	PFDoDA	0.1		No		
	PFOS	4.6		No		
	FOSA	24		No		
	PFOA	13		No		
	PFNA	5.0		No		
	PFDA	2.9		No		
	PFUnDA	1.9		No	Charleston location: striped mullet → dolphin	
	PFDoDA	0.2		No		
	PFHxS	4.0		No		
	PFOS	2.6		No		
	FOSA	8.3		No		
	PFOA	13		No		
	PFNA	3.2		No		
	PFDA	8.8		No		
	PFUnDA	2.4		No		
	PFDoDA	0.1		No		
	PFOS	4		No	Charleston location: pinfish → dolphin	
	FOSA	30		No		
	PFOA	2.7		No		
	PFNA	1.4		No		
	PFDA	2.4		No		
	PFUnDA	3.2		No		
	PFDoDA	0.4		No		
	PFHxS	14		No		
	PFOS	1.2		No		
	FOSA	3.4		No		
	PFOA	2.3		No	Charleston location: Atlantic croaker → dolphin	
	PFNA	24		No		
	PFDA	2.5		No		
	PFUnDA	2.1		No		
	PFDoDA	1.8		No		
	PFOS	2.2		No		
	FOSA	1.5		No		

Table A-4: Bio-accumulation Factors								
Report	Compound	BMF	TMF	TL adjustment	Prey (known or assumed) or diet → Predator	Comments		
	PFOA	6.4		No	Charleston location: spotfish → dolphin			
	PFNA	4.6		No				
	PFDA	2.8		No				
	PFUnDA	3.9		No				
	PFDoDA	0.6		No				
	PFHxS	6.0		No				
	PFOS	0.8		No				
	FOSA	4.4		No				
	PFOA	1.8		No	Charleston location: seatrout → dolphin			
	PFNA	2.1		No				
	PFDA	2.4		No				
	PFUnDA	2.5		No				
	PFDoDA	0.6		No				
	PFHxS	3.3		No				
	PFOS	0.9		No				
	FOSA	1.3		No				
	PFOA			13 / 6.3			Charleston location: Trophic levels from 3.4 to 4.4	
	PFNA			4.7 / 2.4				
	PFDA			3.4 / 2.2				
	PFUnDA			3.0 / 2.3				
	PFDoDA			0.7 / 0.6				
	PFHxS			0.2 / 0.1				
	PFOS			4.9 / 1.8				
	FOSA			5.9 / 5.0				
	PFOS			11 / 6.3			Sarasota Bay location: Trophic levels from 2.0 to 4.1	
	PFOS			7.9 / 1.4			Sarasota Bay location: Trophic levels from 2.4 to 4.1 (i.e., zooplankton excluded)	
	Sinclair <i>et al.</i> (2006)	PFOS	8.9		No		Fish (liver) → piscivorous waterfowl (liver)	Study conducted on a freshwater food web in New York State. The BMFs are defined as the ratio of predator concentrations to prey concentrations, with no adjustment for TL difference.

Table A-4: Bio-accumulation Factors						
Report	Compound	BMF	TMF	TL adjustment	Prey (known or assumed) or diet → Predator	Comments
Haukås <i>et al.</i> (2007)	PFOS	0.32		3	Ice amphipod (whole) → polar cod (liver)	<p>Study conducted on a Barents Sea (Norwegian Arctic, east of Svalbard) marine food web, including seabirds.</p> <p>The BMF, adjusted for TL differences, is defined by the equation $BMF_{TL} = ([X]_{predator} / [X]_{prey}) / (TL_{predator} - TL_{prey})$, where the TL values are deduced from $\delta^{15}N$ measurements, with TL = 2.0 being assigned for the ice amphipod.</p> <p>For the BMFs based on two individual species, the assumed prey considered did not necessarily constitute the sole or predominant diet of the corresponding predator. On the other hand, the mixed-diet BMFs (for PFOS) were based on the following feeding patterns (justified in the paper):</p> <ul style="list-style-type: none"> • Black guillemot: 20 % ice amphipods, 80 % polar cod • Glaucous gull: 20 % ice amphipods, 50 % polar cod, 30 % black guillemot.
	PFOS	1.54		3	Ice amphipod (whole) → black guillemot (liver)	
	PFNA	8.76		3	Polar cod (liver) → black guillemot (liver)	
	PFHxS	6.0		3		
	PFOS	10.1		3		
	PFNA	11.6		3	Polar cod (liver) → glaucous gull (liver)	
	PFHxS	7.20		3		
	PFOS	38.7		3		
	PFNA	9.34		3	Black guillemot (liver) → glaucous gull (liver)	
	PFHxS	8.49		3		
	PFOS	27.0		3		
	PFOS	5.66		3	Mixed diet → black guillemot (liver)	
	PFOS	11.3		3	Mixed diet → glaucous gull (liver)	
Powley <i>et al.</i> (2008)	PFDA	0.5		No	Zooplankton (whole) → arctic cod (whole)	<p>Study conducted on a Western Canadian Arctic marine food web.</p> <p>The BMFs are defined as the ratio of predator concentrations to prey concentrations, for assumed predator-prey relationships, with no adjustment for TL difference.</p>
	PFDoDA	0.3		No		
	PFOS	8.7		No		
	PFDA	1.4		No	Arctic cod (whole) → seal (blood)	
	PFUnDA	3.1		No		
	PFDoDA	0.8		No		
	PFOS	7.0		No		
Butt <i>et al.</i> (2008)	PFOA	119		No	Ringed seal (liver) → polar bear (liver)	<p>Samples of liver were taken from ringed seals at 11 locations in the Canadian Arctic between 2002 and 2005 and PFAS levels were determined by Butt <i>et al.</i> (2008).</p>
		125		No		
		107		No		
		45		No		
	PFNA	111		No		<p>For the purpose of calculating BMFs as the ratio of levels in polar bear livers to those in ringed seal livers, the polar bear data was taken from the paper by Smithwick <i>et al.</i> (2005), which reported PFAS levels in liver samples taken in 2001-2002 in the Canadian Arctic.</p> <p>The ringed seal populations were grouped and matched to similarly located polar bear populations. Four broad areas were thus defined and identified as Southeast Beaufort Sea, Hudson Bay, South Baffin Island and Labrador, and High Arctic. The four numerical values for each PFAS listed in the BMF column of this table refer to results from these 4 areas in the stated order.</p>
		63		No		
		40		No		
		35		No		
	PFDA	43		No		
		23		No		
		17		No		
		21		No		
	PFUnDA	21		No		
		10		No		
		8.8		No		
		7.1		No		
	PFDoDA	3.5		No		
2.9			No			

