Analytical methods for priority and emerging contaminants – a literature review
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Acknowledgements

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Executive summary

The availability of analytical methodology with sufficient detection sensitivity and selectivity is crucial to effective management of environmental contaminants. This review has considered the analytical methodology available for a range of Contaminants of Emerging Concern (CECs) and assessed the measurement-related needs on the basis of two key criteria: the relevance of each contaminant to the Australian environment and the degree to which appropriate analytical capability is available in Australia. Quality assurance tools essential for ensuring comparability of results between laboratories, such as availability of proficiency testing (PT) studies and reference materials were also considered.

The first task of this project was to develop a shortlist of contaminants for detailed investigation using a combination of CRC CARE end-user input and international peer-reviewed literature. The former included the findings of a CEC Forum held by the CRC in February 2012 which generated a ‘first tier priority’ list of contaminants (Priority 1: methyl tertiary butyl ether (MTBE), perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), weathered hydrocarbons, benzo(a)pyrene (BaP) and polybrominated diphenyl ethers (PBDEs)). Another four classes of contaminants determined from the literature and discussions with Australian and international experts to be important emerging contaminants were selected for review as Priority 2. These were perfluorinated alkyl substances (PFASs) other than PFOS and PFOA, novel flame retardants (FRs), short-chain chlorinated paraffins (SCCPs) and methylsiloxanes. Other contaminants nominated by CRC CARE end-users or found in literature reports were selected as Priority 3, requiring further investigation regarding their relevance in the Australian remediation context, based on their likely use and environmental prevalence. The Priority 3 contaminants were 1,4-dioxane, benzotriazoles, ionic liquids, benzidine dyes, musk fragrances, microbicides, organoboron, organoplatinum, arsenic species and nanoparticles.

The project team then undertook a more detailed literature review into each of the Priority 1, Priority 2 and Priority 3 contaminants. As part of the review, a voluntary and anonymous survey of NATA-accredited laboratories was also conducted to assess the availability of analytical capabilities in Australia.

The key findings of the review were that:

- Significant analytical methodology gaps were not found for any of the Priority 1 compounds, although tools to assess laboratory performance such as easily accessible proficiency testing (PT) schemes are lacking. This may seem surprising in view of their identification by the CEC Forum as a ‘first tier priority’. It should be noted, however, that the research requirements specified by that Forum were much more wide-ranging than the analytical methodology focus of this review and that in the cases of MTBE and BaP, the research needs identified by the Forum were explicitly focussed on areas other than measurement. In addition, there has already been considerable research into all the Priority 1 compounds in recent years, which has in turn resulted in substantial progress in analytical method development for these compounds.

- Analytical capability gaps in Australia were identified for SCCPs, PFASs other than PFOS and PFOA, novel FRs other than PBDEs, synthetic musks, benzidine dyes,
benzotriazoles, methylsiloxanes, organoplatinum compounds and nanomaterials. There appear to be suitable methods in the literature for PFOS, PFOA, PBDEs, novel FRs including tetrabromobisphenol A (TBBPA) and hexabromocyclododcanes (HBCDD), and synthetic musks. Development of local analytical capability for SCCPs, PFSAs and selected FRs including TBBPA and HBCDD appears to present the most significant priority for Australia given the relatively high level of usage in this country.

- Gaps in the availability of matrix reference materials in areas where analytical capability exists or where it has been recommended were identified for PFASs including PFOS and PFOA, SCCPs, TBBPA and HBCDD, benzotriazoles, synthetic musks and arsenic species.

- Gaps in the availability of proficiency testing studies by Australian providers in areas where analytical capability exists or where development has been strongly recommended were identified for MTBE, PAHs including BaP, PFASs including PFOS and PFOA, PBDEs, arsenic species, SCCPs, HBCDD and TBBPA.

The recommendations from the review were that:

- For the very diverse groups of PFASs and novel FRs, especially TBBPA and HBCDD, analytical methodology is not adequate in Australia. Many of these compounds will be used in Australia as they have important commercial applications, and many are subject to long-range transport and may be found in the Australian environment whether they are used here or not. Further investigation into which analytes will be most significant for the Australian environment is recommended. The development of methods, production of reference materials and coordination of PT schemes can then be considered for the more relevant analytes.

- The development of methods, production of reference materials and coordination of PT schemes for short-chain chlorinated paraffins (SCCPs) is strongly recommended.

- The development of analytical methods for benzotriazoles and synthetic musks is recommended, to allow the distribution and environmental impact of these contaminants in Australia to be assessed.

- The production of reference materials and coordination of PT schemes for arsenic species in environmental matrices is strongly recommended.

- Activities of interest would be the development of methodology to allow studies to be conducted into the extent of contamination by methylsiloxanes, benzidines arising from dyestuffs and organoplatinum anticancer drugs.
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AICS  Australian Inventory of Chemical Substances
ANZ  Australia(n) and New Zealand
ANZECC  ANZ Environment and Conservation Council
APEO  alkylphenoxyethanol
APHA  American Public Health Association
APVMA  Australian Pesticides and Veterinary Medicines Authority
ARMCANZ  Agriculture and Resource Management Council of ANZ
ASTM  American Society for Testing and Materials
BaP  benzo(a)pyrene
BFR  brominated flame retardant
BTEX  benzene, toluene, ethylbenzene, xylene
CAS No  Chemical Abstracts Service registry number
CEC  contaminants of emerging concern
COMAR  Code d’Indexation des Matériaux de Référence (database)
CRC CARE  Cooperative Research Centre for Contamination Assessment and Remediation of the Environment.
CRM  certified reference material
DBP  disinfection by-product
DMA  dimethylarsenic acid
DSEWPaC  Department of Sustainability, Environment, Water, Population and Communities
ECD  electron capture detector
ECL  environmental concern level
ECHAM  European Chemical Agency
ECIS  existing chemical information sheet
ECNI  electron capture negative ionisation
EDC  endocrine disrupting compound
EI  electron ionisation
EPA  Environmental Protection Agency
EPHC  Environment Protection and Heritage Council
EQS  environmental quality standard
ESI  electrospray ionisation
ESL  ecological screening level
e-waste  electronic waste
FFF  field-flow fractionation
FID  flame-ionisation detector
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>FR</td>
<td>flame retardant</td>
</tr>
<tr>
<td>FTOH</td>
<td>fluorinated telomer alcohol</td>
</tr>
<tr>
<td>FTS</td>
<td>fluorotelomer sulfonate</td>
</tr>
<tr>
<td>GC</td>
<td>gas chromatography</td>
</tr>
<tr>
<td>GILs</td>
<td>groundwater investigation levels</td>
</tr>
<tr>
<td>GPC</td>
<td>gel permeation chromatography</td>
</tr>
<tr>
<td>HBCDD</td>
<td>hexabromocyclododecane</td>
</tr>
<tr>
<td>HGAAS</td>
<td>hydride generation atomic absorption spectrometry</td>
</tr>
<tr>
<td>HILs</td>
<td>health-based investigation levels (soil)</td>
</tr>
<tr>
<td>HPLC</td>
<td>high-pressure liquid chromatography</td>
</tr>
<tr>
<td>HPA</td>
<td>Health Protection Agency</td>
</tr>
<tr>
<td>HR(MS)</td>
<td>high resolution (mass spectrometry)</td>
</tr>
<tr>
<td>HSLs</td>
<td>health screening levels</td>
</tr>
<tr>
<td>IARC</td>
<td>International Agency for Research on Cancer</td>
</tr>
<tr>
<td>ICP</td>
<td>inductively coupled plasma</td>
</tr>
<tr>
<td>IL</td>
<td>ionic liquid</td>
</tr>
<tr>
<td>IRMM</td>
<td>Institute for Reference Materials and Measurements (Belgium)</td>
</tr>
<tr>
<td>ISO</td>
<td>International Standards Organisation</td>
</tr>
<tr>
<td>JIS</td>
<td>Japanese Industrial Standard</td>
</tr>
<tr>
<td>LC</td>
<td>liquid chromatography</td>
</tr>
<tr>
<td>LC-MS-MS</td>
<td>liquid chromatography tandem mass spectrometry</td>
</tr>
<tr>
<td>LLE</td>
<td>liquid-liquid extraction</td>
</tr>
<tr>
<td>MAE</td>
<td>microwave assisted extraction</td>
</tr>
<tr>
<td>MCL</td>
<td>maximum contaminant level</td>
</tr>
<tr>
<td>MS</td>
<td>mass spectrometry</td>
</tr>
<tr>
<td>MTBE</td>
<td>methyl t-butyl ether</td>
</tr>
<tr>
<td>NATA</td>
<td>National Association of Testing Laboratories</td>
</tr>
<tr>
<td>NEPM</td>
<td>National Environment Protection Measure</td>
</tr>
<tr>
<td>NICNAS</td>
<td>National Industrial Chemicals Notification and Assessment Scheme</td>
</tr>
<tr>
<td>NIST</td>
<td>National Institute of Standards and Technology (USA)</td>
</tr>
<tr>
<td>NMI</td>
<td>National Measurement Institute (Australia)</td>
</tr>
<tr>
<td>NPD</td>
<td>nitrogen-phosphorous detector</td>
</tr>
<tr>
<td>NRMMC</td>
<td>Natural Resource Management Ministerial Council</td>
</tr>
<tr>
<td>NWQMS</td>
<td>National Water Quality Management Strategy</td>
</tr>
<tr>
<td>OECD</td>
<td>Organisation for Economic Cooperation and Development</td>
</tr>
<tr>
<td>OEH</td>
<td>Office of Environment and Heritage</td>
</tr>
<tr>
<td>OP</td>
<td>organophosphorous</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>OSPAR</td>
<td>Oslo and Paris Convention for the Protection of the Marine Environment</td>
</tr>
<tr>
<td>PAH</td>
<td>polycyclic aromatic hydrocarbon</td>
</tr>
<tr>
<td>PBDE</td>
<td>polybrominated diphenyl ether</td>
</tr>
<tr>
<td>PCB</td>
<td>polychlorinated biphenyl</td>
</tr>
<tr>
<td>PE</td>
<td>phthalate ester</td>
</tr>
<tr>
<td>PEC</td>
<td>priority existing chemical</td>
</tr>
<tr>
<td>PFAS</td>
<td>perfluoroalkyl substance</td>
</tr>
<tr>
<td>PFCA</td>
<td>perfluorinated carboxylic acid</td>
</tr>
<tr>
<td>PFECHS</td>
<td>perfluoroethylcyclohexane sulfonic acid</td>
</tr>
<tr>
<td>PFOA</td>
<td>perfluorooctanoic acid</td>
</tr>
<tr>
<td>PFOS</td>
<td>perfluorooctanesulfonate</td>
</tr>
<tr>
<td>PFPA</td>
<td>perfluorinated phosphonic acid</td>
</tr>
<tr>
<td>PFPIA</td>
<td>perfluorinated phosphinic acid</td>
</tr>
<tr>
<td>PFSA</td>
<td>perfluorinated sulfonic acid</td>
</tr>
<tr>
<td>PFTHP</td>
<td>perfluoroperhydrophenanthrene</td>
</tr>
<tr>
<td>PLE</td>
<td>pressurised liquid extraction</td>
</tr>
<tr>
<td>POP</td>
<td>persistent organic pollutant</td>
</tr>
<tr>
<td>(P)PCPs</td>
<td>(pharmaceuticals and) personal care products</td>
</tr>
<tr>
<td>PT</td>
<td>proficiency testing</td>
</tr>
<tr>
<td>QTOF</td>
<td>quadrupole time-of-flight</td>
</tr>
<tr>
<td>QUASIMEME</td>
<td>Quality Assurance of Information for Marine Environmental Monitoring in Europe</td>
</tr>
<tr>
<td>REACH</td>
<td>Registration, Evaluation, Authorisation and Restriction of Chemicals</td>
</tr>
<tr>
<td>SCCP</td>
<td>short-chain chlorinated paraffin</td>
</tr>
<tr>
<td>SFE</td>
<td>supercritical fluid extraction</td>
</tr>
<tr>
<td>SIL</td>
<td>soil investigation level</td>
</tr>
<tr>
<td>SPE</td>
<td>solid phase extraction</td>
</tr>
<tr>
<td>SPME</td>
<td>solid phase microextraction</td>
</tr>
<tr>
<td>SRM</td>
<td>standard reference material</td>
</tr>
<tr>
<td>TBA</td>
<td>tertiary butyl alcohol</td>
</tr>
<tr>
<td>TBBPA</td>
<td>tetrabromobisphenol A</td>
</tr>
<tr>
<td>TEQ</td>
<td>toxic equivalence</td>
</tr>
<tr>
<td>TGA</td>
<td>Therapeutic Goods Administration</td>
</tr>
<tr>
<td>TOF</td>
<td>time-of-flight</td>
</tr>
<tr>
<td>TPBP</td>
<td>triphenylborane pyridine</td>
</tr>
<tr>
<td>TPH</td>
<td>total petroleum hydrocarbon</td>
</tr>
<tr>
<td>2D GC</td>
<td>two dimensional GC</td>
</tr>
<tr>
<td>UNEP</td>
<td>United Nations Environment Program</td>
</tr>
</tbody>
</table>
US EPA  United States Environmental Protection Agency
UV    ultra-violet
UNIDO United Nations Industrial Development Organization
VD    vacuum distillation
VOC   volatile organic compound
WFD   Water Framework Directive
WHO   World Health Organisation
WWTP  wastewater treatment plant
1. Introduction

The availability of analytical methodology with sufficient detection sensitivity and selectivity is crucial to effective management of environmental contaminants. This review has considered the analytical methodology available for a range of contaminants of emerging concern (CECs), their relevance to the Australian environment and the analytical capability available locally. This review is limited to laboratory-based methodology, and does not include field-based testing.

Quality assurance tools essential for ensuring comparability of results between laboratories, such as availability of proficiency testing (PT) studies and reference materials, were also considered. The availability of good quality reference materials is critical to permit generation of accurate and comparable analytical results. Reference materials range from technical grade standards of target compounds to fully certified reference materials (CRMs) with documentation of metrological traceability. The metrological traceability and measurement uncertainty associated with an analytical result is dependent on the material used for method calibration and identification (de Bievre et al. 2011; ISO 2009).

1.1 Selection of contaminants

A list of possible contaminants was compiled using information derived from CRC CARE meetings identifying a range of contaminants of concern amongst members. The list was extended following a search of the analytical chemistry literature. This literature has been effectively summarised in the most recent of an extensive series of reviews by Susan Richardson of the US Environmental Protection Agency (EPA) (Richardson 2010; Richardson 2012; Richardson and Ternes 2011). The United Nations Environment Program (UNEP) report on Emerging Chemical Management Issues in Developing Countries provided by Professor MH Wong was also reviewed for potential contaminants of interest to Australia (STAP 2012).

1.1.1 Contaminants considered but not selected

The very large contaminant classes of endocrine-disrupting compounds (EDCs) and emerging contaminants among the pharmaceuticals and personal care products (PPCPs), pesticides and herbicides and their metabolites and degradation products, surfactants and dispersants, phthalates and plasticisers have been extensively studied and reviewed, including in the following publications. Zuloaga et al. (2012) reviewed extraction methods for sewage sludge in the 10 years to 2012. Methods are tabulated by extraction technique, and analytes from all these categories are mentioned. Richardson’s most recent reviews of water (Richardson and Ternes 2011) and environmental analysis (Richardson 2012) include discussion of pharmaceuticals and hormones, sunscreens, musks and pesticide transformation products. The omission of surfactants (other than PFASs), phthalates and plasticisers suggests that Richardson no longer considers them to be new and active fields of research. Wille et al. (2012) reviewed chromatographic methods with mass spectrometric (MS) detection for PPCPs (including musk fragrances, UV filters, insect repellents, paraben preservatives and the microbicides triclosan and triclocarban), pesticides, estrogenic compounds and surfactants. Petrovic et al. (2010) reviewed liquid-chromatography (LC)-MS in environmental samples and included sections on pharmaceuticals and polar pesticides. Giger (2009) reviewed advanced analyses for water pollutants and included methods...
for surfactants and metabolites, pharmaceuticals and polar herbicides and metabolites. Closer to home, Shareef et al. identified EDCs and PPCPs likely to be present in Australian domestic wastewater and surveyed their occurrence in 2010, developing analytical methods where required (Shareef et al. 2008; Shareef et al. 2010). In 2007, the CRC for Water Quality and Treatment published a report on CECs in waste water treatment plant (WWTP) effluent in Australia, discussing EDCs and pharmaceuticals (CRC WQT 2007). They found that established analytical methods were available for many of the classes of EDCs, however methodology for classes such as hormones, drugs, PCP ingredients and metabolites and degradation products of pharmaceuticals was less well developed. Howard and Muir (2010) made extensive lists of potentially persistent and bioaccumulative organics among chemicals in commerce. In their Part I report, mention is made of the microbicides triclocarban, tribromsalan and tetrachlorosalicylanilide – triclosan is considered well monitored. They also mention the synthetic musk galaxolide, and the use of linear and cyclic siloxanes in PCPs. Part II specifically considers pharmaceuticals, and lists 106 chemicals used in high volumes in North America, and over 300 used in lower volumes, that could be persistent and bioaccumulative and which are not being routinely monitored in the environment (Howard and Muir 2011).

Chemicals associated with clandestine labs were of interest to at least one CRC member. The measurement gap in this area would not be in the analysis for known drugs, reagents and intermediates but in the identification of compounds associated with novel drugs. The measurement problem for herbicide and pesticide degradation products is also the need to identify them first. Methods to identify these contaminants are briefly considered in the section on non-targeted analysis.

Disinfection by-products (DBPs), algal and cyanobacterial toxins and chloropropanols were considered to be issues of public health for drinking water rather than environmental contamination and so were not further investigated in this review.

Pathogens are likely to be an important issue, particularly in the reuse of sewage sludge for soil improvement, but they were also considered to be beyond the scope of this review of chemical analysis.

Polycyclic aromatic hydrocarbons (PAHs), the original 12 Stockholm Convention persistent organic pollutants (POPs), the volatile aromatics benzene, toluene, ethylbenzene and xylene (BTEX), chlorinated solvents, cyanide, glycols and glycol ethers, sulfates, nitrate, perchlorate and volatile fatty acids were all considered whilst developing the shortlist, but were not included because there is adequate analytical methodology available for these CECs. Some were included in the survey of analytical laboratories.

Bioavailability of total petroleum hydrocarbon (TPH) and PAHs, TPH ‘fingerprinting’ and phytosterols as biomarkers for the petroleum industry were also raised, but these issues were considered to be matters for research requiring interpretation of results rather than analytical methodology.

### 1.1.2 The shortlist of contaminants for review

A February 2012 CRC CARE end-user workshop (the ‘CEC Forum’) generated a ‘first tier priority’ list to be reviewed in this project (methyl tertiary butyl ether (MTBE), perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), weathered
hydrocarbons, benzo(a)pyrene (BaP) and polybrominated diphenyl ethers (PBDEs)). These contaminants are listed in Table 1 as Priority 1.

Table 1: Contaminants selected for review

<table>
<thead>
<tr>
<th>Priority 1 (CRC First Tier Priority)</th>
<th>Priority 2</th>
<th>Priority 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>MTBE</td>
<td>Other PFASs</td>
<td>1,4-dioxane</td>
</tr>
<tr>
<td>PFOS, PFOA</td>
<td>Novel FRs</td>
<td>1,4-dioxane</td>
</tr>
<tr>
<td>weathered hydrocarbons</td>
<td>SCCPs</td>
<td>benzotriazoles</td>
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<tr>
<td>benzo(a)pyrene</td>
<td>methylsiloxanes</td>
<td>organoboron</td>
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<tr>
<td>PBDEs</td>
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<td>benzotriazoles</td>
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<td></td>
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<td>organophosphorous</td>
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<td></td>
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<td>benzidine dyes</td>
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<td>arsenic speciation</td>
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<tr>
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<td></td>
<td>musk PCP fragrances</td>
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</tbody>
</table>

The broader class of perfluoroalkyl substances (PFASs) was considered in addition to PFOS and PFOA. Howard and Muir (2010) proposed a number of fluorinated compounds in use but not currently being monitored in North America that they consider to be potentially persistent and bioaccumulative, while Richardson (2012) mentions perfluorinated iodides as a new group of interest.

Flame retardants (FRs) are very significant environmental contaminants, with a wide variety of chemicals entering use as the PBDEs are phased out, including tetrabromobisphenol A (TBBPA), hexabromocyclododecane (HBCDD), other novel brominated flame retardants and organophosphorous (OP) compounds, many of which also have other uses. Short-chain chlorinated paraffins (SCCPs) are also used as flame retardants, as well as for other industrial uses.

Methylsiloxanes were also highlighted in the literature and in discussions with colleagues as important emerging contaminants (Richardson 2012).

These four classes of contaminants (other PFASs, novel FRs, SCCPs and methylsiloxanes) were selected for review as Priority 2.

Other contaminants found in literature reports were selected as priority 3, requiring further investigation regarding their relevance in the Australian remediation context, based on their likely use and environmental prevalence. These included 1,4-dioxane, benzotriazoles, ionic liquids and nanoparticles.

Benzidine dyes were flagged by a CRC CARE end-user as an area where analytical methodology was lacking. These are of concern to the US EPA and Environment Canada (Environment Canada and Health Canada 2010; US EPA 2010), and are probably in use in Australia. They were added to the priority 3 list and included in the survey of Australian analytical services to determine what analytical methods are available.

Among the contaminants arising from personal care products, it appeared that musk fragrances and the analogues of triclosan might be groups of chemicals that had been less well studied, and these were included in the survey and review (Priority 3).

The measurement problem for the metals (arsenic, chromium, manganese, antimony) and organometallics listed by CRC members are related to speciation. One CRC member specifically commented that better methods were needed for arsenic speciation while another commented that they were not. Jones-Lepp and Momplaisir
(2005) reviewed organometallic analysis by LC-MS and mentioned that very little work had been done on organoboron (replacing organotin) and organoplatinum (chemotherapy drugs) compounds in the environment. Hence these groups were added to the Priority 3 list for review.

1.2 Survey of Australian analytical capabilities

A survey to determine current Australian capabilities for the analysis of possible CECs was compiled and forwarded by email to Australian laboratories listed on the NATA website as holding accreditation for Chemical Testing and providing a public testing service or being conditionally available for public testing. Duplicate entries for the same contact within an organisation and laboratories not providing email addresses were removed from the list however no further filtering of laboratories was performed, to capture the broadest range of capabilities and opinions. The survey was emailed to 358 laboratories and 33 submitted a response, 4 of which left all fields blank. The survey questions and summaries of the responses are presented in Appendix A.

For alkyl phenol ethoxylates (APEOs), bisphenol A and phthalates, where we had expected capability to be adequate, surprisingly few labs responded. Two labs said they could do APEOs in water, and 19 said not in any matrix; for bisphenol A two labs nominated soil/sediments and water, one water only and one air only (18 not in any matrix); and two could do phthalates in air and five in soil/sediments and water. About half the responding laboratories claimed to be able to analyse antimony (not included in our review as we believed methodology was available) and PAHs, which would include benzo(a)pyrene. No labs claimed to be able to analyse benzidine dyes, benzotriazoles, microbicides, nanoparticles, organoboron, organoplatinum or non-brominated flame retardants.

