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Literature Review of Organic Chemicals of Emerging Environmental Concern in Use in Auckland

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1 Executive Summary

This report reviews the environmental hazard of organic chemicals in products of day-to-day use that are manufactured or consumed in high-volume. It covers, among others; plastics; resins and plastic additives (plasticisers, flame retardants); pharmaceuticals and personal care products (eg, disinfectants, antibiotics, fragrances, sunscreens, drugs, natural and synthetic hormones); detergents and other cleaning agents; various petroleum products, pesticides and biocides (eg, weed killers, fumigants, wood preservatives, antifouling agents); and compounds derived from wastewater and drinking water treatment, landfill or incineration.

The primary aim of the report is to identify chemicals of emerging environmental concern in Auckland and their primary uses. A further objective is the comprehensive assessment of their relative environmental hazard. For this purpose, a ranking system is presented that estimates an "environmental hazard profile" for a given chemical class based on its environmental fate characteristics, such as persistence, bioaccumulation and toxicity (PBT). Special attention is given to chemicals with unfavourable environmental characteristics, such as poor degradability (high persistence), elevated bioaccumulation potential and elevated toxicity (or otherwise adverse biological effects, such as neurotoxicity, endocrine disruption, and carcinogenicity). These substances are accordingly termed "chemicals of potential environmental concern" (CPECs).

In contrast to classic "priority organic pollutants" (POPs), which have consistently high environmental persistence, high bioaccumulation and high acute toxicity, many CPECs or so-called "emerging contaminants" have a somewhat lower environmental hazard profile. Notably, many CPECs have lower acute toxicity than POPs. Nevertheless, some CPECs have a potential to exert chronic adverse effects by being neuroactive or acting as hormone mimics (endocrine disrupting chemicals). The ongoing consumption of high production volume (HPV) chemicals, including some CPECs, increases the potential of accumulation of these substances in Auckland's aquatic receiving environment, with currently unknown consequences.

The most likely routes of entry of CPECs into the aquatic environment are during use and upon disposal, such as from landfill leachates, agricultural run-off, and sewage treatment plant effluent and sludge. Currently no, or few, specific guidelines regulate the discharge of CPECs in New Zealand, resulting in a situation of largely unrestricted discharge in the environment as long as basic water quality criteria are met. Whereas acute toxic effects from individual CPECs are presumed to be unlikely at current environmental concentrations (generally assumed to be <1 mg/L) there is a possibility for the occurrence of additive or synergistic effects (eg endocrine disruption) or long-term effects on behaviour, growth, reproduction and the development of cancer.

Currently, no monitoring is carried out in Auckland to assess the environmental concentrations of CPECs or their potential ecotoxicological effects in the city's freshwater or estuarine environments. This lack of baseline data on exposure conditions impedes reliable estimates of their ecological risk. Whereas current inputs of CPECs from sewage treatment plants and landfills are presumed to be low, due to best management practices, ongoing inputs are likely to occur from decommissioned landfills, septic tank leakage, and combined stormwater and sewage overflows. Agricultural or residential land run-off might be a further diffuse source of CPECs. For antifouling biocides, marinas and boat yards are likely to be significant sources.

Environments with the greatest likelihood of receiving CPECs are presumed to be: (1) marinas (antifouling agents), (2) nearshore settling zones receiving agricultural and residential land run-off (pesticides, hormones and antibiotics), (3) water bodies below catchments with decommissioned landfill sites (leachates containing solvents, plasticisers, pharmaceuticals, pesticides and petroleum products), and (4) urban streams downstream of combined wastewater and stormwater overflows (sewage containing endocrine disrupting chemicals such as hormones, surfactants, pesticides and plastic additives). Analyses of environmental samples from these environments would provide valuable information on the magnitude of current CPEC contamination and serve as a benchmark and baseline for future studies and comparisons with overseas locations.

2 Review of Chemicals of Potential Environmental Concern

2.1 General introduction

This report reviews major groups of organic chemicals that are known or presumed to be in use in New Zealand and that have the potential to become an environmental concern in the future, due to the magnitude of their usage, environmental persistence, bioaccumulation characteristics or toxic properties. In contrast to the existing term "emerging chemicals of concern" (ECCs), this report chooses a more general and more neutral term, "chemicals of potential environmental concern" (CPEC), for this group of substances, given the lack of accurate data on their usage and environmental concentrations in New Zealand.

2.1.1 Chemicals in use

Modern industrialised societies, including New Zealand's, rely on thousands of chemicals in everyday life, for agricultural, manufacturing and domestic applications. As of March 21, 2009, there were 44,781,712 organic and inorganic substances listed in the CAS registry of the American Chemical Society (www.cas.org/cgi-bin/cas/regreport.pl), with about 4000 new substances added each day. The exact numbers of chemicals in commercial use in New Zealand is uncertain, but estimates from other countries range between 10,000 and 100,000, with up to 1000 new compounds released each year (Hale & La Guardia 2002).

In Canada, approximately 11,000 substances are believed to be used regularly in consumer applications, according to the Canadian Domestic Substances List, compiled by Environmental Canada in July 2004 (www.ec.gc.ca/substances/ese/eng/dsl/dslprog.cfm). The Canadian list includes approximately 10,600 organic and 1000 inorganic chemicals in regular (domestic) use. The number is considerably higher in the United States: the U.S. EPA maintains an inventory of chemical substances manufactured for commercial use, as required by the Toxic Substances Control Act (TSCA, www.epa.gov/oppt/newchems/pubs/invntory.htm). It should be noted that the term "manufactured" under the TSCA definition also includes imported chemicals. This TSCA inventory currently (2007) contains approximately 75,000 chemicals in use in the United States, both inorganic and organic, grouped into 55 general categories (www.epa.gov/oppt/newchems/pubs/cat02.htm). Any substance that is not on the TSCA inventory is classified as a "new chemical" and requires submission of a pre-manufacture notice (PMN), detailing, among others, toxicological properties. The Household Products Database of the United States National Library of Medicine (www.householdproducts.nlm.nih.gov/index.htm) lists roughly 2800 compounds in daily (household) use, based on a survey of Material Safety Data Sheets (MSDS) of 7000 household products.

Chemicals in use are often further grouped into high production volume chemicals (HPVCs) and low production volume chemicals (LPVCs), depending on the tonnage manufactured per year. In the European Union, HPVCs are defined as chemicals placed on the E.U. market at volumes exceeding 1000 tons/year per manufacturer or importer. The European Chemical Substances Information System (ESIS) currently (Oct 2007) lists 2767 HPVCs and 7802 LPVCs (http://ecb.jrc.it/esis/). For New Zealand, with about 1 per cent of the population size of the E.U. (population 490 million in July 2007), HPVCs would consequently equate to chemicals manufactured or imported into New Zealand at more than 10 tons per year per manufacturer/importer.

In recent years, there has been increasing concern by scientists, regulators and consumer groups that some HPVCs and products in everyday use (eg, plastics and plastic additives, flame retardants, detergents, disinfectants, newer-generation pesticides, cosmetics and pharmaceuticals) contain substances that are less benign or short-lived than originally assumed and have the potential to accumulate in the environment and exert adverse biological effects, given high enough concentrations and long enough exposure periods. These chemicals of potential environmental concern (CPECs) are commonly characterised by a combination of high-volume production and use and incomplete degradation, leading to gradual accumulation in the environment. Moreover, while generally not acutely toxic at environmentally relevant concentrations, some substances have been found to accumulate in biological tissues, with a potential to cause sublethal or long-term changes in biological function and viability, such as neurological or endocrine disruption, or a higher incidence rate of cancers. In contrast to classic "priority pollutants" (or persistent organic pollutants = POPs), such as DDT, PCBs or PAHs, whose primary sources are agriculture, industry and combustion processes, many of the "emerging contaminants" of current interest have domestic waste as their predominant source – either in the form of sewage or septic tank effluent or landfill leachates.

The problem with managing CPECs is that for many of the chemicals in everyday use, only incomplete or scattered information exists on their usage volume, environmental fate, bioaccumulation and effect on biota, despite potentially widespread inputs via the production and waste streams. For certain types of compounds that share a common mode of action (eg, xenoestrogens, narcotic chemicals, and carcinogens), additive and perhaps synergistic effects are conceivable. This means that the small effects of individual compounds can add up and reinforce each other, with potential long-term impacts on growth, reproduction and the development of cancer. Given that there currently exist no generally accepted water and sediment quality guidelines (eg, ANZECC) for many CPECs, their discharge into the environment is currently more or less unrestricted, with little ongoing screening or monitoring of concentrations and potential environmental effects.

One of the main impediments to a systematic monitoring and management approach is the bewildering number of compounds in use. Recent reviews of CPECs have been conducted by Hale & La Guardia (2002), Richardson (2003b), and Richardson & Ternes (2005). In 2004, the Organisation for Economic Co-Operation and Development (OECD) initiated the development of a global database (“ePortal”) for information on chemical substances in order to improve the availability of hazard data on chemicals. This initiative has involved several member countries and major databases, including CHRIP (Japan's Information on biodegradation and bioconcentration of the Existing Chemical Substances in the Chemical Risk information platform), the OECD High Production Volume Chemicals Database (OECD HPV), the Screening Information Datasets for High Volume Production Chemicals database (SIDS, by UNEP), the European Chemical Substances Information System (ESIS, European Commission), and the High Production Volume Chemical Information System (HPVIS, U.S. Environmental Protection Agency). The most recent OECD HPV Chemicals List, compiled in 2004, contains information on 4843 substances and is based on submissions of nine national inventories and the inventory of the European Union. The next list was scheduled to be compiled in 2007.

The hazardous substances databank (HSDB) by the United States National Institutes of Health (http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB) lists peer-reviewed data on the toxicology of about 5000 chemicals. Another effects database, the Integrated Risk Information System (IRIS), prepared and maintained by the U.S. Environmental Protection Agency (U.S. EPA), summarises information on approximately 1600 chemicals with regard to the likelihood of human health effects (ie, carcinogenic and non-carcinogenic) that may result from exposure (oral or respiratory) to various chemicals in the environment (www.epa.gov/iris/index.html). The ECOTOX database compiled by the U.S. EPA (http://cfpub.epa.gov/ecotox/index.html) contains measured single-toxicity data (terrestrial and aquatic) on nearly 9000 chemicals. However, even in cases where animal toxicity data exists, it is often limited to only a handful of animal species and one or two types of effects (mortality, biochemistry, histological, physiological, behavioural, hormonal, growth, accumulation, or population and assemblage responses), requiring extrapolation to other species, types of responses or time scales. Moreover, even given adequate toxicological information, reliable estimates of environmental risk are impeded by a general dearth of information on a substance’s concentration in the environment or in biological tissues or the environment (ie, “dose” or body burden).

2.1.2 Highly persistent, bioaccumulative and toxic (PBT) substances

Notwithstanding the incomplete nature of ecotoxicological information available, pro-active environmental management necessitates keeping abreast of the plethora of substances being discharged into the environment, in order to identify those that have an elevated potential to cause harm to biota and humans. Urban stormwaters and sediments are known to contain a multitude of inorganic and organic chemicals from numerous human sources. While urban stormwaters in Auckland have been reasonably well-characterised in terms of their trace metal composition and sources, a comprehensive list of organic contaminants in Auckland’s waterways is currently lacking. This is due to the very large number (potentially thousands) of synthetic and natural organic compounds in use. Only a relatively small subset of organic chemical compounds is currently monitored by the Auckland Regional Council (ARC). These include polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and a variety of "first generation" organochlorine pesticides and herbicides (OCs) including DDT, chlordane and dieldrin. These so-called "high-PBT substances" are monitored because of their well-known environmental persistence (P), high bioaccumulative potential (B) and high toxicity (T). Without diminishing the value of ongoing monitoring efforts of these "high-PBT" substances, an exclusive focus on only these compounds is likely to overlook other, emerging organic chemicals of potential environmental concern. The likelihood of being "out-of-date" on the inventory of higher risk organic contaminants is ever more likely given the fact that the list of currently monitored organic compounds is based on recommendations by the U.S. EPA and NOAA from the late-1970s, and has remained virtually unchanged since. Over the last three decades, thousands of new organic compounds have been introduced to the market for agricultural, manufacturing, household, medicinal, and other industrial uses. These include newer generation crop protectants and biocides, surfactants, plasticisers, resins, paints and flame retardants. Based on peer-reviewed research conducted overseas, some of these compounds have been found to cause adverse effects in aquatic organisms, such as toxicity or endocrine disruption. Breakdown of these compounds, in the environment or in wastewater treatment plants, may be incomplete and increased urbanisation and inputs of stormwater and wastewater could result in increased discharges of these compounds into the aquatic receiving environment. If these substances accumulate and persist in the environment following discharge, they may contribute to a degradation of water quality and ecological values. To improve current contaminant risk assessment (and monitoring), a comprehensive, up-to-date review of organic chemicals in use and of potential ecotoxicological concern in Auckland was therefore timely.

For this purpose, ARC commissioned NIWA to review major classes of organic chemicals in use in Auckland that have a potential for causing environmental harm. The brief was kept deliberately broad, in order to capture as many substances as possible that may have "slipped under the radar".

2.1.3 Scope of work

The objective of this report is to identify and characterise organic chemicals of potential environmental concern (CPECs) likely to be used in Auckland. The review describes, among others, chemicals contained in:

- Plastics and plastic additives (eg, plasticisers and flame retardants).
- Resins, paints and coatings.
- Petroleum products.
- Tyres and automobile products.
- Roading and building materials.
- Surfactants and detergents.
- Pesticides and herbicides.
- Other biocides: antifoulants, antifungals, antimicrobials.

- Pharmaceutical and personal care products.
- Food additives or food-processing products.

While the intended focus of this review is on chemicals presumed to be in use in Auckland, the reality is that many of the compound categories described are ubiquitous attendants of industrialised societies, varying from one location to another primarily in their degree of prevalence. For this reason, most of the findings of this review should be generally applicable to other New Zealand cities as well. The distinguishing features of Auckland, in comparison to other New Zealand cities can be summarised as its relatively large population size (1.3 Million), and consequently large industrial, transport and public works infrastructure (eg, roads, airport, wastewater treatment plants, landfills). Unique features are its extensive port and recreational boating facilities (marinas, boat ramps, moorings) and very large suburban/semi-rural footprint. Next to the industrial, transport and residential land use, the intensive agriculture (horticulture and viniculture) occurring in Auckland's periphery is likely to add a distinct "agricultural signature" to its urban chemical footprint.

2.1.4 Methodological approach

For producing a readable review it was necessary to structure the characterisation of CPECs into a manageable number of broad product categories, as outlined in the "scope of work". In doing so, we abandoned the originally envisaged output format as an annotated alphabetical index of individual chemicals and their key chemical and ecotoxicological properties (eg, structure, uses, solubility, K_{OW}, environmental persistence, ecotoxicological capacity and likely sources in Auckland). This was decided upon realising that a comprehensive, alphabetical index of individual substances would entail cataloguing more than 10,000 chemicals in terms of their relevant chemical and ecotoxicological properties – a task which would have gone beyond the scope of a concise review, as well as the attention-span of most interested readers. Moreover, searches of existing substance databases from various reputable online sources (ERMA, U.S. National Institutes of Health, United States EPA, Environment Canada) revealed that detailed compound-specific chemical information already existed in compact, user-accessible, and searchable format on the World Wide Web, to which the reader is referred. For this reason, it was decided that a more useful output would be a general overview of the types of chemicals currently in use, highlighting compounds of recently established or currently suspected emerging environmental concern or scientific interest. In the assessment of environmental hazard, we focused on substances with accessible information in the peer-reviewed toxicological literature, minimising the reliance on unpublished and unverified accounts. While this restriction undeniably runs a risk of missing a number of "weak positives", it is likely to capture the "main players" and ensures a greater confidence in the conclusions.

Information sources

The following information sources were consulted:

- Primary scientific literature, using directed searches on academic literature databases ("Web of Science", "ScienceDirect") and table of contents of relevant scientific journals.
- American Chemical Society CAS (Chemical Abstracts Service) Registry (www.cas.org/cgi-bin/cas/regreport.pl).
- Encyclopaedia (eg, Wikipedia, www.wikipedia.org).
- ePortal of the OECD (http://webnet3.oecd.org/echemportal).
- European Chemical Substances Information System (ESIS) (http://ecb.jrc.it/esis).
- Environment Canada Domestic Substances List.
- ERMA online register of approved compounds (incomplete).
- Human and Environmental Risk Assessment on Ingredients in Household Cleaning Products (HERA) website (www.heraproject.com/Index.cfm).
- International Program on Chemical Safety IPCS (www.inchem.org).
- Manufacturer association websites (eg, Plastics New Zealand, Timber, Industrieverband Kosmetik, European Flame Retardants Association (www.cefic-efra.com).
- Pesticide Network of North America (PAN) database (www.pesticideinfo.org/Index.html).
- Toxicological Profiles by the Agency for Toxic Substances and disease Registry of the U.S. Department of Health and Human Services (www.atsdr.cdc.gov/toxpro2.html).
- United States Environmental Protection Agency High Production Volume Chemicals (HPV) list.
- United States Environmental Protection Agency Integrated Risk Information System (IRIS).
- United States Environmental Protection Agency ECOTOX Online Database (http://cfpub.epa.gov/ecotox/index.html).
- United States Geological Survey, Emerging Chemicals List.
- United States National Library of Medicine Household Products Database (compilation of MSDS sheets of common household products).
- Yellow Pages and UBD business directory of industries in Auckland.

2.2 Criteria for assessing potential environmental concern

2.2.1 Rating environmental hazard – using the PBT classification

Any attempt to compare the environmental risk of the thousands of organic chemicals introduced by our industrial societies is invariably doomed to being an incomplete endeavour, given the plethora of compounds, modes of biological action, exposure routes, species sensitivities and complexity of potential interactions. Furthermore, little information commonly exists on environmental concentrations of specific chemicals in a region of concern. Over and beyond the task of compiling existing toxicological and environmental chemical information of thousands of compounds, a reviewer is faced with the principal issue of attempting to assess risk based on incomplete information. Thus, even if it were possible to collate all existing toxicity information in one document, it would be inevitable that relevant species and certain effects have not been studied yet.

To rank relative environmental risk of different chemicals, in order to prioritise their importance, risk is often quantified as the product of "hazard" (ie, the potential to cause adverse effects) multiplied by "dose" (the degree of actual exposure), as summarised in Equation 1.

Equation 1: Risk = Hazard potential x Dose

As a general rule, it is commonly found that chemicals representing an elevated environmental risk are those that occur in the environment at concentrations of 1 mg/L or higher and that are at the same time persistent, bioaccumulative and toxic, since this combination maximises the likelihood of exposure levels high enough to cause adverse effects. Accordingly, such substances are called "high-PBT substances (P for persistent, B for bioaccumulative and T for toxic). Classic high-PBT substances include organochlorine pesticides, such as DDT, chlordane and dieldrin (all of these pesticides are no longer used in New Zealand, but are still measurable in the environment), as well as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs). These substances all show very slow degradation rates (meaning that they are persistent in the environment), possess a high affinity to accumulate in organism lipid reserves (high bioaccumulation), and are toxic or bioactive at concentration encountered in the environment, either by causing direct mortality or causing adverse sublethal responses, such as, endocrine disruption, mutagenicity or teratogenicity. "High-PBT" substances are also known in the literature as "POPs" (persistent organic pollutants), as defined by the Stockholm Convention of Persistent Organic Pollutants.

For the purpose of assessing hazard of "chemicals of potential environmental concern" (CPECs), it was found to be practical to quantify their environmental hazard using the PBT scale, rating each of the three properties using a modified "traffic-light" classification, consisting of the categories "high" (red), "moderate" (amber) and "low" (blue). Thus, a substance with a slow degradation rate would be given a "high-persistence" rating. A substance with a high lipid-affinity (indicated by a high octanol-water partition coefficient; such as log K_{OW} >4.2) would be ranked "highly bioaccumulative", and a substance showing toxicity at concentration of <1 mg/L (or otherwise adverse biological responses, either in experiments or in QSARs, discussed below) would be considered "highly toxic or bioactive".

A summary of the PBT classification scheme is presented in Table 1 for an imaginary "Substance X", having high-persistence (slow degradation rate), moderate accumulation potential (log K_{OW} 4.2-7.5) and low toxicity. A brief explanation of the reason for the ranking score is given as well.

Table 1

Environmental hazard profile of a generic "Substance X", using the PBT classification described above. Qualitative environmental hazard rating scored as H = high (4 points), M = moderate (2 points), L = low (1 point). Multiplication of the individual PBT score gives the "PBT hazard index" (4 x 2 x 1 = 8, for Substance X).

Qualitative environmental hazard rating		8	Reason for ranking
H=4	Persistence	H	High: degradation half-life six months or more.
		M	Moderate: degradation half-life one week to six months.
		L	Low: degradation half-life less than one week.
M=2	Bioaccumulation potential	H	High: log K_{OW} = 4.2-7.5 (or BCF >1000).
		M	Moderate: log K_{OW} = 3.3-4.2 (or BCF 100-1000).
		L	Low: log K_{OW} <3.3 or log K_{OW} >7.5 (or BCF <100).
L=1	Toxicity/adverse effect potential	H	High: actual or estimated acute or chronic EC_{50} <1 mg/L.
		M	Moderate: actual or estimated acute or chronic EC_{50} of 1-100 mg/L.
		L	Low: actual or estimated acute or chronic EC_{50} >100 mg/L.

For comparing relative hazard between substance classes, a scoring system is proposed in which a "low" ranking is given a score of 1, a "moderate" ranking a score of 2 and a "high" ranking a score of 4. The individual PBT scores for each substance are subsequently multiplied for a combined, qualitative environmental hazard rating, or "PBT hazard index". Thus, in the example of "Substance X", a high-P, moderate-B and low-T ranking would be given a combined PBT score of 4x2x1 = 8. Using this classification, the minimum PBT score attainable is 1 (1x1x1), and the maximum score is 64 (4x4x4). Classic POPs such as DDT represent a "worst case" combination in this PBT spectrum, with a high-P, high-B and high-T ranking in all three categories leading to a combined PBT score of 64 (Table 2).

Table 2

Environmental hazard profile of classic persistent organic pollutants, such as PCBs, DDT, PAHs and PCDD/PCDF, characterised by high-persistence, high-bioaccumulation potential and high acute toxicity.

Qualitative environmental hazard rating	64	**Reason for ranking**
H	Persistence	Slow degradation for PCBs, OCs, PCDDs/PCDFs, PAHs (biodegradation half-lives >6 months).
H	Bioaccumulation potential	High hydrophobicity (log K_{OW} >4.2).
H	Toxicity/adverse effect potential	High baseline toxicity (EC_{50} <1 mg/L). Furthermore, neurotoxicity (OCs), phototoxicity (PAHs), carcinogenicity (PAHs, PCDDs) and oestrogenicity (PCBs, DDT, HCH etc.).

Analogously, every major compound category in this report is preceded by a miniature table summarising its presumed environmental hazard, using the PBT score described above. It should be noted that these summary tables and index scores are qualitative only and must not be considered to be comprehensive or replacing a detailed, compound-specific risk analysis, which would also require an estimate of environmental exposure or "dose". As we will see, most CPECs tend to rank intermediate on the PBT scale.

2.2.2 Persistence

The UNEP Stockholm Convention for Organic Pollutants, signed in 2001 (ratified by New Zealand in 2004 and implemented in 2006), restricts the term "persistent organic pollutants" (POPs) to organic substances that demonstrate a combination of the following four characteristic properties: (1) strongly resist degradation, (2) have a strong tendency to bioaccumulate, (3) undergo long range transfer trespassing state boundaries, and (4) have the potential to cause adverse effects to humans and the environment. At present, the UNEP POP lists comprises 12 substances (or classes of substances), namely: aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, mirex, hexachlorobenzene (HCB), toxaphene (670 substances), polychlorinated biphenyls (PCBs. 209 congeners), polychlorinated dibenzo-p-dioxins (PCDDs = "dioxins", 75 congeners), and polychlorinated dibenzofurans (PCDFs = "furans", 135 congeners).

For this report, to capture as well those chemicals of potential concern having only moderately persistence, a more general definition of persistence was chosen, namely: any substance that resists significant degradation or transformation (eg, to 50 per cent its initial concentration = one degradation half-life) for periods significantly longer than the average residence time in the stormwater system or wastewater treatment plant. This equates to time scales of longer than a week. The rationale hereby is that a substance that that does not degrade completely before reaching the aquatic receiving environment (eg, rivers, estuaries, harbours) has the potential to cause adverse effects on resident biota, even if it subsequently degrades. For simplicity, we choose to rate the persistence of a substance using the following three-rank classification:

- low- (non-) persistent = degradation half-life less than one week,
- moderately persistent = degradation half-life of one week to six months, and
- highly persistent = degradation half-life of six months or more.

Thus, any chemical with a degradation half-life of more than a week, toxic or not, shall be deemed "persistent" for the purpose of this report. As a consequence, many plastics, commonly considered ecotoxicologically inert but, nevertheless, having slow degradation rates of many years, would classify as highly persistent under this definition (they would, however, be rated "low" in their bioaccumulation potential). In contrast, a fumigant pesticide such as methyl bromide, having a degradation half-life of six to 60 days (depending on soil type, (Dungan & Yates 2003)), would be characterised as "moderately persistent". Volatile solvents, such as the petrol additives BTEX (benzene, toluene, ethylbenzene and xylene), that quickly disperse under open atmosphere would be ranked "low" in terms of their persistence.

2.2.3 Bioaccumulation potential

In order for an environmental chemical to exert measurable biological effects, it needs to be present in a bioavailable form. This, in most cases, requires incorporation into tissues. Bioaccumulation of a chemical is commonly measured either as the bioconcentration factor (BCF), when most uptake is from water, or as the biota-sediment accumulation factor (BSAF), when most uptake is from sediment. BCF is defined as the ratio of a chemical's concentration in the organism tissue (C_{tiss}) and the chemical's concentration in the water (C_w), as shown in equation 1:

(1) $BCF = C_{tiss}/C_w$

It should be noted that while bioaccumulation is a good indicator of bioavailability, it is not a prerequisite. Thus, there are a (small) number of chemicals than can exert adverse effects on external tissues (eg, gill surfaces) without being incorporated. Furthermore, a compound can be bioavailable without showing evidence of bioaccumulation if it is rapidly metabolised to another compound within the body. In most cases, however, high bioconcentration and bioaccumulation are closely related to high-bioavailability and ultimately toxicity. The toxicological significance of bioaccumulation is that substances that accumulate in tissues tend to be closer to the site of potential toxic action. Furthermore, bioaccumulation extends the exposure time (contact time) of the organism to the chemical, effectively prolonging the experienced "dose" and thereby increasing the chance for adverse effects to occur. For organic chemicals, it is commonly observed that compounds showing the highest bioaccumulation factors are those with a high affinity for fatty tissue. These compounds are termed lipophilic compounds. The lipid-affinity of a chemical is closely related to its hydrophobicity, which is typically expressed as the logarithm of its octanol-water partition coefficient (log K_{OW}, also called log P), describing to which proportion the chemical distributes between a hydrophobic octanol phase and a hydrophilic water phase. It is generally observed that organic compounds with high log K_{OW} values have high BCFs and/or BSAFs (Meador et al. 1995, Di Toro et al. 2000). In fact, empirical evidence supports that substances show significant bioaccumulation if their log K_{OW} is greater than 4.2 (corresponding to BCFs >1000), based on an average organism lipid content of approximately 5 per cent. This trend applies up to "cut-off" log K_{OW} value of approximately 7.5 (Jonker & vanderHeijden 2007), beyond which chemicals tend to be too large to pass through biological membranes or become so hydrophobic that they dissolve to only a negligible extent in water, which greatly slows down their uptake rate. The log K_{OW} value has further utility in ecological risk assessment since hydrophobic chemicals also tend to be more toxic than less hydrophobic ones. Thus, a direct relationship exists between toxicity and log K_{OW}. This general relationship has led to "target lipid model" of toxicity (Di Toro et al. 2000) which assumes organism lipid (including phospholipid cell membranes) to be the main site of toxic action for hydrophobic substances with a non-specific, narcotic mode of action (for a definition of non-polar narcosis, see below). So far, the relationship has been shown to be valid for 156 organic chemicals and 33 species, including fish, amphibians, arthropods, molluscs, polychaetes, coelenterates and protozoans, up to log K_{OW} values of about 5.3. The United States EPA's New Chemicals Program (NCP), mandated under the Toxic Chemicals Control Act (TSCA), requires Tier 3 ecotoxicity testing for any new chemical having a log K_{OW} >4.2 (BCF>1000), and a degradation (transformation) half-life of more than 60 days (two months). For the purpose of this report it was therefore decided to employ the following definition of bioaccumulation potential:

- Low bioaccumulation potential: substances with log K_{OW} <3.3 (or BCF <100) or log K_{OW} >7.5
- Moderate bioaccumulation potential: substances with log K_{OW} = 3.3-4.2 (or BCF 100-1000).
- High bioaccumulation potential: log K_{OW} 4.2-7.5 (or BCF >1000).

2.2.4 Toxicity and adverse biological effects

The ultimate criterion for determining whether a chemical is "hazardous" is its potential to cause adverse biological effects at environmentally relevant concentrations and biologically relevant time scales. Adverse effects can manifest themselves either as direct toxicity (ie, increased mortality) or as sublethal changes in normal body processes or ecological function. They can occur over a range of time scales, from short-term (acute; eg, up to 96 hours) to chronic responses (eg, requiring several weeks or more). Toxicity is strongly dependent on a chemical's structure, speciation (charge density) and size (molecular weight), which, among other factors, set an upper limit to its uptake across cell membranes. The majority of toxic substances tend to have molecular weights of less than 1000 amu, with the exception of biomolecules such as proteins, or chemicals resembling hormones. Toxicity can be determined empirically using standardised toxicity tests (eg, dose-response assays to determine the EC_{50}, or effective concentration that causes an observable adverse effect in 50 per cent of the test population). Alternatively, toxicity can be estimated using quantitative structure activity relationships (QSARs) that employ relevant physical-chemical properties of a compound to predict its toxicity (Veith & Mekenyan 1993, Cronin & Dearden 1995, Swartz et al. 1995). Many QSAR studies that have been conducted over the last decade have found good agreement between QSAR predicted toxicity and actually measured toxicity for non-polar and polar organic chemicals (Dalzell et al. 2002, Maeder et al. 2004, Martin & Young 2001, Oberg 2004, Oberg 2006, Parkerton & Konkel 2000, Pasha et al. 2007, Salvito et al. 2002, Verhaar et al. 1996, Zhao et al. 1998). As a result, use of QSARs has become accepted practice for estimating ecotoxicity for new industrial chemicals with unknown toxicity. Accordingly, the U.S. EPA now uses QSARs to predict the aquatic toxicity of new industrial chemicals in the absence of toxicity test data. Their ECOSAR software estimates toxicity for fish, invertebrates and algae using the parameters log K_{OW}, molecular weight, charge density and a chemical's structure. As mentioned before, greater hydrophobicity (log K_{OW}) tends to increase toxicity, until a compound's water-solubility eventually becomes so low that that negligible amounts are dissolved for any significant biological uptake (around log K_{OW} 7 to 7.5). Classic high priority pollutants, such as organochlorine pesticides, PCBs and PAHs have log K_{OW} values between 3.5 to 7.5, and tend to be acutely toxic to aquatic invertebrates at concentrations much less than 1 μmol/L (EPA ECOTOX database). Their non-specific mode of action is called "baseline toxicity" or "non-polar narcosis". However, some chemicals can have more than one mode of toxic action and can exert sublethal adverse effects at environmental concentrations much lower than the LC_{50} (ie, the concentration leading to 50 per cent mortality of test organisms).

The issue with many "chemicals of potential environmental concern (CPECs) does not concern so much their acute, baseline toxicity but rather additional, less acute modes of action, such as endocrine disruption or carcinogenicity. To appreciate the multitude of adverse biological effects possible, a brief summary of mechanisms of toxicity is therefore warranted.

Acute effects: toxicity

Baseline (membrane) toxicity or non-polar narcosis

Many hydrophobic organic chemicals display non-polar narcosis as a common mode of action. This acute, non-specific mode of toxicity is often called "baseline toxicity" and involves hydrophobic molecules passively interfering with transport processes in the cell membrane. As a general rule, narcotic toxicity increases with a chemical's molecular weight. Thus, the PAH contaminant naphthalene (MW 128) is less toxic than fluoranthene (MW 202), with a higher estimated final chronic water concentration of 322 μg/L, compared to only 12 μg/L for fluoranthene (Di Toro et al. 2000). On the other hand, while more hydrophobic, higher molecular weight chemicals tend to be more toxic, they are also less water-soluble and therefore tend to accumulate in tissues at slower rates. In the absence of a specifically known mode of action, acute toxicity is usually due to non-polar narcosis. Many hydrophobic "emerging chemicals of concern" are likely to exhibit some degree of baseline toxicity.

Genotoxicity

Beyond baseline toxicity at the cell membrane, many substances (eg, some PAHs, vinyl chloride, aflatoxins) furthermore have the ability to interact and damage DNA. This is often not due to the original compound, but rather due to its break-down products ("metabolites"), which can be more reactive and can form covalent bonds with the DNA molecules (so-called "DNA-adducts"). Damaged DNA will prompt cellular repair processes, which require extra energy expenditure by the organism and can interfere with normal cell function. Furthermore, formation of DNA adducts can result in incomplete replication of the DNA, leading to strand breaks and the formation of micronuclei. If cells with damaged and unrepaired DNA subsequently divide, they can produce mutant cells that can be functionally compromised, non-viable or turn cancerous. Hence, the strong relationship between short-term genotoxicity and carcinogenicity is probably causal (Walker, C.H. et al. 2006).

Cytotoxicity

Toxicity to cell function can manifest itself in many ways, one common one being interference with energy production by the mitochondria. This can occur via uncoupling of oxidative phosphorylation, whereby the proton gradient across the mitochondrial membrane breaks down, stopping the production of ATP. As an example, the chemical 2,4-dinitrophenol (traditionally used in the manufacture of dyes, wood preservatives and explosives, and as a dieting aid) acts as an uncoupler of oxidative phosphorylation. Other mitochondrial poisons, including the fish toxin and insecticide rotenone, can inhibit the electron transport chain (preventing NADH from being converted into ATP). Rotenone is classified by the USDA National Organic Program as a non-synthetic pesticide and is allowed to be used to grow "organic" produce. Cytotoxicity may also result from inhibition of ATPases (Na^+, K^+, Ca^{2+} ATPase), which are centrally involved in osmoregulation and calcification (eg, in the oviduct). For example, the inhibition of Ca^{2+} ATPase by DDE (a metabolite of DDT) is believed to be the reason for DDE-induced eggshell thinning in birds. Further cell damage may occur by destabilisation of lysosomal membranes, which normally sequester toxic substances from the cytoplasm.

Neurotoxicity

A significant number of chemicals, notably insecticides, can disturb the transmission of impulses along nerves and across synapses (Walker et al. 2006). A distinction can be made between compounds that act upon the receptors (or pores) of the nerve membrane (eg, Na^+ or Cl^- channels, or GABA receptor), or on the release of neurochemicals such as acetylcholine esterase (AChE) from nerve synapses. For example, pyrethroid insecticides and DDT disturb the function of the Na^+ channel, leading to retarded closure of the channel, which can lead to unco-ordinated muscle tremors. Chlorinated cyclodiene insecticides, or their active metabolites (eg, dieldrin, endrin, heptachlor epoxide) act as GABA antagonists, by reducing the flow of Cl^- through the nerve membrane, leading to convulsions. The receptors for acetylcholine on the postsynaptic membrane are the site of action of a number of other chemicals, such as nicotine. However, the most neurotoxic compounds are generally those that inhibit the enzyme AChE, responsible for the rapid breakdown of acetylcholine after a nerve impulse. They include organophosphorus insecticides, such as diazinon and dimethoate, and certain (insecticidal) carbamates (note that herbicidal and fungicidal carbamates do not have anti-acetylcholinesterase properties). Impeded breakdown of acetylcholine can lead to synaptic block, resulting in non-specific tetanus (muscular cramp).

Hepatotoxicity

Hepatotoxicity is chemically-induced damage to the liver (in vertebrates, including fish) or hepatopancreas (in invertebrates). The liver is particularly prone to damage, as it acts as a central hub for the detoxification of harmful substances. Detoxification by liver enzymes usually involves converting a substance into a more hydrophilic metabolite (eg, hydroxylation of PAHs by cytochrome c oxidase), accelerating their excretion and shortening the chemical's residence time in the tissue. As a consequence, the enzymatic activity of certain liver enzymes (eg, cytochrome c-oxidase enzyme P450 1A) is used as a biomarker of xenobiotic exposure in fish and in some invertebrates (Sarkar et al. 2006). As a downside, the generation of more water-soluble ("activated") metabolites can have negative side effects, such as increasing reactive oxygen species generation or increasing the frequency of DNA-adduct formation and cancers (Hylland 2006). Liver tissue is characterised by high lipid content, leading to concentration of many hydrophobic contaminants in the liver, further amplifying the likelihood of adverse effects. Liver toxicity may manifest itself in the form of hepatitis (inflammation), cirrhosis (damage of tubules), cholestasis (jaundice due to accumulation of bile products), steatosis (fatty liver due to triglyceride or phospholipid accumulation), granuloma, lesions, necrosis (death of liver tissue), as well as neoplasms, carcinoma, angiosarcoma and adenoma (different types of cancers due to long-term exposure). Examples of hepatotoxins (at high doses) include carbon tetrachloride, vinyl chloride, bromobenzene (Zurita et al. 2007), microcystins (from blue-green algal-blooms) and numerous pharmaceutical drugs such as acetaminophen (paracetamol), dichlofenac, aspirin, ketoprofen, anabolic steroids, contraceptive pills, tetracyclines and penicillin.

Nephrotoxicity

A number of chemicals including chlorothalonil, diphenylamine, lead and aircraft-deicers have been shown to damage or adversely affect kidney histology or function (Caux et al. 1996, Drzyzga 2003, Hartell et al. 1995, Johnson, F.M. 1998). Impacted ion-pumps in the kidney can affect salt and water balance (osmoregulation) and excretion.

Phytotoxicity

Phytotoxicity is the capacity of a chemical (such as an herbicide, trace metal (eg, Zn) or any other compound) to cause temporary or long-lasting damage to plants (OEPP 2007). For the purpose of this report, this definition shall apply to algae as well. Phytotoxicity can manifest itself in numerous ways, such as modifying a plant's development cycle (ie delaying or inhibiting seed germination, emergence, growth, flowering, fruiting, ripening or appearance of certain organs), reducing abundance/survival of offspring, changing colour or causing other morphological modifications in plant tissues (deformations or necrosis) or reducing yield (of crops). Specifically, phytotoxins can disrupt plant-specific amino acid synthesis (eg, glyphosate) or cell membrane function (paraquat), or they can inhibit photosynthesis (atrazine), lipid or pigment synthesis (eg, aryloxyphenoxypropionates) or seedling growth (eg by inhibition of shoot growth, microtube assembly (eg, acetochlor or trifluralin)) or auxin transport). Other phytotoxins can interfere with the normal development of specific plant tissues or organs by acting as synthetic auxins (eg dicamba, 2.4-D). Extreme physicochemical conditions such as low pH or high salinity can also be phytotoxic.

Chronic effects and sublethal responses

Long-term exposure to toxic substances at sublethal concentrations can lead to chronic adverse responses at different biological time scales. Sublethal responses can be as subtle as up-regulated cellular repair processes (eg, higher gene expression, higher antioxidant enzyme titres or elevated repair protein levels) which require additional energy expenditure by the affected organism. More severe effects might include modified physiology and behaviour, delayed development or reduced growth, impaired endocrine regulation or reproductive success, or the development of lesions or cancer. These long-term changes, if severe enough, can ultimately affect species fitness and thereby alter recruitment and community structure. Usually, the smaller the scale of a biological response (eg, cellular, biochemical), the faster it is detectable, but the more difficult it is to relate to ecological effects (Adams et al. 2000). In other words, there tends to be an inverse relationship between the time scale and size scale of biological responses and their ecological significance and interpretability.

Biochemical responses

In the last decade a lot of progress has been made in understanding molecular and biochemical responses to contaminant exposure. Common short-term responses include up-regulation of anti-oxidant enzymes, such as catalase, superoxide dismutase or the glutathione-enzyme complex including glutathione reductase, glutathione peroxidase and glutathione-S-transferase. On the other hand, detoxification can also occur by up-regulation of mixed-function oxygenases (Lee 1981), such as cytochrome c oxidase (Rewitz et al. 2006), mentioned previously. Other biochemical responses include expression of chaperone proteins, such as heat shock proteins and ubiquitin, functioning as repair or recycle proteins.

Endocrine disruption

Although endocrine disrupting chemicals (EDCs) have been know for many years, this topic has only recently attracted worldwide interest due to growing concerns about industrial by-products that may disrupt endocrine function in natural animal populations and humans (Porte et al. 2006). Endocrine-disrupting chemicals possess a structure that more or less resembles natural hormones and therefore enables them to bind to the corresponding cellular hormone receptors (eg, oestrogen receptor, progesterone receptor or androgen receptor), which may adversely affect endocrine regulation, leading to feminisation, masculinisation or impaired growth. Substances are commonly distinguished according to the receptor they affect, eg, oestrogens, androgens, thyroxin antagonists (eg, certain PCB metabolites), or ecdysone-agonists (mimicking the arthropod moulting hormone ecdysone). EDCs can either activate or block receptor activity. At present, most interest focuses on oestrogens (“xenoestrogens”), which are substances that imitate an oestrogen hormone. Known oestrogenic substances include natural and synthetic sex hormones (from contraceptive pills or hormone treatment), organochlorine insecticides, tributyl tin, some phthalate plasticisers and nonylphenols (breakdown products of a class of industrial and agricultural surfactants). The relative magnitude of oestrogenic potency of these chemicals varies by several orders of magnitude. The best documented effects of endocrine disruption by environmental chemicals have been the induction of vitellogenin production (an egg-yolk protein) in masculine fish after exposure to sewage effluent (Harries et al. 1997, Harries et al. 1996, Jobling et al. 1995) and the feminisation of male snails upon exposure to tributyltin-containing antifouling paints. However, oestrogenic activity of industrial, domestic or agricultural effluent has been observed many times over since then (Sonnenschein & Soto 1998).

Behavioural effects

Neuroactive substances can affect an animal's normal behaviour, such as orientation, foraging and predator-avoidance. For example predation risk in fish increases upon exposure to certain insecticides, pentachlorophenol, as well metal and thermal stress (Beitinger 1990).

Growth inhibition

Exposure of an organism to chemical stressors might not lead to direct adverse biochemical or physiological effects if it possesses well-functioning detoxification or repair mechanisms. Nevertheless, increased detoxification and regulation is likely to involve an energetic cost, leading to possible trade-offs with growth or reproduction. The effect of pollution on production can be measured as scope for growth (Widdows et al. 1995, Widdows & Johnson 1988), defined as the difference between energy intake and total metabolic losses. Higher metabolic losses as a consequence of contaminant exposure result in reduced energy available for growth or reproduction (eg, reduced fecundity or egg quality). Reduced scope for growth has been observed in mussels following exposure to tributyltin, petroleum hydrocarbons, organochlorine and organophosphate insecticides, PCB and sewage (Widdows et al. 1997, Roast et al. 1999, Widdows et al. 2002).

Other developmental or reproductive effects

Reproductive success can be furthermore impacted by increased mortality or deformation of juveniles or embryos (eg, teratogenicity). Increased juvenile mortality can also result from maternal transfer of accumulated contaminants vial yolk lipids (Pelletier et al. 2000). Examples of teratogens include alcohol (ethanol), PCBs, dioxins, organic mercury, coumarin, ethidium bromide, various hormones (diethylstilbestrol, androgenic hormones); and numerous pharmaceutical agents such as tetracyclines, aminopterin, busulfan, captopril, enalapril, cyclophosphamide, diphenylhydantoin, etretinate, thalidomide, trimethadione and valproic acid.

Mutagenicity/Carcinogenicity

A number of chemicals can bind to DNA, forming "adducts", or produce reactive oxygen species (eg, hydroxyls or radicals), which can increase the frequency of mutation or lead to changes in gene regulation and gene repair. Some examples of known (human) carcinogens (Group 1, as classified by the International Agency for Research on Cancer, IARC) are benzene, formaldehyde, asbestos, Cr (VI) compounds, aflatoxins, diethylstilbestrol (a synthetic oestrogen), vinyl chloride and coal tar.

As is evident from the descriptions above, potential adverse biological responses to environmental chemicals may vary greatly in their mechanisms and time and size scales, with acute toxicity representing only a small (albeit most severe) response scenario. In contrast to priority organic pollutants (POPs), many chemicals of potential or emerging concern (CPECs) currently occur in the environment at concentrations presumed to be below the threshold for acute toxicity. Thus, any biological response to them, if occurring at all, would be assumed to occur at the sublethal, chronic level. To capture these "bioactive" chemicals that presently occur at sublethal environmental concentrations, it was decided, for the purpose of this report, to define a substance's potential to cause toxicity or adverse effects to aquatic organisms as follows:

- Low toxicity/adverse effect potential: substances with an actual or estimated acute or chronic EC50 >100 mg/L.
- Moderate toxicity/adverse effect potential: substances with an actual or estimated acute or chronic EC50 of 1-100 mg/L.
- High toxicity/adverse effects: substances with an actual or estimated acute or chronic EC50 <1 mg/L.

3 Common Organic Compounds and Materials in Use

The following sections describe in greater detail roughly 20 major classes of high production volume chemicals in use in industrial and domestic applications in Auckland or New Zealand in general. While this overview does not pretend to be an exhaustive list of all potentially hazardous chemicals, it strives to cover the majority of compound classes of potential or identified concern. It should be noted that a chemical's listing under a given category reflects its most prevalent use, but it is often the case that one chemical may find more than one application.

3.1 Plastics

Table 3

Environmental hazard profile of plastics.

Qualitative environmental hazard rating	8	Reason for ranking
H	Persistence	Slow degradation of polymer backbone.
L	Bioaccumulation potential	Generally biologically inert; excluding plasticisers.
M	Toxicity/adverse effects potential	Generally biologically inert (excluding plasticisers and flame retardants) .Moderate-to-high for PVC combustion residues (acids, dioxins).

The term "plastic" encompasses a large variety of synthetic organic polymerization products with malleable properties or capable of undergoing continuous deformation. All plastics are composed of organic condensation or addition polymers and may contain additives to improve performance, such as plasticisers (eg, phthalates). Common types of plastics are listed in Table 4. While the majority plastics are inert in polymerised form, there is some concern about the environmental effects of certain starting materials (monomers), catalysts and additives, as well as some breakdown products. For example, bisphenol-A, one of the components in epoxy resin and polycarbonate, has been shown to have mild oestrogenic activity. Similarly, phthalate plasticisers in PVCs, as well as breakdown products of PVC combustion (eg, HCl and small traces of polychlorinated dibenzodioxins and polychlorinated dibenzofurans) have the potential to cause adverse effects at elevated doses.

Table 4

Major types of plastics, including the six most common types in use in New Zealand (No. 1 to 6). Source: Plastics New Zealand website.