Table A-4: Bio-accumulation Factors							
Report	Compound	BMF	TMF	TL adjustment	Prey (known or assumed) or diet → Predator	Comments	
		3.6		No		The BMFs are defined as the ratio of predator concentrations to prey concentrations, for assumed predator-prey relationships, with no adjustment for TL difference.	
		2.3		No			
	PFTrDA	2.7		No			
		3.4		No			
		2.0		No			
		1.6		No			
		1.4		No			
	PFTeDA	3.1		No			
		8.5		No			
		3.0		No			
		3.0		No			
	PFPeDA	1.7		No			
		3.3		No			
		10		No			
		251		No			
	PFHxS	373		No			
		163		No			
		285		No			
		137		No			
	PFOS	163		No			Ringed seals (liver) → polar bears (liver)
		80		No			
		91		No			
		6.0		No			
	FOSA	116		No			
36			No				
3.6			No				
3.6			No				
de Vos et al. (2008)	PFOS	3.5		No	HD → PC	Study conducted on a Western Scheldt (Netherlands) food chain. BMF values are geometric means, based on levels observed in previous campaigns. HD = herbi-detrivores: lugworm (whole); PC = primary carnivores: brown shrimp (soft tissue only), sprat (whole), sandeel (whole); P-SC = primary-secondary carnivores: green crab (soft tissue only), sole (whole and fillet); plaice (liver), bib (liver), eel (fillet), seabass (liver); SC = secondary carnivorous birds: common tern (eggs). The BMFs are defined as the ratio of predator concentrations to prey concentrations, for assumed predator-prey relationships, with no adjustment for TL difference.	
	PFOS	4.0		No	HD → P-SC		
	PFOS	1.1		No	PC → P-SC		
	PFOS	2.4		No	PC → SC		
	PFOS	2.1		No	P-SC → SC		

Table A-4: Bio-accumulation Factors						
Report	Compound	BMF	TMF	TL adjustment	Prey (known or assumed) or diet → Predator	Comments
Li <i>et al.</i> (2008)	PFOS		(6.4)		Outfall of wastewater treatment plant: see Comments column	Study conducted at outfall of Beijing wastewater treatment plant. Species considered were zooplankton (whole) and 4 fish species (serum). The TMF was not reported by Li <i>et al.</i> (2008), but it was calculated here from Figure 3 of the paper, which shows a plot of ln[PFOS, wet-weight] versus trophic level (TMF being given by e^{slope}).
Houde <i>et al.</i> (2008)	PFOS	66 / 16		No/2	Zooplankton → lake trout	Study conducted on a Lake Ontario freshwater food web, with the main objective of determining how bio-accumulation of commercial PFOS depends on the structure of its constituent isomers. All results were calculated on a whole-organism basis. Only the results for “overall PFOS” (generally very close to those for the linear isomer) are presented here. The first BMF value in the x / y pair is defined as the ratio of predator concentrations to prey concentrations. The second value is adjusted for TL using the equation $BMF_{TL} = ([X]_{\text{predator}} / [X]_{\text{prey}}) / (TL_{\text{predator}} / TL_{\text{prey}})$, where TLs are deduced from $\delta^{15}N$ measurements, with zooplankton being assigned TL = 1.0.
	PFOS	7.5 / 4.1		No/2	Crustacean (<i>Diporeia</i>) → forage fish (sculpin)	
	PFOS	13 / 6.2		No/2	Crustacean (<i>Mysis</i>) → lake trout	
	PFOS	1.2 / 0.5		No/2	Crustacean (<i>Diporeia</i>) → lake trout	
	PFOS	1.6 / 0.9		No/2	Forage fish (alewife) → lake trout	
	PFOS	0.84/0.64		No/2	Forage fish (smelt) → lake trout	
	PFOS	0.17/0.13		No/2	Forage fish (sculpin) → lake trout	
	PFOS		3.8		Benthic organisms (<i>Diporeia</i> and sculpin) included	
	PFOS		4.2		Benthic organisms excluded	
Tomy <i>et al.</i> (2009)	PFOA	2.2		2	Arctic copepod (whole) → cod (liver)	Study conducted on a Western Canadian Arctic marine food web. The BMF is adjusted for TL difference according to the equation $BMF_{TL} = ([X]_{\text{predator}} / [X]_{\text{prey}}) / (TL_{\text{predator}} / TL_{\text{prey}})$, where the TL is deduced from $\delta^{15}N$ measurements, with the arctic copepod being assigned TL = 2.0.
	PFNA	0.7		2		
	PFDA	0.4		2		
	PFUnDA	0.3		2		
	PFDODA	1.2		2		
	PFOS	0.1		2		
	FOSA	0.5		2		
	PFOA	0.8		2		
	PFNA	0.3		2	Pelagic amphipod (whole) → cod (liver)	
	PFDA	0.1		2		
	PFUnDA	0.3		2		
	PFDODA	1.3		2		
	PFOS	0.01		2		
	FOSA	1.2		2		
	PFOA	0.7		2	Arctic cisco (liver) → beluga (liver)	
	PFNA	2.9		2		
	PFDA	44		2		
	PFUnDA	181		2		
PFDODA	4.0		2			
PFOS	141		2			

