Cadmium metal and cadmium oxide: Environment tier II assessment

12 December 2019

CAS Registry Numbers: 7440-43-9, 1306-19-0, 69011-70-7, 69011-69-4

Preface

This assessment was carried out by staff of the National Industrial Chemicals Notification and Assessment Scheme (NICNAS) using the Inventory Multi-tiered Assessment and Prioritisation (IMAP) framework.

The IMAP framework addresses the human health and environmental impacts of previously unassessed industrial chemicals listed on the Australian Inventory of Chemical Substances (the Inventory).

The framework was developed with significant input from stakeholders and provides a more rapid, flexible and transparent approach for the assessment of chemicals listed on the Inventory.

Stage One of the implementation of this framework, which lasted 4 years from 1 July 2012, examined 3000 chemicals meeting characteristics identified by stakeholders as needing priority assessment. This included chemicals for which NICNAS already held exposure information, chemicals identified as a concern or for which regulatory action had been taken overseas, and chemicals detected in international studies analysing chemicals present in babies' umbilical cord blood.

Stage Two of IMAP began in July 2016. We are continuing to assess chemicals on the Inventory, including chemicals identified as a concern for which action has been taken overseas and chemicals that can be rapidly identified and assessed by using Stage

One information. We are also continuing to publish information for chemicals on the Inventory that pose a low risk to human health or the environment or both. This work provides efficiencies and enables us to identify higher risk chemicals requiring assessment.

The IMAP framework is a science and risk-based model designed to align the assessment effort with the human health and environmental impacts of chemicals. It has 3 tiers of assessment, with the assessment effort increasing with each tier. The Tier I assessment is a high throughput approach using tabulated electronic data. The Tier II assessment is an evaluation of risk on a substance-by-substance or chemical category-by-category basis. Tier III assessments are conducted to address specific concerns that could not be resolved during the Tier II assessment.

These assessments are carried out by staff employed by the Australian Government Department of Health and the Australian Government Department of the Environment and Energy. The human health and environment risk assessments are conducted and published separately, using information available at the time, and may be undertaken at different tiers.

This chemical or group of chemicals are being assessed at Tier II because the Tier I assessment indicated that it needed further investigation.

For more detail on this program please visit: www.nicnas.gov.au.

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Acronyms & Abbreviations

Grouping Rationale

The focus of this Tier II assessment is the environmental risks associated with the manufacture of cadmium metal. The metal is manufactured at two facilities in Australia where it is a secondary product of processes that are used to manufacture zinc and/or lead metal from mineral concentrates.

The manufacture of cadmium metal is known to be a source of anthropogenic emissions of cadmium compounds to the Australian environment. Emissions of cadmium compounds to the environment are of concern because they can release bioavailable cadmium(2+) ions which are toxic to wildlife and humans. Ionic cadmium is also of concern in soil because it is taken up rapidly by agricultural crops and can contaminate the human food chain. The environmental fate and effects of ionic cadmium were assessed under the IMAP Framework and the findings are published in the IMAP Environment Tier II Assessment for water soluble cadmium(2+) salts (NICNAS, 2017). This previous assessment should be consulted for details on the environmental hazards associated with ionic cadmium.

The manufacture of cadmium metal involves the deliberate and/or incidental formation of cadmium oxide (CAS RN 1306-19-0) and two inorganic mixtures containing cadmium which are listed chemicals on the Inventory. Cadmium oxide is formed as a process intermediate during the roasting of mineral concentrates and/or when cadmium metal is heated. The two inorganic mixtures containing cadmium are both unknown or variable composition, a complex product of a chemical reaction, or a biological material (UVCB) substances. The first of these process related UVCB substances is cadmium, sponge (CAS RN 69011-70-7), which is described as a precipitate obtained by treatment of slurried dusts from lead manufacturing with zinc (US EPA, 2019b). The second UVCB substance is cadmium, dross (CAS RN 69011-69-4), which is described as a scum formed on the surface of molten cadmium (REACH, 2019a; US EPA, 2019a). The formation and any use of cadmium oxide and the two cadmium UVCB substances during the manufacture of cadmium metal is expected to contribute to total cadmium emissions resulting from manufacturing facilities in Australia. Metallic foams such as cadmium sponges have reported applications in heat exchangers, energy absorption, flow diffusion and lightweight optics (American Elements, 2019). However, it is unclear whether these are direct uses or uses from the manufactured cadmium compounds. Hence, the environmental risks resulting from manufacture of cadmium metal must also consider the risks arising from any industrial use of these three additional cadmium chemicals.

