NeuroToxicology 58 (2017) 187–193

Contents lists available at ScienceDirect

NeuroToxicology

Full length article

Aquatic environmental risk assessment of manganese processing industries

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ARTICLE INFO

Article history:
Received 12 February 2016
Accepted 12 April 2016
Available online 23 April 2016

Keywords:
Manganese
Risk assessment
Freshwater

ABSTRACT

An environmental risk assessment (ERA) has been conducted for sites producing and processing manganese and its inorganic compounds, focussing on potential risks to freshwater. A site specific questionnaire was used to collect information. Sites fall into three broad categories: mining sites, refining sites, and sites producing chemicals and pigments. Waste disposal is principally carried out by the treatment of liquid wastes to separate solids for disposal off-site with a consented wastewater discharge, or disposal on-site using evaporation or settlement ponds in order to maintain the waste materials in a suitable manner following site closure. The main source of emissions from refining and alloying sites is from the treatment of emissions to air using wet scrubber air filters. There is also the potential for fugitive environmental emissions of manganese from stockpiles of raw material held on-site.

Data provided from the questionnaires were both site-specific and also commercially sensitive. Therefore, this paper has undertaken the manganese exposure assessment, using a probabilistic approach to reflect the distribution of emissions of manganese and also to maintain the confidentiality of site specific data. An inverse correlation was observed between the total annual tonnage of manganese processed at the site and the emission factor, such that sites processing larger quantities resulted in lower emissions of manganese per tonne processed. The hazard assessment determined a Predicted No Effect Concentration (PNEC) for freshwater using a species sensitivity distribution approach, resulting in a freshwater PNEC of 0.075 mg L^{-1} for soluble manganese. Based on the exposure data and the freshwater PNEC derived for this study, the distributions of risk characterisation ratios using the probabilistic approach indicates that two thirds of manganese processing sites would not be expected to pose a potential risk to the local aquatic environment due to wastewater emissions, although local risks are possible at some sites.

1. Introduction

Manganese is a naturally occurring essential element, and as such natural background concentrations of manganese are present in the environment, which need to be taken into account in risk assessment analysis. Organisms can regulate internal manganese concentrations, however if external concentrations become too high or too low this internal regulation is not sufficient, leading to toxicity at high concentrations or deficiency at low concentrations.

Environmental risk assessments are required to ensure the safe use of products, demonstration of responsible environmental stewardship and often for regulatory purposes (ICMM, 2007). Although risk assessment approaches can vary in different countries and jurisdictions, the basic principles of a risk assessment remain the same; exposure assessment, hazard assessment and risk characterisation. The process is iterative, with revisions to the hazard and exposure assessment possible if an acceptable level of risk cannot be demonstrated based on default data. An assessment of sites producing and using manganese compounds has therefore been conducted as part of a global environmental risk assessment.

The exposure assessment is undertaken to determine a predicted environmental concentration (PEC) for the substance being assessed, for the environmental compartments of interest (e.g fresh or marine water, sediment). The PEC for each environmental compartment is determined based on emissions of the substance, taking into account any treatment carried out on-site or at a municipal wastewater treatment plant (WWTP), dilution in the receiving water and behaviour of the substance in the

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http://dx.doi.org/10.1016/j.neuro.2016.04.011
0161-813X/

environment, based on the partitioning characteristics. There are default values that can be used in the exposure assessment if site-specific data are not available, for example emission factors can be included based on specific environmental release categories (SpERCs) which are determined for different uses based on sector data, and default dilution factors can be used if information on the receiving water is not known (ECHA, 2012). However, these default values provide a reasonable worst case assessment for some sites and using site-specific data allows a more accurate assessment of the processes occurring at the site. In addition to these direct site discharges, which are often regulated, indirect discharges, via leaching or wind-blown dust, can also occur. These indirect emissions can be much harder to quantify, but sources of potential emissions can be identified and compared between sites.

The aim of this risk assessment was; using site-specific data for a number of different manganese production and use sites develop a generic risk assessment for manganese production and use. The outcomes of the assessment are to be used to identify potential unacceptable risks, the key factors that drive the characterisation of the potential manganese risks and where mitigation measures and best-practices might be best targeted.

