Environmental Issues of Zinc

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INTRODUCTION

It is well established that the risks of excessive Zn in the environment (soils, waters) is related to its effect on primary production. Zinc toxicity to plants starts at soil total Zn concentrations as low as 50 mg Zn/kg in soils with low cation exchange capacity. Toxicity of Zn to algae in soft waters with low dissolved organic matter concentrations starts at about 20 µg Zn/L (Heijerick *et al.*, 2002). Such thresholds appear in the range of natural background concentrations encountered in the environment. The toxicity on primary production limits excessive Zn transfer via the food chain, therefore Zn toxicity to mammals, birds or humans via the environment less relevant than that to primary production. In the environment, Zn toxicity is often found around pyrometallurgic Zn smelters or in the vicinity of mining sites. The development of Zn tolerant biota (plants and soil microorganisms) in such environments is the evolutionary response to Zn toxicity. Gradual addition of Zn to agricultural soils through applications of sewage sludge or animal manure leads to more subtle Zn effects on soil biota. However, the long-term build up of soil Zn from agronomic application requires that limits must be imposed to warrant soil quality in the future. Soil limits, as a reflection of Zn toxicity, range widely across jurisdictions (Table 1). The use of Zn supplements in animal food is a major diffuse route of Zn to soil in areas with intensive animal production. However, sewage sludge is a more important vector of Zn in soils where it is applied. Sewage sludge often contains over 1000 mg Zn/kg dry weight and adverse effects on soil biota have been reported after repeated applications.

ZINC TOXICITY AS AFFECTED BY BIOAVAILABILITY

Total soil Zn concentrations are not predictive for toxicity on soil organisms. Toxicity of Zn in sewage sludge is confounded by the beneficial effects of nutrients and organic matter and because of co-contaminants. The assessment requires several reference treatments to exclude these confounding factors. More in general, three main processes affect the toxic limits of Zn to a soil organism: (i) the differences in soil properties in soils when soils are spiked with a readily available form of Zn (e.g. $ZnSO_4$); (ii) the effects of long-term ageing on Zn bioavailability and the Zn speciation in environmentally contaminated soil (Figure 1); (iii) the adaptation of soil organisms to Zn, e.g. soil microbial activities that may be restored when communities adapt. Leaving aside the adaption process, we now have evidence to state that ecotoxicity of Zn is related to the free ion activity of Zn^{2+} in soil, however this is modified by the concentrations of ions that compete with Zn^{2+} in solution for exerting toxic effects on biota. This means that soil solution Zn^{2+} , in contrast with total soil Zn, becomes *more* toxic at low concentrations of H^+, i.e. as pH rises. This is the basis of the terrestrial *Biotic Ligand Model (BLM),* i.e. ion competition effects affecting the free Zn^{2+} in solution often counteract those at the biotic ligand. The BLM concept was adopted in an empirical model (Smolder set al. 2009) predicting that Zn toxicity decreases by ageing after spiking and decreases with increasing soil cation exchange capacity. As a result, soil limits calibrated to >100 toxicity tests have been derived and total soil Zn limits range 30-300 mg Zn/kg depending on soil properties (Table 1).

Table 1. A selection of soil Zn limits in various jurisdictions. Geological background values range 5-150 mg Zn/kg, with global estimated means about 50 mg Zn/kg. Ecological Soil Screening Limits (ECOSSLs) or predicted no-effect concentrations (PNEC) are derived to evaluate current emissions and should not be considered as clean-up values since the degree of protection is large (i.e. conservative limits).

Legislations	Protection goal	Soil Zn limit (and name)	Reference
US-EPA-2005	Plants	160 mg kg^{-1} ECOSSL	[1]
US-EPA-2005	Soil invertebrates	120 mg kg^{-1} ECOSSL	[1]
EU-risk of chemicals - 2008	Plants, invertebrates, soil microorganism	30-300 mg kg^{-1} PNEC	[2]Range based on soil cation exchange capacity and soil pH
EU countries, Switzerland, USA and Canada	Unknown	100-23000 mg kg^{-1} clean up values for residential areas 360-100000 mg kg^{-1} clean up values for industrial landuse	[3]
UK sludge amended soils	Soil microorganism	200 mg kg^{-1}	[4](based on survival data of rhizobia
EU-sewage sludge limits 86/278/EEC	Unknown	150-300 mg kg^{-1}	[5]

[1.]US-EPA (2005). Ecological Soil Screening Levels for Zinc; [2.]EU (2008). *European Union risk assessment report. Zinc metal. Part I Environment*.; [3]Provoost, J., Cornelis, C., & Swartjes, F. (2006). *Journal of Soils and Sediments, 6*, 173-181.; [4]DoE (1996). Code of Practice for Agriculture Use of Sewage Sludge. DoE Publications, UK. [5]EU (1986). EU sludge directive 86/278/EEC (European Commission).

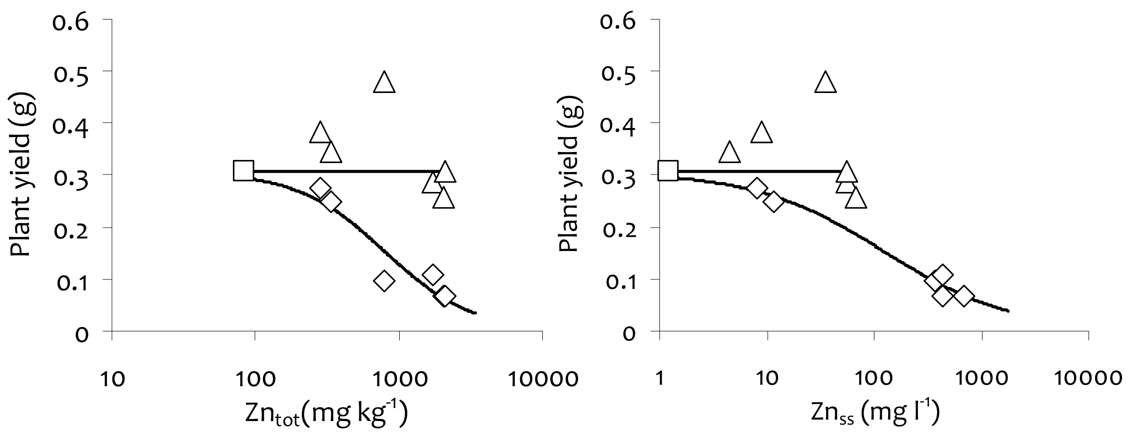

Fig. 1 Difference in Zn toxicity between freshly spiked (diamonds) and long-term contaminated soils under a galvanized pylon (triangles). The uncontaminated control soil is indicated with a square. Toxicity is larger in freshly spiked soils than in soils when expressed as total soil Zn (left) but differences disappear when expressed on a soil solution (Zn_{ss}) basis (right; Smolders&Waegeneers, unpublished data).

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