Chemical Identity

CAS RN	7440-43-9
Chemical Name	Cadmium
Synonyms	cadmium metal elemental cadmium
Atomic Weight (g/mol)	112.41

CAS RN	1306-19-0
Chemical Name	Cadmium oxide (CdO)
Synonyms	cadmium monoxide cadmium fume cadmium oxide brown monteponite
Molecular Formula	CdO
Molecular Weight (g/mol)	128.41

CAS RN	69011-70-7
Chemical Name	Cadmium, sponge

Synonyms	lead smelter, sponge precipitate

CAS RN	69011-69-4
Chemical Name	Cadmium, dross
Synonyms	cadmium oxide residues cadmium skimmings

Physical and Chemical Properties

Elemental cadmium is a soft and ductile metal. It has a relatively low melting point of 320°C and the molten metal has a significant vapour pressure (133.2 Pa at 392°C) (Carr, 1999). The metal is slowly oxidised in moist air to cadmium oxide, and when heated it produces a brown vapour of cadmium oxide (Stoeppler, 1991). Cadmium metal forms alloys with a range of metals (e.g., zinc, copper, and silver) and these have industrial uses in applications such as brazing and soldering (Carr, 1999).

Cadmium metal is insoluble in water. However, the metal reacts with both oxidising and non-oxidising acids to release cadmium(2+) ions in acid solution (Cotton and Wilkinson, 1988). Cadmium oxide is also typically considered insoluble in water, although as a basic metal oxide it is soluble in acids and will, therefore, also release ionic cadmium in acid solution (Haynes, et al., 2016).

A quantitative estimate of the water solubility of cadmium oxide at pH 8 has been obtained by use of a transformation/dissolution test on powdered cadmium oxide. Summary details of this study are reported in the European Union (EU) Risk Assessment report for Cadmium Oxide and Cadmium Metal (EU RAR, 2007). Under the conditions of this test, the solubility of cadmium oxide is reported to be in the range of 0.1–0.23 milligrams dissolved cadmium per litre (mg Cd_{diss}/L). A similar value was determined for the water solubility of powdered cadmium metal (0.14–0.19 mg Cd_{diss}/L at pH 8). Although not discussed in the report, it is assumed that the measured water solubility for cadmium metal actually reflects dissolution of cadmium oxide that is naturally present on the surface of cadmium metal. Hence, for the purposes of this assessment, the water solubility of cadmium oxide measured in the transformation/dissolution test is taken to be a useful indicator of the potential for cadmium metal to release ionic cadmium into water under environmentally relevant conditions.

No physical or chemical property data for the two cadmium UVCBs in this group were identified. However, based on the description of these substances and the way they are formed they are both inorganic solids. Cadmium dross is understood to be a mixture of cadmium metal and cadmium oxide with minor impurities (REACH, 2019b; US EPA, 2019c). This substance is, therefore, expected to share some of the properties of both the metal and the oxide, including their pH dependent water solubility.

Import, Manufacture and Use

Australia

Cadmium metal is manufactured at two locations in Australia. The metal has industrial uses in the manufacture of solders and brazing alloys.

Cadmium metal is manufactured in Australia as a secondary product of zinc and lead refining (Bartel and Gowan, 2013; Ramshaw, 2013). Available information indicates it is primarily produced at the zinc refinery in Hobart with smaller quantities also produced at the Port Pirie lead-zinc smelter (Nyrstar, 2015; Ramshaw, 2013).

Cadmium metal is listed on the 2006 High Volume Industrial Chemicals List (HVICL) with a total reported introduction volume of < 1000 tonnes (NICNAS, 2016). Available information indicates that between 1997 and 2016 production of cadmium in Australia was stable at 310 to 550 tonnes per year, accounting for 3% of global supply (Department of Environment, 1997; UNEP, 2010 ; USGS, 2011; 2017).

Cadmium metal is alloyed with other metals to make specialty solders as well as fusible and brazing alloys in Australia (CAGroup, 2017; SBA, 2019). These alloys typically contain between 5 and 20% cadmium by weight (Carr, 1999; IARC, 1993; Schulte-Schrepping and Piscator, 2012). Cadmium containing solders are used for joining aluminium and alloys to copper, brass, or stainless steel. Other uses include soldered connections on glass and ceramics.

International

Internationally, elemental cadmium and cadmium oxide are primarily used in nickel-cadmium (Ni-Cd) batteries, alloys and corrosion resistant coatings (Herron, 1999; Schulte-Schrepping and Piscator, 2012). Global cadmium metal production in 2016 was estimated at over 21 000 tonnes annually. The majority of global cadmium metal production occurs in China, the Republic of Korea, and Japan (USGS, 2017).

Cadmium metal is used to make certain brazing and low melting alloys used in bearings, solders and as a hardener for copper. Metal alloys containing cadmium are used as a filler for bending thin walled pipes. Cadmium metal is also used as a component of glass lens grinding blocks, foundry patterns and casting moulds where it is present from 5–20% by weight (Carr, 1999).