2. Methods

A questionnaire was developed and sent to manganese mining and processing facilities across the world in order to obtain information on manganese uses and emissions. The questionnaire was designed to be applicable to different types of manganese uses, but also to be site-specific. The questionnaire covered site information, processes involving manganese that are applicable to the site, manganese tonnage per use and releases of manganese to water.

The risk assessment is focussed upon manganese, irrespective of the original manganese compound – the source; therefore emissions data was collected based on manganese concentrations only. Only emissions to the water compartment were considered, as emissions data to soils or sediments tends to be rarely documented by industrial sites and therefore, it was likely to deliver too few data to undertake a robust assessment. The questionnaire collected information on the manganese substances used at the site, and their tonnages, and the processes occurring at the site (e.g. mining, smelting, alloying, or production of compounds). Questions included whether releases to water occur from the site, whether there are discharge limits for manganese from the site, information on any treatment of water emissions (either on-site or off-site at a municipal Wastewater Treatment Plant (WwTP)), the fate of sludge from any on-site waste water treatment, whether any measured emissions data for manganese was available, and information on background manganese concentrations and other potential sources of manganese in the surrounding area. It was understood that not all sites would be able to complete every section of the questionnaire and therefore participants were encouraged to provide as much information as possible, and to add additional comments if a question was not directly applicable to their site.

The approach to waste management at some sites is to contain the waste materials on-site using settlement or evaporation ponds. This approach is especially common at mining sites, but is also used by some manganese processing sites. Sites of this type were not directly included in the aquatic environmental risk assessment because they do not have any regular direct emissions of manganese into surface waters.

The exposure assessment follows a probabilistic approach, both to reflect the distribution of emissions of manganese to the environment from manganese processing sites, and also to maintain the confidentiality of site specific data. The exposure assessment approach followed current European guidance for industrial chemicals (ECHA, 2012). The input frequency distributions were set to reflect as closely as possible the distribution of site specific values provided by the individual sites, and the input parameters used are detailed in Table 1. The probabilistic calculations were performed using Oracle Crystal Ball (release 11.1.2.3.000).

The probability distributions assumed for each of the input parameters was selected based upon the dataset reported by the individual sites in order for the predicted results to best reflect the range of potential exposures posed by manganese processing industries. In several cases triangular distributions were used because the range and diversity of the actual values for sites could not be adequately accommodated with common statistical distributions. The fraction of manganese removed during sewage treatment could not be identified from the information provided by the sites, and this was based on existing literature information (Ward, 1978). In addition, several of the parameters were found to co-vary between sites. Where co-variation of parameters was identified it was taken into account in the probabilistic calculations using the correlation coefficients derived from the site data.

For the hazard assessment, using a threshold derived under one particular piece of legislation was not considered to be appropriate. Instead, a hazard dataset was compiled based on chronic, reliable and relevant ecotoxicity data for a wide range of species representative of different environments. The foundation of the dataset was the Environmental Quality Standard (EQS) under the Water Framework Directive in the (Peters et al., 2010). However, additional data generated since this review were identified and as the focus of this evaluation is a global risk assessment, including data generated by the Australian Government (Harford et al., 2014). The data points used in the generation of the PNEC are shown in Table 2. The method of PNEC derivation for the aquatic environment followed the current European guidance for industrial chemicals (ECHA, 2008).

3. Results

Questionnaire responses were received from thirteen sites, in Europe, Asia, Africa and Australasia.

The information received from manganese processing sites indicated that there is a range of tonnages of manganese which are processed annually by individual sites, covering a range of between approximately 1000 and 1000,000 t of manganese per year. Annual

Table 1
Parameters of distributions of input parameters for the probabilistic exposure assessment.

	Tonnage of manganese used on site (tonnes/year)	Annual emission of manganese to wastewater	Effluent flow rate (m3/day)	Mean emission concentration	Mean fraction of influent manganese released in the effluent	Flow rate of final receiving water
Distribution	Triangular	Triangular	Uniform	Log-normal	Normal	Triangular
Minimum	1000	100	10	Mean 2, standard	Mean 0.55, standard deviation 0.1	100
Likeliest	100000	500	–	deviation 2		4000
Maximum	1000000	10000	1000			400000