



# Effects of alternating wetting and drying versus continuous flooding on chromium fate in paddy soils



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## ABSTRACT

Anthropogenic chromium (Cr) pollution in soils poses a great threat to human health through the food chain. It is imperative to understand Cr fate under the range of conditions suitable for rice growth. In this study, the effects of irrigation managements on dynamics of porewater Cr(VI) concentrations in rice paddies and Cr distribution in rice were investigated with pot experiments under greenhouse conditions. Soil redox potential in continuous flooding (CF) treatments showed that reducing conditions remained for the whole duration of rice growing period, while soil redox potential in alternating wetting and drying (AWD) treatments showed that soil conditions alternately changed between reducing and oxic. As soil redox potential is an important factor affecting Cr(VI) reduction in paddy soils, dynamics of Cr(VI) concentration were clearly different under different irrigation managements. In CF treatments, porewater Cr(VI) concentrations decreased with time after planting, while in AWD treatments porewater Cr(VI) concentrations were increased and decreased alternately response to the irrigation cycles. Chromium(VI) concentrations in the CF treatments were lower than those in AWD treatments for most part of rice-growing season. Moreover, Cr concentrations in rice tissues were significantly influenced by irrigation with relatively higher values in the AWD treatments, which might be attributed to the higher porewater Cr(VI) concentrations in AWD treatments. Therefore, it would be better to use CF than AWD management in Cr-contaminated paddy soils to reduce Cr accumulation in rice, and thus to reduce the potential risk to human health.

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## 1. Introduction

As the 21st most abundant element in Earth's crust (Barnhart, 1997), chromium (Cr) has been extensively used in industrial activities such as ore refining, electroplating industry, tanning, paper making, steel production and automobile manufacturing (Francisco et al., 2002). As a consequence, there is a continual influx of Cr contaminants into the environment. The most stable oxidation states of Cr in the environment are Cr(III) and Cr(VI). Chromium (III), an essential trace element for mammals (Dayan and Paine, 2001), is generally considered immobile and nonbioavailable due to the low solubility of Cr(III) (hydr)oxides at neutral pH (Rai et al., 1987). Conversely, Cr(VI) exists as highly soluble oxyanionic species, i.e.,  $\text{CrO}_4^{2-}$  (chromate),  $\text{HCrO}_4^-$  (bichromate), and  $\text{Cr}_2\text{O}_7^{2-}$  (dichromate), is a known human carcinogen (Costa and Klein, 2006). The mobility, toxicity and plant uptake of Cr depend strongly on its

oxidation states. Once released to the environment, Cr is susceptible to oxidation–reduction reactions that dramatically alter its physical and chemical properties. The reduction of Cr(VI) by Fe(II) sustained through the activity of Fe-reducing bacteria are able to couple the oxidation of organic compounds to the reduction of Fe (III) (Li et al., 2012; Liu et al., 2011).

The lack of appropriate disposal facilities has led to severe Cr pollution in waters and soils (Sethunathan et al., 2005), thus posing a great threat to human health through the food chain (Lavado et al., 2007). As rice (*Oryza sativa* L.) is the major stable food crop for nearly 40% of the world population and more than 60% of the population in China (Mae, 1997), strategies to reduce rice plant exposure to Cr are therefore urgently needed and require a detailed understanding of Cr behavior under the range of conditions suitable for rice growth.

Generally, rice cultivation is carried out in flooded paddy fields because the flooded water supplies micronutrients, washes out substances harmful to rice growth, and weakens the activities of pathogenic bacteria and fungi under the reductive conditions of the soil. However, as water shortage during the dry season of

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irrigated rice farming in Northeast China for climate change and human development (Yang et al., 2007), alternating wetting and drying (AWD) practices are commonly used as a water-saving practice in China (Cabangon et al., 2004). For AWD practices, the fields are managed as irrigated lowland rice but top soil layer is allowed to dry out to some degree before irrigation is applied again (Bouman and Tuong, 2001). The number of days under non-flooded soil conditions vary depending on plant development stages and availability of water. Compared to continuous flooding, the alternating oxic and anoxic top soil conditions imposed by AWD irrigation may lead to the dynamic changes of soil redox potential and Cr redox state, thus the mobility, toxicity and plant uptake of Cr. This makes it crucially relevant to understand the behavior of Cr in intermittently irrigated rice paddies subject to varying soil redox conditions. However, very little research has been done to investigate the impact of irrigation managements on Cr behavior in rice paddies.

The influence of AWD practice on Cr behavior as compared to conventional continuous flooding practices are generally unknown. Hence, we conducted a study with the following main objectives: (i) to determine the effects of irrigation managements on dynamic changes of soil redox potential and porewater Cr(VI) concentration; (ii) to examine whether introduced cycles of AWD affect Cr uptake by rice; and (iii) to investigate the practical use of irrigation management to reduce the potential Cr risk to human health.

## 2. Materials and methods

### 2.1. Soil sample collection and preparation

Two typical soils classified as Oxisols and Phaeozems according to World reference base for soil resources (IUSS-FAO, 2014), were collected at 0–20 cm depth from Guilin City (104°40′–119°45′E, 24°18′–25°41′N) and Ha'erbing City (126°32′–129°55′E, 44°92′–46°32′N), China. After removal of large pieces of plant materials, grit, earthworms, etc. soil samples were air-dried, ground, and passed through a 2-mm sieve prior to use. Soil samples were analyzed for total Cr (Shentu et al., 2008), Cr(VI) (James et al., 1995), pH (Chaturvedi and Sankar, 2006), cation exchange capacity (CEC) (Hendershot and Duquette, 1986), organic matter (OM) contents (Rashid et al., 2001), Fe(II) contents (Schnell et al., 1998), easily reducible Mn [Mn(ER)] contents (Bartlett and James, 1996), and particle size distribution (PSD) (Day, 1965). Relevant physicochemical properties of the soils are shown in Table 1.