Globally, 82% of cadmium metal is processed into cadmium oxide which is used in rechargeable Ni-Cd batteries (UNEP, 2010). Recycling of Ni-Cd batteries to recover cadmium accounts for approximately 17% of global supply. Cadmium oxide has reported use in plastics, and is also used to make most of the economically significant cadmium compounds, such as cadmium sulfide (Herron, 1999; REACH, 2012).

Cadmium oxide is used as a source of soluble cadmium(2+) ions in salt baths for cadmium electroplating. The main application of cadmium plating is for metals used in military applications such as weaponry (IARC, 1993; Schulte-Schrepping and Piscator, 2012). Cadmium oxide has further uses as contact material in metal switches and as a catalyst in organic synthesis (Herron, 1999; Schulte-Schrepping and Piscator, 2012).

Environmental Regulatory Status

A detailed discussion of the regulatory status of cadmium in Australia and internationally is provided in the IMAP Environment tier II assessment for water soluble cadmium(2+) salts (NICNAS, 2017). The discussion below highlights selected regulations and standards of particular relevance for this assessment.

Australia

The emission of cadmium and other pollutants at the two sites where cadmium is manufactured in Australia is regulated under state legislation. Licensing arrangements made by each state specify emission standards requiring monitoring and reporting of emissions as well as other activities.

In Tasmania, the *Environmental Management and Pollution Control Act* (1994) issues Environmental Protection Notices (EPN) which regulate environmentally relevant activities. The EPN for the zinc refinery in Hobart limits emissions of cadmium from the plant’s outfall point to the Derwent River to 30 micrograms of total cadmium (dissolved and particulate) per litre (µg Cd/L), with a threshold limit of 70 µg Cd/L. The concentration of cadmium in process gases released to the atmosphere is limited to 3 milligrams of cadmium per cubic meter (mg Cd/m^3). Annual reporting of emissions and activities to reduce environmental impact of the plant are also required (EPA Tasmania, 2013; Nyrstar, 2013).

In South Australia, emissions of cadmium and other pollutants at the Port Pirie smelter are regulated under the *Environmental Protection Act* (1993) through an operating licence issued by the Environment Protection Authority (EPA) of South Australia. Wastewater discharge to First Creek has a ‘target threshold’ of 230 µg Cd/L and a ‘reportable limit’ of 615 µg Cd/L (SA EPA, 2019). The notice does not specify if emissions relate to total or dissolved cadmium. Notification in writing to the EPA is required where a 7 day rolling average exceeds the reportable limit.

Cadmium and cadmium compounds are subject to reporting under the Australian National Pollutant Inventory (NPI). Under the NPI, emissions of cadmium and cadmium compounds are required to be reported annually by facilities that exceed emission, fuel and electricity demand thresholds (Department of the Environment, 2019b). Industries relevant to this assessment report emissions of cadmium compounds based on measured or estimated values in effluent streams. Emissions include direct release to air, surface water and land as well as those resulting from fuel combustion and other off-site activities (Department of Environment, 1999). Emissions to groundwater are not included in NPI reporting.

Australian Guidelines for Fresh and Marine Water Quality include high reliability default guideline values (DGV) for cadmium. The hardness modified DGV adopted for low hardness freshwater is 0.2 μg Cd/L which will protect 95% of species in *slightly-moderately disturbed* freshwater ecosystems. The 99% DGV of 0.7 μg Cd/L is recommended for use in *slightly-moderately disturbed* marine ecosystems (ANZECC, 2019b).

Groundwater guidelines follow those given for surface waters and are based on current and possible uses scenarios. Where groundwater is used as a source of drinking water a limit of 2 μg/L is adopted (NEPC, 2013).

Sediment DGVs have been developed for the fine sediment fraction (grain size less than 2 mm). The DGV and Guideline Value-high (GV-high) represent, respectively, the concentration at which 10% and 50% of toxic effects on sediment dwelling organisms are observed. For cadmium the DGV and GV-high are 1.5 milligrams of cadmium per kilogram of dry sediment (mg Cd/kg dw) and 10 mg Cd/kg dw, respectively (ANZECC, 2019a).

United Nations

The United Nations Environment Programme (UNEP) received a mandate to address the environmental and health risks of cadmium in 2001 (UNEP, 2019). UNEP published a review of scientific information on cadmium including sources of emissions and the effects of cadmium on human health and the environment which was last updated in 2010 (UNEP, 2010).

OECD

Cadmium metal and cadmium oxide are both listed as high production volume chemicals (HPV) by the OECD indicating that they are produced in volumes greater than 1000 tonnes in at least one member country (OECD, 2009).