Laboratories were also asked about other contaminants for which they believed there to be a measurement research or development need in Australia. Five responses were received: isocyanates and pesticides; human pollution tracers e.g. caffeine; mercury species; chlorinated paraffins and PPCPs. Chlorinated paraffins have been addressed in this review. PPCPs and pesticides were considered in the initial selection of contaminants, but not included for the reasons discussed above. Human pollution tracers are a very interesting tool for environmental monitoring, however tracers can and should be chosen that do not provide an analytical challenge (such as caffeine). Isocyanates are highly reactive industrial chemicals used in the manufacture of foams and coatings. These chemicals are toxic by inhalation, and irritants, particularly of the respiratory tract, and hence are an issue for workplace safety and monitoring, however they are rapidly hydrolysed on contact with water and are inherently biodegradable, and so are not an environmental concern unless spilled in large volumes (IPCS INCHEM 1987; IPCS INCHEM 2001a; IPCS INCHEM 2004). Mercury speciation may be a challenge however there appear to be methods available and laboratories accredited by NATA for analysis of some mercury species (www.nata.asn.au).
2. Contaminants of emerging concern

2.1 Methyl tert-butyl ether (MTBE)

CAS no: 1634-04-4
Chemical name: 2-methoxy-2-methylpropane
Molecular formula: C$_5$H$_{12}$O
Assessed by NICNAS: no

2.1.1 Occurrence of MTBE in the environment

The analysis of MTBE in the aquatic environment was reviewed by Atienza et al. (2005) and Rosell et al. (2006). MTBE is also discussed in the scoping review of natural attenuation by McLaughlan et al. (2006). Detailed reports and studies providing information on the occurrence, use, fate and remediation of contaminated sites in the USA, Europe and Canada have also been published (Environment Canada 2010b; ITRC 2005; Moyer and Kostecki 2003; Stupp et al. 2012; US EPA 2012c).

Over the last few decades MTBE has been produced in large amounts worldwide. It is primarily used as an oxygenate and added to petrol to increase the octane rating. In 1999 more than half of the global use of MTBE was in the USA, where it was typically added to petrol at concentrations around 11%. This use is being phased out and a number of US states have now banned the addition of MTBE to fuel.

MTBE is highly soluble in water and can quickly move through soil and groundwater. The World Health Organisation (WHO) declined to set health-based guidelines for drinking water as they would be significantly higher than the levels at which taste and odour problems become apparent (WHO 2005). The health effects of MTBE on humans are still being debated however the overall evaluation by the International Agency for Research on Cancer (IARC) is that it ‘is not classifiable as to its carcinogenicity to humans (Group 3) based on inadequate studies in humans and limited studies in animals’ (IARC 1999). In June 2008 the advisory group for the IARC recommended MTBE be added to the list of agents for evaluation of medium priority for future monographs (IARC 2008). MTBE is one of the 40 compounds on the Danish EPA’s List of Undesirable Substances (Danish EPA 2012a) and will be surveyed in 2013 to collect information to assess the need for further regulation and management (Danish EPA 2013).

Balducci et al. (2012) discussed MTBE in the atmosphere. While it is very volatile, and hence can be transported in air, its water solubility leads it to partition significantly into precipitation.

2.1.2 Methods and measurement issues

There are a number of US EPA and other standard methods for volatile organic compounds (VOCs) that are applicable to the analysis of MTBE, including those listed in Table 2 below, which all incorporate separation by gas chromatography (GC). The review by Atienza et al. (2005) discusses both US EPA and standard methods and the application, performance and limitations of other published techniques including purge
and trap, headspace, direct aqueous injection, membrane introduction mass spectrometry and solid phase micro extraction (SPME) to the analysis of MTBE.

Analytical issues include false positives due to co-elution of interferences (non-selective detectors or common ions with MS detection), hydrolysis during sampling and analysis (McLoughlin et al. 2004), low recoveries due to high water solubility (White et al. 2002) and poor detection limits. Instrument calibration, careful selection of GC columns, sample pH and headspace temperature have been used to address these issues.

tertiary-Butyl alcohol (TBA) is often found with MTBE in ground water samples as a result of biodegradation or hydrolysis of MTBE to TBA during sampling and analysis.

<table>
<thead>
<tr>
<th>Table 2: Standard methods for MTBE</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ASTM D5790-95:</strong> Standard Test Method for Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry</td>
</tr>
<tr>
<td><strong>ISO 22155:2011:</strong> Soil quality -- Gas chromatographic determination of volatile aromatic and halogenated hydrocarbons and selected ethers -- Static headspace method</td>
</tr>
<tr>
<td><strong>ASTM D4815-09:</strong> Standard Test Method for Determination of MTBE, ETBE, TAME, DIPE, tertiary-Amyl Alcohol and C1 to C4 Alcohols in Gasoline by Gas Chromatography</td>
</tr>
<tr>
<td><strong>US EPA 502.2:</strong> Volatile organic compounds in water by purge and trap capillary column gas chromatography with photoionization and electrolytic conductivity detectors in series, and <strong>US EPA 524.2:</strong> Measurement of purgeable organic compounds in water by capillary column gas chromatography /mass spectrometry.</td>
</tr>
<tr>
<td><strong>US EPA 5030C:</strong> Purge and trap for aqueous samples Heated purge and careful column selection required for MTBE</td>
</tr>
<tr>
<td><strong>US EPA 8015C:</strong> Non-halogenated organics by gas chromatography (GC-FID) A detection method, suffers from interferences, does not provide positive identification</td>
</tr>
<tr>
<td><strong>US EPA 8021B:</strong> Aromatic and halogenated volatiles by gas chromatography using photoionization and/or electrolytic conductivity detectors A detection method, issues with co-elution and false negatives and positives due to high ionisation potential required for detection of MTBE and lack of selectivity of detectors.</td>
</tr>
<tr>
<td><strong>US EPA 8260C:</strong> Volatile organic compounds by gas chromatography/mass spectrometry (GC/MS) A detection method, positive confirmation in a single run.</td>
</tr>
<tr>
<td><strong>US EPA 8261:</strong> Volatile organic compounds by vacuum distillation in combination with gas chromatography/mass spectrometry (VD/GC/MS) This method is applicable to nearly all types of matrices including of water, soil, sediment, sludge, oil, and biota.</td>
</tr>
</tbody>
</table>

**2.1.3 Australian measurement services**

A search of the National Association of Testing Authorities, Australia (NATA) website (www.nata.asn.au) lists ten Australian laboratories accredited for the analysis of MTBE in environmental samples and providing a public testing service. One additional laboratory is accredited to provide workplace environment testing and another liquid fuels testing. In-house methods using purge and trap with GCMS detection are the most commonly listed techniques. Only five of the laboratories in the survey conducted as part of this review indicated they performed testing of MTBE in some or all of the
matrices listed with three having NATA accreditation for all matrices, one for some of the matrices and one not having accreditation. Frequency of analysis ranged from daily to yearly for these laboratories.

2.1.4 Regulation of MTBE

MTBE is not routinely used as a fuel additive in Australia. The Australian 2001 Fuel Standard (Petrol) Determination, 8 October 2001, made under the Fuel Quality Standards Act 2000, limits fuel content to 1% MTBE by volume from January 2004 (DSEWPaC 2001). Prior to this Determination Western Australia, Queensland and South Australia introduced maximum levels of 0.1%, 0.5% and 1%v/v respectively for MTBE in petrol. Approvals of applications to vary section 13 of the Fuel Quality Standards Act 2000 are published by the Department of Sustainability, Environment, Water, Population and Communities (DSEWPaC 2013). Permits for use of specialised racing fuels containing up to 55% MTBE were operating in 2012.

MTBE is not used by Australian refineries however it is used by overseas refineries to achieve required octane ratings. In 2002–03 Australia’s refineries were able to meet most of the domestic demand and imports of refined fuel were minimal (ACCC 2012). In 2011–12 imports contributed approximately 20% of petroleum products consumed around the country. In 2002 Woolworths received criticism in the press for importing fuel (Petrol Plus) containing MTBE at levels averaging 2–3% v/v (max. 7%v/v) from Asian refineries (Wade 2002).

The New South Wales Office of Environment and Heritage (OEH) Guidelines for assessing service station sites (NSW OEH 2012) do not specify threshold levels for MTBE or VOCs in general, however, it is apparently not uncommon to find MTBE near service stations (Moritz 2012).

The Australian Inventory of Chemical Substances (AICS) listing for MTBE notes that it has been assigned to the National Industrial Chemicals Notification and Assessment Scheme (NICNAS) Priority Emerging Contaminants list as a part of the Priority Existing Chemical (PEC) assessment process.

Australian National Environment Protection Measures (NEPMs) and water quality guidelines do not specifically mention MTBE (DSEWPaC 2012; EPHC 1999). Health screening levels (HSLs) have not been derived for MTBE (Friebel and Nadebaum 2011). Guidelines in British Columbia, Canada, range from 20 µg/L for aesthetic reasons to 3400 µg/L for aquatic life (Environment Canada 2010b). The US EPA has not set a national standard for MTBE in drinking water however some individual US states have set maximum contaminant levels (MCL) (US EPA 2000). California has set an MCL of 13 µg/L to address health concerns and a secondary MCL of 5 µg/L to address taste and odour concerns, with a detection limit of 3 µg/L set for reporting purposes (CDPH 2009). MTBE is listed on the US EPA's Contaminant Candidate List CCL-3 and previously CCL-2 with the aim of providing data toward a determination for drinking water regulations.

2.1.5 Reference materials and proficiency testing studies

Solution and matrix reference materials are available for MTBE. Various reference materials and standards can be obtained from LGC standards. MTBE solution certified reference materials (CRMs) are available commercially (e.g. Sigma Aldrich, Restek,
Cerilliant). A mixed surrogate solution containing methyl-d3-tert-butyl ether is also available (Restek). RTC produce solution standards as well as a number of CRMs in various soil types for VOCs and BTEX that have reference values for MTBE. Reference materials for gasoline components certified for MTBE (6.9 to 15% v/v) are produced by the US National Institute of Standards and Technology (NIST) and the Japan Petroleum Institute.

Various overseas PT providers including ERA (www.eraqc.com/), NSI Solutions Incorporated (www.nsi-es.com), RTC (www.rt-corp.com) and CALA (www.cala.ca) run regular PT programs for MTBE in environmental samples. Meeting Australian quarantine requirements may hamper participation in overseas studies or possibly compromise sample integrity. No Australian run PT studies including MTBE could be identified however the NMI (www.measurement.gov.au) runs annual PT programs for BTEX in soil and water that could feasibly be extended to include MTBE.

### 2.1.6 Analytical methodology gaps in Australia

The inclusion of MTBE in this review is as a result of its being identified as a ‘first tier priority’ by the CEC Forum. The research requirements identified by that Forum were the extent of contamination, risk threshold/criteria and remediation options, rather than the need for development of analytical techniques (Scott 2012). MTBE has been effectively banned in Australian fuel since 2004, and fuel is the major source of contamination overseas. Standard methods are available for analysis of MTBE in environmental matrices and a large number of peer-reviewed methods have been published detailing the use of these methods for remediation studies and possible measurement and sampling issues. A testing service for the analysis of MTBE in environmental samples is currently provided by a number of Australian NATA accredited laboratories. MTBE reference materials are available from various commercial suppliers and overseas PT providers conduct regular studies. Australian-run PT programs for this contaminant in environmental samples are not available. Improved analytical methodology for measurement of MTBE in environmental samples is not a major priority at this time. Tools to assess laboratory performance such as easily accessible PT studies are lacking.
### 2.2 Perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA)

<table>
<thead>
<tr>
<th>CAS no:</th>
<th>Chemical name</th>
<th>Molecular formula</th>
<th>On AICS*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1763-23-1</td>
<td>perfluorooctane sulfonic acid</td>
<td>( \text{C}<em>8\text{H}</em>{17}\text{O}_3\text{S} )</td>
<td>no</td>
</tr>
<tr>
<td>2795-39-3</td>
<td>perfluorooctane sulfonic acid potassium salt</td>
<td>( \text{C}<em>8\text{H}</em>{17}\text{O}_3\text{SK} )</td>
<td>yes</td>
</tr>
<tr>
<td>70225-14-8</td>
<td>perfluorooctane sulfonic acid diethanolamine salt</td>
<td>( \text{C}<em>8\text{H}</em>{17}\text{O}_3\text{S} \cdot \text{C}<em>4\text{H}</em>{11}\text{NO}_2 )</td>
<td>yes</td>
</tr>
<tr>
<td>29081-56-9</td>
<td>perfluorooctane sulfonic acid ammonium salt</td>
<td>( \text{C}<em>8\text{H}</em>{17}\text{O}_3\text{SNH}_4 )</td>
<td>yes</td>
</tr>
<tr>
<td>29457-72-5</td>
<td>perfluorooctane sulfonic acid lithium salt</td>
<td>( \text{C}<em>8\text{H}</em>{17}\text{O}_3\text{SLi} )</td>
<td>yes</td>
</tr>
<tr>
<td>335-67-1</td>
<td>perfluorooctanoic acid</td>
<td>( \text{C}<em>8\text{H}</em>{15}\text{O}_2 )</td>
<td>yes</td>
</tr>
</tbody>
</table>

*None of these compounds have been assessed by NICNAS*

Richardson has been discussing perfluoroalkyl substances (PFASs) including PFOS and PFOA in her biennial environmental review since 2004 and most of the following information is from the 2012 review (Richardson 2004; Richardson 2006; Richardson 2008; Richardson 2010; Richardson 2012). PFASs are both hydrophobic and lipophobic. They have been used for more than 50 years to make stain repellents for fabrics and carpets, grease-proof food packaging and in the manufacture of paints, adhesives, waxes, polishes, metals, electronics, fire-fighting foams and caulks. Perfluorooctanesulfonic acid (PFOS) was heavily used in the manufacture of anti-stain fabric treatment. Perfluorooctanoic acid (PFOA) is used in the manufacture of fluoropolymers for non-stick coatings and waterproof clothing membranes (US EPA 2012a). A United Nations Industrial Development Organization (UNIDO) report summarises the production and use of PFOS world-wide to 2009 (Carloni 2009). PFOS and PFOA are on the Danish EPA List of Undesirable Substances (Danish EPA 2012a) and were scheduled for survey in 2012. The version of the survey for public consultation is now available and provides extensive information related to regulation, manufacture and usage, waste management, environmental effects and health effects in addition to monitoring data and alternative compounds for PFOS, PFOA and other per- and polyfluoroalkyl substances (Danish EPA 2012b).

NICNAS Alert No. 8 indicates that while there was no PFOS imported into Australia in 2005, annual imports had increased to 1350 kg by 2008, primarily for mist suppression in metal plating (NICNAS 2008). In 2007 there were estimated to be stockpiles of fire-fighting foam in Australia containing approximately 7.6 tonnes of PFOS. This foam may be used or discarded as it reaches its use-by date, and will be replaced by alternative products. A survey reporting on the status of PFOS and perfluoroalkyl sulfonate in Australia was published in 2009 (NICNAS 2009a).

NICNAS Alert No. 6 reports that very little PFOA (~80 kg) was imported into Australia in 2007 (NICNAS 2007a). It was contained at less than 10% in an antifoam product for a dying process, and at <100 ppm (concentration since reduced to <10 ppm) in an industrial de-dusting product and a consumer paint product. NICNAS advises industry to actively seek alternatives.

#### 2.2.1 Occurrence of PFOS and PFOA in the environment

The carbon to fluorine bond is one of the strongest chemical bonds known, and PFASs are very persistent in the environment. They undergo long-range transport, being found in the Arctic, and in humans and animals all over the world. Due to their lipophobicity,
they accumulate in blood rather than fatty tissue, and health concerns include developmental toxicity, bioaccumulation and carcinogenicity (Richardson 2012).

Thompson et al. have studied perfluorinated alkyl acids including PFOS and PFOA in Australian drinking water and in the Sydney Harbour environment. Results from samples of drinking water from 34 locations around the country were comparable with the lower ranges of concentrations found in international studies (Thompson et al. 2011a). Most samples contained at least traces of one or more PFAS, most commonly PFOS, which was found above the instrument detection limit in 75% of the samples, or PFOA, in 96% of samples. The Parramatta River environment was found to be moderately contaminated, comparable internationally with other urban areas (Thompson et al. 2011b). PFOS was the most prevalent PFAS in water, followed by PFOA. In sediment and most types of biota, PFOS accounted for more than half of the PFASs in the samples, and PFOA was only found in some of the samples, at much lower levels. The authors concluded that at the levels found there was little likelihood of adverse biological effects on wildlife or humans.

Tanabe and Ramu (2012) report widespread, uniform distribution of PFOS, PFOA and similar PFASs in the marine environment of Asia-Pacific. Overall levels are increasing although PFOS levels are now decreasing. Zhao et al. (2012) discussed environmental distribution in Asia, finding it to be most prevalent in aquatic ecosystems, and more so in industrialised areas.

2.2.2 Methods and measurement issues

Richardson (2012) described over a dozen studies and new methods for PFASs including PFOS and PFOA in various environmental matrices. Petrovic et al. (2010) and Wille et al. (2012) included PFASs in their reviews of MS methods for CECs in the environment. Both reviews gave over 10 references to methods for the long-chain acid type PFASs including PFOS and PFOA, in aqueous and solid matrices.

Diaz Cruz et al. (2009) reviewed CEC analysis in sludge and mentioned the problem of laboratory contamination from fluorinated polymers, giving two references (from 2003 and 2005) for extraction, and references to three reviews of LC-MS analysis of the acidic types of PFASs. Zuloaga et al. (2012) in a similar review found two more recent methods.

Garcia Jares et al. (2009) reviewed methods for indoor air and house dust, and included one method for PFOS and PFOA. Most of the methods were for perfluoroalkyl sulfonamides and fluorinated telomer alcohols (FTOHs).

Wille et al. (2012) stated that ‘the occurrence of PFASs in the environment has been extensively studied’, however there are problems with the quality of data. They cite the results of the third interlaboratory study on PFASs in environmental matrices as showing wide variance in results. The difficulties with the analysis include cross contamination due to their prevalence, adsorption of the analytes to surfaces, matrix interference and the occurrence of branched isomers. The results of the third study do not appear to have been published in the open literature yet1, however the results of the second study, including PFOS and PFOA, were published in 2009 (van Leeuwen et al. 2009). The co-ordinators reported that accurate and precise analysis was possible if good standards and isotopically-labelled internal standards were used and a suitable cleanup was applied to minimise matrix effects. The study provided the same native

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1 Note added in proof: see Weiss (2013)
and isotopically-labelled standards to all participants, and spiked the water and fish samples with PFASs to ensure ng/L concentrations, as the environmental sub-ng/L concentrations were difficult to detect.

Standard and US EPA methods are only available for these compounds in waters. International Standards Organisation (ISO) method 25101:2009 is applicable to the determination of PFOS and PFOA in drinking water, ground water and surface water (fresh and sea water) while the Japanese Industrial Standard (JIS) K 0450-70-10:2011 is applicable to industrial water and waste water. US EPA method 537 is applicable to the determination of selected perfluorinated alkyl acids in drinking water only. All three methods employ solid phase extraction and liquid chromatography tandem mass spectrometry (LC-MS-MS).

Table 3: Standard methods for PFOS and PFOA

<table>
<thead>
<tr>
<th>Method</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISO 25101:2009</td>
<td>Water quality - Determination of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) - Method for unfiltered samples using solid phase extraction and liquid chromatography/mass spectrometry</td>
</tr>
<tr>
<td>US EPA METHOD 537</td>
<td>Determination of selected perfluorinated alkyl acids in drinking water by solid phase extraction and liquid chromatography/tandem mass spectrometry (LC/MS/MS)</td>
</tr>
<tr>
<td>JIS K 0450-70-10:2011</td>
<td>Testing methods for perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) in industrial water and wastewater</td>
</tr>
</tbody>
</table>

2.2.3 Australian measurement services

A search of the NATA chemical testing website (www.nata.asn.au) lists three Australian laboratories accredited for the analysis of PFOS and PFOA in soil and waters. All three laboratories use in-house methods and LC-MS-MS for separation and detection. The survey data indicates at least one other testing service for these compounds that does not have NATA accreditation. Additional capability for analysis of these compounds is indicated by published studies from Australian laboratories that were not included or did not respond to the survey.

2.2.4 Regulation of PFOS and PFOA

PFOS was added to the annexes of the Stockholm Convention in 2010, and so Australia is committed to significantly reduce its use (DSEWPaC 2011). Unlike most of the other POPs, PFOS is listed with a number of acceptable purposes and specific exemptions for use. In Australia, PFOS is used primarily for mist suppression in metal plating, which can be done in accordance with the Stockholm Convention listing (NICNAS 2008). PFOS and its salts are on the OSPAR list of Chemicals for Priority Action (OSPAR 2002).

PFOS and some of its salts are restricted under EU REACH legislation (EC 2006), being listed in Appendix 5 as toxic to reproduction. An Environmental Quality Standard (EQS) dossier deriving tentative EQSs (EC WFD 2011b) has been prepared for PFOS under the EU Water Framework Directory (WFD). It is proposed for addition to the list of priority substances (EC 2011) with the following EQSs:
- annual average of $6.5 \times 10^{-4}$ μg/L in inland surface waters, $1.3 \times 10^{-4}$ μg/L in other surface waters; maximum allowable concentration of 36 μg/L in inland surface waters, 7.2 μg/L in other surface waters; 9.1 μg/kg in biota.
The German Drinking Water Commission has suggested a guideline value of 0.3 µg/L for total PFOS and PFOA (TWK 2007). The UK Health Protection Agency (HPA) advises that the maximum acceptable concentrations of PFOS and PFOA in drinking water are 0.3 µg/L and 10 µg/L respectively (UK HPA 2007). The Australian Drinking Water Guidelines (NHMRC and NRMMC 2011) do not address perfluorinated compounds.

PFOS and PFOA are listed on the US EPA's Contaminant Candidate List CCL-3 (US EPA 2012a). These are contaminants that the EPA is evaluating to determine if drinking water regulations are required. Provisional guidelines of 0.2 and 0.4 µg/L respectively have been set (US EPA 2009). In 2007, the state of New Jersey set an unusually low health-based guideline level of 0.04 µg/L for PFOA, in response to concerns of a water supplier near a DuPont chemical plant (Renner 2007). The US EPA also regulates industrial use of PFOS and other perfluoroalkylsulfonates under Significant New Use Rules (SNURs) that limit their use to specified activities, considered to be essential and relatively low risk for human or environmental exposure (NICNAS 2008).

A residential soil screening level of 6 mg/kg for PFOS and 16 mg/kg for PFOA is recommended for US EPA Region 4 (US EPA 2012b).

2.2.5 Reference materials and proficiency testing studies

Native and isotopically-labelled analytical standards are commercially available for a range of perfluoroalkylcarboxylic acids and perfluoroalkylsulfonates (e.g. Cambridge Isotope Laboratories, Wellington Laboratories).

COMAR searches for PFOA, PFOS, and the potassium, diethanolamine, ammonium and lithium salts of PFOS found two certified reference materials from NMIJ: PFOA certified at 0.959 kg/kg (#4056) and potassium PFOS in methanol solution certified at 9.93 mg/kg (#4220). NIST have provided reference values on the certificates of three human serum SRMs (1950, 1957 and 1958) for a number of perfluorinated alkanoic and sulfonic acids, including PFOS and PFOA.

QUASIMEME (Quality Assurance of Information for Marine Environmental Monitoring in Europe) conducted a proficiency study for PFOS/PFOA in mid-2011 (round 70, http://www.quasimeme.org/workshops-studies-and-conferences). Australian-run PT studies for this class of compounds are not available.

2.2.6 Analytical methodology gaps in Australia

The inclusion of PFOS and PFOA in this review is as a result of their being identified as a 'first tier priority' by the CEC Forum. The research gaps identified by that Forum were risk threshold, analytical techniques and ability to treat and dispose.

PFOS and its salts were added to the annexes of the Stockholm Convention in 2010 and their use restricted to specific applications in accordance with Stockholm Convention listing. These are being phased out as suitable alternatives become available. Standard methods are available for water and wastewater but not for other environmental matrices. Numerous methods have been reported for these matrices in the literature. A testing service for the analysis of PFOS and PFOA in soil and water is currently provided by three Australian NATA-accredited laboratories. Literature reports indicate that there are a number of other Australian laboratories with capabilities in this area. Suitable native and isotopically-labelled standard materials are available from...
commercial suppliers for PFOS and PFOA. CRMs in environmental matrices are not available. One overseas PT provider conducts studies for these compounds. Australian-run PT programs for this contaminant in environmental samples are not available.