Table A-4: Bio-accumulation Factors							
Report	Compound	BMF	TMF	TL adjustment	Prey (known or assumed) or diet → Predator	Comments	
	FOSA	26		2	Herring (liver) → beluga (liver)		
	PFOA	1.3		2			
	PFNA	5.8		2			
	PFDA	87		2			
	PFUnDA	353		2			
	PFDODA	7.9		2			
	PFOS	276		2			
	FOSA	52		2			
	PFOA	0.9		2	Cod (liver) → beluga (liver)		
	PFNA	12.9		2			
	PFDA	55		2			
	PFUnDA	229		2			
	PFDODA	3.2		2			
	PFOS	179		2			
	FOSA	31		2			
	PFOA	0.1		2	Cod (liver) → ringed seal (liver)		
	PFNA	1.2		2			
	PFDA	2.5		2			
	PFUnDA	6.6		2			
	PFDODA	0.1		2			
	PFOS	27.7		2			
	FOSA	0.1		2			
	PFOA		2.1		TMF regression performed on same concentration basis as for BMF values above (whole organism or liver)		The TMF is derived from a plot of the logarithm of the concentration of the PFAS in various organisms versus TL. The TL is deduced from $\delta^{15}\text{N}$ measurements, with the arctic copepod being assigned TL = 2.0.
	PFNA		3.8				
	PFDA		6.3				
	PFUnDA		13.7				
	PFOS		6.3				
	FOSA		1.9				
	PFNA		4.8		TMF regression performed on whole-body concentration basis		The species considered for the regression are those listed for the BMF measurements, ranging from the arctic copepod (TL = 2.0) to the beluga (TL = 3.8).
	PFDA		19.8				
	PFOS		19.6				
	Kelly <i>et al.</i> (2009)	PFHpA		1.43			TMF based on overall Arctic marine food web, using "as measured" concentrations, not adjusted to protein levels
PFOA			3.28				
PFNA			7.03				
PFDA			8.29				
PFUnDA			7.98				
PFDODA			4.79				
PFTTrDA			2.37				
PFOS			17.4				
FOSA			5.09				
PFHpA			0.76				
PFOA			1.93		TMF based on overall	The TMF is derived from a plot of the logarithm of the concentration of the PFAS in various organisms versus TL, with the TLs being deduced from $\delta^{15}\text{N}$ measurements	

Table A-4: Bio-accumulation Factors						
Report	Compound	BMF	TMF	TL adjustment	Prey (known or assumed) or diet → Predator	Comments
	PFNA		4.23		Arctic marine food web, using concentrations expressed relative to protein levels (ng/g protein)	conducted previously on the food web studied.
	PFDA		4.81			
	PfUnDA		4.79			
	PFDoDA		2.96			
	PFTTrDA		1.97			
	PFOS		11.0			
	FOSA		4.46			
	PFHpA		0.75		TMF based on marine piscivorous food web only, using concentrations expressed relative to protein levels (ng/g protein)	
	PFOA		0.40			
	PFNA		0.63			
	PFDA		0.60			
	PfUnDA		1.09			
	PFDoDA		1.01			
	PFTTrDA		0.34			
	PFOS		0.47			
	FOSA		4.53			
Quinete <i>et al.</i> (2009)	PFOA	1.3-2.6		No	Scabbard fish (liver) or croaker (liver) → tucuxi dolphin (liver)	Study conducted at two locations in Brazil: the Paraíba do Sul river and Guanabara Bay, both in Rio do Janeiro State. The BMFs are defined as the ratio of predator concentrations to prey concentrations, for assumed predator-prey relationships, with no adjustment for TL difference.
	PFOS	7.7-63		No		
	FOSA	5.6-35		No		
Müller <i>et al.</i> (2011)	PFOA	0.9 / -		No	Lichen (whole) → caribou (muscle)	Study conducted on terrestrial food webs (lichen/plants → caribou → wolf) from two remote areas in northern Canada, designated here as Porcupine (P) and Bathurst (B). The two numerical values (x / y) shown in the BMF column refer respectively to the P (x) and B (y) locations. The BMFs are defined as the ratio of predator concentrations to prey concentrations, for assumed predator-prey relationships, with no adjustment for TL difference. Two approaches were applied, one based on single-tissue concentrations, the other using estimated whole-body concentrations for caribou and wolf.
	PFNA	1.2 / 0.9		No		
	PFDA	1.3 / 1.1		No		
	PfUnDA	1.9 / 4.3		No		
	PFDoDA	1.9 / 5.2		No		
	PFTTrDA	2.1 / 5.0		No		
	PFOS	2.0 / 3.6		No		
	PFOA	- / 11		No	Lichen (whole) → caribou (liver)	
	PFNA	40 / 32		No		
	PFDA	75 / 33		No		
	PfUnDA	46 / 78		No		
	PFDoDA	16 / 110		No		
	PFTTrDA	17 / 47		No		
	PFOS	4.0 / 3.1		No		
	PFOA	3.8 / 2.6		No	Caribou (muscle) → wolf (muscle)	
	PFNA	6.9/12.4		No		
PFDA	3.3 / 2.8		No			
PfUnDA	2.1 / 3.2		No			
PFDoDA	- / 1.2		No			
PFTTrDA	- / 4.9		No			