Cadmium metal and cadmium oxide were assessed under the Cooperative Chemicals Assessment Programme (CoCAP) and a Screening Information Dataset (SIDS) Initial Assessment Report (SIAR) was published in 2004 (OECD, 2004). Both chemicals were considered candidates for further work.

Canada

Chemicals containing cadmium are listed as a broad class of compounds (‘Inorganic cadmium compounds’) under Schedule 1 (the Toxic Substance List) of the *Canadian Environmental Protection Act 1999* (Government of Canada, 2016). All chemicals in this group are listed on the Domestic Substances List (DSL).

European Union

All chemicals in this group are regulated as containing cadmium and are listed in Annex XVII (Restriction) under the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) legislation as a broad class of compounds (‘Cadmium and its compounds’) (REACH, 2019a). The restrictions relate to the use of these chemicals in polymers (plastic material), plastic articles, paints, painted articles, articles containing recovered PVC, cadmium metal plating, cadmium plated articles, brazing fillers and jewellery.

The European Parliament amended the EU Battery Directive (2006/66/EC) to prohibit the inclusion of Ni-Cd batteries in cordless power tools beginning December 31, 2016, after which Ni-Cd batteries could only be used in emergency systems and medical equipment in the EU (European Union, 2006).

United States of America

All of the chemicals and substances in this group are listed on the inventory of chemicals manufactured or processed in the USA, as published under the Toxic Substances Control Act 1976 (TSCA) (US EPA, 2019b). Except for cadmium dross, they are all registered as ‘active’ on the TSCA Inventory, which indicates that they have recently been manufactured, imported or processed by industry in the USA.

‘Cadmium and cadmium compounds’ are on the 2014 Update to the TSCA Work Plan list of existing chemicals for assessment (US EPA, 2014).

Environmental Exposure

Cadmium metal is a secondary product from the zinc refinery in Hobart and the lead-zinc refinery in Port Pirie. The majority of cadmium is manufactured at the zinc refinery in Hobart, which uses a zinc-iron sulfide concentrate as a feedstock. Zinc and cadmium metal are extracted concurrently using a hydrometallurgical process which involves calcination, leaching and electrolysis (Ramshaw, 2013).

At the Hobart refinery, initial processing involves oxidising the zinc-iron sulfide concentrate at high temperature (calcination) to remove sulfide (Ramshaw, 2013). Waste gases produced during smelting at other facilities contained cadmium oxide particulates of approximately 2 micrometres (µm) in diameter (Stoeppler, 1991). Electrostatic precipitators, wet scrubbing, chemical absorption and fabric filters are used to remove particulate matter before release to the atmosphere (Nyrstar, 2018; Ramshaw, 2013). Cadmium emissions to the atmosphere are monitored at the Hobart refinery with air concentrations typically ten to one hundred times below the limit of 3 mg Cd/m^3 specified in the EPN (Nyrstar, 2013; 2018).

The material resulting from calcination undergoes an acid leaching process to sequentially dissolve the target metals. This process produces concentrated zinc and cadmium solutions (Ramshaw, 2013). The solutions have the potential to be released to groundwater through spills and seepage of containment facilities (Nyrstar, 2013; 2018). The Hobart refinery undertakes a range of programs to reduce historical and modern contaminants in groundwater being discharged to the Derwent Estuary. Programs have focused on sealing processing facilities to prevent leaks as well as intercepting and decontaminating groundwater (Nyrstar, 2018).

Following acid leaching the concentrated cadmium solution is refined to cadmium metal by electrolysis (Ramshaw, 2013). Loss of concentrated solutions of ionic cadmium to groundwater may also occur at this stage, and this is managed onsite using the methods described above (Nyrstar, 2013; 2018).

The manufacturing process at the Hobart refinery generates significant quantities of process waste water, stormwater and recovered groundwater that are contaminated with cadmium compounds. Contamination of these waters arises from both modern and historical production. Contaminated water is treated by lime neutralisation, flocculation, reverse osmosis and dilution before being discharged to the Derwent River (Nyrstar, 2018). Twenty-four hour composite samples are taken from the discharge stream to monitor cadmium and other pollutants. Monitoring data show that the concentration of cadmium is typically significantly below the regulatory discharge limit for total cadmium of 30 µg Cd/L (Nyrstar, 2018).

Less information is available regarding specific sources of cadmium emissions at the Port Pirie lead-zinc refinery. Emission estimates indicate that cadmium compounds are released primarily to the air compartment (Department of Environment, 2018). Reports have identified elevated levels of cadmium in sediments, biota and soils surrounding the plant, but do not enable a systematic evaluation of exposure (Cartwright, et al., 1976; Gaylard, et al., 2011 ; Lafratta, et al., 2019; SA EPA, 2004; Ward and Hutchings, 1996). Pollution management at the site has focused on reducing emissions of lead to air and it is expected that this program will also improve cadmium emissions (Department of Environment, 2019b; Nyrstar, 2013; SA EPA, 2004).