While analytical services for PFOS and PFOA in environmental samples are available in Australia, the infrastructure to ensure the quality and comparability of the measurements appears to be lacking.
2.3 Other perfluoroalkyl substances (PFASs)

Other perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFSAs) are used as replacements for PFOS and PFOA, especially shorter chain analogues (particularly butyl) as they are thought to be less bioaccumulative (Richardson 2012). Strempel et al. (2012), however, comment that in some cases these are no less persistent and even sometimes as bioaccumulative. Richardson (2012) also mentioned some new perflourinated surfactants, including fluorinated alkyl ethers and esters, and perflurorinated iodides. Perfluorinated iodides are intermediates in the production of other PFASs which have recently become much more extensively produced and used because an alternative production process was discontinued (Ruan et al. 2010). They are volatile and appear to have sufficient atmospheric persistence to be subject to long-range transport.

Howard and Muir (2010) in their calculations of potentially persistent and bioaccumulative industrial chemicals noted that many of the PFASs can form PFCAs or PFSAs in the environment. The Organisation for Economic Cooperation and Development (OECD) has compiled lists of almost 900 known PFOS, PFAS, PFOA, PFCA, related compounds and chemicals that may degrade to PFCA (OECD 2007).

Howard and Muir (2010) also mention perfluoroalkyl phosphonates (PFPAs) and perfluorinated cyclic compounds used as fluids in electronics industry, including perfluoroerythrohydrophenanthrene (PFTHP, CAS no. 306-91-2), which are volatile and persistent but have low bioaccumulation potential.

Clement et al. (2012) listed FTOHs, fluorotelomer acrylates and methacrylates, perfluoroalkane sulfonamides and sulfonamidoethanols, perfluorinated phosphate surfactants and perfluoroethylcyclohexane sulfonic acid (PFECHS, CAS no. 335-24-0).

Perfluorinated phosphate surfactants include phosphonic acids (PFPAs), phosphinic acids (PFPIAs) and phosphoric acid diesters, and are used as leveling and wetting agents in waxes and coatings, and as foam dampening agents in the textile, pharmaceutical and metal industries (Guo et al. 2012). Phosphonic and phosphinic acids were listed as high-production volume chemicals by the US EPA in 2002. Phosphoric acid diesters potentially degrade in the environment to PFCAs.

PFECHS was first reported in the environment by de Silva et al. (2011), found in fish in the Great Lakes of North America. It is used as a corrosion inhibitor in aircraft hydraulic fluids and this use is permitted in the USA and Canada based on the lack of alternatives and the low probability of environmental release. Howard and Muir (2010) calculated it to be potentially persistent and bioaccumulative.

2.3.1 Occurrence of PFASs in the environment

Thompson et al. (2011a) in their study of Australian drinking water from 34 locations around the country found PFOS and/or PFOA in more than 75% of the samples but also found one or more other PFCAs and PFSAs at most locations, usually at trace or low levels. In their study of the Sydney Harbour environment, PFOS and PFOA were again most prevalent but other PFCAs and PFSAs were found in many water, sediment and biota samples (Thompson et al. 2011b).

Eggen et al. (2010) presented a summary of the concentrations of PFCA (C4–C12), PFSA (C4–C10) and three other PFAS found in landfill leachate and sediment from treatment systems in their 2010 study and five other studies published 2005 – 2010.
Not all PFASs were tested for in each study, but when they were most were detected, at least in trace amounts.

### 2.3.2 Regulation of PFASs

Heptadecafluorooctane-1-sulfonic acid and some of its salts are restricted under EU REACH, being listed in Appendix 5 (with PFOS) as toxic to reproduction (EC 2006). Perfluorooctanesulfonyl fluoride (CAS no. 307-35-7) is listed with PFOS and salts in Annex B of the Stockholm Convention, as a POP with production and use allowed for specific purposes.

### 2.3.3 Methods and measurement issues

Many methods are available for PFCAs and PFSAs (see PFOS/PFOA methods above). D’eon et al. (2009) reported detecting PFPAs for the first time in the environment using a solid-phase-extraction (SPE)-LC-MS method also suitable for PFCAs and PFSAs. Zhang et al. (2010a) described a method for PFCAs, PFSAs and seven other PFASs described as precursor compounds, including sulfonamides and sulfonamido acetic acids, in digested sewage sludge by ion-pair extraction, SPE and LC-MS. Clement et al. (2012) summarised methods used for detection of a range of PFASs in fish in the Great Lakes, including a method by Guo et al. (2012) which determined PFPAs, PFPIAs, phosphoric acid diesters, PFCAs and PFSAs. Extraction is mostly by ion-pairing liquid-liquid extraction (LLE) and LC-MS, in methods similar to those used for PFCAs and PFSAs, although attention needs to be paid to pH to extract some of the phosphorous compounds.

Ruan et al. (2010) published methods for polyfluorinated iodides in air by thermal desorption-GC-high resolution (HR)-MS and in soil using SPME-GC-MS.

Several methods for perfluoroalkyl sulfonamides and FTOHs in indoor air and house dust were reviewed by Garcia Jares et al. (2009). Xie and Ebinghaus (2008) reviewed methods for CECs in the atmosphere and presented several methods for FTOHs and perfluorinated sulfonamides and sulfonamidoethanols.

The measurement issues of background contamination, adsorption and analysis of branching isomers, mentioned above for PFOS and PFOA, apply to PFASs in general. As discussed previously, there has been a series of three international interlaboratory studies on PFCAs and PFSAs in environmental samples. The results of the third study do not appear to have been published in the open literature yet\(^2\), however Wille et al. (2012) commented that there was a significant degree of variance in the results from aqueous samples. The results of the second study, including C4–C12 PFCAs, C4–C8 PFSAs and perfluorooctane sulphonamide, were published in 2009 (van Leeuwen et al. 2009). The co-ordinators reported that accurate and precise analysis was possible under the conditions described previously where the same native and isotopically-labelled standards were provided to all participants.

Two Australian laboratories that submitted survey responses provide services for the analysis of PFOS and PFOA. These laboratories also reported capabilities for other PFSAs and PFCAs, and PFASs including sulfonamides and sulfonamidoacetic acids, alcohols and fluorotelomer sulfonates (FTSs), in a range of matrices. The studies by Thompson et al. (2011a, 2011b) discussed above also demonstrate additional Australian analytical capabilities.

\(^2\) Note added in proof: see Weiss (2013)
2.3.4 Reference materials and proficiency testing studies

Native and isotopically-labelled analytical standards are available for a number of perfluorinated compounds, including telomer alcohols and PFPAs (e.g. Cambridge Isotope Laboratories, Wellington Laboratories, Chiron). PFECHS standards are available, at least as the potassium salt.

NIST states on its website that 'methods are being developed for perfluorinated compounds and applied to SRMs' (http://www.nist.gov/mml/csd/emergecontam.cfm). As discussed above for PFOS and PFOA, reference values for some PFCAs and PFSAs have been added to the certificates of three human serum SRMs. The levels of PFCAs and perfluoroctane sulfonamide (PFOSA) in fish tissue (SRMs 1946, 1947), bovine liver (SRM 1577c), and mussel tissue (SRM 2974a) have also been reported (Reiner et al. 2012).

2.3.5 Analytical methodology gaps in Australia

There are no standard methods for these compounds although there appear to be suitable methods in the literature for these analytes in soil and water. Application of these methods requires careful attention to detail and significant technical capability. Limited commercial analytical capability appears to exist in Australia for PFSAs, PFCAs, and PFASs including sulfonamides and sulfonamidoacetic acids, alcohols and fluorotelomer sulfonates, in a range of matrices. The studies by Thompson et al. provide evidence of Australian analytical capabilities for PFCAs and PFSAs. Analytical standard solutions are commercially available for a large number of these compounds. Suitable matrix reference materials and proficiency testing studies do not appear to be available. Australian studies on the environmental prevalence of all PFAS classes are not yet available. Current LC-MS-MS methods are capable of screening for a wide range of these compounds although it is not clear which of these compounds will be of most interest as alternatives for PFOS are sought.
2.4 Benzo(a)pyrene (BaP)

CAS no: 50-32-8
Chemical name: benzo(a)pyrene
Molecular formula: C_{20}H_{12}
Assessed by NICNAS: no

2.4.1 Occurrence of benzo(a)pyrene in the environment

The IARC have classified benzo(a)pyrene as a Group 1 carcinogen (IARC 2012b). It is a PAH formed as a by-product of combustion, and major sources in the environment include wood or coal burning, motor-vehicle exhaust and industrial emissions. Benzo(a)pyrene is one of the most toxic PAHs and is often used as the basis for expressing the toxic equivalence (TEQ) of other PAHs (Delistraty 1997).

Deng et al. (2006) analysed PAHs in air in an e-waste recycling area of China and found levels to be higher than those of one of the countries’ most polluted cities, probably reflecting the significant emission of PAHs from the open burning of plastic and metal scraps. Wang et al. (2010a, 2010b) found significant contamination with PAHs in aquaculture sediments in China, attributed to vehicle emissions, burning coal and even to contamination from fish feed.

Analytical methodology and data from Australian studies for PAHs in ambient air between 1990 and 1999 were reviewed by Berko (1999) for Environment Australia, and the Environment Australia (2001) state of knowledge report provides additional data. Benzo(a)pyrene was one of the most widely studied compounds in ambient air over this period with the maximum reported particulate phase concentrations of 34.3 ng/m³ over a 24 hour averaging time. It was noted in the report that comparison of results from the various studies was difficult due to the different measurement methods in use.

2.4.2 Methods and measurement issues

Guidelines on the laboratory analysis of potentially contaminated soils, Schedule B3 of the NEPM, 1999 and the draft variation NEPM 2011, provide information on sampling, storage, quality control, extraction and analysis of samples and specifies methodology for the analysis of PAHs (EPHC 1999; EPHC 2010).

Standard methods for PAH analysis in environmental matrices are available and applicable to the analysis of benzo(a)pyrene, including those in Table 4.

<table>
<thead>
<tr>
<th>Table 4: Standard methods for PAHs</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISO 17993:2002 : Determination of 15 polycyclic aromatic hydrocarbons (PAH) in water by HPLC with fluorescence</td>
</tr>
<tr>
<td>ISO 7981-1:2005 (6 PAHs) : Determination of polycyclic aromatic hydrocarbons (PAH) -- Part 1: Determination of six PAH by high-performance thin-layer chromatography with fluorescence detection after liquid-liquid extraction</td>
</tr>
<tr>
<td>ISO 7981-2:2005 (6 PAHs) : Determination of polycyclic aromatic hydrocarbons (PAH) -- Part 2: Determination of six PAH by HPLC with fluorescence detection after LLE</td>
</tr>
<tr>
<td>Code</td>
</tr>
<tr>
<td>--------------</td>
</tr>
<tr>
<td>EN 15549:2008</td>
</tr>
<tr>
<td>EN 15980:2011</td>
</tr>
<tr>
<td>US EPA IP-7</td>
</tr>
<tr>
<td>US EPA 3510*</td>
</tr>
<tr>
<td>US EPA 3540C</td>
</tr>
<tr>
<td>US EPA 3545A</td>
</tr>
<tr>
<td>US EPA 3550C</td>
</tr>
<tr>
<td>US EPA 3561</td>
</tr>
<tr>
<td>US EPA 8270D*</td>
</tr>
<tr>
<td>US EPA 8275A</td>
</tr>
<tr>
<td>US EPA 8310</td>
</tr>
<tr>
<td>Californian EPA Air Resources Board Method 429</td>
</tr>
<tr>
<td>EPA METHOD TO-13A</td>
</tr>
</tbody>
</table>


*Methods recommended in the NSW OEH Guidelines for assessing service station sites (NSW OEH 2012)

Thirty-nine Australian laboratories are listed on the NATA website as providing a public testing service for the analysis of PAHs in a range of environmental samples including soils, waters (waste, ground, surface, potable and saline), sediments, sludges, aggregates, ambient air, stack gases, emissions, air filters, sorbent tubes, badges, trade waste, industrial and municipal waste, biosolids and biota. The scope of accreditation for many of these laboratories includes benzo(a)pyrene. GC-MS detection is used by the majority of these laboratories for this analysis.

### 2.4.3 Regulatory limits

The Australian drinking water guidelines state that PAHs have not been found in Australian drinking waters and sets a guideline maximum concentration based on health considerations of 0.010 μg/L (NHMRC and NRMMC 2011). Australian NEPMs and New South Wales environmental guidelines set SILs at 1 – 5 mg/kg and GILs at 0.01 μg/L in drinking water (EPCH; NSW OEH 2012).

The National Water Quality Management Strategy (NWQMS) ANZ Guidelines for Fresh and Marine Water Quality (ANZECC and ARMCANZ 2000) found insufficient data to derive reliable trigger values for this compound and so provide only a low reliability trigger value of 0.2 μg/L for fresh and marine water (Section 8.3.7.7, p 8.3–193). In the same document, the guideline for water for recreational purposes is 0.01 μg/L and for sediment the trigger value is 430 μg/kg (DSEWPaC 2012).

Schedule B1 of the draft varied Assessment of Site Contamination NEPM (EPHC 2010) lists a range of health-based investigation levels (HILs) for BaP (TEQ) in soil from 3 mg/kg in low density residential areas to 40 mg/kg in commercial industrial premises and ecological screening levels (ESLs) in fine and course sand as 1.4 and 0.7 mg/kg respectively.

Australia’s National Environment Protection (Air Toxics) Measure (Air Toxics NEPM 2011) sets the monitoring investigation level for BaP at 0.3 ng/m³ (annual mean of 24 hour monitoring periods) and lists US EPA method TO-13A as the reference method for PAHs.

### 2.4.4 Reference materials and proficiency testing studies

Various overseas PT providers including ERA (www.eraqc.com/), NSI Solutions Incorporated (www.nsi-es.com), RTC (www.rt-corp.com), CALA (www.cala.ca) and FAPAS (www.fapas.com) run regular PT programs for PAHs in environmental samples. Wepal (The Netherlands) offers PAHs in sediments, and in marine environmental samples via QUASIMEME. The European PT information system (EPTIS) (www.eptis.bam.de) is a useful database run by BAM (Federal Institute for Materials Research and Testing, Germany) for finding suitable PT schemes from 300 PT providers. Meeting Australian quarantine requirements may hamper participation in...
overseas studies or possibly compromise sample integrity. There does not appear to be a regular Australian-run PT program for PAHs in environmental samples.

Certified pure material (e.g. Fluka, Dr Ehrenstorfer) and solution standards (Fluka, Dr Ehrenstorfer, NIST, Chiron) are available for benzo(a)pyrene, as are solutions of both the $^{13}$C and deuterium labelled material (Cambridge Isotope Laboratories, Cerilliant Corporation, C/D/N isotopes, NIST, Aldrich, Chiron). Mixed PAH calibration solutions that include benzo(a)pyrene are also available from a number of suppliers (Sigma, Supelco, Restek, Dr Ehrenstorfer). A search of COMAR by CAS number (50-32-8) listed 25 certified reference materials in solvent, biota and environmental matrices (Table 5).

<table>
<thead>
<tr>
<th>Reference Material</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ERM-CZ100</td>
<td>Fine dust (PM10-like) (mg/kg)</td>
</tr>
<tr>
<td>BCR-524</td>
<td>Contaminated industrial soil (mg/kg)</td>
</tr>
<tr>
<td>BCR-535</td>
<td>Freshwater harbour sediment (mg/kg)</td>
</tr>
<tr>
<td>BCR-683</td>
<td>Beech wood (mg/kg)</td>
</tr>
<tr>
<td>BCR-459</td>
<td>Coconut oil (μg/kg)</td>
</tr>
<tr>
<td>BROC-03</td>
<td>Mussels [RIVO]</td>
</tr>
<tr>
<td>NIST SRM 1580</td>
<td>Organics in Shale Oil</td>
</tr>
<tr>
<td>NIST SRM 1582</td>
<td>Petroleum Crude Oil</td>
</tr>
<tr>
<td>NIST SRM 1597</td>
<td>PAHs from Coal Tar</td>
</tr>
<tr>
<td>NIST SRM 1649b</td>
<td>Urban Dust</td>
</tr>
<tr>
<td>NIST SRM 1650b</td>
<td>Diesel Particulate Matter</td>
</tr>
<tr>
<td>NIST SRM 1941b</td>
<td>Organics in Marine Sediment</td>
</tr>
<tr>
<td>NIST SRM 1944</td>
<td>New York/New Jersey Waterway Sediment</td>
</tr>
<tr>
<td>NIST SRM 1974c</td>
<td>Organics in Mussel Tissue (Mytilus edulis)</td>
</tr>
<tr>
<td>NIST SRM 2585</td>
<td>Organic Contaminants in House Dust</td>
</tr>
<tr>
<td>NIST SRM 2974a</td>
<td>Organics in Freeze-Dried Mussel Tissue (Mytilus edulis)</td>
</tr>
<tr>
<td>NIST SRM 2975</td>
<td>Diesel particulate matter</td>
</tr>
<tr>
<td>NIST SRM 2975</td>
<td>Diesel Particulate Matter</td>
</tr>
<tr>
<td>NIST SRM 2786</td>
<td>Fine Particulate Matter (&lt;4 μm)</td>
</tr>
<tr>
<td>NIST SRM 2787</td>
<td>Fine Particulate Matter ( &lt;10 μm)</td>
</tr>
<tr>
<td>NIST SRM 2779</td>
<td>Gulf of Mexico Crude Oil (reference value only)</td>
</tr>
<tr>
<td>ERM-AC213</td>
<td>PAHs in acetonitrile/toluene</td>
</tr>
<tr>
<td>NIST SRM 1647e</td>
<td>Priority Pollutant PAHs (in Acetonitrile)</td>
</tr>
<tr>
<td>NIST SRM 2270</td>
<td>Perdeuterated PAH-II Solution in Hexane/Toluene</td>
</tr>
<tr>
<td>NIST SRM 2260a</td>
<td>Aromatic Hydrocarbon in Toluene</td>
</tr>
</tbody>
</table>

A European Commission Joint Research Centre (JRC) fact sheet intended to improve the measurement of PAHs provides useful links that includes information on PT
providers, reference materials, standard methods, toxicity, occurrence, EU regulations and directives (Lerda 2011).

2.4.5 Analytical methodology gaps in Australia

The inclusion of benzo(a)pyrene in this review is as a result of its being identified as a ‘first tier priority’ by the CEC Forum. The research requirements identified by that Forum were bioavailability and toxicity, rather than analytical techniques or evidence of a measurement gap (Scott 2012). Numerous standard methods are available for the determination of the polycyclic aromatic hydrocarbon benzo(a)pyrene in a wide range of environmental matrices. Thirty-nine Australian laboratories are listed on the NATA website as providing a public testing service for the analysis of PAHs in a range of relevant samples. Suitable certified reference standards and matrix materials are commercially available. Regular proficiency testing studies for PAH analysis are available but only from international PT providers.
2.5 Weathered hydrocarbons

Brassington et al. (2007) wrote a review of characterisation, risk assessment and bioremediation of weathered hydrocarbons. They point out that petroleum products are complex mixtures of hydrocarbons whose composition varies according to the source material and the nature and degree of processing. When released to the environment, these mixtures undergo a range of weathering processes which further change their composition, and hence availability, toxicity and partitioning.

### 2.5.1 Regulation of hydrocarbons

Hydrocarbon characterisation is required for risk assessment and the management, treatment and monitoring of contaminated sites. It is also used to identify the source of the contamination and determine liability and responsibility for cleanup.

Assessment of site contamination is performed within the NEPM framework (EPHC 2010) using a three-tiered approach for human health risk assessment of contaminated land (draft variation NEPM Schedule B4). The draft variation of the NEPM now includes HSLs and ESLs for petroleum hydrocarbons (Schedule B1), based on revised carbon chain fractions. The HSLs for TPH compounds were developed by CRC CARE in consultation with an advisory group consisting of experts from regulatory, industry, health, environment assessment and remediation areas (Friebel and Nadebaum 2011).

### 2.5.2 Methods and measurement issues

Petroleum samples are very complex and contain thousands of different compounds including acyclic alkanes, cyclic alkanes, aromatics and unsaturated alkanes (Adahchour et al. 2006). Discrimination between biogenic and petrogenic hydrocarbons is also an analytical issue that can confound remediation efforts.

Brassington et al. (2007) discussed various extraction methods, as well as the issue of harsher methods extracting hydrocarbons that are no longer bioavailable, and whether it is sometimes more appropriate to use a ‘weaker’ extraction. The review also discussed the performance of various extraction techniques that have been extensively compared and reported in the literature such as Soxhlet, microwave assisted extraction (MAE), sub-critical water extraction, supercritical fluid extraction (SFE), shake/vortex, ultrasonic and pressurised liquid extraction (PLE). Risdon et al. (2008) reported the development of a sequential ultrasonic extraction method for weathered hydrocarbons from contaminated soil to meet the needs of the UK risk-based framework and discussed the extraction efficiencies of various sonication methods and alternate extraction solvents.

There are a number of US EPA methods suitable for extraction, cleanup and analysis of various hydrocarbon fractions. The Australian Guideline on Laboratory Analysis of Potentially Contaminated Soil, Schedule B3 of the Site Contamination NEPM (EPHC 1999), refers to US EPA methods 3540B or C, 3550B, 3560 or 3561 for extraction of soils by Soxhlet, sonication or SFE; method 1664 for silica gel cleanup; methods 8015 or 8270B for GC-flame ionisation detection (FID) or -MS analysis; and method 8440 for silica cleanup and infrared detection (EPHC 1999). Standard methods in addition to those listed above are available for hydrocarbon analysis and identification of waterborne oil spills (Table 6).
A full characterisation and forensic analysis of petroleum materials for source identification and liability investigations requires data from an array of analytical techniques in addition to statistical analysis and expert interpretation of data (Wang et al. 1999). Biomarker fingerprinting may be used for identification of source and estimation of degree of weathering. Wang and Stout (2010) provide a comprehensive overview of oil spill fingerprinting and oil spill source identification and the analytical techniques employed including two-dimensional GC (2D GC), GC-MSMS and stable isotope measurement.

A project undertaken by the Office of Environment and Heritage (NSW OEH 2009) aimed to use ‘a combination of advanced environmental forensic techniques to develop chemical and isotopic fingerprints of petroleum residues so that the pollutants can be matched to the source(s)’, indicating an Australian capability in the area of environmental forensic techniques.

The use of 2D GC for elucidation of TPH unresolved complex material (UCM) was raised by a stakeholder during the consultative process for this review. The characterisation of petrochemicals was the primary application for 2D GC when first developed and is widely reported in the literature (Mao et al. 2009; Mao et al. 2008; van de Weghe et al. 2006; von Mühlen et al. 2006). It is used for risk assessment and remediation as well as source identification purposes. 2D GC technology is not widely available in Australia for commercial analysis although a number of research groups are working in this area (Eiserbeck et al. 2012; Harvey and Shellie 2012; Tran et al. 2006).

### 2.5.3 Reference materials and proficiency testing studies

PT programs for TPH, PAHs and phenols are available and potentially useful to demonstrate competency in the application of extraction techniques used for characterisation of weathered hydrocarbons. Suitable programs can be identified using the EPTIS (www.eptis.bam.de) database. The Bonn Agreement Oil Spill Identification Network of Experts (OSINET) also organises ‘round robins’ for identification of oil spills. Australian-run PT programs in this area are not available.

Pure standard materials and solutions for many hydrocarbons are available through commercial suppliers. However standards will not be available for all possible compounds of interest due to the large number of potential compositional changes and
biotransformations that can occur during weathering. Synthetic ‘weathered’ hydrocarbon solutions of hydrocarbons categorised by loss of mass are also available (e.g. Restek).

Matrix reference materials are available for individual hydrocarbon compounds and classes of compounds such as TPHs and PAHs. A CRC CARE project to develop, produce and certify an Australian reference material and conduct a proficiency study for TPH in soil aims to assist laboratories to demonstrate comparability of results for TPH in soil (CRC CARE 2012). The weathering of petroleum products can involve the changes in concentration of hundreds of compounds in the mixture. The concept of weathering encompasses a wide range of environmental effects. Preparation and certification of meaningful weathered hydrocarbon reference materials would require careful specification of the starting material and the particular combination of weathering effects experienced.