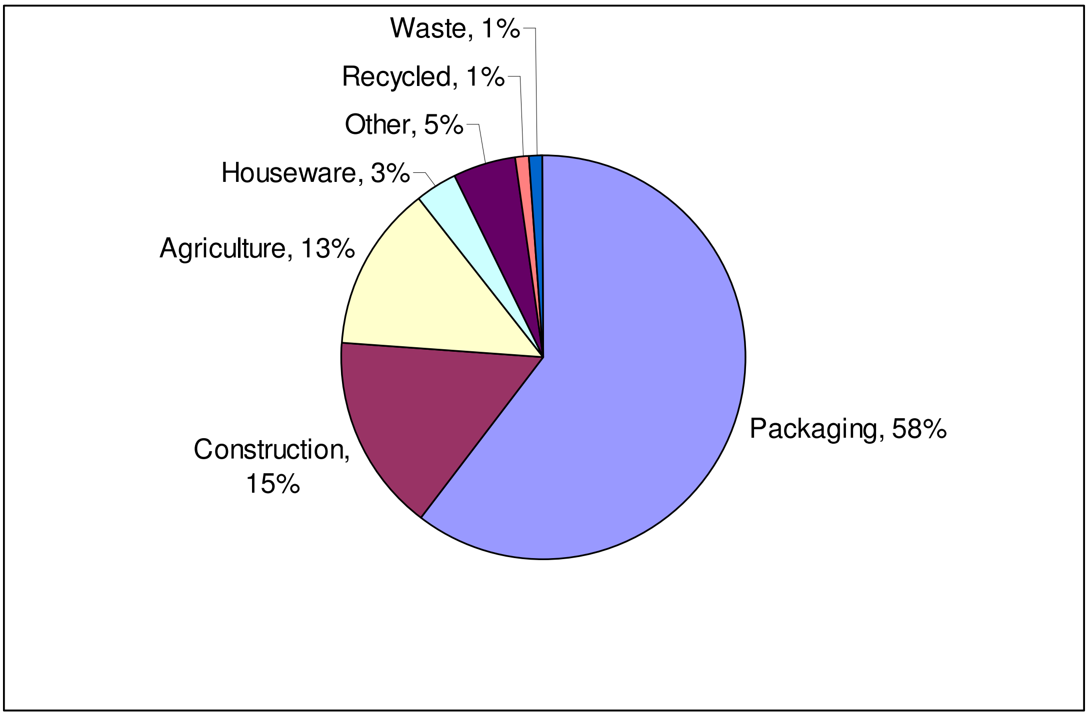
Plastic type	Symbol/Abbreviation	Common use
Polyethylene terephthalate	♳ PET (or PETE)	Soft drink and water bottles, food trays, salad dressing and peanut butter containers, pillow and sleeping bag filling, clothing, carpet.
High-density polyethylene (HDPE)	♴ PE-HD	Crinkly shopping bags, freezer bags, milk bottles, ice cream containers, juice bottles, shampoo, chemical and detergent bottles, recycling bins, compost bins, buckets, posts, fencing, pipes.
Low-density polyethylene (LDPE)	♶ PE-LD	Plastic food wrap, garbage bags, squeeze bottles, black irrigation tube, garbage bins, pallet sheets.
Polyvinyl chloride	♵ PVC	Unplasticised: cosmetic containers, electrical conduit, plumbing pipes and fittings, blister packs, wall cladding, roof sheeting, flooring, mats, sheets, speed bumps, bottles, packaging, binders, mud flaps. Plasticised: clear film, garden hoses, inflatables, shoe soles, cable sheathing, tubing.
Polypropylene	♷ PP	Dip bottles and ice cream tubs, potato chip bags, straws, microwave dishes, kettles, garden furniture, lunch boxes, pegs, bins, pipes, pallet sheets, oil funnels, car battery cases, trays.

Plastic type	Symbol/Abbreviation	Common use
Polystyrene	♸ PS	CD cases, plastic cutlery, imitation “crystal glassware”, low-cost brittle toys, video cases, coat hangers, coasters, white ware components, stationery trays. Expanded polystyrene (EPS): Foam cups, takeaway containers (clamshells), foamed meat trays, protective packaging, underfloor insulation.
Acrylonitrile butadiene styrene	ABS	Automotive body parts, hubcaps, piping, protective head gear.
High-impact polystyrene	HIPS	Toys and electronic product casings.
Polycarbonate	PC	Sunglasses, visors, domelights CDs and DVDs.
Polyvinylidene chloride	PVDC	Food wrap.
Polyester	-	Clothing, bedlinen, curtains, tarpaulins, resins (alkyd paints).
Polyamide	PA	Automobile airbags, intake manifolds, petrol tanks, bushings, nylon ropes, pantyhose, sails.
Polylactic acid	PLA	Medical sutures, clothing.
Polytetrafluoroethylene	PTFE	Non-stick coatings.
Polysulphones	PSU	Specialty material, dielectric in capacitors, dialysis membranes.
Epoxy resin	-	Adhesives, putties, fibreglass, castings.
Polyurethane	PU	Primarily foams, for upholstery flotation devices.
Acrylates (polymethyl methacrylate)	PMMA	Perspex, acrylic resins, nappy gels.
Phenolic resin	-	Household utensils (saucepan handles), electrical switches.
Melamine resin	-	Countertops, fabrics, food packaging.

According to information from the industry producer forum Plastics New Zealand, the New Zealand plastics industry is exclusively a processing industry. This means that no polymer raw materials are manufactured in New Zealand but all are imported, primarily from North America and Asia. Over 50 per cent of the plastics manufactured are re-exported as packaging, primarily for the dairy, meat and horticultural sector. A summary of the types and amounts of plastics produced in 2003 is given in Figure 1. In the period 1990-2000, plastic imports and production in New Zealand more than quadrupled. Recent plastic production (2003) in New Zealand was approximately 242,000 tons, compared with 1.2 million tons in Australia, and 334 million tons in Western Europe. The plastics industry estimates that 300,000 tons/a of raw plastic material will be imported by 2030.

Figure 1

Plastics production statistics for 2003 (in per cent) by sector (adapted from the Plastics New Zealand website).



According to information from Plastics New Zealand, all current manufacturers comply with the Resource Management Act (RMA), and all polymers and substances in use have approval under the Hazardous Substances and New Organisms Act (HSNO). More than 90 per cent of all production waste plastic is recycled in-house, meaning that they are ground – up and reused. No information was available whether this percentage related to weight or volume.

Six types of plastics dominate the New Zealand market, all imported as raw material: polyethylene terephthalate (PET), low-density and high-density polyethylene, PVC, polypropylene and polystyrene. Common plastics are summarised in Table 4. Low-density polyethylene (LDPE) makes up the largest fraction of New Zealand imports, with roughly 80,000 tons/a. High-density polyethylene (HDPE) imports are 40,000 tons/a, and polyvinyl chloride (PVC) and polypropylene (PP) each comprise approximately 30,000 tons/a. Polyethylene terephthalate (PET), polystyrene (PS) and expanded polystyrene (EPS) imports amount to about 10,000 to 20,000 tons each. Further to the six main types of plastic raw materials described above, there is a multitude of other plastic types and plastic mixtures in use in New Zealand, which together comprise another 10,000 tons/a.

3.1.1 Polyester

Polyesters are a general category of polymers that contain the ester functional group in their main chain. Synthetic polyesters include polycarbonate (PC) and polyethylene terephthalate (PET). The term “polyester” in day-to-day use refers to fibres of PET, such as nylon. Polyesters are used in many types of fabrics, such as clothing, bed sheets, bedspreads and curtains. Polyesters are also used to make tarpaulin, liquid crystal displays and a wide variety of films (eg, dielectric films for capacitors, insulation for wire, and insulating tapes).

Polyester resins are widely used as casting materials or as fibreglass laminating resins and in non-metallic auto-body fillers. In such applications, polymerization and cross-linking are initiated through an exothermic reaction involving organic peroxides, such as methyl ethyl ketone peroxide or benzoyl peroxide (see Section 3.7 “organic peroxides”). Polyester is also widely used as a finish on high-quality wooden products like guitars, pianos and vehicle/yacht interiors.

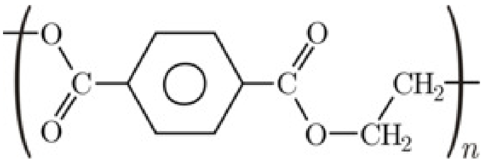
3.1.2 Polyethylene terephthalate

Polyethylene terephthalate (Figure 2; also known as PET, PETE, PETP or PET-P) is a thermoplastic polyester resin used in synthetic fibres, beverage, food and other liquid containers, thermoforming applications and engineering resins, often in combination with glass fibre. The majority of the world's PET production (60 per cent) is for synthetic fibres (“polyester”), with bottle production accounting for around 30 per cent. In the textile industry, PET is referred to as “polyester", with nylon being the most important polyester fibre). The term "PET" is generally used to refer to packaging applications.

PET is synthesised by the esterification between terephthalic acid and ethylene glycol (with water as a by-product), or the transesterification reaction between ethylene glycol and dimethyl terephthalate (with methanol as a by-product). Polymerization is via a polycondensation reaction of the monomers. These production steps would be performed by raw material suppliers overseas. PET readily degrades at high temperature, releasing acetaldehyde.

Figure 2

Chemical structure of polyethylene terephthalate (PET). (Source: www.wikipedia.org.)



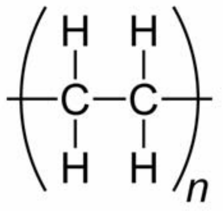
Next to being used as a homopolymer (100 per cent PET), PET can be modified by copolymerization, which changes properties of the plastic such as lowering the melting point and moulding properties. Common co-polymerisation agents include cyclohexane dimethanol (CHDM) and isophthalic acid; the latter of which is acutely toxic (96h LC_{50}) to fathead minnows at concentrations of 31 to 113 µg/L (EPA ECOTOX database, for isophthalic acid, dioctyl ester). Antimony trioxide (Sb_2O_3) is a commonly used catalyst in the production of PET and remains in the final product. No adverse metabolic fate has been observed for CHDM, which is fully excreted in rat trials (Divincenzo & Ziegler 1980). Antimony trioxide, on the other hand, is mutagenic and causes DNA damage in bacterial assays (Kuroda et al. 1991). It is highly toxic to green algae (EC_{50} 0.2 to 1 mg/L), but has low-toxicity to crustaceans, fish and oligochaetes (EPA ECOTOX database).

3.1.3 High- and low-density polyethylene

Polyethylene (or polyethene) is a polyolefin polymer consisting of long chains of the monomer ethylene (Figure 3).

Figure 3

Chemical structure of polyethylene. (Source: www.wikipedia.org.)



Polyethylene is classified into several different categories based on its density and branching. The most widely used types are: (1) high-density polyethylene (HDPE), found in many containers (milk jugs, Tupperware, laundry detergent bottles, automobile fuel tanks), and some domestic water pipes, and (2) low-density polyethylene (LDPE), as used in rubbish and grocery bags, films and soft, pliable plastic parts. Production of PE involves polymerisation catalysts such as chromium.

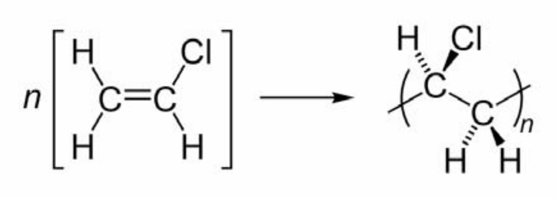
Polyethylene-copolymers

Polyethylene can be copolymerised with a wide range of monomers and ions, including alpha-olefins (eg, 1-butene, 1-hexene, and 1-octene; resulting in linear low-density polyethylene, or LLDPE), vinyl acetate (resulting in ethylene-vinyl acetate copolymer, or EVA, used in sport shoe soles), and a variety of acrylates (for packaging and sporting goods). The vinyl acetate monomer ($CH_3COOCH{=}CH_2$) is a known skin irritant and a suspected carcinogen. In addition to its use in EVA, vinyl acetate is also a starting material in the production of polyvinyl acetate, polyvinyl alcohol, ethylene and polyvinyl chloride-vinyl acetate, used in the production of adhesives, paints and food packaging. Vinyl acetate is rapidly metabolised to acetaldehyde and acetic acid, of which acetaldehyde is known to be cytotoxic and genotoxic. Few data exist on the direct toxicity or vinyl acetate aside from a small number of studies on rats. Vinyl acetate can cause nasal tumours in rats upon inhalation at concentrations of 200 ppm (Bogdanffy et al. 1997) and causes tumours and carcinomas when administered to rats in drinking water at high doses of 1000 to 10,000 ppm over two years (Minardi et al. 2002, Umeda et al. 2004). One study found lower body weights and smaller litters in rats exposed to vinyl acetate from drinking water at concentrations of 5000 ppm (Mebus et al. 1995). Human exposure to vinyl acetate occurs mainly by inhalation or dermal contact during production of the monomer (ie, overseas) or during production of polymers and water-based paints.

3.1.4 PVC

Polyvinyl chloride, or PVC (Figure 4), is among the most widely used plastics in the world, and ranks third in production in New Zealand. In 2002, over 30,000 tons of PVC products were manufactured in New Zealand, of which 82 per cent were used in construction and 10 per cent in agricultural products. PVC has a greater variety of uses than any other plastic, since its structural and colour properties can be greatly modified by use of different additives. Over 90 per cent of PVC is used in long-life products such as irrigation and sewer piping, tubing, electrical insulation, floor coverings and automotive parts. The remainder is used for stationery, packaging and medical products. More than half of the weight of PVC is due to chlorine. The advantage of this is that PVC is inherently fire resistant as well as resistant to acids and many other chemicals (the chlorine acts as a free radical scavenger). The disadvantage is that combustion of PVC (and any other waste containing carbon and chlorine) has the potential to generate dioxins (see below), next to corrosive acid (HCl). Even though currently disposed of in landfill in New Zealand, PVC is well-suited for recycling.

Figure 4
Chemical structure of PVC. (Source: www.wikipedia.org.)



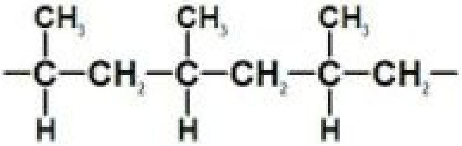
PVC is used both as a hard and soft plastic. As a hard plastic, it is used as vinyl siding, window profiles, pipes and plumbing and conduit fixtures. PVC pipes for household use are typically made of chlorinated polyvinyl chloride (CPVC), which provides better thermal stability. PVC pipe plumbing is typically white or grey, in contrast to acrylonitrile butadiene styrene (ABS, see below) which is generally black. Chlorinated PVC can have chlorine content as high as 70 per cent. PVC can be made softer and more flexible by the addition of plasticisers, the most widely used ones being phthalates (see below). Soft PVC is used in clothing and upholstery, to make flexible hoses and tubing (eg, garden hoses and Tygon PVC tubing), flooring, roofing membranes and electrical cable insulation. Environmental concern about PVC centres on phthalate plasticisers, as well as the potential toxicity of production intermediates and waste products upon disposal. Some phthalates have been banned overseas, for example DEHP (diethylhexyl phthalate) and DINP (diisononyl phthalate) in soft PVC baby toys in the European Union. Long-term exposure to DEHP, such as via medical implants, poses a health risk (Tickner et al. 2001). Incineration of PVC leads to generation of PCDDs and PCDFs ("dioxins") as well as coplanar PCBs, with a direct correlation between dioxin formation and chlorine content (Katami et al. 2002, Takasuga et al. 2000). Occupational exposure to the PVC starting monomer vinyl chloride has been linked to liver angiosarcoma in production workers (Bosetti et al. 2003).

3.1.5 Polypropylene

Polypropylene (PP, Figure 5) is a thermoplastic polymer, used in a wide variety of applications, including food packaging, ropes, textiles, plastic parts and reusable containers of various types, thermal textiles, laboratory equipment, loudspeakers, automotive components, and polymer banknotes, such as in use in New Zealand. Thin sheets of polypropylene are used as a dielectric in capacitors. Due to its high melting point (160°C), polypropylene features in many plastic items for medical or laboratory use. Furthermore, many plastic tubs for dairy products are made of polypropylene and sealed with aluminium foil, allowing hot-filling after pasteurisation. The clear lids, added after cooling are made of LDPE. Rugged, translucent, reusable plastic food containers, such as Rubbermaid and Tupperware, are commonly made of polypropylene, with lids made of more flexible LDPE. Plastic pails, car batteries, wastebaskets, cooler containers, dishes and pitchers are often made of polypropylene (or HDPE). PP is also widely used for outdoor, cold-weather clothing ("polypro"). PP is sometimes used as insulation for cables (instead of PVC), because it generates less smoke and caustic fumes when scorched. Most commercially available polypropylene contains a catalyst such as titanium chloride, which ensures correct (isotactic) orientation of the monomers.

Figure 5

Structure of polypropylene (Source: www.wikipedia.org).



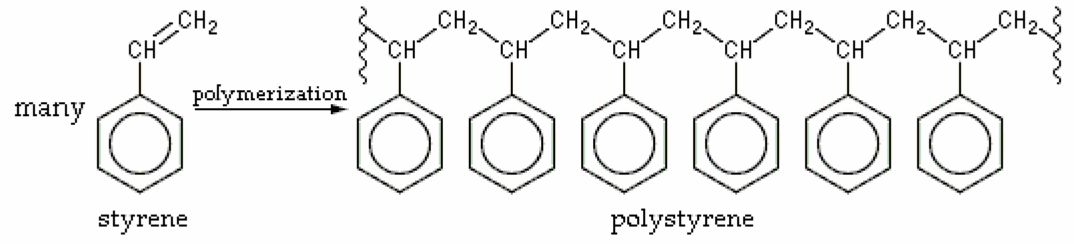
$$-\underset{\mathrm{H}}{\underset{|}{\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}}}-\mathrm{CH_2}-\underset{\mathrm{H}}{\underset{|}{\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}}}-\mathrm{CH_2}-\underset{\mathrm{H}}{\underset{|}{\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}}}-\mathrm{CH_2}-$$

3.1.6 Polystyrene

Polystyrene (Figure 6) is a polymer made from the aromatic monomer styrene. Polystyrene is used for producing plastic model assembly kits, plastic cutlery, CD "jewel" cases, and many types of laboratory plasticware (Petri dishes, test tubes, cuvettes). High-impact polystyrene (HIPS) is used in toys and product casings (eg, telephones). Acrylonitrile butadiene styrene (ABS) is a copolymer of acrylonitrile and styrene, toughened with polybutadiene. Most electronics cases are made of this form of polystyrene, as well as sewer pipes. Other co-polymerising agents are divinylbenzene.

Figure 6

Structure of polystyrene. (Source: www.wikipedia.org.)



Expanded polystyrene (EPS) foam

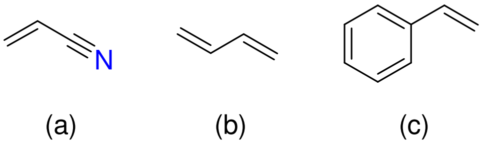
Polystyrene's most common use is as expanded or foamed polystyrene (EPS). EPS is prized for its properties as an insulator and shock absorber and because of its high flexural strength to weight ratio. Furthermore, it is moisture resistant and resists microbial breakdown. 7000 tons of EPS were manufactured in NZ in 2002, of which 67 per cent was used in construction products and 26 per cent in packaging. EPS is produced from a mixture of about 90 to 95 per cent polystyrene resin and 5 to 10 per cent gaseous blowing agent, most commonly pentane or carbon dioxide. However, the blowing agents are expended during production, such that the final void volume in EPS consists of trapped air. EPS is used as insulation in building structures and as packaging material (eg, packing "peanuts"). Another use for EPS is as a lightweight fill for embankments in the civil engineering industry. Expanded polystyrene used to contain CFCs (chlorofluorocarbons), but other, more environmentally-safe blowing agents are now used (ie, pentane and carbon dioxide). Production methods include sheet stamping (PS) and injection moulding. EPS and PS products are currently not recycled due low cost-effectiveness. All polystyrene raw material used for EPS production in New Zealand is imported, in the form of granular polystyrene beads, which are produced by a polymerisation process. During the polymerisation process, pentane (a low boiling point hydrocarbon) is added to the material to assist expansion during subsequent processing. New Zealand manufacturers convert the raw material into EPS using a three-stage process. The first stage involves thermal expansion of the polystyrene beads (at ca. 100 °C) to 40 to 50 times their volume. This is followed by cooling, drying and maturing (the second stage), to stabilise the inflated beads. During the final stage, beads are conveyed into a mould and further expanded under heat, fusing the material into the desired shape. During this stage, pentane is expended so that the final EPS contains no residual pentane. EPS is moulded either into large blocks, which are subsequently cut into sheets, or shaped directly into its final form. All EPS used in construction products in New Zealand contains a flame retardant (such as hexabromocyclodecane). EPS manufacturers include BASF New Zealand Ltd, Huntsman Chemical Company NZ Ltd and Shell New Zealand NZ Ltd.

High impact polystyrene (HIPS) and acrylonitrile butadiene styrene (ABS)

High impact polystyrene (HIPS) is a co-polymer of polystyrene and butadiene (Figure 7), with good impact strength, heat resistance and machinability. It is typically used for automotive parts, structural and electrical components (eg, telephone casings). The butadiene (actually polybutadiene) is added at about 7 per cent, and acts to "rubber-toughen" the polymer (polybutadiene is one of main types of synthetic rubber; see Section 3.10 "Tyres and automotive products").

Figure 7

Monomers making up ABS: a. acrylonitrile, b. 1,3-butadiene and c. styrene.



(a) (b) (c)

Acrylonitrile butadiene styrene (ABS) is a co-polymer structurally similar to HIPS, made by polymerizing styrene and acrylonitrile in the presence of polybutadiene. ABS is used to make light, rigid, moulded products such as automotive body parts, wheel covers, enclosures, piping, musical instruments, golf club heads, toys, and protective head gear. The proportions can vary from 15 to 35 per cent acrylonitrile, 5 to 30 per cent butadiene and 40 to 60 per cent styrene. ABS polymers are resistant to aqueous acids, alkalis, concentrated hydrochloric and phosphoric acids, alcohols and animal, vegetable and mineral oils, and are only attacked by concentrated acids or very hydrophobic solvents (eg, carbon tetrachloride and aromatic hydrocarbons). ABS is soluble in esters, ketones and ethylene dichloride and degrades when exposed to acetone. The aging characteristics of the polymers are largely influenced by the polybutadiene content, and it is normal to include antioxidants in the composition. HIPS and ABS are unlikely to degrade to any significant extent and can be considered toxicologically inert.

3.1.7 Polycarbonate

Polycarbonate plastics are polymers whose monomers are linked together by carbonate groups. Polycarbonate is considered a high quality plastic because of its temperature resistance, impact resistance and transparency and is becoming more common in housewares as well as in laboratories and in industry. Typical products include glasses (sunglasses, eyeglass lenses, and safety glasses), automotive headlamp lenses, CDs and DVDs, lab equipment, visors and shields, domelights and some computers. Polycarbonate resins are known under the commercial brand names "Calibre" (Dow), "Lexan" (GE), "Makrolon" (Bayer) and "Panlite" (Teijin). Polycarbonate plastics are manufactured from bisphenol-A, in the presence of carbonyl dichloride, in which groups of bisphenol-A are linked together by carbonate groups in a polymer chain. Bisphenol-A (BPA) is a mild xenoestrogen, which can exert endocrine-disruption at high doses. There is an ongoing controversy about what constitutes a "safe dose" of BPA. Recent studies, using rats, suggest that BPA is a more potent oestrogen than previously assumed, with about 1/100th of the activity of ethinylestradiol (Timms et al. 2005, vom Saal & Hughes 2005). Bisphenol-A has been found to leach from polycarbonate plastic containers (Chang et al. 2005, Sajiki & Yonekubo 2003, Yamamoto & Yasuhara 1999).

3.1.8 Polyvinylidene chloride

Polyvinylidene chloride (PVDC) is a polymer derived from vinylidene chloride. The most popularly known product of polyvinylidene chloride was "Saran Wrap", used as plastic food wrap from the 1960s up to a few years ago. Nowadays, most food wraps are made of low-density polyethylene (LDPE). Polyvinylidene chloride is also applied in packaging as a water-based coating to other plastic films to increases the barrier properties of the film (eg, reducing oxygen permeability), thereby extending the shelf life of foods. Evidence in the peer-reviewed literature for toxic effects of PVDC is restricted to products of PVDC pyrolysis, such as dioxins and PAHs (Blankenship et al. 1994, Yasuhara et al. 2006).

3.1.9 Polyamide

Polyamides (PA) are polymerised monomers joined by peptide bonds. Polyamides include natural protein fibres such as wool and silk and synthetic fibres such as nylon (marketed by DuPont) and Aramid. Production of polyamide intermediates is carried out by BASF NZ, based in Auckland. However, production of polyamide raw material in NZ is likely to be negligible, with most raw material imported from overseas. Aramid and nylon fibres are widely used in dress and shirt fabrics, pantyhose, sails, bridal veils, carpets, guitar strings and ropes. Solid nylon is used in mechanical parts (bushings) and as an engineering material. Other uses include fishing lines, Velcro, auto parts (air bags, intake manifolds, and petrol tanks), metallised nylon balloons and sports equipment (racquetball, squash, and tennis racquet strings).

3.1.10 Polylactic acid

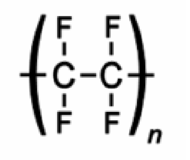
Polylactic acid or polylactide (PLA) is an aliphatic polyester derived from fermented starch. It is synthesised from lacitide by a ring-opening polymerisation using a tin-based catalyst (stannous octoate or tin(II) chloride). PLA is currently used in only a small number of applications, such as in easy-iron shirts, microwavable trays and biomedical applications, such as sutures. Because of its biodegradability it has a great potential in the packaging industry.

3.1.11 Polytetrafluoroethylene

PTFE (Figure 8) is one of many fluoropolymers, best known as a non-stick coating such as Teflon, produced by DuPont. PTFE is very non-reactive and is used to contain reactive and corrosive chemicals. It is also used as a lubricant, and as a low-friction plastic in bearings, bushings, gears, slide plates. Due to its dielectric properties, it is used as an insulator in cables and connector assemblies and as a material for printed circuit boards used at microwave frequencies. It is also used in high-tech fabrics, such as Gore-Tex.

Figure 8

General Chemical structure of PTFE.



While the production of PTFE is quite toxic (involving reacting polyethylene with fluorine gas or polymerisation of tetrafluorethylene or perfluorooctanoic acid, PFOA) all PTFE raw material is synthesised overseas. PTFE degrades above 350°C.

3.1.12 Polysulphones

Polysulphone (PSU) is a specialty thermoplastic with very high temperature resistance acid and alkali tolerance. Chemically, polysulphone consists of repeating units of $C_{27}H_{22}O_4S$. It is produced by step polymerization of bisphenol-A and bis(4-chlorophenyl)sulphone, forming a polyether by elimination of hydrogen chloride. It is used as a dielectric in capacitors and for membranes used in wastewater recovery, food and beverage processing, and gas separation. It is furthermore used in medical devices (due to its autoclavability), food processing and in the automotive and electronic industry as a superior (but more expensive) alternative to polycarbonate.

3.2 Synthetic resins

Table 5

Environmental hazard profile of synthetic resins.

Qualitative environmental hazard rating 16		**Reason for ranking**
🟥 H	Persistence	Polymer backbone, flame retardants (monomers have low persistence).
🟨 M	Bioaccumulation potential	Flame retardants (monomers have low-moderate bioaccumulation).
🟨 M	Toxicity/adverse effect potential	Monomers: oestrogenic and moderately toxic. Flame retardants: oestrogenic.

3.2.1 Epoxy resin

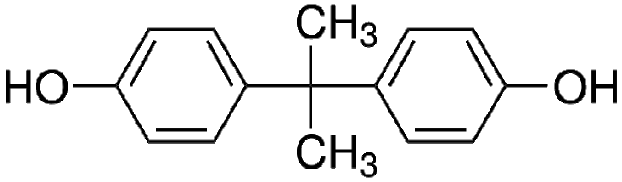
Epoxy polymer resins (polyepoxides) are used in many kinds of adhesives, putties, sealants, composites and as protective coatings on metal cans to maintain the quality of canned food and beverages. Most epoxy resins are produced from a reaction between epichlorohydrin and bisphenol-A, or diglycidyl ethers of bisphenol-A, in the presence of a catalysing agent ("hardener"). Most large overseas primary epoxy manufacturers (eg, Huntsman or Dow) do not sell epoxy resins directly to end users, but rather to intermediate "formulators" (eg, West System) who modify epoxies for final use by adding proprietary mineral fillers, flexibilisers, viscosity reducers, colorants, thickeners, accelerators and adhesion promoters. Some of the major industrial and domestic applications for epoxy-based materials include paints and coatings (eg, powder coatings for washers and other "whiteware", corrosion protection of steel pipes and concrete reinforcing rebar, primers to improve the adhesion of automotive and marine paints, coatings for food tins to prevent rusting, and flooring applications, such as terrazzo flooring, chip flooring and coloured aggregate flooring), structural adhesives (aircraft, cars, boats and sports equipment), fibre reinforced composites materials (eg, fibreglass), and industrial tooling applications (moulds, laminates and castings and fixtures, and electrical insulation for electrical motors, generators, transformers, switchgear, bushings, and circuit boards). For consumer use, epoxy resin is typically sold as a two component kit (eg, "Araldite" glue).

Bisphenol-A and epichlorohydrin

Bisphenol-A (BPA), or 4,4'-dihydroxy-2,2-diphenylpropane (IUPAC name), is one of the primary monomers in epoxy resins (Figure 9). BPA is also used as a starting material of polycarbonate plastics, as an antioxidant in plasticisers, as a polymerization inhibitor in PVC and as a polymer for dental fillings (Soderholm & Mariotti 1999). BPA can leach from epoxy resins and plastic wastes (Bae et al. 2002, Latorre et al. 2003, Takao et al. 2002, Yamamoto & Yasuhara 1999). It appears to have a short degradation half-life of a few days (even though another study reported negligible degradation over 81 days (Ying et al. 2003)) and is likely to bioaccumulate only moderately (log K_{OW} ca. 3.3). BPA has weak oestrogenic activity (Sonnenschein & Soto 1998) and can cause genotoxicity at high doses (Iso et al. 2006). BPA is moderately toxic to aquatic organisms, with LC_{50} values of 1 to 10 mg/L for algae, crustaceans (water fleas) and various fish species (EPA ECOTOX and ESIS databases). Compared to typical surface water concentrations of BPA in the range of 0.001 to 0.10 µg/L, it has been suggested that BPA is unlikely to cause adverse effects on aquatic populations or ecosystems (Staples et al. 2002).

Figure 9

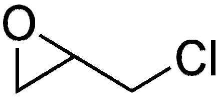
Chemical structure of bisphenol-A.



Epichlorohydrin is a small, highly reactive organochlorine epoxide (Figure 10), which will polymerise upon treatment with acid or strong base. It is used as a building block in the manufacture of epoxy resins, phenoxy resins and other polymers. It is also used as a solvent for cellulose and as an insect fumigant. Epichlorohydrin is flammable and is suspected to have mutagenic and carcinogenic properties, based on laboratory tests with mammalian species (Giri 1997, Kolman et al. 2002). Alternatively, chlorendic acid is also used. As epichlorohydrin is highly polar, it is unlikely to bioaccumulate (log K_{OW} <1). Its calculated degradation half-life is approximately one-week. Epichlorohydrin is moderately toxic to crustaceans and fish, with EC_{50}s of 10-50 mg/L for most species investigated.

Figure 10

Chemical structure of epichlorohydrin.



3.2.2 Polyurethane

Polyurethanes (PUs) are widely used in flexible and rigid foams, durable elastomers and high performance adhesives. They are furthermore used in sealants, elastic fibres, gaskets, carpet underlay, and hard plastic parts. Polyurethanes are produced by reacting a liquid isocyanate with a liquid blend (or "resin") of polyols, usually a polypropylene glycol or polyester polyol, in the presence of a catalyst (eg, a tertiary amine, such as dimethylcyclohexylamine or organometallic salts). The isocyanates can be aromatic or aliphatic compounds, and include diphenylmethane diisocyanate (=methylene diphenyl 4,4'-diisocyanate, MDI), toluene diisocyanate (TDI); hexamethylene diisocyanate (HDI), and isophorone diisocyanate (IPDI). Other resin additives include chain extenders, cross-linkers, surfactants, flame retardant, pigments, fillers, and blowing agents (halocarbons or water). Isocyanates are highly reactive and toxic and are known to cause asthma in humans (Krone & Klingner 2005).

Over three quarters of the global consumption of polyurethane products is in the form of foams. Flexible polyurethane foams are widely used for furniture upholstery, rigid foams for thermal insulation (eg, in refrigerators). Foamed polyurethane is also widely used in automobiles (for car seats, headrests, bumpers, and steering wheels). Other uses of polyurethane foam include sound deadening, flotation (providing buoyancy for small boats and surfboards) and as a packing material. Polyurethanes are furthermore used in paints and varnishes to protect or seal wood (eg, hardwood floors) and as woodworking glue. Polyurethanes are used for making solid tyres (eg, for skateboards) and foam tyres, used on wheelchairs. One disadvantage of PUs is their generally poor resistance to acids, solvents and UV weathering.

3.2.3 Acrylate polymers

Acrylate polymers, also known as "acrylics" or "polyacrylates" include products such as Plexiglas (= Perspex), superglue (cyanoacrylate), and acrylate "gels" for absorbing moisture. Acrylates are derivatives of acrylic acid, characterised by an unsaturated carbonyl group ("acrylic group"), containing a carbon-carbon double bond and a carbon-oxygen double bond, separated by a carbon-carbon single bond, making them very reactive. The simplest acrylic compound is acrolein, used in the preparation of polyester resin, polyurethane, propylene glycol, acrylic acid, acrylonitrile, and glycerol.

Common acrylate monomers used to form acrylate polymers are acrylic acid, butyl acrylate, 2-ethylhexyl acrylate, methyl acrylate, ethyl acrylate, acrylonitrile, n-butanol methyl methacrylate, and TMPTA (trimethylolpropane triacrylate). One widely used acrylate polymer is polymethyl methacrylate (PMMA) or poly(methyl 2-methylpropenoate), sold as acrylic glass under the trade names Plexiglas, Perspex, Plazcryl, Acrylite, Acrylplast, Altuglas, and Lucite. Sodium polyacrylate is known as a super absorbent polymer (SAP) or polyelectrolyte, because it can absorb up to 1000 times its weight in distilled water. It is used in disposable nappies, bed pads, fire control, spray drift control, seed germination, soil conditioning, sanitary pads, and hydroponics. Sodium polyacrylate is also used in many industrial applications, as a thickening agent, as an aid for dissolving soaps, and as a spill absorbing media. Known as "water crystals", it is used as a water storage agent for soils, soaking up excess water and discharging it when the soil becomes drier. Acrylate-based resins are widely used in dentistry. Some acrylate monomers are known to cause skin irritation or contact allergies (Geukens & Goossens 2001, Kanerva 2001, Lindstrom et al. 2002). Acrylic acid, methyl acrylate, ethyl acrylate, and butyl acrylate may bioaccumulate and is moderately toxic to aquatic organisms, with effect concentrations (LC_{50} or EC_{50}) for fish and invertebrates of 1.1 to 8.2 mg/l for methyl acrylate, ethyl acrylate, and butyl acrylate (Staples et al. 2000). Aquatic toxicity of acrylic compounds has also been evaluated by Freidig et al. (1999), who assumed a multiple mode of action model involving narcosis and reactive toxicity. Acrylic compounds, including acrolein, are reactive compounds and can undergo electrophilic reactions with cellular glutathione, which may lead to glutathione depletion as well as non-specific narcosis. However, it is estimated that acrylate concentrations emanating from household wastes in sewage treatment plant effluent are below levels likely to cause adverse effects (Hamilton et al. 1995, Hamilton et al. 1996).

3.2.4 Polyacrylamide

Polyacrylamide (PAM) or (PAA) is an acrylate polymer formed from cross-linking of acrylamide monomers. Polyacrylamides are highly water-absorbent and are used as thickeners in papermaking, in wastewater treatment (Kroening et al. 2004) and for making permanent press fabrics. PAM is also widely used in biochemical laboratories. While polyacrylamide itself is not toxic, the acrylamide monomer is carcinogenic and neurotoxic (LoPachin 2004) and traces of unreacted acrylamide monomer can be present in polymerised acrylamide. Natural sources of acrylamide include fried or baked foods (eg, French fries or chips), as well as coffee and tobacco smoke. Ingested acrylamide appears to be destroyed by stomach acids. On the other hand, direct skin exposure to large doses or acrylamide can cause damage to the male reproductive glands (Shipp et al. 2006).

3.2.5 Phenolic resins

Phenolic resin (or "Phenolic") is a type of thermosetting resin created by reacting a phenol with an aldehyde (eg, formaldehyde) and a filler material (such as paper, cotton, wood flour, or glass), followed by curing and cross-linking. The most common phenolic is phenol-formaldehyde, commercially known as "Bakelite". Due to its electrical non-conductive and heat-resistant properties, Bakelite was widely used in household utensils, but its use has declined in recent decades. It is still used in saucepan handles, electrical plugs and switches, and disc brake cylinders. Some disadvantages include the low resistance to oxidisers and emission of volatiles (phenol and formaldehyde) during cure. The final Bakelite product is chemically highly inert, so toxic effects are likely to be associated with the raw materials only.

3.2.6 Melamine resin

Melamine resin is a durable thermosetting plastic produced by reacting melamine base (1,3,5-triazine-2,4,6-triamin) with formaldehyde. It is widely used in countertops, fabrics, glues and flame retardants. The raw material melamine is also used to make fertilisers and has caused a recent controversy overseas by being illegally used as an additive in pet and livestock food to boost nitrogen content ("melamine scrap"). Melamine appears to be minimally toxic, with an oral LD_{50} of >3000 mg/kg, based on rat toxicity data. On the other hand, melamine cyanurate (formed by reacting melamine with cyanuric acid, a commonly used fire retardant in melamine resin), can increase toxicity, even though nitrogen-based flame retardants are generally considered to have low toxicity (Horacek & Grabner 1996). NZFMA rules out melamine use in food production in New Zealand.

3.3 Paints and coatings

Table 6

Environmental hazard profile of paints and coatings, including antifouling paints.

Qualitative environmental hazard rating	16	Reason for ranking
H	Persistence	Polymers in binder.
M	Bioaccumulation potential	Some antifouling biocides.
M	Toxicity/adverse effect potential	Biocides, plasticisers, solvents, flame retardants.

There are three primary components to paint: pigments, binder (or resin), and solvent. Natural pigments include clays, calcium carbonate, mica, silicas, and talcs. Synthetic pigments include calcined clays, calcium carbonate and synthetic silicas. The dominant white pigment in modern paints is titanium dioxide. Zinc oxide is used as the primary white pigment in road-marking paint. In previous times, lead pigments were used widely until their ban several decades ago.

Paint binders include synthetic or natural resins such as acrylics, polyurethanes, polyesters, melamine resins, epoxy, and oils. Binders can be categorised according to curing mechanism. The most common curing mechanisms are solvent evaporation, oxidative cross-linking, catalyzed polymerization, and coalescence. Most classic paints (eg, enamels) cure by a combination of solvent evaporation and oxidative cross-linking. Paints curing by catalyzed polymerization include epoxies or polyurethanes and are generally two package coatings. Acrylic paints (or "latex" paints) cure by coalescence of the micronised binder particles upon evaporation of the solvent. A fifth category, wax-paints, hardens upon cooling.

Besides the three main categories of ingredients, paint can have a wide variety of miscellaneous additives, usually present in only small amounts. Some examples include additives to improve wetting, to improve fluxing, to impart antifreeze properties, to control foaming, to control skinning, to inhibit bacterial growth, or to improve pigment stability. Other types of additives include catalysts, thickeners, fillers, stabilisers, emulsifiers (eg, cationic surfactants such as quaternary ammonium compounds), texturisers, adhesion promoters, flatteners (de-glossing agents), anti-rust compounds and antifouling agents (discussed in Section 3.15).

3.3.1 Oil-based (alkyd) paints

The dominant binders in oil based paints are alkyd resins, and the terms "alkyd paint" and "oil-based paint" are generally used interchangeably. Alkyds are a class of polyester that is derived from the reaction of a (polyhydric) alcohol and a (polybasic) acid or acid anhydride. Alkyd coatings are typically manufactured from acid anhydrides (such as phthalic anhydride or maleic anhydride) and polyols (such as glycerine or pentaerythritol) that are modified with unsaturated fatty acids (from plant and vegetable oils) to give them air drying properties. Alkyd paints are relatively cheap to produce because of their primarily vegetable origin. Typical sources of drying oils for alkyd coatings are sunflower oil, safflower oil, soybean oil, fish oil, corn oil, and tall oil (resinous oil by-product from pulp and paper manufacturing). Alkyd coatings are typically sold in three classes, "Long", "Medium", and "Short", depending on the content of drying oil. For speeding up the cross-linking of the oils, organic lead salts were traditionally employed, but have been replaced with cobalt and other alternative driers such as zirconium, zinc, calcium, and iron. Acetaldehyde, one of the intermediates in alkyd resin production (ie, for making pentaerythritol), is a carcinogen at high doses. Solvent-based paints ("oil paints") contain various combinations of organic solvents including aliphatic and aromatic alcohols, esters, ethers and ketones. Common paint thinners comprise acetone, mineral spirits, mineral turpentine ("turps"), wood turpentine, naphtha, toluene and xylene. Toxic properties of paints are largely attributable to the solvent component and lead-based additives, rather than the pigment or resin component. After the ban of leaded fuel, the major remaining source of lead is paint in older housing stock (Needleman 2004, Skerfving et al. 1998, Zarcinas & Rogers 2002).

3.3.2 Acrylic paint

Acrylic paint (or "latex" paint) is fast-drying paint containing pigment suspended in an acrylic polymer emulsion. Water is the main solvent for acrylic based paints. Acrylic paints can be diluted with water, but become water-resistant when dry. Indoor house paints tend to be a combination of different copolymer binders (ie, acrylic, PVC, PVA and others), filler, pigment and water. Exterior latex house paints tend to have a higher acrylic content, with the highest quality exterior water-based paints being 100 per cent acrylic. There is no evidence in recently published literature of toxicity emanating from acrylic paint.

3.3.3 Paint strippers

Paint strippers (or paint removers) comprise a variety of solvents designed to remove old paint and other finishes, as well as clean underlying surfaces. The most common active ingredient is dichloromethane (DCM), although formulations based on tetrachloroethylene, terpene solvents (eg, orange oil), N-methylpyrrolidone, various esters, aromatic hydrocarbons, dimethylformamide, nitromethane and other solvents are used as well (see Section 3.8 "Common solvents"). Various co-solvents, such as ethanol, methyl ethyl ketone, phenols, cresols and benzyl alcohol are added to the primary active ingredient to assist with penetration into the old paint layer. Further additives include activators (such as amines, strong acids and strong alkalis), various surfactants (mostly anionic, eg, dodecyl benzene sulphonate or sodium xylene sulphonate, but also cationic and non-ionic surfactants), and thickeners (such as hydroxypropyl cellulose, fumed silica, waxes and polyacrylate gels). Corrosion inhibitors are sometimes added to protect the underlying surface and include antioxidants such as dimethylmethane (propane), polyphosphates, silicates, borates and chromate-based inhibitors. Chelating agents are added to complex metals and usually comprise EDTA, tributyl phosphate, and sodium phosphate. Few data exist on the toxicological effects of paint strippers by themselves. Presumably of greater relevance to the aquatic environment are the effects of paint stripping residue, that is, the combination of old paint (including metals) and paint stripper, such as under bridges or in boatyards (Zarcinas & Rogers 2002).

3.3.4 Other coatings

Polychlorinated naphthalene

Polychlorinated naphthalene (PCN) products were widely used from the 1920s until the 1980s as an insulating coating for electrical wires, wood preservation, as rubber and plastic additives, for capacitor dielectrics and in lubricants. They are now banned, due to adverse health effects (skin rashes and liver disease in manufacture workers). However, due to low degradation rates of PCN products, residues are likely to be widespread. Ongoing sources are waste incineration.

3.4 Silicone sealants, oils and polymers

Table 7

Environmental hazard profile of silicones and silicone oils.

Qualitative environmental hazard rating (8)		Reason for ranking
H	Persistence	Inert polymer backbone.
L	Bioaccumulation potential	Low bioconcentration observed despite log K_{OW} of 3-5.
M	Toxicity/adverse effect potential	Silicone oils: Primarily physical effects (silicone resins non-toxic).

3.4.1 Siloxanes and polysiloxanes (silicones)

Siloxanes are a class of organosilicon compounds with the empirical formula R_2SiO, where R is an organic group. Polymerised siloxanes are commonly known as silicones. The most common silicone is linear polydimethylsiloxane (PDMS), a type of silicone oil, widely used as a sealant and recently in antifouling coatings. The second largest group of silicone materials are silicone resins (or gels), which are formed by branched and cage-like oligosiloxanes.

Siloxanes can be found in medical implants, cosmetics, deodorants, water-repelling windshield coatings, and some soaps. They occur in landfill gas and are being evaluated as alternatives to perchloroethylene for dry-cleaning. Polysiloxanes are widely used as sealants in building construction and maintenance, to seal gaps, joints and crevices in buildings. In the plumbing and automotive fields, silicone grease is often used as a lubricant and silicon oil as a gasket seal. Automotive spark plug wires are often insulated by multiple layers of silicone, and silicone grease is typically used in brake lubricants due to its temperature stability. The hydrophobic nature of silicone oils confers antifouling properties, explaining the increasing use of silicone products in antifouling applications (Truby et al. 2000, Wood et al. 2000, Stein et al. 2003a, Stein et al. 2003b, Meyer et al. 2006). It is important to realise that silicone oils in antifouling applications are not bound by the matrix and can therefore leach into the surroundings. Silicone products are also widely used for cooking, such as in non-stick baking paper, cooking utensils (spatulas) and bakeware (silicone rubber). Silicones are also used to encapsulate drugs or electronic components in order to protect circuitry from environmental influences. While silicone resins appear to be relatively inert and non-toxic, silicone oils give some reason for ecotoxicological concern.

Silicone oils, having a molecular weight of 2400 to 10,000, are persistent and moderately toxic (Nendza 2007). Inhalation of octamethylcyclotetrasiloxane (D-4) at high doses of 890 ppm led to reversible changes in the reproductive tract of female rats (Burns-Naas et al. 2002). Phenyl-methyl siloxanes exert slight oestrogenic activity (Nilsson 2000), and octamethylcyclotetrasiloxane (D4), decamethyltetrasiloxane (M10TS), and 1,3,5,7-tetramethyltetravinylcyclotetra-siloxane (TMTV-D4) show cytotoxicity in mammalian cells at high concentrations of 30 to 50 µM (Felix et al. 1996). Similarly, exposure of rat fibroblast cells to 50 µM of tetravinyl-tetramethyl-cyclo-tetrasiloxane (tetravinyl D4) resulted in a modest 1.7-fold increase of mutant frequencies over controls (Felix et al. 1998). Moderate intrinsic aquatic toxicity has been observed at concentrations of 100 to 1000 mg/L towards microorganisms, plankton, invertebrates, molluscs and fish (review in Nendza (2007)). Toxicity appears to be due to physical-mechanical effects of the small silicone oil droplets rather than biochemical effects.

Most siloxanes, including dimethyl siloxane, are slow to biodegrade and will therefore persist in sediments for some time. The majority of silicone degradation appears to be abiotic (Graiver et al. 2003). PDMS has been shown to degrade if molecularly dispersed, and is removed during wastewater treatment (Frye 1988). Despite their lipophilicity (log K_{OW} >3), methyl siloxanes do not bioconcentrate in organisms and do not show significant ecotoxicity. It is also considered unlikely that methyl siloxanes are capable of transferring methyl groups to mercury. This lead Frye (1988) to conclude that "significant adverse ecological impacts related to environmental methyl siloxanes are highly improbable".

3.4.2 Silanes

Silanes are the silicon analogue to carbon-based alkanes, with silicon atoms covalently bound to each other or hydrogen atoms, following the general formula Si_nH_{2n+2}. Silanes are used as coupling agents to attach glass fibres to a polymer matrix and stabilise the composite material, and in the semiconductor industry. Other applications include water repellents, masonry protection (control of graffiti) and as sealants. Silane (SiH_4) and similar compounds containing Si-H-bonds are also used as reducing agents in organic chemistry. The toxicities of silane (SiH_4), tetraethoxysilane ($Si(OC_2H_5)_4$, TEOS) and dichlorosilane (SiH_2Cl_2, DCS), used in the semiconductor industry, have been reviewed by Nakashima et al. (1998). Silane and TEOS caused acute nephrotoxicity at high concentrations of 2500 ppm (Silane) and 1000 ppm (TEOS), and tubulo-interstitial nephritis at inhalation doses of 100 ppm. TEOS also injured nasal mucosa. DCS showed another type of adverse effect: it was an irritant and/or a corrosive agent to the respiratory tract at acute doses of 64 ppm for 1 h, and chloride appears to play a role in the toxicity of DCS. No published reports were available on the toxicity of silanes to aquatic organisms. Based on available effects data, they are considered to be low to moderately toxic

3.4.3 Silanols

Silanols are the silicon equivalent to carbon-based alcohols, characterised by the presence of a hydroxy (-OH) group. The best known example is trimethylsilanol (TMS), which is an organic derivative of silane, substituted with three methyls and one hydroxyl group. TMS is used as a hydrophobic coating. Trialkylsilanols, including TMS, have recently been reported to exhibit unexpectedly strong antimicrobial and disinfectant properties, exceeding those of aliphatic alcohols and phenols (Kim et al.

2006, 2007). Silanols have the potential to become commercially more important in the future.

3.5 Plasticisers and other plastic additives

Table 8

Environmental hazard profile of plasticisers.

Qualitative environmental hazard rating	16	Reason for ranking
M	Persistence	Phthalates: degradation half-life several weeks, other plasticisers even longer.
H	Bioaccumulation potential	High: Phthalates: log K_{OW} >4.2; other plasticises generally lower.
M	Toxicity/adverse effect potential	Moderate: phthalates (endocrine disruption), benzoates (metabolites), maleates, sebacates, sulphonamides. High: organophosphates.

