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Research article

Derivation of ecological criteria for copper in land-applied biosolids and biosolid-amended agricultural soils

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ABSTRACT

The difference in availability between soil metals added via biosolids and soluble salts was not taken into account in deriving the current land-applied biosolids standards. In the present study, a biosolids availability factor (BAF) approach was adopted to investigate the ecological thresholds for copper (Cu) in land-applied biosolids and biosolid-amended agricultural soils. First, the soil property-specific values of $HC5_{add}$ (the added hazardous concentration for 5% of species) for Cu^{2+} salt amended were collected with due attention to data for organisms and soils relevant to China. Second, a BAF representing the difference in availability between soil Cu added via biosolids and soluble salts was estimated based on long-term biosolid-amended soils, including soils from China. Third, biosolids Cu $HC5_{input}$ values (the input hazardous concentration for 5% of species of Cu from biosolids to soil) as a function of soil properties were derived using the BAF approach. The average potential availability of Cu in agricultural soils amended with biosolids accounted for 53% of that for the same soils spiked with same amount of soluble Cu salts and with a similar aging time. The cation exchange capacity was the main factor affecting the biosolids Cu $HC5_{input}$ values, while soil pH and organic carbon only explained 24.2 and 1.5% of the variation, respectively. The biosolids Cu $HC5_{input}$ values can be accurately predicted by regression models developed based on 2–3 soil properties with coefficients of determination (R^2) of 0.889 and 0.945. Compared with model predicted biosolids Cu $HC5_{input}$ values, current standards (GB4284-84) are most likely to be less protective in acidic and neutral soil, but conservative in alkaline non-calcareous soil. Recommendations on ecological criteria for Cu in land-applied biosolids and biosolid-amended agriculture soils may be helpful to fill the gaps existing between science and regulations, and can be useful for Cu risk assessments in soils amended with biosolids.

1. Introduction

Land application of biosolids is commonly recognized as a promising practice for its disposal and returning valuable nutrients and organic matter to reclaim degraded soils and improve crop growth (Bernal et al., 1998). However, essential elements such as copper (Cu) in agricultural soils are of increasing concern due to repeated applications of biosolids, which increases soil concentrations of these elements to potentially toxic levels. Despite the fact that the bioavailability and/or toxicity of biosolids-borne elements decreases with increased metal binding sites in soils, and with time due to attenuation (Ma et al., 2006a, 2006b; Smolders et al., 2009), ecological risks of land-applied biosolids remain existing (McBride, 2003).

China's national land-applied biosolids standards (GB4284-84, Environmental Protection Leading Group of the State Council, 1984) are based on soil pH only, and consist of a maximum allowable Cu concentration in the biosolids (e.g. 250 mg Cu/kg biosolid for soil pH < 6.5, and 500 mg Cu/kg biosolid for soil pH ≥ 6.5, on biosolid dry weight basis), which largely follows the China national environmental quality standards for agricultural soils (e.g. 50 mg Cu/kg soil at pH < 6.5, 100 mg Cu/kg soil at pH ≥ 6.5, GB15618-1995, State

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Environmental Protection Administration Council, 1995). The plant availability of Cu in soils previously amended with heavy applications of sewage sludge was affected by total soil Cu concentration, soil pH and clay content in soil (Hooda et al., 1997). The phytotoxicity of soil Cu added as soluble salts was affected mainly by soil cation exchange capacity (CEC) in a wide range of European soils (Rooney et al., 2006) and mainly by soil pH, organic carbon (OC) and CEC in a wide range of Chinese soils (Li et al., 2010). Furthermore, GB15618-1995 does not consider metal and contaminant concentrations in agricultural soils amended with biosolids in which the bioavailability of metals is lower than in metal salt amended soils, the latter being the basis of soil regulations (Smolders et al., 2012).

In recent years, the ecological criteria for Cu in agricultural soils, expressed as predicted no effect concentrations (PNEC), were derived using quantitative normalization relationships between soil properties and Cu bioavailability, toxicity and uptake by organisms, expressed as the hazardous concentration for 5% of species (HC5), extrapolated using species sensitivity distribution (SSD) methods (Smolders et al., 2009; Heemsbergen et al., 2009). All of these studies were carried out by spiking soils with soluble Cu salts, and thus the PNEC outcomes might be unsuitable to regulate the same soils amended with biosolids, which might result in over-protection. The bioavailability of Cu in soils amended with biosolids is typically less than for Cu in soils spiked with soluble Cu salts, even after correcting for differences in equilibration time in soil (Heemsbergen et al., 2010; Oliver et al., 2004). This is due to the presence of mineral or organic particulates to which the metals bind, i.e. binding material is added along with the biosolids (Hooda and Alloway, 1994). It is therefore important to benchmark the eco-toxicological effects of Cu in biosolids with those from soluble Cu salts, preferably under conditions that mimic the field environment, by quantifying the difference between the bioavailability of Cu from biosolids and that from soluble salts. One such option is to develop a translator, i.e. a factor expressing the difference in bioavailability between salt spiked soils and biosolid-amended soils.