2.5.4 Analytical methodology gaps in Australia

The inclusion of weathered hydrocarbons in this review is as a result of their being identified as a ‘first tier priority’ by the CEC Forum. The research requirements identified by that Forum were characterisation, risk assessment and treatment (Scott 2012). Assessment of risk requires identification of the hydrocarbons. Analytical techniques for hydrocarbons are well established, but these techniques generally give information about groups and ranges of aliphatic and aromatic hydrocarbons. Determination of the composition of weathered hydrocarbons in contaminated soil samples is not a routine task. It is a forensic analysis and needs to be performed on a case-by-case basis, taking into account not only what is known about the contamination but also the use to which the results will be put. It requires expert interpretation of data from the multiple analytical measurements used to fingerprint and characterise samples and identify marker compounds. Full characterisation will be limited to laboratories with access to very high-resolution chromatographic techniques such as two-dimensional GC coupled to mass spectrometry. At least one Australian laboratory currently advertises this service and evidence from the literature indicates additional expertise in this area.
2.6 Polybrominated diphenyl ethers (PBDEs)

<table>
<thead>
<tr>
<th>CAS no:</th>
<th>pentaBDE</th>
<th>octaBDE</th>
<th>decaBDE</th>
</tr>
</thead>
<tbody>
<tr>
<td>32534-81-9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>32536-52-0</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>1163-19-5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Chemical name: pentaBDE, octaBDE, decaBDE
Molecular formula: $C_{12}H_5Br_5O$, $C_{12}H_3Br_8O$, $C_{12}Br_{10}O$
Assessed by NICNAS: yes, yes, yes

Wang and Li (2010) have written a review that gives a good introduction to the PBDEs and then discusses in detail the application of mass spectrometry to their analysis. The class of polybrominated diphenyl ethers consists of 209 congeners, substituted with between one and 10 bromine atoms. The major commercial products, decaBDE, octaBDE and pentaBDE, are mixtures of congeners that do not have fixed compositions. They are added to a range of matrices including plastics, textiles and electronic circuitry as flame retardants (FRs). PBDEs are persistent in the environment and not very water soluble, leading to accumulation in soils and sediments. Some congeners are sufficiently volatile that they are subject to long-range atmospheric transport, and have been found to move towards polar regions. Various mixtures of PBDEs have shown a range of modes of toxicity including neurotoxicity, endocrine disruption and cellular toxicity, in various organisms. The less-brominated congeners are generally more toxic, and the potential for bioaccumulation is high for tetra- and pentaBDEs then decreases with increasing bromination. The highly-brominated congeners can be debrominated to other congeners by environmental degradation.

The Australian Government commissioned a series of three studies in 2004, of PBDEs in aquatic sediments, indoor environments and human blood. The report on aquatic environments found PBDEs in sediments from 35 of 46 sites sampled; five industrial/urban sites in Sydney and Melbourne at over 10 ng/g and 11 WWTPs, urban and urban/industrial sites with 1–10 ng/g (Toms et al. 2006). Overall levels were low compared to Europe, Asia and North America.

2.6.1 Occurrence of PBDEs in the environment

PBDEs are extensively used in electronic devices, and PBDE contamination is associated with e-waste disposal, particularly when it occurs in a crude or unregulated manner in developing countries (Deng et al. 2007; Leung et al. 2007; Lopez et al. 2011a).
Tanabe and Ramu (2012) reported that the occurrence of PBDEs in the marine environment of the Asia-Pacific region is widespread and has increased over the last 30 years.

A 2010 investigation into the presence of PBDEs in articles being used, recycled and disposed of in New Zealand concluded that ‘properly designed and managed landfills are a secure final depository for BDE containing plastics’ after testing leachate from three landfill sites (Keet et al. 2010).

### 2.6.2 Regulation of PBDEs

Tetra-, penta-, hexa- and heptaBDE were listed as POPs under the Stockholm Convention in 2009. Hence parties to the convention must take steps to eliminate production and use of these chemicals. Specific exemptions were listed for these PBDEs to allow recycling of articles containing PBDEs and use and disposal of the recycled articles in environmentally sound ways.

PBDEs are also on the OSPAR list of Chemicals for Priority Action (OSPAR 2002).

In Australia, the draft NEPM 2010, Schedule B1, Table 1A(1) specifies HILs for ‘PBDE Flame Retardants (Br1 to Br9)’ of 1–10 mg/kg depending on the land use (EPHC 2010).

An EQS dossier deriving tentative EQSs (EC WFD 2011c) has been prepared for PBDEs under the EU WFD. They were included in the Priority Substances Directive (EC 2008) and are listed in the proposed revised WFD (EC 2011) with the following updated EQSs (for the sum of six tri–hexaBDE congeners): annual average of $4.9 \times 10^{-8} \mu g/L$ in inland surface waters, $2.4 \times 10^{-9} \mu g/L$ in other surface waters; maximum allowable concentration of 0.14 μg/L in inland surface waters, 0.014 μg/L in other surface waters; 0.0085 μg/kg in biota.

### 2.6.3 Methods and measurement issues

The extensive review by Wang and Li (2010) showed that a great deal of work has been done on the analysis of PBDEs in environmental matrices. Methodology is well established, however the inherent difficulties of the analysis means that it is expensive. PBDEs are strongly bound to soils and sediment, and so rigorous extraction is required, which in turn requires extensive cleanup of extracts. Environmentally significant levels may be very low, requiring sensitive detection methods. The variety of analytes calls for a variety of labelled internal standards. The difficulties of separating and distinguishing between the large numbers of congeners means expensive methods of detection such as HRMS are required. Wang and Li did note that advances are being made in the use of triple-quadrupole and ion-trap mass spectrometry, and LC-MS with atmospheric-pressure photoionisation (APPI), which might allow the use of less expensive instrumentation. They also call for further work on the accuracy of methods for highly-brominated congeners, and congener-specific analysis for some tetra- to hexa-brominated congeners.

Xie and Ebinghaus (2008) reviewed methods for atmospheric analysis and Garcia Jares et al. (2009) reviewed methods for analysis of indoor air, and noted that background levels of PBDEs can be expected in any laboratory containing electronic equipment. Care must be taken, including appropriate cleaning of sampling and analysis equipment, to reduce contamination.
Some standard methods for PBDEs are given in Table 7.

<table>
<thead>
<tr>
<th>Method</th>
<th>Description</th>
<th>MDLs (μg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISO 22032:2006</td>
<td>Water quality – Determination of selected polybrominated diphenyl ethers in sediment and sewage sludge – Method using extraction and GC-MS</td>
<td>tetra- to octaBDEs: 0.05, decaBDE: 0.3</td>
</tr>
<tr>
<td>US EPA 1614</td>
<td>Brominated diphenyl ethers in water, soil, sediment and tissue by HRGC/HRMS</td>
<td>mono- to heptaBDEs: 20–50, decaBDE: 700</td>
</tr>
</tbody>
</table>

### 2.6.4 Reference materials and proficiency testing studies

Solutions of calibration standards are commercially available (e.g. AccuStandard, Cambridge Isotope Laboratories, Wellington Laboratories), as are solutions of isotopically-labelled PBDE congeners (Cambridge Isotope Laboratories). A number of matrix reference materials are also available, including many in environmental matrices (Table 8).

PT programs for PBDEs in environmental samples are available from international providers. Wepal (The Netherlands) offers PBDEs in sediments and in marine environmental samples via QUASIMEME. The Institute for Interlaboratory Studies (Spijkenisse, The Netherlands) have run PT schemes for PBDEs in granulates. BIPEA (Gennevilliers, France) offers PBDEs in waters, including feed, waste and industrial waste waters. RTC (Wyoming, USA) offers PBDEs in sediments, drinking water and waste water. There does not appear to be an Australian-run PT program for PBDEs in environmental samples.

### 2.6.5 Analytical methodology gaps in Australia

The measurement need identified by the CRC CARE forum for PBDEs was measurement and risk assessment. Standard methods are available for these compounds. Analysis of environmental samples for these compounds can be expensive due to the use of high resolution mass spectrometry to separate congeners and achieve adequate detection limits. Three Australian laboratories have NATA accreditation for this class of compounds. The data from the survey indicate that the demand for this service does not exceed current capacity. Suitable certified reference standards and matrix materials are commercially available. A limited number of PT studies are available internationally but there are no Australian PT providers currently offering this service.
Table 8: Matrix reference materials available for PBDEs

<table>
<thead>
<tr>
<th>Reference Material</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluka CNS329</td>
<td>PCBs and PBDEs on Sandy Loam Sediment (Soil), pkg of 50 g</td>
</tr>
<tr>
<td>IRMM ERM-EC590 &amp; ERM-EC591</td>
<td>Polybrominated diphenyl ethers in polymers</td>
</tr>
<tr>
<td>NMIJ CRM 8108-b, 8109-a &amp; 8110-a (disk)</td>
<td>Polybrominated diphenyl ethers in polymers</td>
</tr>
<tr>
<td>JSAC CRM 0641 &amp; 0642 (chips)</td>
<td>Plastics (PBDEs) for Chemical Analysis (each 25g) (Japan Society for Analytical Chemistry)</td>
</tr>
<tr>
<td>IJE PBDE-ABS-PE</td>
<td>ABS and PE resin (PBDE) (IJE Research Laboratory)</td>
</tr>
<tr>
<td>BROC-01</td>
<td>PBDEs in Flounder [manufactured by RIVO (Netherlands)]</td>
</tr>
<tr>
<td>BROC-02</td>
<td>PBDEs in Marine Sediment –RIVO.</td>
</tr>
<tr>
<td>NIST SRM 1588c</td>
<td>Organics in Fish Oil</td>
</tr>
<tr>
<td>NIST SRM 1589a</td>
<td>PBDEs etc in Human Serum</td>
</tr>
<tr>
<td>NIST SRM 1945</td>
<td>Organics in Whale Blubber</td>
</tr>
<tr>
<td>NIST SRM 1946</td>
<td>Lake Superior Fish Tissue</td>
</tr>
<tr>
<td>NIST SRM 1947</td>
<td>Lake Michigan Fish Tissue</td>
</tr>
<tr>
<td>NIST SRM 1974c</td>
<td>Organics in Mussel tissue</td>
</tr>
<tr>
<td>NIST SRM 1947</td>
<td>Lake Michigan Fish Tissue</td>
</tr>
<tr>
<td>NIST SRM 1944</td>
<td>New York/New Jersey Waterway Sediment (Reference Values only for PBDEs)</td>
</tr>
<tr>
<td>NIST SRM 2257</td>
<td>PBDE congeners in 2,2,4-Trimethylpentane</td>
</tr>
<tr>
<td>NIST SRM 2258</td>
<td>BDE 209 in 2,2,4-trimethylpentane</td>
</tr>
<tr>
<td>NIST SRM 2585</td>
<td>Organic Contaminants in House Dust</td>
</tr>
<tr>
<td>NIST SRM 2786</td>
<td>Fine particulate Matter (&lt;4 um)</td>
</tr>
<tr>
<td>NIST SRM 2787</td>
<td>Fine Particulate Matter (&lt;10 um)</td>
</tr>
<tr>
<td>NIST SRM 2974a</td>
<td>Organics in freeze-dried Mussel Tissue</td>
</tr>
<tr>
<td>WMF-01</td>
<td>Reference fish tissue for organic contaminant analysis (Wellington Laboratories)</td>
</tr>
</tbody>
</table>
2.7 Tetrabromobisphenol A (TBBPA) and hexabromocyclododecane (HBCDD)

CAS no: 79-94-7 25637-99-4 & 3194-55-6*
Chemical name: 4,4’-(2,2-propanediyl)bis(2,6-dibromophenol) (TBBPA) 1,2,5,6,9,10-hexabromo-cyclododecane (HBCDD)
Molecular formula: C\textsubscript{15}H\textsubscript{12}Br\textsubscript{4}O\textsubscript{2} C\textsubscript{12}H\textsubscript{18}Br\textsubscript{6}
Assessed by NICNAS: yes yes

*Two CAS numbers are listed, one including position numbering, but both are the same compound and a mixture of isomers.

TBBPA and HBCDD are brominated flame retardants (BFRs) that have been extensively used as replacements for PBDEs. In 2001 they were the two highest-volume BFRs used in the European Union (Covaci et al. 2006). Concerns have also been raised about their effects on health and the environment. Neither TBBPA nor HBCDD are manufactured in Australia.

TBBPA is primarily used in printed circuit boards as a reactive FR, becoming part of the polymer into which it is incorporated (NICNAS 2001a). It is therefore unlikely to enter the environment by volatilising from polymer products; however it may be released from discarded products in landfill. It has low water solubility and so partitions to soils and sediments, and has a relatively high bioconcentration factor, however it is generally excreted quite rapidly and so is not normally found in environmental biological samples (INCHEM 1995).

Most HBCDD is used in polystyrene foams for thermal insulation in the construction industry, with some used in electronic components and some in textiles for furniture (Jensen and Bergman 2010). HBCDD has six stereogenic centres, giving rise to 16 possible isomers, however the commercial product is mainly a mixture of three isomers, known as α-, β- and γ-HBCDD (over 75% of the technical grade material is usually γ) (Covaci et al. 2006). It is an additive FR, not chemically bound to the polymer, hence easily emitted from FR-containing products, and it has been found to be ubiquitous in the environment. HBCDD is lipophilic, and usually adsorbs strongly to soils and sediments (Jensen and Bergman 2010). It is persistent in the environment, has a moderate capacity for long-range transport, and is bioaccumulative.

NICNAS prepared a PEC report and an Existing Chemical Information Sheet (ECIS) on BFRs that discussed TBBPA. The PEC report concluded that as TBBPA had been found to partially or completely degrade in the environment, as it is a reactive FR and so less likely to be released to the environment, and as its use was declining, no further assessment was required (NICNAS 2001a). The ECIS, however, showed that usage in
fact increased in the next few years, with 69 tonnes imported in the year 2003–04 (NICNAS 2005a), presumably because of the phasing out of PBDEs.

The NICNAS PEC report on HBCDD says that the amount of raw material imported is decreasing, however imports of polystyrene resin containing HBCDD appear to be increasing (NICNAS 2012b). A total of approximately 61 tonnes was imported into Australian in the year 2009–10.

2.7.1 Occurrence in the environment

Tanabe and Ramu (2012) reported distribution of HBCDD to be widespread and increasing over the last 30 years in the marine environment of the Asia-Pacific region. Covaci et al. (2006) found that HBCDDs were being detected in remote Arctic regions, that concentrations from the North American environment appeared to be lower than similar samples from Europe, and that data from Asia was lacking. They did note that many studies had concentrated on areas near manufacture or usage of HBCDD and there was little data for the wider environment. NICNAS found no Australian environmental monitoring data was available for HBCDD (NICNAS 2012b). Kefeni et al. (2011) reviewed the international literature on distribution of PBDEs, TBBPA and HBCDD and reported that TBBPA is widely distributed in the environment. Due to its use as a reactive FR, concentrations found were usually significantly lower than those for PBDEs.

2.7.2 Regulation of TBBPA and HBCDD

In Australia, use of HBCDD is not regulated, however NICNAS has recommended that industrial users should discontinue use where possible, and that the Council of Australian Governments Standing Council for Environment and Water should prepare an action plan to address the unacceptable risk to the environment and occupational safety and the possibility of HBCDD being listed under the Stockholm Convention (NICNAS 2012b).

Internationally, TBBPA and HBCDD (under ‘brominated flame retardants’) are on the OSPAR list of Chemicals for Priority Action (OSPAR 2002).

A Stockholm Convention committee concluded in 2010 that HBCDD met the criteria for a POP, and the eighth meeting in 2012 recommended listing it in Annex A with some specific exemptions (POP RC 2012a). HBCDD was identified in 2008 by the European Chemicals Agency as one of 14 substances of ‘very high concern’, and was added to the REACH authorisation list in 2010. An Environmental Quality Standard (EQS) dossier deriving tentative EQSs (EC WFD 2011a) has been prepared for this substance under the EC WFD. (This document appears to erroneously describe CAS no. 15637-99-4 as 1,3,5,7,9,11-hexabromocyclododecane). HBCDD is proposed for addition to the list of priority substances (EC 2011) with the following EQSs: annual average of 0.0016 µg/L in inland surface waters, 0.0008 µg/L in other surface waters; maximum allowable concentration of 0.5 µg/L in inland surface waters, 0.05 µg/L in other surface waters; 167 µg/kg in biota.

The US EPA lists HBCDD on the Office of Pollution Prevention and Toxic Substances Index I Master Testing list and is considering (as of June 2012) a series of further regulations (NICNAS 2012b). Canada has added it as a toxic substance to Schedule 1 of the Canadian Environmental Protection Act, 1999 (Government of Canada 2012a).
2.7.3 Methods and measurement issues

The American Society for Testing and Materials (ASTM), ISO and the US EPA do not have standard methods for TBBPA or HBCDD.

Clement et al. (2012) discussed details of extraction and cleanup techniques for TBBPA and HBCDD from biota, and noted that LC-MS is a suitable analytical technique because of the polarity of TBBPA and the interconversion of the HBCDD isomers at GC temperatures. Diaz Cruz et al. (2009) reviewed two methods for TBBPA and three for HBCDD in sewage sludge, using Soxhlet extraction or centrifugation; one or more of gel permeation chromatography (GPC), silica gel, SPE or HPLC for cleanup; and LC- or GC-MS detection. Covaci et al. (2006) reviewed environmental studies on HBCDD, covering air and dust, sediments and soils, marine biota, birds and humans. Wu et al. (2009) described an MAE-LC-MS method for HBCDD in marine sediments. Li et al. (2011) reported methods for TBBPA and HBCDD in soil, cabbage and radish by Soxhlet extraction, silica cleanup and LC-MS. Garcia Jares et al. (2009) and Xie and Ebinghaus (2008) have reviewed analysis in air and included methods for TBBPA and HBCDD. TBBPA is detected in three methods (one including PBDEs) by GC-MS, after derivatisation, and one LC-MS method is reported in each review. HBCDD is analysed along with PBDEs and other novel BFRs by GC with atomic emission detection or electron capture detection (ECD), by GC-electron ionisation (EI)-MS, or by a GC and an LC method.

The isomers of HBCDD and their interconversion above 160°C present a challenge in the measurement of this contaminant. From an ecotoxicological perspective the isomer profile is important, as differing solubilities, and apparently bioavailability, lead to different environmental impacts (Covaci et al. 2006). De Boer and Wells (2006) reported the results of three consecutive annual international studies on BFRs in environmental matrices, and found that only a minority of laboratories undertook reliable TBBPA and HBCDD analyses.

None of the respondents to our survey of Australian laboratories claimed analytical capabilities for TBBPA or HBCDD, and no mention of these analytes was found in the ‘Test Type Search’ of NATA accredited laboratories on the NATA website (www.nata.asn.au).

2.7.4 Reference materials and proficiency testing studies

Analytical standards of TBBPA and the three main isomers of HBCDD are available commercially, neat or as solutions. Isotopically-labelled TBBPA and HBCDD isomers are also available.

NIST describe a ‘Methods and Measurements for Emerging Contaminants’ program on their website (http://www.nist.gov/mml/csd/mergecontam.cfm), and they state that methods are currently being developed for the newer BFRs, without specifying which ones.

Wepal (The Netherlands) offers PT studies for BFRs in sediments and in marine environmental samples via QUASIMEME (Quality Assurance of Information for Marine Environmental Monitoring in Europe), and this appears to cover TBBPA and HBCDD (de Boer and Wells 2006).
2.7.5 Analytical methodology gaps in Australia

There appear to be suitable methods in the literature for these analytes, although they require careful attention to detail and significant technical capability. The methodology does not appear to be available commercially in Australia. TBBPA and HBCDD are widespread internationally and almost certainly present in the environment, so development of an analytical capability is required. There also appears to be a need for suitable matrix reference materials.
### 2.8 Novel flame retardants

#### Table 9: Brominated, chlorinated and organophosphorous flame retardants

<table>
<thead>
<tr>
<th>CAS no.</th>
<th>Chemical name</th>
<th>Mol. formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>26040-51-7</td>
<td>bis-(2-ethylhexyl)-tetrabromophthalate (BEH-TEBP)</td>
<td>C_{24}H_{36}Br_{4}O_{4}</td>
</tr>
<tr>
<td>32588-76-4</td>
<td>ethylene bis(tetra bromophthalimide) (EBTBPI)</td>
<td>C_{18}H_{4}Br_{6}N_{2}O_{4}</td>
</tr>
<tr>
<td>155613-93-7</td>
<td>octabromo-1,3,3-trimethyl-1-phenylindane (OBTMPI)</td>
<td>C_{18}H_{12}Br_{6}</td>
</tr>
<tr>
<td>84852-53-9</td>
<td>decabromodiphenyl ethane (DBDPE)</td>
<td>C_{14}H_{4}Br_{10}</td>
</tr>
<tr>
<td>37853-59-1</td>
<td>1,2-bis(2,4,6,-tribromophenoxy)ethane (Firemaster 680, BTBPE)</td>
<td>C_{14}H_{8}Br_{6}O_{2}</td>
</tr>
<tr>
<td>35109-60-5</td>
<td>2,3-dibromopropyl-2,4,6-tribromophenyl ether (Dpte)</td>
<td>C_{9}H_{7}Br_{5}O</td>
</tr>
<tr>
<td>87-82-1</td>
<td>hexabromobenzene (HBB)</td>
<td>C_{6}Br_{6}</td>
</tr>
<tr>
<td>183658-27-7</td>
<td>2-ethylhexyl 2,3,4,5-tetabromobenzoate (EH-TBB)</td>
<td>C_{15}H_{18}Br_{6}O_{2}</td>
</tr>
<tr>
<td>87-83-2</td>
<td>pentabromotoluene (PBT)</td>
<td>C_{7}H_{3}Br_{5}</td>
</tr>
<tr>
<td>85-22-3</td>
<td>pentabromoethylbenzene (PBE)</td>
<td>C_{8}H_{5}Br_{5}</td>
</tr>
<tr>
<td>632-79-1</td>
<td>tetrabromophthalic anhydride (TBP-Anh)</td>
<td>C_{6}Br_{6}O_{3}</td>
</tr>
<tr>
<td>20566-35-2</td>
<td>1,2-benzenedicarboxylic acid 3,4,5,6-tetabromo-2-(2-hydroxyethoxy)ethyl 2-hydroxypropyl ester (TBP-diol)</td>
<td>C_{15}H_{16}Br_{4}O_{7}</td>
</tr>
<tr>
<td>21850-44-2</td>
<td>TBBPA-bis(2,3-dibromopropylether) (TBBPA-BDBPE)</td>
<td>C_{21}H_{28}Br_{6}O_{2}</td>
</tr>
<tr>
<td>25327-89-3</td>
<td>TBBPA-bis(allyl) ether (TBBPA-BAE)</td>
<td>C_{21}H_{28}Br_{6}O_{2}</td>
</tr>
<tr>
<td>3278-89-5</td>
<td>2,4,6-tribromophenyl allyl ether (TBP-AE)</td>
<td>C_{9}H_{7}Br_{3}O</td>
</tr>
<tr>
<td>118-79-6</td>
<td>2,4,6-tribromophenol (TBP)</td>
<td>C_{9}H_{7}Br_{3}O</td>
</tr>
<tr>
<td>58965-66-5</td>
<td>1,4-(pentabromophenoxy)tetrabromobenzene</td>
<td>C_{18}H_{12}Br_{6}O_{2}</td>
</tr>
<tr>
<td>25713-60-4</td>
<td>2,4,6-tris(2,4,6-tetrabromophenoxy)-1,3,5-triazine (TBP-TAZ)</td>
<td>C_{21}H_{28}Br_{6}N_{3}O_{3}</td>
</tr>
<tr>
<td>23488-38-2</td>
<td>tetrabromo-p-xylene</td>
<td>C_{8}H_{6}Br_{4}</td>
</tr>
<tr>
<td>87-84-3</td>
<td>pentabromochlorocyclohexane</td>
<td>C_{6}H_{8}Br_{5}Cl</td>
</tr>
<tr>
<td>39569-21-6</td>
<td>tetrabromo-o-chlorotoluene (TBCT)</td>
<td>C_{7}H_{3}Br_{4}Cl</td>
</tr>
<tr>
<td>126-72-7</td>
<td>tris(dibromopropyl)phosphate (Firemaster T 23P, TDBPP)</td>
<td>C_{9}H_{15}Br_{6}PO_{4}</td>
</tr>
<tr>
<td>51936-55-1</td>
<td>hexachlorocyclopentadienyldibromocyclooctane (HCDBCO)</td>
<td>C_{13}H_{12}Br_{6}Cl_{6}</td>
</tr>
<tr>
<td>13560-89-9</td>
<td>dechlorane</td>
<td>C_{18}H_{12}Cl_{12}</td>
</tr>
<tr>
<td>57583-54-7</td>
<td>resorcinol bis(diphenyl phosphate) (RDP)</td>
<td>C_{30}H_{24}P_{2}O_{8}</td>
</tr>
<tr>
<td></td>
<td>tris(chloroalkyl)phosphates</td>
<td></td>
</tr>
<tr>
<td>115-96-8</td>
<td>tris(2-chloroethyl) phosphate (TCEP)</td>
<td>C_{9}H_{12}Cl_{3}PO_{4}</td>
</tr>
<tr>
<td>13674-84-5</td>
<td>tris(1-chloro-2-propyl) phosphate (TCPP)</td>
<td>C_{9}H_{18}Cl_{3}PO_{4}</td>
</tr>
<tr>
<td>13674-87-8</td>
<td>tris(1,3-dichloro-2-propyl) phosphate (TDCPP)</td>
<td>C_{9}H_{15}Cl_{6}PO_{4}</td>
</tr>
<tr>
<td></td>
<td>triarylyphosphates</td>
<td></td>
</tr>
<tr>
<td>115-86-6</td>
<td>triphenylphosphate (TPP)</td>
<td>C_{18}H_{18}PO_{4}</td>
</tr>
</tbody>
</table>

CRC CARE Technical Report no. 24
Analytical methods for priority and emerging contaminants – a literature review
Halogenated and phosphorous containing flame retardants work by capturing the high energy H and OH radicals that are part of the flame propagation process. They can also inhibit combustion by helping to form a charred layer on the outside of the polymer (Clariant). Brominated, chlorinated and organophosphorous compounds are likely to be persistent in the environment. Howard and Muir (2010) have included most of the flame retardants in Table 9 in their list of potentially persistent and bioaccumulative chemicals. The San Antonio Statement on Brominated and Chlorinated Flame Retardants concludes that ‘brominated and chlorinated flame retardants as classes of substances are a concern for persistence, bioaccumulation, long-range transport, and toxicity’ (DiGangi et al. 2010).