Plastics contain a wide variety of compounds to enhance their properties. Plastic additives include plasticisers, fillers, flame retardants, heat stabilisers, UV-stabilisers, anti-oxidants, antistatic agents, impact modifiers, pigments, anti-microbials, fragrances, and process aids such as blowing agents (Table 9).

Table 9

Common plastic additives (adapted from British Plastics Federation website www.bpf.co.uk).

Additive	Function	Example
Plasticisers	To make plastics softer and more flexible and to enhance the degradability of the product.	Phthalates, adipates, trimellitates, organophosphates.
Fillers/Extenders	To improve strength, increase "bulk" and lower the cost of the material. Usually mineral-based.	-
Flame retardants	To prevent ignition or spread of flame in plastic material. Used in textile, electrical and transport applications to meet fire safety standards.	PBDEs, chlorendic acid, aluminium oxides.
Heat stabilisers	To prevent thermal decomposition of the polymer during manufacture or use (food processing).	Methyl-, dibutyl- and octyl tin thioesters (for PVC).
Light stabilisers	To inhibit the chemical degradation from exposure to UV light.	Benzophenones, benotriazoles, amine stabilisers.
Antioxidants	To prevent degradation of the polymer by oxidation, leading to reduced impact strength, elongation, surface cracks and discolouration.	Phosphites, phenolics, thio-compounds, diphenylamine.
Impact modifiers	To enable plastic products to absorb shocks and resist impact without cracking. Particularly relevant for polyvinyl chloride (PVC), polystyrene (PS) and polypropylene (PP).	Polybutadiene.
Antistatic agents	To prevent the build up of static electric charge.	Cationic surfactants.
Reinforcements	To improve tensile strength, flexural strength and stiffness of the material. Often fibre-based.	-
Pigments and clarifiers	To create a particular colour or improve transparency.	Benzoic acid.
Antimicrobials	To prevent deterioration of plastic materials by microbiological attack which can cause staining, discolouration, odour, loss of aesthetics, loss of electrical insulating properties, loss of hygiene and overall loss of mechanical properties.	-
Fragrances and deodorants	To improve odour properties. Used in food and beverage packaging.	-
External lubricants	Processing aid to prevent damage to plastics or the mould during processing.	-
Internal lubricants	Processing aid to improve processability of plastics by increasing the flowability.	-
Blowing agents	Processing aid to produce a foam material.	Pentane.

3.5.1 Plasticisers

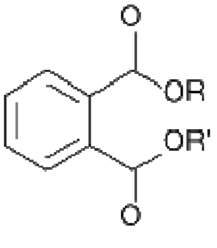
Plastic plasticisers give hard plastics like PVC flexibility and also provide water-repellent properties. The most common plasticisers are phthalates, although there is a myriad of other chemicals with plasticising properties, such as adipates, maleates, trimellitates, and sulphonamides. Most plasticisers (including phthalates) are derivatives of esters of polycarboxylic acids, with linear or branched aliphatic alcohols of moderate-chain length. Plasticisers work by embedding themselves between the chains of polymers, and spacing them apart. Plasticisers are typically volatile and tend to evaporate from the matrix over time.

There is concern about the slow breakdown of some plasticisers, as well as their metabolites. Whereas plasticisers generally do not exhibit acute toxicity, their metabolites can be toxic, and they can exert other biological activity, such as endocrine disruption. For example, microbial breakdown of some plasticisers leads to the formation of 2-ethylhexanoic acid and 2-ethylhexanol, which resist further degradation. The presence of these metabolites have been detected in environmental samples and have been shown to exhibit acute toxicity in Microtox, *Daphnia*, rainbow trout and fathead minnow toxicity assays (Horn et al. 2004)

Phthalates

Phthalates, or phthalate esters, are among the most widespread plasticisers currently in use. They are added to increase the flexibility of hard plastics, especially PVC, or wherever materials with high flexibility and good resistance to water are required. Phthalates are dialkyl or alkyl aryl esters of 1,2-benzenedicarboxylic acid (Figure 11), characterised by low water solubility, high oil solubility, and relatively low volatility.

Figure 11
General chemical structure of phthalate.



The most widely used phthalates are di-2-ethyl hexyl phthalate (DEHP), diisodecyl phthalate (DIDP) and diisononyl phthalate (DINP, Table 10). DEHP is the dominant plasticiser in PVC. DIDP is widely used in electrical insulation and in artificial leather. DINP is used in garden hoses and various consumer goods. Another phthalate plasticiser, benzylbutylphthalate (BBP), is used in the manufacture of foamed PVC in flooring material. Phthalates with short side chains are used as solvents in perfumes and pesticides. Examples include dimethyl phthalate, diethyl phthalate and dibutyl phthalate. Phthalates are also frequently used in nail polish, fishing lures, adhesives, caulk, paint pigments, and toys. Phthalates have been found to reach high concentrations in the environment, especially in wastewater and sewage (Fromme et al. 2002). The 2003 Ministry of Environment (MfE) biosolids study measured DEHP concentrations in sewage sludge from 10 New Zealand wastewater treatment plants as high as 200 mg/kg (Northcott 2007). Whereas toxicity of phthalates in vertebrates and aquatic benthos is moderate to very low (EC_{50} >1000 mg/kg; Api (2001), Call et al. (2001)), phthalates have been found to have oestrogenic activity (Forget-Leray et al. 2005, Jobling et al. 1995, Kim et al. 2002, Ortiz-Zarragoitia & Cajaraville 2005, Stahlschmidt-Allner et al. 1997, Waring & Harris 2005). This appears to be due to interference with the inactivation of oestrogen by sulphation, leading to an increased level of oestrogen (Waring & Harris 2005). As a result, the ESIS database lists DEHP as "may impair fertility". Phthalates are rapidly deactivated by metabolic processes (van den Berg et al. 2003), and degradation half-lives in temperate environments range from days to several months (Staples et al. 1997).

Table 10

Common phthalates in use. (Source: www.wikipedia.org, modified and amended.)

Name	Abbreviation	Use
Dimethyl phthalate	DMP	Insect repellent, sunscreen creams, explosives, solvent, fixative, wetting agent.
Diethyl phthalate	DEP	Insect repellent, sunscreen creams, explosives.
Diallyl phthalate	DAP	-
Di-n-propyl phthalate	DPP	-
Di-n-butyl phthalate	DBP/DnBP)	Cellulose plastics, food wraps, adhesives, perfumes and also in cosmetics – about a third of nail polishes, glosses, enamels and hardeners contain it, together with some shampoos, sunscreens, skin emollients, and insect repellents.
Diisobutyl phthalate	DIBP	-
Butyl cyclohexyl phthalate	BCP	-
Di-n-pentyl phthalate	DNPP	-
Dicyclohexyl phthalate	DCP	-
Butyl benzyl phthalate	BBP	Vinyl tiles, traffic cones, food conveyor belts, artificial leather and plastic foams.
Di-n-hexyl phthalate	DNHP	Materials, tool handles and automobile parts.
Diisohexyl phthalate	DIHxP	-
Diisoheptyl phthalate	DIHpP	-
Butyl decyl phthalate	BDP	-
Di(2-ethylhexyl) phthalate	DEHP	Flexible PVC, construction materials, food packaging, children toys, medical devices, cling wrap.

Name	Abbreviation	Use
Di(n-octyl) phthalate	DNOP	Flooring materials, carpets, notebook covers, and explosives. Together with DEHP, DNOP was the most common plasticiser, but now is suspected of causing cancer.
Diisooctyl phthalate	DIOP	All-purpose plasticiser for polyvinyl chloride, polyvinyl acetate, rubbers, cellulose plastics and polyurethane.
n-Octyl n-decyl phthalate	ODP	-
Diisononyl phthalate	DINP	Garden hoses, shoes, toys, and building materials.
Diisodecyl phthalate	DIDP	Insulation for wires and cables, car undercoating, shoes (artificial leather), carpets, pool liners.
Diundecyl phthalate	DUP	-
Diisoundecyl phthalate	DIUP	-
Ditridecyl phthalate	DTDP	-
Diisotridecyl phthalate	DIUP	-

Adipates

Adipates are plasticisers used in plastics for high and low temperature applications or resistance to ultraviolet light. They are also used in antiperspirants. Some examples are bis (2-ethylhexyl) adipate (DEHA, also called "dioctyl adipate" or DOA), dimethyl adipate (DMA, or DMAD), monomethyl adipate (MMAD), and dibutyl adipate (used in cosmetics). Dioctyl adipate (DOA) is a typical, cold-resistant plasticiser for polyvinyl chloride, chloroethylene copolymer, polystyrene, nitrocellulose, ethyl cellulose and synthetic rubber, imparting softness at low temperature and light stability. Its application is often in combination with phthalate plasticisers such as DOP and DBP for making cold-resistant agricultural plastic thin film, packing membrane for freezing food, cable, coating, leatherette, sheet materials and water pipes. DOA (=DEHA) is tumorigenic in rats at concentrations of 500 mg/kg (Astill et al. 1996), whereas no adverse effects (in humans) have been observed for dibutyl adipate (Anon. 2006). Polyethylene adipate polyesters have intermediate biodegradability (Gimeno et al. 2003).

Trimellitates

Trimellitates are used in automobile interiors and other applications where resistance to high temperature is required. They are branched esters of benzenetricarboxylic acids and have extremely low volatility. Furthermore, they are used as an emollient in cosmetics. Examples include trimethyl trimellitate (TMTM), tri-(2-ethylhexyl) trimellitate (TEHTM-MG), tri-(n-octyl, n-decyl) trimellitate (ATM), tri-(heptyl, nonyl) trimellitate (LTM), n-octyl trimellitate (OTM), tridecyl trimellitate, and trioctyl trimellitate (TOTM). TOTM is widely used in covering material of vinyl electrical wires as a heat resistant plasticiser. It is also used for heat resistant leather and films. The U.S. EPA ECOTOX, IRIS and OECD eChem Portal databases returned no records on the toxicity of trimellitates.

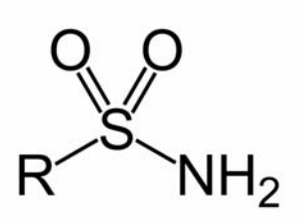
Benzoates

Benzoate plasticisers are used as alternatives to phthalates in the manufacture of PVC (Wardzinska & Penczek 2005). According to an unverified review (Stanhope & Netzel 2003) diethyleneglycol dibenzoate, dipropyleneglycol dibenzoate and triethyleneglycol dibenzoate have low toxicity, with a LD_{50} 3 to 5 g/kg body weight). Few data concerning their oestrogenic activity, metabolism, toxicity to aquatic organisms and biodegradability are available. Based on information from the EPA ECOTOX database, benzoate esters generally have LC_{50} values (to fish) of 5 to 50 mg/L, indicating moderate toxicity. Benzoate plasticisers are claimed to quickly undergo biodegradation in the environment and do not show the tendency to accumulate in the organisms (Stanhope & Netzel 2003). However, a Canadian study found that metabolites from the breakdown of benzoate plasticisers (dipropylene glycol dibenzoate and diethylene glycol dibenzoate) showed elevated toxicity to yeast cells (Gartshore et al. 2003). The authors conclude that these results do not support the use of these two benzoate plasticisers as environmentally safe alternatives to classic plasticisers such as bis-2-ethylhexyl adipate, dioctyl phthalate, and dioctyl terephthalate.

Sulphonamides

Sulphonamide plasticisers, like sulphonamide drugs, are characterised by having a sulphonamide group (Figure 12). Sulphonamide plasticisers include isomers of N-ethyl toluene sulphonamide (o/p ETSA) and benzene sulphonamide. No specific information exists on the environmental toxicity and fate of sulphonamide plasticisers. However, other sulphonamides, used as antibacterial agents (“sulfa drugs”) have been measured at concentrations of up to 6 ng/l in surface waters (Diaz-Cruz, M. S. & Barcelo 2005). They are moderately toxic to aquatic organisms, with LC_{50}s ranging between 1 and 100 mg/L. It may be conjectured that sulphonamide plasticisers also possess, to some degree, antibacterial properties.

Figure 12
Sulphonamide group. (Source: www.wikipedia.org.)



Organophosphates

Organophosphorus compounds are mostly known for their use as insecticides, accounting for an estimated 34 per cent of world-wide insecticide sales (Singh &

Walker 2006). However, next to being used as pesticides, organophosphorus compounds are also used as plasticisers, solvents, air fuel ingredients and chemical warfare agents. Organophosphate plasticisers include the compounds tricresyl phosphate (TCP), and tributyl phosphate (TBP). TCP is acutely toxic (EC_{50} <1 mg/L) to some fish (eg, sticklebacks) and moderately toxic to many other fish species. TBP, used as an industrial solvent and in nuclear fuel processing, is moderately toxic to algae, crustaceans and fish. Organophosphates in general have very high neurotoxicity towards mammals (leading to their, now banned, use as warfare agents). TBP biodegrades rapidly, with roughly 90 per cent degradation within 28 days.

Maleates

Common maleate plasticisers are dibutyl maleate (DBM), diisobutyl maleate (DIBM) and dioctyl maleate. Dioctyl maleate is used as a plasticiser in emulsion-type paints, paper, textile coating, adhesives, and oil additives. It is furthermore used in surfactants and wetting agents and as an emollient in various skin and hair care products such as cleansers, moisturisers, sunscreens, eye shadows, hair relaxers, and hair styling products (Chan & Wakelin 2006). The European ESSI database lists dibutyl maleate to be moderately toxic to fish with 96h LC_{50} values ranging between 1 and 12 mg/L. The EPA ECOTOX database lists diethyl maleate to be moderately toxic to fish, with a 96h LC_{50} of 18 mg/L. No ecotoxicological information was found for dioctyl maleate. The hydrophobicity of most maleates is around log $K_{OW} \approx 4$. Degradation in domestic sewage is 95 per cent after 28 days and 99 per cent after five days in industrial activated sludge, indicating low persistence.

Sebacates

Sebacates are low-volume production polyester-type plasticisers used in specialty applications. Common sebacates include bis(1,2,2,6,6-pentamethyl-4-piperidinyl)sebacate, bis(2,2,6,6-tetramethyl-4-piperidinyl) sebacate, di(2-ethylhexyl) sebacate, dibutyl sebacate (DBS), dimethyl sebacate (DMS), dinonyl sebacate, dioctyl sebacate and disodium sebacate. Dimethyl sebacate (DMS) is used as a PVC plasticiser, as a softening agent and as a solvent for various types of resin (cellulose, polyethylene). DMS is also widely used as a plasticiser and solvent for synthetic rubber and as an intermediate to produce other organic chemicals, including UV light stabilisers, pharmaceuticals and colorants. Dioctyl sebacate is used in PVC applications, such as frost-resistant cables, leatherette for aircraft and motor transport, and PVC linoleum. Dibutyl sebacate is used as a PVC and PVDC plasticiser and as a rocket propellant, as well as a cold-resistant plasticiser for synthetic resin. Only scattered information exists on the ecotoxicity and environmental fate of sebacates. Bis(1,2,2,6,6-pentamethyl-4-piperidinyl) sebacate and di(2-ethylhexyl) sebacate show moderate acute toxicity to fish at 1 to 20 mg/L (OECD eChem Portal) and are moderately persistent (degradation half-lives on the order of 28d). In general, sebacates appear to have relatively low-biodegradability compared to other polyester-type plasticisers (Doi et al. 1996).

Other plasticisers for plastics

In the search for plasticisers that are more biodegradable and have fewer biochemical side-effects, some newer plasticisers are finding increasing use. For example, alkyl citrates are compatible with PVC and are being used as alternatives to phthalates in food packaging, medical products (chewing gums and controlled-release medicines), cosmetics, ink and children's toys. Examples include triethyl citrate (TEC), acetyl triethyl citrate (ATEC), tributyl citrate (TBC), acetyl tributyl citrate (ATBC), trioctyl citrate (TOC), acetyl trioctyl citrate (ATOC), and trihexyl citrate (THC). Current data suggest no measurable toxic risk (to humans) from exposure to alkyl citrates (Johnson 2002). Other types of plasticisers include nitrate-based plasticisers, used as propellants (eg, nitroglycerine, butanetriol trinitrate, metriol trinitrate, diethylene glycol dinitrate and 2,2,2-trinitroethyl 2-nitroxyethyl ether), as well as glycol and polyether based plasticisers, also used as propellants. They are likely to be of little significance in New Zealand. Further plasticisers with specialty applications include nitrobenzene, carbon disulfide and carbon naphthyl salicylate, the latter of which is also used in propellants.

3.5.2 Heat stabilisers

While being banned as antifouling agents, organotins such as dibutyltin are still used in plastic products such as PVC pipe as heat stabilisers. Their toxicity follows the order trialkyltin > dialkyltin > monoalkyltin. Dibutyltin has been found to leach from PVC pipe at concentrations on the order of 1 µg/L (Richardson, S.D. & Ternes 2005).

3.6 Flame retardants

Table 11

Environmental hazard profile of organic flame retardants.

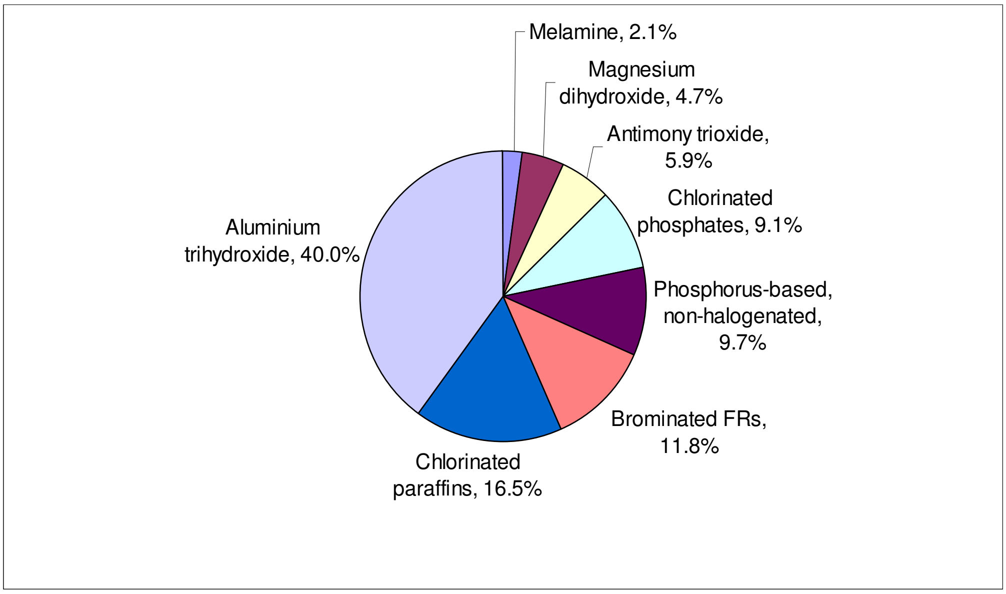
Qualitative environmental hazard rating (32)		**Reason for ranking**
H	Persistence	PBDEs, PBBs, TBBA.
H	Bioaccumulation potential	PBDEs (up to octa), PBBs, TBBA, chlorinated paraffins.
M	Toxicity/adverse effect potential	PBDEs, PBBs, TBBA: endocrine disruption. Organophosphates: neurotoxicity (but low-moderate persistence) Short-chain chlorinated paraffins: baseline toxicity.

Flame retardants are added to otherwise flammable materials to inhibit or resist the spread of fire. Common organic flame retardants include halocarbons, such polybrominated diphenyl ether (PBDEs), polychlorinated biphenyls (PCBs), polybrominated biphenyls (PBBs), tetrabromobisphenol-A (TBPPA), chlorinated paraffins and chlorendic acid derivates. Other organic flame retardants include organophosphates, such as tricresyl phosphate (TCP) and the discontinued tris(2,3-dibromopropyl) phosphate (called "TRIS"; but not to be confused with the buffer salt trishydroxymethylaminomethane), and tris(1-aziridinyl)-phosphine oxide (TEPA). In the past, perfluorinated surfactants, such as perfluorooctanesulfonate (PFOS) and PFOS derivatives were used in fire fighting foams because of their flame-retardant properties (see Section 3.13.3). Beyond the organic compounds mentioned above, many inorganic chemicals are or have been used as flame retardants as well, including asbestos (discontinued), aluminium and magnesium hydroxides and various hydrates, as well as halogenated phosphorus compounds, red phosphorus and borates, none of which will be discussed in this review. However, it should be noted that inorganic flame retardants (primarily aluminium oxide) comprise over 40 per cent of the flame retardant market share by volume (Figure 13).

Given that flame retardants are commonly added to plastics during the manufacture of the raw material, which occurs outside of New Zealand (Section 3.1) inputs by the production stream are likely to be negligible in Auckland. Thus, the main route of flame retardant entry into the environment in Auckland is likely to be via domestic wastewater (eg, laundering of fireproofed clothing, such as baby clothes) and leaching from plastic and textile wastes (eg, electronic equipment, furniture, fabrics) in landfills.

Figure 13

Market share (by volume) of different flame retardant types, European flame retardant market survey, 2001. (Source: European Flame Retardants Association www.flameretardants.eu.)



3.6.1 Chlorinated flame retardants

Traditionally, chlorinated hydrocarbons such as PCBs and chlorinated paraffins (CPs) were widely used as flame retardants. Halogenated (ie, chlorinated and brominated) flame retardants act by radical quenching: upon thermal degradation, these compounds release hydrogen chloride and hydrogen bromide, which quench radicals (but are also highly corrosive). Due to their persistent, bioaccumulative and bioactive nature, PCBs were phased out in the late-1970s and replaced by brominated flame retardants (BFRs) as the main flame retardants. Chlorinated paraffins and chlorendic acid derivates are still in use.

Chlorinated paraffins

Chlorinated paraffins (CPs) are a complex mixture of polychlorinated n-alkanes and have been in use since the 1930s. The chlorination degree of CPs can vary between 30 and 70 per cent. CPs are subdivided according to their carbon chain length into short chain CPs (SCCPs, C10-13), medium-chain CPs (MCCPs, C14-17) and long-chain CPs (LCCPs, C>17). Currently, over 200 CP formulations are in use for a wide range of industrial applications, not only as flame retardants but also as plasticisers and as additives in metal working fluids, in sealants, paints and coatings. In the textile industry, chlorinated paraffins are commonly used for rainproof applications (eg, tents). SCCPs are classified as persistent and have a high potential for bioaccumulation (log K_{OW} 4.4 to 8, depending on the degree of chlorination). SCCPs have been found to be moderately toxic to aquatic organisms at concentrations of 1 to 20 mg/L (daphnids, shrimp, blue mussels and trout), according to information summarised by the Priority Substance Assessment Program of Environment Canada. They are furthermore a reproductive or developmental toxin and a suspected carcinogen. Medium- and long-chain CPS show little long-term toxicity to aquatic organisms at test concentrations of up to 5 mg/L. Reported water concentrations of CPs are 100 to 1000 times lower, such that CPs are not considered to present an imminent hazard to aquatic organisms (Iino et al. 2005). ERMA lists short-chain chlorinated paraffins (C10-C13) as candidates for reassessment for priority listing.

Chlorendic acid and derivates

Chlorendic acid is a high-volume industrial chemical used for the production of flame-resistant composites, also known as HET acid, Hetron 92, Hetron 92C, among other names. Chlorendic acid is used as an intermediate in the synthesis of unsaturated flame-retardant polyester resins and the flame retardants dibutyl chlorendate and dimethyl chlorendate. It is also used for making plasticisers and as a finishing flame-retardant treatment for wool (even though wool is relatively fire-resistant). Another major use is in the production of fibreglass-reinforced resins for chemical industry equipment. It can also be used to make alkyd resins for special inks and paints. It is also used as a hardening agent in epoxy resins in printed circuit boards (see Section 3.2 "Synthetic resins"). When reacted with non-halogenated glycols, it forms halogenated polyols used as flame retardants in polyurethane foams. It is an intermediate in the production of dibutyl chlorendate and dimethyl chlorendate, which are used as reactive flame retardants in plastics. In limited amounts, it is used as an additive in acrylonitrile butadiene styrene copolymer (ABS), and (in salt-form) as an extreme pressure additive in synthetic lubricants. In Europe, 80 per cent of chlorendic acid is used in production of flame-resistant composites for building and transportation, while the rest is used in materials for corrosion-resistant fluid storage. In the USA, Latin America, and Asia, 20 to 30 per cent is used in flame retardant applications and the rest is used in corrosion-resistant plastics (Wikipedia).

When used in polymers, whether as a curing agent or as a flame retardant, chlorendic acid bonds covalently to the polymer matrix, which reduces its leaching to the environment. It may, however, be released when such materials are subjected to hydrolysis, and can also be formed by oxidation of chlorinated cyclodiene insecticides (eg, endosulfan, chlordane, heptachlor, aldrin, dieldrin, endrin, and isodrin). Its half-life in soil is 140 to 280 days, making it relatively persistent. Chlorendic acid is only mildly toxic to fish, with a 48h EC_{50} of 383 mg/L to *Oryzias latipes* (CHRIP database, accessed via OECD eChem Portal). Chlorendic acid has been classified as possibly carcinogenic to humans (Group 2B) by the International Agency for Research on Cancer (IARC).

Chlorinated phosphates

As an alternative to PBDEs in upholstery (primarily pentaBDE), a variety of chlorinated phosphate esters (chloroalkyl phosphate esters) have been introduced to the market. Two examples are tris(1-chloro-2-propyl) phosphate (TCPP) and tris(1,3 dichloro-2 propyl phosphate, TDCPP), used extensively in polyurethane foams (up to 12 per cent weight) and fabrics (eg, polyester sleepwear for children). They are structurally-related to the banned compound tris(2,3-dibromopropyl) phosphate (TRIS). The environmental fate of TDCPP and TCPP is largely unknown. Entry into the aquatic environment can be through production waste streams or from use and disposal of the final product. For example, Ahrens et al. (1979) determined the rate of release of TDCPP as a function of the number of launderings of children's polyester sleepwear and observed that about 37 per cent of the flame retardant was lost after 20 washings.

TCPP and TDCPP are moderately persistent compounds, with degradation half-lives of several months in water. Bioaccumulation in fish has been found to be relatively low (BCF generally <100). Toxicity to aquatic organisms is moderate, with EC_{50} values ranging between 12 to 48 mg/L for algae and 5 to 131 mg/L for water fleas. Toxicity to fish is variable, ranging from 1 mg/L for trout to 180 mg/L for bluegill sunfish. Spinal deformities have been observed in killifish exposed to TDCPP at concentrations of 3.5 mg/L for 24 h. (IPCS database).

Another chlorinated phosphate is tris(2-chloroethyl) phosphate (TCEP). It has been used as a flame retardant mainly in the production of polyurethane foams and liquid unsaturated polyester resins, but also in textile back-coating formulations and PVC. Its production has been in decline since the 1980s so it is probably no longer used. Its log K_{OW} is 1.7 and it does not bioaccumulate to any significant extent (BCF in fish generally <5). It is only weakly toxic to aquatic organisms, with EC_{50}s of 100 to 1000 mg/L.

3.6.2 Brominated flame retardants

Brominated flame-retardants (BFRs) are high-volume industrial chemicals that have been in use for about 30 years. Even though they generally comprise less than 20 per cent of the market share in terms of volume, they have the highest market share by value (ie, sales). BFRs are produced in approximately 75 variants with different chemical properties (European Flame Retardants Association website). Four main groups (including obsolete PBBs) are commonly distinguished:

1. Brominated cyclohydrocarbons (eg, hexabromocyclododecane HBCD).
2. Tetrabromobisphenol-A (TBBPA).
3. Polybrominated diphenyl ethers (PBDEs).
4. Polybrominated biphenyl (PBBs).

In addition to these four main classes, many other brominated organic compounds are being marketed. BFRs are commonly used in electronic products, clothes (flame-retardant back-coating) and furniture (50 per cent of furniture uses PBDEs as the main flame retardant). The electronics industry accounts for the greatest consumption of BFRs. Bromine based flame retardants are applied to 2.5 million tons of polymers annually, with the annual consumption of PBDEs alone being estimated at over 40,000 metric tons (Wikipedia). In computers, BFRs are used in printed circuit boards, connectors, plastic housings and cables. BFRs are also added to plastic housings of television sets, carpets, paints, upholstery and domestic kitchen appliances. A summary of typical BFR content in various plastics is presented in Table 12.

The majority of environmental studies on BFRs conducted to date have focused on PBDEs and to some extent on TBBPA and HBCD. The current concern about the environmental hazard posed by BFRs relates to their high persistence, high bioaccumulation potential and their capacity to bind to various hormone receptors (Meerts et al. 2001), potentially leading to endocrine disruption in wildlife (Darnerud 2003, de Wit 2002). This concern is further exacerbated by the finding that BFR levels in the environment and in humans have strongly increased over the last two decades (Vos et al. 2003), in contrast to classic persistent pollutants such as polychlorinated biphenyls (PCBs), which have decreased or remained static during the same time period. Humans may be exposed to PBDEs through consumption of fatty food of animal origin (eg, fish, milk), through skin contact with textiles protected with flame retardants or through inhalation of BFRs volatilised from electronic and electric equipment. In a long-term study of PBDEs in human milk in Sweden, a doubling of PBDE concentration was found every five years over the period 1972 to 1997. The levels of penta- and hexa-brominated diphenyl ethers (two common PBDEs) also increased at the same rate in ringed seals collected in the Canadian Arctic from 1981 to 2000 (Ikonomou et al. 2002). PBDEs are potential endocrine disrupters. They are structurally and toxicologically similar to PCBs, polychlorinated dibenzofurans (PCDFs), and polychlorinated dibenzo-p-dioxins (PCDDs), by affecting the aryl hydrocarbon, oestrogen and thyroid receptors. The compound TBBPA, on the other hand, has been implicated in potentially affecting thyroid hormone homeostasis, and there is evidence that some BFRs might be neurotoxic at high doses (Eriksson et al. 2001). Bioactivity depends greatly on the bromine substitution pattern and other structural characteristics (Hamers et al. 2006, Harju et al. 2007).

Table 12

Typical BFR content in plastics. (Source: Arias, 2001.)

Polymer	Content (%)	Primary flame retardant(s)
Polystyrene foam	0.8–4	HBCD
High impact polystyrene	11–15	DecaBDE, brominated polystyrene
Epoxy resin	19–33	TBBPA
Polyamides	13–16	DecaBDE, brominated polystyrene
Polyolefins	5–8	DecaBDE, propylene dibromo styrene
Polyurethanes	10–18	PentaBDE, esters of TBBPA
Polyterephthalate	8–11	Brominated polystyrene, TBBPA derivative
Unsaturated polyesters	13–28	TBBPA
Polycarbonate	4–6	Brominated polystyrene, TBBPA derivative
Styrene copolymers	12–15	OctaBDE, brominated polystyrene

Hexabromocyclododecane

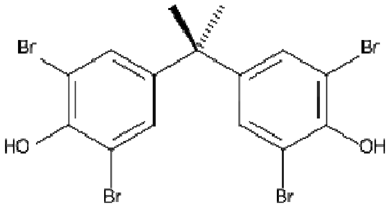
Hexabromocyclododecane (HBCD or HBCDD) is a brominated cycloalkane primarily used in extruded and expanded polystyrene foam (XPS and EPS) for thermal insulation in the building industry. Typical HBCD levels in EPS are 0.7 per cent and in XPS 2.5 per cent. Other uses are as a textile back-coating, in upholstered furniture, automobile interior textiles, car cushions and insulation blocks in trucks, packaging material, video cassette recorder housing and electric and electronic equipment. HBCD is relatively non-toxic to fish (EC_{50} (48h) = 363 mg/L to *Oryzias latipes;* CHRIP database), but acutely toxic to algae (EC_{50} = 0.01 to 0.1 mg/L for *Skeletonema costatum* and *Thalassiosira guillardi*; EPA ECOTOX database). It has very low-biodegradability under aerobic conditions but degrades quickly (within days) anaerobically (EPA HPVIS database). HBCD shows strong bioaccumulation (BCF 18,000) in fathead minnow, *Pimephales promelas*; EPA ECOTOX database). HBCD has been measured in tissues and egg yolk of birds at concentrations of up to 60 ng/g wet weight (Gauthier et al. 2007, Verreault et al. 2007) and in cetaceans at concentration of up to 380 ng/g lipid (Isobe et al. 2007). In the Dutch Scheldt estuary, total HBCD concentrations in sediment and mysid shrimp were 14 to 71 ng/g dw and 562 to 727 ng/g lipid, respectively (Verslycke et al. 2005).

Tetrabromobisphenol-A

Tetrabromobisphenol-A (TBBPA, Figure 14) is primarily used in electronic circuit boards. Since it is covalently bound to the resin of the printed circuit board, leachability into the aquatic environment is presumed to be negligible. TBBPA is persistent, potentially bioaccumulative (log K_{OW} 4.5 to 5.3) and toxic to water-living organisms (EC_{50} <1 mg/L to algae, crustaceans and fish; EPA ECOTOX database). TBBPA's molecular structure is similar to that of the thyroid hormone thyroxine, except that iodine atoms have been replaced by bromines. However no unequivocal evidence of thyroid stimulation by TBBPA has been documented to date. TBBPA has oestrogenic activity, interfering with oestradiol metabolism (Jurgella et al. 2006). Furthermore, TBBPA is hepatotoxic (to rats) at very high concentrations of 250 mg/kg (Szymanska et al. 2000). Sediment concentrations of TBBPA as high as 430 ng/g have been measured downstream of a Swedish plastics manufacturer. However typical concentrations in sewage sludge are generally 10 to 50 ng/g dry weight (de Wit 2002).

Figure 14

Structure of tetrabromobisphenol-A.

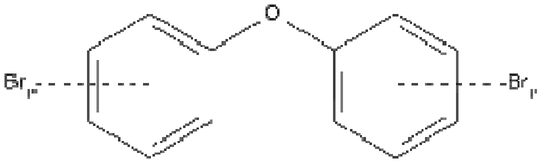


Polybrominated diphenyl ethers (PBDEs)

The family of polybrominated diphenyl ethers consists of 209 different congeners (Figure 15). All are highly hydrophobic, with log K_{OW} values ranging between 4.4 and 8.1, depending on the degree of bromination (Kurz & Ballschmiter 1999).

Figure 15

Generic chemical structure of a polybrominated diphenyl ether (PBDE).



PBDEs are used (or have been used) as flame retardants in many industrial and household products, including fabrics (polyester), furniture, and electronics. They are contained in epoxy resins, phenol resins and polyurethane foams, as well as in ABS foam. Three technical mixtures are commonly used, known as pentaBDE, octaBDE and decaBDE, depending on the degree of bromination of the dominant congeners. However, each technical mix will also contain PBDEs with other numbers of bromine atoms than the dominant congener. For example, technical “pentaBDE” contains 50 to 60 per cent penta-brominated diphenyl ethers, 24 to 38 per cent tetra BDEs and 4 to 8 per cent hexa BDEs (de Wit 2002). The E.U. has explicitly banned the use of penta-and octaBDE since 2004 (Restriction of Hazardous Substances in Electric or Electronic Equipment (RoHS)), as well as any other brominated flame retardant with the exception of decaBDE, tetrabromobisphenol-A (TBBPA) and hexabromocyclododecane (HBCD). PBDEs have also been banned by some U.S. States, such as Washington. In New Zealand, PBDEs fall under the HSNO Act but currently have no classification.

There is evidence that PBDEs are hepatotoxic, neurotoxic, and can affect the reproductive and endocrine system (thyroid and oestrogen receptors). PentaBDE is also suspected of being carcinogenic (de Wit 2002). Lower brominated PBDEs (having

1 to 5 bromine atoms) are regarded as more hazardous because their smaller molecular weight (and intermediate log K_{OW}) allows them to be absorbed more readily by organisms. PentaBDE is classified by the E.U. as "very toxic" to aquatic organisms. It has a weak dioxin-like toxicity to rats. OctaBDE has been classified as a potential teratogen and reproductive toxin. The half-life of pentaBDE is estimated to be 150 days in soil, 600 days in aerobic sediment, 150 days in water and 11 to 19 days in air. Breakdown processes such as de-bromination of higher brominated PBDEs can lead to the formation of more toxic and bioaccumulative lower brominated PBDEs. Long-range transport of PBDEs is considered to be likely.

A New Zealand study by Harrad & Porter (2007) measured penta PBDEs in human blood serum samples from 23 donors in Wellington. Average PBDE concentrations (sum of the common congeners 47, 99, 100, 153, 154, and 183, spanning the range of tetra BDE to hepta BDE), were approximately 7 ng/g lipid, which was within the range reported for human tissues in Europe, but lower than in Australia and North America. The most likely source of this contamination was considered to be the release of PBDEs from imported consumer goods. The congener pattern observed is in line with that reported for human tissues outside North America, but shows a lower contribution of congener BDE 47 to the total amount of accumulated PBDEs than observed in North Americans. No significant differences between concentrations in males and females were detected, and no relationship between donor age and ΣPBDE concentration was observed. One donor displayed concentrations that were significantly elevated (ie, >average +2 standard deviations) above those in others in this study.

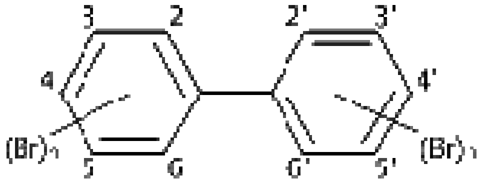
PBDE concentrations in environmental samples range from ten to several hundred ng/g in sewage sludge, from <1 to several thousand ng/g dry weight in river sediments, and from <1 to around 1000 ng/g in shellfish and fish samples (de Wit 2002). Concentrations of individual congeners (such as BDE 47 or BDE-99) can often reach several hundred or thousand ng/g dry weight.

Polybrominated biphenyls (PBBs)

Polybrominated biphenyls PBBs (Figure 16) are a class of obsolete brominated flame retardants, no longer in use, but intensively utilised from 1970 to the mid-1980s in consumer plastic products such as electrical appliances, textiles, acrylonitrile butadiene (ABS) foams and electronic equipment housing (eg, business machine housings, motors, radio and TV parts). For this reason, PBBs are likely to be present in older landfills. Production and use of PBBs was voluntarily stopped in the U.S. in the mid-1970s upon the emergence of adverse effects in people and animals exposed to PBBs during production or in agricultural contamination, after which other countries followed suit. Three technical mixtures were manufactured commercially: hexabromobiphenyl, octabromobiphenyl, and decabromobiphenyl. Nearly 90 per cent of PBBs in use worldwide were hexabromobiphenyl (known under the trade names "FireMaster BP-6" and "FireMaster FF"). Octabromobiphenyl and decabromobiphenyl were never used in the United States, probably because the hexabromobiphenyl was less expensive and equally effective as a fire retardant (Neufeld et al. 1977). Production of highly brominated PBBs (decabromobiphenyl) continued in Europe until 2000, and is now banned under the European Restriction of Hazardous Substances in Electric or Electronic Equipment (RoHS). PBBs were replaced by PBDEs.

Figure 16

Figure generic structure of PBBs. (Source: www.wikipedia.org.)



PBBs are stable and persistent in the environment. PBBs appear to be fairly resistant to microbial degradation. Breakdown by purely abiotic chemical reactions (excluding photodegradation) is considered to be unlikely. PBBs are persistent under field conditions. For example, soil samples from a former PBB manufacturing site, analysed several years after accidental release, still contained PBB and follow-up surveys over a three-year period following the termination of PBB production showed no significant decline in PBB levels.

PBBs are lipophilic (log K_{OW} 3.4-7.0, up to hexabromobiphenyl) and have a high potential to bioaccumulate. For example, fathead minnows (*Pimephales promelas*) caged in a river where water levels of PBB remained consistently below 0.1 µg/litre, concentrated PBBs in their bodies more than 10,000 fold in two weeks of exposure. From this, a bioconcentration factor (BCF) of more than 10,000 can be inferred.

Not much data is available on the effects of PBBs on organisms in the environment, and no information is available on the effects of PBBs on ecosystems. Studies in animals exposed to large amounts of PBBs for a short period or to smaller amounts over a longer period show that PBBs can cause weight loss, skin disorders, nervous and immune systems effects, as well as effects on the liver, kidneys, and thyroid gland. A number of chronic toxic effects have been observed in experimental animals at doses around 1 mg/kg body weight per day following long-term exposure. There is also evidence that PBBs may cause skin problems, such as acne, in consumers of PBB-contaminated food. Some workers exposed to PBBs by breathing and skin contact for days to months also developed acne. PBBs can induce cancers at a dose of 0.5 mg/kg body weight per day. The International Agency for Research on Cancer (IARC) has classified hexabromobiphenyl as a possible human carcinogen (IARC group 2B).

Given the discontinued use of PBBs in industry, their main source in New Zealand is release from electronic waste via landfills. Since PBBs are not chemically bound to the polymer matrix, there is a potential for them to migrate out of the matrix with time.

Other brominated flame retardants

In addition to the four major BFR categories described above, a variety of other brominated compounds are currently marketed as alternative BFRs for textile back-coatings and fireproofing adhesives and cables, roofing, furniture (including aircraft seats) and circuit boards. These include tetrabromophthalate esters, tribromophenyl allyl ether, bis(tribromophenoxy) ethane and dibromostyrene. A number of proprietary mixes with partially specified composition are marketed as well, such as "Great Lakes FireMaster CP-44 HF" (= brominated polystyrene and brominated benzene, ethenyl homopolymer) or "Great Lakes FireMaster 2100" (= decabromodiphenylethane and 1, 1'-(1, 2-ethanediyl)bis[2, 3, 4, 5, 6]-pentabromobenzene). Many of these compounds are structurally similar to commonly used BFRs (eg, PBDEs) but have not been classified in terms of their risk to the environment or restricted in use.

3.6.3 Other flame retardants

Organic phosphorus flame retardants

As alternatives to brominated flame retardants, organic phosphate esters, phosphonates and phosphinates are finding wide use in the textile industry. Examples are TRIS (2,3 tribromopropyl phosphate and TEPA (tris aziridinyl phosphine oxide) which were extensively used in clothing and fibre products, but manufacture has been discontinued in Europe. Tricresyl phosphate (TCP) is one of several aromatic phosphate esters still in commercial use. It is applied as a back-coating to fabrics when used as a flame retardant in upholstered furniture and as a flame retardant in plastics and rubbers. TCP is also used as a plasticiser in nitrocellulose and acrylate lacquers and varnishes, in PVC, as a petrol additive (in leaded petrol, as a lead scavenger for tetra-ethyl lead), and as a lubricant. Commercial TCP is a complex mixture containing the isomers meta TCP (TMCP), para TCP (TPCP) and traces of ortho TCP (TOCP), as well as mixed tricresyl and dicresyl phosphate esters. TCP released into water is readily adsorbed on to sediment particles. TCP is readily biodegraded in activated sewage sludge to 70 to 99 per cent of initial concentrations within 24 h (IPCS database), depending on feed concentrations and conditions. This equates to a biodegradation half-life of 3.6 to 14 hours for TCP. TCP is almost completely degraded within five days in river water. Although TCP breaks down rapidly, it is lipophilic (log K_{OW} = 5.11) and has been shown to bioaccumulate in fish (BCF = 165-2768). TOCP is a neurotoxin, with moderate toxicity (EC_{50}) to algae, aquatic insects and fish, on the order of 1 to 5 mg/L.

Other organophosphate flame retardants are tri(dichloroisopropyl) phosphate and tri(2-chloroethyl) phosphate (mentioned above), which are applied to plastics, especially in flexible foams used in automobiles and furniture, and in rigid foams used for building insulation. They occur with high frequency of detection in many U.S. streams (Kolpin et al. 2002). Further organic phosphorus-based flame retardants and plasticisers, primarily used as additives in hydraulic fluids and lubricants, are triphenyl phosphate, trixylenyl phosphate, cresyl diphenyl phosphate and phenyl dicresyl phosphate, as well as isopropylated triarylphosphates. The majority of these organophosphates are toxic to aquatic organisms.

3.7 Organic peroxides

Table 13

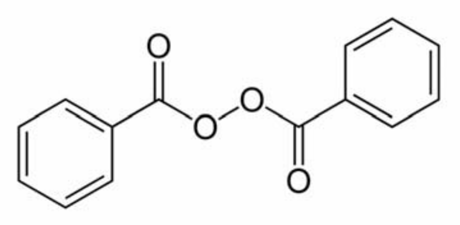
Environmental hazard profile of organic peroxides.

Qualitative environmental hazard rating	2	**Reason for ranking**
L	Persistence	Not evident.
L	Bioaccumulation potential	Not evident.
M	Toxicity/adverse effect potential	Potential carcinogens. Moderate toxicity in activated pulp mill effluent.

Organic peroxides (Figure 17) are organic compounds containing the peroxide functional group (ROOR'). The class includes dialkyl peroxides, alkyl hydroperoxides, peroxy esters, diacyl peroxides and peroxy acids, which generally have a MW <500.

Figure 17

Chemical structure of benzoyl peroxide. (Source: www.wikipedia.org.)



Organic peroxides are used as accelerators, activators, catalysts, cross-linking agents, curing and vulcanization agents, hardeners, initiators and promoters. They are very versatile catalysts for many types of polymerisation reactions, such as in epoxy and polyester resin. They are also powerful bleaching agents. The most common organic peroxides are methyl ethyl ketone peroxides (MEKP) and benzoyl peroxide. Other peroxides include acetone peroxide, pinane hydroperoxide and cumene hydroperoxide. Most organic peroxides are highly flammable, explosive materials, often volatile and of short environmental persistence.

MEKP and benzoyl peroxide are used as initiators for polymerization of polyester resins and silicone polymers. Benzoyl peroxide (and to some extent acetone peroxide) is also used as a bleaching agent for dyeing hair, whitening teeth and curing acne, and for treating flour to accelerate gluten release. Pinane hydroperoxide is used in the production of styrene-butadiene synthetic rubber. Organic peroxides can also form as an unwanted by-product during the oxidation of organic solvents (such as during long-term storage of chemicals). To minimise the risk of explosion, dilute solutions of 30 to 60 per cent MEKP are commonly used. MEKP is typically dissolved in dimethyl phthalate, cyclohexane peroxide, or diallyl phthalate to further reduce sensitivity to shock. Solutions of MEKP are severe skin and eye irritants, and some organic peroxides (eg, benzoyl peroxide) have been identified by the U.S. EPA as possible carcinogens. Benzoyl peroxide breaks down to benzoic acid and oxygen.

3.8 Organic solvents

Table 14

Environmental hazard profile of organic solvents.

Qualitative environmental hazard rating 8		**Reason for ranking**
M	Persistence	Problematic where continuous inputs occurring.
M	Bioaccumulation potential	Low-to-moderate (log K_{OW} generally <4.2).
M	Toxicity/adverse effect potential	Non-polar: moderate (narcotic at concentrations >1 mg/kg. Polar: generally low. Some compounds are potentially carcinogenic.

3.8.1 Common solvents

Many industrial processes involve organic solvents. Organic solvents are also used in domestic applications for cleaning, degreasing, or painting (see Section 3.3 "Paints and coatings"). A list of commonly used organic solvents is given in Table 15. Organic solvents are typically small molecules (MW <150), with relatively high volatility, medium- to high-persistence, low- to moderate-bioaccumulation potential (log K_{OW} generally <4.2) and low- to moderate-toxicity.

For example, the high production volume solvent cyclohexane has moderate bioaccumulation potential (log K_{OW} of 3.44; BCF approximately 200), an EC_{50} (to fish) of 10 to 50 mg/L, and low biodegradation rates. Other non-polar solvents, such as hexane and heptane and have higher bioaccumulation potential (log K_{OW} 3.6 and 4.6, respectively), but degrade rapidly and are less toxic to fish (EC_{50} >100 mg/L). Hexane (usually as a mixture of five isomers) is a common constituent of petrol and glues used for shoes, leather products and roofing.

Compared to non-polar solvents, polar solvents generally pose a lower environmental hazard, by being less bioaccumulative and less persistent. For example, the polar solvent acetonitrile has a short degradation half-life of 28d, a low bioaccumulation potential (log K_{OW} -0.34) and low toxicity (EC_{50} >>100 mg/L). Ethanol has an even shorter degradation half-life (five to seven days), low bioaccumulation potential (log K_{OW} -0.31), and low toxicity to aquatic organisms (EC_{50} >500 mg/L to most fish).

Chlorinated hydrocarbons, including chloroform and carbon tetrachloride, have been phased out over the last two decades because of their ozone-depleting characteristics (see section below).

Table 15

Common organic solvents and toxicity, adapted from Dr. Steven L. Murov's website, Modesto Junior College; http://virtual.yosemite.cc.ca.us/smurov/orgsoltab.htm#TABLE%201.