Table A-4: Bio-accumulation Factors							
Report	Compound	BMF	TMF	TL adjustment	Prey (known or assumed) or diet → Predator	Comments	
	PFOS	4.5 / 1.8		No	Caribou (liver) → wolf (liver)		
	PFOA	0.0 / 0.9		No			
	PFNA	2.1 / 2.3		No			
	PFDA	1.0 / 1.4		No			
	PFUnDA	1.4 / 2.0		No			
	PFDODA	- / 1.1		No			
	PFTrDA	- / 1.1		No			
	PFOS	2.1 / 0.8		No			
	PFOA	1.4 / 2.6		No	Lichen (whole) → caribou (whole)		
	PFNA	2.8 / 2.7		No			
	PFDA	6.1 / 2.9		No			
	PFUnDA	3.8 / 8.2		No			
	PFDODA	2.9 / 11		No			
	PFTrDA	2.4 / 6.9		No			
	PFOS	4.8 / 9.1		No			
	PFOA	1.8 / 0.3		No			Vegetation (whole) → caribou (whole)
	PFNA	8.5 / 5.3		No			
	PFDA	12.4/7.2		No			
	PFUnDA	9.8/14.5		No			
	PFDODA	4.5 / 8.0		No			
	PFTrDA	7.1 / 9.0		No			
	PFOS	9.1 / 7.9		No			
	PFOA	2.4 / 2.1		No	Caribou (whole) → wolf (whole)		
	PFNA	3.8 / 5.4		No			
	PFDA	1.7 / 2.1		No			
	PFUnDA	2.0 / 2.8		No			
	PFDODA	1.2 / 1.4		No			
	PFTrDA	0.8 / 3.2		No			
	PFOS	3.3 / 1.2		No			
	PFOA		2.4 / 2.2			Lichen (whole) → caribou (liver) → wolf (liver)	See above. The two numerical values (x / y) shown in the BMF column refer respectively to the P (x) and B (y) locations. The TMF is derived from a plot of the logarithm of the wet-weight concentration in various organisms versus TL, the latter being determined by $\delta^{15}\text{N}$ measurements performed on the actual samples. The approximate range of TLs was from 1.0 to 3.7 at the Porcupine location and from 0.6 to 3.9 at the Bathurst location.
	PFNA		6.7 / 4.5				
	PFDA		7.1 / 5.1				
	PFUnDA		6.6 / 6.1				
	PFDODA		4.1 / 5.2				
	PFTrDA		3.7 / 4.2				
	PFOS		6.7 / 5.2				
	PFOA		1.3 / 1.3		Lichen (whole) → caribou (whole) → wolf (whole)		
	PFNA		2.7 / 2.2				
	PFDA		2.6 / 2.3				
	PFUnDA		2.5 / 2.8				
	PFDODA		1.4 / 2.2				
						Two approaches were applied, one based on single-tissue concentrations, the other	

Table A-4: Bio-accumulation Factors						
Report	Compound	BMF	TMF	TL adjustment	Prey (known or assumed) or diet → Predator	Comments
	PFTrDA		1.4 / 2.0		Vegetation (whole) → caribou (whole) → wolf (whole)	using estimated whole-body concentrations for caribou and wolf.
	PFOS		2.6 / 2.4			
	PFOA		1.1 / 1.3			
	PFNA		2.0 / 1.9			
	PFDA		2.3 / 2.3			
	PFUnDA		2.2 / 2.9			
	PFDoDA		1.3 / 2.0			
	PFTrDA		1.4 / 1.8			
	PFOS		2.2 / 2.3			
Loi <i>et al.</i> (2011)	PFOA		(1.0)		Subtropical brackish aquatic food web in Hong Kong	The TMF is derived from a plot of the logarithm of whole-body wet-weight concentration in various organisms versus TL, with TL varying from 0.7 (phytoplankton) to 5.5 (small snakehead fish), as determined by $\delta^{15}\text{N}$ measurements performed on the actual samples, with zooplankton being assigned a TL of 2.0. There was no significant trend of concentration with TL for PFOA or PFNA.
	PFNA		(1.0)			
	PFDA		1.5			
	PFUnDA		1.74			
	PFDoDA		1.38			
	PFOS		1.3			
Zhou <i>et al.</i> (2012)	PFHxA	(1.0)	(1.0)	No	The trophic chain considered included: plankton (whole), floating aquatic plants (whole), river snail (whole), shrimp (whole), crab (whole), loach (whole) and common carp (muscle)	Study conducted on a freshwater food chain in Baiyangdian Lake (China). Reported concentrations were expressed on a dry-weight basis. Only those PFASs and organisms reported in Table 1 of the paper are listed here. TLs were calculated from stable N isotope ratios. On the basis of the authors' statement "There was no significant correlation between concentrations of PFCs and TLs in aquatic organisms from Baiyangdian Lake", BMFs and TMFs have been assigned unit values here, although such numerical values were not reported in the original paper.
	PFOA	(1.0)	(1.0)	No		
	PFNA	(1.0)	(1.0)	No		
	PFDA	(1.0)	(1.0)	No		
	PFUnDA	(1.0)	(1.0)	No		
	PFOS	(1.0)	(1.0)	No		
Wang <i>et al.</i> (2013)	PFNA	0.6		No	Silver carp (whole) → alligator (serum)	Study conducted on endangered Chinese alligators and their prey species in a research habitat. The BMFs are defined as the ratio of predator concentrations to prey concentrations, for assumed (but
	PFDA	17		No		
	PFUnDA	26		No		
	PFDoDA	6.2		No		
	PFTeDA	110		No		
	PFOS	3.7		No		
	PFNA	3.0		No	Oriental river prawn (whole) → alligator (serum)	
	PFDA	10		No		
	PFUnDA	6.5		No		
	PFDoDA	2.7		No		
	PFTeDA	2.2		No		

