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Evaluation of bioavailability of light rare earth elements to wheat (*Triticum aestivum L.*) under field conditions

Jing Fang, Bei Wen, Xiao-Quan Shan *, Huan-hua Wang, Jin-ming Lin, Shu-zhen Zhang

State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, China

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Abstract

Current bioavailability assessments of light rare earth elements (LREEs) are often carried out under greenhouse conditions. This work was to identify which soil properties are mostly related to LREE bioavailability and what extraction method is the most promising approach for assessing bioavailability of LREEs to wheat under field conditions. A comparison was made between four commonly used extractants (DTPA, EDTA, $CaCl_2$ and CH_3COOH), and the results suggested that the LREE concentrations in wheat roots significantly correlated with soil pH and amorphous Fe oxide contents in soils, but were independent of soil organic matter (SOM), crystalline Fe and Mn oxide contents, and cation exchange capacity (CEC). The contents of LREEs in shoots were independent of any soil properties. Both DTPA- and EDTA-extractable LREEs were significantly correlated to LREE concentrations in wheat roots and shoots. DTPA extractable LREEs were comparable to LREEs in wheat roots, however, the EDTA exctractable LREEs overestimated the LREE accumulation in wheat roots. Neither root nor shoot LREEs showed significant correlation with CH_3COOH extractable LREEs, suggesting that the CH_3COOH extraction method was not suitable for predicting LREE bioavailability. $CaCl_2$ method was unable to estimate the LREE bioavailability due to poor data distribution in correlation analysis. Overall, DTPA extraction method was preferred to other extraction methods for estimating bioavailability of LREEs to wheat.

Keywords: Light rare earth elements; Extraction method; Bioavailability; Wheat; Field study; Soil properties

1. Introduction

Fertilizers containing rare earth elements (REEs) with predominant proportion La and Ce are widely used in agriculture in China in order to increase crop yields of some plant species, particularly if moisture is limited (Xu et al., 2002; Shtangeeva, 2004). Since 1990s, millions of tons of such fertilizers have been applied. As a result, REEs in China have been found to be accumulated in soils, crops, and enter the food chain (Chua et al., 1998; Wen et al., 2001). Others sources (sewage sludge, incinerator bottom ashes and rainwater) can also contribute to environmental contamination by REEs (Zhang et al., 2001; Zhang and Liu, 2004). The adverse health effect and potential detrimental environmental issue caused by REEs are concerned by environmental scientists. Possible health risks for humans could not be excluded and health status of children should be examined from health risk assessment perspective in rare earth mining areas (De Boer et al., 1996; Tong et al., 2004). High concentrations of REEs may cause significant damage to ecosystem (Barry and Meehan, 2000). Some studies also focused on the toxic effects of REEs to plants from occupational and environmental exposures and the long-term hazardous environment effects (Sax, 1984; Suzuki et al., 1992). To evaluate the ecotoxicological risks of REEs, the first step is to estimate the bioavailability of REEs.

REE bioavailability is measured by assessing the proportion of REEs that is accumulated by an organism or that can cause a biological response. It is the common concept nowadays that total concentration of metals in soils is not a good indicator of bioavailability, and a good tool for potential risk assessment neither (Qian et al., 1996; Chen et al., 1996). Extraction procedures using a selective chemical extractant, such as strong chelating agents, mild neutral salts, organic or inorganic acid

* Corresponding author. Tel.: +86 10 62923560; fax: +86 10 62923563.
E-mail address: xiaoquan@rcees.ac.cn (X.-Q. Shan).

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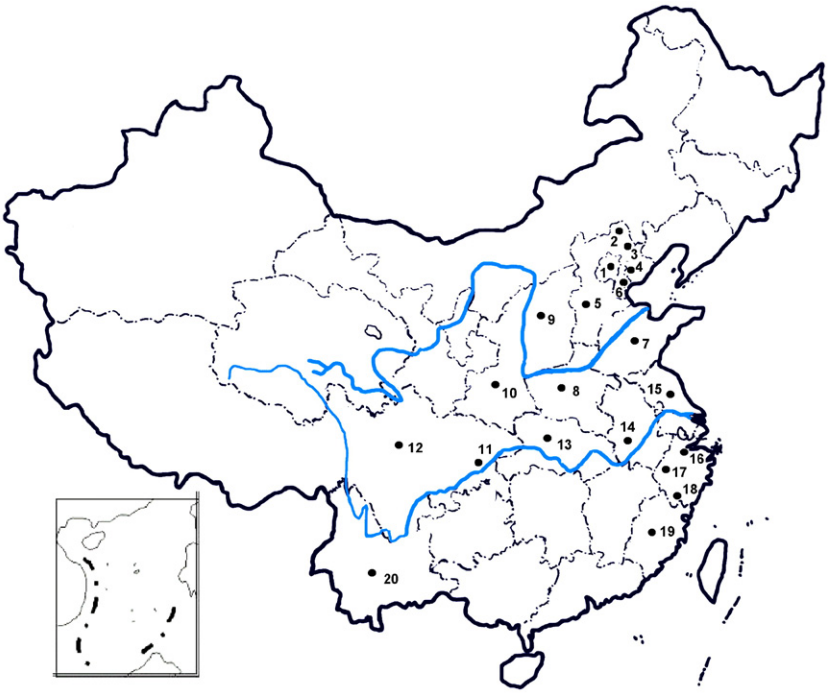