Solvent	Formula	LD_{50} (oral-rat; g/kg)	Polarity
Acetic acid	$C_2H_4O_2$	3.3	Polar, protic
Acetone	C_3H_6O	9.8	Polar, aprotic
Acetonitrile	C_2H_3N	3.8	Polar, aprotic
Benzene	C_6H_6	4.9	Polar, aprotic
1-butanol	$C_4H_{10}O$	0.79	Polar, protic
2-butanone	C_4H_8O	2.7	Non-polar
t-butyl alcohol	$C_4H_{10}O$	3.5	Polar, protic
Carbon tetrachloride (tetrachloromethane)	CCl_4	2.8	Non-polar
Chloroform	$CHCl_3$	1.2	Non-polar
Cyclohexane	C_6H_{12}	13	Non-polar
Diethylene glycol	$C_4H_{10}O_3$	13	Polar, protic
Diethyl ether	$C_4H_{10}O$	1.2	Non-polar
Diglyme ((bis(2-methoxyethyl) ether)	$C_6H_{14}O_3$	-	Non-polar
Dimethoxy-ethane (glyme, DME, dimethyl cellosolve)	$C_4H_{10}O_2$	10	Non-polar
Dimethyl formamide (DMF)	C_3H_7NO	2.8	Polar, aprotic
Dimethyl sulphoxide (DMSO)	C_2H_6OS	18	Polar, aprotic
1,4-dioxane	$C_4H_8O_2$	4.2	Polar, aprotic
Ethanol	C_2H_6O	7.1	Polar, protic
Ethyl acetate	$C_4H_8O_2$	11	Non-polar
Ethylene glycol	$C_2H_6O_2$	4.7	Polar, protic
Formic acid	$C_2H_2O_2$		Polar, protic
Glycerine	$C_3H_8O_3$	13	Polar, protic
Heptane	C_7H_{16}		Non-polar
Hexane	C_6H_{14}	29	Non-polar
Methanol	CH_4O	5.6	Polar, protic
Methyl *t*-butyl ether (MTBE)	$C_5H_{12}O$	4	Non-polar
Methylene chloride (DCM)	CH_2Cl_2	1.6	Non-polar

Solvent	**Formula**	**LD_{50} (oral-rat; g/kg)**	**Polarity**
Pentane	C_5H_{12}		Non-polar
1-propanol	C_3H_8O	1.9	Polar, protic
2-propanol (IPA)	C_3H_8O	5	Polar, protic
Tetrahydrofuran (THF)	C_4H_8O	2.8	Polar, aprotic
Toluene	C_7H_8	5	Non-polar
p-xylene	C_8H_{10}	5	Non-polar

3.8.2 Halogenated solvents

Until recently, halogenated hydrocarbons were widely used as solvents, cleaning agents (eg, degreasers) and for bleaching of cardboard, before many were banned by the Montreal Protocol because of their ozone-damaging properties. Examples of halogenated solvents include tetrachloromethane , chloroform (trichloromethane), 1,1,1-trichloroethane and 1,1,2-trichloroethane, bromochloromethane, 1,2,2,2-tetrachloroethane and 1,1,1,2-tetrachloroethane and pentachloroethane. Further examples are 1,1 dichloroethylene, trichloroethylene and 1,2,4 trichlorobenzene. Chlorinated solvents that are still in use are dichlomethane (widely used as a paint stripper, see Section 3.3.3) and tetrachloroethylene, which is the most commonly used solvent in dry cleaning. Tetrachloroethylene is also used to degrease metal parts in the automotive and other metalworking industries. Methyl bromide, banned under the Montreal Protocol, is still used in New Zealand as a fungicide (as a fumigant for strawberry horticulture), as a result of an exemption. Chlorobenzene is used in the manufacture of herbicides, dyes and rubber, being an intermediate in the production of nitrochlorobenzenes and diphenyl oxide. It was also used as an intermediate in the manufacture of DDT. Chlorobenzene is also used as a high-boiling solvent in organic synthesis as well as many industrial applications. Bromobenzene is used as an additive in motor oils

Most halogenated solvents are small, volatile compounds that have low persistence and low bioaccumulation potential (log K_{OW} generally <3) and generally cause acute (primarily narcotic) toxicity only at moderate (bromobenzene; EC_{50} = 10-100 mg/L) or very high concentrations (eg, chloroform, 1,1,1-trichloroethane, tetrachloromethane). Their toxicity to aquatic organisms is therefore ranked as low-to-moderate. However, some halogenated solvents are classified as likely carcinogens (eg, chloroform), or can act as hepatotoxins (bromobenzene), teratogens or cause long-term organ damage (Zurita et al. 2007).

3.9 Petrol, diesel, and fuel additives

Table 16

Environmental risk profile of petrol, diesel and fuel additives.

Qualitative environmental hazard rating		**8**	**Reason for ranking**
M	Persistence		Generally rapid volatilisation and biodegradation of low molecular weight alkanes and aromatics, but high persistence of PAHs and large aliphatics and some branched compounds.
M	Bioaccumulation potential		Low for light distillates; moderate-to-high for diesel and fuel oils.
M	Toxicity/adverse effect potential		Acute EC_{50}s generally 1-100 mg/L. However chronic effects observed at concentrations considerably lower.

3.9.1 Petrol

Petrol is a mixture of aliphatic hydrocarbons (alkanes, such as hexane, and alkenes), enhanced by aromatic hydrocarbons such as toluene, benzene , xylene , naphthalene and ethyl benzene or various kinds of ethers or alcohols, to function as oxygenates or to increase octane ratings (iso-octane can be added directly as well for this purpose). New Zealand has comparatively strict petrol specifications by international standards. According to the New Zealand Petroleum Products Specifications Regulations 2002, regular and premium grade petrol may contain no more than 18 per cent olefins (alkenes), 42 per cent aromatics (incl. benzene), 1 per cent benzene, 1 per cent oxygenates (10 per cent, if ethanol), 2 mg/L manganese, 1.3 mg/L phosphorus, 150 mg/kg sulphur, and 5 mg/L lead. The environmental persistence of petrol in the open aquatic environment (eg, after spills), is on the order of days, but can be considerably longer in groundwater.

3.9.2 Diesel and fuel oil

Diesel fuel, jet fuel (kerosene), heating oil and marine diesel are higher-boiling petroleum distillate fractions than petrol, and contain a higher percentage of long-chain aliphatic hydrocarbons and polycyclic aromatic hydrocarbons. Fuel oils are largely similar in composition, in being a complex mixture of aliphatic and aromatic hydrocarbons. Home heating oil (fuel oil No. 2) and kerosene (fuel oil No. 1) are composed of 80 to 90 per cent aliphatics (alkanes = paraffins and cycloalkanes = naphthenes), 10 to 20 per cent aromatics (eg, benzene) and 1 per cent olefins (eg, styrene and indene). Kerosene (Fuel oil No. 1) is a lighter distillate consisting primarily of hydrocarbons in the C9 to C16 range. Fuel oil No. 2 is heavier, with hydrocarbons in the C11 to C20 range. Diesel fuels are essentially a mixture of fuel oils No. 1, No.2 and

No. 4 (marine diesel), and are dominated by hydrocarbons in the C10 to C19 range. Diesel contains approximately 64 per cent aliphatic hydrocarbons, 1 to 2 per cent olefins, 35 per cent aromatic hydrocarbons, as well as additives. The PAH content in diesel, kerosene and heating oils is generally less than 5 per cent. Marine diesel (fuel oil No. 4) contains up to 15 per cent residues from the distillation process and is generally more complex in composition and higher in impurities. Marine diesel is less volatile than regular diesel and may contain more than 5 per cent polycyclic aromatic hydrocarbons and up to 4 per cent sulphur. The majority of compounds in diesel and kerosene have low environmental persistence of several days to weeks, due to their high volatility (Table 17). However, PAHs can persist in the environment for months or years. Furthermore, despite high physical volatility and degradability, the biodegradability of diesel oil residues is very low. Bulk diesel fuel has a moderate-to-high bioaccumulation potential (log K_{OW} 3.3 to 7.1; ASTDR database) and moderate acute toxicity to aquatic organisms, with EC_{50}s on the order of 20 to 50 mg/L to fish and algae. However, chronic adverse effects on marine benthos (reductions in abundance) have been observed at concentrations of 90 ppb (= 90 μg/L) by Oviatt et al. (1982).

Table 17

Relative persistence of various petroleum products in the aquatic environment following a spill; relative ranking with "1" being least persistent to "1600" being extremely persistent. Adapted and modified from Watts et al. (2004). Note that the qualitative persistence ratings in the third column relate primarily to the volatility and physical presence of bulk petroleum product spills, rather than the biodegradability and persistence of individual compound classes (such as BTEX, PAHs etc.).

Petroleum product	Relative persistence ranking	Persistence time scale of oil spill	Biodegradability and persistence of individual compounds
Petrol (gasoline)	1	Days	Weeks-months M
Jet fuel (kerosene)	2		
No. 2 fuel oil and diesel	8		
Lube oils	55	Weeks	Months-years
Light crude oil	320	Months	Years H
No. 6 fuel oil	400		
Medium crude oil	450		
Heavy crude oil	590	Years	Decades H
Residual asphaltenes	1600		

3.9.3 BTEX

The abbreviation BTEX stands for benzene, toluene, ethylbenzene, and xylenes, which constitute the predominant aromatic fraction of petrol (next to PAHs). Among these, toluene is usually the dominant compound. Ethylbenzene is also an important intermediate in the production of tyrine (vinyl benzene), used for the production of polystyrene. Next to the four compounds, trimethylbenzene and naphthalene may also be present in the aromatic fraction. BTEX chemicals have log K_{OW} values less than three and tend to volatilise rapidly when exposed to air. However, when evaporation is impeded or where there is continuous discharge of these compounds into the environment (eg, leakage from production facilities, petrol stations or underground storage tanks) they can chronically contaminate soil and groundwater. BTEX compounds biodegrade on the time-scale of several weeks (degradation half-life 7-28d) under oxic conditions. Benzene, toluene, ethylbenzene, and xylene have adverse effects on the central nervous system of animals and are moderate toxic to many aquatic species (EC_{50} 1-100 mg/L; ESIS database). Furthermore, benzene is a known carcinogen, explaining its restricted use in petrol to 1 per cent.

3.9.4 Fuel additives

Petrol and diesel additives have the purpose of increasing a fuel's octane rating or acting as corrosion inhibitors or lubricators. Additives include oxygenates, antioxidants, metal deactivators, corrosion inhibitors and dyes.

Oxygenates (alcohols and ethers)

Oxygenates improve the octane rating of a fuel and reduce engine misfiring (engine "knock"). Their percentage in NZ petrol is currently limited to 1 per cent. In the past, tetra-ethyl lead was used for this purpose, but has been banned in New Zealand since 1996 (nevertheless, currently sold petrol may still contain a very small amount of lead; 5 mg/L). The most commonly used fuel oxygenate is MTBE (methyl tert-butyl ether, or 2-methoxy-2-methylpropane). Alternatively, ETBE (ethyl tertiary butyl ether) and, increasingly, ethanol are used. In the case of ethanol, its percentage is permitted to be as high as 10 per cent. Other petrol oxygenates include other alcohols such as methanol, isopropanol and butanol, and various ethers, such as tertiary amyl methyl ether (TAME), tertiary hexyl methyl ether (eg, 2-methoxy-2,3-dimethyl butane (MDMB)), tertiary amyl ethyl ether (TAEE) and diisopropyl ether (DIPE). All of these compounds have relatively high volatility, low bioaccumulation potential, and cause primarily narcotic toxicity at high concentrations (>100 mg/L). Their biodegradability varies strongly, from readily biodegradable within days (ethanol) to very slow biodegradability (>six months) for MTBE. MTBE contamination in drinking water aquifers has been a concern in the United States, and has lead to a phasing out of MTBE since 2006 in favour of other oxygenates, such as ETBE.

Antioxidants and stabilisers

Antioxidants contained in petrol reduce corrosion and fuel degradation. They are commonly low molecular weight aromatic hydrocarbons, such as 2,6-di-tert-butylphenol (2,6-DTBP), 2,4-dimethyl-6-tert-butylphenol, p-phenylenediamine and derivatives or ethylenediamine (Table 18).

Table 18

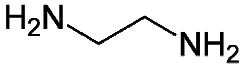
Common antioxidants used in fuels, greases and waxes. (Source: www.wikipedia.org.)

Compound	Applications
N,N'-di-2-butyl-1,4-phenylenediamine	Turbine and transformer oils, hydraulic fluids, waxes and greases.
N,N'-di-2-butyl-1,4-phenylenediamine	Low temperature oils.
2,6-di-tert-butyl-4-methylphenol	Turbine oils and transformer oils, hydraulic fluids, waxes, greases, and petrol.
2,4-dimethyl-6-tert-butylphenol	Jet fuels and petrol.
2,4-dimethyl-6-tert-butylphenol	Jet fuels and petrol.
2,4-dimethyl-6-tert-butylphenol and 2,6-di-tert-butyl-4-methylphenol	Jet fuels and petrol.
2,6-di-tert-butylphenol	Jet fuels and petrol.
Ethylenediamine	Petrol, corrosion inhibitor.

In addition to being a fuel additive, ethylenediamine (Figure 18) is used in large quantities for production of many industrial chemicals, due to its high reactivity with acids and amines. It is an important precursor to chelating agents like EDTA (ethylenedinitrilotetraacetic acid), the laundry bleaching activator tetra acetyl ethylene diamine (TAED), chemicals for colour photography developing, lubricants for the moulding and processing of plastics, carbamate fungicides, binders, adhesives, fabric softeners, surfactants, curing agents for epoxies, and dyes. It is highly water soluble, has low bioaccumulation potential (log K_{OW} ca. -1.3) and degrades rapidly (55 per cent after 10d). While it is alkaline, its toxicity to aquatic organisms is very low (>1000 mg/L).

Figure 18

Chemical structure of ethylenediamine.



Of the three isomers of phenylenediamine, two are widely used in industry (Figure 19): ortho-phenylenediamine (1,2-diaminobenzene) is used as a fuel additive, but also in the production of fungicides, corrosion inhibitors, various pigments and some pharmaceuticals. The isomer m-phenylenediamine (1,4-diaminobenzene) is used in the production of plastic composites and polymers, rubber products, and many types of dyes and pigments, including hair dye.

Figure 19

Chemical structure of m-phenylenediamine and 0-phenylenediamine.

Antiknock agents

In replacement of tetra-ethyl lead, no longer used in New Zealand, a variety of other compounds are used as anti-knock agents in petrol: first and foremost is toluene, followed by isooctane. Other agents include organo-metal compounds such as ferrocene ($Fe(C_5H_5)_2$), and methylcyclopentadienyl manganese tricarbonyl (MMT), the latter of which is used in Australia but not New Zealand. Ferrocene is also used in diesel fuel for reducing soot formation.

Detergents and deposit-control additives

Some petrol manufacturers have started marketing fuels with detergent additives to reduce deposit build-up in the engines (eg, "Techron", patented by Chevron), promising better engine performance and cleaner emissions. Compounds such as Techron are polyether amines, large organic molecules, in which primary amino groups are attached to the terminus of a polyether backbone.

Other fuel additives

Other compounds added to petrol to improve optical properties, handling or engine performance include:

- Fuel dyes (eg, Solvent Red 24, Solvent Red 26, Solvent Yellow 124, Solvent Blue 35.
- Nitromethane (used in drag racing to increase engine power).
- Butyl rubber (as polyisobutylene succinimide, detergent to prevent fouling of diesel fuel injectors).
- Ferox (catalyst additive that increases fuel economy, cleans engine, lowers emission of pollutants, prolongs engine life).
- Ferrous picrate (diesel additive to improve combustion and reduce soot formation).
- Silicones (anti-foaming agents for diesel, damage oxygen sensors in gasoline engines).
- Ethylene glycol.

3.10 Tyres and automobile products

Table 19

Environmental hazard profile for tyres, engine oil, lubricants and other automotive fluids.

Qualitative environmental hazard rating	16	**Reason for ranking**
H	Persistence/environmental concentration	Vulcanisation accelerators; rubber polymers.
M	Bioaccumulation potential	Moderate for TPH, vulcanisation accelerators (benzothiazoles, sulphenamides, thiuram), detergents and anti-wear additives.
M	Toxicity/bioactivity	Moderate for TPH, anti-wear additives and most vulcanisation accelerators (EC_{50} typically 1-10 mg/L). High for thiuram (vulcanisation accelerator).

Innumerable chemicals are used in the manufacture and operation of automotive vehicles. Whereas the majority of materials remain locked in the vehicle's body and componentry throughout the vehicle's operational lifetime, some components such as tyres, brake liners, engine oil, hydraulic fluid and coolants undergo continuous wear and tear and incremental release into the environment. Tyres are one of the main wearing components, with a product lifetime of one to several years before needing replacement.

During its lifetime a tyre loses approximately 20 per cent of its mass due to abrasion. According to information from the U.S. Rubber Manufacturers Association, approximately 281 million scrap tyres were generated in the United States in 2001, equating to approximately 5.7 million tons. With a population of 285 million, this equates to roughly one scrap tyre per inhabitant. Roughly 84 per cent of scrap tyres are derived from passenger cars, and 14 per cent from light to heavy trucks (1 per cent due to other heavy equipment). Assuming similar patterns of vehicle ownership and use, New Zealand, with a population of roughly four million, is likely to generate on the order of four million scrap tyres per year, with Auckland estimated to contribute roughly one third of this (1.3 million).

Tyres are made up of a variety of compounds, the foremost being rubber and fillers, summarised in Table 20. The category "other additives" in the table below includes silica and phenolic resin (acting as reinforcing chemicals, in addition to carbon black), various oils (aromatic, naphthenic, paraffinic, acting as tackifiers and softeners), fabric (eg, polyester, used for strengthening), petroleum waxes and fatty acids (used as anti-degradants), pigments (eg, zinc oxide, titanium dioxide; for optical properties), accelerators and activators (such as benzothiozoles, sulphur and sulphur compounds and zinc oxide) and adhesion promoters (eg, brass and cobalt salts).

Table 20

Average composition of passenger car and truck tyre. (Source: Rubber Manufacturers Association website, USA www.rma.org.)

Compound	Percent of total weight
Natural rubber	14%
Synthetic rubber (BR and SBS)	27%
Carbon black	28%
Steel wire	14-15%
Other additives: fabric, fillers, accelerators, antiozonants	16-17%
Average weight (new)	Car 11.3 kg (25 lbs) Heavy Truck 54.4 kg (120 lbs)
Average weight (scrap)	Car 9.1 kg (20 lbs) Heavy Truck 45.4 kg (100 lbs)

In Auckland, scrap tyres are disposed of through a combination of landfill and recycling. In contrast, in the United States, the majority of states no longer allow disposal of scrap tyres to landfill. Thus, the majority of scrap tyres get recycled, either for energy generation or for re-use. Of 281 million scrap tyres produced in the U.S. in 2001, roughly 77 per cent went to market, with the remainder being stockpiled. Of the 218 million tyres going to market, roughly 50 per cent (115 million) were used for fuel generation (in cement kilns, pulp and paper mills, and industrial and utility boilers), whereas 15 per cent were processed into ground rubber and 4 per cent were stamped into new products. An emerging market for recycling scrap tyres is their use in rubber-modified asphalt, as used in California, Arizona and in the UK.

Only one tyre recycling business operates in Auckland. According to the operator's website, recycled, shredded tyres are used for erosion control, as a sub-base for private roads, for surface water diversion, for embankment retention, sports turf-management, for horse arena surfaces and as a backstop for firing ranges. Future uses of finely ground scrap tyres (crumb) for road-building and for the manufacture of rubber bollards and road dividers are also being considered in New Zealand. Furthermore, re-use as a fuel (by catalysed pyrolysis) is being considered, but is currently not in effect.

3.10.1 Rubber and rubber additives

Rubber-like compounds are used in large volumes in the automotive industry and for other consumer applications (eg, footwear and adhesives). Synthetic and natural rubbers are very large polymers (called "elastomers"), which are produced by cross-linking the rubber monomers, usually by using sulphur compounds in a process called vulcanisation. Due to their large molecular weight (>100,000) most rubber polymers are too large to bioaccumulate in organisms to any measurable extent and can be considered toxicologically inert. Nevertheless, rubber products are persistent, high-production volume materials with large loadings into the environment. Furthermore, they contain a variety of additives with more pronounced toxicity and bioaccumulation, as described below.

Styrene butadiene rubber (SBR)

Styrene butadiene rubber is a copolymer of butadiene (ca. 76 per cent) and styrene (ca. 24 per cent) and is the most widely used synthetic rubber. It is predominantly used in tyre treads (and re-treads), but also in mats, rolls and gaskets. Next to automotive applications SBR is also widely used in footwear (shoe soles), sponge articles, rubber toys, and adhesives. SBR is also suitable for asphalt modification.

Polybutadiene rubber (BR)

Polybutadiene (BR) is the second largest volume synthetic rubber produced, after styrene-butadiene rubber (SBR). The major use of polybutadiene is in tyres (for treads and sidewalls), due to its excellent abrasion resistance (good tread wear). Other flexible car parts like belts, hoses, and gaskets are also made from polybutadiene rubber.

Acrylonitrile butadiene rubber (NBR)

Nitrile rubber (NBR) is a copolymer of acrylonitrile and butadiene. In automobiles, NBR is used in fuel and oil handling hoses, seals and grommets, and water handling applications. NBR is also used in industry in hydraulic hoses, conveyor belting and seals for all kinds of plumbing and appliance applications.

Hydrogenated nitrile butadiene rubber (HNBR)

Hydrogenated nitrile butadiene rubber is an extremely durable and heat-resistant rubber that is used in the automotive industry for static seals, hoses, and belts because of its resistance to attack by common automotive fluids.

Polyisoprene rubber (“natural rubber”)

Polyisoprene is the main component of natural rubber (derived from gum trees) and synthetic polyisoprene rubber. Synthetic polyisoprene is used in a wide variety of applications requiring high tensile strength, good resilience, good tack as well as low water swell. For example, black-loaded polyisoprene is used in tyres, motor mounts, pipe gaskets, shock absorber bushings and many other moulded goods. Mineral filled polyisoprene rubber is used in footwear, sponges and sporting goods. Pure polyisoprene is used in rubber bands and old-type baby bottle nipples.

Butyl rubber

Butyl rubber, also known as polyisobutylene is a copolymer of isobutylene (2-methyl-1-propene) with a small amount of isoprene. Structurally, polyisobutylene resembles the plastic polypropylene. Being gas-impermeable, it is used for tyre inner tubes and inner liners of balls. However, it is also widely used in adhesives, agricultural chemicals, fibre optic compounds, caulks and sealants, cling film, electrical fluids, lubricants (2 cycle engine oil), paper and pulp, personal care products, pigment concentrates, and as a gasoline/diesel fuel additive. Butyl rubber in tyres is commonly halogenated (halobutyl), either chlorinated or brominated. Butyl rubber is commonly vulcanised by elemental sulphur or thiuram or thiocarbamates. However for halobutyl, zinc oxide is commonly used. Butyl rubber is added in small amounts to engine oil to minimise generation of oil mist, and as a fuel additive, where it conveys detergent properties. Added to diesel fuel, it minimises fouling of fuel injectors, leading to reduced hydrocarbon and particulate emissions. Even though exact fuel additive formulations are trade secrets, polyisobutylene is usually blended with other detergents and additives to make a "detergent package" that is added to petrol and diesel fuel to resist build-up of deposits and reduce engine knock.

Styrenic block polymers

Styrenic block polymers (SBC) are a hybrid rubber-plastic material (“thermoplastic elastomer”) widely used in adhesives, sealants, coatings, and in footwear. They are also used to enhance grip, feel, and appearance in automotive products, toys, personal hygiene products, and packaging. SBC polymers consist of two “hard” polystyrene end blocks and one soft, elastomeric midblock (polybutadiene, polyisoprene, either or not hydrogenated).

Ethylene-propylene rubber

Ethylene-propylene rubbers and elastomers (also called EPDM and EPM) are a slow production volume rubber class that is finding increasing use because of its versatility. EPDM is used in automotive weather-stripping and seals, glass-run channels, radiator, garden and appliance hoses, tubing, belts, electrical insulation, roofing membrane and motor as a motor oil additive. Ethylene-propylene rubbers use the same monomers as polyethylene (PE) and polypropylene (PP) plastics, by combining these in a random manner to produce a rubbery polymer.

Polychloropene rubber (Neoprene)

Polychloropene, commonly known by its trade name “Neoprene”, is a specialty elastomer used for rubber applications, but also for adhesives, latex applications (dipped gloves), moulded foam and improvement of bitumen. It is especially resistant to oil and used in automobiles in moulded parts, cables and transmission belts. Main manufacturers of polychloropene are DuPont and Bayer.

Polyolefin elastomers

Polyolefin elastomers (or POEs) are a relatively new class of polymers. Most commercially available POEs are copolymers of either ethylene-butene or ethylene-octene. In the last decade, POEs have emerged as a leading material for automotive exterior and interior applications. They are also used for wire and cable coatings, extruded and moulded goods, films, medical goods, adhesives, footwear, and foams, replacing a number of generic polymers including ethylene propylene rubbers, ethylene vinyl acetate (EVA), styrene-block copolymers and polyvinyl chloride (PVC).

Fluoroelastomers

Fluoroelastomers (FKM polymers) are a class of synthetic rubber used in seals, o-rings, gaskets and fuel hoses, providing very high levels of resistance to chemicals, oil and heat, while providing useful service life above 200°C. Most fluoroelastomers are either fluorine co-polymers or ter-polymers that are cured by either bisphenol or peroxide.

Silicone rubber

Silicone rubber is a type of polysiloxane with elastic properties (see Section 3.4). The majority of silicone rubbers vulcanise at high temperatures and are also known as solid silicone and high consistency rubber. Silicone rubbers have a wide number of applications spanning the automotive, medical and household sector. Softer silicone is also widely used for caulking and as a lubricating oil (see Section 3.4). The high utility of silicone rubbers is largely attributable to their wide temperature stability, high biocompatibility, inertness and low flammability. Silicone rubber is considered to be toxicologically inert.

Vulcanisation accelerators

Modern tyre rubber is vulcanised using accelerators. The most common ones are benzothiazoles (eg, 2-mercaptobenzothiazole (MBT), sulphenamides and diphenyl guanidine. Other rubber vulcanisation accelerators include dithiocarbamates and thiuram sulphides (Table 21). Only incomplete information is available on the ecotoxicological characteristics of many of these chemicals. The compound 2-mercaptobenzothiazole is moderately toxic to aquatic organisms (EC_{50} 1-10 mg/L to fish, EPA ECOTOX database) but unlikely to bioaccumulate to any great extent (log K_{OW} approximately 2.4). It has moderate persistence in the aquatic environment (15 per cent degradation after seven days), but breaks down rapidly in the presence of sunlight. This is likely to limit accumulation of MBT in the environment. Similar arguments are likely to apply to other benzothiazoles as well.

Zinc diethyldithiocarbamate is highly toxic to algae, crustaceans and fish (EPA ECOTOX database). It is structurally-related to the pesticide Ziram (dimethyl dithiocarbamate). It has a log K_{OW} of 7.04 and an estimated BCF of 100, suggesting moderate bioaccumulation potential. It degrades relatively quickly, namely, 50 per cent after five days at pH 7.0 (50 per cent after 18 days at pH 8.0).

Diphenylguanidine is moderately persistent (18 per cent degradation after 1000 h = 41 days). Its partition coefficient of log K_{OW} = 3.1 suggests a low tendency to bioaccumulate. It is moderately toxic to aquatic organisms with an EC_{50} of 1 to 10 mg/L for algae and various fish species and 10 to 60 mg/L for water fleas.

Tetramethylthiuram monosulphide (thiuram) is a highly persistent chemical (no biodegradation in sewage after 28 days), with an estimated log K_{OW} of 3.2. It has moderate acute toxicity to fish and algae, with EC_{50}s of 1 to 10 mg/L. However, it exerts chronic toxicity to fish (*Oncorhynchus mykiss* and *Brachydanio rerio*; seven to 60 days) and crustacea (*Daphnia magna*, 21 days) at concentrations of only 0.01 to 0.2 mg/L (ESIS IUCLID database).

The compound 2-morpholinothiobenziothiazole (= N-(oxydiethylene) benzothiazole-2-sulfenamide) is highly persistent (no degradation after 28d), moderately toxic (EC_{50} 1-5 mg/L) and moderately bioaccumulative (log K_{OW} 3.5; estimated BCF 100).

Table 21

Vulcanisation accelerators. Source: Alliger & Sjothun (1964).

Compound	Abbreviation
2-Mercaptobenzothiazole	MBT
2-2'-Dithiobisbenzothiazole	MBTS
N-Cyclohexylbenzothiazole-2-sulfenamide	CBS
N-t-Butylbenzothiazole-2-sulfenamide	TBBS
2-Morpholinothiobenzothiazole	MBS
N-Dicyclohexylbenzothiazole-2-sulfenamide	DCBS
Tetramethylthiuram monosulphide	TMTM
Tetramehylthiuram disulfide	TMTD
Zinc diethyldithiocarbamate	ZDEC
Diphenylguanidine	DPG
Di-o-tolyolguanidine	DOTG
Phenolics	-
Benzoquinone derivatives	-
Metal oxides	-
Organic peroxides (eg, cumene hydroperoxide)	-

3.10.2 Engine oil, lubricants and automotive fluids

Engine oil

Most engine (motor) oils are made from heavier petroleum hydrocarbon distillates derived from crude oil, with additives to improve lubricating properties. These are often referred to as “mineral” engine oils. In contrast, “synthetic” engine oils are based on either poly-alpha olefins (PAO), polyol esters, polyalkylene glycols (PAG oils) or perfluoropolyalkylethers (PFPAEs). Most everyday engine oils are “mineral” oils (ie, petroleum distillates) even though they are often marketed as being “synthetic”.

A typical “mineral” motor oil consists of approximately 80 to 90 per cent petroleum distillates (heavy paraffinic, solvent-dewaxed and naphthenic), up to 20 per cent detergents and solvents (including naphthalene, xylene, acetone and isopropanol), and various types of “anti-wear additives”, such as PTFE (“Teflon”), methacrylate polymer, zinc dialkyldithiophosphate (ZDDP), and molybdenum disulfide, with sometimes unproven performance-enhancing characteristics. For example, the alleged benefit of PTFE in engine oil has been the subject of recent controversy and has led to a decline of its use in favour of ZDDP. ZDDP is an oil-soluble organophosphate that is marketed as providing corrosion protection and antioxidant properties. Tricresyl phosphate (TCP), also used as a flame retardant (Section 3.6) is used for high pressure, high temperature operations (such as turbine engines) but is also found in some crankcase oils and hydraulic fluids. Other lubricating anti-wear agents (not commonly used in motor oils) include chlorinated paraffins, trichloromethyl phosphine acids, organic esters of acetoxy-trichloroethyl phosphonic acid, trichloromethyl esters of phosphoric acid, trichloromethyl derivates of sulphur, trichloroacetoxy compounds, and esters or amine salts of chlorendic acid.

In terms of ecotoxicological hazard, discarded engine oil has a strong potential to foul water quality when poured into drains or discharged into water ways. Due to its hydrophobic nature, it will rapidly spread on the water surface (or in aquifers), diminishing gas exchange and affecting surface-dwelling biota (insects, water fowl). Upon evaporation and photodegradation, heavier petroleum fractions will clump and deposit to sediments, where they can smother benthic organisms at high concentrations and lead to increased biological oxygen demand. Contamination by motor oil is readily detectable in GC-FID analysis of total petroleum hydrocarbons (TPH), where it will show up as a broad band in the long-chain hydrocarbon region of the chromatogram (ie, C_{20}-C_{44}). High sediment TPH concentrations (>500 mg/kg) are correlated with adverse ecological effects. Several petrol additives, such as surfactants and anti-wear agents, have moderate environmental persistence and toxicity. For example zinc dialkyldithiophosphate (ZDDP= zinc salts of phosphorodithioic acid, O,O-di-C1-14-alkyl esters, zinc salts) is moderately toxic to aquatic organisms (EC_{50} 1-5 mg/L; ESIS database), having some structural similarity to the organophosphorus insecticide “dimethoate” (phosphorodithioic acid, O,O-dimethyl S-(2-(methylamino)-2-oxoethylyl) ester. The main toxic hazard from engine oil is, however, likely to emanate from the petroleum distillates.

Automatic transmission fluid

Automatic transmission fluid is a highly refined mineral oil that is optimised to meet the performance demands in gearboxes (ie, balancing friction, torque conversion and gear lubrication requirements). A typical transmission fluid contains ca. 85 to 95 per cent refined petroleum distillates, 10 to 25 per cent antioxidants and detergents, up to 4 per cent viscosity improvers, up to 4 per cent corrosion inhibitors (eg, zinc dialkyldithiophosphate, ethoxylated long-chain alkylamines and metal sulphonates), and <1 per cent dye. In terms of ecological hazard, it is comparable to engine oil, although the percentage of corrosion inhibitors is generally higher.

Other automotive fluids

Brake fluid and power steering fluid

Hydraulic fluids such, as brake fluid and power steering fluid, differ from engine oils in their primary function of transferring pressure rather than lubrication. However, they often contain similar ingredients. Brake fluids are composed of either castor oil; mineral oils, glycol esters or ethers; synthetic oils, or silicone oils. The majority of automobiles use mineral-based power steering fluid and glycol-ester or ether based brake fluids. For example, the MSDS sheet for an unnamed brake fluid product, lists 0 to 3 per cent glycol, 17 to 20 per cent diethylene glycol, 0 to 3 per cent 2-(2-methoxyethoxy)ethanol, 1 to 7 per cent diethylene glycol ethyl ether, 0 to 3 per cent triethylene glycol, 4 to 12 per cent diethylene glycol monobutyl ether, 3 to 8 per cent ethoxytriglycol, 15 to 30 per cent butoxytriglycol, 8 to 11 diethylene glycol monopropyl ether, 6 to 9 per cent polyethylene ethers, and 6 to 11 per cent hexyl poly(oxyethylene) ether. Some brake fluids also contain alkylamines, presumably acting as detergents, and other "trade secrets". Power steering fluid is typically composed of refined heavier mineral oils, and often contains anti-wear additives, such as zinc dialkyldithiophosphate (ZDDP).

Antifreeze

Antifreeze used in automobiles is commonly ethylene glycol, and sometimes propylene glycol. Ethylene glycol has very low toxicity to aquatic organisms (EC_{50} >1000 mg/L), and does not bioaccumulate (log K_{OW} -1.9). It is highly water-soluble and biodegrades readily (100 per cent after 20 days in domestic sewage). The primary hazard from ethylene glycol is likely to be accidental ingestion by humans and animals due to its sweet taste. Propylene glycol is sometimes marketed as a "non-toxic" alternative.

Next to its use as antifreeze (25 per cent of the production), ethylene glycol is also used as a hydraulic brake and thermal exchange fluid, as a humidifying and plasticising agent (food and tobacco industry), dehydrating agent, softener for textiles, solvent (for dyes and inks) and as a synthetic intermediate in chemical production.

3.10.3 Brake pads

A review commissioned by MfE of organic and inorganic substances in brake pads estimates that there are more than 400 different types of brake pads on the New Zealand market (Gadd & Kennedy 2000, Kennedy & Gadd 2000). Until 20 years ago, the majority of brake pads were dominated by asbestos. Nowadays, composite materials prevail, which can be classified into three main categories, semi-metallic, organic and non-asbestos organic. The frictional material is commonly metal powder, carbon fibre, glass fibre or kevlar fibre held together by an organic matrix consisting of phenolic resins, rubber or other binders and fillers. Graphite is sometimes used as a frictional additive. Fillers are based on clay and calcium. Given the inertness of the organic matrices used, the environmental hazard emanating from brake pads concerns primarily the metal frictional material.

3.11 Roading materials

Table 22

Environmental hazard profile of roading materials.

Qualitative environmental hazard rating 16		**Reason for ranking**
M	Persistence (excl. PAHs in coal tar)	Surfactants: persistent, but concentrations generally low. Asphaltenes: high.
H	Bioaccumulation potential	Surfactants, adhesion promoters (excluding asphaltenes).
M	Toxicity/adverse effect potential (excl. PAHs in coal tar)	Surfactants and extender oils.

Modern sealed road pavements are essentially a mixture of inorganic aggregate (gravel and sand), contained in a binder, such as asphalt or cement. In addition to these main ingredients, a variety of other chemicals are used in road construction and for road maintenance, ranging from soil stabilisers, dust-suppressing agents ("palliatives"), to asphalt additives such as primers, surfactants, anti-strip agents and paints.

3.11.1 Asphalt (bitumen)

There is a common confusion between the terms tar, bitumen and asphalt. Tar is the result of the distillation of coal (and therefore commonly called "coal tar"), while bitumen and asphalt are synonyms for the residue produced from the distillation of crude oil. While being synonymous to bitumen, the term "asphalt" is often restricted to a type of bitumen-based pavement called asphalt concrete (see below). Since the 1970s, crude-oil based bitumen has been the primary binder for sealed road construction in New Zealand. Most residential, "low-traffic" roads in Auckland are surfaced with chip-seal (sometimes also called "sprayed seal") due to its cost-effectiveness. Chip seal is constructed by spraying a thin base of bitumen onto an existing pavement and then embedding finely graded aggregate into it. It makes for a relatively rough pavement of short lifetime. A top layer or polymer additives can improve the properties of the bitumen binder and increase the pavement's lifetime, by preventing cracking and increasing stone retention.

Higher-volume roads, such as main arteries or motorways, are constructed of asphalt concrete (commonly called "asphalt"). Several types of asphalt concrete are distinguished:

- Hot mix asphalt concrete (HMAC or HMA) is produced by heating the asphalt to decrease its viscosity and drying the aggregate to remove moisture from it prior to mixing. HMAC is the form of asphalt concrete most commonly used on highly trafficked roads such as those on major highways and airfields ("tarmac"). It contains relatively few additives.

- Warm mix asphalt concrete (WMA or WAM) is produced by adding zeolites, waxes, or asphalt emulsions to the mix. This allows significantly lower mixing and laying temperatures, saving fuel costs and leading to more rapid availability of the surface for use.
- Cold mix asphalt concrete is produced by emulsifying the asphalt in water with detergents prior to mixing with the aggregate. It is also called slurry sealing. While in its emulsified state, the asphalt is less viscous and the mixture is easy to work and compact. The emulsion will break after enough water evaporates and the cold mix will set similarly to HMAC. Slurry sealing with cold mix is finding increasing use in New Zealand for main road construction.
- Cut-back asphalt concrete is produced by dissolving the binder in kerosene or another lighter fraction of petroleum (eg, naphtha) prior to mixing with the aggregate. While in its dissolved state, the asphalt is less viscous and the mix is easy to work and compact. After the mix is laid down the solvent fraction evaporates.
- Mastic asphalt concrete (= sheet asphalt) is produced by "cooking" bitumen in a kiln until it reaches the desired viscosity. Mastic asphalt concrete is used for footpath and road applications.

While the manufacture of asphalt is associated with the release of volatile (and often odorous) "nuisance" organic compounds into the environment (light petroleum fractions), asphalt itself is a rather inert material, once laid down, with an environmental persistence of years to decades. Compared to coal tar it contains 10,000 times less PAHs, and also fewer other leachable organic compounds, such as phenols. Most environmental effects from road-building are therefore related primarily to earthworks t (eg, turbidity generation) and the use of non-asphalt materials, such as detergents, soil stabilisers and residual coal tar binders. In recent years, blends of asphalt and of phenolic tars (a large tonnage by-product from phenol and acetone production) are being marketed overseas, claiming to enhance physical characteristics of regular asphalt. However, it is unknown to which extent such phenolic-asphalt blends are utilised in New Zealand.

3.11.2 Coal tar

In contrast to bitumen, coal tar is a product from coal distillation in gasworks. Until the 1970s (ie, before the commissioning of the Marsden Point Oil Refinery), coal tar was widely used throughout Auckland and the rest of New Zealand (up to 1985 in Christchurch) as a road-binder. Coal tar is a very durable, hydrophobic material, but contains high concentrations (up to 20 per cent by weight) of polycyclic aromatic hydrocarbons (PAHs), which are persistent, bioaccumulative and toxic, as well as carcinogenic. Coal tar also contains high concentrations of phenols. Even though modern-day road seals are based on bituminous binders, there are still numerous "coal tar-era" roads in Auckland and throughout New Zealand that have not been reconstructed and that contain PAH-rich coal tar binders underneath the topmost asphalt layer, or buried in roadside soils. In older Auckland catchments (eg, Westmere, St Lukes, Western Springs), this “coal tar legacy” is suspected to be the primary source of ongoing PAH inputs into the environment (Ahrens, M. & Depree 2006).

In recent years, there has been a “revival” of coal tar-based products overseas for re-sealing parking lots and driveways (Mahler et al. 2005). In the U.S., for example, coal tar “black top” is applied as a durable sealcoat on parking lots, with subsequent marked increases in PAH run-off concentrations. It is conceivable that coal tar based products might also be reintroduced to the New Zealand market.

With an increasing trend in New Zealand (and overseas) towards recycling of old road pavements, there is an elevated risk of re-mobilising old, deeply-buried coal tar seal layers, by re-applying them in surface road layers and potentially releasing previously “locked-up” PAHs and phenols. The European Asphalt Pavement Association (EAPA) recommends that reclaimed asphalt with more than 0.1 per cent coal tar content should be considered hazardous waste (European Asphalt Pavement Association 2005).

3.11.3 Soil stabilisers and dust-suppressing agents

Soil stabilisers

Soil stabilisers are added to soils to improve their weight-bearing capacity and diminish swelling and shrinking of the pavement base by removing inter-molecular water. Most of the marketed formulations are proprietary, but commonly used materials include lime (calcium oxide), ion exchange resins (eg, silicates), sulphur-based compounds (eg, lignosulphates or sulphonated limonene), and acrylic polymers. Enzymes are used as well. Soil stabilisers get applied on the surface of the pavement base or are pressure-injected into it. Their main mode of action is ionic exchange, displacing bound water from the clay minerals by other ions and reducing the clays’ ability to take up (or lose) water. Lignosulphates further prevent water uptake by making the surface more hydrophobic (more “oily”). Little information exists on the biological effects of soil stabilisers. From first principles, it may be assumed that any kind of ion exchange with clay is likely to involve pH changes (by release of H^+ ions). Lignosulphates are marketed as “environmentally friendly”.

Dust-suppressing agents

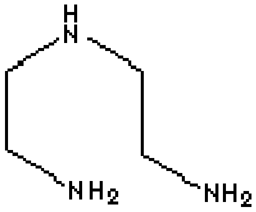
Dust suppressing agents are added to loose road base or unsealed roads to prevent resuspension of dust, by increasing the stickiness of the wearing surface. Commonly used materials include saponified pitch, lignosulphonates, anionic surfactants, acrylic polymers and waste oil (Robinson 2003). Insufficient information was available to assess potential ecological impacts of theses additives.

3.11.4 Asphalt additives

Asphalt additives include surfactants and anti-strip agents. For applying asphalt onto road surfaces and facilitating its adhesion to gravel, the viscosity and surface energy of the asphalt material needs to be reduced. This can be achieved either by heating, making a solution with a solvent ("cutback") or creating an asphalt-in-water emulsion that is stabilised by a dispersing agent (commonly a cationic surfactant). Anti-strip agents promote adhesion between the mineral aggregate and the asphalt. Asphalt emulsions are used for chip sealing, slurry sealing and cold-mix. Asphalt emulsions commonly contain up to 70 per cent asphalt and typically less than 1.5 per cent chemical additives. Asphalt additives include derivatives of higher molecular weight ethyleneamines and fatty acids. Examples of these include mono- and bis-amidoamines and imidazolines, such as diethylenetriamine (DETA, Figure 20), triethylenetetramine (TETA), tetraethylenepentamine (TEPA), aminoethylpiperazine (AEP), and complex mixtures of ethyleneamines. Another detergent for slow-setting asphalt emulsions is nonylphenol ethoxylate. TETA, DETA, TEPA and AEP, in addition to being used as asphalt additives, are also used as general surfactants, corrosion inhibitors, epoxy curing agents, lube and fuel oil additives, mineral processing aids and textile additives. DETA is furthermore used as a fabric softener and chelating agent, and as a catalyst for urethane and as a component in polymer resins. TEPA is furthermore used as a wood preservative and in the manufacture of carbamate insecticides, antihelminthics and psychoactive drugs. Diethylenediamine is the simplest cyclic ethyleneamine (C-4), called piperazine. Various types of rubber (eg, styrene butadiene rubber) from scrap tyres are suitable as asphalt modifiers (see Section 3.10).

Figure 20

Chemical structure of DETA, an asphalt surfactant and drying agent.



3.12 Building materials

Table 23

Environmental hazard profile of building materials.

Qualitative environmental hazard rating	16	Reason for ranking
H	Persistence	High for flame retardants and wood preservatives, but slow release.
M	Bioaccumulation potential	High for flame retardants.
M	Toxicity/adverse effect potential	High for wood preservatives.

Building construction uses vast amounts of raw materials – concrete, timber, brick, glass, various metals, as well as paints and plastic materials. Conversely, renovation and demolition of old buildings generates large quantities of refuse, and discarded construction materials constitute one of the biggest inputs to the urban waste stream and landfill volume. A large variety of chemicals find use in the building industry as solvents, foams, sealants, cements and coatings, for water-proofing or insulation purposes, or to protect against rot and unwanted pests. Many product and chemical classes are described in other sections of this report, such that their treatment in this section will be brief.

3.12.1 Soils

Building construction commonly involves a considerable amount of earthworks, such as levelling, infilling or re-contouring. Next to the increased likelihood of generating fine particulate run-off and elevated turbidity, at former agricultural or industrial sites there is the potential to remobilise soil-bound contaminants, such as pesticide residues or legacy chemicals. Pesticides, petroleum by-products and solvents are discussed in Sections 3.8, 3.10 and 3.14.

3.12.2 Treated timber

Vast amounts of timber are used in construction, of which the majority requires treatment to inhibit decay by fungi or insects. Timber treatment chemicals are discussed in detail in Section 3.16.

3.12.3 Resin composites and engineered wood products

A variety of composite materials are used in construction, for counter tops, shelving and flooring. These include phenolic and formaldehyde-based resins, such as melamine and various engineered wood products such as chipboard, MDF (medium-density fibreboard), hardboard and plywood.

Melamine and Formica

Many counter tops are made of Formica or similar resin-based composites. Formica is a plastic laminate of paper or fabric, bound together by melamine resin (a mixture of a triazine amine and formaldehyde). Formaldehyde and phenol-based resins are discussed in greater detail in Section 3.2.

Fibreboard

Fibreboard is an engineered wood product that is made out of wood fibres held together by resin. Three types of fibreboard are commonly distinguished: particle board (= chipboard), medium-density fibreboard (MDF) and high-density fibreboard (= hardboard). Fibreboard, particularly MDF, is heavily used in the furniture industry instead of conventional wood. In 2005, New Zealand produced 855,000 m^3 of fibreboard, most of which was MDF (822,000 m^3; FAOStat). Fibreboard has been controversial due to its formaldehyde resin content and the associated health risks. Chipboard is made from wood particles, wood chips, sawmill shavings, or saw dust, and a synthetic resin or other suitable binder, which is pressed and extruded. Particle board is cheaper, denser and more uniform than conventional wood and plywood and is made more attractive by painting or the use of wood veneers that are glued onto surfaces that will be visible (eg, kitchen counters). 240,000 m^3 of particle board was produced in NZ in 2005. Hardboard is similar to particleboard and medium-density fibreboard, but is denser and much harder because it is made out of exploded wood fibres that have been highly compressed. 9000 m^3 were produced in NZ in 2005. Hardboard is used in construction, furniture, appliances, automobiles and cabinetry. Tempered hardboard is made by adding an oil that becomes a polymer when the board is formed under high temperature and pressure, giving it more water resistance, hardness, rigidity and tensile strength. Hardboard is also used in construction siding.

Plywood

Plywood is made from thin sheets of wood veneer bonded under heat and pressure with strong adhesives, usually phenol formaldehyde resin. Plywood meant for indoor use generally uses less expensive urea-formaldehyde as a glue, which has limited water resistance, while outdoor and marine grade plywood are designed to withstand rot and use a water resistant phenol-formaldehyde glue to prevent delamination and to retain strength in high humidity. In 2005, 400,000 m^3 of plywood were produced in New Zealand (FAOStat). Plywood is used in any application that needs high quality wooden sheet material, resistant to cracking, breaking, shrinkage, twisting and warping.