2.8.1 Brominated flame retardants (BFRs)

A 2009 report from the Norwegian Pollution Control Authority reviewed uses, toxicity and environmental levels and behaviour of 21 novel BFRs (Harju et al. 2009). Annual production volume was roughly estimated at 100,000 tonnes. The OECD's Pov&LRTP Screening Tool was used to assess the potential for POP behaviour. Fourteen of the compounds (TBBPA-DBPA, TBBPA-BAE, HBB, PBT, PBE, TBP-AE, DPTE, TBP, DBDPE, BTBPE, EBTBPI, TBP-Anh, BEH-TEBP and EH-TBB in Table 9) were prioritised for further monitoring.

NICNAS has prepared a PEC report on BFRs (NICNAS 2001a). The main route to the environment for all of the BFRs considered was expected to be from landfill at the end of the useful life of products containing FRs. The main BFRs in use in Australia at the time were PBDEs, HBCDD and TBBPA (dealt with in other sections of this report), brominated styrenes (not being considered in this review), brominated aliphatic phosphates, TBBPA-BDBPE and BTBPE (for which little toxicity data was available, although what was known at the time did not give rise to concern). The toxicity and carcinogenicity (group 2A according to the IARC) of the brominated aliphatic trisphosphate TDBPP was reported, as were international restrictions on its use, although it was not in use in Australia at the time. A PEC report was issued on TDBPP (NICNAS 2005b). This compound is listed in Annex III of the Rotterdam Convention (www.pic.int), requiring signatories (including Australia) to notify the secretariat if they wish to allow its importation. NICNAS therefore annotated the AICS listing for TDBPP to indicate that it is not to be imported except for the purposes of research and development. TDBPP has been used as a FR in textiles and clothing, and so trace amounts may enter the Australian environment as a result of washing clothing manufactured in countries that have not banned the use of TDBPP.

Gouteux et al. (2006) showed that oligomeric BRFs, which are not considered an environmental hazard as they are embedded in polymer products, can still contain smaller brominated molecules as synthetic impurities, or give rise to these compounds on breakdown of the polymeric structure, particularly under thermal stress. Among the compounds released were PEBE and PBT.

2.8.2 Chlorinated and organophosphorous (OP) FRs

The original dechlorane, also known as Mirex, was developed as a pesticide and then also used as a FR (Feo et al. 2012). Mirex was one of the original 12 Stockholm POPs and so its use has been discontinued. To replace it, other similar highly chlorinated compounds such as Dechlorane Plus and dechloranes 602, 603 and 604 were
developed. However, these are also environmentally persistent, bioaccumulative and subject to long-range transport.

Chlorinated trisphosphates were the subject of a NICNAS Priority Existing Chemical report (NICNAS 2001c). Generally, they are not as persistent in the environment or as toxic as the BFRs, however there are concerns about their volatility leading to blooming from the surface of treated products, and they are found in environmental water due to their water solubility. Trisphosphates are also used as additives in hydraulic fluids, lubricants, and transmission and motor oils to prevent surface damage, and a Swedish study found that some are subject to long-range air transport (Marklund et al. 2005).

Reemtsma et al. (2008) reviewed the occurrence and fate of OP ester FRs and plasticisers. Trichloroalkyl and triaryl phosphates are more commonly used as FRs while the non-chlorinated trialkyl phosphates tend to be used as plasticisers and anti-foaming agents. The authors described OP esters as 're-emerging rather than emerging' pollutants as they were first discussed in the 1970s, then concern died away as the aryl and alkyl phosphates in use at the time were found to degrade in the environment. Later they were found in indoor environments and chlorinated alkyl phosphates were found to be more persistent in the environment. Many OP FRs are high-production-volume chemicals, with estimated combined usage in Western Europe in the mid 2000s, for example, approaching 100,000 tonnes/year and apparently increasing. Bisphosphates such as RDP were used to a minor extent at the time of the review. Properties such as hydrophobicity and volatility vary quite considerably across the range of OP FRs, depending on the alkyl or aryl substituents, but most are quite stable to hydrolysis at neutral pH.

2.8.3 Occurrence of FRs in the environment

Many of the novel BFRs are likely to be associated with e-waste, and Zhang et al. (2010b) detected HBB, PBT, PBEB, BTBPE and dechlorane (among other CECs) in aquatic biota of an e-waste recycling region in China.

Feo et al. (2012) reviewed studies reporting Dechlorane Plus in biota in many parts of the world, however many of these were near production facilities and little information was available on the wider environment.

Reemtsma et al. (2008) reviewed studies on the occurrence of OP esters in waters and air. Seven studies in Europe between 2002 and 2005 showed that OP FRs were prevalent in wastewater and that chlorinated alkyl phosphates were often not well removed by WWTPs. The bisphosphate RDP was included in one study but not found. Studies of surface and ground waters since the 1970s showed some OP FRs to be omnipresent. Due to their addition to building materials, furnishings and electrical appliances, levels of OP FRs in indoor air can be high, and while they are lower in outdoor areas, significant levels have been found, particularly in urban areas affected by traffic or airports. Some OP esters have been detected in remote areas, indicating that they undergo long-range air transport.

Two more recent reviews of emerging contaminants report the frequent finding of TCEP in water in Europe and the USA (Lapworth et al. 2012; Wells et al. 2010), and Andrews et al. (2012) reported finding trialkylphosphates in leachates from three different old and new landfill sites in Oklahoma, as did Eggen et al. (2010) in Europe.
2.8.4 Regulation of flame retardants

TDBPP is listed in Annex III of the Rotterdam Convention.

The Australian water recycling guidelines for augmenting drinking water supplies recommended values for TDCPP, TCEP and TPP of 1 μg/L (NRMMC, EPHC and NH&MRC 2008).

The Minnesota Department of Health are currently reviewing TDCPP with the aim of publishing health-based guidance values for drinking water (MDH 2012).

2.8.5 Methods and measurement issues

Covaci et al. (2011) and Papachlimitzou et al. (2012) recently reviewed the analysis of novel BFRs. Standard methods are not generally available for these contaminants. Usually the methods used are optimised for PBDEs and HBCDD. Papachlimitzou et al. concluded that ‘mainly, they involve the detection and analysis of a limited number of [novel] BFR compounds using GC–[electron-capture negative ionization]ECNI-MS. This technique is associated with several problems such as thermal decomposition and isomerization of some of the compounds of interest, lack of standards and certified reference materials, and co-elution of relevant pairs of organobromine compounds.’

Lopez et al. (2011b) described a method for eight of the BFRs in Table 9 in sediments by PLE, chromatography and SPE, then GC-EI or ECNI-MS. Clement et al. (2012) reviewed methods used to analyse biota in the US Great Lakes. Many of the methods are GC-EI- or NCI-MS, but there are also some LC-MS methods. The authors noted that as FRs are designed to break down and release halogen radicals when heated, they can be difficult to analyse by GC.

Garcia Jares et al. (2009) and Xie and Ebinghaus (2008) reviewed methods for brominated and OP FRs in air. Nearly all the methods reported for BFRs are for PBDEs. Only a few of the BFRs from Table 9 are included in some methods, with Soxhlet or ultrasonic extraction of the sampling device and GC-AED (one method) or – NCI-MS detection.

Stapleton et al. (2008, 2009) reported methods for brominated and OP FRs in house dust and furniture foam by GC-EI and ECNI-MS. Cristale et al. (2012) reported a multiresidue chromatographic method for the determination of halogenated and OP FRs by GC-EI or ECNI-MS in water.

In Part II of their discussion of OP FRs and plasticisers in water and air, Quintana et al. (2008) reviewed analytical methodology. They again noted the diversity of properties such as polarity and volatility that have to be considered if these compounds are to be analysed as a class. One aspect of this diversity is the requirement for a suitable range of internal standards and surrogates, to adequately reflect the behaviour of all analytes. OP FRs are often detected by NPD or flame-photometric detection, as these detectors give good specificity for phosphorus-containing compounds, and for these methods OP esters that are not expected to occur in the samples are usually used as surrogates and internal standards. For MS detection, some deuterated alkyl and aryl phosphates are available, but at the time of review no isotopically-labelled chlorinated alkyl phosphates were available. LLE or SPE are often used for extraction of waters, however more volatile compounds can be lost during concentration steps, very polar compounds are hard to retain by SPE and hydrophobic compounds may be lost to particulate matter during SPE. Modern microextraction techniques address some of
these problems. Air sampling is usually done using active sampling, and most OP esters are retained using simple devices. Solid samples are usually extracted by sonication, Soxhlet, PLE or MAE using medium-polarity solvents. The selectivity of NPD or MS detection allows analysis of raw extracts, but a cleanup such as SPE, GPC or silica or alumina chromatography is usually applied to prolong column lifetime. LC-MS analyses have also been reported.

Rodil et al. (2005) reported an LC-MS method for 11 OP FRs and plasticisers in wastewater, including trialkyl, trichloroalkyl and triaryl phosphates and two bisphosphates (including RDP). The LC-MS method reported by Kim et al. (2011) for a range of contaminants in fish included nine non-halogenated, primarily trialkyl organophosphates. Another multiresidue LC-MS method for 53 multi-class analytes in water included 19 OP FRs (Rodil et al. 2009). Mahugo-Santana et al. (2011) referenced four methods for OP FRs in air and water in their review of liquid-phase microextraction applications, and Sanchez-Prado et al. (2010) discussed two MAE methods for house dust (GC-NPD detection) and sediment (GC-inductively coupled plasma (ICP)-MS).

Feo et al. (2012) reviewed analysis of Dechlorane Plus and related compounds in biota. They have similar physiochemical properties to PBDEs and so similar sample preparation techniques are usually used. Very little work has been done on dechloranes 602–604, or degradation products. Most of the dechloranes are produced commercially as mixtures of stereoisomers.

Only two Australian laboratories responded to the survey questions about FRs other than PBDEs, one stating that they could do BFRs in air, without specifying which analytes, and the other mentioning analysis of another BFR, hexabromobiphenyl, in several matrices.

2.8.6 Reference materials and proficiency testing studies

Analytical standards are available for many of the FRs in Table 9 and some dechlorane related substances, and isotopically-labelled standards are available for at least DBDPE, BTBPE, HBB, pentabromobenzene, dechlorane and triethyl-, tributyl- and triphenylphosphates (e.g. Cambridge Isotope Laboratories, Wellington Laboratories). Isotopically-labelled standard for chlorinated OP FRs appear to be lacking.

NIST describe a ‘Methods and Measurements for Emerging Contaminants’ program on their website (http://www.nist.gov/mml/csd/emergetest.cfm) and they state that methods are currently being developed for the newer BFRs, without specifying which ones.
2.8.7 Analytical methodology gaps in Australia

Some work on most of the compounds in Table 9 is reported in the literature. However, methodology for these classes of compounds generally does not appear to be well established, and analysis does not appear to be performed routinely in Australia. With the phasing out of the PBDEs and HBCDD, a large number of possible replacements have appeared and it is not clear which are most important in Australia. Some are subject to long-range transport and may be found in the Australian environment whether they are used here or not. Further investigation into which analytes will be most significant for the Australian environment is recommended. The development of methods, the production of reference materials and the coordination of proficiency testing schemes can then be considered for the more relevant analytes.
2.9 Short-chain chlorinated paraffins (SCCPs)

CAS no: 85535-84-8*
Chemical name: alkanes, C₁₀-₁₃, chloro
Assessed by NICNAS: yes

*Several other CAS numbers represent groups of chlorinated alkanes with chain lengths including or overlapping the C₁₀ – C₁₃ range (NICNAS 2001b)

SCCPs are chlorinated linear alkanes containing between 10 and 13 carbon molecules. Commercial SCCPs are complex mixtures. In 2012, annual global production was estimated to be of the order of a megatonne (Clement et al. 2012). Information about their use in Australia from the PEC report, (NICNAS 2001b), and the ECIS (NICNAS 2004) includes the following: SCCPs are widely used in manufacturing of metalworking fluids and as flame retardants in a range of products such as fillers, adhesives and coating materials used in the building industry. They could be released into the environment at any stage in their life-cycle, including release from products in use or after disposal. In the environment they are toxic to aquatic organisms, persistent (binding to soils and sediments), bioaccumulative, and undergo long-range transport through air. SCCPs are not manufactured in Australia. In the two years to 2000, around 360 tonnes were imported. In 2004, usage was found to have reduced significantly, however NICNAS recommended that industry voluntarily phase out the use of these chemicals in metalworking fluids.

2.9.1 Occurrence of SCCPs in the environment

Bayen et al. (2006) noted that SCCPs have been produced since the 1930s and have been detected in air, water, soils and sediments, and biota. Clarke and Smith (2011) reviewed SCCPs in the context of agricultural use of biosolids and found them to be of concern given the high levels detected. The NICNAS analysis of environmental exposure considered that most of the SCCPs used in Australia as industrial lubricants would be disposed of to landfill bound to sludge, and the proportion from building materials and other uses would also end up in landfill (NICNAS 2001b). SCCPs will bind strongly to soil and are unlikely to leach. A fraction of the lubricants will be released to waste water and, as SCCPs are practically insoluble in water; this fraction will largely bind to sediments.

The Centre for Australian Weather and Climate Research prepared a report on indoor air pollutants for which they measured SCCP levels at 10 dwellings in Melbourne (Gillett et al. 2010). Indoor air levels were between 34 and 122 ng m⁻³ and outdoor air levels were between 56 and 164 ng m⁻³. They found only two previous studies, of levels in outdoor air at rural or remote locations in Europe, both of which reported much lower levels of SCCPs than the Australian urban study.

2.9.2 Regulation of SCCPs

SCCPs were nominated for listing as a POP under the Stockholm Convention in 2006. At its eighth meeting in 2012, the POP Review Committee was unable to agree to accept the draft risk profile presented (POP RC 2012c), and decided to establish further working groups to continue to discuss the risk profile and the information required, and to collect further information to add to the risk profile (POP RC 2012b).

Internationally, SCCPs are considered to be of concern by many organisations (NICNAS 2001b). The US EPA regulates them under the Toxic Substances Control Act.
and the Clean Air Act. The EU assessed them as part of their first priority list of substances, and found health concerns. Member states were directed to establish monitoring programs and are reporting declining usage. European REACH regulation EC 1907/2006, Annex XVII, restricts their use in metalworking and leather production. Canada declared them ‘toxic’ in 1993, and conducted a risk assessment. In 2012 they were added to the Schedule 1 List of Toxic Substances of the Canadian Environmental Protection Act, 1999 (Government of Canada 2013). OSPAR initiated a phase-out of their use in 1995.

### 2.9.3 Methods and measurement issues

One standard method was found for SCCPs in waters:

**ISO 12010:2012** Water quality – Determination of short-chain polychlorinated alkanes (SCCPs) in water – Method using gas chromatography-mass spectrometry (GC-MS) and negative-ion chemical ionization (NCI). Method is applicable to a range of waters, approximate range 0.1 to 10 μg/L.

Bayen et al. (2006) have reviewed the analysis of SCCPs and Clement et al. (2012) reviewed extraction methods for fish. Extraction and clean-up can be similar to those used for other organochlorine compounds, including polychlorinated biphenyls, however more clean-up is usually needed due to the complexity of the quantification. Water samples are extracted by LLE, SPE or SPME, and usually do not require clean-up. Soils, sediments and biota are usually subjected to Soxhlet extraction, although PLE or MAE can be used. Extracts are often treated to remove sulfur, then cleaned up using silica or GPC. SCCPs are not ionised by the atmospheric pressure ionisation sources normally used for LC-MS, so analysis is usually by GC. The very complex mixtures have not been resolved on a single GC column and are usually quantified as a band. Some separation has been achieved by 2D GC. For environmental samples, analysis is usually by ECNI-MS. HRMS is preferred, as it reduces interferences, but requires complex data processing to overcome the sensitivity bias towards higher congeners (Zencak et al. 2005).

Only one Australian laboratory responded that they could analyse for SCCPs, in air only. It appears that no laboratories have NATA accredited methods for these analytes (www.nata.asn.au).

Analysis of SCCPs is difficult due to the large numbers of compounds involved (over 10,000) (Clarke and Smith 2011), and interference from matrix components such as lipids and other polychlorinated compounds (Bayen et al. 2006). The choice of representative congeners to use as analytical standards is difficult as there are so many compounds, with a range of masses and retention times, and MS response varies with the degree of chlorination.

### 2.9.4 Reference materials and proficiency testing studies

Some analytical standards are available commercially (e.g. Chiron). Standards are also available as technical mixtures which can be described by degree of chlorination, by chain length or by branching. Some isotopically-labelled standards may be available, but they are difficult to find. Clement et al. (2012) mentioned the lack of reference standards as a challenge to analysis.

Bayen et al. (2006) could not find any reference materials – IRMM were considering producing a sludge material, and a number of NIST materials (SRMs 1588, 1945 and
1974a) had been analysed (but not certified) for SCCPs. Searching COMAR for this review did not find any reference materials.

In 2010, QUASIMEME coordinated an interlaboratory study on the analysis of chlorinated paraffins in isooctane solutions (van der Veen et al. 2012). Their 2012 report discussed only two previous intercomparison studies, one of SCCP solutions and the other of industrial oil extract. Chlorinated paraffins in biota (DE-15) is listed on the QUASIMEME website (http://www.quasimeme.org) as one of their test materials, under the heading Development Exercises.

### 2.9.5 Analytical methodology gaps in Australia

SCCPs have been widely used in Australia and have been found in quite high levels in urban air. As there is very limited analytical capability, there is a need in Australia for development of methods for all environmental matrices. Reference materials and proficiency testing schemes are also lacking.
2.10 Methylsiloxanes

CAS no: Chemical name: Molecular formula:
541-05-9 hexamethylcyclotrisiloxane (D3) C₆H₁₈O₃Si₃
556-67-2 octamethylcyclohexasiloxane (D6) C₁₂H₃₆O₆Si₆
541-02-6 decamethylcyclopentasiloxane (D5) C₁₀H₃₀O₅Si₅
540-97-6 dodecamethylcyclohexasiloxane (D7) C₁₄H₄₂O₇Si₇
107-50-6 tetradecamethylcycloheptasiloxane (D8) C₁₄H₄₂O₇Si₇
107-46-0 hexamethyldisiloxane (L2) C₆H₁₆OSi₂
107-51-7 octamethyltrisiloxane (L3) C₈H₂₄O₃Si₃
141-62-8 decamethyldisiloxane (L4) C₁₀H₃₀O₃Si₄
141-63-9 dodecamethylpentasiloxane (L5) C₁₂H₃₆O₄Si₅

All of the above siloxanes are listed on the AICS but none have been assessed by NICNAS

Cyclic and linear siloxanes are used as precursors in the production of silicone polymers and in a range of consumer products such as cosmetics, deodorants, soaps, hair conditioners, hair dyes, car waxes, baby pacifiers, cookware, cleaners, furniture polishes, and water-repellent windshield coatings (Kierkegaard et al. 2010; Richardson 2012). D5 is also used as a dry-cleaning solvent (Brooke et al. 2009a). Howard and Muir (2010) calculated that cyclic siloxanes with four to six siloxane groups are likely to be particularly bioaccumulative. They cited a 2005 report that found siloxanes in a variety of samples from Nordic environment, with cyclic siloxane concentrations around two orders of magnitude higher than linear siloxane concentrations in spite of widespread use of both types (Kaj et al. 2005). The report found only a limited amount of toxicity data for most siloxanes, and possible fertility and carcinogenic effects for some of the cyclic compounds. Siloxanes are resistant to chemical reactions and so may be persistent in the environment.

2.10.1 Regulatory activity regarding siloxanes

NICNAS classify D4 as a hazardous substance. D3–D7 and L2–L5 are all listed on the AICS.

Environmental risk assessment reports by the Environment Agency of England and Wales, published in 2009, found no risks to health or the environment from the use of D4 in PCPs and household products. D5 was determined to be very persistent and very bioaccumulative, but no risks to the environment or health in the UK were identified. D6 was not considered to be bioaccumulative or toxic, although it may be persistent. There are industrial sites using D4–6 in the UK, which may be of environmental concern, and the reports mentioned further studies to be undertaken,
including development of analytical methodology (Brooke et al. 2009a; Brooke et al. 2009b; Brooke et al. 2009c).

Environment Canada assessed D4–D6, L3 and another siloxane (M4Q, known to be an industrial byproduct) as part of the Canadian Chemical Management Plan Challenge. In February 2012, the Government of Canada declared that it was satisfied that D5 was not harmful to the environment, following a toxicological review (Siloxane D5 Board of Review 2011). They found that D5 was not bioaccumulative. Screening assessment of D4 (2008) found that it may be entering the environment in ways that could be harmful to the environment, but was not constituting a threat to human health. In June 2012, the Canadian Minister of Environment published requirements for Pollution Prevention Plans for D4. Screening assessment of D6 (2009) concluded that exposure to D6 is not harmful to human health or the environment. The D4–D6 assessments can be accessed from the Batch 2 summary web page (Government of Canada 2012b).

Assessment of L3 (2011) found that it may be entering the environment in ways that could be harmful to the environment, but was not constituting a threat to human health. In the same Challenge Batch 12, assessment of hexamethyl-3,3-bis[(trimethylsilyl)oxy]trisiloxane (M4Q, CAS no. 3555-47-3, assessed 2011) found that M4Q is potentially persistent, is not bioaccumulative, and would not be released to the Canadian environment in quantities sufficient to cause harm. M4Q is a reaction by-product in siloxanes. These assessments can be accessed from the Batch 12 summary webpage (Government of Canada 2011).