There are several methods to estimate the bioavailability of metals in soils (McLaughlin et al., 2000). In general, measuring metal concentrations in organism tissue is most likely to critically reflect the real level of metal uptake by soil biota such as plants and invertebrates. The isotopic dilution technique is a method that quantifies the relative availability of a metal salt, added as an isotope, compared to the total concentration in the soil. This method allows to develop a translator, termed biosolids availability factor (BAF), provided that it is applied to biosolid amended soils and corresponding metal salt spiked soils (Smolders et al., 2012). This method can give an assessment of long-term availability of metals in biosolids amended soils (Merrington et al., 2003; Oliver et al., 2004).

This study was set up to develop ecological criteria for Cu in land-applied biosolids and biosolid-amended agricultural soils by implementing a biosolids availability factor (BAF) into the existing ecological criteria for Cu in agricultural soils with due attention to the Chinese situation.

2. Materials and methods

2.1. Framework for deriving ecological criteria for Cu in land-applied biosolids and amended soils

The proposed framework is presented in Fig. 1. In brief, the procedures included, first, the collection of Cu-salts $HC5_{add}$ values (HC5 values expressed as added Cu to soils), along with soil properties of different scenarios. These added risk approach-based values are produced from normalized $EC10_{add}$ (the added Cu concentrations that cause 10% toxicity effect on soil biota during a specified time interval) values of Cu in soils spiked with soluble Cu salts. The $HC5_{add}$ is derived using the species sensitivity distribution method, which is more advanced than the traditional method for derivation of ecological soil standards. The HC5 was corrected by leaching and aging factors to represent the availability of Cu in long-term equilibrated soils (Wang et al., 2015). The second step is the estimation of a BAF accounting for the difference in availability between Cu added as soluble salts and biosolids in the same soils with similar aging times. The third step is the derivation of biosolids Cu $HC5_{input}$ values as a function of soil properties by dividing the Cu-salts $HC5_{add}$ values by the corresponding BAF value. Finally, the PNECs were calculated. This approach is similar to the one suggested by others (Heemsbergen et al., 2009) for developing guidelines controlling metal and contaminant concentrations in biosolids and biosolid-amended soils.

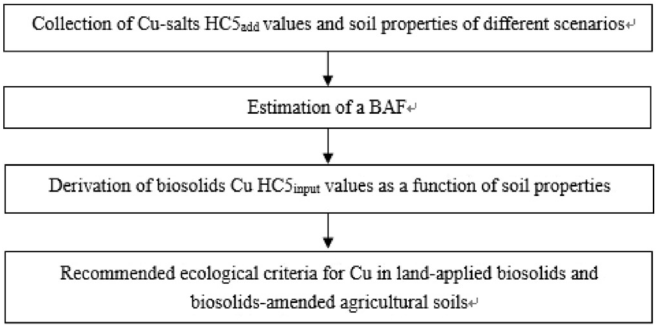

Fig. 1. Overview of the proposed framework for deriving ecological criteria for Cu in land-applied biosolids and biosolid-amended agricultural soils.

2.2. Collection of eco-toxicological data for Cu added as soluble salts

The Cu-salts $HC5_{add}$ values along with soil properties of different scenarios, used to derive the ecological criteria for Cu in land-applied biosolids and biosolid-amended agricultural soils, were collected from Wang et al. (2015) and shown in Table 1. Correction of leaching/aging effect on Cu-salts $HC5_{add}$ values and field trial data validation were also considered by Wang et al. (2015).

2.3. Estimation of BAF

BAF represents the difference in partitioning of isotopically exchangeable Cu added from biosolids and soluble Cu salts

Table 1
The calculated Cu-salts $HC5_{add}$ values (in mg Cu/kg soil) according to the regression equations of the $HC5_{add}$ values as a function of soil properties (Wang et al., 2015).

pH	OC (%)	CEC (cmol/kg)		
		5	15	30
		Cu-salts $HC5_{add}$ value (mg/kg)		
5.5	1	9.4	24.8	39.7
	4	10.2	26.8	48.5
7	1	13.8	33.9	49.0
	4	13.4	36.8	68.2
7.5	1	15.9	36.5	50.5
	4	14.9	41.4	75.7

Note: the pH is soil pH (1:5 H_2O); OC is organic carbon (%), CEC is cation exchange capacity (cmol/kg) and Cu-salts $HC5_{add}$ is the hazardous concentration for 5% of the biota species when exposed to soluble Cu salt added to soils (mg/kg).