Assessing the potential terrestrial risks from manganese

Three previous fact sheets have described the advance in understanding of the fate and behaviour of manganese in freshwaters, with a focus on accounting for bioavailability in order to produce more realistic estimates of potential ecological risks. This fact sheet is focused upon the soil or terrestrial compartment and summarises the findings of a recent scoping study performed by UK, Australian and Chinese scientists to assess the regulatory and technical value of undertaking an investigative testing programme to develop a terrestrial limit value for manganese also based on bioavailability.

1. Introduction

Manganese is a naturally occurring and abundant element that is essential in biological systems. Historically, much of the research effort on manganese in soils has been on understanding soil factors leading to deficiencies in crop plants that result in yield reduction. However, manganese can also be toxic to plants and soil organisms at certain concentrations and under certain soil conditions.

Regulatory interest in the assessment of the potential risks to soil from manganese exposures has increased with increasing anthropogenic activity and industrial development. A recent study by Herndon et al.\(^1\) estimated that aerial deposition from anthropogenic sources contributed 50% of the manganese in EU soils and 60% in US soils. However, these estimates greatly exceed those predicted from regulatory exposure models based on manganese production and use data.

Nevertheless, as with all metals, there are some familiar challenges for those attempting to derive limit values to assess potential terrestrial risks, including the variability of ambient soil background concentrations, the changing form and subsequent ecotoxicology of manganese with changing soil conditions and the poor relationship between standard ecotoxicity test data for all trophic levels and the reality in the field. The influence of speciation (form) and soil properties on metal behaviour are well established through extensive research and development programmes undertaken by several other metals commodity groups (copper, nickel, zinc, lead, cobalt)\(^2\) in order to meet European regulatory drivers. However, some of the methods used in these programmes may not be wholly applicable to manganese.

2. Background concentrations of manganese in soils

Natural background concentrations of manganese in soils are, like other metals, highly variable (Figure 1). However, unlike many other metals, there tends not to be a strong relationship between total soil manganese and parent material due to the reduction and oxidation facilitated mobilisation and precipitation behaviour of manganese in soils.

Despite the variability of soil manganese background concentrations from different continents, the median concentrations are of a similar order of magnitude and the mean manganese concentrations of Chinese and European topsoils are relatively close.

Table 1. Concentrations of manganese in topsoils in Europe, Australia and China.

<table>
<thead>
<tr>
<th></th>
<th>GEMAS European topsoils(^4)</th>
<th>Australian topsoils(^3)</th>
<th>Chinese topsoils(^5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum</td>
<td>2</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>Maximum</td>
<td>14969</td>
<td>14969</td>
<td>5888</td>
</tr>
<tr>
<td>Median</td>
<td>445</td>
<td>279</td>
<td>540</td>
</tr>
<tr>
<td>Mean</td>
<td>564</td>
<td>-</td>
<td>583</td>
</tr>
<tr>
<td>Number of samples</td>
<td>4210</td>
<td>-</td>
<td>4094</td>
</tr>
</tbody>
</table>

3. How does manganese behave in soils?

In soils both Mn\(^{3+}\) and Mn\(^{4+}\) are only stable in the soil solid-phase as poorly soluble and therefore relatively immobile (hydr)oxide minerals. Under anaerobic or acidic soil conditions (pH <6) mobile Mn\(^{2+}\) is released from these

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minerals, either into solution or in readily exchangeable forms. It is these latter forms of manganese that can be considered to be bioavailable and so potentially toxic to soil organisms.

Solid-solution partitioning ($k_p$) is often used to describe the mobility of reactive solutes in solution, accounting for both adsorption and precipitation reactions. A low $k_p$ indicates that the reactive solute does not interact strongly with the soil solid phase. For manganese, at high soil pH the dissolved Mn$^{2+}$ concentration is independent of the total soil manganese and $k_p$ will increase with increasing total soil manganese concentration, whereas at low pH the dissolved manganese concentration will be proportional to the total soil manganese and $k_p$ will be independent of the manganese in the soil. Relationships have been developed following the schematic shown in Figure 2, from which the manganese concentration in solution and partitioning ($k_p$) can be predicted from total soil manganese and pH for European soils.

These relationships show a rapid decline in solution manganese concentrations, and increase in $k_p$ with increasing soil pH (3.5 - 7.5) at soil concentrations up to 3200 mg kg$^{-1}$. However, these relationships only hold for aerobic soils, as under saturated or waterlogged conditions Mn$^{3+}$ and Mn$^{4+}$ oxides may be reduced therefore increasing the Mn$^{2+}$ solution concentration and so potentially manganese bioavailability. The reduction of manganese oxides and potential increase in dissolved Mn$^{2+}$ can occur relatively rapidly (in days) resulting in ecotoxicity symptoms very quickly. It is also important to note that even at natural background concentrations under certain soil conditions (low pH and/or relatively high water content) manganese toxicity may be observed in soil organisms.

4. What are the options for deriving a terrestrial limit value for manganese?

Despite the relatively long history of studying the (mostly deficiency) effects of manganese in soils there are relatively few reliable or relevant ecotoxicity data when compared to other metals (e.g. zinc). The most studied trophic level is plants, with some invertebrate tests and no soil microbial function tests. Furthermore, there is relatively poor predictability of soil measures of manganese availability, such as chemical extractants, to plants with differences attributed to plant species, variety and genotype factors. Therefore, deriving a single value for manganese through which the terrestrial ecosystem can be protected is clearly a challenge. Those values that have been derived, including under the REACH regulations, are below the background concentrations of most soils making their use in the assessment of potential risks relatively limited$^7, 8$. It has been acknowledged by the WHO that, due to the highly variable natural background concentrations and the dramatic influence of transient water logging and pH changes on manganese speciation, deriving a single guidance value for the terrestrial environment is inappropriate$^9$. 

5. Summary

At this time, with the current knowledge and understanding of the fate and behaviour of manganese in soil and with the paucity of reliable ecotoxicity data, an extensive ecotoxicity testing programme, as undertaken for other metals, may not deliver to any clear regulatory endpoints. Clear challenges remain in relation to differentiating between manganese added to soils from anthropogenic sources and natural manganese and the relatively rapid change in toxicity status of manganese in soils with soil water status. Regulatory organisations in China and Australia have a pragmatic view of the assessment of terrestrial risks from manganese exposures and are likely to be informed by the scientific evidence available. They are therefore unlikely to adopt an unimplementable limit value for manganese.

Further information:
There are more fact sheets in this series: Fact Sheet 1. The derivation of limit values for manganese and its compounds in freshwaters: data availability. Fact Sheet 2. Construction of the biotic ligand models for manganese, and Fact Sheet 3. Accounting for bioavailability in assessing potential risks of manganese in freshwaters, and can be found at: http://www.manganese.org. For more information contact ohes@manganese.org.

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$^7$http://www.esdat.net/Environmental%20Standards/Australia/NEPM%20Tables.pdf