2.10.2 Methods and measurement issues

Analytical methodology for siloxanes is not well established (Howard & Muir 2010). Richardson has included them in her reviews since 2009 but only refers to two methods for environmental samples (Richardson 2009; Richardson 2010; Richardson 2012; Richardson & Ternes 2011). These are both by Sparham et al. (2008, 2011) for D5, one using headspace GC-MS for waters and the other comparing ASE and liquid extraction from sediments. The first report referred to a few other analytical methods for siloxanes, primarily in biological samples, and both discussed measures to minimise background levels, which can be very high in laboratories due to silicone polymers in equipment and consumables, and the use of cleaning and personal care products. Kierkegaard et al. (2010) described a purge-and-trap GC-MS method for D4–6 in biota, and Companioni-Damas et al. (2012) reported a solvent-extraction GC-MS method using a large-volume injection technique for D3–D6 and linear tri- to pentasiloxanes (L3–L5).

Clarke and Smith (2011) in their review of CECs in biosolids and wastewater treatment determined that while polydimethylsiloxanes are found in sludge and little occurrence data is available, levels observed are not of concern for biosolid reuse in agriculture due to their relatively low toxicity. Balducci et al. (2012) reviewed the few existing studies of methylsiloxanes in the atmosphere as an example of a CEC for which insufficient information on their atmospheric distribution is available to properly determine the environmental risk. Due to their volatility, more than 90% of cyclic methylsiloxanes released to the environment diffuse to the atmosphere.

Only one respondent to the laboratory survey claimed to be able to analyse for methylsiloxanes, in air. It appears that no laboratories have NATA accredited methods for these analytes (www.nata.asn.au).
2.10.3 Reference materials and proficiency testing studies

Analytical standards for some siloxanes are available (e.g. Sigma-Aldrich, Moravek). Some isotopically-labelled standards are also available, including hexamethyl-d18-disiloxane (Dr Ehrenstorfer) and $^{13}$C labelled D4–D6 (Moravek).

No matrix reference materials or proficiency testing studies were found.

2.10.4 Analytical methodology gaps in Australia

Analytical methodology is lacking in Australia. Given their widespread use, volatility and persistence siloxanes are likely to be common in the environment; however, their environmental toxicity is low compared to other CECs so they are probably a low priority.
2.11 1,4-Dioxane

CAS no: 123-91-1
Chemical name: 1,4-dioxane
Molecular formula: C₄H₈O₂
Assessed by NICNAS: yes

Richardson (2012) included 1,4-dioxane in her review, describing it as a high production chemical in the USA, used as a solvent stabiliser in a range of manufacturing processes. Dioxane is a probable human carcinogen, and was included on the contaminant candidate list CCL-3 by the US EPA (US EPA 2012a).

1,4-Dioxane was assessed as part of the Canadian Challenge and found not to be of concern as an environmental contaminant in Canada (Environment Canada 2010a).

In Australia, NICNAS prepared a PEC report in June 1998 (NICNAS 1998). 1,4-Dioxane is not manufactured in Australia, and only small quantities are imported, mainly for laboratory and research use. Public exposure is more likely to occur from contamination in consumer products than from environmental contamination. This chemical does not appear to be of concern in the context of this review.
2.12 Benzotriazoles

<table>
<thead>
<tr>
<th>CAS no</th>
<th>Chemical name</th>
<th>Mol. formula</th>
<th>AICS*</th>
</tr>
</thead>
<tbody>
<tr>
<td>95-14-7</td>
<td>benzotriazole</td>
<td>C₆H₅N₃</td>
<td>yes</td>
</tr>
<tr>
<td>29385-43-1</td>
<td>4-methylbenzotriazole</td>
<td>C₇H₇N₃</td>
<td>yes</td>
</tr>
<tr>
<td>136-85-6</td>
<td>5-methylbenzotriazole</td>
<td>C₇H₇N₃</td>
<td>yes</td>
</tr>
<tr>
<td>29385-43-1</td>
<td>tolyltriazole (mix of 4- and 5-Me)</td>
<td>C₇H₇N₃</td>
<td>yes</td>
</tr>
<tr>
<td>4184-79-6</td>
<td>xylitriazole</td>
<td>C₆H₆N₃</td>
<td>no</td>
</tr>
<tr>
<td>94-97-3</td>
<td>5-chlorobenzotriazole</td>
<td>C₆H₅ClN₃</td>
<td>yes</td>
</tr>
<tr>
<td>2440-22-4</td>
<td>2-(2H-benzotriazol-2-yl)-4-methylphenol (UV-P)</td>
<td>C₁₃H₁₁N₃O</td>
<td>yes</td>
</tr>
<tr>
<td>2170-39-0</td>
<td>2-(2H-benzotriazol-2-yl)-4-methyl-6-(2-propen-1-yl)phenol (UV-9)</td>
<td>C₁₆H₁₅N₃O</td>
<td>no</td>
</tr>
<tr>
<td>70321-86-7</td>
<td>2-(2H-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol (UV-234)</td>
<td>C₂₃H₂₉N₃O</td>
<td>yes</td>
</tr>
<tr>
<td>3846-71-7</td>
<td>2-(2H-benzotriazol-2-yl)-4,6-bis(1,1-dimethylethyl)phenol (UV-320)</td>
<td>C₂₀H₂₅N₃O</td>
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<tr>
<td>3896-11-5</td>
<td>2-(2'-hydroxy-3'-tert-butyl-5'-methylphenyl)-5-chlorobenzotriazole (UV-326)</td>
<td>C₁₇H₁₈ClN₃O</td>
<td>yes</td>
</tr>
<tr>
<td>3864-99-1</td>
<td>2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)-5-chloro-2H-benzotriazole (UV-327)</td>
<td>C₂₀H₂₂ClN₃O</td>
<td>yes</td>
</tr>
<tr>
<td>25973-55-1</td>
<td>2-(2H-benzotriazol-2-yl)-4,6-bis(1,1-dimethylpropyl)phenol (UV-328)</td>
<td>C₂₂H₂₉N₃O</td>
<td>yes</td>
</tr>
<tr>
<td>3147-75-9</td>
<td>2-(2-hydroxy-5-tet-ocetylphenyl)benzotriazole (UV-329)</td>
<td>C₂₀H₂₅N₃O</td>
<td>yes</td>
</tr>
<tr>
<td>103597-45-1</td>
<td>2,2'-methylenebis[6-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol (UV-360)</td>
<td>C₃₁H₅₀N₆O₂</td>
<td>yes</td>
</tr>
<tr>
<td>125304-04-3</td>
<td>2-(benzotriazol-2-yl)-6-dodecyl-4-methylphenol (UV-571)</td>
<td>C₂₈H₃₅N₃O</td>
<td>no</td>
</tr>
</tbody>
</table>

*Most of the above benzotriazoles are listed on the AICS but none have been assessed by NICNAS

Benzotriazoles are complexing agents used as anticorrosives in engine coolants, antifreeze and aircraft de-icing fluids, and as silver protection in dishwasher detergents (Richardson 2012). They may be carcinogenic and have estrogenic effects. They are water soluble, resistant to biodegradation and only partially removed by wastewater treatment, and appear to be widespread in the environment. Weiss and Reemtsma (2005) reported that four benzotriazoles were expected to occur in the aquatic environment – benzotriazole, 4- and 5-methylated tolyltriazole and xylitriazole.

2-Hydroxyphenol benzotriazole derivatives are used as UV stabilisers in personal care products and industrial products. Kim et al. (2011) noted that they may have endocrine-disrupting effects in the aquatic environment and can cause coral bleaching. Their
continuous release to the aquatic environment due to their widespread use makes them pseudo-persistent in the environment, irrespective of their biodegradability. Carpinteiro et al. (2010) reported that the phenolic benzotriazoles are hydrophobic, accumulate and persist in sediments and bioaccumulate in the marine food chain.

2.12.1 Occurrence of benzotriazoles in the environment

Studies in Switzerland, Europe and Scandinavia show the corrosion inhibitors to be ubiquitous and abundant contaminants in the aquatic environment (Giger 2009; Loos et al. 2009). The UV stabilisers have been found in various environmental matrices in Europe, Asia and North America (Montesdeoca-Esponda et al. 2012). Liu et al. (2011) found four corrosion inhibitors and six UV stabilisers in waters and biosolids at a sewage treatment plant in South Australia.

2.12.2 Regulation of benzotriazoles

Australian guidelines for recycled water to augment drinking water supplies list a level of 7 ng/L for tolyltriazole (NRMMC, EPHC & NH&MRC 2008).

2.12.3 Methods and measurement issues

There do not appear to be any standard methods for benzotriazoles in environmental matrices.

Farre et al. (2008), Giger (2009) and Richardson (2012) included benzotriazoles in their various reviews, with only a few methods referenced. LC-MS methods for the corrosion inhibitors included those by Weiss and Reemtsma (2005), Hogenboom et al. (2009) and Carpinteiro et al. (2012). Jover et al. (2009) published a method for the corrosion inhibitors in water by SPE and 2D GC-time of flight (TOF)-MS. LC-MS methods for the UV stabilisers include those by Kim et al. (2011) and Montesdeoca-Esponda et al. (2012). Carpinteiro et al. (2010) have also published GC-MS methods for the UV stabilisers. Liu et al. (2011) published a GC-MS method for analytes from both groups of benzotriazoles.

Carpinteiro et al. (2010) noted that the most hydrophobic UV stabilisers (UV-327 and UV-328) are prone to adsorption on glass and PTFE, and for this reason they discounted SPE as an enrichment technique, using SPME instead. Jover et al. (2009) used 2D GC and Liu et al. (2011) used GC-MSMS to reduce matrix effects which are often found when using LC-MS or GC-MS for these compounds in complex environmental samples.

No laboratory survey respondents indicated that they could analyse for benzotriazoles. It appears that no laboratories have NATA accredited methods for these analytes (www.nata.asn.au).

2.12.4 Reference materials and proficiency testing studies

Analytical standards are commercially available, however none of the methods described above include isotopically-labelled internal standards. 1H-Benzotriazole-d4 is commercially available (e.g. Dr Ehrenstorfer).

COMAR searching by the CAS numbers tabulated above did not find any reference materials.
2.12.5 Analytical methodology gaps in Australia

Some methods for benzotriazoles are available in the literature, but there does not appear to be any commercial analysis in Australia. Benzotriazoles and hydroxyphenol benzotriazole derivatives are likely to be common in dishwasher and personal care products in use in Australia and so be as widespread in the aquatic environment here as overseas. There appears to be a need for development of analytical methodology and reference materials to determine the extent of contamination.
2.13 Ionic liquids (ILs)

Ionic liquids (ILs) are low-melting-point salts with a bulky, asymmetric organic cation and a weakly-coordinating anion. The cation is generally a nitrogen-containing ring or quaternary amine with alkyl substituents. Their solvating properties can be tailored to suit any chemical process by varying the structure of the cation substituents. Richardson and Ternes (2011) described them as a ‘contaminant on the horizon’ and ‘currently one of the hottest areas in chemistry’. ILs are not yet widely used in industry, but are a ‘green chemistry’ research area of great interest, being considered alternatives to traditional organic solvents because of their low volatility and flammability. They are being enthusiastically adopted as solvents, stationary phases and other reagents in analytical chemistry (Sun & Armstrong 2010). Pham et al. (2010) reviewed the environmental fate and toxicity of ILs. Those that have been studied are generally toxic, although the toxicity varies with the organism and with chemical structure. Their high chemical and thermal stability means that mostly they are not readily biodegradable, although again this varies with structure. There appears to be scope for tailoring chemical structure to reduce toxicity and improve biodegradability, as well as affecting solvation properties. The solubility of ILs means that if they are adopted by industry, they are likely to end up in environmental waters, although some affinity has been observed for certain types of soils and sediments. Their low volatility means they are not likely to be found in the atmosphere.

2.13.1 Methods and measurement issues

There do not appear to be methods specifically designed for environmental analysis of ionic liquids. Pham et al. (2010) listed commonly used anions as alkyl-substituted imidazolium, pyridinium, pyrrolidinium, morpholinium, piperidinium, quinolinium and quaternary ammonium or phosphonium. Commonly used cations are chloride, bromide, tetrafluoroborate, hexafluorophosphate, bis(trifluoromethylsulfonyl)imide and dicyanamide. Screening methods would have to address the variety of possible structures.

2.13.2 Analytical methodology gaps in Australia

Ionic liquids are still very new and not widely used commercially, and there appears to be very little discussion in the literature of their analysis in the environment. They are unlikely to be an environmental contaminant in Australia, and so are not a high priority at this time.
2.14 Benzidine-based pigments and dyes

Benzidine-based pigments and dyes are members of a very large family of azo compounds used widely as colourants because of their intense absorption of visible wavelengths of light and their high degree of stability against environmental and biological degradation (Øllgaard et al. 1999). The benzidines shown in Table 10 are the basis for many azo pigments and dyes used in the production of textiles, paints, printing inks, paper and pharmaceuticals (US EPA 2010).

Table 10: Benzidines

<table>
<thead>
<tr>
<th>Cas no.</th>
<th>Chemical name</th>
<th>Molecular formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>92-87-5</td>
<td>4,4’-biphenyldiamine (benzidine)</td>
<td>C_{12}H_{12}N_{2}</td>
</tr>
<tr>
<td>91-94-1</td>
<td>3,3’-dichlorobenzidine</td>
<td>C_{12}H_{10}Cl_{2}N_{2}</td>
</tr>
<tr>
<td>119-90-4</td>
<td>3,3’-dimethoxybenzidine</td>
<td>C_{14}H_{16}N_{2}O_{2}</td>
</tr>
<tr>
<td>119-93-7</td>
<td>3,3’-dimethylbenzidine</td>
<td>C_{14}H_{16}N_{2}</td>
</tr>
</tbody>
</table>

None of the above benzidines have been assessed by NICNAS

The IARC has found benzidine and dyes metabolised to benzidine to be carcinogenic to humans (Group 1) (IARC 2012a). The Canadian Technical Background Document on these compounds gives extensive information on their physical and chemical properties (Environment Canada & Health Canada 2010).

Most of the benzidine-based pigments and dyes on the Canadian list are on the AICS, and CI Pigment Yellow 13 (CAS No. 5102-83-0) is on the Australian High-Volume Industrial Chemicals list, so there is potential for these compounds to occur in association with sites of use or disposal in Australia. Most colourants are designed to be resistant to degradation so that they can maintain their colour and these materials may be expected to have a significant degree of environmental persistence in their original form. A distinction needs to be made between dyes and pigments. Benzidine-based pigments such as CI Pigment Yellow 13 have been reported to be particularly insoluble and stable against photolysis, hydrolysis and biological degradation (Øllgaard et al. 1999) and were not considered to represent an exposure concern by the US EPA (2010). However, dyes generally are more soluble and therefore somewhat more bioavailable. The US EPA action plan listed 44 benzidine-based dyes that may be capable of being metabolised to the carcinogenic parent benzidine congener.

The Danish EPA Miljoproject report no. 509 discussed the toxicity and fate of these pigment compounds (Øllgaard et al. 1999). The high stability of the benzidine-based pigments suggests that most will end up in landfill or soil/sediment near sites of use. Their environmental degradation to benzidine congeners will only generally occur under anaerobic conditions and be very slow. Benzidine-based pigments are not recommended for use in applications where they will be heated above 200°C because of potential decomposition at higher temperatures. This suggests that use of high temperatures to treat solids contaminated with these pigments could result in release of toxic degradation products, although no reports of investigation into this were found.

The constantly changing commercial need for colourants results in older compounds falling into disuse and new ones being developed. The composition of some will be confidential. Efficiency for environmental monitoring is therefore more likely to be achieved by use of analytical methodology to focus on the parent benzidines (Table 10), which are the toxic potential environmental degradation products. The International
Program on Chemical Safety (IPCS INCHEM 1998) described 3,3’-dichlorobenzidine as having relatively low volatility and very short residence time in the atmosphere, and binding strongly to soil and aquatic sediment, so it is unlikely to remain in water, reducing the likelihood of leaching from the original site. They found that available data indicated it was likely to have reduced bioavailability and pose negligible risk to aquatic organisms.

### 2.14.1 Regulation of benzidines

Benzidine-based dyes are regulated or under assessment in Europe, the US and Canada. The European REACH regulation EC 1907/2006, Annex XVII, restricts the use of azocolourants and azodyes that may release the aromatic amines listed in Appendix 8 (EC 2006). The US EPA prepared a Benzidine Dyes Action Plan in 2010 to further regulate use of these substances, and a new rule was issued in March 2012 (US EPA 2010). Environment Canada intends to assess around 360 aromatic azo- and benzidine-based substances by 2015 as part of the Canadian Chemical Management Plan, and a Draft Technical Background Document was produced in July 2012 (Environment Canada & Health Canada 2010).

The ANZ guidelines for fresh and marine water quality (ANZECC and ARMCANZ 2000, section 8.3.7), in the absence of sufficient data on benzidine and dichlorobenzidine, suggest Environmental Concern Levels (ECLs) derived from US EPA data for use as indicative working levels. These are 2.5 and 0.5 \( \mu \text{g}/\text{L} \) respectively.

### 2.14.2 Methods and measurement issues

Development of generic methods for the large family of dyes would be difficult. Methods for environmental monitoring are more likely to target the corresponding aromatic amines. Standard methods for benzidines are given in Table 11, and do not appear particularly modern. The Concise International Chemical Assessment Document for 3,3’-dichlorobenzidine reported that analysis of that compound in environmental air or water samples was usually by GC with MS or infrared detection or by HPLC, and that no methods were found for soil or sediments (IPCS INCHEM 1998).

<table>
<thead>
<tr>
<th>Table 11: Methods for unsubstituted benzidines</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Standard Methods for the Examination of Water and Wastewater (APHA, AWWA, WEF):</strong></td>
</tr>
<tr>
<td><strong>Method 6410-B</strong> Extractable Base/Neutrals and Acids by LLE-GC-MS; MDL 16–44 ( \mu \text{g}/\text{L} ) (method notes that it is not the most suitable for benzidine, but does not specify an alternative)</td>
</tr>
<tr>
<td><strong>US EPA 553:</strong> Determination of benzidines and nitrogen-containing pesticides in water by liquid-liquid extraction or liquid-solid extraction and reverse phase high performance liquid chromatography/particle beam/mass spectrometry (1992); MDL 2–8 ( \mu \text{g}/\text{L} ) and</td>
</tr>
<tr>
<td><strong>US EPA 605:</strong> Benzidines; (LLE HPLC ECD) MDL 0.08–0.13 ( \mu \text{g}/\text{L} )</td>
</tr>
<tr>
<td><strong>Matrices:</strong> Benzidines; (LLE HPLC ECD) MDL 0.08–0.13 ( \mu \text{g}/\text{L} )</td>
</tr>
</tbody>
</table>

In the course of this review it was not possible to determine whether all of the relevant dyes are expected to persist in the environment in their substituted forms or to break down quickly to benzidines. If they persist, it may be necessary to include reductive steps in analytical methods, as in the method reported by Ahlstrom et al. (2005) for analysis of banned dyes in leather. This report described the optimisation of European methods required to support the REACH legislation regarding azo dyes. Leather samples were treated with sodium dithionite to reduce the dyes and the aromatic
amines were extracted from the leather by MAE and detected by HPLC with UV
detection.

No laboratory survey respondents indicated that they could analyse for benzidine dyes.
It appears that no laboratories have NATA accredited methods for benzidines or
benzidine derivatives (www.nata.asn.au).

2.14.3 Reference materials and proficiency testing studies

Some analytical standards may be commercially available, however the large number
and changing range of compounds means that there are unlikely to be reference
materials available for many benzidine-based pigments. Analytical standards for the
toxicologically important benzidines in Table 10 are commercially available.

In the USA, the NELAC Institute (www.nelac-insitute.org), an organisation for
accreditation of environmental laboratories, included benzidine and 3,3'-
dichlorobenzidine in its non-potable water fields of proficiency testing until recently but
are considering their deletion due to poor quality results that may stem from the use of
unsuitable methodology by accredited laboratories (GC instead of HPLC). Laboratories
seeking accreditation are required to satisfactorily analyse samples from proficiency
testing providers. Hence PT samples are available in the USA for benzidine and 3,3'-
dichlorobenzidine (eg NSI Solutions).

No matrix reference materials were found in COMAR, for substituted or unsubstituted
benzidines.

2.14.4 Analytical methodology gaps in Australia

There does not appear to be any commercial testing for benzidine-based colourants in
Australia, and methods applicable to the environmental matrices in which they are most
likely to be found are not well established internationally.

‘Azo dyes – benzidines and degradation products’ were nominated as chemicals of
concern by one CRC affiliate with the comments ‘only a few analysed – relatively
unknown as a contaminant – HPLC rarely used as a screening tool’ and ‘activity
causing or impacted – chemicals manufacture’. CI Pigment Yellow 13 is on the
NICNAS High-Volume Industrial Chemicals (2006) list, used in the paper and pulp
industry, however it seems unlikely that there are grounds for a serious environmental
concern related to usage of benzidine dyes in Australia and that the class would be a
significant environmental contaminant. They do not appear to be a high priority for
method development.
2.15 Synthetic musk fragrances

Synthetic musks are widely used as fragrances in personal care products and consumer products such as detergents. The common nitromusks and polycyclic musks, and the terpenoid-like OTNE, are listed in Table 12. Another class of fragrances, macrocyclic musks, are apparently more easily degradable in the environment. In 2009 there had been no reports on the analysis of macrocyclic musks in the environment, and they are not as extensively used as the other classes, presumably because they are more expensive (Bester 2009). They are not discussed further in this review.

Table 12: Synthetic musks

<table>
<thead>
<tr>
<th>CAS no.</th>
<th>Chemical name</th>
<th>Mol. formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>81-15-2</td>
<td>1-t-butyl-3,5-dimethyl-2,4,6-trinitrobenzene (musk xylene, MuX)</td>
<td>C₁₂H₁₅N₃O₆</td>
</tr>
<tr>
<td>81-14-1</td>
<td>4-t-butyl-2,6-dimethyl-3,5-dinitroacetophenone (musk ketone, MuK)</td>
<td>C₁₄H₁₈N₂O₅</td>
</tr>
<tr>
<td>116-66-5</td>
<td>4,6-dinitro-1,1,3,3,5-pentamethyldiane (musk moskene, MuM)</td>
<td>C₁₄H₁₉N₂O₄</td>
</tr>
<tr>
<td>145-39-1</td>
<td>1,2,3-trimethyl-5-t-butyl-4,6-dinitrobenzene (musk tibetine, MuT)</td>
<td>C₁₃H₁₈N₂O₄</td>
</tr>
<tr>
<td>1506-02-1</td>
<td>7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene (AHTN; tonalide)</td>
<td>C₁₈H₂₈O</td>
</tr>
<tr>
<td>1222-05-5</td>
<td>1,3,4,6,7,8-hexahydro-4,6,6,8-hexamethylcyclopenta(g)-2-benzopyran (HHCB; galaxolide)</td>
<td>C₁₈H₂₆O</td>
</tr>
<tr>
<td>13171-00-1</td>
<td>4-acetyl-6-tert-butyl-1,1-dimethyldian (ADBI; celestolide)</td>
<td>C₁₇H₂₄O</td>
</tr>
<tr>
<td>33704-61-9</td>
<td>6,7-dihydro-1,1,2,3,3,3-pentamethyl-4(5H)-indanone (DPMI; cashmeran)</td>
<td>C₁₄H₂₂O</td>
</tr>
<tr>
<td>15323-35-0</td>
<td>5-acetyl-1,1,2,3,3,6-hexamethyldian (AHMI; phantolide)</td>
<td>C₁₇H₂₆O</td>
</tr>
<tr>
<td>68140-48-7</td>
<td>5-acetyl-1,1,2,6-tetramethyl-3-isopropylindene (ATII; traseolide)</td>
<td>C₁₈H₂₆O</td>
</tr>
<tr>
<td>54464-59-4</td>
<td>1,2,3,4,5,6,7,8-octahydro-2,3,8,8-tetramethylnaphthalen-2yl] ethan-1-one (OTNE; Iso-E-super)</td>
<td>C₁₆H₂₄O</td>
</tr>
</tbody>
</table>

All of the above musks are listed on the AICS but none have been assessed by NICNAS.