Fig. 1. Soil and wheat sampling locations. (1) Beijing, (2) Hebei 1, (3) Hebei 2, (4) Hebei 3, (5) Hebei 4, (6) Tianjin, (7) Shandong, (8) Henan, (9) Shanxi, (10) Sha'anxi, (11) Chongqing, (12) Sichuan, (13) Hubei, (14) Anhui, (15) Jiangsu, (16) Zhejiang 1, (17) Zhejiang 2, (18) Zhejiang 3, (19) Fujian, (20) Yunnan.

(Lu et al., 2003; Wang et al., 2003; Wang et al., 2004) could provide information on the potential mobility and bioavailability of REEs. Bioavailability of REEs depends on the chemical speciation of REEs in soils and plant species (Zhang and Shan, 2001; Hu et al., 2002; Wang et al., 2004). Shan et al. (2003) found that REEs in the labile rhizosphere soil solution, including free metal ions and inorganic and organic complexes, were mostly bioavailable. REEs in water soluble, exchangeable and carbonate bound fractions were significantly correlated with REE uptake by wheat (Wang et al., 2001) and alfalfa (Cao et al., 2000). $CaCl_2$ and CH_3COOH extracted REEs were reported to be best correlated with REE contents in shoots of wheat (Lu et al. 2003). 0.1 mol l^{-1} HCl gave a good estimate of the wheat available REEs in soils (Li et al. 2001). A mixture of malic and citric acids could be also used as a predictor of available REEs (Zhang et al. 2000). The above studies were inconsistent and made comparisons difficult. However, most of the results were obtained under greenhouse conditions. Extrapolation of the results to the field might be problematic due to the complicated growth conditions. Therefore, the aims of this work are (1) to identify which soil properties are mostly related to LREE bioavailability; (2) to search for the most efficient extraction method for evaluation of LREE bioavailability to wheat under field conditions by comparing EDTA, DTPA, $CaCl_2$ and CH_3COOH extraction methods.

2. Materials and methods

2.1. Soil and wheat samples

Twenty cultivated surface soils and the corresponding wheat seedlings from the same field were collected from 15 different Chinese provinces during February 2005 (Fig. 1). Within each sampling unit, both soil and wheat subsamples were taken from several different locations (5–10 locations, depending on the uniformity and size of the sampling unit), and were mixed into one composite sample. Moist soils and wheat samples were preserved separately in polyethylene bags during transport to the laboratory. All wheat seedlings were cut to the size of 3–7 cm for

Table 1
Extraction procedures used in this study

Extractant	Procedure	Fraction	Reference
$CaCl_2$	2.00 g soil was mixed with 20 ml 0.01 mol l^{-1} $CaCl_2$ in a 50 ml plastic centrifuge tube, and shaken for 3 h	Easily exchangeable	Novozamsky et al. (1993)
CH_3COOH	1.00 g soil was mixed with 20 ml 0.11 mol l^{-1} acetic acid in a 50 ml plastic centrifuge tube, and shaken for 16 h	Exchangeable and carbonate bound	Ure et al. (1993)
EDTA	2.00 g soil was mixed with 20 ml 0.05 mol l^{-1} EDTA and its pH was adjusted with ammonia solution to 7.0 in a 50 ml plastic centrifuge tube, and the suspension was shaken for 1 h	Organically bound and metals occluded in oxides and secondary clay minerals in part	Wear and Evans (1968)
DTPA	10.0 g soil was mixed with 20 ml 0.005 mol l^{-1} DTPA+0.01 mol l^{-1} $CaCl_2$+0.01 mol l^{-1} TEA, pH of suspension was adjusted to pH 7.3 in a 50 ml plastic centrifuge tube, and shaken for 2 h	Iron and manganese oxides bound	Lindsay and Norvell (1978)