Table A-4: Bio-accumulation Factors						
Report	Compound	BMF	TMF	TL adjustment	Prey (known or assumed) or diet → Predator	Comments
	PFOS	31		No	Northern snakehead (whole) → alligator (serum)	unconfirmed) predator-prey relationships, with no adjustment for TL difference.
	PFNA	1.3		No		
	PFDA	3.2		No		
	PFUnDA	2.0		No		
	PFDODA	1.1		No		
	PFTeDA	3.2		No		
	PFOS	4.6		No		
	PFNA	18		No	Common carp (whole) → alligator (serum)	
	PFDA	200		No		
	PFUnDA	90		No		
	PFDODA	17		No		
	PFTeDA	9.9		No		
	PFOS	76		No		
	PFNA	2.7		No	Tire track eel (whole) → alligator (serum)	
	PFDA	38		No		
	PFUnDA	20		No		
	PFDODA	11		No		
	PFTeDA	14		No		
	PFOS	13		No		
	PFNA	6.7		No	Crucian carp (whole) → alligator (serum)	
	PFDA	68		No		
PFUnDA	44		No			
PFDODA	14		No			
PFTeDA	11		No			
PFOS	58		No			
Vestergren <i>et al.</i> (2013)	PFOA	0.68		No	Feed → cow (liver)	Study conducted over a 6-month period on a herd of adult cows on a Swedish dairy farm. The animals were generally confined to a barn, but were allowed to graze on a pasture in the summer months. They were exposed to “background” levels of PFASs through their feed and drinking water.
	PFNA	4.87		No		
	PFDA	10.4		No		
	PFUnDA	12.2		No		
	PFDODA	3.28		No		
	PFOS	19.8		No		
	PFOA	0.53		No	Feed → cow (muscle)	Based on previously published studies by other scientists, it was assumed that the cows reached a steady state with their feed, which is reasonable, given the short observed half-lives of the PFAAs studied.
	PFNA	1.42		No		
	PFDA	1.12		No		
	PFUnDA	1.08		No		
	PFDODA	0.81		No		
	PFOS	3.09		No		
	PFOA	0.22		No	Feed → cow (blood)	The BMFs are defined as the ratio of PFAA concentrations in the liver, muscle or blood, divided by the concentrations in silage, which was shown to constitute 75-81 % of the total intake of the various PFAAs.
	PFNA	5.62		No		
	PFDA	4.63		No		
PFUnDA	2.63		No			
PFDODA	0.70		No			
						The exact numerical BMF values, not published in the paper, were obtained from

Table A-4: Bio-accumulation Factors						
Report	Compound	BMF	TMF	TL adjustment	Prey (known or assumed) or diet → Predator	Comments
	PFOS	15.0		No		Vestergren (personal communication, 15 December 2013).
Xu <i>et al.</i> (2014)	PFOA		(1.0)		The TMFs were derived from observations on phytoplankton (TL 1.05), zooplankton (TL set to 2.0), zoobenthos (TL 2.53), herbivorous fish (TLs 2.94-2.95), omnivorous fish (TLs 3.24-3.76), carnivorous fish (TLs 3.66-4.30), shrimp (TL 4.11) and egrets (TL 4.61).	Study conducted on a sub-tropical freshwater aquatic and avian food web in Lake Taihu, China. The TMFs are derived from plots of the logarithm of wet-weight concentration in various organisms versus TL, with TL determined by $\delta^{15}\text{N}$ measurements performed on the actual samples, and zooplankton being assigned a TL of 2.0. The concentrations were expressed relative to the whole organism for plankton, zoobenthos, shrimps and small fish, and relative to muscle for the larger fish and egrets. No significant trend of TMF with TL was observed for PFOA
	PFNA		2.1			
	PFDA		3.7			
	PFUnDA		3.1			
	PFDoDA		2.4			
	PFOS		2.9			
Braune <i>et al.</i> (2014)	Σ PFCAs	4.0			Arctic cod → thick-billed murre liver (TBM-L)	Study conducted on seabirds (female thick-billed murre) and various fish species in northern Hudson Bay (Canada). The BMFs were the ratios of concentrations in bird liver to those in the fish. No adjustment for exact TL difference was applied. <u>BMFs were not reported for individual PFASs, but only for the sum of the PFCAs present.</u>
		12			Capelin → TBM-L	
		6.4			Sand lance → TBM-L	
		29			Arctic shanny → TBM-L	
		32			Daubed shanny → TBM-L	
		5.8			Banded gunnel → TBM-L	
		9.2			Fish doctor → TBM-L	
		42			Fourline snake blenny → TBM-L	
		31			Arctic staghorn sculpin → TBM-L	
		4.1			Sculpin (<i>Triglops</i> spp.) → TBM-L	
		14			Snailfish → TBM-L	
D'Hollander <i>et al.</i> (2014)	PFOS	302 ± 67		No	Berries (whole) → wood mouse (liver)	Study conducted at two sites near Antwerp (Belgium), one of them adjacent to a fluorochemical plant, the other 2 km away. The invertebrates studied were earthworms, slugs, millipedes and woodlice. The plant samples included the fruits of common blackberry and European elder. No adjustment for exact TL difference was applied.
		46 ± 12		No	Berries (whole) → wood mouse (kidney)	
		202 ± 39		No	Berries (whole) → bank vole (liver)	
		2.0 ± 0.4		No	Invertebrates (whole) → wood mouse (liver)	
		0.30 ± 0.08		No	Invertebrates (whole) → wood mouse (kidney)	
		1.3 ± 0.3		No	Invertebrates (whole) → bank vole (liver)	
Fang <i>et al.</i> (2014)	PFOA		2.13		The TMFs reported here were derived from observations on a number of fish species at various TLs (i.e.,	Study conducted on a freshwater food chain in Lake Taihu, China. The TMFs were derived from plots of the logarithm of wet-weight muscle concentration in various fishes versus TL, with TL determined by
	PFNA		2.19			
	PFDA		2.53			
	PFUnDA		2.25			