3.12.4 Concrete

While concrete is primarily an inorganic building material, it can contain organic chemicals to improve its properties. Concrete consists of cement (commonly Portland cement), aggregate (generally gravel and sand, but increasingly also recycled aggregates from construction or fly-ash from power plants), water as well as admixtures, such as cement plasticisers (see below). Portland cement consists of a mixture of oxides of calcium, silicon and aluminium, made by heating limestone and clay, grinding it and adding gypsum. Other admixtures, added either as powder or fluids at the time of batching/mixing, confer to the concrete desirable handling characteristics. Admixtures typically comprise less than 5 per cent by mass of cement. The most common types of admixtures are:

- Accelerators, to speed up the hydration (hardening) of the concrete.
- Retarders, to slow the hydration of concrete, used in large or difficult pours where partial setting before the pour is complete is undesirable.
- Air-entrainers, to add and distribute tiny air bubbles in the concrete, which will reduce damage during freeze-thaw cycles thereby increasing the concrete's durability.
- Plasticisers and organic polymer-based superplasticisers, to increase the workability, allowing concrete to be placed more easily. They are particularly important when strong, water-less concrete is desired and are usually added at 2 per cent per unit weight of cement. Examples of concrete plasticisers are lignosulphonates (a by-product from the paper industry), sulphonated naphthalene formaldehyde or sulphonated melamine formaldehyde ("superplasticisers"), conveying a negative charge to cement particles which enhances electrostatic repulsion and dispersion. Newer generation plasticisers are based on polycarboxylic ethers. Sodium lignosulphonate is not acutely toxic to fish and shows moderate toxicity to molluscs (Pacific oyster LC50 40 mg/L). Insufficient data exist to rank it as an endocrine disruptor, developmental toxin or neurotoxin (PAN Pesticides database).
- Pigments, to change the appearance of the concrete.
- Corrosion inhibitors, to minimise the corrosion of steel and steel bars in concrete.
- Bonding agents, to create a bond between old and new concrete.
- Pumping aids, to improve pumpability, thicken the paste, and reduce dewatering of the paste.

3.12.5 Panels and flooring

Linoleum

Linoleum is a floor covering made from solidified linseed oil (linoxyn) in combination with wood flour or cork dust over a burlap or canvas backing. Pigments may be added for aesthetic purposes. Modern day "lino" flooring is actually not linoleum but PVC.

PVC flooring

Linoleum as a floor covering has been largely replaced with polyvinyl chloride, which has similar properties of flexibility and durability, but greater brightness and translucency and low flammability. PVC is discussed in detail in Section 3.1.

Ceiling panels

Ceiling panels are fabricated from a variety of materials, including perlite (an expanded volcanic glass), mineral wool, plastic, tin, aluminium, and composites of pulp or recycled paper.

Plasters

Plaster of Paris, or simply plaster, is based on calcium sulphate hemihydrate (gypsum). It usually does not contain significant amounts of organic admixtures. Plaster is widely used in pre-fabricated panelling (GIB-board).

3.12.6 Plastics

Foams and sealants

Expanded polystyrene foam (EPS) is widely used as under-floor insulation. Polyurethane foams are used in furniture and beds, and silicone and other sealants are used for setting and insulating windows and bathroom fixtures. Foamed plastics usually contain flame retardants. EPS, foams and resins, sealants and flame retardants are discussed in Sections 3.1, 3.2, 3.4 and 3.6.

Other plastic building materials

Plastics such as PVC are widely used in construction, in pipes, spouting, flooring and siding (weatherboard). Of environmental concern are PVC plasticisers, although hard PVC usually contains none or only negligible amounts of these. PVC, other plastics and plasticisers are discussed in greater detail in Sections 3.1 and 3.5.

3.12.7 Paints, varnishes and wood-preservatives

The building sector is one of the main consumers of paints, which are discussed in greater detail in 3.2. Of environmental concern are old, lead-based paints and paint-stripping residues. Brush-on wood preservatives typically contain fungicides and insecticides, which are described in greater detail in Sections 3.14 and 3.16.

3.12.8 Metals

While not the topic of this review, large amounts of metal are used as building materials, in the form of reinforcement bars, galvanised and zincalume roofing, copper spouting and flashing. Corrosion of metals can be accelerated by contact with certain wood preservatives (eg, CCA) and exposure to mist, salt-laden air, as is typical for some areas in Auckland.

3.12.9 Paving materials

Driveways and footpaths are constructed from various materials, including brick, concrete, loose gravel and asphalt. Asphalt and asphalt additives are discussed in greater detail in Section 3.11.

3.13 Surfactants and other detergent additives

Table 24

Environmental hazard profile for surfactants.

Qualitative environmental hazard rating		**32**	**Reason for ranking**
H	Persistence		Cationic surfactants and perfluorinated surfactants: high. Most surfactants: moderate.
M	Bioaccumulation potential		Most surfactants: moderate. Fatty alcohols and perfluorinated surfactants: high.
H	Toxicity/adverse effect potential		Anionic surfactants: low-to-moderate; Cationic surfactants: moderate-to-high Nonylphenols: high and oestrogenic.

3.13.1 Detergents

The definition of a detergent is a mixture of compounds to assist with cleaning. A typical detergent product will contain all or most of the following ingredients:

- Surface-active compounds (“surfactants”; sometimes also called “tensides”), to solubilise grease and wet surfaces.
- Inorganic abrasives, to scour.
- Stabilisers, to modify or maintain pH or to affect performance or stability of other ingredients.
- Acids or bases (“caustics”), for de-scaling and destroying dirt.
- Water softeners, such as EDTA, to counteract the effect of "hardness" ions (such as Mg and Ca).
- Oxidants, for bleaching and oxidation of dirt.
- Non-surfactant materials, to keep dirt in suspension.
- Enzymes, to digest proteins, fats, or carbohydrates or to modify fabric feel.

- Ingredients that stabilise or counteract foam.
- Other ingredients, to modify aesthetic properties, such as optical brighteners, fabric softeners (in laundry detergents), colours and fragrances.

3.13.2 Surfactants

Surfactants usually make up the highest percentage of active ingredients in a detergent formulation. In addition to their use in detergents, surfactants are used in many other domestic or commercial applications requiring mixing, wetting, and dispersion of substances with limited water solubility. Thus, surfactants are important ingredients in products such as hair shampoos, carpet cleaners, emulsifiers, adhesives, paints, waxes, herbicides and insecticides (to allow penetration of the pesticide through the water-repellent cuticle of the pest organism), fire extinguishers, spermicides, fabric softeners and lubrication products (see Section 3.10).

Surfactants are amphiphilic molecules, consisting of a hydrophilic (water-friendly) and a hydrophobic (water-repellent) domain, typically a long-chain hydrocarbon. Surfactants are formally classified by the presence of charged groups in the hydrophilic domain of the molecule. Four types are usually distinguished: A **nonionic** surfactant has no charge groups in its head, whereas the head of an **anionic** or **cationic** surfactant carries a negative or positive charge, respectively. A surfactant molecule containing a head with two oppositely charged groups is termed **zwitterionic** (or **amphoteric**). Examples of the four types of surfactants are listed in Table 25.

Many commercial surfactants are made by ethoxylation of a fatty acid residue (ie, adding of an ether linkage by addition of an epoxide (= cyclic ether), such as ethylene oxide), rendering it more water-soluble. Thus, sodium laureth sulphate (an anionic surfactant) is made by ethoxylation of sodium dodecyl sulphate, and alkylphenol ethoxylate surfactant (a non-ionic surfactant) is made by ethoxylation of nonylphenol or octylphenol.

For assessing the bioaccumulation potential of surfactants, it should be noted that a physically meaningful log K_{OW} cannot be measured for these compounds due to their amphiphilic nature, but it can be modelled from molecular structure. Thus, all assessments based on partitioning coefficients should be considered only as rough estimates.

Table 25

Examples of the four main classes of surfactants.

Surfactant type	Description	Examples
Anionic	Often based on sulphate, sulphonate or caboxylate anions.	Sodium dodecyl sulphate (SDS) = sodium lauryl sulphate, Sodium laureth sulphate (SLES) =sodium lauryl ether sulphate, Linear alkylbenzene sulphonate (LAS), Soaps and fatty acids Perfluorinated surfactants (PFS).
Cationic	Often based on quaternary ammonium cations.	Benzalkonium chloride (BAC), Benzethonium chloride (BZT), Cetrimonium bromide (CTAB), Cetylpyridinium chloride (CPC), Polyethoxylated tallow amines (POEA).
Zwitterionic (amphoteric)	-	Dodecyl betaine, Dodecyl dimethylamine oxide, Cocamidopropyl betaine (CAPB), Coco ampho glycinate.
Nonionic	Based on alkylphenol ethoxylates (APEOs), alcohol ethoxylates (AEs), alcohol propoxylates, cocamides, fatty alcohols or alkyl polyglucosides.	Nonylphenol ethoxylates, Cocamide MEA, cocamide DEA, cocamide TEA, Cetyl alcohol, oleyl alcohol, Octyl glucoside, decyl maltoside.

3.13.3 Anionic surfactants

Anionic surfactants are the most widely-used type of surfactant for laundering, dishwashing liquids and shampoos. Being negatively charged when in solution, they are very effective in keeping the dirt away from fabrics, and removing residues of fabric softener from fabrics. Anionic surfactants are effective for oily soil cleaning and oil/clay soil suspensions. Their great disadvantage is that they interact with positively charged water hardness ions (eg, Ca^{2+} and Mg^{2+}), which can lead to partial deactivation. To prevent this, Ca/Mg sequestrants are added, called "builders" (eg, zeolites). The most commonly used anionic surfactants are classic soaps, alkyl sulphates, alkyl ethoxylate sulphates, and linear alkylbenzene sulphonates.

Soaps

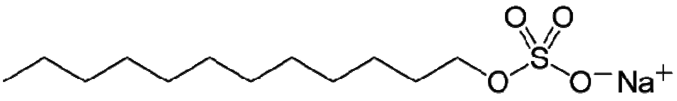
Classic ("true") soaps, rank first (in tonnage) of anionic surfactants used worldwide. They are widely used in soap bars and laundry detergents. True soaps are based on potassium or sodium salts of long-chained fatty acids, commonly derived from palm oil, coconut oil, palm kernel oil, tallow (beef fat), lard (pig fat), rice bran oil, ground nut oil, and castor oil. Most bar soaps on the market are true soaps. Combination bars (“combars”) or “syndet bars” contain additional types of surfactants, chelators, pigments, antibacterials and antioxidants to enhance product performance and appeal. For example, the MSDS of a popular combar soap brand lists various fatty acid-type soaps such as sodium stearate, sodium tallowate, sodium cocoate, sodium palm kernelate, stearic acid and coconut fatty acid, but also other anionic surfactants, such as SDS, sodium alkylbenzene sulphonate, sodium cocoyl isethionate (a sulphonate), and amphoteric surfactants such as cocoamidopropyl betaine, as well as BHT, EDTA, trisodium etidronate, titanium dioxide, sodium chloride, water and fragrance. Fatty acid-based soaps are generally readily biodegradable and have low toxicity. Due to their elevated log K_{OW} values they have moderate-to-high bioaccumulation potential.

Alkyl sulphates

Among anionic surfactants, alkyl sulphates (AS) rank third in tonnage used, after soaps (#1) and linear alkylbenzene sulphonates (#2). The best known alkly sulphate surfactants are ammonium lauryl sulphate (ALS, Figure 21) and sodium lauryl sulphate (SLS or SDS). They are the sodium or ammonium salts of dodecyl sulphate. ALS is found primarily in shampoos and body-wash as a foaming agent. SDS is contained in toothpastes, shampoos, shaving foams and bubble baths for its thickening effect and its ability to create a lather. Lauryl sulphates are very high-foam surfactants. SDS and ALS have low bioaccumulation potential (log K_{OW} = 1.6) and are readily biodegradable (85-100 per cent degradation after 30d = moderately persistent). They are moderately toxic, with EC_{50}s on the order of 1 to 10 mg/L for most fish species and 1 to 30 mg/L for crustaceans.

Figure 21

Chemical structure of sodium dodecyl sulphate. (Source: www.wikipedia.org.)

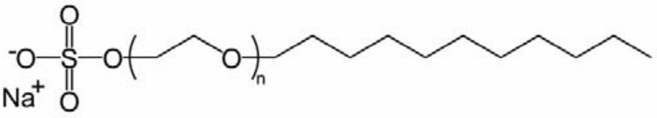


Alkyl ethoxylated sulphates

This group includes sodium laureth sulphate (Figure 22), also known sodium lauryl ether sulphate (SLES) or sodium polyoxyethylene lauryl ether sulphate, derived from the ethoxylation of SDS. Being inexpensive and a very efficient foamer, it is used as a surfactant in many personal care products (soaps, shampoos, toothpaste etc.). A study by the Danish Ministry of the Environment (Larsen & Andersen 2006) found SLES in 39 out of 50 hand soaps tested, commonly in concentrations of 5-15 per cent. SLES has low bioaccumulation potential (log K_{OW} = 1.14) and is moderately toxic to crustaceans (EC_{50} 1-30 mg/L). It is fully degradable in 28d biodegration tests.

Figure 22

Chemical structure of sodium laureth sulphate. (Source: www.wikipedia.org.)



Linear Alkylbenzene sulphonates

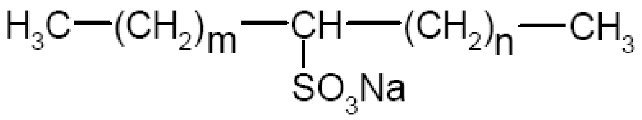
Linear alkylbenzene sulphonates (LAS) have been used since the 1960s in replacement of less biodegradable highly branched alkylbenzene sulphonates (ABS). LAS represent a mixture of closely related isomers and homologues, each containing an aromatic ring sulphonated at the para position and attached to a linear alkyl chain. LAS are one of the major anionic surfactants used on the market, particularly used in laundry powders, laundry liquids, dishwashing products and all-purpose cleaners. They are also used for textile and fibres and in agriculture. LAS have low bioaccumulation potential (log K_{OW} = 3.3; measured BCF 16-66) and biodegrade rapidly, on the order of a few days under aerobic conditions (HERA 2004). LAS concentrations in sludge are <0.5 m/kg (aerobic) and up to 30 g/kg under anaerobic conditions. Typical LAS values measured in sediments below sewage outfalls were in the range of 0.5 to 5.3 mg/kg with an arithmetic mean of 2.9 mg/kg (HERA 2004). Toxicity of LAS depends on chain length, with longer chained compound generally being more toxic. LAS have high-to-moderate toxicity to aquatic organisms, with average EC_{50}s ranging between 0.5 to 40 mg/L for fish and 1.5 to 17 mg/L for *Daphnia magna*. In addition to LAS, alkyl sulphonates are used as well, for example sodium cocoyl isethionate. However, due to their lower solubility, their use tends to be restricted to bar soaps

Secondary alkane sulphonates and other sulphonates

Secondary alkane sulphonates (SAS) are another group of major anionic surfactants used in dishwashing, laundry and cleaning products. The commonly used SAS (on the European market, but presumably globally as well) are "sulphonic acids, C13-17-sec-alkane, sodium salts" (Figure 23).

Figure 23

Chemical structure of a secondary alkane sulphonate. (Source: www.hera.org.nz.)

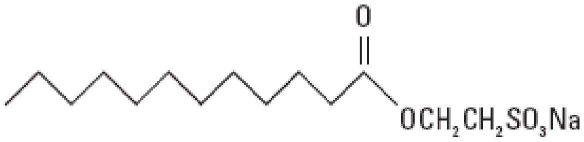


$$H_3C-(CH_2)_m-\underset{\underset{SO_3Na}{|}}{CH}-(CH_2)_n-CH_3$$

SAS degrade readily in water (88 to 96 per cent in 28d). Few experimental data on biodegradation of SAS in sediments are available, but it is estimated that their biodegradation half-lives are similar to those of LAS, on the order of seven days. Their bioaccumulation potential is low (log K_{OW} <3). Aquatic toxicity to fish and crustaceans is moderate (EC_{50} = 1 to 30 mg/L). Another commonly used alkyl sulphonate is sodium cocoyl isethionate (Figure 24), used in bar soaps.

Figure 24

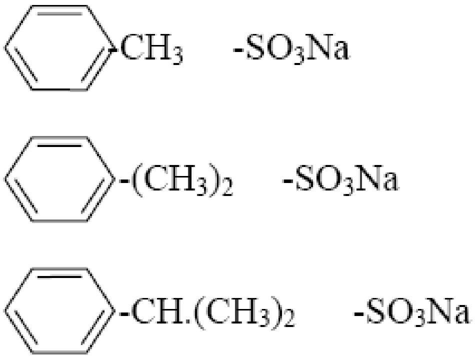
Idealised chemical structure of sodium cocoyl isethionate.



Other sulphonate-based anionic surfactants include aromatic hydrotropes such as toluene, xylene and cumene sulphonates (Figure 25), used as coupling agents to solubilise water-insoluble and often incompatible functional ingredients of household and institutional cleaning products and personal care products. They are low-volume production chemicals. Hydrotrope sulphonates have moderate persistence (biodegradation half-life on the order of 15 days), very low bioaccumulation potential (log K_{OW} <0), and low toxicity to aquatic organisms (EC_{50} >100 mg/L).

Figure 25

Generic chemical structure of the sodium salts of toluene sulphonate, xylene sulphonate and cumene sulphonate. (Source: www.hera.org.nz.)



Perfluorinated surfactants

Perfluorinated surfactants (PFSs) are a class of low production volume, fluorine-based, anionic surfactants that have attracted regulatory attention in recent years because of their very low biodegradability and high bioaccumulation potential. They are used primarily as mist suppressants in automotive metal plating, and, furthermore, for photographic processing (as antistatic), as fabric and carpet protectors and oil/water repellency agents in food packaging, in fire fighting foams (discontinued) and in aviation hydraulic fluids. Some PFS are also used as pesticides. The most common compounds (or production intermediates) are perfluorooctanoic acid (PFOA), perfluorooctanesuphonate (PFOS); n-alkyl perfluorooctanesulphonamides (FOSA) and n-alkyl perfluorooctanesulphonamidoethanol (FOSE). Other kinds of PFSs include perfluorinated derivatives of carboxylates, amides, amines, silanes, alkoxylates, fatty acid esters, adipates, urethanes, acrylates, oxazolidinones and phosphate esters (Footitt et al. 2004). PFOA, also known by the name “C8”, is used in making PTFE (eg, Teflon), but also constitutes a by-product in the manufacture of perfluorinated alcohols (for household surface finishes), non-stick food packaging and stain repellants. All PFOA production currently occurs overseas (N. America, Europe, Asia), but PFOA is believed to also enter the environment via the waste stream. PFOS (eg, heptacecanofluorooctane-1 sulphonic acid) is a key ingredient in fabric protectors and numerous stain repellants. As such, it is used as an impregnation agent (conferring water/oil repellency) for textiles, paper, leather, metal surfaces, and carpets and as a surfactant in waxes, polishes, paints, and cleaning products. PFOS is highly persistent (no measurable biodegradation over 28d) and highly bioaccumulative (BCF = 1124 to 4013 for bluegill sunfish, and 200 to1500 for carp). PFOS has been detected in fatty tissues of various vertebrates, including seals, dolphins, whales, cormorants, eagles, swordfish and tuna (Footitt et al 2004). PFOS has moderate toxicity to aquatic organisms with EC_{50}s of 5 to 200 mg/L for different fish species, 27 mg/L for daphnids, and 3.6 mg/L for mysids (Footitt et al. 2004). In a German study, PFOS concentrations as high as 0.6 µg/L were measured in river water (Skutlarek et al. 2006). The US EPA recommends phasing-out of PFSs over the next decade.

3.13.4 Cationic surfactants

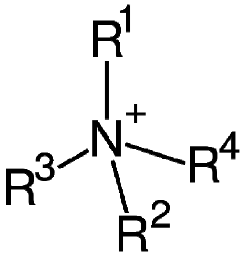
Cationic surfactants are used in fabric softeners, laundry detergents, and in bathroom and household cleaners, due to their additional disinfecting properties. They are also used as drying aids in automatic car wash facilities. The majority of cationic surfactants is based on quaternary ammonium salts (also known as quats). These are often dimeric (also called “gemini surfactants”), composed of two monomeric surfactants whose head groups are bonded together by a spacer. This provides greater solubilising capacity as well as viscoeleastic properties. Cationic surfactants in general (including gemini surfactants) are more toxic and less biodegradable than anionic surfactants, posing a greater environmental hazard.

Quaternary ammonium surfactants

Quaternary ammonium cations (quats) are positively charged polyatomic ions of the structure NR_4^+ with R being alkyl groups (Figure 26). Unlike the ammonium ion (NH_4^+) and primary, secondary, or tertiary ammonium cations, the quaternary ammonium cations are permanently charged, independent of the pH of their solution, providing an affinity to adsorb to negatively charged surfaces (eg, textiles), imparting “softness”. In laundry detergents, the positive charge of the cationic head furthermore improves the packing of anionic surfactant molecules at the stain/water interface, resulting in more efficient dirt removal. Quats are also inherently biocidal (see Section 3.14). As a consequence of these characteristics, quats are used as disinfectants, pesticides, laundry detergents, household cleaners, fabric softeners, and as antistatic agents (eg, in shampoos). Quats are also a common ingredient in many spermicidal jellies. Many commercial formulations are chloride or sulphate salts of quaternary ammonium compounds. Liquid fabric softeners are commonly based on chloride salts of gemini quats (eg, dioctadecyldimethyl ammonium chloride = DSDMAC; Figure 27) whereas sheets and dryer anti-cling strips tend to be based on sulphate salts (eg, (C14-C18)

Dialkyldimethylammonium methyl sulphate). Over the last decade, triethanolamine (TEA)-based esterquats (Figure 28) have replaced older-type tallow amines such as DSDMAC and ditallow imidazoline quat. The quats in many laundry detergents are typically mono alkyl quats. Quats in general have poor biodegradability and elevated toxicity. As a consequence, there have been efforts in industry to develop more degradable types. A recent outcome has been cleavable gemini cationic surfactants, such as esterquats.

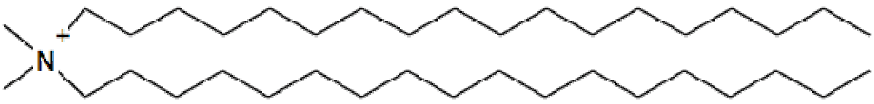
Figure 26
General structure of a quaternary ammonium cation.



Distearyldimethylammonium chloride and other gemini quats

Distearyldimethylammonium chloride (DSDMAC = DODMAC = DHTDMAC), also known as dioctadecyldimethylammonium chloride, or dihydrogenated tallow dimethyl ammonium chloride (Figure 27), is a gemini quat cationic surfactant that was the main active ingredient in fabric softeners up to the 1990s. It was characterised by very poor biodegradability (biodegradation half-life >>180d) and very high toxicity to algae (EC_{50} generally 0.01 to 1 mg/L) and high toxicity 0.5 to 5 mg/L to fish and crustaceans. DSDMAC and structurally similar gemini quats such as (C14-C18) dialkyldimethylammonium methyl sulphate have been phased out in Europe but are still in use elsewhere in the world.

Figure 27
Generic chemical structure of a gemini surfactant such as DSDMAC.



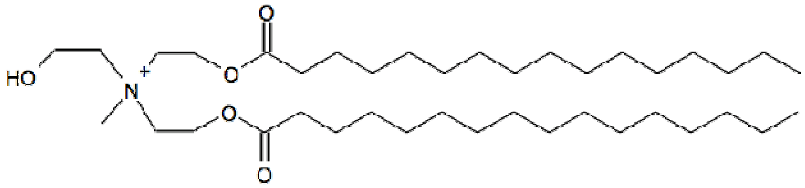
Esterquats and betainates

In recent years, dimeric esters of quaternary amines, generally called esterquats (Figure 28), have replaced DSDMAC as fabric softeners, driven by environmental concerns about the poor degradability of the latter. Esterquats are described as "cleavable surfactants", having an ester bond inserted between the hydrocarbon tail(s) and the quaternary ammonium head group. Depending on the orientation of the carbonyl group, esterquats (outwards) and alkyl betainates (inwards) are distinguished.

While being labelled as more readily biodegradable, few peer-reviewed studies are actually available to confirm this. From the evidence available, it appears that biodegradation half-lives of gemini esterquats and gemini-betainates are on the order of 30 to 40 days. However, even with cleavable groups, biodegradation of gemini quats is much slower than for the corresponding cleavable monomers. This effect appears to be due to one of the primary degradation products, a dicationic species, being very resistant to biodegradation (Tehrani-Bagha et al. 2007). Therefore it is conceivable that esterquat cationic surfactants, currently marketed as being more environmentally friendly, will likewise be superseded by more biodegradable quats in coming years.

Figure 28

Chemical structure of a triethanolamine-based esterquat.



Benzalkonium chloride

Benzalkonium chloride (alkyl dimethyl benzyl ammonium chloride) is a cationic surfactant belonging to the quaternary ammonium salt group. It is a mixture of alkylbenzyl dimethylammonium chlorides of various alkyl chain lengths. Benzalkonium chloride is commonly used as an antiseptic and spermicide, in products such as eyewashes, hand and face washes, mouthwashes, spermicidal creams, various cleaners, sanitisers, and disinfectants. It is also used as for the elimination of bacteria in waterbeds. It is furthermore used as an herbicide for gardening (against mosses). The greatest bactericidal activity is associated with the C12-C14 alkyl derivatives.

Cetrimonium bromide

Cetrimonium bromide (CTAB = hexadecyl-trimethyl-ammonium bromide) is an effective antiseptic agent against bacteria and fungi. It is widely used in hair conditioning products and in laboratories (DNA extraction). The closely related compounds cetrimonium chloride and cetrimonium stearate are also used as topic antiseptics, and may be found in many household products such as shampoos and cosmetics. Cetrimonium bromide has low biodegradability, and high bioaccumulation (BCF 400 to 700, CHRIP database). Reported log K_{OW} values are not very reliable, ranging from 3.2 to 5.2. It is highly toxic to algae (EC_{50} <0.1 mg/L) and fish and crustaceans (EC_{50} 0.1 to 1 mg/L).

Polyethoxylated tallow amines (POEA)

POEAs are commonly used as surfactants in herbicide formulations (eg, roundup; constituting ca. 15 per cent) to enhance the penetration of waxy plant cuticle. They have an alkaline pH in water (pH 8 to 9.5) and are moderately toxic to crustacean and fish, with EC_{50}s around 1 to 50 mg/L. Little information exists on bioaccumulation and persistence of POEAs. However, their precursors, tallow amines, have high log K_{OW} values of >6, biodegradation half-lives of approximately 20 days and high toxicity to aquatic organisms (EC_{50} 0.1 to 1 mg/L; ESIS database).

3.13.5 Amphoteric (zwitterionic) surfactants

These surfactants are used in personal care and household cleaning products for their "mildness" (ie, pH neutrality or low irritation to skin). They are frequently used in shampoos and other cosmetic products, and also in hand dishwashing liquids because of their high foaming properties. Amphoteric surfactants may contain two charged groups of different sign. They can be anionic (negatively charged), cationic (positively charged) or non-ionic (no charge) in solution, depending on the acidity or pH of the water. They are compatible with all other classes of surfactants and are soluble and effective in the presence of high concentrations of electrolytes, acids and alkalis. Whereas the positive charge is almost always ammonium, the source of the negative charge may vary (carboxylate, sulphate, sulphonate). One class of amphoteric/zwitterionic surfactants are the alkyl betaines, such as CAPB.

Cocamidopropyl betaine

Cocamidopropyl betaine (CAPB) is a zwitterionic surfactant with a quaternary ammonium cation in its molecule. It is commonly used as a surfactant in bath products like shampoos and hand soaps, and in cosmetics as an emulsifying agent and thickener, usually at concentrations of 1 to 5 per cent. It also serves as an antistatic agent in hair conditioners. CAPB is a medium-strength surfactant that causes relatively low irritation to skin or mucous membranes and has replaced cocamide DEA to a significant degree. CAPB is fully degradable in a 28-day standard test for ready biodegradability. It is also degradable under anaerobic conditions. CAPB is moderately toxic to aquatic organisms, with EC/LC_{50} values between 1.8 to 22 mg/L. With an estimated log K_{OW} value of 2.65, CAPB has low bioaccumulation potential. Because it is considered to be fully degradable in wastewater treatment plants, CAPB is unlikely to cause long-term adverse effects in the aquatic environment.

Ethylene amine derivatives

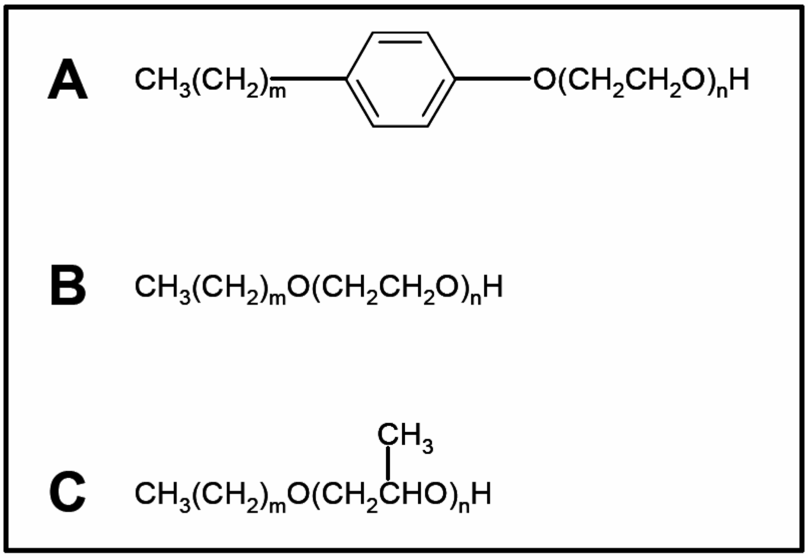
Ethylene amides such as diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA), ethyleneamine E-100 (E-100), aminoethylpiperazine (AEP) and aminoethylethanolamine (AEEA) are used, among other applications (see Section 3.11.4 – Asphalt additives), as amphoteric surfactants, being active over a wide pH range. AEEA and TETA are also used as a starting material to make other amphoteric surfactants. Amphoteric surfactants have been produced from the reaction products of alkoxylated ethyleneamines and fatty acids. A variety of additives useful in laundry detergents has been made from ethyleneamines such as a clay suspension additive made from TEPA and ethylene oxide which prevent the re-deposition of suspended soil on laundry.

3.13.6 Nonionic surfactants

These surfactants do not have an electrical charge, which makes them resistant to water hardness deactivation. They are excellent grease removers that are used in laundry products, household cleaners and hand dishwashing liquids. Most laundry detergents contain both non-ionic and anionic surfactants as they complement each other's cleaning action. Non-ionic surfactants contribute to making the surfactant system less hardness sensitive. The most commonly used non-ionic surfactants are ethers of fatty alcohols.

A commercially important group of non-ionic surfactants are alkylphenol ethoxylates (APEOs), and alcohol polyethers such as alcohol ethoxylates (AEOs) and alcohol propoxylates (APOs; Figure 29).

Figure 29
Chemical structure of three types of non-Ionic surfactants: A) alkylphenol ethoxylate B) alcohol ethoxylate C) alcohol propoxylate (from Hoffman, 2004).



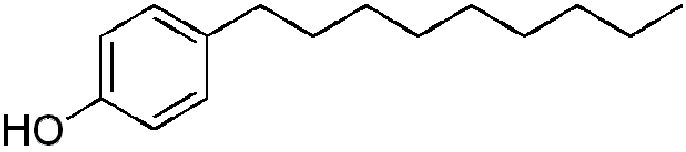
Alkylphenol ethoxylates (including nonylphenol)

Alkylphenol ethoxylates (APEOs), also called ethoxylated alkylphenol (APEs), are high production volume surfactants that have been used commercially since the mid-1940s. They are used primarily in industry, for the manufacture of wool and leather (scouring), paper (dispersing agent) and metal (degreasing), as laboratory detergents (eg, Triton X), as emulsifiers in pesticides and in some household detergents (15 per cent of production). They are also used in lubricating oils, resins, plasticisers, petroleum demulsifiers and as antioxidants for rubbers and plastics. The commercially most important APEOs are ethoxylates of nonylphenol (NP) and octylphenol (OP), comprising approximately 80 per cent and 20 per cent of the total annual production (annual worldwide usage is estimated to be 600,000 tons/a). Octylphenol ethoxylate is known under the trade name "Triton X". Nonylphenol ethoxylates are marketed under the trade name "Nonoxynol". A common formulation is Nonoxynol-9, used as an ingredient in various cleaning and cosmetic products, in shaving creams and in contraceptives for its spermicidal properties.

The current environmental concern surrounding alkylphenol ethoxylated surfactants centres on their breakdown products, since some of these, particularly nonylphenols, are more toxic, lipophilic and persistent than their parent material. Nonylphenols consist of a hydrocarbon chain with nine carbon atoms attached to a phenol ring in either the ortho, meta or para position, with the most common ring isomers being ortho or para (Figure 30). The alkyl chain can either be a linear n-alkyl chain or branched and nonylphenols commonly occur as a mixture of isomers. The isomer p-nonylphenol (= 4-nonylphenol = 4-NP; with substitution in the para position) has been found to be oestrogenic in fish, birds, and mammals. Initial breakdown of APEOs occurs relatively rapidly in sewage treatment plants (STPs), producing a variety of intermediates of varying stability, usually mono and diethoxylates or carboxylates, depending on ambient conditions (aerobic or anerobic). Ultimately, these intermediates break down further to form nonylphenols, which are a common residue in municipal wastewater. Discharge of APEOs and nonylphenols in effluent from primary sewage treatment plants has been reported to be on the order of 300 μg/L and 30 μg/L, respectively.

Figure 30

Chemical structure of 4-nonylphenol (4-NP). (Source: www.wikipedia.org.)



Acute toxicity of nonylphenol to aquatic organisms (crustaceans, bivalves and fish) is roughly 10 to 100 times greater than for nonylphenol ethoxylates (NPEOs) and other associated degradation products (ie, mono- and diethoxylates and carboxylates; Hale & La Guardia 2002). Acute EC_{50}s for 4-NP commonly range between 0.05 and 1 mg/L, supporting their ranking as "highly toxic".

Nonylphenols are moderately bioaccumulative, with reported BCFs generally ranging between of 100 to 1000. However, BCFs as high as 10,000 have been reported for algae. Being relatively hydrophobic (log K_{OW} ca. 4.5), NPs will partition readily to sediment organic carbon and accumulate in sediments. Nonylphenol concentrations of up to 54 mg/kg have been reported in sediments near a STP outfall in the United States (Hale & La Guardia 2002), and 4-NP concentrations in New Zealand sewage sludge are as high as 12 to 1800 mg/kg (Northcott 2007). Little information exists on the toxicity of sediment-associated NPs, but no observable effects concentrations (NOECs) greater than 20 mg/kg have been suggested.

Nonylphenols degrade slower than the parent NPEOs, leading to higher concentrations in the environment: for example, the biodegradation of NPs in river water is 30 per cent at 7°C and 70 per cent at 25°C , compared to 68 per cent at 7°C and 96 per cent at 25°C for NPEOs.

A number of alkylphenols, including nonylphenol, octylphenol and 4-butylphenol have the ability to bind to the oestrogen receptor of mammals, acting as xenoestrogens and leading to endocrine disruption. 4-NP concentrations of 1.6 to 3.4 µg/L have been reported to cause alterations in gonad histology of male fathead minnows, and NP appears to impede smoltification of salmon. Octylphenol inhibits testicular growth and increases vitellogenin production in fish and also affects sexual behaviour in laboratory assays. Increased vitellogenin production and higher intersex frequency has also been observed in wild fish populations in the UK in the vicinity of STP, although these effects may have been caused by other xenoestrogens as well.

As a result of their xenoestrogenic potential, nonylphenol and nonylphenol ethoxylates have been banned by the European Union, where they have been replaced by alcohol ethoxylates and alcohol polyethers (see below). Nonylphenol ethoxylates are currently not banned in New Zealand.

Alcohol ethoxylates

Alcohol ethoxylates (AEs or AEOs) and propoxylates are polyethers composed of an alkyl chain (usually 12 to 18 carbons) combined with some ethylene oxide units (three to 14). The majority are based on fatty alcohols derived from coconut oil and tallow (eg, Genpol C100 or T110). By far, the greatest use of AEs is in domestic detergents, household cleaners, and personal care products such as shampoos. However they are also used as penetration promoters in insecticides. AE are readily biodegradable under aerobic and anaerobic conditions. Total measured removal rates in wastewater treatment plants vary from 99.6 to 99.9 per cent. The acute toxicity of AE is dependent on the alkyl chain length and the number of EOs. Toxicity to aquatic organisms, measured by EC_{50}, ranges from highly toxic (<1 mg/L) to moderate (between 10 and 100 mg/L).

Cocamides

Another common group of nonionic surfactants are alkanolamides, such as cocamide monoethanolamine (MEA), cocamide diethanolamide (DEA) and cocamide triethanolamide (TEA), widely used as foaming agents in bath products such as shampoos and hand soaps, and in cosmetics as an emulsifying agent. They are often used in concentrations of 1 to 5 per cent. Cocamides are derivates of coconut oil (eg, lauric, palmitic and myristic acid), but other fatty acid acids can be used, such as stearic acid. Cocamides have moderate hydrophobicity (log K_{OW} ca 4) and moderate persistence (biodegradation half-life in aerobic sewage ca. 30 days). They are moderately toxic to aquatic organisms, with EC_{50}s of 10 to 30 mg/L for most fish and crustaceans, and highly toxic (approximately 1 mg/L) for algae (ESIS database). Cocamide DEA is generally more toxic than cocamide MEA.

Fatty alcohols and sugar-based surfactants (glucosides)

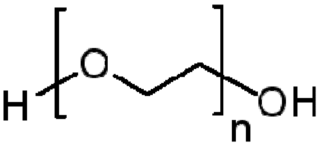
Long-chained alcohols such as cetyl alcohol and oleyl alcohol are used in shampoos, or as emollients, emulsifiers or thickening agents in skin creams and lotions. They are also used as lubricants for nuts and bolts. Oleyl alcohol is furthermore used as a plasticiser for softening fabrics, and as a hair coating agent in shampoos and hair conditioners. Fatty alcohols are strongly hydrophobic (log K_{OW} 6-7), but degrade readily in oxic sewage treatment (half-life one to two weeks). From the little information available, they seem to have low toxicity to aquatic organisms (EC_{50} to algae >>100 mg/L; ESIS database). Sugar-based surfactants, such as glucosides and maltosides are low-volume production surfactants with no significant commercial application. They are considered environmentally friendly, but there is little toxicological data available to prove this.

Polyethylene glycol and PEG-based surfactants

Polyethylene glycol (PEG, Figure 31) and PEG-based surfactants are used in a wide spectrum of industry applications. In the rubber industry, PEG is used as a releasing agent for foam rubber and latex rubber. It is also used as an airpack releasing agent, inner releasing agent, and lubricant in the tyre industry. In the textile industry, PEG is used as a softener, antistatic agent, scouring agent, sizing agent, and dyeing auxiliary. In paper industries, PEG has a softening effect on paper. In metal industries, PEG is used in grinding powder, for anticorrosion-treatment and for cleaning of metal surfaces. In the timber industry, PEG is used to minimise shrinking and cracking of wood. In pharmaceuticals and cosmetics, PEG is used as a base material of ointments and can be used in shampoos, hand creams, lotions. PEG is also used as a raw material in paints and resins. Hydrophobically modified PEGs, called PEG-surfactants or PEO-lipids, consist of a hydrophilic PEG chain covalently attached to hydrophobic end groups via an ether, ester, or urethane linkage (Rangelov & Tsvetanov 2001). One subgroup are polysorbates (see below). PEG ethers include various surfactants under the trade name "Brij" and are used in biomedical research applications. Examples are Brij 30 (tetraethylene glycol dodecyl ether) and Brij 76 (decaethylene glycol octadecyl ether). PEG esters such as PEG dilaurate and PEG laurate are used in a wide variety of cosmetic formulations as surfactants and emulsifying agents. They are considered to be non-carcinogenic and of low reproductive toxicity, in contrast to PEG-ethers. Alkylphenol polyethoxylate surfactants can be seen as a special type of a PEG-ether. The PEG monomer, ethylene glycol, is considered to be a reproductive and developmental toxin (Lanigan 2000a, Lanigan 2000b, Lanigan 2000c), and ethoxylated fatty acids, in general, can contain traces of 1,4-dioxane, which is a carcinogen and an irritant.

Figure 31

Chemical structure of polyethylene glycol.



Polysorbates and sorbates

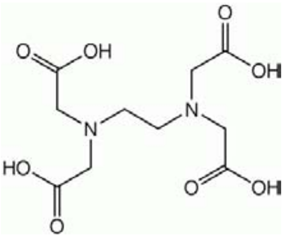
Polysorbates and sorbates are used as emulsifiers and wetting agents in laboratory, pharmaceutical and food applications. In cosmetic products, polysorbates are used to solubilise essential oils into water-based products. Polysorbates are esters of fatty acids with PEG-ylated sorbitan (a derivative of sorbitol). They are commonly known as "Tween". Different tweens are distinguished by the length of the fatty acid tail. For example, Tween 20 is an ester of polyoxyethylene sorbitan monolaurate and is widely used in laboratories and as a food additive. Surfactants that are esters of plain (non-PEG-ylated) sorbitan with fatty acids are commonly known as "Span". Analogous to the tweens, various types exist, differing in the length of the fatty acid tail, ie, Span 20 (Sorbitan monolaurate), Span 40 (Sorbitan monopalmitate), Span 60 (Sorbitan monostearate), and Span 80 (Sorbitan monooleate). Polysorbates and sorbates have low toxicity (EC_{50} >1000 mg/L) and moderate persistence (biodegradation half-life approximately two weeks). They do not appear to be carcinogenic.

3.13.7 Water softeners

Water softeners include the chelating agent EDTA (ethylenediaminetetraacetic acid, Figure 32), which is effective in complexing metal ions such as Mg^{2+} and Ca^{2+} during laundering. EDTA is also used in textile manufacture for chelating heavy metals. EDTA has poor biological degradability (degradation half-life generally <20 per cent after 28 days), but low toxicity to fish and crustaceans (EC_{50} >100 mg/L) and very low bioaccumulation potential.

Figure 32

Chemical structure of the chelating agent EDTA, used as a water softener in detergents.



3.13.8 Bleaching agents and activators

Most household bleaches are inorganic chemicals, such as sodium hypochlorite (NaClO "chlorine bleach") or hydrogen peroxide (H_2O_2) or peroxide-releasing compounds, such as sodium perborate or sodium percarbonate ("oxygen bleach"). Tetraacetylethylenediamine (TAED) is a bleaching activator in laundry detergents that improves the low temperature efficiency of hydrogen peroxide releasing chemicals such as sodium perborate, sodium percarbonate, sodium perphosphate, sodium persulphate and urea peroxide.

3.14 Pesticides

Table 26

Environmental hazard profile for pesticides.

Qualitative environmental hazard rating 16		Reason for ranking
M	Persistence	Biodegradation half-life generally <30d.
M	Bioaccumulation potential	BCFs generally <100.
H	Toxicity/adverse effect potential	High: dithiocarbamate fungicides; organophosphorus insecticides. Low: phenoxy and carbonyl herbicides.

Worldwide, roughly 2000 chemicals are regularly used (or have been used in the past) to control unwanted biological "pests". The term "pesticides" for purpose of this review shall be taken to comprise animal biocides (eg, insecticides, acaricides, molluscicides, nematicides rodenticides, etc.) as well as herbicides, plant growth regulators and fungicides. Bactericides are treated separately in Section 3.17. Most pesticides are known by their trade names, of which there is a bewildering variety. The pesticide product information system (PPIS) of the Untied States EPA lists 1400 pesticides that are registered under the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA). Roughly 1100 official pesticide common names have been assigned by the International Organization for Standardization (ISO), in accordance with an established system of nomenclature. Of the commonly used pesticide compounds, herbicides, insecticides and fungicides each comprise approximately 25 per cent of the total compound list (Table 27). Acaricides make up another 10 per cent, and the remaining 15 per cent are due to plant and animal hormones, molluscicides, nematicides, avicides and mammalian toxins.

Table 27

Commonly used pesticides (February 2006), grouped by target organism. (Source: Alan Wood Compendium of Pesticide Common Names website, www.alanwood.net/pesticides/index.htm.)

Pesticide type (by target organism)	Number of compounds
Acaricides	201
Algaecides	12
Antifeedants	4
Avicides	5
Bactericides	19
Bird repellents	9
Chemosterilants	17
Fungicides	409
Herbicides	534

Pesticide type (by target organism)	**Number of compounds**
Herbicide safeners	17
Insect attractants	28
Insecticides	470
Mammal repellents	4
Mating disruptors	3
Molluscicides	17
Nematicides	44
Pesticide-miscellaneous	12
Pesticide-synergists	6
Plant activators	2
Plant growth regulators	95
Rodenticides	36
Virucides	2
Grand Total	**1946**

The list of pesticides in use grows every year, as new pesticides are continuously being introduced in an effort to develop more effective or less hazardous products, or to overcome pest resistance. Pesticides can be classified in numerous ways – by their use or target organism, by their primary site of action, by chemical compound type, or by their hazard to non-target organisms. Within a classification, a given pesticide might fit several sub-categories (eg, being an acaricide as well as an insecticide). In this report, a classification system by chemical compound type, also adopted by the UN World Health Organisation (WHO) and Food and Agricultural Organization (FAO), is followed to a large extent. However, pesticide categories of particular relevance to Auckland's urban and suburban character (eg, rodenticides or molluscicides) are discussed as separate groups. It should be noted that the list of pesticides discussed in this report is not exhaustive and focuses only on the major classes of pesticides in agricultural and domestic use in New Zealand (ie, substances commanding approximately 1 per cent or more of the market).

The greatest use of pesticides in New Zealand is without doubt attributable to the agricultural, horticultural and forestry sector. Further to these sectors, a sizable amount of pesticides (ca. 20 per cent) is estimated to be used in domestic and roadside applications in the urban and suburban landscape, although no accurate market figures exist at present. Nevertheless, it may be assumed that pesticide use is widespread throughout Auckland's environment, despite its primarily residential, industrial and commercial land use.

According to a recent report by MfE on trends in pesticide use in New Zealand (Manktelow et al. 2005), approximately 3900 tons of pesticide were sold in New Zealand in 2003, based on sales data by the New Zealand Association for Animal Health and Crop Protection (Agcarm). These sales data include organic as well as inorganic pesticides (eg, sulphur). The report states: "Pesticide use in New Zealand has increased approximately 27 per cent from 1999-2003. Comprehensive and detailed data on pesticide use is difficult to obtain, due to the broad classifications used and the fact that only about 80 per cent of pesticide sales are covered" (ie, excluding domestic and roadside applications). "Herbicides are used primarily in the pastoral and forestry sector, whereas fungicides and insecticides are primarily used in horticulture (including wine growing). In terms of active ingredients applied per hectare (kg active ingredient/ha), the horticultural sector is by far the intensive pesticide user (13.2 kg a.i./ha), followed by the arable (2.4 kg a.i./ha), forestry (0.3 kg a.i./kg) and pastoral (0.2 kg a.i./ha) sector. The recent (1999-2003) increase in pesticide use is most likely due to the large increase (76 per cent) in wine grape plantings, where elemental sulphur is the most commonly used pesticide. There is a current trend to remove broad spectrum pesticides, such as organophosphates (OP) for more selective ones, such as growth regulators."

The MfE report alerts to a significant lack of reliable data on domestic and urban pesticide use. The report makes several recommendations, such as (1) improving the system for recording pesticide sales and use data, (2) standardisation of pesticide categories within the customs importation records to allow tracking of generic pesticide active ingredients imported into New Zealand that are not fully represented in Agcarm's current recording system, and (3) introducing spray diary records for individual pesticide users as key building blocks for an effective pesticide use recording system.

Table 28 lists most commonly used pesticides in New Zealand (in per cent of sales), according to the MfE report (Manktelow et al. 2005), not counting mineral oils (ca. 25 t/y). Next to the compounds listed as high-volume agricultural pesticides in Table 28, a number of other pesticides are used in domestic, roadside and specialty applications, including pyrethroids, neonicotinoids, and anticoagulant rodenticides. Some of these, while used in much lower volumes, are likely to be more hazardous to the environment.

Table 28

Most commonly used pesticides in New Zealand (excluding domestic), Source: (Manktelow et al. 2005), modified.