The musks above are lipophilic and so tend to bioaccumulate in aquatic organisms. Howard and Muir (2010) included all the compounds in Table 12 (except AHTN) in their list of potentially persistent and bioaccumulative chemicals in commerce. In addition to any specific environmental concerns, these compounds are of analytical interest as tracers for treated water because of their reliable occurrence in domestic wastewater.
The nitroaromatic musks were the first to be used commercially in the 1930s but began to be replaced in the 1950s as evidence arose of their toxicity, probably due to their transformation to nitroanilines (Bester 2009; Clarke & Smith 2011). Most of the polycyclic musks are chiral (some even have two chiral centres), with only one enantiomer (or two stereoisomers) having the desired fragrance (Bester 2009; Wong 2006). Syntheses are usually racemic and the different enantiomers may well have different environmental toxicities. Polycyclic musks have been shown to disrupt endocrine functions in aquatic organisms (Schreurs et al. 2004). Bridges (2002) discussed health and environmental concerns arising from the widespread use of fragrances. Difrancesco et al. (2004) showed OTNE to dissipate from soils at a similar relatively slow rate to HHCB and some of the other musks. OTNE has a different type of scent to the nitro and polycyclic musks, and so its popularity is probably due more to changing fashions in fragrance than environmental concerns (Bester 2009).

### 2.15.1 Occurrence of synthetic musks in the environment

In 1998, OTNE was the most commonly used fragrance in Europe, followed by HHCB, AHTN, MuX then MuK (Bester 2009), however usage patterns may be different in other parts of the world, and may have changed in the past decade. Lapworth et al. (2012) found galaxolide (HHCB) to be among the most frequently reported contaminants in groundwater in studies from Europe, the Middle East, North America and Asia. Tonalide (AHTN) was also mentioned as a frequent contaminant. Tanabe and Ramu (2012) reported the distribution of HHCB in the Asia-Pacific marine environment to have significantly increased since the 1990s. Clarke and Smith (2011) found high levels of polycyclic musks reported in their review of biosolids studies, but this was not of great concern for sludge reuse in agriculture as significantly higher exposure occurs from household use.

### 2.15.2 Regulation of synthetic musks

Australian water recycling guidelines for augmenting drinking water supplies include guideline values derived from reported No Observed Effect Levels (NOELs) for musk ketone and musk xylene of 350 μg/L and galaxolide of 1750 μg/L. Values for musk tibetine and musk moskene of 0.35 μg/L were derived by extrapolation from values for other compounds.

MuX is on the OSPAR list of Chemicals for Priority Action (OSPAR 2002). The EU has identified it as a Substance of Very High Concern (ECHA 2012) and have prohibited the use of nitromusks in cosmetics (Richardson & Ternes 2011).

There are German proposals to set biosolids limits for HHCB and AHTN of 10 and 15 mg/kg respectively (Clarke & Smith 2011).

### 2.15.3 Methods and measurement issues

There do not appear to be US EPA, ISO or ASTM standard methods for these compounds.

Richardson has been reviewing synthetic musks as emerging contaminants since 2010, and references a few new methods each year (Richardson 2010; Richardson 2012; Richardson & Ternes 2011). Bester (2009) reviewed the analysis of musks in environmental samples and reported that nitromusks can be analysed by alkali-FID or ECD, but the other musks require MS detection. GC is a suitable chromatographic technique as the fragrances are naturally volatile, and not thermo-labile. A range of
methods were referenced for waters, sludges, sediments, biota, air and commodities. Zuloaga et al. (2012) also included more than 10 references to methods for sewage sludge. Garcia Jares et al. (2009) reviewed analysis of various pollutants in indoor air, and referenced five methods for nitroaromatic and polycyclic musks. As the musks are often in air fresheners, very high levels can be found in indoor environments.

OTNE is not mentioned frequently in the literature, however it appears it can be detected using methods for the polycyclic musks, as Difrancesco et al. (2004) and Simonich et al. (2000) reported related methods for most of the musks tabulated above, including OTNE, in aqueous and solid matrices. Kubwabo et al. (2012) reported a method for all the musks above (except MuT) in house dust.

There are well established methods for analysis of musks, the main challenges lie in avoiding sampling and laboratory contamination, due to their prevalence in PCPs and indoor environments. There is also the issue of chiral analysis of the polycyclic musks. Bester (2009) commented that better availability of library spectra would facilitate detection of the musks as non-targeted contaminants.

None of the respondents to the survey of Australian laboratories claimed analytical capabilities for musks, and no mention of these analytes was found in the ‘Test Type Search’ of NATA accredited laboratories on the NATA website (www.nata.asn.au).

2.15.4 Reference materials and proficiency testing studies

Bester (2009) reported that all of the tabulated musks were available as commercial standards except HHCB (50%, mixed with phthalate). Kubwabo et al. (2012) reported obtaining all the compounds above commercially, and did not comment on the purity of the HHCB. Both used commercially available deuterated MuX as an internal standard. Apparently deuterated AHTN is available but is known to suffer problems with deuterium exchange. Simonich et al. (2000) used a number of deuterated musks synthesised in-house.

In 2007, NIST reported analysis of six NIST SRMs (marine biota, domestic sludge and house dust) for ADBI, AHMI, HHCB, ATII, AHTN, MuX and MuK (Peck et al. 2007). All the polycyclic musks were found in the sludge, and all seven musks in the house dust. Only HHCB and AHTN were found in two of the four biota SRMs. The concentrations reported are described in the conclusion as reference values.

No CRMs were found in the COMAR database for the CAS numbers tabulated.

2.15.5 Analytical methodology gaps in Australia

There appear to be suitable methods in the literature for these analytes, however the methodology does not appear to be available commercially in Australia. The compounds are almost certainly present in the environment due to their use in PCPs, so method development is warranted. There also appears to be a need for additional matrix reference materials.
2.16 Microbicides

Table 13: Microbicides

<table>
<thead>
<tr>
<th>Cas no.</th>
<th>Chemical name</th>
<th>Mol. formula</th>
<th>Assessed by</th>
</tr>
</thead>
<tbody>
<tr>
<td>3380-34-5</td>
<td>2',4,4'-trichloro-2-hydroxydiphenyl ether (TCS)</td>
<td>C₁₂H₇Cl₃O₂</td>
<td>yes</td>
</tr>
<tr>
<td>101-20-2</td>
<td>3,4,4'-trichlorocarbanilide (TCC)</td>
<td>C₁₃H₉Cl₃N₂O</td>
<td>no</td>
</tr>
<tr>
<td>87-10-5</td>
<td>3,4',5-tribromosalicylanilide (TBS)</td>
<td>C₁₃H₈Br₃NO₂</td>
<td>no</td>
</tr>
<tr>
<td>1154-59-2</td>
<td>3,3',4',5-tetrachlorosalicylanilide</td>
<td>C₁₃H₇Cl₄NO₂</td>
<td>not on AICS</td>
</tr>
</tbody>
</table>

Howard and Muir (2010) described the microbicides in Table 13 as potentially persistent and bioaccumulative. Triclosan (TCS) and triclocarban (TCC) are frequently used in soaps, toothpastes and other personal care products. Tribromosalan (TBS) can be used as an antiparasitic for cattle so methods exist for its determination in matrices such as milk (Sakamoto et al. 2010). There do not appear to be any products containing tribromosalan registered by the Australian Pesticides and Veterinary Medicines Authority (APVMA) however, so presumably it is not used in veterinary medicine in Australia. Tetrachlorosalicylanilide is not on the AICS, and in fact is on a Therapeutic Goods Administration (TGA) list of substances subject to import controls (http://www.tga.gov.au/consumers/import-controlled-substances.htm). A Web of Science (Thomson Reuters 2013) search did not find analytical methods, but did find many references to its use as an ‘uncoupler’, particularly in the reduction of sewage sludge volume in WWTPs (Chen et al. 2000). Presumably it is not used for this application in Australia.

NICNAS completed a PEC report on triclosan in 2009, including the following information (NICNAS 2009c): the first US patent for triclosan was issued in 1964 and it has been marketed for over 30 years. It is not manufactured in Australia. In 2001–2005, 20–30 tonnes per year were imported, mostly as raw material but some in products. About half of this was formulated into cosmetics and PCPs. Most of the remainder was used in therapeutic goods, either as the active ingredient or as a preservative. Triclosan is not toxic to mammals, but is very toxic to some aquatic organisms. Its rate of removal by WWTPs depends on the processes used and the prevailing conditions. Triclosan adsorbs to sediment, and as it can be toxic to some plants and soil-dwelling organisms this may affect agricultural reuse of sludge.

2.16.1 Occurrence of microbicides in the environment

Ying and Kookana (2007) reported a study on the occurrence of triclosan associated with WWTPs in Australia. Triclosan was found in all samples.
Clarke and Smith (2011) reported that triclosan and triclocarban are incompletely removed by WWTPs, and have been found upstream of discharges indicating persistence in the environment. They tend to partition into sludge, and have been reported in biosolids in studies from many countries.

2.16.2 Regulation of microbicides

The EU has set a maximum content of 0.3% for triclosan as a preservative in cosmetics and PCPs (Cosmetics Directive 76/768/EEC, 1999). Canada has a similar regulation and Japan has also set limits for use in cosmetics (NICNAS 2009c).

2.16.3 Methods and measurement issues

Although there do not appear to be US EPA, ISO or ASTM standard methods for triclosan and triclocarban, they have been frequently analysed. Peck (2006) tabulates around 40 methods for triclosan and/or triclocarban in aqueous and solid matrices, mostly published between 2002 and 2005, in his review of methods for PCP ingredients in environmental matrices. These include LLE or SPE extraction of waters; LLE, Soxhlet, PLE or MAE extraction of solids; and analysis by GC- or LC-MS. Chen et al. (2012) recently reported a multiresidue LC-MS method for 19 biocides in aqueous and solid matrices, demonstrating that triclosan and triclocarban can be analysed with azole fungicides, insect repellents, isothiazolinone anti-fouling agents and parabens. The NICNAS PEC reviews methods of analysis (NICNAS 2009c). Ying and Kookana (2007) used SPE (following LLE for biosolids), trimethylsilyl derivatisation and GC-MS for their WWTPs study.

No laboratory survey respondents indicated that they could analyse for these microbicides. One Australian laboratory has NATA accredited methods for PPCPs including triclosan, and another for PPCPs without specifying which compounds (www.nata.asn.au).

2.16.4 Reference materials and proficiency testing studies

Triclosan, triclocarban and \textsuperscript{13}C labelled analogues are commercially available. No CRMs were found in the COMAR database when searching by CAS number.

2.16.5 Analytical methodology gaps in Australia

Triclosan and triclocarban are well studied, and although there appears to be very limited commercial capability in Australia, presumably methodology could easily be implemented if there were commercial demand. As with other constituents of PCPs, such as musks and siloxanes, the lack of interest in environmental analysis is probably due to the low human toxicity and the familiarity of widespread use.
2.17 Organoboron

Organoboron was included as Priority 3 in the pre-selection of contaminants, with further investigation required into relevance in Australia. Triphenylborane pyridine (TPBP, CAS 971-66-4) is a novel marine anti-fouling biocide used mainly in Japan, and very little is known about its fate and effects in the environment (Thomas & Brooks 2010). It was included because it was noted in a review by Jones-Lepp and Momplaisir (2005) of the US EPA that triphenylboranes were being used as substitutes for organotin in antifouling paints, but they found only one LC-MS method for triphenylborons in environmental waters (Hanada et al. 2002). Searching the Web of Science (Thomson Reuters 2013) found only one additional analytical method applicable to environmental samples, which referred to another published SPE procedure that could be used for extraction from seawater (Fukushi et al. 2010). However, the use of anti-fouling biocides in Australia is regulated by the APVMA and no products containing TPBP are registered with that agency. Thomas and Brooks (2010) mentioned other novel antifouling biocides (not organoboron compounds) but products containing these are not registered with the APVMA either, and so this is an area where Australian analytical capabilities are not currently required.
2.18 Organoplatinum

Organoplatinum compounds have been used in chemotherapy since the 1970s. Cisplatin was the first compound discovered, followed by carboplatin, then others including iproplatin and satraplatin (Meermann & Sperling 2012). Upon treatment, significant amounts of these drugs are excreted in the patient’s urine and so the platinum compounds end up in the wastewater stream. Chemotherapy may be administered as an inpatient or an outpatient treatment, so the drugs are not limited to hospital wastewater. These drugs are extremely toxic, and in fact it appears they may be human carcinogens. Hann et al. (2005) noted that some of the drugs (cisplatin in particular) are largely excreted intact, but for others (such as oxaliplatin, around one third excreted intact), there may be significant formation of organoplatinum metabolites. The same group studied the fate of organoplatinum compounds in a model wastewater treatment system and found that significant amounts remained intact in the treated effluent (Lenz et al. 2007).

2.18.1 Methods and measurement issues

Standard methods are not available for these compounds in environmental matrices. Hann et al. (2005) reported an HPLC-ICP-MS method for organoplatinum speciation, and in their paper they noted that methods for analysis of these compounds are usually developed for pharmacological or toxicological studies, where only a single drug is administered. Some of the organoplatinum drugs and metabolites are positively charged and others are neutral, so multiresidue LC separation is challenging and Hann et al. (2005) used an LC stationary phase that provided both reversed-phase and ion-exchange based retention. Meermann and Sperling (2012) reviewed metal-based pharmaceutical speciation and referred to several methods for platinum speciation in plasma and urine (some by the group of Hann et al.) by LC-ICP-MS. They noted that ICP-MS is a sensitive and selective detector for these compounds, and its species-independent sensitivity means that species-specific standards are not required.

Nussbaumer et al. (2011) reviewed the analysis of anticancer drugs, and Popp et al. (2010) reviewed speciation in environmental samples by ICP-MS. The only methods for environmental matrices either group reported are those from Hann et al. for wastewater (Hann et al. 2005; Lenz et al. 2007). Nussbaumer et al. mentioned that capillary electrophoresis (CE) is a useful separation technique for intact platinum metal complexes, having been applied to biological samples. Popp et al. referred to hydrophilic interaction LC (HILIC) as an ‘analytical novelty’ for platinum speciation, including a method for plasma from their group.

No laboratories responding to the survey claimed capabilities for organoplatinum.

2.18.2 Reference materials and proficiency testing studies

Analytical standards are commercially available (e.g. Sigma-Aldrich). There are US Pharmacopeial Convention USP reference standards (http://www.usp.org/reference-standards) available for several organoplatinum drugs.

There are no matrix reference materials for these compounds.
2.18.3 Analytical methodology gaps in Australia

If these compounds were considered an environmental contaminant of concern in Australia, then there would be need for development of methods, production of reference materials and organisation of proficiency testing. Organoplatinum compounds are used to treat cancer in Australia in much the same way as in other developed countries, but it is unclear how much of a problem excreted drugs are in waste water. Any problem is likely to be confined to highly urbanised areas.
2.19 Arsenic speciation

Arsenic speciation was considered because CRC members surveyed prior to commencement of this review had conflicting opinions on the need for better methods. Research publications in this field are copious and it is the subject of numerous reviews. The International Programme on Chemical Safety Environmental Health Criteria document on arsenic gives an overview of sources, occurrence, analytical procedures and effects on human health and the environment (IPCS INCHEM 2001b).

Many arsenic compounds are naturally present in the environment with a broad range of toxicity. The inorganic species of arsenic (As\text{III} and As\text{V}) are much more toxic than the organoarsenic forms, and As\text{III} is 60 times more toxic than As\text{V} (Ratnaike 2006, p. 300). Evaluating environmental contamination and risk to ecosystems or humans must take into account the chemical form (species) of arsenic present. Quantification of total arsenic by aggressive sample decomposition (measurement of ‘total arsenic’) in many cases will overestimate the risk of arsenic toxicity. Consequently, it is necessary to use species-specific analysis rather than measuring total arsenic content. A frequently cited example is seafood. Arsenic is commonly metabolised in fish to arsenobetaine, the arsenic analogue of trimethylglycine. Unlike the inorganic forms of arsenic (As\text{III} and As\text{V}), arsenobetaine is non-toxic and therefore presents no risk for human consumption. This illustrates the requirement of distinguishing between different species of arsenic, a requirement that increases the analytical level of difficulty considerably.

Arsenic contamination in the environment can occur from natural and anthropogenic causes. Arsenic is a moderately abundant element in the earth’s crust which has led to numerous instances of arsenic in groundwater above safe levels for human consumption. Bangladesh is a prominent example where over 85% of the population is at risk of arsenic toxicity from contaminated groundwater (Naidu et al. 2006, p. 5). Industrial sources of environmental arsenic contamination include smelting, mining, banned pesticides, and by-products of chemical manufacture. The main source of human exposure to arsenic is the diet (Ratnaike 2006, p. 299). Drinking water, seafood, rice and seaweed are some of the major contributors to dietary arsenic.

Inorganic arsenic is metabolised by humans to organoarsenic metabolites. As\text{V} is first converted to the more toxic As\text{III}. Then the majority of As\text{III} is methylated producing monomethylarsonic acid (MMA) and dimethylarsonic acid (DMA). Methylation is to some extent a detoxification process however both methylated forms still have toxic effects (Ratnaike 2006, p. 301). Chronic arsenic poisoning causes numerous dermatological symptoms, gastric disruption and increased risk of cardiovascular disease, neurological disorders and cancer.

2.19.1 Regulation of arsenic

Many environmental guideline documents only list investigation levels for total arsenic. In soil these are in the order of 100–500 mg/kg (EPHC 1999; NSW OEH 2012). The Australian Drinking Water Guidelines (NHMRC & NRMMC 2011) and World Health Organisation Drinking Water Guidelines (WHO 2006) list a guideline value of 10 μg/L total arsenic. The NWQMS guidelines for fresh and marine water quality (ANZECC & ARMCANZ 2000) trigger values for 99% level of protection in freshwater ecosystems are 1 μg/L for As\text{III} and 0.8 μg/L for As\text{V}. 
2.19.2 Methods and measurement issues

Species selective quantification is the major measurement issue for arsenic.

Several published standard methods for inorganic arsenic, mostly in foodstuffs, are shown in Table 14.

Table 14: Standard methods for inorganic arsenic

<table>
<thead>
<tr>
<th>Method</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BS EN 15517:2008</td>
<td>Foodstuffs. Determination of trace elements. Determination of inorganic arsenic in seaweed by hydride generation atomic absorption spectrometry (HGAAS) after acid extraction</td>
</tr>
<tr>
<td>BS EN 16278:2012</td>
<td>Animal feeding stuffs. Determination of inorganic arsenic by hydride generation atomic absorption spectrometry (HG-AAS) after microwave extraction and separation by solid phase extraction (SPE)</td>
</tr>
<tr>
<td>GB/T 5009.11-2003</td>
<td>Determination of total arsenic and abio-arsenic in food (HG-AFS)</td>
</tr>
<tr>
<td>GB/T 23372-2009</td>
<td>Determination of inorganic arsenic in food by LC-ICP-MS</td>
</tr>
<tr>
<td>GB 17055-1997</td>
<td>Determination of total arsenic and abio-arsenic in food (HG-AFS)</td>
</tr>
<tr>
<td>PN 92/Z-04011.06:1992</td>
<td>Airborne particulates, HGAAS, (Poland)</td>
</tr>
<tr>
<td>US EPA 1632</td>
<td>Chemical Speciation of Arsenic in Water and Tissue by Hydride Generation Quartz Furnace Atomic Absorption Spectrometry</td>
</tr>
<tr>
<td></td>
<td>range: 0.01–50 µg/L for inorganic As and As species in water</td>
</tr>
<tr>
<td></td>
<td>0.01–500 µg/g dry weight for inorganic As and As species in tissue</td>
</tr>
</tbody>
</table>

A method widely used in the 1970s, particularly for seafood analysis, for determination of inorganic arsenic involves conversion of the inorganic arsenic species to arsenic trichloride (AsCl₃) and separation from organoarsenic species by distillation or solvent extraction. The extract is then subjected to total arsenic quantification (e.g. HGAAS, ICPMS, etc) to quantify the inorganic arsenic content of the original sample. Some more recent developments of the extraction-based approach have been published (Almela et al. 2002; Muñoz et al. 1999). Concerns have been raised about selectivity of the method and applicability for various sample types (EFSA 2009). In general, arsenic speciation analysis has moved to LC techniques. The majority of ‘expert laboratories’ participating in the 12th proficiency test focussing on total and inorganic arsenic in plant materials organised by the European Union Reference Laboratory for Heavy Metals in Feed and Food used HPLC-ICPMS (de la Calle et al. 2011).

Akter and Naidu (2006) provided an overview of analytical techniques used for arsenic speciation and tabulated data from 50 references that summarised the method limitations and detection limits for determination of AsIII and AsV in environmental and biological samples using a large range of hyphenated techniques. They concluded that the technique selected will be dependent on the required sensitivity and availability of instrumentation and that careful control of sample preparation and preservation is essential for true speciation.

Popp et al. (2010) reviewed LC-ICP-MS analysis of environmental samples for elemental speciation and referred to nine methods for arsenic species. They described arsenic in speciation analysis as ‘probably one of the most intensely studied elements.’ They did highlight problems with some methods including matrix-dependent As recoveries from leachates and large non-extractable As fractions from biological
samples, demonstrating the difficulties of extracting arsenic species intact. They also noted that polyatomic interferences in ICP-MS analysis can arise from chloride, so special care needs to be taken with chloride rich samples and sample preparation involving hydrochloric acid.

Zwiener and Frimmel (2004) reviewed LC-MS for emerging contaminants in aqueous matrices and included a section on arsenic speciation, referencing 12 methods published 1999–2002. They also referred to the review of arsenic speciation by Gong et al. (2002), considering environmental as well as biological matrices. Gong et al. described methods with separation by ion-pairing-, ion-exchange-, ion- and size-exclusion- and multidimensional-LC, capillary electrophoresis and even GC separation; and detection by ICP-atomic emission spectrometry (AES), ICP-MS, electrospray-MS and other techniques. They included a section on sample handling emphasising the techniques for preserving the arsenic species profile throughout storage and analysis.

Francesconi and Kuehnelt (2004) in their review of analytical methods for arsenic speciation tabulated over 400 papers published from 2000–2003 and classified them according to instrumentation/technique and sample type. The review included discussion of sample extraction, extraction solvents and stability of arsenic species during collection, extraction and analysis.

Ten Australian laboratories specified in their response to the survey that they could measure arsenic species, with five having NATA accreditation. Many of these clarified their response, listing the particular species, and these are included in Appendix A as footnotes to the Table summarising the responses to the first survey question. A Test Type Search’ of NATA accredited laboratories (www.nata.asn.au) for ‘arsenic species’ and the individual arsenic species identified two laboratories with accreditation in one or more matrices for determination of As\textsuperscript{III}, As\textsuperscript{V}, MMA, DMA and arsenobetaine. This discrepancy in number of accredited labs appears to result from insufficient detail in the laboratory’s scope to allow searching.

2.19.3 Reference materials and proficiency testing studies

There are currently no certified reference materials available for quantification of inorganic arsenic in environmental samples apart from marine biota. National Measurement Institute, Japan (NMIJ) have certified a white rice flour CRM (#7503-a) for DMA, As\textsuperscript{V}, As\textsuperscript{III} and total arsenic. NMIJ Seaweed CRM (#7405-a) is certified for total arsenic and As\textsuperscript{V}.

NIST SRM 1568a (rice flour) has a certified value for total arsenic and has been the subject of several research efforts quantifying inorganic arsenic (Tyson). Literature values for inorganic arsenic in NIST SRM 1568a range from 80–110 μg/kg. Variation is likely to be caused by extraction efficiencies and inter-conversion of arsenic species in the different methods that have been used.

There are several reference materials with certified values for particular organoarsenic compounds, including arsenobetaine, dimethylarsinic acid and tetramethylarsionium (BCR 627 and BCR 710 from the Community Bureau of Reference, Belgium; DORM-2 from the Canadian Institute for National Measurement Standards). Wahlen et al. (2004), from the Canadian Institute for National Measurement Standards, published the results of a study on arsenic speciation in three marine biota CRMs (DORM-2, DOLT-2 and TORT-2). They had trouble getting consistent results for some species, which demonstrates measurement difficulties. Two CRMs are available relevant to biological
monitoring of arsenic exposure in human urine (NIES CRM No.18 from the National Institute for Environmental Studies, Japan; NIST SRM 2669).