Table A-4: Bio-accumulation Factors						
Report	Compound	BMF	TMF	TL adjustment	Prey (known or assumed) or diet → Predator	Comments
	PFDoDA		3.19		invertebrates were excluded). The fish TLs ranged from 2.50 to 4.24.	δ ¹⁵ N measurements performed on the actual samples, and zooplankton being assigned a TL of 2.0. The TMF values for PFOA and PFOS refer to weighted-average values for the sum of a number of linear and branched isomers.
	PFOS		3.74			
Numata <i>et al.</i> , (2014)	PFHxS	20.1			Whole Pig	Mean for all 24 pigs.
	PFHpS	12.7				
	PFOS	17.9				
	PFOA	7.9				
	PFHpA	2.7				
	PFBS	1.2				
	PFHxA	0.13				
	PFHxS	13.1			Pig Meat	
	PFHpS	8.3				
	PFOS	9.7				
	PFOA	5.3				
	PFHpA	1.8				
	PFBS	0.8				
	PFHxA	0.08				
	PFHxS	48				
	PFHpS	81				
	PFOS	503				
	PFOA	32.8				
	PFHpA	7.0				
	PFBS	6				
PFHxA	0.42					

Notes: Table adopted from Concawe, 2016

Table A-5: Crop plant part analysed, initial PFAS concentrations (mg/kg soil), soil organic matter (SOM) or organic carbon (OC) contents and bioconcentration factors (concentration in plant parts/initial concentration in soil).					
Plant Species and parts	Compounds and initial concentrations (mg/kg)	PFBA,PFBS Bioconcentration Factors	PFOA, PFOS Bioconcentration Factors	SOM or OC contents	References
Maize straw	PFOA: 0 - 50 PFOS: 0 - 50	--	Values at 0.25 and 1 mg/Kg: PFOA: 0.272; 0.126 PFOS: 0.132; 0.104	na	Stahl et al.,2009
Maize straw	PFAA mixture: 0.25 and 1 per each of 10 compounds	Values at 0.25 and 1 mg/Kg: PFBA: 63.64; 35.23 PFBS: 3.85 a; 1.84a	Values at 0.25 and 1 mg/Kg: PFOA: 0.56 a; 0.65 a PFOS: 0.32; 0.62	OC: 0.274%	Krippner et al.,2015
Maize stover	Full-scale field study, PFAA mixture from urban 2x biosolid addition. PFBA: 0.00010 PFBS: 0.00039 PFOA: 0.00128 PFOS: 0.00282	PFBA: 64.8 PFBS: --	PFOA: -- PFOS: --	OC: 0.57%	Blaine et al., 2013
Maize leaves	PFOS: 38.5 PFBS: 0.02	PFBS: 4.00 ^b	PFOS: 0.80 ^b	na	Navarro et al., 2017
Maize ears	PFOA: 0 – 50 PFOS: 0 - 50	--; --	Values at 0.25 and 1 mg/Kg: PFOA: 0.008; 0.004 PFOS: 0; .003	na	Stahl et al., 2009
Maize grains	PFAA mixture: 0.25 and 1 per each of 10 compounds	Values at 0.25 and 1 mg/Kg: PFBA: 0.133 ^a ; 0.229 ^a PFBS: 0.008 ^a ; 0.005 ^a	Values at 0.25 and 1 mg/Kg: PFOA: --; 0.002 PFOS: --; --	OC: 0.274%	Krippner et al., 2015
Maize root	PFOS: 38.5 PFBS: 0.02	PFBS: 5.00 ^b	PFOS: 8.82 ^b	na	Navarro et al., (2017)
Oat straw	PFOA: 0 – 50 PFOS: 0 - 50	--	Values at 0.25 and 1 mg/Kg: PFOA: 0.88; 0.69 PFOS: 0.224; 0.150	na	Stahl et al., 2009

Table A-5: Crop plant part analysed, initial PFAS concentrations (mg/kg soil), soil organic matter (SOM) or organic carbon (OC) contents and bioconcentration factors (concentration in plant parts/initial concentration in soil).

Plant Species and parts	Compounds and initial concentrations (mg/kg)	PFBA,PFBS Bioconcentration Factors	PFOA, PFOS Bioconcentration Factors	SOM or OC contents	References
Oat grains	PFOA: 0 – 50 PFOS: 0 - 50	--	Values at 0.25 and 1 mg/Kg: PFOA: 0.048; 0.054 PFOS: 0.004; .0170	na	Stahl et al., 2009
Ryegrass, Four cuttings	PFOA: 0 – 50 PFOS: 0 - 50	--	Range within the four cuttings at 0.25 and 1 mg/Kg: PFOA: 0.128 -7.52 PFOS: 0.048 –0.47	na	Stahl et al., 2009
Wheat straw	PFOA: 0 – 50 PFOS: 0 - 50		Values at 0.25 and 1 mg/Kg: PFOA: 3.20; 1.90 PFOS: 0.20; 0.27	na	Stahl et al., 2009
Wheat straw	PFAA mixture from the highest biosolid addition: PFBA: 0.0135 PFBS: 0.0312 PFOA: 0.0261	PFBA: 1.64 PFBS: 0.635	PFOA: 0.847 PFOS: 0.270	SOM: 2.76%	Wen et al., 2014
Wheat grains	PFOS: 0.0408 Wheat grains PFOA: 0 – 50 PFOS: 0 - 50	--	Values at 0.25 and 1 mg/Kg: PFOA: 0.096; 0.009 PFOS: --; --	na	Stahl et al., 2009
Wheat grains	PFAA mixture from the highest biosolid addition: PFBA: 0.0135 PFBS: 0.0312 PFOA: 0.0261 PFOS: 0.0408	PFBA: 0.48 PFBS: --	PFOA: 0.111 PFOS: 0.062	SOM: 2.76%	Wen et al., 2014

Table A-5: Crop plant part analysed, initial PFAS concentrations (mg/kg soil), soil organic matter (SOM) or organic carbon (OC) contents and bioconcentration factors (concentration in plant parts/initial concentration in soil).