Chemical compound type (FAO category)	Active ingredient	Percentage of sale	Mode of action
Phenoxy hormones	MCPA, 2,4-D, mecoprop, MCPB.	25%	Synthetic auxin (herbicides).
Dithiocarbamates	Mancozeb, metiram, thiram, Ziram.	11%	Lipid synthesis inhibitors (fungicides).
Phosphonyls	Glyphosate, glufosinate-ammonium.	8.4%	Amino acid inhibitor (herbicides).
Triazines	Terbuthylazine, hexazinone, atrazine.	7.6%	Photosynthesis inhibitors (herbicides).
Plant growth regulators	Hydrogen cyanamide, ammonium thiosulphate, chlomequat-chloride, mepiquat-chloride.	6.9%	Growth inhibitors/retardants (herbicides).
Inorganics	Copper compounds, sulphur compounds, phosphorous acid.	6.9%	Mostly fungicides.
Organophosphates	Diazinon, methamidophos, chlorpyrifos, fenamiphos, pirimiphos-methyl, phorate.	3.6%	Neurotoxic (insecticides).
Chloroacetanilides	Acetochlor, alachlor, propachlor.	3.0%	Seedling shoot inhibitors (herbicides).
Other fungicides	Captan, chlorothalonil, metalaxyl-m, tolylfluanid.	2.4%	Fungicides.
Urea derivatives	Isoproturon, linuron.	2.0%	Photosynthesis inhibitors (herbicides).
Other hormone types	Triclopyr, pichloram.	1.3%	Synthetic auxin (herbicides).
Dinitroanilines	Trifluralin.	0.4%	-
Carbamate insecticides	Carbaryl.	0.4%	-

3.14.1 Pesticide formulations

Most pesticides get sold as a pesticide formulation, which is a mixture of the active biocidal ingredient and additional (toxicological inert) additives, such as solvents, carriers adjuvants (eg, surfactants) and synergists. For example, an insecticide containing pyrethroids as the active ingredient will often contain piperonyl butoxide or n-octyl bicycloheptene dicarboximide as a synergist, to enhance insecticidal action.

3.14.2 Likely pesticide sources in Auckland

Agricultural run-off

Even though land use in Auckland is dominated by residential, commercial and industrial uses, a sizable amount of agricultural and horticultural land use remains. Contributions from agricultural run-off are therefore to be expected. Pastoral land use is likely to contribute primarily herbicides such as phenoxy hormones, which pose a relatively low hazard to most non-target organisms. Greater inputs are likely to derive from arable land use. According to a MAF report (Holland & Rahman 1999), onions, which are grown in the Franklin district, receive very high doses of pesticides. The average use of herbicides in onions exceeds 6 kg/ha. Insecticide use is also relatively intense, and use of fungicides in onions exceeds 25 kg/ha. Commonly used pesticides are dithiocarbamates (eg, mancozeb) and benzimidazoles ("MBC-compounds"), such as benomyl and carbendazim. Use of MBC fungicides has been reduced in recent years, but onion production is still strongly reliant on dithiocarbamate fungicides.

Horticulture and viniculture is common in Auckland's surroundings. For example, a small amount of kiwifruit is grown in the Auckland area, as are strawberries and wine. According to Holland & Rahman (1999), in the last two decades, pesticide use in kiwifruit has decreased markedly, from eight to nine broad-spectrum sprays (commonly organophosphates such as azinphos-methyl, phosmet, diazinon and chlorpyrifos, as well as dicarboximid and benzimidazole fungicides) to three sprays in 1998. In recent years, more selective insecticides (eg, *Bacillus thuringiensis*), mineral oil products, and the growth regulator hydrogen cyanamide are widely used in kiwifruit orchards.

The strawberry industry relies heavily on the use of fungicides. Up to 2007, methyl bromide, banned by the Montreal Protocol as an ozone-depleting substance, was used as a fumigant, requiring an extension of a critical use exemption from the UN. In future years, growers will have to rely on alternative fungus control measures. For most growers, the most likely alternatives will be chloropicrin (trichloronitromethane).

Roadside weed control

According to information from Auckland City Council (www.aucklandcity.govt.nz/council/documents/resources/weed/section4-1.asp), weed control along roadsides and parks and gardens relies primarily on glyphosate-based (eg, Roundup) and sulphonylurea (eg, Escort) herbicides.

Domestic use

No comprehensive, quantitative information exists on pesticide use in New Zealand households. A survey of MSDS sheets of common household pesticide product on the U.S. market (using the NLM website) reveals that a wide variety compounds are used as herbicides, insecticides, fungicides and molluscides (Table 29). A similarly broad suite of ingredients may be assumed to be present in household pesticides available in New Zealand.

Antifouling paints

A number of fungicides and herbicides are used as co-biocides in antifouling paints on ship hulls and moorings. These are discussed in more detail in Section 3.15.

Table 29

Compounds frequently encountered in pesticide formulations for household use (based on MSDS information compiled by NLM household products database).

Compound	Category	Use	Weight percentage in formulation
Sulphur, elemental	Fungicide	Fruit	4-98%
Thiophanate	Fungicide	Fruit	up to 50%
Captan and derivatives	Fungicide	Trees	6-50%
Tridadimefon	Fungicide	Lawns	0.5-50%
Mancozeb	Fungicide	Fruit	up to 40%
Ridomil	Fungicide	Seeds	ca. 30%
Chlorothalonil	Fungicide	Flowers	1-30%
Methoxychlor	Fungicide	Rosesand shrubs	6-12%
Triforin	Fungicide	Rosesand shrubs	0.1-6.5%
Myclobutanil	Fungicide	Multi-purpose	0.1-1.5%
Glyphosate	Herbicide	Total vegetation	0.5-50%
2.4-D	Herbicide	Lawn weeds	0.2-25%
Diquat dibromide	Herbicide	General weeds	0.2-2.5%
Dimethylamine	Herbicide	Lawn weeds	0.1-8%
Prometon	Herbicide	Total vegetation	2-2.5%
Dicamba	Herbicide	Lawn weeds	0.1-1.5%
Imazapyr	Herbicide	Total vegetation	<0.1%
Trifluralin	Herbicide	Garden weeds	1.5%
Diazinon	Insecticide	General	n.a.
Malathion	Insecticide	General use	3-50%
Permethrin	Insecticide	General use, flies, mosquitoes, ticks, ants, roaches	0.1-45%
Carbaryl	Insecticide, molluscicide, miticide	Multi-purpose	0.5-25%
Chlorpyrifos	Insecticide	Ants, wasps, termites	0.1-13%
Piperonyl butoxide	Insecticide	Ticks, ants, roaches, wasps	0.2-10%
Imidacloprid	Insecticide	Grubs	ca. 10%

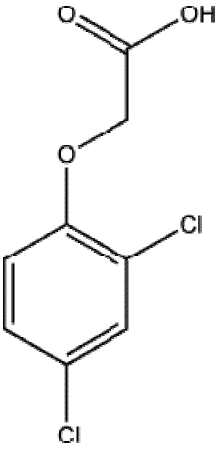
Compound	Category	Use	Weight percentage in formulation
MGK 264 (N-octyl bicycloheptene dicarboximide)	Insecticide	Ants	0.2-8%
Rotenone	Insecticide	Garden	0.5-6%
d-methoprene	Insecticide	Pets, carpets	0.01-3%
Bifenthrin	Insecticide	Lawn	0.01-2.5%
Lambda cyhalothrin	Insecticide	Lawn and turf	0.002-0.5%
Tetramethrin	Insecticide	General use	0.05-0.2%
Deltamethrin	Insecticide	Ants	0.02-0.1%
Tralomethrin	Insecticide	Ants	0.01-0.1%
Acephate	Insecticide	Ants and mites	0.01-0.1%
Metaldehyde	Molluscicide	Slugs	ca. 3%
3-Iodo-2-propynylbutylcarbamate	Molluscicide	Slugs	0.2-1%
1080 (sodium monofluoroacetate)	rodenticide	Rats and mice	n.a.
Bromethalin	rodenticide	Rats and mice	0.01%
Brodifacoum	rodenticide	Rats and mice	0.01%
Chlorophacinone	rodenticide	Rats and mice	0.01%
Ziram	animal deterrent	Rabbits	23%

3.14.3 Phenoxy hormone herbicides

Phenoxy herbicides constitute the single most important group of agricultural herbicides in New Zealand, as well as worldwide. Familiar examples include 2,4-D ((2,4-dichlorophenoxy) acetic acid, Figure 33) and MCPA (2-methyl-4-chlorophenoxyacetic acid). Another example is 2,4,5-T, although it is no longer used. Phenoxy herbicides are plant growth regulators (also known as "synthetic auxins") that are selectively toxic to dicotyledonous ("broadleaf") plants. They are widely used to control dicot weeds in monocot crops (eg, cereals and grasses). In New Zealand, phenoxy hormones are the dominant pesticides used in the pastoral sector. They are also likely to be used around the home by consumers to control weeds on lawns.

Figure 33

Chemical Structure of 2,4-dichlorophenoxy) acetic acid (2,4-D).



Phenoxy herbicides are readily biodegradable and moderately persistent (biodegradation half-life approximately 15d), and have a low bioaccumulation potential (log K_{OW} <3.3). Due to their specific mode of action (plant hormone), they have low toxicity to fish and crustacea (EC_{50} >>100 mg/L) and moderate toxicity to algae (EC_{50} 33 mg/L to *Selenastrum capricornutum*, five-day test; ESIS database). Their environmental hazard relates primarily to unwanted (terrestrial) plant toxicity as a result of spray drift. In the past, some phenoxy herbicides (such as 2,4-D and 2,4,5-T (2,4,5-trichlorophenoxyacetic acid) became notorious because of contamination of certain formulations ("Agent Orange" = mixture of 2.4.5-T and 2.4-D) by dioxin residues, such as 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) from the production process. The compound 2,4.5-T was widely used to control broadleaf weeds until the 1970s before being phased out, primarily because of contamination issues by TCDD.

3.14.4 Other synthetic auxin herbicides

Next to phenoxy herbicides, several other herbicides act as synthetic growth regulators, namely pyridine carboxylic acids, benzoic acids and quinoline carboxylic acids.

Pyridine carboxylic acids

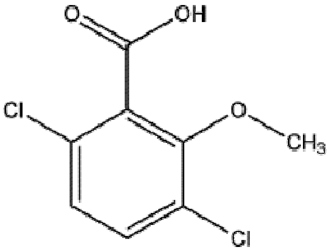
Pyridine carboxylic acids are mainly used to control unwanted woody plants in pastures and at edges of fields. Being a synthetic plant hormone, they have low-to-moderate acute toxicity to animals. An example is picloram, used for control of deeply rooted herbaceous weeds and woody plants (in pasture and forestry). It has very low bioaccumulation potential (BCF<1) and moderate-to-low toxicity to fish, crustacea and amphibia (EC_{50} values of 10 to 100 mg/L). However, picloram is highly persistent, with a biodegradation half-life of 167 to 513 days. A related compound, triclopyr, is used as a broadleaf (dicot) herbicide. It also has very low bioaccumulation potential (BCF generally <1) and low toxicity to crustaceans. However, it is moderately toxic to algae (LC_{50} ca. 20 to 30 mg/L) and acutely toxic to fish, such as salmon (LC_{50}s on the order of

0.5 to 10 mg/L). No information was available on its biodegradation rate. Another herbicide belonging to the pyridine carboxylic acid group is clopyralid, used for the control of noxious thistles.

Benzoic acid type herbicides

Benzoic acid herbicides are a third type of synthetic auxins. They include dicamba (Figure 34), which is used as a broadleaf herbicide as an alternative to phenoxy compounds such as 2,4,5-T. Dicamba products are widely used in domestic applications. They have moderate persistence (biodegradation half-life ca. 30d), low bioaccumulation potential (log K_{OW} 2.2) and low toxicity to fish and crustaceans (EC_{50} >100 mg/L), thereby constituting a relatively low environmental hazard.

Figure 34
Chemical structure of dicamba, a benzoic acid herbicide used for landscaping and lawn weed control.

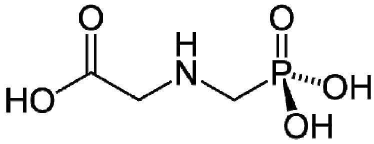


3.14.5 Phosphonyl herbicides

Phosphonyls (or phosphonoglycines) are organophosphorus herbicides that inhibit a plant-specific enzyme (enolpyruvylshikimate-phosphate synthase = EPSPS). Examples include glyphosate and its salts and esters. Glyphosate (Figure 35) is the active ingredient in Roundup products. Glyphosate is a systemic, non-selective herbicide used for no-till burndown and general weed control. In domestic use it is marketed as a "total vegetation control" herbicide. Glyphosate is one of the most widely used herbicides worldwide and is also widely used in New Zealand, both in the agricultural and domestic sector. Due to its presumed plant-specific mode of action, it is generally considered to have low toxicity to animals. However, actual measured toxicity data are highly variable, with four-day EC_{50} values to crustacea and fish ranging from 1 to 1000 mg/L, with high inter- and intraspecific variability. As a conservative estimate, toxicity shall be assumed to be moderate. Being an ionic compound with a log K_{OW} <0 and measured bioconcentration factors (BCF) of generally <50, its bioaccumulation potential is low. Environmental persistence is assumed to be low-to-moderate, with 13 to 30 per cent biodegradation (aerobic) after 45d in one study and >90 per cent after 15 days in another study (ISES database). An INCHEM review reports a biodegradation half-life of <14 days under aerobic conditions, and 14 to 22 days under anaerobic conditions (in the laboratory), with no references cited. However, persistence in the field could be higher, especially under anaerobic conditions. At any rate, glyphosate's environmental persistence is sufficiently long for it to occur in domestic sewage sludge in concentrations on the order of 1 to 10 mg/kg, as shown in a French study (Ghanem et al. 2007).

Figure 35

Chemical structure of glyphosate, a phosphonoglycine herbicide.

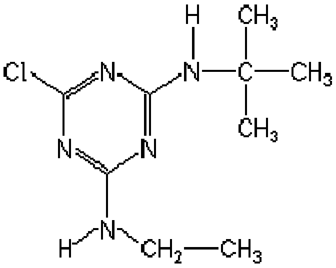


3.14.6 Triazine herbicides

Triazines belong to a large group of photosynthesis inhibiting herbicides that also include triazinones, uracils, phenylureas and amides. Examples of triazine herbicides include terbuthylazine (Figure 36), used as an algaecide, and atrazine, widely used in corn (maize) cultivation for control of broadleaf weeds and grasses.

Figure 36

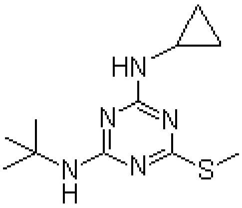
Chemical structure of terbuthylazine. (Source: Alan Wood compendium of pesticides www.alanwood.net/pesticides/index.htm.)



Another triazine herbicide is irgarol (Figure 37), used as an algaecide and as an antifouling agent in boat paints. Terbuthylazine is used as algaecide, microbicide and microbiostat to control slime-forming algae, fungi, and bacteria in commercial and industrial water cooling systems, and in residential and commercial ornamental ponds, fountains and aquaria (EPA R.E.D. Factsheet for terbuthylazine). Terbuthylazine is stable to hydrolysis and to aqueous photolysis and degrades very slowly under aerobic aquatic conditions. It is moderately toxic to both cold and warm water fish and invertebrates (EC_{50} 1 to 100 mg/L) and is highly toxic to aquatic algae (EC_{50} <1 mg/L). Its bioaccumulation potential is low, with BCFs generally <10.

Figure 37

Chemical structure of irgarol, a common triazine herbicide, also found in antifouling paints. (Source: www.chemblink.com database of chemicals from China.)

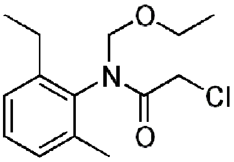


3.14.7 Chloroacetanilide herbicides

Chloroacetanilide herbicides include compounds such as acetochlor (Figure 38), alachlor, propachlor and metolachlor. They act by inhibiting shoot elongation and are often found in mixed herbicide formulations with atrazine, glyphosate, trifluralin, and imazaquin to control weeds in corn. Acetochlor and alachlor are highly to moderately toxic to fish, crustaceans and molluscs (LC_{50} 0.1 to 20 mg/L, EPA ECOTOX database). They have low bioaccumulation potential (BCF for alachlor <50). Environmental persistence is moderate, with a biological half-life in soil on the order of seven to 16 days (Ma et al. 2004). In contrast, metolachlor's half-life in soil is estimated to vary between 15 to 132 days, depending on soil type and environmental conditions, and its hydrolysis half-life of is estimated to be over 200 days (at 20° C) for a broad range of pH values (Rivard 2003).

Figure 38

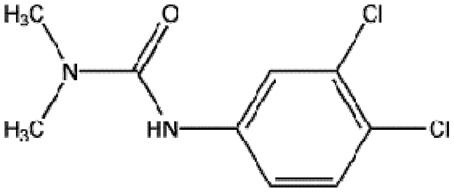
Chemical structure of acetochlor.



3.14.8 Urea derivative herbicides

Urea based herbicides, readily identifiable by the suffix "uron" in their name (eg, linuron and isoproturon), include a large variety of compounds, such as phenylureas, sulphonylureas and thiadiazolylureas. Linuron and isoproturon are non-selective phenylurea herbicides used for the control of grasses and broad-leafed weeds. Their mode of action is by inhibiting photosynthesis. Diuron (Figure 39) is used as an algaecide in antifouling paints.

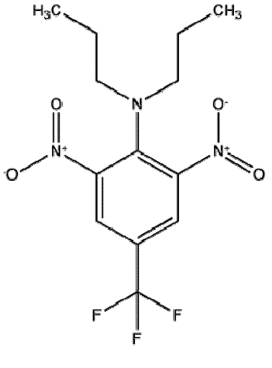
Figure 39
Chemical Structure of diuron.



3.14.9 Dinitroaniline herbicides

Dinitroanilines (derivatives of 2,6-dinitroaniline) are used as herbicides for vegetable growing, nurseries and landscaping. Examples include trifluralin and other "alin" and "amine" substances (oryzalin, benfluraline and prodiamine). Trifluralin (Figure 40), as well as other dinitroanilines, is highly toxic to amphibians, crustacea and fish (LC_{50} <1 mg/L). It has low bioaccumulation potential (BCF generally <100). It has moderate persistence in soils (biodegradation half-life ca. 30d), but degrades rapidly in water (half-life on the order of 24 hours).

Figure 40
Chemical structure of trifluralin, a dinitroaniline herbicide used for arable crops.



3.14.10 Other common herbicides

Other than the selection of herbicide classes described above, there are numerous other herbicides in use, with different mode of action. Some of these are specific plant enzyme inhibitors, such as imidazolinones, triazolopyrimidines and sulfonylureas, or quaternary ammonium herbicides.

Imidazolinones

Imazolinones (IMIs) are a relatively new class of herbicidal compounds, with low acute toxicity to animals. They act by inhibiting specific plant enzymes called acetolactate synthase (ALS/AHAS). One example is imazapyr, a non-selective herbicide used for the control of a broad range of weeds including terrestrial annual and perennial grasses and broadleaved herbs, woody species, and for riparian and emergent aquatic species.

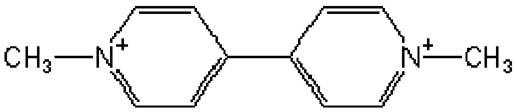
Another example is imazapic, which is a selective herbicide for both the pre- and post-emergent control of some annual and perennial grasses and some broadleaf weeds. Other ALS inhibitors, not belonging to the imidazolinone family include sulfonylureas, triazolopyrimidines, pyrimidinyl oxybenzoates, and sulfonylamino carbonyl triazolinones.

Bipyridilium herbicides

Bipyridilium herbicides contain two pyridine rings, joined through a C-C bond. They belong to the general class of quaternary ammonium herbicides (quats), acting by disrupting the cell membrane. Common examples are paraquat (Figure 41), diquat and morfamquat. In New Zealand, paraquat is used to control weeds in clover seed crops, drains, forestry, industrial sites, lucerne, streets, waterways, pasture, strawberries, vegetables, citrus or deciduous fruit orchards and vineyards. No paraquat formulations are known to be available to the general public in New Zealand. Most bipyridilium herbicides (including paraquat) are acutely toxic to mammals.

Figure 41

Chemical structure of paraquat, a quaternary ammonium herbicide.



Other quaternary ammonium herbicides

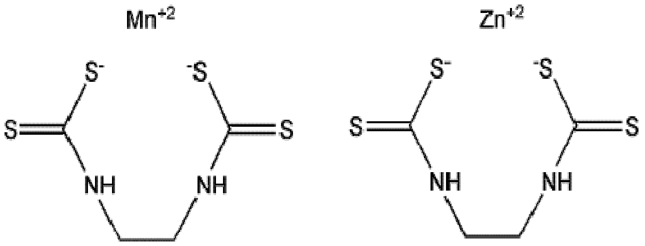
Nearly 200 quaternary ammonium compounds (quats) are used as herbicides, usually as algaecides or microbiocides, although some are used as fungicides and growth regulators. Having surfactant properties, they are often simultaneously used as adjuvant wetting agents. Benzalkonium chloride is used as a domestic moss killer in New Zealand.

3.14.11 Dithiocarbamate fungicides

Dithiocarbamates are lipid synthesis inhibiting fungicides that are commonly used to preserve plant seeds and inhibit bulb rot. Examples include mancozeb (Figure 42), metiram and thiram. Mancozeb is used for onion and potato cultivation, some of which is occurring around Auckland, as well as in a variety of household fungicides. Mancozeb is acutely toxic to algae, crustaceans, amphibia and fish, at LC_{50}s of 0.1 to 10 mg/L. It is moderately bioaccumulative (log K_{OW} = 3.8; BCF ca. 100) and moderately persistent (biodegradation half-life in water ca. 15 days). Due to its widespread use, it is likely to be present in the aquatic environment.

Figure 42

Chemical structure of mancozeb, an example of a dithiocarbamate fungicide. (Source: Pesticide Action Network database www.pesticideinfo.org.)



3.14.12 Other common fungicides

Other fungicides include substituted benzenes, such as chlorothalonil (Figure 43), thiophthalamides, such as captan (Figure 44), phenylsulfamides such as trifluralin, tolylfluanid (Figure 45) and dichlofluanid, as well as azoles, such as tebuconazole (Figure 46). Many fungicides including chlorothalonil and trifluralin are also used as antifouling agents and timber treatment chemicals. Trifluralin is a suspected carcinogen and endocrine disruptor, acting on the thyroid gland. Tebuconazole is used as a fungicide for horticulture (grapes, cherries, peaches) and as a timber treatment chemical. It is moderately toxic to algae, fish and crustaceans, at LC_{50}s generally <10 mg/L.

Figure 43

Chemical structure of chlorothalonil, as substituted benzene fungicide.

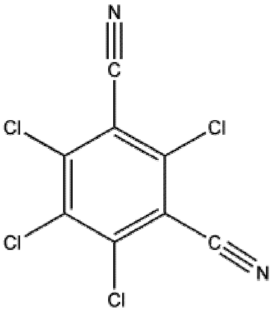


Figure 44

Chemical structure of captan.

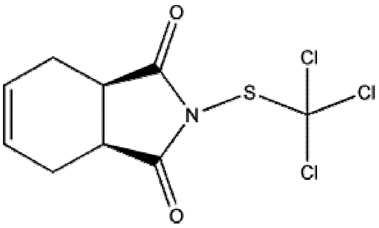


Figure 45

Chemical structure of tolylfluanid, a phenylsulfamide fungicide.

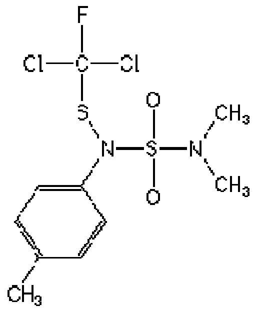
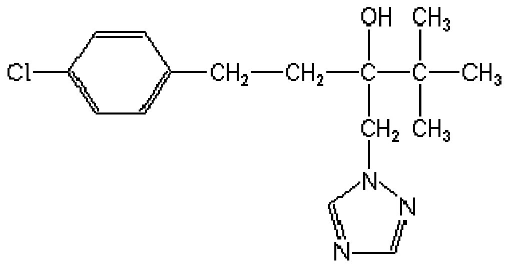


Figure 46

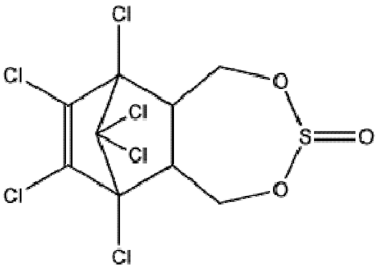
Chemical structure of tebuconazole, an azole-type fungicide.



3.14.13 Organochlorine pesticides

Use of classic organochlorines (OCs) such as DDT, dieldrin and lindane has virtually ceased in New Zealand. However, certain OCs such as endosulfan (Figure 47) are still used in New Zealand (eg, for vegetable, ornamental and berry fruit crops) and there is an environmental legacy of these persistent pesticides in New Zealand from their widespread use, as well as from dumps and spillages. DDT was also used as an antifouling agent in previous times, with direct inputs into the aquatic environment as a consequence. The three most commonly known organochlorine compound classes are DDT (and related compounds), chlorinated cyclodiene insecticides (eg, aldrin, dieldrin, heptachlor, endosulfan and chlordane) and hexachlorocyclohexanes (HCHs), such as lindane. Some organochlorine flame retardants, such as chlorendic acid, have close resemblance to cyclodiene organochlorine pesticides such as endosulfan. Organochlorines are highly toxic (LC_{50} <1µg/L for fish and crustacea), highly persistent and bioaccumulative, enabling them to exert chronic effects on non-target organisms, including neurotoxicity, eggshell-thinning and endocrine disruption. Next to the compound classes described above there are a variety of other chlorine-containing pesticides still in use, such as chloracetanilides, phenoxy herbicides, some urea herbicides, some pyrethroid insecticides, as well as substituted benzene fungicides.

Figure 47
Chemical structure of endosulfan, a cyclodiene organochlorine pesticide still registered for use in New Zealand.



3.14.14 Organophosphorus pesticides

Organophosphorus pesticides (OPs) are esters of phosphoric acid. They are potent neurotoxins, irreversibly inhibiting the enzyme acetylcholinesterase, which is responsible for regulating acetylcholine (ACh) at neuromuscular junctions and at certain synapses in the central and peripheral nervous systems. Examples include diazinon (Figure 48), malathion (Figure 49), chlorpyrifos, dimethoate and trichlorfon. Diazinon is an all-purpose insecticide that is used in both horticultural pesticides and veterinary medicines. Diazinon is applied to apples, kiwifruit, grapes, cereals, lettuce, tomatoes and onion and is also used as a commercial insecticide on lawns and soil. Target pests include whitefly, aphids, caterpillars and grass grubs. Diazinon is also used as an ectoparasiticide against fleas and ticks in cat and dog flea collars, sheep dips and dusting powders for sheep, dogs and horses. Trichlorfon is also used for this purpose. Many OPs are formulated as emulsions for spraying using surfactants. Others are incorporated into seed dressing or into granular formulations, often used for the most toxic compounds, such as phorate, making them easier to handle. However, while this limits acute toxicity, it can lead to continuous, slow release into the environment. OPs are also used to control parasites of salmon in fish farms. Most OPs tend to be short-lived when in the environment, such that their toxicity is primarily acute. However, being highly neurotoxic, sublethal effects at low doses are a potential concern (eg, modified behaviour). For example diazinon has a very low LC_{50} of 0.0008 mg/L for fish and an EC_{50} of 0.0002 mg/L for crustacea. It is also very ecotoxic to terrestrial vertebrates such as birds, and very ecotoxic to honeybees. Diazinon degrades rapidly in aerobic soil with a half-life of less than 20 days and seven to 15 days in natural river water and pond water/soil systems under aerobic conditions. Diazinon has a moderate potential for bioaccumulation, with a reported BCF of 5 to 300 for several species of fish and crustacea. An exception appears to be the common eel (*Anguilla anguilla*), for which BCFs range between 500 and 3000.

Figure 48

Chemical structure of diazinon, an organophosphorus insecticide (Source PAN database).

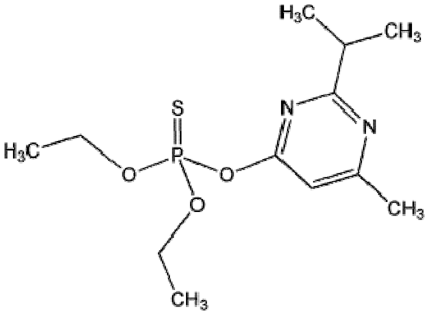
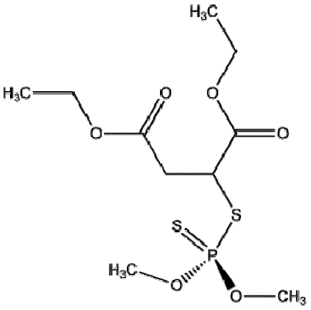


Figure 49

Chemical structure of malathion, an organophosphorus insecticide used in sewage treatment plants for midge control. (Source: PAN database www.pesticideinfo.org.)

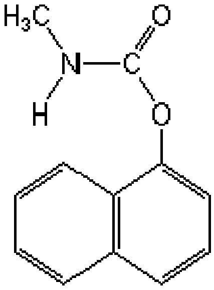


3.14.15 Carbamate pesticides

Carbamates are a newer type of pesticide that act as neurotoxins by reversibly inhibiting the neurotransmitter acetylcholinesterase (ACh). They are primarily used as insecticides, but are also effective as miticides, molluscicides and nematicides. Examples include aldicarb, carbaryl (Figure 50), carbofuran, and methiocarb, the latter of which is used as a molluscide. In New Zealand, carbaryl is the most commonly used carbamate, applied as a broad-spectrum insecticide on fruit trees, vegetables, ornamentals, lawns and to control wasp nests. It is also used in veterinary applications. Carbamates vary greatly in water-solubility and are frequently applied as solids. Carbamates are extremely toxic, but degrade rapidly. For example, the acute toxicity (48-h and 96-h LC_{50}) of carbaryl to a variety of crustaceans is as low as 0.005 mg/L, and is generally lower than 1 mg/L. Carbaryl is moderately toxic to molluscs and fish (LC_{50} 1 to 30 mg/L) and has been used to control pests in oyster farms. It degrades rapidly, with biodegradation half-lives in natural water on the order of a few days, with a maximum of two weeks. It has a low bioaccumulation potential (log K_{OW} <3; BCF <100). Thus, toxicity in the environment, if at all, is likely to occur from acute exposure only.

Figure 50

Chemical structure of carbaryl, a carbamate insecticide.



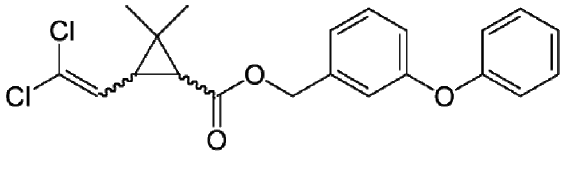
3.14.16 Pyrethroid pesticides

This group of insecticides has gained recent popularity due its perceived "natural" character and relatively low environmental persistence. Although some pyrethroid compounds occur naturally in *Chrysanthemum* flowers, the majority of pyrethroids in use are actually synthetic. Commercial pyrethroids, found in household and agricultural insecticides, as well as in various outdoors applications (mosquito nets, fabric coatings), include permethrin (Figure 51), allethrin, bifenthrin, cypermethrin, tetramethrin, deltamethrin, cyhalothrin, tralomethrin and phenothrin. Pyrethroids and insect growth regulators are also currently used as sheep dips and footbaths, in replacement of arsenic-based compounds (used until the 1950s), organochlorine pesticides (eg, dieldrin, lindane and DDT) and organophosphates (eg, diazinon).

All pyrethroids are potent neurotoxins that affect sodium regulation at nerve synapses. Some pyrethroids, such as bifenthrin, also act as ATPase inhibitors. Pyrethroids are highly toxic to insects and arthropods (LC_{50} generally <0.001 mg/L), and moderately toxic to fish (LC_{50}s generally <5 mg/L). Bifenthrin can interfere with ATP synthesis and osmotic regulation. Pyrethroids have low water solubility, low bioaccumulation potential (low Kow <3), and moderate environmental persistence (biodegradation half-lives generally <six weeks). The hazard from pyrethroids relates primarily to short-term toxicity to fish and non-target invertebrates (eg, bees and dragonflies). Pyrethroids are usually combined with piperonyl butoxide, acting as a "synergist", preventing liver enzymes from metabolising the pyrethroid compound, thereby increasing lethality. Some pyrethroids such as phenothrin are used in combination with methoprene, an insect growth regulator (see below) that interrupts the insect's biological life cycle by killing the eggs.

Figure 51

Chemical structure of permethrin, a pyrethroid insecticide.

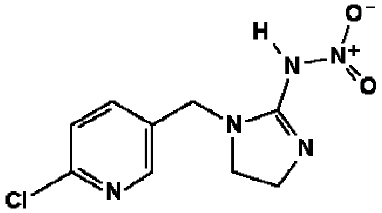


3.14.17 Neonicotinoid pesticides

Another group of neurotoxic insecticides, introduced since the pyrethroids, are neonicotinoids. They are structurally-related to nicotine, and act by affecting cholinergic synapses of animals (eg, acetylcholinesterase). An example is imidacloprid (Figure 52), used in spray formulations (eg "Confidor"). Neonicotinoids have high toxicity to insects, but relatively low or moderate toxicity to many other animals, including daphnids and some fish (LC_{50} >100 mg/L). However, imidacloprid has been found to be toxic to some crustaceans such as ostracods and opossum shrimp. Neonicotinoids are used for flea treatments for pets, control of beetle larvae in lawns, eradication or prevention of termite infestation in buildings, and other uses where animals and people may be exposed. There is concern that imidacloprid might adversely affect non-target insect populations, such as honey bees.

Figure 52

Chemical structure of imidacloprid, a neonicotinoid insecticide, showing structural resemblance to nicotine.



3.14.18 (Animal) growth regulators

A number of insecticides do not act as neurotoxins but instead affect the growth or development of pest organisms, usually by interfering with the moulting process.

Moulting disruptors

These compounds include tebufenozide, methoxyfenozide ("Intrepid") and azadirachtin ("Neemix").

Chitin inhibitors

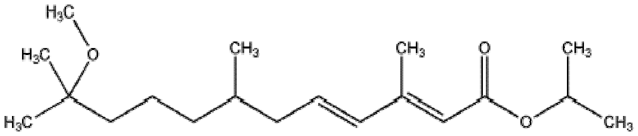
Chitin inhibitors interfere with the synthesis of chitin in insects and other arthropods. They tend to have very low toxicity for vertebrates, but are harmful to crustaceans. An example is diflubenzuron.

Juvenile hormone analogues

Juvenile hormone analogues prevent metamorphosis in arthropods, such as the metamorphosis from pupa to adult in insects. For this to occur, levels of juvenile hormone must be low. Juvenile hormone analogues will therefore prevent or stall development and break the biological life cycle of the pest insects. Examples include methoprene (Figure 53), pyriproxyfen, and diofenolan. Methoprene is used most widely as a mosquito larvicide (eg, Altosid) and for indoor control of fleas and ticks. It is also used to control fire ants.

Figure 53

Chemical Structure of methoprene



3.14.19 Rodenticides

Rodenticides are pesticides used to control rats and mice, as well as rabbits and possums. They comprise substances such as strychnine (no longer registered in New Zealand), anticoagulants and sodium monofluoroacetate (“1080”).

Anticoagulants

Anticoagulant rodenticides include warfarin, and second-generation compounds (“super warfarins") such as brodifacoum, diphenacoum, bromadiolone and flocumafen. Most anticoagulants are coumarin based and act as vitamin K antagonists (competing with vitamin K in the liver), severely interfering with blood clotting. Anticoagulants are toxic to mammals and birds and have long biological half-lives in tissues (120 days), leading to biomagnification through the food chain (eg, accumulation in predators such as owls). Brodifacoum is also highly to moderately toxic to fish (EC_{50}s 0.1 to 10 mg/L) and moderately toxic to daphnids, but apparently has little adverse effect on other crustaceans, such as land crabs (Pain et al. 2000).

Sodium monofluoroacetate (1080)

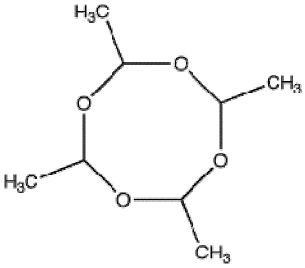
Another common mammal poison used for rabbit and possum control in New Zealand is sodium monofluoroacetate, better known as “1080”. It’s mode of toxic action is by affecting the Krebs cycle, leading to respiratory failure. Available evidence suggest that 1080 is only moderately toxic to fish (EC_{50} >50 mg/L) and weakly toxic to water fleas (EC_{50} >100 mg/L). The biological half-life of 1080 in soils is around 10 days at 23°C, 30 days at 10°C and 80 days at 5°C. In water, 1080 degrades within one to two weeks depending on temperature. In the field, 1080 concentrations measured in natural streams were less than 0.0006 mg/L, four weeks after application (Hamilton & Eason 1994). In tissues, 1080 has a relatively short biological half-life of less than seven days, significantly shorter than that of anticoagulant rodenticides.

3.14.20 Molluscicides

The majority of slug and snail poisons on the market are based on metaldehyde (Figure 54). It is ubiquitously used in agriculture, horticulture and for controlling slugs in the garden. Metaldehyde is moderately toxic to non-target aquatic organisms (EC_{50} for fish, crustacea and algae generally >20 mg/L). It has a low bioaccumulation potential (BCF ca. 10), but is moderately to highly persistent (6 to 18 per cent biodegradation after 28 days). Another molluscicide is methiocarb, a carbamate pesticide used for citrus growing and in nurseries (see Section 3.14.15).

Figure 54

Chemical structure of Metaldehyde, the most common molluscicide.



3.14.21 Nitrification and urease inhibitors

Nitrification inhibitors are used in the pastoral grazing industry to reduce nitrate leaching from soils, either by inhibiting the microbial conversion of ammonium to nitrate and nitrogen-containing gases or by inhibiting the conversion of urea to ammonium. Three kinds of nitrification inhibitors are available: Nitrapyrin (2-chloro-6trichloropyridine), dicyandiamide (DCD) and 3,4 dimethylpyrazole-phosphate (Environment Waikato 2004). The most common nitrification inhibitor in New Zealand is DCD. Three different formulations of DCD are currently available in New Zealand, Eco-N (Ravensdown), DCn (Ballance) and Taurine (Summit Quinphos). One urease inhibitor is registered in New Zealand: nBTPT (N-(n-butyl) thiophosphoric triamide, trade name Agrotain). Their environmental fate is largely unstudied.

3.15 Antifouling agents

Table 30

Environmental hazard profile for antifouling agents.

Qualitative environmental hazard rating	8	**Reason for ranking**
M	Persistence	Generally readily biodegradable within a month.
L	Bioaccumulation potential	Generally low; except for TBT (high).
H	Toxicity/adverse effect potential	Short-term acute toxicity to target organisms.

Antifouling agents are potentially important environmental contaminants in Auckland, given the high-density of marinas and boat mooring sites. Antifouling paints are applied to ship hulls, docks, fishnets and other objects (eg, buoys) to prevent the build-up of aquatic fouling organisms, such as barnacles, algae, bryozoans and bivalves. According to information from ERMA (ERMA Evaluation sheet, March 2007), there are currently over 35 antifouling paints approved for use in New Zealand. All antifouling formulations currently approved in New Zealand use copper as the primary biocide (either as copper oxide or as copper thiocyanate), but many paint formulations include mixtures of additional booster biocides ("co-biocides"), to enhance the paint's efficacy against a broader spectrum of fouling organisms. These co-biocides are commonly fungicides or herbicides, which are also used in agriculture and wood preservation, or in pharmaceuticals and personal care products (eg, Sea-Nine 211 and zinc omadine). Up to 1990, tributyltin (TBT)-based biocides (primarily bis (tri-n-butyltin) oxide) were very popular antifouling compounds, before being banned on recreational and small vessels because of their bioaccumulative properties, high toxicity and endocrine disrupting effects on molluscs. Despite their discontinued use on small water craft, they are still used on larger vessels and as wood preservatives. TBT is likely to be present in old hull coatings, with the potential to enter the aquatic environment in the course of hull-washing and repainting operations. Comprehensive reviews of previously and currently used antifouling compounds, as well as emerging technology can be found in Konstantinou & Albanis (2004) and Yebra et al. (2004). The majority of antifouling paints currently used in New Zealand and worldwide contain one or more of the following co-biocides listed in Table 31.

Table 31

Common antifouling co-biocides, present in copper-based antifouling paint formulations.

Co-biocide name	**Type**	**Chemical class**
Chlorothalonil	Fungicide	Substituted benzene
Copper pyrithione	Fungicide	Inorganic pyrithione
Dichlofluanid	Fungicide	Phenylsulfamide

Co-biocide name	Type	Chemical class
Diuron	Herbicide	Urea
Irgarol 1051	Herbicide	Triazine
Mancozeb	Fungicide	Dithiocarbamate
Octhilinone	Microbicide, fungicide	Isothiazolone
Sea-Nine 211	General microbicide	Isothiazolone
Thiram	Fungicide	Dithiocarbamate
Tolylfluanid	Fungicide, insecticide	Phenylsulfamide
Zinc pyrithione	Microbicide	Inorganic pyrithione
Zineb	Fungicide	Dithiocarbamate

Little knowledge exists of the actual concentrations of antifouling co-biocides in waters and aquatic sediments around New Zealand marinas and mooring facilities. In a survey of 12 recreational boating facilities of two co-biocides irgarol and diuron, Stewart (2003) found diuron to be widespread and detectable in 24 out of 26 samples at concentrations ranging from <10 to 830 ng/L. Irgarol was found only at four locations, at concentrations of <5 to 45 ng/L. Highest concentrations were found in the vicinity of boat washing and re-painting facilities, but interestingly, diuron concentrations were not restricted to marinas, with concentrations of up to 190 ng/L found in open coastal waters. Corresponding sediment concentrations were up to 9410 ng/g for diuron and 1450 ng/g for irgarol, compared to background concentrations of <10 ng/g. These high sediment concentrations near marinas are likely to be attributable to paint flakes.

Bellas (2006) compared the toxicity of several antifouling co-biocides (chlorothalonil, Sea-Nine 211, dichlofluanid, tolylfluanid and irgarol 1051) on early developmental stages of marine invertebrates (the bivalve *Mytilus edulis*, the sea-urchin *Paracentrotus lividus* and the ascidian *Ciona intestinalis*). The author found strong differences in toxicity between different compounds and species: toxicity followed the general order chlorothalonil >Sea-Nine 211 >dichlofluanid=tolylfluanid >irgarol 1051, with EC_{50} values ranging from 25 to 160 nM (for chlorothalonil), 38 to 372 nM (for Sea-Nine), approximately 200 to 4000 nM for the phenylsulfamide compounds tolylfluanid and dichlofluanid, and over 6000 nM for irgarol. Effective concentrations were compared to worst-case environmental concentrations reported in the literature in order to evaluate the hazard posed by these biocides to those invertebrate species. These comparisons indicated that predicted concentrations of chlorothalonil, Sea-Nine 211 and dichlofluanid have the potential to reach concentrations in marinas that represent a threat to *M. edulis*, *P. lividus*, and *C. intestinalis* populations, whilst the risk for irgarol was negligible.

3.16 Timber treatment chemicals

Table 32

Environmental hazard profile of timber preservatives.

Qualitative environmental hazard rating 16		Reason for ranking
M	Persistence	Moderate for most co-biocide. High: inorganic components (CCA, Zn) and creosote-derived PAHs.
M	Bioaccumulation potential	BCF generally <100. High for creosote-derived PAHs.
H	Toxicity/adverse effect potential	High for organic co-biocides and creosote-derived PAHs.

The high reliance on timber as a construction material in New Zealand entails considerable use of chemicals for timber preservation purposes, primarily to fend off fungal and insect attack. Up to recently, there used to be three methods of wood treatment: creosote pressure-treated wood, pentachlorophenol pressure-treated wood, and inorganic metal-arsenical (CCA) pressure-treated wood. Over the last two decades, creosote and pentachlorophenol have dropped out of favour because of environmental concerns about their persistence and toxicity, and CCA has become the prevailing wood-preservation method in New Zealand. In recent years, a wide spectrum of timber preservative formulations containing metals (usually copper oxide) in combination with pesticides have emerged, similar to trends observed for antifouling paints. Common timber treatment co-biocides include compounds such as tributyltin oxide, alkaline copper plus a quaternary ammonium compound (ACQ), and a variety of other pesticides such as tebuconazole, chlorothalonil, chlorpyriphos, carbendazim and carbamate (Table 33).

Table 33

Common biocides or preservatives in timber treatment formulations (Source: Ibach (1999), Koppers Arch website, TimTech website and Osmose website). n.d. = no data available.

Compound/Formulation	Typical concentration in formulation
4,5-dichloro-2-n-octyl-3(2H)-isothiazolone (“Sea-Nine”).	n.d.
Alkaline copper quaternary (ACQ): mixture of copper oxide and didecyldimethylammonium chloride (DDAC).	Cu: 66% DDAC: 33%
Ammoniacal copper citrate (CC): mixture of copper oxide and citric acid.	Cu: 62% citric acid: 36%
Ammoniacal copper zinc arsenate (ACZA): mixture of chromium trioxide, zinc oxide, arsenic pentoxide dehydrate.	Cr: 50% Zn: 25% As: 25%
Benzalkonium chloride.	50%
Bifenthrin.	n.d.

Compound/Formulation	**Typical concentration in formulation**
Bis (tri-n-butyltin) oxide (TBTO).	95%
Borates (Na-octaborate, Na-tetraborate, Na-pentaborate, boric acid).	n.d.
Carbendazim.	7-10%
Chlorothalonil.	45%
Chlorpyrifos.	n.d.
Chromated copper arsenate (CCA): mixture of chromium trioxide, copper oxide, arsenic pentoxide dehydrate.	Cr: 45-55% Cu: 15-20% As: 25-35%
Coal tar creosote.	n.d.
Copper azole: mixture of Cu, boric acid and tebuconazole.	Cu: 49% B: 49% tebuconazole: 2%
Copper bis(dimethyldithiocarbamate) (CDDC): mixture of Cu-ethanolamine and DDC.	Cu: 5% DDC: 2.5%
Copper naphthenate.	10-20%
Didecyldimethylammmonium chloride (DDAC): active ingredient in alkaline copper quaternary.	n.d.
Iodocarb; 3-iodo-2-propynyl butyl carbamate (IPBC).	1-5%
Light organic solvent preservative (LOSP): mixture of waxes and petroleum resin, used in combination with pyrethroid insecticides and azole fungicides.	30%
Linseed oil.	n.d.
Methylene bisthiocyanate.	6%
Octhilinone.	1-2%
Oxine-copper: mixture of copper-8-quinolinolate and nickel 2-ethylhexanoate.	4-10%
Pentachlorophenol (PCP).	95%
Permethrin.	1-2%
Propiconazole.	2-5%
Tebuconazole.	0.5-3%
Zinc naphthenate.	n.d.

3.16.1 Pentachlorophenol

Pentachlorophenol (PCP) is a potent fungicide and insecticide that is no longer used as a wood preservative or in consumer products because of concerns about its toxicity, persistence in the environment and highly toxic residues. The use of PCP in the timber industry ceased in 1988 and PCP was formally deregistered in New Zealand by the Pesticides Board in 1989. Despite its discontinued use for nearly 20 years, PCP may still enter the environment from old PCP treated timber sources and landfills. Closely related tetrachlorophenols are still used as wood preservatives and as anti-sapstains.

PCP is extremely toxic to aquatic organisms, including algae, crustaceans, fish, and amphibians, at LC_{50}s generally less than 1 mg/L (EPA ECOTOX database). Measured log K_{OW} values for PCP range from about 2.7 to 3.7, depending on pH, and measured bioconcentration (BCF) values generally range between 100 to 1000, indicating moderate bioaccumulation potential. Nevertheless, BCF values as high as 45,000 have been measured in molluscs, such as zebra mussels (*Dreissena polymorpha*) and blue mussels (*Mytilus edulis*). Measured aqueous biodegradation half-lives range from 23 to 178 days under aerobic conditions, and from 42 days to greater than a year under anaerobic conditions, indicating high persistence of PCP.

Next to its high environmental persistence, PCP also contains dioxins (eg, tetra-, hexa- and octachlorodibenzo-p-dioxin) and hexachlorobenzene as manufacturing by-products. Furthermore, incineration of old PCP-treated wood (as well as other chlorine-containing wood wastes) can generate polychlorinated dibenzodioxins (PCDD/PCDFs), (Lavric et al. 2004).

3.16.2 Coal tar creosote

Creosote is a tar-based preservative that has commonly been used for impregnating telephone and utility poles and railroad ties. It is one of the oldest wood preservatives, and was originally derived from a wood distillate, although all creosote manufactured today is from the distillation of coal tar. Creosote is a complex mixture of more than 300 compounds, containing mainly PAHs, plus small amounts of phenols, cresols, diphenylene oxide, quinoline base and indoles, which also have biocidal properties. The environmental concern about coal tar creosote centres on the very high PAH concentrations (see coal tar, Section 3.11). Creosote is basically a concentrated PAH-paste, with all the associated environmental hazards. For this reason, creosote is highly toxic to fish and crustaceans (LC_{50} <1 mg/L), highly bioaccumulative (PAHs) and highly persistent.