The soil samples (Oxisols and Phaeozems) were spiked with Cr as  $K_2Cr_2O_7$  (with a purity > 98% from Aldrich Chemical Co.) to establish three contaminant levels of CK (background values), 200, and 400 mg Cr  $kg^{-1}$  soil. All spiked soil samples were aged for 1 year at a moisture content of 70% of water holding capacity prior to pot experiments.

### 2.2. Pot experiment

The rice (*O. sativa* L.) variety used was Zhongzheyou 1, which is a single season indica variety with an average plant height of 120 cm. This long duration variety takes about 140 days to mature. The seed of the variety was obtained from the Zhejiang Seed Company. Seeds were surface-sterilized by washing with 70% ethanol for 1 min and soaking in 0.01 g  $mL^{-1}$  sodium hypochlorite for 5 min, rinsed thoroughly in deionized water, and then imbibed in deionized water for 48 h at 30 °C (Wu et al., 2011). The seeds were germinated in quartz sand washed with 5% (v/v) HCl. For the first two weeks, only deionized water was supplied. After 14 days when seedlings grew onto two-leaf stage, nutrient solution was

**Table 1**  
Physio-chemical properties of the soils.

Soil	Oxisols	Phaeozems
<b>Chromium (mg <math>kg^{-1}</math>)</b>		
Total Cr (mg $kg^{-1}$ )	68.5 ± 2.54	65.5 ± 2.01
Cr(VI) (mg $kg^{-1}$ )	0.28 ± 0.01	0.45 ± 0.01
<b>Chemical characteristics<sup>a</sup></b>		
pH	5.03 ± 0.05	7.23 ± 0.03
OM (g $kg^{-1}$ )	19.1 ± 0.56	32.2 ± 0.34
CEC (cmol <sub>c</sub> (+) $kg^{-1}$ )	17.3 ± 1.96	34.0 ± 2.51
Fe(II) (mg $kg^{-1}$ )	34.4 ± 1.48	30.5 ± 0.56
Mn(ER) (mg $kg^{-1}$ )	2.64 ± 0.23	109 ± 5.21
<b>Soil texture</b>		
Sand (%)	10.6 ± 0.15	20.6 ± 1.54
Silt (%)	39.8 ± 1.26	60.2 ± 2.21
Clay (%)	49.6 ± 1.19	19.2 ± 1.24

<sup>a</sup> CEC, cation exchange capacity; Mn(ER), easily reducible Mn; OM, organic matter.

supplied. The composition of nutrient solution was the same as described by Yang et al. (2004).

On May 30, 2012, 4 seedlings (thirty days old) were transplanted to individual pots with a diameter of 21 cm and depth of 25 cm. Each pot had 5 kg of soil. Before transplanting, the standard recommended dose of NPK fertilizer was applied to all pots at the rates of 187.5 kg N  $ha^{-1}$  (70% applied as basal dose and 30% as topdressing at panicle initiation stage), 70 kg  $P_2O_5$   $ha^{-1}$  and 93 kg  $K_2O$   $ha^{-1}$  (Wei et al., 2012). The irrigation management factor had two levels: (1) alternating wetting and drying (AWD), the irrigation method is characterized by a mid-season drainage during the late tillering stage of the rice crop, and periodic soil drying of 2–3 days between irrigation events from panicle initiation to grain filling with water level kept at 0–2 cm above the soil surface, and the soil was not irrigated from 100 day until the harvest (Fig. 1); (2) continuous flooding (CF), in which water depth was maintained at 3 cm above the soil surface for the whole duration of the experiment (Fig. 1). All treatments were conducted in triplicate, and the pots were randomly arranged in a greenhouse under a photo flux density of 400  $\mu mol m^{-2} s^{-1}$ , a light/dark period of 16/8 h, day/night temperatures of 30/25 °C, and day/night relative humidity of 75/85% (Wu et al., 2010). Portions of fresh soil (100 g, oven-dry basis) were sampled for Cr(VI) determination at the intervals of 28, 34, 45, 48, 63, 66, 81, 84, 99, 102, 108, and 114 days after transplanting, and then soil samples were immediately stored in sealed plastic containers at 4 °C (Hopp et al., 2008). Each pot contained three permanently-installed platinum electrodes for redox measurement, placed in three pairs at the depth of 7.5 cm, and horizontally distributed around the perimeter about 1 cm from the walls (Johnson-Beebout et al., 2009). The depth was chosen to represent root-zone depth (Patrick and DeLaune, 1972). Soil redox potential was monitored on each day of Cr(VI) measurement with platinum-tipped electrodes and a portable Eh meter (EH-120; Fujiwara Scientific Company Co. Ltd., Tokyo, Japan).

Plants were harvested at maturity and air dried. Plant samples were manually threshed to separate grains, then the dry weights of grains and straws were recorded. The brown rice was prepared by removing the husk using a laboratory de-husker (JLGJ4.5, Taizhou Cereal and Oil Instrument Co. Ltd., Zhejiang, China), the polished rice was prepared by polishing the bran by a laboratory polishing machine (JNMJ3, Taizhou Cereal and Oil Instrument Co. Ltd., Zhejiang, China). The husk, brown rice, and polished rice samples were ground using a ball mill (Retsch, MM-301, Germany) and passed through a 60-mesh sieve, then keep at –20 °C prior to Cr analysis.

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