Plant Species and parts	Compounds and initial concentrations (mg/kg)	PFBA,PFBS Bioconcentration Factors	PFOA, PFOS Bioconcentration Factors	SOM or OC contents	References
Wheat husk	PFAA mixture from the highest biosolid addition: PFBA: 0.0135 PFBS: 0.0312 PFOA: 0.0261 PFOS: 0.0408	PFBA: 0.43 PFBS: --	PFOA: 0.160 PFOS: 0.054	SOM: 2.76%	Wen et al., 2014
Notes: 1. <i>a</i> = no significant difference between the two different concentrations 2. <i>b</i> = obtained from mean values of <i>t</i> =0 and <i>t</i> = final soil concentrations 3. <i>na</i> = not available 4. Σ = total amount					

Table A-6: Initial PFAS concentrations (mg/kg soil) and their amount in different vegetable plants parts (µg/kg d.w.)				
Plant Species and Parts	Compounds	Type of treatment and initial soil concentrations	Concentrations in plant tissues	References
Carrots (peeled)	PFOA; PFOS Tub 1	Soil + spiked biosolids. 0.681; 0.010	PFOA: 31.3 ^a ; 333 ^b PFOS: 0.5 ^a ; 5.3 ^b	Lechner and Knapp (2011)
Carrots (peeled)	PFOA; PFOS Tub 2	Soil + spiked biosolids. 0.676; 0.458	PFOA: 30.8 ^a ; 32 ^b PFOS: 18.4 ^a ; 196 ^b	Lechner and Knapp (2011)
Carrots (peeled), <i>Chantenay</i> variety	PFOA and PFOS in separate pots	Soil 2.4 + spiked compost. 0.528; 0.445	PFOA: 148 PFOS: 240	Bizkarguenaga et al., 2016
Carrots (peeled), <i>Nantesa</i> variety	PFOA and PFOS in separate pots	Soil 2.4 + spiked compost. 0.485; 0.335	PFOA: 144 PFOS: 162	Bizkarguenaga et al., 2016
Celery shoots	PFAA mixture	Soil + biosolids. Industrially impacted: PFBA: 0.00468 PFBS: 0.04858 PFOA: 0.07852 PFOS: 0.04966 ΣPFASs = 0.329;	PFBA: 231.69 PFBS: 107.13 PFOA: 55.40 PFOS: 69.27 ΣPFASs = 817.3	Blaine et al., 2014 a
Celery shoots	PFAA mixture	Soil + biosolids. Municipal: PFBA: 0.00090 PFBS: 0.00021 PFOA: 0.01491 PFOS: 0.31949 ΣPFASs = 0.427	PFBA: < LOQ PFBS: 4.49 PFOA: 1.99 PFOS: 17.21 ΣPFASs = 39.3	Blaine et al., 2014 a
Cucumbers Tub 1	PFOA; PFOS	Soil + spiked biosolids. 0.406; 0.010	PFOA: 11.3 ^a ; 323 ^c PFOS: ND	Lechner and Knapp (2011)
Cucumbers Tub 2	PFOA; PFOS	Soil + spiked biosolids. 0.805; 0.556	PFOA: 23.8 ^a ; 680 ^c PFOS: 1.3 ^a ; 37.1 ^c	Lechner and Knapp (2011)
Lettuce leaves	PFAA mixture	Soil + biosolids. Industrially impacted: PFBA: 0.00468 PFBS: 0.04858 PFOA: 0.07852 PFOS: 0.04966 ΣPFASs = 0.329	PFBA: 266.08 PFBS: 205.24 PFOA: 197.91 PFOS: 82.90 ΣPFASs = 1245	Blaine et al., 2013

Table A-6: Initial PFAS concentrations (mg/kg soil) and their amount in different vegetable plants parts (µg/kg d.w.)				
Plant Species and Parts	Compounds	Type of treatment and initial soil concentrations	Concentrations in plant tissues	References
Lettuce leaves	PFAA mixture	Soil + biosolids. Municipal: PFBA: 0.00090 PFBS: 0.00021 PFOA: 0.01491 PFOS: 0.31949 ΣPFASs = 0.427	PFBA: 25.50 PFBS: 3.03 PFOA: 20.01 PFOS: 101.62 ΣPFASs = 240	Blaine et al., 2013
Lettuce leaves	Field-scale trial plots PFAA mixture	Soil + biosolids, 4x PFBA: 0.00069 PFBS: 0.00080 PFOA: 0.00517 PFOS: 0.01391 PFASs = 0.03477	PFBA: 27.5 PFBS: 1.62 PFOA: < LOQ PFOS: 1.39 ΣPFASs = 47.43	Blaine et al., 2013
Lettuce leaves	PFOA and PFOS in separate pots	Soil 2.4 + spiked compost: 0.560; 0.508	PFOA: 1029 PFOS: 77	Bizkarguenagae t al., 2016
Pea fruits	PFAA mixture	Soil + biosolids. Industrially impacted: PFBA: 0.00468 PFBS: 0.04858 PFOA: 0.07852 PFOS: 0.04966 ΣPFASs = 0.329	PFBA: 150.14 PFBS: 16.18 PFOA: 2.65 PFOS: 1.28 ΣPFASs = 236	Blaine et al., 2014 a
Pea fruits	PFAA mixture	Soil + biosolids. Municipal: PFBA: 0.00090 PFBS: 0.00021 PFOA: 0.01491 PFOS: 0.31949 ΣPFASs = 0.427	PFBA: < LOQ PFBS: < LOQ PFOA: < LOQ PFOS: < LOQ ΣPFASs = < LOQ	Blaine et al., 2014 a
Potatoes (peeled)	PFOA, PFOS	Spiked soil. 0 – 50 for each compound	At 1 mg/Kg soil: PFOA: 0 PFOS: 0	Stahl et al., 2009
Potatoes (peeled)	PFOA; PFOS Tub 1	Soil + spiked biosolids. 0.276; 0.015	PFOA: 2.9 ^a ; 17.9 ^b PFOS: < LOD	Lechner and Knapp (2011)
Potatoes (peeled)	PFOA; PFOS Tub 2	Soil + spiked biosolids. 0.795; 0.317	PFOA: 7.7 ^a ; 47.5 ^b PFOS: 0.7 ^a ; 4.3 ^b	Lechner and Knapp (2011)