3.16.3 Chromated copper arsenate (CCA)

Chromated copper arsenate (CCA) is by far the most popular wood treatment in New Zealand, offering good protection from moisture and decay fungi, as well as against insects. CCA-treated timber is also known as "tanalised wood". The copper acts as the primary fungicide, arsenic as a secondary fungicide as well as an insecticide, and chromium is a fixative that also provides UV light resistance. The disadvantage of CCA is that, being water-based, the active compounds will gradually leach out of the timber into the surrounding environment. For example 10 to15 per cent of the CCA have been found to leach out of treated wood buried in compost over a time-period of 12 months (Ibach 1999). Furthermore, incineration of CCA-treated timber can release substantial amounts of Cu, Cr and As, and the inorganic components do not degrade. This has lead to efforts by regulatory agencies overseas (eg, U.S. EPA and the Australian Pesticides and Veterinary Medicines Authority, APVMA) to restrict use of CCA-treated wood for certain applications (eg, children's play equipment and furniture). CCA has been replaced to a certain extent by alkaline copper quaternary, copper azole and the borates.

3.16.4 Alkaline copper quaternary

Alkaline copper quaternary (ACQ) is used as an alternative to CCA. It contains copper (acting as a fungicide) and a quaternary ammonium compound such as didecyldimethylammonium chloride (DDAC), a gemini-quat type cationic surfactant (see Section 3.13) that acts as an insecticide as well as a fungicide. Due to its high levels of copper, ACQ-treated lumber is highly corrosive, requiring the use of double-galvanised fasteners. Quat pesticides tend to have moderate environmental persistence.

3.16.5 Copper azole

Copper azole type wood preservatives are used in a few low-volume commercial formulations in New Zealand (eg, Tanalith E), but have come into wide use in the USA, Europe, Japan and Australia following restrictions on CCA. Copper azole formulations contain an alkaline amine copper complex similar to that in ACQ as well as organic triazoles such as tebuconazole or propiconazole as co-biocides. Azoles are effective against fungicides but not insects. They have moderate toxicity to aquatic organisms (LC_{50} 1-10 mg/L). Their environmental hazard relates to their high persistence. The reported aqueous photolysis half-life of tebuconazole is 600 days; the soil photolysis half-life is 191 days; the aerobic metabolism half-life in a field study is 610 days; and the anaerobic metabolism half-life is 400 days. As azoles contain chlorine, incineration of triazole treated wood can generate dioxins, as recently shown for tebuconazole and permethrin treated wood (Tame et al. 2007).

3.16.6 Other copper compounds

Other primarily inorganic timber preservatives include copper chromate, copper citrate, acid copper chromate and ammoniacal copper zinc arsenate (ACZA). AZCA is generally used for marine applications. The prevailing environmental hazard of this group relates to the inorganic metal and metalloid ingredients, which are toxic and non-biodegradable.

3.16.7 Borates

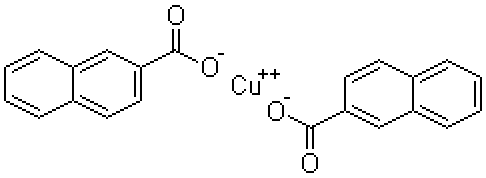
Boric acid, oxides and salts (borates) are used in timber treatment formulations for indoors applications. While the boron compounds are an effective preservative (as well as flame retardant), they are water-soluble and will readily leach out of the wood. For this reason, boron preservatives are used primarily for framing and other indoor applications.

3.16.8 Naphthenates

Metal naphthenates (eg, Cu and Zn-naphthenate) are used for superficial wood treatment (eg, brush-on application). Naphthenates based on calcium, cobalt, lead and mercury or based on quaternary ammonium are used as well. Copper naphthenate (Figure 55) is highly toxic to fish and zinc naphthenate has moderate toxicity. Mercury naphthenate is not commonly used for wood preservation, presumably due to its high toxicity.

Figure 55

Chemical structure of copper naphthenate. (Source: www.chemblink.com database of chemicals from China.)



3.16.9 Other timber preservatives

As shown in Table 33, a number of inorganic and organic agricultural fungicides and insecticides find use as timber treatment chemicals, including dithiocarbamates (eg, CDDC), carbamates (eg, IPBC) organophosphates (eg, chlorpyrifos) and substituted benzenes (eg, chlorothalonil). Furthermore, general microbicides such as tributyl tin oxide (TBTO) or tributyl tin naphthenate (TBTN) and Sea-Nine (4,5-dichloro-2-n-octyl-3(2H)-isothiazolone = DCOIT) are used as well. Some formulations use pyrethroid insecticides such as bifenthrin and permethrin, mostly for envelope-treating wood (ie, brush-on application). Pyrethroids are often used in combination with light organic solvent preservatives (LOSP), consisting of petroleum waxes and white spirit as a solvent. In New Zealand, the most common pyrethroid formulations use permethrin as an insecticide, and propiconazole and tebuconazole as fungicides. Incineration of tebuconazole and permethrin treated wood has been shown to produce PCDDs/PCDFs (Tame et al. 2007).

3.17 Pharmaceuticals, hormones and personal care products

Table 34

Environmental hazard profile of pharmaceuticals and personal care products, including hormones.

Qualitative environmental hazard rating	32	**Reason for ranking**
H	Persistence	High: Sulphonamide antibiotics, some pharmaceuticals. Moderate: Ethinylestradiol (months).
M	Bioaccumulation potential	Moderate for certain antibiotics and surfactants. Oestrogens: low-to-moderate (log K_{OW} 2.6-4.2, depending on compound).
H	Toxicity/adverse effect potential	Moderate-to-high for some drugs: antineoplastics (cancer treatment) and cardiovascular drugs, but these substances occur at concentrations several orders below toxic effects level. The main concern is about chronic effects, eg, the potential to cause endocrine disruption or promote antibiotic resistance (antibiotics, plasticisers, surfactants, oestrogens).

Over the last decade, pharmaceuticals and personal care products (PPCPs) have received increasing attention from environmental and health agencies in the European Union and in North America (Sanderson et al. 2004b). It is estimated that approximately 3000 to 4500 different chemicals are used as pharmaceuticals (Fent et al. 2006, Sanderson et al. 2004b). Nearly 8000 compounds are used as ingredients for personal care products, according to a list by the German manufacturers association for cosmetics and detergents (Industrieverband Körperpflege und Waschmittel, IKW). Since 1997, the European Union has been labelling cosmetic ingredients according to the International Nomenclature of Cosmetic Ingredients (INCI), classifying ingredients according to roughly 60 uses. Since its introduction 10 years ago, the INCI nomenclature has been adopted nearly everywhere in the world, but is not yet consistently used in New Zealand. Personal care product formulations comprise, among other others, oils, moisturising agents, surfactants (Section 3.13), emulsifiers, bleaches, oxidisers, buffers, colours, fragrances, kerolytics, solvents, UV-filters, and various kinds of disinfectants and preservatives. Only a selection of theses will be discussed in this report.

Pharmaceuticals are engineered to have specific effects on the intended target organisms. They include antimicrobials (including antibiotics, antifungals, antivirals, and antiparasitics), analgesics and anti-inflammatory drugs (eg, aspirin, paracetamol), stimulants (eg, caffeine), depressants (eg, benzodiazepines), prescription drugs (eg, cardiovascular, antineoplastics and anti-tumour agents, and anti-asthmatics) as well as steroid hormones, including natural and synthetic sex hormones and corticosteroids.

Given the high number of substances in use, the ecotoxicity, environmental fate or alternative metabolic pathways of PPCPs are often not fully known. In fact, ecotoxicological data are available for less than 1 per cent of pharmaceuticals in the open peer-reviewed literature (Sanderson et al. 2004a). The main route of entry into the environment for pharmaceuticals is via sewage treatment plants (STPs). During use or during breakdown in STPs, pharmaceutical chemicals may be metabolised and converted into new products, which may be modified again when released into the environment, constituting a potential ecotoxicological "Pandora's box" of uncertain magnitude. Furthermore, there is a potential for the occurrence of interactive toxicity. While most studies examining pharmaceutical release have focussed on fate of drugs in STPs, pharmaceuticals may also be released from landfills, following disposal of unused or expired drugs. Another important source of pharmaceuticals, notably hormones and growth promoting antibiotics, is agricultural effluent and run-off from livestock operations. Because many pharmaceuticals tend to be relatively water-soluble, they tend to leave STPs in the aqueous effluent rather than partitioning to biosolids.

Commonly detected drugs in STP effluent include antibiotics, β-blockers, antiepileptic drugs, and lipid regulators, usually at concentrations below 1 µg/L. A comprehensive survey of 95 common pharmaceuticals and hormones in 139 streams across the United States by Kolpin et al. (2002) found 82 of these, in 95 per cent of the occurrences, at concentrations <1 µg/L. The most frequently encountered substances (frequency of detection 50 to 85 per cent) were coprostanol (a faecal steroid), cholesterol (a plant and animal steroid), N,N-diethyltoluoamide (= DEET, an insect repellent), caffeine (a stimulant), triclosan (an antimicrobial), tri(2-chloroethyl) phosphate (a fire retardant), and 4-nonylpehnol (a nonionic surfactant metabolite). Other frequently encountered substances (detection frequency 20 per cent or greater) were cotinine (a breakdown product of nicotine), acetaminophen (ie, paracetamol), estriol (a natural sex hormone), as well as certain kinds of antibiotics (eg, sulfamethoxazole). The detection of PCPPs in stream waters indicates prolonged environmental persistence of many PPCPs beyond sewage treatment. According to a German study of 32 common drugs, removal efficiencies in STPs ranged from seven to 96 per cent, with an average of 60 per cent (Ternes 1998). The concern about PPCPs is their potential to cause reproductive impairment, abnormal physiological processes, increased incidence of cancer, promoting antibiotic resistance and the potential for interactive toxic effects of complex mixtures (eg, synergism or additive toxicity).

Sanderson et al. (2004a), using QSARs, assessed the toxicity of four main pharmaceutical classes: antibiotics (n = 226), antineoplastics (anti-cancer drugs; n = 81), cardiovascular (n = 272) and sex hormones (n = 92), focusing on environmental hazards other than baseline toxicity (ie, resistance, endocrine disruption, and mutagenicity). The predicted rank order of toxicity to daphnids, fish and algae was as follows: sex hormones > cardiovasculars = antibiotics > antineoplastics, with daphnids being the most susceptible and algae the least. The finding of comparatively low toxicity of antineoplastic (cancer-treatment) drugs to algae, invertebrates and fish is surprising given the cytostatic nature of these drugs, but their action might be presumed to be greater in mammals.

3.17.1 Disinfectants, antiseptics and antimicrobials

In addition to pesticides, wood preservatives and antifouling biocides discussed previously, a variety of chemicals are used as disinfectants in human and veterinary pharmaceuticals and personal care products. These include antibiotics (antibacterials and bacteriostatics), antifungals and general, broad-spectrum disinfectants and topical antiseptics. Some chemicals are also used as insect repellents (eg, DEET).

Table 35

Classes of antibiotics (adapted from www.wikipedia.org).

Antibiotic class	Examples
Aminoglycosides	Amikacin, Gentamicin, Kanamycin, Neomycin, Netilmicin, Streptomycin, Tobramycin.
Ansamycins	Geldanamycin, Herbimycin.
Carbacephem	Loracarbef.
Carbapenems	Ertapenem, Imipenem/Cilastatin, Meropenem.
Cephalosporins	Cefadroxilm Cefazolin, Cephalexin, Cefaclor, Cefamandole, Cefoxitin, Cefprozil, Cefuroxime, Cefixime, Cefdinir, Cefditoren, Cefoperazone, Cefotaxime, Cefpodoxime, Ceftazidime, Ceftibuten, Ceftizoxime, Ceftriaxone, Cefepime.
Glycopeptides	Teicoplanin, Vancomycin.
Ionophores	Lasalocid, Monensin, Salinomycin, Narasin.
Macrolides	Azithromycin, Clarithromycin, Dirithromycin, Erythromycin, Roxithromycin, Troleandomycin, Tylosin.
Monobactams	Aztreonam.
Penicillins	Amoxicillin, Ampicillin, Azlocillin, Carbenicillin, Cloxacillin, Dicloxacillin, Flucloxacillin, Mezlocillin, Nafcillin, Penicillin, Piperacillin, Ticarcillin.
Polypeptides	Bacitracin, Colistin, Polymyxin B, Virginiamycin.
Quinolones	Ciprofloxacin, Enoxacin, Gatifloxacin, Levofloxacin, Lomefloxacin, Moxifloxacin, Norfloxacin, Ofloxacin, Trovafloxacin.
Sulphonamides	Mafenide, Prontosil, Sulfacetamide, Sulfamethizole, Sulfanilimide, Sulfasalazine, Sulfisoxazole, Trimethoprim, Trimethoprim-Sulfamethoxazole.
Tetracyclines	Demeclocycline, Doxycycline, Minocycline, Oxytetracycline, Tetracycline.
Others	Arsphenamine, Chloramphenicol, Clindamycin, Ethambutol, Fosfomycin, Fusidic acid, Furazolidone, Isoniazid, Linezolid, Metronidazole, Mupirocin, Nitrofurantoin, Platensimycin, Pyrazinamide, Quinupristin/Dalfopristin, Rifampin, Spectinomycin, Telithromycin.

Antibiotics

Antibiotics are bactericidal substances that are used in medical and veterinary applications and for livestock feeding. While the term "antibiotic" was originally restricted to substances extracted from a fungus (eg, penicillin), it has now come to include many synthetic and semi-synthetic drugs that have antibacterial effects (Table

35). Antibiotics are high-production volume pharmaceuticals, of which a large fraction is used in agriculture to treat animal diseases or promote weight gain. In many instances, antibiotics are used in a purely preventative role. Use and environmental fate of veterinary antibiotics worldwide has recently been reviewed by Sarmah et al. (2006a). In New Zealand, antibiotic use on agricultural livestock is estimated to be around 80,000 kg/annum, for the year 2000 (MAF 2001) (Table 36). Of this, roughly 70 per cent (55,725 kg) was used for purely prophylactic purposes in cattle, pigs and poultry. Antibiotics are also used in fish farms, currently not relevant to the Auckland region.

Antibiotic resistance

The concern about antibiotics in the environment does not relate as much to their toxicity, persistence of bioaccumulation properties, but rather to their potential of promoting antibiotic resistance in free-living bacteria, increasing the chance of transferring this resistance to pathological bacteria, with unforeseen long-term consequences for human health. Increasing antibiotic resistance is a worldwide concern, and it is feared that elevated levels of antibiotics in the environment enhance selection of genes coding for antibiotic resistance which can be transferred between bacteria via plasmids, making it possible for bacteria never exposed to an antibiotic to acquire resistance from those which have it.

Table 36

Veterinary antibiotics sold for agricultural livestock production in New Zealand (kg/annum; 2000 data). Source: MAF (2001).

Type	Kg	% of total	Primary use
Penicillins	10423	13%	Cattle
Aminoglycosides	2122	3%	Cattle and unspecified
Cephalosporins	839	1%	Cattle and unspecified
Tetracyclines	3167	4%	Pigs and unspecified
Macrolids/Lincosamides	6601	8%	Pigs and poultry
Sulphonamides	5570	7%	Unspecified
Ionophores	36215	45%	Poultry and Cattle
Others (non-ionophores)	15461	19%	Poultry
TOTAL	80400	100%	

Environmental persistence and toxicity of antibiotics

Some antibiotics such as sulphonamides have high excretion rates in urine and faeces and degrade only slowly (Kahle & Stamm 2007). In most cases more than 50 per cent of an administered antibiotic leaves the body unchanged (Hirsch et al. 1999). For animal manure, which is often re-applied to land by irrigation, there is a high potential for excreted antibiotics to directly enter the aquatic receiving environments. Consequently, veterinary and medical antibiotics have been detected in groundwater near animal feeding operations and in streams below STP outfalls at concentrations of 0.1 to 1 µg/L (Sarmah et al. 2006a). Near intensive animal feedlots, antibiotic concentrations can be as high as 1 mg/L. The frequency of detection is usually highest for sulphonamides and lincomycin, followed by tylosin (a macrolide). Tetracyclines can also be persistent and have been measured in marine sediments at concentrations of 0.25-4 mg/kg bellow fish farms.

Most antibiotics have only moderate-to-low toxicity to non-target aquatic microorganisms and invertebrates, with EC_{50}s ranging around 1 to 100 mg/L. Environmental concentrations are commonly at least three orders lower, such that acute toxic effects are unlikely to occur. Most antibiotics, such as sulphonamides, have low bioaccumulation potential, with log K_{OW} values generally less than 1 (Diaz-Cruz et al. 2006). However, other antibiotics such as penicillins have higher log K_{OW} values of 3 to 4, suggesting moderate bioaccumulation potential. Reported BCFs for various antibiotics range between 0.34 (chloramphenicol) to 54 (clarithomycin), according to Richardson et al. (2005).

Antiseptic agents

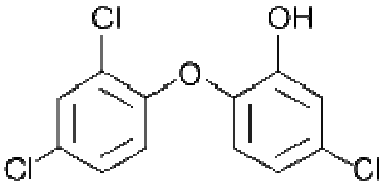
Antiseptic agents are antimicrobials that are generally topically applied (ie, to the skin) or added to products to prevent degradation. Common antiseptic agents include triclosan, chlorophenols, other phenols and cresols, parabens, benzalkonium chloride, cetrimonium bromide, chlorhexidine, hexachlorophene, iodine compounds, mercury compounds, various alcohols, hydrogen peroxide, hexamine hippurate, cetylpyridinium chloride, dequalinium and boric acid.

Triclosan

Many cosmetic and pharmaceutical products contain preservatives to inhibit microbial activity. One widely used antibacterial substance that has been in use for several decades is triclosan (5-chloro-2-(2,4-dichlorophenoxy) phenol; Figure 56), a chlorinated diphenyl ether. It is a potent wide-spectrum antibacterial and is used in shampoos, soaps, deodorants, toothpaste and medicines. Triclosan, or structurally similar substances, are also infused or coated onto solid consumer products such as kitchen utensils, clothing, bedding and trash bags to confer anti-microbial properties. Such plastics and fibres are marketed under trade names “Microban-treated”, “Sanitized” or “Amicor”.

Figure 56

Chemical structure of triclosan, a common antibacterial agent in personal care products.

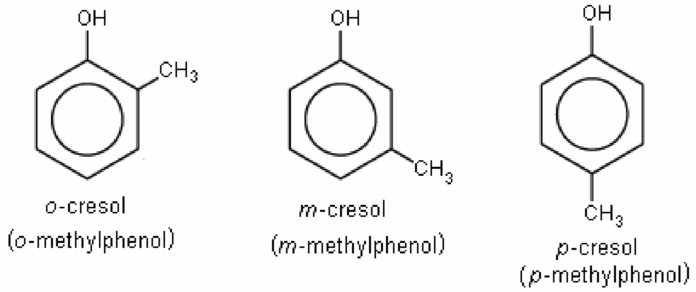


Triclosan’s chemical structure resembles a halogenated diphenyl ether, structurally-related to brominated diphenyl ethers (BDEs). It has a moderate bioaccumulation potential (log K_{OW} ca. 3.3) and a weak endocrine disrupting potential, with the potential to interfere with thyroid function. Triclosan does not degrade completely during sewage treatment and has been detected in wastewater, sediments and river water. For example, Northcott (2007) reported triclosan concentrations of 1 to 20 mg/kg in sewage sludge from 10 New Zealand wastewater treatment plants. Dissolved triclosan concentrations in STP effluent can be as high as 40 µg/L, although other authors report concentrations more than two orders lower (Hale & La Guardia 2002). Removal efficiency of triclosan in STPs is estimated to be around 80 per cent, with 5 per cent leaving as effluent and 15 per cent as sludge. There has been concern, similar to other antibiotics, that the widespread use of triclosan at sublethal concentrations could promote biocide resistance in natural bacterial populations. Triclosan's bacteriostatic or biocidal property seems to be due to multiple action at the cell membrane and by inhibiting fatty acid synthesis in bacteria.

Phenolics

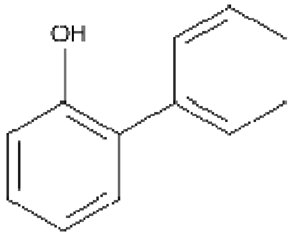
Phenol and its substituted derivatives such as cresols (= methylphenols, Figure 57) and xylenols (dimethylphenols) and cresylic acid are often lumped under the term "phenolics". They are potent antiseptics used as household cleaners and disinfectants, such as "Lysol". In previous times, cresol solutions were widely used as antiseptics in surgery, but they have been largely superseded by less toxic agents, such as cationic surfactants. Other phenolics include thymol, used in antiseptic mouthwashes, menthol, used as an analgesic and flavouring agent, and salicylic acid, used as a cleaning agent in mouthwashes and vasodilator in liniment oils.

Figure 57
Chemical structure of the three cresol isomers, used as antiseptics. (Source: www.wikipedia.org.)



Yet another phenol derivative is 2-phenylphenol (Figure 58), used as an agricultural fungicide for waxing citrus fruits. It is also used for disinfection of seed boxes. It is a general surface disinfectant, used in households, hospitals, nursing homes, farms, laundries, barber shops, and food processing plants. It can be used on fibres and other materials and is used to sterilise hospital and veterinary equipment. Other uses are in rubber industry and as a laboratory reagent. It is also used in the manufacture of other fungicides, dye stuffs, resins and rubber chemicals. Phenylphenol is contained in low concentrations in some household products such as spray disinfectants and aerosol or spray underarm deodorants.

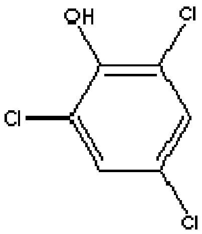
Figure 58
Chemical structure of 2-phenyl phenol, a fungicide for waxing citrus fruit and sterilising agent in hospitals.



Chlorophenols

Chlorophenols are phenol-derivatives with one to five chlorine atoms, resulting in 19 possible congeners. All chlorophenols have biocidal properties, resulting in their primary use as antiseptics, disinfectants, pesticides and wood and leather preservatives. Monochlorophenols (2,MCP, 3-MCP and 4 MCP) are water-soluble and are used as antiseptics in homes, hospitals, farms and in dentistry. However, they have largely been replaced by other chemicals. Dichlorophenols are either used directly as fungicides, algaecides and bactericides, or for formulating herbicides such as 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-T. 2,4-dichlorophenol is also used for mothproofing, as an alternative to naphthalene, and as a nematicide. Among the trichlorophenols, 2,4,5-TCP and 2,4,6-TCP (Figure 59) are the most widely used TCP congeners, used in germicidal soaps, as fungicides, bactericides, algaecides; and germicides for preservation for plywood. Tetrachlorophenols are also used as wood preservatives, anti-sapstains, and as preservatives for latex, leather and plywood. Pentachlorophenol, discussed earlier (Section 3.16.1), used to be an important timber treatment chemical, but is now banned in New Zealand.

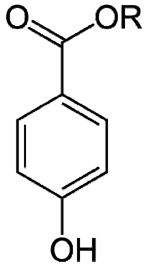
Figure 59
Chemical structure of 2,4,6-trichlorophenol, an antibacterial agent used in germicidal soaps.



Parabens

Parabens are esters of para-hydroxybenzoic acid (Figure 60). They have bactericidal and fungicidal properties and are widely used as preservatives in cosmetic and pharmaceutical products. Common parabens include methylparaben, ethylparaben, propylparaben and butylparaben. Less common parabens include isobutylparaben, isopropylparaben and benzylparaben. Parabens are found in shampoos, bath soaps, commercial moisturisers, shaving gels, cleansing gels, personal lubricants, pharmaceuticals and toothpaste. They are also used as food additives. Parabens generally have low toxicity to aquatic organisms. Some parabens such as butylparaben are weakly estrogenic, approximately 2.5 billion times weaker than estradiol at typical use concentrations.

Figure 60
General chemical structure of a parabens (such as pare-hydroxybenzoate).



Isothiazolinones

Isothiazolinones such as 5-chloro-2-methyl-4-isothiazolin-3-one, are used as broad-spectrum biocides and preservatives in antiseptic agents, bactericides, slimicides, and fungicides. The biggest application, however, is in marine antifouling paints, where the compound is called "Sea-Nine" (see Section 3.15). It is also used for timber treatment, discussed earlier (Section 3.16). Isothiazolinones are also used in cosmetics, adhesives, cutting oils, water systems, household goods and in horticulture (for protecting pruning cuts). They are also used as pulp and wood impregnating agents as well as in leather and fur processing.

Zinc pyrithione

Zinc pyrithione (also known as pyrithione zinc, zinc omadine, zinc bis(pyridine-N-oxide-2-thiolate), or bis(1-hydroxy-2(1H)-pyridinethiolato-O,S) zincate) is an antifungal and antibacterial agent used for treating dandruff and seborrheic dermatitis. It is also used for treating psoriasis, eczema, ringworm, fungus, athlete's foot, dry skin, atypical dermatitis and tinea, and is also an effective algaecide. Due to its low solubility in water, zinc pyrithione is also suitable for use in outdoor paints, including antifouling paints (see Section 3.15), and in products requiring protection against mildew and algae. It breaks down rapidly under UV light, but little is known about its fate in sediments.

Quaternary ammonium surfactants

As discussed in Section 3.13.4 ("Cationic surfactants"), several quaternary ammonium salts such as benzalkonium chloride and cetrimonium bromide are used as disinfectants and preservatives in many cosmetic products, including antiseptic shampoos and face washes. Like other cationic surfactants, they have elevated toxicity towards aquatic organisms and have moderate environmental persistence.

Iodine compounds

Iodine compounds have very broad anti-infective effectiveness against bacteria, fungi, spores, protozoa, viruses, and yeasts. They are used in aqueous or alcoholic solutions. Povidone-iodine is a common over-the-counter iodine antiseptic (eg, trade name "Betadine").

Other antiseptics

Chlorhexidine is used as an antiseptic or disinfectant to prevent body infection and in oral rinses for treating sore gums and mouth ulcers and preventing plaque on teeth. It is used in the form of acetate, gluconate or hydrochloride, either alone or in combination with other antiseptics such as cetrimide. Cetylpyridinium chloride is used in oral rinses and treating minor throat or mouth infections and teething problems. Another oral antiseptic is dequalinium chloride, used for treating bacterial or fungal infections of the mouth and throat. Hexamine hippurates are used for preventing and treating infections of the urinary system. They act by being transformed to formaldehyde.

3.17.2 Mosquito repellents

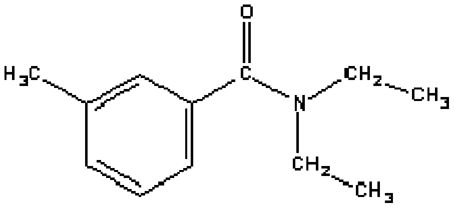
DEET

DEET (meta-N,N-diethyl toluamide; Figure 61) is the active ingredient in most insect and tick repellents currently on the market. Its repellent action is based on blocking certain insect receptors (notably those which detect carbon dioxide and lactic acid) which are used to locate hosts. DEET is sold and used in concentrations up to 100 per cent. It is also used as a solvent for resin and film formers. DEET has a low bioaccumulation potential (log K_{OW} 2.0) and moderate toxicity to aquatic organisms (LC_{50} ca. 75 mg/L for daphnids and trout). However, it has poor biodegradability (no biodegradation over four weeks). Thus, even while applied primarily on clothes and on skin, it is commonly detected in environmental samples (75 per cent detection rate in 139 U.S. streams; Kolpin et al. (2002)).

Next to DEET, natural and synthetic repellents such as citronella oil, permethrin and "Bayrepel" (1-piperidinecarboxylic acid, 2-(2-hydroxyethyl), 1-methylpropyl ester) are also used.

Figure 61

Chemical structure of DEET.



3.17.3 Synthetic musk fragrances

Synthetic musks are used extensively as fragrances in personal care products such as shampoos, detergents, cosmetics and toiletries. Typically, two classes of musk are distinguished; namely, "nitro musks" and "polycyclic musks" (Table 37). Polycyclic musks make up the majority of the market share (66 per cent of world production, estimated at 7000 t/a in 1988; Hale & La Guardia (2002)). The environmental concern about musk fragrances centres on their pheromone-like activity and steroid-like structure, with a potential to evoke endocrine disruption. Furthermore, all musks have relatively high hydrophobicity (log K_{OW} >4) and appear to be bioaccumulative. The log K_{OW} values for musk ketone and xylene (nitro musks) are 4.1 and 5.2, respectively. The log K_{OW} values for the polycyclic musks galaxolide and tonalide are 5.9 and 5.8, respectively. Bioaccumulation factors in trout are 4200 to 5100 for musk compounds. A Japanese study found musk-related compounds ubiquitously occurring in fish, shellfish, and river water samples, as well as in STP effluent. An American study measured musk compound concentrations of 10 to 7000 ng/L in wastewater samples from two STPs, with an estimated removal efficiency of 72 to 98 per cent and a daily discharge of 20 to 30 g/day per plant (Horii et al. 2007). Gatermann et al. (1998) measured musk xylene and musk ketone concentrations of 150 to 550 ng/L in STP influent and 6 to 10 ng/L in effluent. The same authors found high concentrations of musk ketone and galaxolide in tissues of lobster, winter flounder, American eel, lake trout, clams and mussels in the vicinity of densely populated areas (Gatermann et al. 1999). Clams generally had the highest tissue concentrations (17,000 ng/g lipid and 3000 ng/g lipid, respectively). Concentrations of musk breakdown products can increase considerably in STP effluent and some of them (eg, amino derivatives) appear to be more toxic than the parent compound.

Table 37

Synthetic musk fragrances in commercial use (Reiner et al. 2007).

Generic name	Chemical name	Category	Use
Musk ketone	4-*tert*-butyl-2,6-dimethyl-3,5-dinitroacetophenone.	Nitro musk	Most commonly used nitro musk.
Musk xylene	1-*tert*-butyl-3,5-dimethyl-2,4,6-trinitrobenzene.	Nitro musk	Second most commonly used nitro musk.
Musk ambrette	1-(1,1-dimethylethyl)-2-methoxy-4-methyl-3,5-dinitrobenzene.	Nitro musk	Rarely used.

Generic name	Chemical name	Category	Use
Musk moskene	2.3-dihydro-1,1,3,3,5-pentamethyl-4,6-dinitro-1H-indene.	Nitro musk	Rarely used.
Musk tibetene	1-(1,1-Dimethylethyl)-3,4,5-trimethyl-2,6-dinitrobenzene.	Nitro musk	Rarely used.
AHTN (tonalide)	7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene.	Polycyclic musk	95% of European and U.S. market share; together with HHCB.
HHCB (galaxolide)	1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta[γ]-2-benzopyran.	Polycyclic musk	95% of European and U.S. market share; together with AHTN.
HHCB-lactone	1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta[γ]-2-benzopyran-1-one	Polycyclic musk	Oxidation product of HHCB.

3.17.4 Sunscreen compounds

Sunscreen compounds (Figure 62) protect against UV radiation and are either based on organic chemicals that absorb ultraviolet light or opaque inorganic materials that reflect light (usually metallic oxides, such as zinc oxide and titanium oxide, in nanoparticulate form). Next to absorbing or reflecting light, sunscreens are usually also good at dissipating the absorbed energy, thereby preventing the generation of reactive oxygen species and effectively acting as anti-oxidants. To achieve broad-spectrum protection, several compounds are often mixed. Furthermore, antioxidants are added to sunscreens as free-radical scavengers.

Common sunscreen compounds, used as personal care products, are listed in Table 38. Several of these are lipophilic (log K_{OW} 3 to 7; Kunz et al. (2006)) and therefore potentially bioaccumulative, and some have estrogenic activity, such as benzophenone-3, homosalate, 4-MBC, octyl-methoxycinnamate and octyl-dimethyl PABA (Kunz et al. 2006, Schlumpf et al. 2001).

Figure 62

Chemical structure of 4-Methylbenzylidene-Camphor (4-MBC), a common sunscreen compound with weak estrogenic activity.

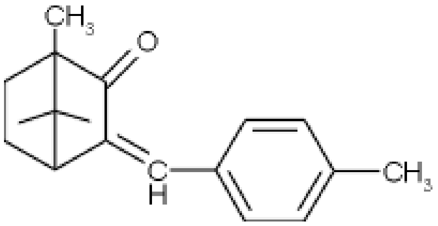


Table 38

Commonly used sunscreen compounds in personal care products.

Compound	Use
4-Methylbenzylidene-camphor (4-MBC)	Widely used sunscreen, at dosage of 4%. Good UVB protection. However, can cause contact dermatitis. Estrogenically active.
Benzophenones	Good UVA and UVB absorbers, but can cause contact dermatitis. One example is benzophenone-3 (BP-3). Estrogenically active.
Cinnamates	Good UVB blockers. Often used in combination with other sunscreen agents. Examples include ethyl hexylmethoxycinnamate, isoamyl p-methoxycinnamate, and octylmethyl cinnamate. Estrogenically active.
Dibenzoylmethanes	Good UVB protection and estrogenically inert, but not very stable. One example is butyl-methoxydibenzoylmethane.
Homosalate	Good UVB protection and solvent for other sunscreen; used at concentrations of 10-15%. Estrogenically active.
Menthyl anthranilate	Good UVA blocker, lipid soluble, used at concentrations of 5% (only approved in the U.S.).
Octocrylene	Good UVB protection, used in combination with ethylhexyl methoxycinnamate, phenylbenzimidazole sulphonic acid, or menthyl anthranilate.
p-aminobenzoic acid (PABA) and derivatives	Extensively used until the 1960s, but no longer common because of poor-water solubility and allergic properties. One example is octyldimethyl-p-aminobenzoic acid (ODPABA). Poor UVA and only partial UVB protection. Estrogenically active.
Phenylbenzimidazole sulphonic acid	Good UVB protection. Usually contained in sunscreen formulations at concentrations of 4-8%.
Salicylates	Good UVB protection. Used in waterproof sunscreens.

3.17.5 Steroid hormones and xenoestrogens

Natural hormones and hormone-like substances are being detected with increasing frequency in the aquatic environment (Hale & La Guardia 2002, Kolpin et al. 2002). They are released into the environment at elevated concentrations from humans, livestock, as well as wildlife and plants. Many hormones and hormonal drugs belong to the class of steroids (derivates of a hydrogenated cyclopentanoperhydrophenanthrene ring system). Natural steroids include the female and male sex hormones estradiol, estrone, estriol, progesterone and testosterone, as well as the synthetic oestrogen ethinyl estradiol (Table 39). These compounds are commonly referred to as oestrogens and androgens. All the corticosteroid hormones (glucocorticoids or mineralocorticoids), all vitamins of the Vitamin D group (calciferol), the bile acids (ursodeoxycholic acid and analogues), cardiac aglycones, sterols like cholesterol, coprostanol, plant saponins, and some corticosteroid drugs (eg, prednisone) are also steroids.

As a consequence of their natural excretion by humans and animals as well as use in drugs such as contraceptives, steroids are ubiquitous components of sewage and agricultural run-off. Oestrogen concentrations in the environment can be as high as 1000 ng/L in farm effluent and up to 100 ng/L in STP effluent. For example, Sarmah et al. (2006b) measured concentrations of β-estradiol of 14.8 ng/L and estrone of 84.7 ng/L in effluent from the Taupo STP. In contrast, dairy farm effluent from the Waikato contained β-estradiol concentrations as high as 331 ng/L and estrone concentrations as high 3057 ng/L. Estriol and ethinyl estradiol were not detected. Estrone has been detected in buried, 120-year-old river sediment in the United Kingdom (Labadie et al. 2007), indicating down-core migration of oestrogens or prolonged persistence.

The environmental concern about oestrogens and oestrogen-like substances relates to their ability to bind to hormone receptors in living organisms and potentially cause endocrine disruption of normal hormone regulation. For example, exposure to oestrogenic substances has been shown to increase vitellogenin production in fish, which can lead to reduced male fish survival and lower egg production in females (Thorpe et al. 2007). The oestrogen β-estradiol is generally used as the "benchmark" for oestrogenicity, and changes in biomarkers in fish have been reported after exposure to estradiol concentrations as low as 0.5 ng/L. The synthetic oestrogen 17α ethinyl estradiol is even more potent, eliciting a response at concentrations as low as 0.1 ng/L (Hale & La Guardia 2002).

Anabolic steroids

Anabolic steroids are based on the male hormone testosterone. They are used as prescription drugs to treat hormonal disorders. Steroidal supplements, used by some body builders to increase muscle and skeletal mass, are based on dehydroepiandrosterone (DHEA) or androstenedione.

Corticosteroids

Corticosteroids mimic the activity of the hormone cortisone, regulating inflammation. Corticosteroids are used in the treatment of many diseases like asthma, eczema, allergies, arthritis, colitis and kidney disease. They include glucocorticoids such as prednisone and mineralocorticoids such as aldosterone.

Sex hormones

Sex hormones are extremely bioactive compounds that are effective at very low concentrations of less than 1 ng/L. Oestrogens are the primary female sex hormones, and include 17-estradiol, estriol and estrone. They are normally produced and excreted by humans, particularly women of childbearing age. Conjugated and unconjugated oestrogens (including estrone) are also prescribed as hormone replacement drugs for postmenopausal women and to prevent osteoporosis. Progestagens include progesterone, 17-hydroxyprogesterone and progestins. Androgens include testosterone, dihydrotestosterone and androsterone. Oestrogens and androgens are lipophilic substances that are weakly (estriol) to moderately bioaccumulative (eg, estradiol, estrone and ethinylestradiol), with log K_{OW} values ranging between 2.6 to 4.2). Their biodegradation half-lives range from two days (estradiol) to 81 days (ethinylestradiol) under oxic conditions (Ying et al. 2003), and more than two months under anaerobic conditions, rendering them moderately persistent. Next to naturally occurring sex hormones, a large variety of synthetic oestrogens and androgens are used as pharmaceuticals and contraceptives (Table 39).

Table 39

Natural sex hormones and hormonally active drugs.

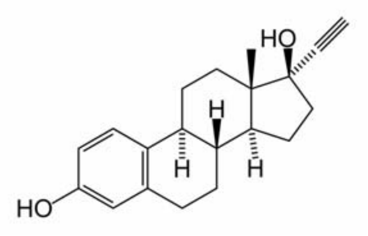
Hormone type	Example
Progestogens	Progesterone, Desogestrel, Drospirenone, Dydrogesterone, Ethisterone, Etonogestrel, Ethynodiol diacetate, Gestodene, Gestonorone, Levonorgestrel, Lynestrenol, Medroxyprogesterone, Megestrol, Norelgestromin, Norethisterone, Norethynodrel, Norgestimate, Norgestrel, Norgestrienone, Tibolone. Inhibitors: Mifepristone.
Androgens	Testosterone, Androstanolone, Fluoxymesterone, Mesterolone, Methyltestosterone. Inhibitors: Bicalutamide, Cyproterone, Flutamide, Nilutamide, Spironolactone.
Oestrogens	Estradiol, estriol, estrone, Chlorotrianisene, Dienestrol, Diethylstilbestrol, Ethinylestradiol, Fosfestrol, Mestranol, Polyestradiol phosphate. Modulators: Bazedoxifene, Clomifene, Fulvestrant, Raloxifene, Tamoxifen, Toremifene. Inhibitors: Aminogluthetimide, Anastrozole, Exemestane, Formestane, Letrozole, Vorozole.
Gonadotropins	FSHR/LHCGR, Clomifene, Urofollitropin. Inhibitors: Danazol, Gestrinone.
Gonadotropin releasing hormones	GnRH, Buserelin, Goserelin, Histrelin, Leuprorelin, Nafarelin, Triptorelin, Inhibitors: Abarelix, Cetrorelix, Ganirelix.

Synthetic oestrogens

Synthetic oestrogens such as 17α-ethinylestradiol (EE2, Figure 63) are widely used in oral contraceptives, mimicking the natural hormone 17β-estradiol. EE2 is the active ingredient in almost all modern formulations of oral contraceptive pills. It is also used for the management of menopausal symptoms and female hypogonadism (called "Estinyl"). It is more resistant to degradation than 17β-estradiol and is metabolised in the liver, involving the P450 enzyme complex and is excreted in both faeces and urine, as a glucuronide and sulphate conjugate. EE2 is only incompletely broken down in the secondary stage of sewage treatment and has been detected in STP effluent, surface waters and fish tissue, at trace concentrations (Sarmah et al. 2006b). EE2 bioaccumulates in fish, and there is concern that EE2 acts in concert with other environmental oestrogens to cause feminisation and infertility of male fish. For example, exposure to EE2 retards the differentiation of testis in zebra fish, which can lead to the development of intersex, where ova begin to appear in the testis. The degree of intersex in roach is correlated with lower sperm quality and quantity and reduced reproductive capability (review by Walker et al. 2006). EE2 has been measured in STP effluent (in the Netherlands) at concentrations of up to 7.5 ng/L (Hale & La Guardia 2002) and in a U.S. STP at 3.66 ng/L, even though it was undetectable in effluent from two New Zealand STPs.

Figure 63

Chemical structure of the synthetic oestrogen 17α-ethinylestradiol (EE2).



Diethylstilbestrol is another synthetic oestrogen (nonsteroidal) that was widely used until the 1970s for treating menopausal symptoms, breast and prostate cancer and various female hormonal disorders. It is still used for veterinary purposes in small quantities.

Xenoestrogens

Many chemicals with a structural similarity to natural oestrogens have the ability to bind to the oestrogen receptor (ER) of animals. Chemicals shown to have oestrogenic (or antagonistic) effects include atrazine (herbicide), alkylphenols (surfactant derivatives; eg, nonylphenol and octylphenol), bisphenol-A (plasticiser and polymerising agent), DEHP (phthalate plasticiser), dieldrin, DDT, hexachlorocyclohexane, endosulfan and methoxychlor (insecticides), polychlorinated biphenyls (transformer fluids, lubricants, adhesives, paints), polybrominated diphenyl ethers and tetrabromobisphenol-A (flame retardants), parabens (cosmetic preservatives) and 4-methylbenzylidine camphor (4-MBC; sunscreen compound). The "oestrogenic potency", or strength of binding to the ER receptor varies by several orders of magnitude, but can potentially lead to endocrine disruption at high enough doses. Table 40 compares the relative potencies of various oestrogenic substances in terms of their binding affinity to the human oestrogen receptors, α-ER and β-ER (Gutendorf & Westendorf 2001). This comparison shows a 10000 fold difference in potency between estradiol and weak xenoestrogens such as bisphenol-A. However, given that environmental concentrations of some xenoestrogens are generally 1000 to 10,000 times higher (eg, 1 ng/L vs. 10 µg/L), high concentrations of these can potentially elicit a similar oestrogenic response.

Table 40

Effects concentrations (EC_{50}) and relative potency (compared to 17β-estradiol = 1) of various oestrogenic compounds, as determined by competitive binding to ER-α and ER-β. Adapted from Gutendorf & Westendorf (2001).

Compound	Chemical group	ER-α binding EC_{50} (nM)	ER-α binding Rel. potency	ER-β binding EC_{50} (nM)	ER-β binding Rel. potency
17-β Estradiol	Nat. oestrogen	3.5	1	65	1
Estriol	Nat. oestrogen	50	0.07	250	0.6
Estrone	Nat. oestrogen	500	0.007	1000	0.065
Ethinylestradiol	Nat. oestrogen	3	1.16	45	1.44
Diethylstilbestrol	Nat. oestrogen	2	1.75	50	1.3
4-nonylphenol	Xenoestrogen	20000	0.000175	30000	0.0023
4-octylphenol	Xenoestrogen	5000	0.0007	10000	0.0065
Bisphenol-A	Xenoestrogen	15000	0.00023	25000	0.0026
Genistein	Phytooestrogens	35000	0.0001	2000	0.032
β-Sitosterol	Phytooestrogens	4000	0.000875	4000	0.016
Coumestrol	Phytooestrogens	3000	0.00117	3000	0.022
Tamoxifen	ER-antagonist	1.5	0.023	40	0.054
OH-Tamoxifen	ER-antagonist	150	1.25	1200	-
ICI 182 384	ER-antagonist	1	3.25	20000	-

3.17.6 Analgesics and anti-inflammatory drugs

Non-steroidal anti-inflammatory drugs include several popular, non-prescription pain killers such as acetylsalicylic acid (aspirin), paracetamol ("Panadol"), ibuprofen, naproxen, codeine, ketoprofen and dichlofenac. Their removal efficiency in STPs is generally high (90 to 100 per cent elimination) and concentrations in STP effluent are generally less than 1 μg/L, although concentrations up to 10 μg/L have been reported (Fent et al. 2006). Acute toxicity to aquatic organisms (algae, daphnids, fish) is generally low-to-moderate (EC_{50} >10 mg/L).

3.17.7 Antineoplastics

Antineoplastic drugs are used in cancer treatment to kill off cancerous cells (chemotherapy). Befitting their use, they are highly cytotoxic, but also genotoxic, mutagenic, carcinogenic, teratogenic and fetotoxic, warranting concern about their potential effect on the environment. Two of the most common antineoplastics are cyclophosphamide and ifosfamide, belonging to the class of oxazaphosphorines. Approximately 14 to 53 per cent of the administered antineoplastic drug is excreted unmetabolised into the urine (Sanderson et al. 2004a). Antineoplastics have poor biodegradability and have been found in STP effluent at concentration up to 3 μg/L.

Their log K_{OW} values are around 1, indicating low bioaccumulation potential. Predicted toxicity ranges between 8 and 1800 mg/L, indicating moderate-to-low acute toxicity.

3.17.8 Cardiovascular drugs

Cardiovascular drugs are highly prescribed compounds, of which five are among the 10 most prescribed drugs in the United States (Sanderson et al. 2004a). Cardiovasculars include statins (eg, atorvastatin), β-blockers (eg, atenolol, metoprolol, and propranolol), diuretics (eg, furosemide and hydrochlorothiazide), calcium channel blockers (eg, amlodipine) and blood-lipid lowering agents (eg, bezafibrate, gemfibrozil, fenofibric acid and clofibric acid). Lipoprotein lipase activators such as bezafibrate were widely used in the past, but have come to be replaced by statins (in the U.S. and the E.U.). Reported concentrations of these compounds in STP effluent commonly range between 0.2 and 1 μg/L. Their maximum removal efficiency in STPs is typically less than 90 per cent and on average around 50 per cent (Fent et al. 2006). Cardiovascular drugs are designed to inhibit or enhance the activity of various enzymes, conferring upon them the potential to cause additional toxicity beyond narcosis. For example, low concentrations (0.5 μg/L) of β-blockers such as propranolol have been shown to decrease the number of eggs in fish. Such effective concentrations are lower than the highest environmental propranolol concentrations (ca. 2 μg/L) that have been measured in the U.S. and the E.U. In a QSAR study of nearly 3000 pharmaceutical compounds, comprising 51 classes, cardiovascular drugs were ranked fourth in terms of ecological risk (behind paraffins, surfactants and pesticides), based on toxicity, bioaccumulation potential and persistence (Sanderson et al. 2004b).

3.17.9 Neuroactive substances

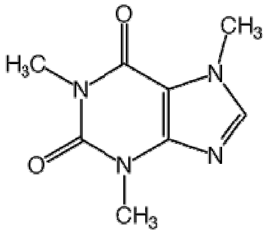
This category comprises stimulants, depressants and antiepileptic drugs.

Stimulants

Chemicals with stimulating properties include caffeine (Figure 64), nicotine, various prescription drugs (eg, antidepressants and anti-asthmatics) and illegal psychoactive drugs (eg, amphetamines). They are neuroactive substances that affect the central nervous system of vertebrates, with the potential to cause neurotoxicity at high concentrations.

Figure 64

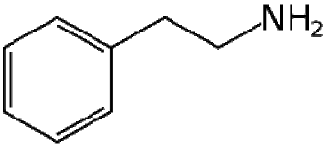
Chemical structure of caffeine. (Source: www.lycaeum.org.)



Many stimulants are alkaloids, including caffeine, nicotine, cocaine and phenethylamine derivatives (Figure 65), such as albuterol and clenbuterol (used as bronchodilators), catecholamines (dopamine, epinephrine and norepinephrine), amphetamines (including methylenedioxymethamphetamine, the active ingredient in the drug ecstasy) and ephedrine and pseudoephedrine (used in decongestants).

Figure 65

Chemical structure of the alkaloid phenethylamine, which is backbone of many stimulants.



Other, non-steroidal stimulants include antidepressants, such as methylphenidate ("Ritalin", "Concerta") and bupropion ("Wellbutrin"), as well as recently introduced ampakines, including modafinil and adrafinil (marketed as "Provigil" and "Olmifon"), used to enhance alertness. Another antidepressant that has been detected at median concentrations of 0.012 µg/L in U.S. streams is fluoxetine. It is one of the more toxic pharmaceuticals, with an EC_{50} <1 mg/L. However, given its nearly 100,000 times lower measured concentration in the environment, acute toxic effects on wildlife are highly unlikely.