Despite the adoption of emission reduction technologies, cadmium manufacturing remains one of the most significant sources of cadmium emissions to the Australian environment (DEP, 2015; Department of Environment, 2019a; Department of the Environment, 2019a; Nyrstar, 2018). Significant historical contamination at these sites is also a source of emissions of cadmium from these manufacturing facilities. However, emissions arising from past contamination are beyond the scope of this assessment (DEP, 2015; Gregory, et al., 2013).

Lead, zinc and cadmium refining involves the release of multiple pollutants that are of environmental concern. They include mercury, concentrated acids, sulfur dioxide, fluoride and arsenic (Department of Environment, 2018; 2019b). The environmental impacts from these other pollutants are beyond the scope of this assessment.

Environmental Fate

A detailed discussion of the environmental fate of ionic cadmium is available in the IMAP Environment Tier II Assessment for water soluble cadmium(2+) salts (NICNAS, 2017). A summary is presented here of fate characteristics which are relevant to cadmium compounds emitted during manufacturing of cadmium metal.

Partitioning and transport

Cadmium compounds are released to all environmental compartments during the manufacture of cadmium metal. Cadmium compounds emitted to air and water predominantly partition to sediments and soils. Cadmium compounds may be sequestered in sediments and soils but are able to be remobilised.

Particles of cadmium oxide emitted to the atmosphere during calcination have diameters of the order of 2 μm. This fine particle size promotes wind dispersion and solubility (Alloway, 1990; Cartwright, et al., 1976; Ettler, et al., 2012; Schaider, et al., 2007; Stoeppler, 1991). Cadmium oxide is removed from the atmosphere by deposition to soils and surface water.

The fate of cadmium compounds in soils is influenced by their solubility and mobility under local environmental conditions. The fraction of total soil cadmium dissolved in pore water is strongly influenced by pH, salinity, clay content, age, the presence of sulfides and dissolved organic matter (Alloway, 1990; Rieuwerts, et al., 1998; Sauve, et al., 2000; Smolders, et al., 2009). Fine particles collected from refinery waste gases have been found to readily release soluble cadmium to soil pore water (Ettler, et al., 2012). The solubility of inorganic cadmium compounds in soils is known to decline on aging (Smolders, et al., 2009).

Despite receiving significant inputs from cadmium manufacturing facilities, estuarine waters adjacent to the Hobart refinery have low total cadmium concentrations (Nyrstar, 2013). This is typical of many receiving estuaries where partitioning to sediments reduces cadmium levels in the water column (Alloway, 1990; DEP, 2015; Förstner, 1980 ; Luoma and Rainbow, 2008).

Sediments in the Derwent Estuary are heavily contaminated with cadmium compounds from the Hobart refinery (DEP, 2015; Macleod and Coughanowr, 2019; Nyrstar, 2018). In sediments, cadmium may be present as sulfides or bound to iron and manganese oxyhydroxides, clays and organic material (Gregory, et al., 2013; Luoma and Rainbow, 2008). About 10% of cadmium compounds in the surface layer of sediments in the Derwent Estuary are readily exchangeable with the water column (Gregory, et al., 2013). Sediment cadmium concentrations that exceed the default guideline value of 1.5 mg Cd/kg extend approximately 25 km from the refinery (DEP, 2015).

Sediment layers have been used to observe changes in emissions from Australian cadmium manufacturing facilities over time. Sediment cores indicate that modern industrial practices and risk management activities at the Hobart refinery have contributed to significant improvements in emissions from cadmium manufacturing. Despite these efforts modern sediment concentrations associated with cadmium manufacturing remain over ten times above the Australian sediment guideline value-high of 10 mg/kg, typically used for disturbed estuarine environments (Gregory, et al., 2013; Nyrstar, 2013; Simpson, et al., 2013).

Some cadmium bound to sediments may be remobilised if disturbed (DEP, 2010). Monitoring programs at the Hobart refinery have observed the remobilisation of zinc from sediments to the water column. This flux may indicate a possible route for the remobilisation of cadmium (Nyrstar, 2018). Construction and dredging have the potential to disturb and remobilise metals from sediments (Nayar, et al., 2004).