The International Measurement Evaluation Program (IMEP) has run several proficiency testing schemes for inorganic arsenic measurement (IMEP-30, 107, 109 and 112) in seafood, rice, wheat, vegetable food and algae. FAPAS (UK) run PT schemes for inorganic arsenic in crab meat and powdered rice however frequently results are too few and varied to assign an accurate reference value.

2.19.4 Analytical methodology gaps in Australia

There are numerous methods for extraction and quantification of arsenic species in environmental samples in the literature, however official standard methods have not been established. Certified reference materials for method development and quality control are unavailable for environmental matrices. Ten Australian laboratories provide commercial testing services for As\textsubscript{III} and As\textsubscript{V} and organoarsenic species as identified via the survey and further capability is evidenced by publications in scientific literature. Tools to assess laboratory performance such as easily accessible PT studies are lacking.
2.20 Nanomaterials

Nanomaterials are generally described as materials with at least one dimension less than 100 nm, although there are numerous definitions, and the value of 100 nm does not have a basis in any particular physical property or effect (SCENHIR 2010). NICNAS are using the following working definition: ‘Industrial materials intentionally produced, manufactured or engineered to have specific properties or specific composition, and one or more dimensions typically between 1 and 100 nanometers’ (NICNAS 2009b). There is currently a great deal of research in the field. Richardson has included nanomaterials in her reviews of drinking water analysis and environmental mass spectrometry since 2008 (Richardson 2008; Richardson 2009; Richardson 2010; Richardson 2012; Richardson & Ternes 2011) and in 2012 she reported that she found nearly 5000 citations on the Web of Science (Thomson Reuters 2013) from the previous two years, including over 500 review articles. There is such a variety of nanomaterials, and so much research reported, that anything more than a brief overview is beyond the resources and the scope of this review.

Nanomaterials can be natural or engineered. Farre et al. (2011) classified engineered nanomaterials into five groups: carbon (including fullerenes and nanotubes), metal oxide nanoparticles, zero-valence metal nanoparticles, quantum dots (reactive semiconductor cores contained in an inert shell such as silica) and dendrimers (single molecules with a branching, layered structure). Uses listed by Richardson (2008) are in products including cosmetics, sunscreens, clothing, paints, automobile tyres, tennis rackets, lubricants, electronics, soaps, shampoos, and detergents and in environmental remediation (zero-valent iron). Farre et al. (2011) mentioned catalysis, water purification, plastics, orthopaedic implants, adhesives and sensors for carbon nanomaterials; mortar, metallurgical, glass and ceramics for metal oxides; the antibacterial properties of zero-valent silver; quantum dots in medical imaging, solar cells and security inks; and dendrimers in drug delivery, polymers and sensors. Tiede et al. (2008) discussed nanomaterials as food ingredients, additives, supplements and contact materials.

Nanoformulations of pesticides include emulsions, spheres and capsules formed with polymers and porous hollow silica nanoparticles (Kah et al. 2012). Many of these techniques are currently used for microformulations. They are designed to improve solubility, slow or target release or protect against premature degradation of the pesticide. In many cases, the nanoformulation is designed to allow the use of less active ingredient, which should be beneficial to the environment; however the effects on the environmental fate of differing solubility, degradation or transport will need to be considered.

NICNAS put out voluntary calls for information to industry in 2006 and 2008 on the usage of nanomaterials in Australia, but received limited response. Materials reported were acrylic latex for surface coatings in volumes of thousands of tonnes per year, zinc oxide for cosmetics, catalysts and coatings at a few tonnes per year, and a few other metal oxides in small amounts (NICNAS 2012a).

2.20.1 Toxicity and occurrence of nanomaterials in the environment

Information on toxicity – human and particularly environmental – and environmental fate is scarce for most nanomaterials (Farre et al. 2011; Gottschalk et al. 2009; Perez et al. 2009; Tiede et al. 2008). Farre et al. (2011) concluded that much work needs to
be done on environmental fate, which is hampered by the lack of analytical methods. Environmental concentrations are sometimes modelled due to the dearth of information about actual concentrations (Gottschalk et al. 2009). Priestly (2009) was commissioned by NICNAS to review the literature available on toxicity of fullerenes, carbon nanotubes, and nanoforms of zinc oxide, titanium oxide, cerium oxide and silver.

Nanomaterials found in PCPs are likely to enter the environment through the wastewater system. Other nanomaterials, such as carbon nanomaterials in electronic components, are more likely to go to landfill. Materials finding their way into waters and WWTPs are expected to end up in sludge and sediment because of their tendency to aggregate and adsorb and interact with natural organic material (Gottschalk et al. 2009; Klaine et al. 2008).

Batley and McLaughlin (2010) reported on the fate of manufactured nanomaterials in the Australian environment. They considered seven classes of nanomaterials – carbon, metal oxide nanoparticles, zero-valence metal nanoparticles, quantum dots, dendrimers, nanoclays and nanoemulsions. Their recommendations include the development of measurement techniques to perform environmental measurements. The National Measurement Institute (NMI) and Entox (the National Research Centre Environmental Toxicology at UQ) completed a review of the fate of engineered nanoparticles in wastewater in October 2012 as a Water Quality Research Australia (WQRA) funded project and a summary is available at http://www.wqra.com.au/project-details/135.

2.20.2 Regulatory activity regarding nanomaterials

The NICNAS regulatory framework is currently being reviewed to address nanomaterials. The process is summarised on their website (NICNAS 2012a). If a chemical is already listed on the AICS, i.e. it is an ‘existing’ chemical, there is currently no regulatory framework to distinguish between conventional and nanoscale forms. In January 2011, the administrative arrangements for the regulation of ‘new’ chemicals were changed to provide that nanoforms must be notified and assessed before they can be marketed. The 2009 Discussion Paper for reform found on the website describes the regulatory framework being proposed for ‘existing’ chemicals: having voluntary, then mandatory (when legislation can be enacted) pre-introduction notification requirements, meanwhile working on a regulatory framework for assessment of all nanoforms, possibly where each user will have to apply, rather than the nanoform being entered on the register (NICNAS 2009b).

The US EPA (http://epa.gov/oppt/nano/) completed a Nanoscale Materials Stewardship Program where they requested (and received) data from industry. They have also come to the conclusion that currently use of the nanoforms of ‘existing’ chemicals is permitted because they are not considered to be different chemicals.

The OECD Working Party on Manufactured Nanomaterials (www.oecd.org/env/nanosafety) is coordinating an international sponsorship program to test the safety of 13 different types of manufactured nanomaterials. Australia is co-sponsoring the testing of cerium oxide, zinc oxide and silver for physical chemical properties, environmental fate and behaviour, ecotoxicity and mammalian toxicity. At present, the data are being analysed to assess if test protocols developed for chemicals are suitable for nanomaterials or whether there is a need for them to be adapted or if new test methods are required for nanomaterials.
2.20.3 Methods and measurement issues

Tiede et al. (2008) reviewed analysis of engineered nanoparticles in food and the environment. They discussed methods for the detection and characterisation of nanomaterials, categorised as microscopy and related techniques; chromatography and related techniques (including field-flow fractionation); centrifugation and filtration; spectroscopic; mass spectrometric and ‘other’. In sample preparation they highlighted the importance of minimising any effect on nanoparticle structure and composition e.g. aggregation state.

The category of carbon nanomaterials probably has the best developed analytical methodology for complex samples (Farre et al. 2011). Perez et al. (2009) reviewed the analysis, behaviour and ecotoxicity of carbon-based nanomaterials in the aquatic environment. They also mentioned ‘the analytical artefacts caused by sample preparation’ as well as difficulties due to the lack of reference materials and the matrix of the sample. Nanomaterials in general and fullerenes in particular, are likely to be very sensitive to the effects of parameters such as pH and organic content on their state and partitioning. Isaacson et al. (2009) also concentrated on carbon nanomaterials, specifically fullerenes, and reviewed their quantitative analysis in environmental samples. Fullerenes can be naturally occurring or man-made, but increasingly the synthetic ones are being surface-modified. An example given by Isaacson et al. of a problem of material state is the conversion between hydrophobic and water-soluble forms of the same fullerene.

Farre et al. (2011) reviewed analysis of nanomaterials in the environment. Their overview of analytical techniques is divided into qualitative and quantitative analysis. For qualitative analysis they listed microscopic analysis, separation methods, light-scattering techniques and spectroscopic methods. Under quantitative analysis, their first point was the importance of the effect of sample preparation on the state of the nanomaterials. Other problems include complications from the naturally occurring nanoparticles and organic matter in environmental samples, and instrumental limits of detection that are not appropriate for environmental levels.

Ferreira da Silva et al. (2011) reviewed analysis of metallic nanoparticles in natural environments. Filtration, centrifugation or size-exclusion methods are usually used to extract the nanoparticles, and ICP-MS or ICP-optical emission spectroscopy (OES) for detection. However, these methods do not give full information about the state of the nanoparticles, for which microscopy-based or X-ray spectroscopy techniques are useful.

Field-flow fractionation (FFF) is an analytical separation technique suited to the analysis of nanomaterials, and in conjunction with UV or fluorescence spectroscopy and ICP-MS detection, it can be very useful, having the potential to determine the chemical composition of the particles. Von der Kammer et al. (2011) reviewed FFF applied to environmental and food samples. They suggest that if FFF is to become a routine methodology, analytical standards, quality control measures and interlaboratory comparisons are required.

A review of methods for monitoring airborne nanoparticles was published by Morawska et al. (2009), a group based in Queensland.

No laboratory survey respondents claimed to have analytical capabilities for chemical characteristics of nanoparticles. The survey did not seek to determine the extent of
analytical capabilities for physical characteristics of nanoparticles as this is beyond the scope of this review; however the NMI Physical Metrology’s nanoparticle characterisation laboratory in Lindfield will be offering accredited measurement services in the future.

2.20.4 Reference materials and proficiency testing studies

A list of nanoscale reference materials is maintained by the German Federal Institute for Materials Research and Testing in collaboration with ISO Technical Committee TC229 (http://www.nano-refmat.bam.de/en/). Most of the materials provide reference values for mean particle diameter, not particle number or mass concentration. There are no matrix reference materials.

2.20.5 Analytical methodology gaps in Australia (chemical aspects only)

There are very few analytical methods for nanomaterials in environmental samples. For many materials satisfactory analytical techniques are not established. There is no listing of laboratories providing commercial services for measurement of nanomaterials in environmental samples on the NATA website.
3. Non-target analysis – contaminants yet to emerge

Contaminants of emerging concern may, by definition, not yet be properly recognised as environmental contaminants. Non-target analytical methods allow detection and identification of previously unmonitored compounds. These methods would employ sample preparation procedures to extract the broadest range of possible contaminants, and detection techniques (e.g., TOF-MS) that allow the observation of unexpected analytes, or the possibility of re-interrogating the data in the future when new analytes have been discovered.

3.1 Extraction techniques for non-target analysis

Farre et al. (2012) in their review of CEC analysis in the environment by MS and bioanalytical techniques gave an overview of new analytical trends in sample preparation, LC separation and multidimensional GC separation, and discussed detection by MS and biosensors. Zuloaga et al. (2012) also reviewed extraction, clean-up and detection techniques for a wide range of CECs in sewage sludge. They divided extraction procedures into classical and novel techniques.

Soderstrom et al. (2009) discussed the use of passive water sampling devices for monitoring polar CECs.

Sanchez-Prado et al. (2010) described MAE as a rapid, effective, environmentally friendly technique which has been successfully applied to many pollutants in a wide range of samples, and reviewed its application to CECs in solid samples.

Mahugo-Santana et al. (2011) reviewed liquid-phase microextraction (LPME) for the determination of emerging pollutants. They reported LPME techniques to be fast, easy and low-cost compared to traditional extraction methods, applicable to practically all classes of analytes, with low solvent consumption and compatibility with analytical techniques. Yao et al. (2011) described their studies of ionic liquids as novel extraction solvents for dispersive liquid-liquid microextraction.

3.2 Separation and detection techniques

Supercritical fluid chromatography is not a new separation technique, but recent advances in instrumentation have reintroduced it as a convenient alternative to LC, which may have a wider range of applicability (Vollmer and Becker 2011; Waters).

Hernandez et al. (2012) reviewed HRMS in environmental analysis, concluding that combining GC- and LC-HRMS is currently the most efficient strategy for screening for organic pollutants in the environment. The same group described the retrospective detection of pharmaceutical metabolites in wastewater samples previously analysed by LC-quadrupole (Q)TOF (Hernandez et al. 2011).

Holcapek et al. (2012) in their review of recent developments in LC-MS gave examples of combined ion-sources for atmospheric pressure ionisation, which would broaden the range of analytes that could be detected in one chromatographic run.
3.3 Reports of non-target analysis

Eggen et al. (2010) described a non-target screening analysis of landfill leachates by SPE-GC-MS. They used low resolution MS in full-scan mode and classified unknown compounds into classes rather than identifying each one.

A good example of an area where the identity of contaminants is not well-known is the monitoring of transformation products. Del Mar Gomez-Ramos et al. (2011) reported a method using an accurate-mass database of TOF-MSMS fragments of 147 pharmaceuticals, drugs of abuse and pesticides for identifying transformation products in wastewater.

Nurmi and Pellinen (2011) described a multiresidue method for 84 pesticides and pharmaceuticals in water by SPE and ultra-performance LC-TOF-MS. They further described the assessment of this method for post-target and non-target analysis (Nurmi et al. 2012). Post-target analysis was performed by extracting chromatograms for a narrow window (20–50 mDa) around the known mass for a contaminant of interest from the mass spectrometric data set. Tentative identification was achieved for many of the analytes in the spiked test sample, although the authors emphasised that analytical standards will always be required for final identification. For non-target screening, deconvolution software detected ions arising from the same component and attempted to deduce a molecular formula from the exact masses of any ions found. As LC-MS does not usually produce many ions, and matrix interferences are often significant, this was found to be impractical with the software available.

Mueller et al. (2011) described a method for non-target screening in water analysis where samples were analysed by SPE-HPLC-QTOF-MS. Features of each data set were extracted and compared between samples such as water before and after treatment. They gave an example of a groundwater system potentially affected by landfill leachate, where they identified a number of compounds in the leachate, as well as finding 1-adamantyladamantine as a contaminant in treated drinking water originating from the landfill.
4. Conclusion

The first stage of this review was selection of the contaminants to be addressed. After consideration of input from CRC CARE end-users and experts, and searching international peer-reviewed literature, the contaminants in Table 1 were chosen. Detailed conclusions regarding analytical methodology gaps in Australia can be found following the discussion of each contaminant above, and these are summarised below.

4.1 Priority 1 contaminants

- Significant analytical methodology gaps were not found for any of the Priority 1 compounds, although tools to assess laboratory performance such as easily accessible proficiency testing (PT) schemes are lacking. This may seem surprising in view of their identification by the CEC Forum as a ‘first tier priority’. It should be noted, however, that the research requirements specified by that Forum were much more wide-ranging than the analytical methodology focus of this review and that in the cases of MTBE and BaP, the research needs identified by the Forum were explicitly focused on areas other than measurement. In addition, there has already been considerable research into all the Priority 1 compounds in recent years, which has in turn resulted in substantial progress in analytical method development for these compounds.

4.2 Priority 2 contaminants

- Analytical capability certainly exists in Australia for perfluorinated compounds analogous to PFOS and PFOA, although commercial availability is limited. There are a wide range of other PFASs which may be of interest as alternatives to PFOS, many of which could be included in current LC-MSMS screening methods. Further investigation is required into which compounds have the greatest potential to become environmental contaminants in Australia in terms of usage and routes for entry into the environment. Matrix reference materials and proficiency testing studies do not appear to be available.

- There appear to be suitable methods in the literature for TBBPA and HBCDD, the most commonly used FRs other than PBDEs, although they require careful attention to detail and significant technical capability. The methodology does not appear to be commercially available in Australia. The compounds are widespread internationally and almost certainly present in the environment, so development of an analytical capability is required. There also appears to be a need for matrix reference materials.

With the phasing out of the PBDEs and HBCDD, a large number of possible novel FRs have appeared and further investigation into which analytes will be most significant for the Australian environment is recommended. Around 30 novel FRs were considered in this review, and while some work on most of the compounds is reported in the literature, methodology for these classes of compounds generally does not appear to be well established, and analysis does not appear to be performed routinely in Australia.
SCCPs have been widely used in Australia and are expected to be present in the environment. As there is very limited analytical capability, there is a need in Australia for development of methods for all environmental matrices. Reference materials and proficiency testing schemes are also lacking.

Analytical methodology for methylsiloxanes is lacking in Australia, and given their widespread use, volatility and persistence siloxanes are likely to be common in the environment. However, their environmental toxicity is low compared to other CECs so they are probably a low priority for method development.

4.3 Priority 3 contaminants

1,4-Dioxane, ionic liquids and organoboron contaminants are expected to be of little environmental significance to Australia as they are not widely used commercially at this time.

Benzotriazoles and hydroxyphenol benzotriazole derivatives are likely to be common in dishwasher and personal care products in use in Australia and so should be as widespread in the aquatic environment here as overseas. Some methods are available in the literature, but there does not appear to be any commercial analysis in Australia. There appears to be a need for method development and reference materials to determine the extent of contamination.

There does not appear to be any commercial testing for benzidine colourants in Australia, and methods for environmental matrices are not well established internationally. They are not expected to be a significant environmental contaminant and so they do not appear to be a high priority for method development.

There appear to be suitable methods in the literature for synthetic musks, however the methodology does not appear to be available in Australia. The compounds are almost certainly present in the environment due to their use in PCPs, so method development is warranted. There also appears to be a need for matrix reference materials.

The microbicides triclosan and triclocarban are well studied, and although there appears to be very limited commercial capability in Australia, presumably methodology could easily be implemented if there were commercial demand. As with other constituents of PCPs, such as musks and siloxanes, the lack of interest in environmental analysis is probably due to the low human toxicity and the familiarity of widespread use. Perhaps the first priority for such compounds is generating public and regulatory interest in environmental contamination, which would lead to demand for analytical methodology.

Organoplatinum compounds are undoubtedly used to treat cancer in Australia in much the same way as in other developed countries, but it is unclear how much of an environmental problem excreted drugs are in waste water, locally or internationally. If organoplatinum compounds were considered an environmental contaminant of concern in Australia, then there would be need for development of methods, production of reference materials and organisation of proficiency testing.

There are numerous methods for extraction and quantification of arsenic species in environmental samples in the literature, however official standard methods have
not been established. Certified reference materials for method development and quality control are unavailable for environmental matrices. Ten Australian laboratories provide commercial testing services for As\textsuperscript{III} and As\textsuperscript{V} and organoarsenic species as identified via the survey and further capability is evidenced by publications in scientific literature. Tools to assess laboratory performance such as easily accessible PT studies are lacking.

- There is very little analytical methodology available for nanomaterials in environmental samples, locally and internationally. The research field is very active.
5. Recommendations

- For the very diverse groups of PFASs and novel FRs, especially TBBPA and HBCDD, analytical methodology is not adequate in Australia. Many of these compounds will be used in Australia as they have important commercial applications, and many are subject to long-range transport and may be found in the Australian environment whether they are used here or not. Further investigation into which analytes will be most significant for the Australian environment is recommended. The development of methods, production of reference materials and coordination of PT schemes can then be considered for the more relevant analytes.

- The development of methods, production of reference materials and coordination of PT schemes for SCCPs is strongly recommended.

- The development of analytical methods for benzotriazoles and synthetic musks is recommended, to allow the distribution and environmental impact of these contaminants in Australia to be assessed.

- The production of reference materials and coordination of PT schemes for arsenic species in environmental matrices is strongly recommended.

- Activities of interest would be the development of methodology to allow studies to be conducted into the extent of contamination by methylsiloxanes, benzidines arising from dyestuffs and organoplatinum anticancer drugs.
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APPENDIX A.
CRC CARE survey of analytical methodologies for emerging contaminants

Australian laboratories listed on the NATA website as holding accreditation for Chemical Testing and providing a public testing service or being conditionally available for public testing were emailed an invitation to participate in an anonymous and voluntary survey aimed at assessing the availability of analytical methods for a selection of environmental contaminants. Thirty-three responses were received, of which four left all fields blank. The introductory text and questions are shown below, together with the responses to each question. The findings from the survey are discussed in section 1.2 of this report.

Introductory text to survey

The term ‘contaminants of emerging concern’ is used in this survey to refer to chemicals for which concerns have been recently raised about the risk they may pose to human health of the environment. These chemicals may have been newly developed, or they may be chemicals which have only just been recognised as a potential environmental risk, or which are being used in new ways.

As part of a literature review intended to identify contaminants of emerging concern for which there are measurement capability gaps in Australia, CRC CARE (Cooperative Research Centre for Contamination Assessment and Remediation of the Environment) is conducting a brief survey of Chemical Testing laboratories listed on the NATA website. The following survey should only take 5 minutes or less of your time to complete. We would be grateful if you could complete this survey by Friday 14 December 2012.

Please note that all questions are optional, and that your response will be anonymous unless you choose to leave your contact details in the last question of the survey.

Your input would be very much appreciated. For further information on this survey, the literature review or CRC CARE’s work with the remediation sector, please contact Cheryl Lim, CRC CARE Program Leader, Better Measurement Program on (02) 8467 3845 or by email at cheryl.lim@measurement.gov.au.
Please use the drop-down boxes to indicate for each compound or group of compounds (a) in which of the four environmental matrices (air (A), biota (B), soil/sediment (S) and water (W)) your laboratory has analytical capability, (b) whether your laboratory has NATA accreditation, (c) the approximate analysis frequency (combined over all matrices) and (d) the approximate range of the limit of reporting.

Matrices (A=Air, B=Biota, S=Soil/Sediment, W=Water)

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<th>Answer Options</th>
<th>None</th>
<th>None (%)</th>
<th>A only</th>
<th>B only</th>
<th>S only</th>
<th>W only</th>
<th>A and B</th>
<th>A and S</th>
<th>A and W</th>
<th>B and S</th>
<th>B and W</th>
<th>S and W</th>
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<th>A, B, W</th>
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7(one respondent) inorganic
8(four responses) ASB, AsIII, DMA, MMA, AsV; total; As concentration from soluble As compounds in water based matrix; MMA, DMA, Arsenobetaine, AsIII, AsV;
9AsBetaine, MMA, DMA, AsV, AsV all quantitated individually
10(one respondent) Total As
11As3+ and 5+
12major cations
136:2 FTS with a host of carboxylic acids, sulfonates and alcohols, the FOSEs under development.
14Perfluoroalkylsulfonic acids, Perfluorobutanesulfonic acid (PFBS), Perfluorohexanesulfonic acid (PFHxS), Perfluorodecanesulfonic acid (PFDS), Perfluoroalkylicarboxylic acids, Perfluorohexanoic acid (PFHxA), Perfluorohexanoic acid (PFHxNA), Perfluorononanoic acid (PFNNA), Perfluorodecanoic acid (PFDA), Perfluoroundecanoic acid (PFUnA), Perfluorododecanoic acid (PFDoA), Perfluorotridecanoic acid (PFTrA), Perfluorotetradecanoic acid (PFTeA), Other PFCs, Perfluorooctanesulfonamide (PFOSA), N-ethylperfluorooctanesulfonamidoacetic acid (NEtFOSA), N-methyl-perfluorooctanesulfonamidoacetic acid (NMeFOSA), N-ethyl-perfluorooctanesulfonamide (NEtFOSA), N-methyl-perfluorooctanesulfonamide (NMeFOSA), N-ethyl-perfluorooctanesulfonamidothanol (NEtFOSE), N-methyl-perfluorooctanesulfonamidoethanol (NMeFOSE), 1H,1H,2H,2H-perfluorohexanesulfonic acid (4:2 FTS), 1H,1H,2H,2H-perfluorooctanesulfonamidoacetic acid (6:2 FTS), 1H,1H,2H,2H-perfluorooctanesulfonamidoacetic acid (8:2 FTS), PBB153 (hexabromobiphenyl)
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Q 4. Would you like to suggest any other contaminants for which you believe there is a measurement research or development need in Australia?

Five responses given as follows, email contact details provided with each.

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