Depressants

Most commonly used depressants (next to alcohol, opiate derivatives and tranquilisers) fall into two classes: barbiturates and benzodiazepines. Benzodiazepines are used for treating anxiety, insomnia, agitation, seizures, and muscle spasms, as well as alcohol-withdrawal. Examples include diazepam ("Valium") and flunitrazepam ("Rohypnol"). Diazepam has moderate acute toxicity to aquatic organism, with EC_{50}s typically in the range of 1 to 100 mg/L (Fent et al. 2006).

Antiepileptics

The most frequently detected anti-epileptic compound is carbamazepine (5H-dibenzo[b,f]azepine-5-carboxamide), with measured concentrations up to 6.3 µg/L in wastewater. The EPA ECOTOX database shows low acute toxicity of this compound to water fleas (*Daphnia magna*), with EC_{50} values of 414 to 475 µM ≈ 100mg/L). Another antiepileptic drug which also has been detected in sewage is primidone.

3.17.10 Other pharmaceuticals

Other widely used pharmaceuticals, not described further, include antiviral agents, gastrointestinal drugs, thyroid pharmaceuticals, x-ray contrast agents, antihistamines, antidiabetics, prostaglandins, dermatological drugs, cough remedies, local anaesthetics and muscle relaxants. They all have a potential to enter the environment via wastewater, given that their removal efficiency in STPs is estimated to be generally less than 10 per cent (Sanderson et al. 2004b).

3.18 Food additives and residues

Table 41

Environmental hazard profile for food additives and residues.

Qualitative environmental hazard rating	(4)	**Reason for ranking**
L	Persistence	Generally presumed to be low, but exceptions (artificial sweeteners , synthetic oils).
M	Bioaccumulation potential	Generally presumed to be low, but exceptions.
M	Toxicity/adverse effect potential	Generally low, but moderate toxicity to non-human species by some artificial sweeteners; fragrances and stimulants are potentially neuroactive. Acrolein by-products are carcinogenic.

Processed foods can contain a large number of additives and residues. While the majority are likely to be metabolised or broken down during digestion and in wastewater treatment plants, the environmental fate of food additives is not as well studied or monitored as that of other high production volume chemicals. The prevailing route of entry of these substances into the environment is likely to be by way of sewage effluent or sludge. A QSAR study of 2697 industrial chemicals, including roughly 2000 food additives, estimated 20 direct food additives and 13 indirect food additives as being potentially environmentally problematic, (next to 47 industrial chemicals and pesticides and seven pharmaceuticals), having either elevated bioconcentration potential, aquatic toxicity or diminished biodegradability (Walker et al. 2004). While the top-ranked compounds were not named by the authors, most of them were classified as hydrophobic and therefore predicted to partition to sediments.

3.18.1 Acids

Food acids enhance flavour and also act as preservatives and antioxidants. Common food acids include vinegar, citric acid, tartaric acid, malic acid, fumaric acid and lactic acid.

3.18.2 Acidity (pH) regulators

Acidity regulators are pH buffers used to change or otherwise control the acidity and alkalinity of foods. They can be organic or inorganic. Common acidity regulators include citric, acetic and lactic acids. Other acidity regulators for food include adipates, such as sodium adipate and potassium adipate.

3.18.3 Anticaking agents

Anticaking agents are added to powdered or crystalline foods (eg, table salt) to keep the product from forming lumps, facilitating packaging, transport, and appeal to the consumer. Anticaking agents are typically hydroscopic mineral salts, such as sodium bicarbonate, sodium ferrocyanide, potassium ferrocyanide, calcium aluminosilicate, polydimethylsiloxane and many more. They are likely to have low environmental toxicity.

3.18.4 Antifoaming agents

Antifoaming agents reduce or prevent effervescence in foods, such as soft drinks. An example is polydimethylsiloxane.

3.18.5 Antioxidants

Antioxidants prevent food from becoming rancid. They include compounds such as ascorbic acid (vitamin C), propyl gallate, tocopherols, tertiary butylhydroquinone (TBHQ), butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT). Natural antioxidants include carotenoids and flavonoids. Due to their reactive nature, antioxidants generally have a short degradation half-life of only a few days and will not persist in the environment. BHT is moderately toxic to molluscs, daphnids and fish, with EC_{50}s of 1 to 20 mg/L (EPA ECOTOX database).

3.18.6 Food colouring

A variety of natural and synthetic colours are added to certain foods to replace colours lost during preparation, or to make food look more attractive. Common food dyes include Brilliant Blue (FD&C Blue No. 1), Indigotine (FD&C Blue No. 2), Fast Green (FD&C Green No. 3), Allura Red (FD&C No. 40), Erythosine (FD&C Red No. 3), Tartrazine (FD&C Yellow No. 5) and Sunset Yellow (FD&C Yellow No. 6). Tartrazine, a coal tar derivative, is banned in Norway.

3.18.7 Emulsifiers

Emulsifiers allow water and oils to remain mixed together in an emulsion, as in mayonnaise, ice cream, and homogenised milk. For example, commonly used emulsifiers in chocolate include various lecithins, polyglycerol polyricinoleate, citric acid esters, ammoniumphosphatide, and sorbitan tristearate (European Food Emulsifiers Manufacturing Association (EFEMA) website). Other commonly used emulsifiers, used for dairy products, margarine, and baked goods, are mono-and diglycerides of fatty acids, mono- and diacetyl tartaric acid esters of mono- and diglycerides of fatty acids, and sodium and calcium stearoyl-2-lactylates.

3.18.8 Flavours

A countless number of natural and artificial compounds are used as food flavours, many of which are esters. Examples include diacetyl (buttery), isoamyl acetate (banana), cinnamic aldehyde (cinnamon), ethyl propionate (general fruity), limonene (orange), allyl hexanoate (pineapple), ethyl maltol (sugary), methyl salicylate (wintergreen) and benzaldehyde (bitter almond).

3.18.9 Flavour enhancers

Flavour enhancers enhance a food's existing flavours. Common savoury food flavour enhancers include glutamic acid salts (eg, monosodium glutamate, MSG), glycine salts, guanylic salts and inosine salts.

3.18.10 Flour treatment agents

Flour treatment agents are added to flour to enhance whiteness and baking properties. They include bleaching agents, such as organic peroxides (eg, benzoyl peroxide), calcium peroxide and azodicarbonamidem, and maturing agents (helping with forming gluten), such as carbamide, potassium bromate, ascorbic acid and phosphates.

3.18.11 Humectants

Humectants prevent foods from drying out. They include glycerine, propylene glycol and glyceryl triacetate, polyols like sorbitol, xylitol and maltitol, or polymeric polyols like polydextrose, among many others.

3.18.12 Nitrosamines

Nitrosamines are food-processing byproducts that are produced from nitrites and secondary amines. Their formation occurs under acidic conditions (such as in the human stomach) and at high temperatures, as in frying and barbecuing. Nitrosamines are found in beer, fish products, and in meat and cheese products preserved with nitrite pickling salt.

3.18.13 Preservatives

Preservatives prevent or inhibit spoilage of food due to fungi, bacteria and other microorganisms. They include benzoates (benzoic acid, sodium benzoate, potassium benzoate and calcium benzoate), sorbates and sulphites (eg, sulphur dioxide, sodium sulphite, sodium bisulphite and sodium metabisulphite).

3.18.14 Stabilisers, thickeners and gelling agents

Stabilisers, thickeners and gelling agents, give foods a firmer texture. Food thickeners are frequently based on polysaccharides or proteins. Common examples are agar, alginin, carrageen, collagen, cornstarch, gelatin, guar gum, pectin, tapioca, and xanthan gum.

3.18.15 Sweeteners

Sweeteners are classified as nutritive (eg, sucrose, honey, syrups) and non-nutritive. Non-nutritive sweeteners include aspartame (“NutraSweet” or “Equal”), saccharin (“Sweet 'n' Low”), acesulfame potassium, cyclamate and sucralose (“Splenda”). Many soft drinks contain a combination of aspartame and acesulfame potassium. Some artificial sweeteners are highly toxic to amphibians (EC_{50} 10 to 20 µg/L).

3.19 Nanomaterials

Table 42

Environmental hazard profile of nanomaterials.

Qualitative environmental hazard rating ⑧		**Reason for ranking**
H	Persistence	Probably high for inorganic materials; unclear for organic materials.
M	Bioaccumulation potential	Potentially moderate-to-high because of ability to cross membranes.
L	Toxicity/adverse effect potential	Presumed to be low, but greater reactivity than “normal particles’” more information needed.

Nanoparticles (NPs), defined as particles having a size of 1 to100 nanometres, are finding increasing use in industrial and household applications due to their special physical and chemical properties. They include natural environmental colloids (inorganic, humic substances and biopolymers including enzymes, polysaccharides and peptidoglycans), soot, fullerenes, and engineered organic and inorganic nanoparticles, such as micronised zinc oxide (used in sunscreens). The persistence, mobility, reactivity and ecotoxicity of these substances are currently not well-established. A recent review of nanoparticles (Nowack, 2007) concludes that certain NPs are likely to have effects on organisms under environmental conditions, though mostly at elevated concentrations. Estimating exposure to NPs is currently hindered by analytical difficulties of accurately measuring particulate concentrations.

3.20 Drinking water disinfection by-products (DBP)

Table 43

Environmental hazard profile of drinking water disinfection by-products.

Qualitative environmental hazard rating 16		**Reason for ranking**
M	Persistence	Moderate-to-high for many halocarbons, but occurring at low concentrations.
M	Bioaccumulation potential	Moderate-to-high for lipophilic substances.
H	Toxicity/adverse effect potential	Moderate-to-high, but occurring at low concentrations.

Disinfection of drinking water with chlorine and other disinfectants (eg, ozone, chlorine dioxide, and chloramines) can lead to the generation of various halogenated (primarily chlorinated, but also iodinated and brominated) hydrocarbons, termed “disinfection by-products” (DBPs). There is concern that some of these compounds are inherently toxic, with a potential to cause developmental and reproductive effects and possibly cancer. A nationwide U.S. study of DBPs in drinking water, reviewed by Richardson (2003a), found over 60 compounds, including halomethanes, haloacids, halonitomethanes, haloacetonitriles, haloketones, haloaldehydes, haloacetates, haloamides and halogenated furanones (Table 44). Furthermore, potentially carcinogenic nitrosodimethylamines may be formed.

Table 44

Drinking water disinfection by-products detected in U.S. nationwide survey (Richardson, 2003a).

Compound class	**Example**
MX and MX-analogues	3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone (MX)
	3-chloro-4-(dibromomethyl)-5-hydroxy-2(5H)-furanone (BMX-2)
	3-chloro-4-(dichloromethyl)-2-(5H)-furanone (red-MX)
	3-bromo-4-(dibromomethyl)-5-hydroxy-2(5H)-furanone (BMX-3)
	(E)-2-chloro-3-(dichloromethyl)-butenedioic acid (ox-MX)

Compound class	Example
	(E)-2-chloro-3-(bromochloromethyl)-4-oxobutenoic acid (BEMX-1)
	(E)-2-chloro-3-(dichloromethyl)-4-oxobutenoic acid (EMX)
	(E)-2-chloro-3-(dibromomethyl)-4-oxobutenoic acid (BEMX-2)
	2,3-dichloro-4-oxobutenoic acid (mucochloric acid)
	(E)-2-bromo-3-(dibromomethyl)-4-oxobutenoic acid (BEMX-3)
	3-chloro-4-(bromochloromethyl)-5-hydroxy-2(5H)-furanone (BMX-1)
Haloacids	3,3-dichloropropenoic acid
Halomethanes	Chloromethane
	Dibromoiodomethane
	Bromomethane (methyl bromide)
	Chlorodiiodomethane
	Dibromomethane
	Bromodiiodomethane
	Bromochloromethane
	Iodoform
	Bromochloroiodomethane
	Chlorotribromomethane
	Dichloroiodomethane
	Carbon tetrachloride
Halonitromethanes	Bromonitromethane
	Bromochloronitromethane
	Chloronitromethane
	Bromodichloronitromethane
	Dibromonitromethane
	Dibromochloronitromethane
	Dichloronitromethane
	Tribromonitromethane (bromopicrin)
Haloacetonitriles	Bromoacetonitrile
	Bromodichloroacetonitrile
	Chloroacetonitrile
	Dibromochloroacetonitrile
	Tribromoacetonitrile
Haloketones	Chloropropanone
	1,1,1,3-tetrachloropropanone
	1,3-dichloropropanone
	1,1,3,3-tetrachloropropanone
	1,1-dibromopropanone
	1,1,3,3-tetrabromopropanone
	1,1,3-trichloropropanone
	1,1,1,3,3-pentachloropropanone
	1-bromo-1,1-dichloropropanone

Compound class	Example
	Hexachloropropanone
Haloaldehydes	Chloroacetaldehyde
	Bromochloroacetaldehyde
	Dichloroacetaldehyde
	Tribromoacetaldehyde
Haloacetates	Bromochloromethyl acetate
Haloamides	Monochloroacetamide
	Dibromoacetamide
	Monobromoacetamide
	Dichloroacetamide
	Trichloroacetamide
Nonhalogenated aldehydes and ketones	2-hexenal
	Methyl ethyl ketone (2-butanone)
	5-keto-1-hexanal
	6-hydroxy-2-hexanone
	Cyanoformaldehyde
	Dimethylglyoxal (2,3-butanedione)
Volatile Organic Compounds and miscellaneous DBPs	1,1,1,2-tetrabromo-2-chloroethane methyl tert-butyl ether
	1,1,2,2-tetrabromo-2-chloroethaneb benzyl chloride

3.21 Wastewater treatment residues

Table 45

Environmental hazard profile of wastewater treatment residues.

Qualitative environmental hazard rating	16	**Reason for ranking**
H	Persistence	Moderate-to-high: for certain surfactants (cationic), flame retardants, oestrogens, some pharmaceuticals; likely to be higher for sludge-bound chemicals than for effluent-borne substances.
M	Bioaccumulation potential	Treated effluent: low. Sludge: moderate-to-high for lipophilic substances.
M	Toxicity/adverse effect potential	Low-to-moderate acute toxicity, but endocrine disruption and neuroactivity possible for some compounds.

Municipal wastewater represents one of the main vectors for chemicals used in households and industry to enter the aquatic environment. While secondary and tertiary treatment do an adequate job of reducing bulk organic carbon and nutrient loading, biological and chemical breakdown of specific chemicals such as pharmaceuticals, hormones, flame retardants, some plasticisers, surfactants and natural and synthetic oestrogens is often incomplete. Moreover, degradation can sometimes generate more toxic or biologically active breakdown products, such as 4-nonylphenol, which is a breakdown product of alkylphenol ethoxylate nonionic surfactants, discussed earlier (Section 3.13). Removal efficiencies for various PPCPs are often significantly less than 100 per cent (Ternes 1998), leading to detection of these substances in sewage treatment plant effluent and sludge, and in the adjacent aquatic environment. This also applies to compound classes for which nearly complete removal in STPs has been reported, such as anti-inflammatory pharmaceuticals (Kanda et al. 2003).

Auckland currently operates two municipal STPs, in Mangere and Rosedale. These are comparatively modern facilities, with tertiary treatment. As a consequence, removal efficiencies of various chemicals of potential environmental concern (CPECs) may be assumed to range at the higher end of the spectrum reported for STPs worldwide. Next to the sewage treatment plant route, there is the potential for raw sewage to be discharged to the aquatic receiving environment via leaking septic systems and combined sewage/stormwater overflows, which are still present in a few older residential areas in Auckland, such as the Meola Creek catchment and the Coxes Creek catchment. Given the lack of primary treatment for these effluent streams (or secondary and tertiary treatment, in the case of leaking septic tanks) removal efficiencies of CPECs are likely to be low. Furthermore, raw sewage inputs from livestock production operating in the outskirts of Auckland are likely to be an important input vector for agricultural pharmaceuticals such as hormones and antibiotics. It has been estimated that the New Zealand livestock population excretes about 40 times more waste than the human population (Sarmah et al. 2006b).

The environmental fate of a given chemical of concern will be largely governed by its hydrophobicity and solubility in water: Lipophilic substances are likely to partition to particles and settle out with sludge or sediments, whereas dissolved substances will be carried away rapidly and dispersed by water movement. Sewage sludge can be highly enriched in lipophilic substances, as has been shown in an investigation of sewage sludge from 10 New Zealand municipal STPs (Table 46; Speir & Northcott 2006). For example, nonylphenol concentrations as high as 1800 mg/kg have been reported. The same study detected the phthalate compound DEHP at concentrations of over 100 mg/kg, and brominated diphenyl ether (PBDE) flame retardants at concentrations of over 250 ng/kg, for the congeners BDE 47 (=2,2',4,4'tetraBDE) and BDE 99 (= 2,2',4,4',5-pentaBDE; Northcott, 2007).

Table 46

Concentrations of various chemicals in biosolids/sewage sludge from ten NZ sewage treatment plants. (Source: Speir & Northcott 2006.)

Compound class	Concentration range
PBBs	0.01-0.42 ng/kg
PBDEs	5-625 ng/kg
Nonylphenol	12-1800 mg/kg
Phthalates (DEHP)	20-120 mg/kg (ppm)
Bisphenol-A	29-294 µg/g
Triclosan	1-22 mg/kg
Musk fragrances	3.2-40 mg/kg
Pesticide residues	0.01-13 mg/kg

The magnitude and environmental fate of sewage-derived CPECs is poorly studied in New Zealand. From first principles, it may be argued that lipophilic (hydrophobic) chemicals have a higher chance of attaining elevated environmental concentrations, given their tendency to partition to particulate phases, which will lead to their deposition close to their point of origin, with a lesser chance of dilution. However, if these hydrophobic compounds settle within the confines of the STP, they are destined to be removed in the sludge and will be prevented from further entering streams and estuaries. While there is a theoretical potential for sludge-bound chemicals to re-enter the aquatic environment if STP sludge is subsequently applied to land, this route is discounted for Auckland-derived STP sludge: according to industry information from Watercare, all sludge from the Mangere STP (which produces over 100,000 t/a of biosolids since the 2003 upgrade) is currently landfilled on-site, for which an area of 35 ha has been designated. As a consequence, current inputs of sludge-bound, hydrophobic CPECs from Auckland's STPs are likely to be low. It may therefore be argued that if these compounds are detected in the environment, they are likely to be derived from "legacy" inputs, or contributed via untreated waste from combined stormwater overflows, leaking septic systems and agricultural run-off. On the other hand, as has been shown in overseas studies, even lipophilic substances such as oestrogens, various surfactant breakdown products and pesticides have been detected in treated STP effluent, demonstrating that measurable amounts escape flocculation and remain water-borne. This is probably due the fact that these substances have only moderate log K_{OW} values, causing a measurable residual amount to remain associated with the aqueous phase.

3.22 Landfill leachate

Table 47

Environmental hazard profile of landfill leachate.

Qualitative environmental hazard rating 64		**Reason for ranking**
H	Persistence	Old landfills: High for POPs (PCBs, PBBs, PMDEs, metals) from decommissioned landfills. New landfills: moderate-to-high.
H	Bioaccumulation potential	Mostly-low-to moderate for most leachate compounds with high water solubility, but high for lipophilic compounds (PCBs, nonylphenols, xenoestrogens).
H	Toxicity/adverse effect potential	Old landfills: High toxicity for legacy POPs; in-situ generation of more toxic metabolites possible (eg, nonylphenols). New landfills: low-to-moderate acute toxicity of current-day refuse; contained on-site.

More than 200 organic compounds have been identified in municipal landfill leachate (Slack et al. 2005), of which 10 to 20 per cent are estimated to be potentially hazardous. Auckland currently operates three active landfills: Whitford, Redvale and Greenmount, of which the latter one has recently been re-classified as "cleanfill-only". In addition to these active landfills, there are approximately 370 closed landfills around Auckland. Currently operating landfills are complying with management practices for containing and re-capturing leachates, such as the use of liners, capturing of gaseous emissions and collection of leachate fluids in ponds and their re-application onto the landfill. Contamination of the aquatic environment from these currently operating landfills is therefore expected to be minimal.

In contrast, historic landfill sites are likely to have operated under less stringent consent conditions, both in terms of which kinds of wastes were accepted and how they were disposed of. Thus, it can be assumed that the majority of Auckland's historic landfills were not lined. As a consequence, these sites have a high chance of leaching of liquid wastes into groundwater and adjacent aquatic receiving environments. Even upon closure, leaching processes will continue for several decades, and it is estimated that 30 years of post-closure care is usually needed for a given landfill. Furthermore, previous landfills would have received large amounts of wastes containing now banned substances such as PCBs and DDT, and it may be speculated that some would have received sewage sludge ("municipal solid waste") as well.

3.22.1 Landfill leachate composition

Landfill leachate contains inorganic and organic compounds, of which only the organic compounds will be discussed here. The composition of the organic fraction of landfill leachate is determined not only by the types of waste discarded, but also by the conditions under which they are buried and the interaction of these substances with other wastes. Biological and chemical transformations in the solid phase can lead to the formation of toxic substances from relatively innocuous precursors. While the majority of organic leachates, on a volume basis, are attributable to the degradation of vegetation and natural materials, many CPECs described earlier are frequently found in landfill leachate (Table 48). These include BTEX compounds, halogenated solvents, phthalate plasticisers, bisphenol-A, numerous pharmaceuticals, surfactants (and breakdown products), as reviewed by Slack et al. (2005). Given the large number of decommissioned landfill sites in the Auckland region, it is highly probable that many of these substances are leaching into the environment.

Table 48

Chemicals frequently found in landfill sites receiving municipal solid waste (Slack et al. 2005).

Compound	Use
Halogenated solvents	
Bromodichloromethane, 1,3-Dichlorobenzene, 1,2-Dichlorobenzene, 1,2,3-Trichlorobenzene, 1,2,4-Trichlorobenzene, 1,3,5-Trichlorobenzene, 1,1-Dichloroethane, 1,2-Dichloroethane, Tribromomethane, 1,1,1-Trichloroethane, 1,1,2-Trichloroethane, 1,1,2,2-Tetrachloroethane, trans-1,2-Dichloroethylene, cis-1,2-dichloroethylene, Trichloroethylene, Trichloromethane, Carbon tetrachloride, Chloroethene, Dichloromethane, Tetrachloroethylene, 1,4-Dichlorobenzene.	Solvent, degreaser, deodoriser, DBP, PPCP manufacture, plastic additive or pesticide.
Hexachlorobenzene.	Industrial by-product of solvent, pesticide and wood preservation.
Other solvents	
Glycol ethers.	Solvent paint, varnish, inks, pesticides, antifreeze.
Alcohols.	Solvents.
Benzene, Toluene, Xylenes, Ethylbenzene, Trimethylbenzenes, n-Propylbenzene, t-Butylbenzene, Ethyltoluenes, Tetrahydrofuran, Indene, Aldehydes, ketones.	Solvents.
Surfactants	
Nonylphenol, Nonylphenol ethoxylate.	Surfactant and surfactant breakdown products.
Pesticides	
Aldrin, Dieldrin, DDT DDD, DDE, Dichlorvos, Endosulfan, Endrin, -Hexachlorocyclohexane, Malathion, Methyl parathion, Propoxur.	Insecticides.
Ametryn, Ampa, Atrazine, Glyphosate, Bentazon, Chloridazon, Chlorpropharm, Dichlobenil, Hexazinon, Isoproturon, Mecoprop, MCPA, Simazine, Trifluralin, 4-	Herbicides.

CPP, 2,4-D, 2,4,5-T, 2,4-DP.	
Fenpropimorf, Tridimefon.	Fungicides.
Paint, plastic or rubber additives	
Monomethyl phthalate, Dimethylphthalate, Diethyl phthalate, Methyl-ethyl phthalate, Mono-(2-ethylhexyl) phthalate, Di-(2-ethylhexyl) phthalate, Mono-butylphthalate, Di-n-butylphthalate, Di-isobutylphthalate, Mono-benzylphthalate, Butylbenzyl phthalate, Dioctylphthalate, Diheptyl phthalate, Phthalic acid	Phthalate plasticisers or breakdown product.
Diphenylsulphone, N-Butylbenzene sulphonamide, Naphthalene sulphonates, Benzene sulphonates, p-Toluenesulphonate.	Sulphone or sulphonamide plasticiser, dye or detergent.
Tributylphosphate, Triethylphosphate.	Phosphonate plasticiser, solvent, antifoaming agent.
Bisphenol-A.	Epoxy resins.
Benzenetricarboxyl acids.	Carboxylic acid plasticiser.
n-Tricosane.	Plastics and intermediate.
Styrene.	Polystyrene intermediate.
Diphenylethers.	Flame retardant, plasticiser, herbicide.
Siloxanes.	Silicone polymers—varnish, oils/waxes, rubber.
Benzothiazoles, Benzonitrile, Hexachlorobutadiene.	Rubber manufacture.
Polychlorinated biphenyls.	Transformers and capacitors, paint, adhesives, fluorescent lamps, oil
Anilines.	Ink/dye, resins, drugs, agrochemical intermediate.
Food, pharmaceuticals and personal care products	
Borneol, Camphor, 1,8-Cineole, Fenchone, Limonene, Menthol, Pinene, Terpineol, Tetralins, Thymol.	Terpenoid perfume, flavour or fragrance.
Phenylacetic acid, Linoleic acid.	Fragrance, flavour, drugs.
Caffeine Ibuprofen, Propylphenazone, Phenazone, Clofibric acid, Methylpyridine, Nicotine, Cotinine.	Anti-inflammatory/analgesic-OTC.
Benzoic acid, Palmitic acid, Stearic acid.	Food preservative, cosmetics and pharmaceuticals.
N,*N*-Diethyltoluoamide (DEET).	Insect repellent.
Phenol, Ethylphenols, Cresols, Dimethylphenols, 2,4-Dichlorophenol, 3,5-Dichlorophenol, Trichlorophenols, 2,3,4,6-Tetrachlorophenol, Pentachlorophenol, 2-Meth/4-methoxyphenol.	Disinfectant, solvent, antioxidant or wood preservative.
Indoles.	Food colour, drugs and cosmetics.
Esters.	Flavour and other uses.
Fuel and Combustion Products	
PCDD/PCDF.	Incineration by-product.
MTBE.	Fuel additive.
Naphthalene, 2-Methylnaphthalene, 1-Methylnaphthalene.	Coal tar, moth repellent, toilet deodoriser, or chemical intermediate.

Indane.	Fuel and metal cleaning.

3.23 Incinerator waste

Table 49

Environmental hazard profile of incinerator waste.

Qualitative Environmental Hazard Rating	64	Reason for ranking
H	Persistence	High for PCDDs/PCDFs and PAHs.
H	Bioaccumulation potential	High for PCDDs/PCDFs and PAHs.
H	Toxicity/adverse effect potential	High for PCDDs/PCDFs and PAHs.

While Auckland does not perform municipal waste incineration, several smaller incineration facilities operate in the Auckland region for medical and specialty wastes. Furthermore, domestic burning of rubbish or building wastes contributes to a small incineration waste stream. The environmental concern about incineration wastes focuses primarily on the generation of halogenated by-products, such as acids and polychlorinated dibenzodioxins and polychlorinated dibenzodifurans (PCDD/PCDFs). These can be formed whenever organic matter containing chlorine is combusted, be it PVC, chlorinated hydrocarbon solvents, pentachlorophenol-treated timber waste or even salt-water (and hence Cl^-) logged wood. The use of brominated flame retardants (BFRs) has raised the question whether polybrominated dibenzodioxins and furans (PBDD/PBDFs) might be generated during incineration of BFR-containing plastic wastes (Haglund et al. 2007). However, the understanding of sources and potential toxicity of measured PBDD/PBDF concentration in the environment are still in their infancy and require further study.

4 Synopsis

This report summarised major classes of chemicals known or assumed to be used in consumer, industrial and agricultural applications around Auckland. For assessing the environmental hazard profile of these chemicals of potential environmental concern (CPECs), the persistence-bioaccumulation-toxicity (PBT) classification scheme was adopted. Using this classification, it is apparent that most CPECs have unfavourable environmental fate characteristics in at least one category (ie, a ranking of "moderate" or "high" for one or more criterion). While this does not automatically indicate an elevated environmental risk, which also depends on the concentration at which a given compound occurs, it increases the potential for adverse effects, either by having a low effects threshold (eg, low EC_{50}) or an increased exposure "dose" (eg, high bioaccumulation or high persistence).

A summary of all qualitative environmental hazard ratings (PBT scores) assigned to the 24 product categories covered in this report is presented in Figure 66. Highest PBT scores (PBT score of 64) were assigned to priority organic pollutants (POPs), and landfill and incinerator wastes, due to the large number of compounds present, some of which have high persistence, bioaccumulation and toxicity. Lowest environmental hazard (PBT score of 2) was assigned to organic peroxides, due to their short life-time, and food additives. Among specific chemicals of potential environmental concern, halogenated flame retardants, surfactants (and metabolites) and certain pharmaceuticals and personal care products (notably oestrogens) ranked high (PBT score of 32), mostly as a result of high persistence and bioaccumulation, as well as their elevated potential to cause endocrine disruption.

While, as a whole, CPECs do not attain nearly as high an environmental hazard profile as POPs, such as DDT, PCBs or PCDDs/PCDFs, there is no fundamental difference between these two compound categories. POPs simply occupy an "end ember" position in the spectrum of persistence, bioaccumulation and toxicity, scoring high in all three categories. Table 50 compares further the hazard profile of CPECs and POPs. It may be generalised, that at present, CPECs do not appear to attain environmental concentrations sufficiently high enough to elicit acute toxic effects. However, if moderately elevated toxicity or bioactivity is combined with prolonged exposure (ie, by increased residence in the environment or in organism tissues), there is an increased likelihood for the occurrence of chronic adverse effects. Adverse effects might manifest themselves not necessarily as increased mortality, but rather as chronic endocrine or neurological disruption, leading to modified behaviour or impaired scope for growth. Of the possible types of adverse chronic effects, endocrine and neurological disruption have the greatest likelihood of being observed, given the very low concentrations at which natural hormones and neurotransmitters are effective.

A general challenge in assessing the environmental risk of chemicals in the environment is the fact that they do not occur in isolation but as part of "complex mixtures". This raises the likelihood of additive toxicity for chemicals with a common mode of action, such as non-polar narcosis, acetylcholinesterase inhibition or binding to the oestrogen receptor. As a result, chemicals that occur at environmental concentrations well below their EC_{50} or the lowest observed effects concentration (LOEC) might be capable of acting in concert with other chemicals to produce an adverse effect. To check for such additive effects, rather than measuring individual compound concentrations, it is possible to use bioassays to determine an integrated response. For example, to assess the likely effects of complex mixtures presumed to contain xenoestrogens or neurologically-active substances, competitive binding bioassays show high promise.

Table 50

Comparison of risk profile of primary pollutants and chemicals of potential environmental concern.

Characteristic	Priority pollutants	Chemicals of emerging concern
Toxic effects and mode of action	Acute and chronic (eg, narcosis, growth inhibition, carcinogenic).	Not likely to be acutely toxic at environmental doses, but potentially bioactive (eg, estrogenic, neuro-active).
Environmental concentrations	Frequently monitored: stable or decreasing.	Not frequently monitored: assumed to be increasing.
Persistence	High.	Variable: low, medium, high.
Bioaccumulation potential	High.	Variable: low, medium, high.
Sources	Mainly industry and agriculture few domestic.	Some industry, some agriculture, mainly domestic.
Existing water quality guideline?	Yes.	No.
Discharge regulated?	Yes.	No.
Examples	Mercury, lead, arsenic, DDT, PCBs, PAHs, PCDD/PCDF.	surfactants, plasticisers, disinfectants, pesticides, flame retardants, PCPPs.

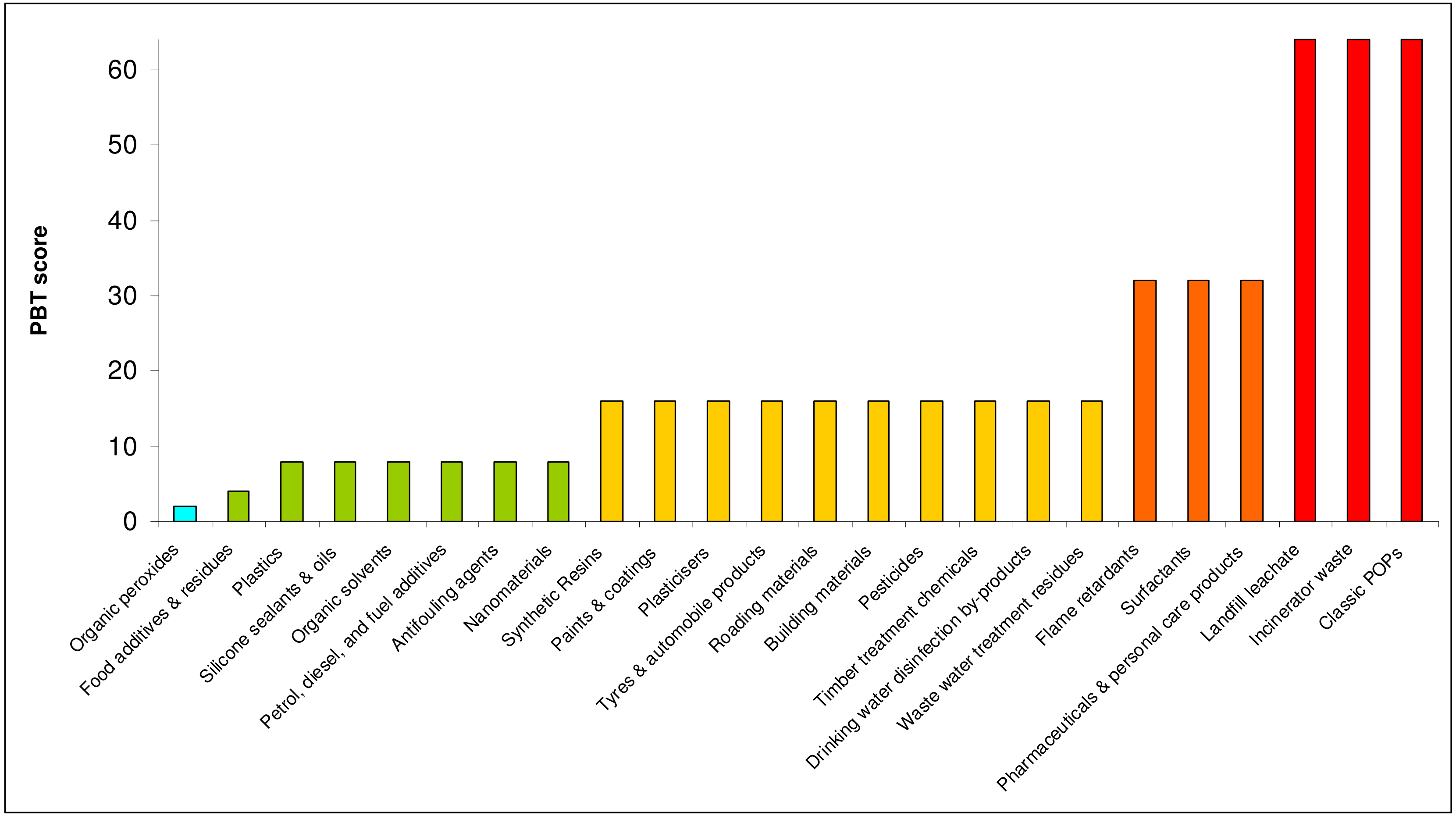
For accurately gauging and managing the risk of CPECs in Auckland, it is necessary to establish the concentrations at which these substances occur in the environment, as well as identify their prevailing sources. The likely routes of entry of CPECs into the aquatic environment are during manufacture and use, from agricultural run-off, from landfill leachates and from sewage treatment plant effluent and sludge. Currently, no monitoring is carried out to determine the environmental concentration of CPECs and their sublethal effects in Auckland's riverine or estuarine environments. Moreover, few guidelines exist at present that regulate the discharge of many of these substances, resulting in a situation of unrestricted discharge into the environment.

Whereas inputs from currently operating, modern sewage treatment plants and landfills are likely to be low, as a consequence of best management practices, ongoing inputs are likely to be occurring from decommissioned landfills, septic tank leakage, and combined stormwater and sewage overflows. Furthermore, agricultural and residential land run-off might be an important diffuse source of some CPECs, notably pesticides and hormones. For antifouling biocides, marinas and boat yards are likely to be significant sources.

Environments with the greatest likelihood of receiving significant inputs of CPECs are estimated to be: (1) marinas (antifouling agents), (2) nearshore settling zones, receiving direct agricultural and residential land run-off (pesticides, hormones and antibiotics), (3) water bodies beneath catchments with decommissioned landfill sites (leachates containing solvents, plasticisers, pharmaceuticals, pesticides and petroleum products), and (4) urban streams downstream of combined wastewater and stormwater overflows (raw sewage containing hormones and xenoestrogens, surfactants, pesticides and plastic additives). Analysis of environmental samples from these environments would provide valuable information on the magnitude of current contamination levels and serve as a benchmark for international comparisons and as a baseline for future studies.

Figure 66

Summary of qualitative environmental hazard ratings (PBT scores) for the 24 general compound classes described in this report.



5 Glossary of common terms and abbreviations

2,4-D	(2,4-dichlorophenoxy) acetic acid, a common phenoxy hormone herbicide.
ABS	Acrylonitrile butadiene styrene, a common type of plastic; alternatively: alkylbenzene sulphonate, a type of surfactant.
Acaricide	Poison for mites.
AChE	Acetylcholine esterase, an enzyme that splits (hydrolyses) the neurotransmitter acetylcholine.
Acute	(when referring to ecotoxicity tests) an adverse effect that manifests itself over a short time period of 48 to 96 hours.
Adjuvant	Substance that is not in itself a pesticide but which enhances or is intended to enhance the effectiveness of the pesticide with which it is used. Adjuvants for use with agricultural pesticides have been categorised as extenders, wetting agents, sticking agents and fogging agents.
Algaecide	Poison for algae.
Analgesic	Pain killing drug.
Androgen	Male sex hormone, or any substance acting on the androgen receptor.
Antagonist	A substance that blocks the action of another substance (for example, at a cellular receptor).
Antineoplastic	Cancer treatment drug.
ANZECC guidelines	An environmental risk assessment framework developed by Australian and New Zealand Environmental and Conservation Council to derive environmental threshold concentrations ("trigger levels") for various contaminants in freshwater, seawater and sediment above which adverse environmental effect are probable.
APEO	Alkylphenol ethoxylates, a class of nonionic surfactant.
ATP	Adenosine triphosphate, a molecule involved in intracellular energy transfer.
BCF	Bioconcentration factor; ratio between the concentration of a chemical in an organism's tissue versus the dissolved concentration in water.
BFR	Brominated flame retardant.
Bioaccumulation	Uptake of a chemical into organism tissues.

BPA	Bisphenol-A, a plastic additive used in the production of polycarbonate plastic.
BTEX compounds	Volatile organic hydrocarbon fraction of petrol consisting of benzene, toluene, ethylbenzene and xylene.
CAPB	Cocamidopropyl betaine, a zwitterionic surfactant.
Carcinogen	Substance causing cancer.
CAS number	Unique number assigned to every known chemical substance in the substance registry of the American Chemical Society.
Catalyst	Substance that accelerates or enhances a chemical reaction without being part of the final product.
CCA	Chromated copper arsenate, an inorganic wood preservative formulation.
Chelating agent	Compound that complexes dissolved metals and renders them less active for chemical reactions.
CHRIP	Chemical Risk Information Platform, a chemical substance database maintained by the Japanese National Institute of Technology and Information.
Chronic	(when referring to ecotoxicity tests) an adverse effect that manifests itself over a time period of seven days or more (usually 28 days).
Congeners	Organic compounds belonging to the same family of compounds (eg, PCBs), differing in the number of rings or substitutions (eg, chlorine atoms).
CP	Chlorinated paraffin, a type of chlorinated flame retardant.
CPEC	Chemical of potential environmental concern.
Cytotoxic	Toxic to biological cells and tissues.
DBT	Disinfection by-products, compounds formed during drinking water disinfection.
DCM	Dichloromethane, an organic solvent commonly used as paint stripper.
DDT	Dichloro-diphenyl-trichloroethane, a common organochlorine pesticide.
decaBDE	Decabrominated diphenyl ether, a mixture of brominated flame retardant with mostly 10 bromine substitutions.
DEHP	Di(2-ethylhexyl) phthalate, a common PVC plasticiser.
DINP	Diisononyl phthalate, a common PVC plasticiser.

Dose	Amount of chemical accumulated or received by an individual (human or organism) over a given time (application) period.
DSDMAC	Dioctadecyldimethyl ammonium chloride, a cationic surfactant widely used as fabric softener.
E.U.	European Union.
EC_{50}	Effects concentration, at which an (adverse) effect is observed in 50 per cent of the specimen in a toxicological assay.
ECC	Emerging chemical of concern.
EDC	Endocrine disrupting chemical (EDC): for example, steroid hormones, phthalates, alkylphenols, bisphenol-A.
EDTA	Ethylene dinitrilotetraacetic acid, a common metal chelating agent.
EE2	17α ethinylestradiol, a synthetic steroid hormone.
Empirical	Based on experimental observation.
EPA ECOTOX	Database of toxicological information maintained by the U.S. Environmental Protection Agency.
EPA HPVIS	High Production Volume Chemical Information System, database maintained by the U.S Environmental Protection Agency.
EPS	Expanded polystyrene foam.
ER	Oestrogen receptor.
ERMA	New Zealand Environmental Risk Management Agency.
ESIS	European Chemical Information System.
FAO	Food and Agriculture Organisation of the United Nations.
FOSA	n-alkyl perfluorooctanesulphonamides, a perfluorinated surfactant intermediary.
FOSE	n-alkyl perfluorooctanesulphonamidoethanol, a perfluorinated surfactant intermediary.
Glyphosate	A non-selective, phosphonyl herbicide.
Halogenated	Containing halogen atoms such as fluorine, chlorine, bromine or iodine.
HBCD	Hexabromocyclododecane, a type of brominated flame retardant that is not a PBDE.
HCH	Hexachlorocyclohexanes, a group of organochlorine pesticide that includes lindane.

Hepatotoxic	Toxic to the liver.
HPVC	High Production Volume Chemical.
HSDB	Hazardous substances databank, maintained by the U.S. National Institutes of Health.
Hydrophobicity	Negative tendency of a compound to partition (solubilise) in water, used to describe fat-soluble chemicals. Often used synonymously with "lipophilicity". Commonly expressed as log $K_{OW.}$
INCHEM	Chemical database maintained by International Program on Chemical Safety (IPCS), as a cooperative agreement between UNEP, FAO, OECD, WHO and other organisations.
IRIS	Integrated Risk Information System, database maintained by the U.S Environmental Protection Agency.
LAS	Linear alkylbenzene sulphonate, an anionic surfactant.
LC_{50}	Lethal concentration, at which mortality is observed in 50 per cent of the specimen in a toxicological assay.
LD_{50}	Lethal dose, accumulated tissue concentration of a chemical at which 50 per cent mortality is observed among experimental specimen.
Leachate	Water and substances dissolved therein after being in contact with a solid material such as landfill waste.
LOEC	Lowest observable effects concentration.
log K_{OW}	Logarithm of the octanol-water partition coefficient, a measure of a chemical's hydrophobicity.
LPVC	Low Production Volume Chemical.
MBC compounds	Fungicide formulation consisting of mancozeb, benomyl and carbendazim.
MBT	2-mercaptobenzothiazole, a vulcanisation accelerator for rubber.
MCPA	2-methyl-4-chlorophenoxyacetic acid, a common phenoxy hormone herbicide.
MDF	Medium-density fibreboard.
MEKP	Methyl ethyl ketone peroxide.
Metabolite	Breakdown product after a biochemical reaction.
MfE	New Zealand Ministry for the Environment.
Molluscicide	Poison for snails and slugs.
MSDS	Material safety data sheet.
MTBE	Methyl tert-butyl ether, a fuel oxygenate in petrol.

MW	Molecular weight.
NADH	Nicotineamide adenine dinucleotide, a co-enzyme found in all living cells that is important for redox reactions
Nematicide	Poison for worms.
Neurotoxic	Toxic to nerves and the central nervous system.
NLM	National Library of Medicine.
nM	Nanomolar.
NOAA	United States National Oceanic and Atmospheric Administration.
NP	4-Nonylphenol, a breakdown product of nonionic alkylphenol ethoxylate surfactants. Alternatively: nanoparticle.
NZFMA	New Zealand Feed Manufacturers Association.
NZFSA	New Zealand Food Safety Authority.
OC	Organochlorine, usually referring to "first-generation" pesticides such as DDT, lindane and HCH.
octaBDE	Octabrominated diphenyl ether, a mixture of brominated flame retardant with mostly 8 bromine substitutions.
Octanol	Eight-carbon alcohol that is very hydrophobic, used as a reference compound when expressing partition coefficients.
OECD	Organisation for Economic Co-operation and Development.
Oestrogen	Female sex hormone, or any substance acting on the oestrogen receptor.
OP	Organophosphate, used as plasticisers, flame retardants and pesticides.
PAH	Polycyclic aromatic hydrocarbon, eg, naphthalene.
PAM	Polyacrylamide.
PBB	Polybrominated biphenyl, a type of brominated flame retardant.
PBT substances	Highly persistent, bioaccumulative and toxic substances.
PCB	Polychlorinated biphenyl.
PCDD/PCDF	Polychlorinated dibenzodioxins and polychlorinated dibenzofurans, often summed as "dioxins".
PCP	Pentachlorophenol.
PDBE	Polybrominated diphenyl ether, a type of flame retardant.
PEG	Polyethylene glycol.
pentaBDE	Pentabrominated diphenyl ether, a mixture of brominated flame retardant with mostly five bromine substitutions.

Persistence	Residence time of a compound in the environment. Inversely related to degradation rate. Often expressed as degradation half-life.
PET	Polyethylene terephthalate, a common type of plastic.
PFOA	Perfluorooctanoic acid, an industrial surfactant and intermediate in the production of PTFE, perfluorinated alcohols and fluorinated fabric protectors such as PFOS.
PFOS	Perfluorooctanesulfonate, a fluorinated industrial surfactant and key ingredient/intermediary in fabric protectors, impregnation agents and fire-fighting foams.
PFS	perfluorinated surfactant; see PFOS, PFOA, FOSA or FOSE.
pH	Negative logarithm of the hydrogen ion activity in water, a measure of acidity.
Phthalate	Common type of plasticiser, often found in soft PVC.
PMMA	Polymethyl methacrylate, the structural compound of acrylic glass (Plexiglas).
POEA	Polyethoxylated tallow amines, a group of cationic surfactants.
Polymer	Organic macromolecule composed of similar repeating sub-units; eg, polyethylene.
POP	Persistent organic pollutant, for example PAH, PCB, DDT.
PPCP	Pharmaceutical and personal care products.
PTFE	Polytetrafluoroethylene, a fluoropolymer commonly known as Teflon.
PU	Polyurethane, a type of plastic commonly used in foamed products.
PVC	Polyvinyl chloride, a common type of plastic.
QSAR	Quantitative structure activity relationships, a modelling approach to estimate a chemical's properties from structural information.
Quats	Quaternary ammonium salts.
RoHS	Restriction of Hazardous Substances in Electric or Electronic Equipment, legislation passed by the European Union.
SDS	Sodium dodecyl sulphate, an anionic surfactant.
Steroid	Terpenoid lipid characterised by a carbon skeleton with four fused rings, generally arranged in a 6-6-6-5 fashion. Includes sex hormones such as oestrogen and testosterone.
STP	Sewage treatment plant.
Sublethal	Having an adverse toxicological effect other than mortality

Surfactant	Surface active compound, the active ingredient in a detergent that helps to solubilise hydrophobic substances in water.
TAED	Tetra acetyl ethylene diamine, a laundry bleaching activator.
TBBPA	Tetrabromobisphenol-A, a type of brominated flame retardant.
TBP	Tributyl phosphate, an organophosphate plasticiser.
TBT	Tributyltin.
TCP	Tricresyl phosphate, a kind of (non-halogenated) flame retardant.
TCSA	Toxic Substances Control Act, U.S. legislation regulating the release of new chemicals into the environment.
TEPA	Tris aziridinyl phosphine oxide, an organophosphorus flame retardant.
Teratogenic	Causing adverse effects to the embryo.
TETA	Triethylenetetramine, a surfactant used as an asphalt additive.
Toxicity	Capacity of a chemical to cause adverse biological effects, such as non-polar narcosis or death. Commonly expressed as an effects concentrations (EC_{50}) or lethal concentration (LD_{50}).
TPH	Total Petroleum Hydrocarbons.
U.S. EPA	United States Environmental Protection Agency.
UNEP	United Nations Environment Programme.
USDA	United States Department of Agriculture.
WHO	World Health Organisation of the United Nations.
Xenobiotic	Foreign substance, a compound commonly not present in the environment.
Xenoestrogen	Chemical that is not a natural female sex hormone (oestrogen) but acts like an oestrogen.
ZDDP	Zinc dialkyldithiophosphate, an anti-wear additive in engine oil.

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