Comparatively little information is available regarding the fate of emissions from cadmium manufacturing at the Port Pirie Facility. A faunal survey conducted in 1982 indicated cadmium accumulation in sediments, while a study of air emissions found cadmium was deposited in soils within 20 km from the facility (Cartwright, et al., 1976; SA EPA, 2004; Ward and Young, 1982). A recent study, that examined two sediment cores taken adjacent to the facility, indicated cadmium concentrations had not declined since the 1970s (Lafratta, et al., 2019). A study from 1976 indicated that soils approximately 20 km from the facility had been contaminated by atmospheric deposition of airborne cadmium compounds (Cartwright, et al., 1976).

Bioaccumulation and biomonitoring

Cadmium is known to be bioaccumulative and a portion of cadmium compounds emitted from cadmium manufacturing is known to be bioavailable. See the IMAP Environment Tier II Assessment for water soluble cadmium(2+) salts for a detailed discussion on cadmium bioaccumulation (NICNAS, 2017).

Bioaccumulation by oysters and mussels has been used to indicate the bioavailability of cadmium compounds emitted from cadmium manufacturing facilities in Hobart and Port Pirie. In the Derwent Estuary, cadmium concentration in oysters (species not specified) was up to 10 times higher than control groups (Nyrstar, 2018).

The median cadmium concentration in blue mussels (*Mytilus galloprovincialis*) deployed in coastal waters adjacent to the Port Pirie smelter showed a 110% increase from baseline measurements (Gaylard, et al., 2011).

Flathead (*Platycephalus bassensis*) sampled near the Hobart facility were found to have low cadmium concentrations in body tissues (Nyrstar, 2013). The report was unclear if organs known to accumulate cadmium were included in these measurements. Limited available information suggests high levels of cadmium in sediment dwelling organisms in the Derwent Estuary (DEP, 2010).

Zinc and calcium have been shown to reduce the toxicity and bioaccumulation of cadmium in several environmental media by limiting cadmium absorption (Chaney, et al., 1996; Gao, et al., 2011; McLaughlin, 1996; Mebane, 2010; Munksgaard, et al., 2017).

Predicted Environmental Concentration (PEC)

A PEC for cadmium compounds was not calculated for this assessment.

Cadmium is a naturally occurring element that occurs at low levels in most environmental compartments. In uncontaminated rocks and soils concentrations range from 0.03–0.4 milligrams per kilogram of solid material (mg Cd/kg), while pristine freshwaters typically have concentrations of 0.07 to 0.1 µg Cd/L (Alloway, 1990). Background cadmium concentrations in some Australian sediments are estimated at 0.1–0.2 mg Cd/kg (Gregory, et al., 2013).

Ambient cadmium concentrations in estuarine waters near the Hobart refinery are typically reported below 5 µg Cd/L total cadmium (Nyrstar, 2018). This concentration is close to the 95% species protection threshold for marine waters of 5.5 µg Cd/L, but is below the 80% protection level of 36 µg Cd/L used in reporting at the site.

Sediments in the Derwent Estuary have accumulated cadmium associated with both modern and historical practices. In the uppermost layers, likely to be indicative of modern contributions, cadmium concentrations above 100 mg Cd/kg are observed (DEP, 2015; Gregory, et al., 2013; Nyrstar, 2013). Sediment concentrations in this area are above ten times the sediment guideline value-high of 10 mg/kg dw. Detailed analysis of shallow sediments indicate that approximately 10% of cadmium in sediments are likely to be readily mobilised. The majority of cadmium is immobilised within the sediment layer (Gregory, et al., 2013).

Limited sediment monitoring is available for the Port Pirie refinery. A study conducted in the 1980s recorded cadmium concentrations between 10 and 260 mg Cd/kg at four sites (Ward and Hutchings, 1996). A recent study indicated modern concentrations at a single location of 7 mg Cd/kg (Lafratta, et al., 2019).

Groundwater monitoring at the Hobart refinery indicates cadmium concentrations are highly spatially variable and dependent on risk management practices. Cadmium concentrations below the waste storage depot were observed of 24 mg Cd/L were measured, while groundwater beneath the electrolysis facility was recorded at over 2000 mg Cd/L. Regular monitoring has been used to identify the most significant sources of cadmium emissions at the facility and target risk management activities (Nyrstar, 2013; 2018).

At the Hobart refinery, deployed oysters (unspecified species) have cadmium concentrations up to 2.5 mg Cd/kg of flesh. Reports do not indicate if these measurements are made on a wet or dry weight basis (Nyrstar, 2018).

Blue mussels (*Mytilus galloprovincialis*) deployed in coastal waters adjacent to the Port Pirie refinery were found to have cadmium concentrations of 2.51 milligrams of cadmium per kilogram of dried tissue mass (mg Cd/kg dw) compared to 1.20 mg Cd/kg dw measured prior to deployment (Gaylard, et al., 2011).