Table A-6: Initial PFAS concentrations (mg/kg soil) and their amount in different vegetable plants parts (µg/kg d.w.)				
Plant Species and Parts	Compounds	Type of treatment and initial soil concentrations	Concentrations in plant tissues	References
Radish roots	PFAA mixture	Soil + biosolids. Industrially impacted: PFBA: 0.00468 PFBS: 0.04858 PFOA: 0.07852 PFOS: 0.04966 ΣPFASs = 0.329	PFBA: 13.67 PFBS: 61.89 PFOA: 66.89 PFOS: 34.86 ΣPFASs = 279	Blaine et al., 2014 a
Radish roots	PFAA mixture	Soil + biosolids. Municipal: PFBA: 0.00090 PFBS: 0.00021 PFOA: 0.01491 PFOS: 0.31949 ΣPFASs = 0.427	PFBA: < LOQ PFBS: 23.88 PFOA: 8.11 PFOS: 21.03 ΣPFASs = 79.3	Blaine et al., 2014 a
Spinach	PFAA mixture	Soil + biosolids W1: PFBA: 0.00045 PFBS: ND PFOA: 0.00019 PFOS: 0.00035 ΣPFASs = 0.00144	PFBA: ND PFBS: ND PFOA: 2.37 PFOS: 1.62 ΣPFASs = 5.33	Navarro et al., 2017
Spinach	PFAA mixture	Soil + biosolids W2: PFBA: 0.00043 PFBS: ND PFOA: 0.00018 PFOS: 0.00022 ΣPFASs = 0.00096	PFBA: ND PFBS: ND PFOA: ND PFOS: 0.99 ΣPFASs = 0.99	Navarro et al., 2017
Tomato fruits	PFAA mixture	Soil + biosolids. Industrially impacted: PFBA: 0.00468 PFBS: 0.04858 PFOA: 0.07852 PFOS: 0.04966 ΣPFASs = 0.329	PFBA: 56.11 PFBS: 19.38 PFOA: 8.81 PFOS: < LOQ ΣPFASs = 337	Blaine et al., 2013
Tomato fruits	PFAA mixture	Soil + biosolids. Municipal: PFBA: 0.00090 PFBS: 0.00021 PFOA: 0.01491 PFOS: 0.31949 ΣPFASs = 0.427	PFBA: < LOQ PFBS: < LOQ PFOA: < LOQ PFOS: < LOQ ΣPFASs = 21.4	Blaine et al., 2013

Table A-6: Initial PFAS concentrations (mg/kg soil) and their amount in different vegetable plants parts (µg/kg d.w.)				
Plant Species and Parts	Compounds	Type of treatment and initial soil concentrations	Concentrations in plant tissues	References
Tomato fruits	Field-scale trial plots PFAA mixture	Soil + biosolids, 4x PFBA: 0.00069 PFBS: 0.00080 PFOA: 0.00517 PFOS: 0.01391 ΣPFASs = 0.03477	PFBA: 12.56 PFBS: < LOQ PFOA: < LOQ PFOS: < LOQ ΣPFASs = 37.7	Blaine et al., 2013
Tomato fruits	PFAA mixture	Soil + biosolids W1: PFBA: 0.00074 PFBS: ND PFOA: 0.0012 PFOS: 0.00047 Σ = 0.00782	PFBA: 12.45 PFBS: ND PFOA: 0.18 PFOS: 0.03 ΣPFASs = 61.30	Navarro et al., 2017
Tomato fruits	PFAA mixture	Soil + biosolids W2: PFBA: 0.00007 PFBS: 0.00013 PFOA: 0.00024 PFOS: 0.00030 ΣPFASs = 0.00088	PFBA: 2.48 PFBS: ND PFOA: ND PFOS: ND ΣPFASs = 3.47	Navarro et al., 2017
<p>Notes:</p> <ol style="list-style-type: none"> 1. <i>a = on a fresh weight basis</i> 2. <i>b = on a dry weight basis calculated assuming the % dry matter values of 9.4 and 16.2 (author's data) for peeled carrots and potatoes, respectively</i> 3. <i>c = calculated on a dry weight basis assuming a 3.5% dry matter content (http://nut.entecra.it/646/tabelle_di_composizione_degli_alimenti.html)</i> 4. <i>LOD = limit of detection</i> 5. <i>LOQ = limit of quantitation</i> 6. <i>ND = not detected</i> 7. <i>Σ = total amount</i> 				