Aquatic birds sampled near the Hobart refinery were found to accumulate cadmium. In birds toxic effects have been associated with feather concentrations of 2 mg/kg dry weight, though these levels were not observed in the study sample (Einoder, et al., 2018).

Environmental Effects

The environmental effects of cadmium metal and the cadmium compounds in this assessment primarily result from the release of ionic cadmium species to the environment. The toxic effects of all chemicals have been collectively assessed by reference to the extensive ecotoxicity data available for ionic cadmium.

A detailed account of the ecotoxicity of ionic cadmium is available in the IMAP Environment tier II assessment for water soluble cadmium(2+) salts (NICNAS, 2017), a summary of which is presented here.

Effects on Aquatic Life

Cadmium bioaccumulates in aquatic organisms and bioavailable forms of cadmium are very toxic to aquatic life in both short and long term exposures. The toxicity of ionic cadmium to aquatic organisms varies considerably between species and is strongly influenced by water chemistry.

Acute toxicity

Dissolved cadmium(2+) causes severe acute toxicological and physiological effects to aquatic organisms. In freshwater fish the primary mode of action is through binding to calcium-binding sites at the gill surface (Mebane, 2010). As a result cadmium toxicity typically decreases with increasing calcium concentration (Mebane, 2010).

The acute toxicity of ionic cadmium varies considerably between aquatic organisms and even between closely related species (UNEP, 2010). The IMAP Environment tier II assessment for water soluble cadmium(2+) salts identified a 96 hour LC50 test on rainbow trout (*Oncorhynchus mykiss*) as the most sensitive endpoint for the acute toxicity of ionic cadmium at 0.77 µg Cd/L (NICNAS, 2017).

Chronic toxicity

Available chronic toxicity data indicate that the sensitivity of aquatic organisms to cadmium decreases in the order invertebrates ≥ fish/amphibians > algae. Long term exposure to cadmium can affect reproduction, endocrine and immune systems, development, growth and behaviour of aquatic organisms (McGeer, et al., 2011) in (US EPA, 2016).

The lowest chronic toxicity value identified in the IMAP Environment tier II assessment for water soluble cadmium(2+) salts was a no-observed effect (NOEC) equivalent for *Daphnia magna* of 0.08 µg Cd/L. The NOEC value was adjusted to a water hardness of 30 mg of calcium carbonate per litre (mg $CaCO_3$/L) (NICNAS, 2017).

In birds toxic effects have been associated with feather concentrations above 2 mg/kg dry weight (Einoder, et al., 2018).

Effects on Sediment Life

Bioavailable forms of ionic cadmium can be toxic to sediment dwelling organisms.

Limited data are available indicating direct toxic effects of cadmium on sediment dwelling organisms in the Derwent Estuary. One study conducted on the bulk toxicity of sediments from the Derwent Estuary indicated behavioural effects on the native brittle star (*Amphiura elandiformis*). These effects were attributed to the synergistic toxicity of the copper, cadmium, mercury, lead and zinc present in the sediments (DEP, 2010).

Effects on Terrestrial Life

Bioavailable forms of ionic cadmium can be toxic to terrestrial organisms.

Soil microbes and plants are more sensitive to cadmium than soil invertebrates. In nutrient solutions, cadmium is toxic to plants at concentrations between 0.1 to 1 mg Cd/L. Both invertebrates and plants accumulate cadmium (UNEP, 2010).

Australian soil guidelines for cadmium have been set to ensure that plant tissue concentrations of cadmium in crops do not exceed food standard guidelines – rather than for the protection of terrestrial life itself (ANZECC, 2000).

Hazards associated with ionic cadmium in soil can be strongly influenced by the presence of other metals as well as pH and salinity (Chaney, et al., 1996; McLaughlin, et al., 1994; Sauve, et al., 2000).

Predicted No-Effect Concentration (PNEC)

In place of PNECs for the water and sediment compartments, the trigger values published for cadmium in the Australian and New Zealand Guidelines for Fresh and Marine Water Quality have been used (ANZECC, 2019a; 2019b). The water quality trigger values represent thresholds above which further assessment of potential toxicity may be required to ensure environmental quality.

For *slightly-moderately disturbed* freshwater ecosystems, the high reliability water quality guideline value for protection of 95% of species is 0.2 µg Cd/L (in low hardness water). For cadmium in *slightly-moderately disturbed* marine waters, the water quality guideline value is 0.7 µg Cd/L.

The Sediment Default Guideline Value (DGV) of 1.5 mg Cd/kg represents the concentration at which 10% of effects on sediment dwelling organisms are observed (ANZECC, 2019a).

Categorisation of Environmental Hazard

It is not currently possible to categorise the environmental hazards of metals and other inorganic chemicals according to standard persistence, bioaccumulation and toxicity (PBT) hazard criteria. These criteria were developed for organic chemicals and do not take into account the unique properties of inorganic substances and their behaviour in the environment (UNECE, 2007).

As a result environmental hazard categorisation according to domestic PBT criteria has not been performed for chemicals in this group. Nevertheless, there is an international consensus that bioavailable forms of ionic cadmium are highly toxic to the environment and that cadmium is a bioaccumulation hazard.

Risk Characterisation

Risk quotients have not been calculated for the chemicals in this group.

Anthropogenic emission of cadmium compounds to the environment are acknowledged to be of concern both domestically and internationally due to the toxicity and potential for bioaccumulation of ionic cadmium. Cadmium metal manufacturing associated with zinc and lead refineries are the major point sources of anthropogenic cadmium emissions in Australia.

The manufacture of cadmium metal occurs at metal refineries in Hobart and Port Pirie. Current practices result in the release of cadmium compounds to all environmental compartments leading to an accumulation of cadmium in sediments and soils.

While sediment concentrations of cadmium have declined in response to risk management measures employed at the Hobart refinery, concentrations still exceed the guideline value-high by over ten times. The risk posed by high sediment concentrations of cadmium in the Derwent Estuary is reduced by strong binding to local sediments.

Cadmium may be sequestered in sediments but is not degraded in the environment. Cadmium sequestered in sediments has the potential to be remobilised through disturbances such as bioturbation or dredging. Ongoing management will be required to reduce the risk posed by the potential for remobilisation of cadmium compounds in sediments.

In estuarine waters adjacent to the Hobart facility, total cadmium is present above the 95% protection level for marine ecosystems, but below the 80% protection level used at this site. Combined with observed bioaccumulation of cadmium in indicator organisms, this indicates that there may be some potential risks to sensitive aquatic organisms at this location.

There are limited data available regarding the impacts of cadmium emissions from the Port Pirie refinery. The limited monitoring data that are available for this site indicate that there is cadmium contamination of sediments and bioaccumulation of cadmium within marine organisms. In light of the limited monitoring data available and considering the toxicity and potential for bioaccumulation of ionic cadmium, the environmental risks associated with cadmium manufacturing at this facility are currently considered to be uncertain.

Key Findings

The principal environmental concern for the chemicals in this group is the potential for release of ionic cadmium to aquatic environments and soil pore water from any industrial uses of these chemicals in cadmium manufacturing facilities. This is of concern because bioavailable forms of ionic cadmium are very toxic to aquatic life and many aquatic and terrestrial species can accumulate cadmium.

The toxicity and bioavailability of cadmium compounds are significantly dependent on local environmental conditions. Given this dependency, detailed environmental and biological monitoring at cadmium manufacturing facilities is necessary to adequately characterise the environmental risks of cadmium emissions.

An extensive data set regarding the environmental impact of cadmium and zinc refining at the Hobart refinery has been compiled. This data set in conjunction with an extensive ongoing chemical and biomonitoring programme has been used to consistently improve practices at the plant over a number of decades. A similar set of publicly available data (including chemical and biomonitoring data) was not identified for the Port Pirie refinery. In the absence of more complete information, the environmental risks associated with cadmium manufacturing at Port Pirie are currently considered to be uncertain.

Based on the available environmental and biomonitoring data, the emission of cadmium compounds during cadmium metal manufacture remains an environmental concern in Australia.

Recommendations

Cadmium is a significant environmental contaminant and the routine collection and publication of environmental and bio-monitoring data from all facilities that manufacture cadmium metal is recommended to assist in formulating risk management recommendations.

Ongoing management of sediments contaminated by cadmium manufacturing is recommended to limit risks arising from remobilisation of cadmium to biota and the water column.

Environmental Hazard Classification

In addition to the classification of environmental hazards according to domestic environmental thresholds presented above, the classification of the environmental hazards of elemental cadmium and cadmium oxide according to the third edition of the United Nations' Globally Harmonised System of Classification and Labelling of Chemicals (GHS) is presented below (UNECE, 2009b):

Hazard	GHS Classification (Code)	Hazard Statement
Acute Aquatic	Category 1 (H400)	Very toxic to aquatic life
Chronic Aquatic	Category 1 (H410)	Very toxic to aquatic life with long lasting effects

The aquatic hazards of elemental cadmium and cadmium oxide have been classified based on the available acute toxicity values for the soluble cadmium(2+) ion in accordance with the classification procedure for metals and metal compounds under the GHS (UNECE, 2007). The classification of each compound was made based on the concentration of dissolved cadmium determined using the 7 day transformation/dissolution test conducted according to guidelines in annex 10 of the GHS (UNECE, 2009a).

The aquatic hazards of cadmium dross and cadmium sponge have not been classified for this assessment.

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