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Evaluation of soil characteristics potentially affecting arsenic concentration in paddy rice (*Oryza sativa* L.)

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Field selection for total As, poorly crystalline Fe and plant available P in soil might contribute to control As content of paddy rice.

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ABSTRACT

Paddy rice may contribute considerably to the human intake of As. The knowledge of soil characteristics affecting the As content of the rice plant enables the development of agricultural measures for controlling As uptake.

During field surveys in 2004 and 2006, plant samples from 68 fields (Italy, Po-area) revealed markedly differing As concentration in polished rice. The soil factors total $As_{(aqua\ regia)}$, pH, grain size fractions, total C, plant available $P_{(CAL)}$, poorly crystalline $Fe_{(oxal.)}$ and plant available $Si_{(Na\text{-}acetate)}$ content that potentially affect As content of rice were determined.

A multiple linear regression analysis showed a significant positive influence of the total $As_{(aqua\ regia)}$ and plant available $P_{(CAL)}$ content and a negative influence of the poorly crystalline $Fe_{(oxal.)}$ content of the soil on the As content in polished rice and rice straw.

Si concentration in rice straw varied widely and was negatively related to As content in straw and polished rice.

1. Introduction

An applicable extraction method for determination of plant available As in flooded soils does not exist. However, to evaluate the potential of a soil resulting in low or high As content in rice is of great importance since As concentration in paddy rice may contribute considerably to human intake of As (Schoof et al., 1999). Soil parameters potentially affecting As accumulation in rice are the total As content, concentration of poorly crystalline iron-(hydr)oxides, plant available P, soil texture and the plant available Si. The total As content defines the pool from which As can potentially be mobilized. It is well described in literature that arsenic is mainly bound to iron-(hydr)oxides in the soil (Inskeep et al., 2002). Due to flooding of paddy rice soil and the subsequent decrease of redox potential the bound arsenic is released. Thus, the concentration of iron-(hydr)oxides may have an influence on the As concentration in soil solution (Marin et al., 1993). In the literature a competition between phosphate and arsenate is often described because of chemical similarities. Phosphate may displace arsenate from binding sites in the soil and thus, increase arsenic availability and As uptake of plant (Sadiq, 1997). On the other hand plants take up phosphate and arsenate by the same transporter (Ullrich-Eberius et al., 1989). Therefore, phosphate may compete with arsenate for uptake which would result in a decrease of As content in the plant (Meharg and Macnair, 1990). A further characteristic affecting As concentration in rice could be the soil texture. Arsenic may be bound to hydrated surfaces and clay contains a high proportion of iron-, manganese- and aluminium-oxides at which surfaces arsenic could be bound (Sadiq, 1997). In addition to this, previous studies showed that high silicic acid concentration in soil solution as well as in nutrient solution reduced the plant As uptake (Bogdan and Schenk, 2008; Guo et al., 2007, 2005). Therefore, the plant available silicic acid content of the soil may affect the As content of rice. Besides the plant available silicic acid content in soil, the silicic acid concentration of irrigation water may influence the plant As uptake as it highly contributed to the silicic acid uptake of the Si accumulator rice (Ma and Takahashi, 2002; Desplanques et al., 2006). The aim of this study was to characterize the contribution of these soil characteristics on arsenic content of rice.

2. Materials and methods

2.1. Soil and plant samples

Soil and plant samples were taken from 33 fields in 2004 and 35 different fields in 2006. All 68 fields were located in the Po-area/Italy. The sampling was conducted from 4 random points from each field and merged to a composite sample. From each point 20 plants were harvested and soil samples were taken to a depth of 30 cm. *Oryza sativa* L. cv. Selenio was sampled which was cultivated according to the

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common agricultural practice in the Po-area. Regarding irrigation practice this means seeding onto the irrigated field. After germination the field was drained for 3–4 days to improve rooting of seedlings. Then the water table was increased up to 10 cm according to the growth of seedlings. In general, fields are kept irrigated until 2–3 weeks before harvest. Plants were harvested at maturity about 5 months after planting. Rice grains were separated from the straw which was cut 5 cm above the soil. Rice straw was dried for three days at 60 °C and milled afterwards. Rice grains were dried at 40 °C over night to reduce moisture content in order to prevent fungi infestation, then grains were processed to white rice. Soil samples were air-dried and homogenized using a jaw crusher.

2.2. Chemical analysis

Soils were characterised for particle-size distribution by fractionation using sieving and sedimentation (DIN ISO 11 277, LUFA Hameln), pH in 0.01 M $CaCl_2$ measured with a pH-Electrode (Sen Tix 41, WTW) (Schlichting et al., 1995), total As by aqua regia extraction according to DIN 38414, S7 (VDLUFA, 1991), oxalate soluble Fe according to Schwertmann (1964). The total C was analysed by a CNS-Autoanalyser (VarioEL, Elementar, Hanau, Germany). The plant available P was determined by the Ca–acetate–lactate method according to Schüller (1969). Plant available silicic acid was determined by the extraction with Na-acetate (Ma and Takahashi, 2002).

Dried and milled straw (350 µg) and polished rice (480 µg) were digested with 4 mL HNO_3 (65%) and 1.5 mL H_2O_2 (30%) in a microwave (ETHOSplus, MLS GmbH, Germany) for 20 and 15 min at 190 °C, respectively, and total As content was measured with ICP-MS 7500c (Agilent Technologies, USA).

2.3. Statistical analysis

Analysis of variance, correlation analysis and multiple linear regression were conducted by using SAS (SAS Institute INC, Cary, USA). Comparison of means was carried out according to Tukey test.

3. Results

In 2004 the total $As_{(aqua\ regia)}$ content in the soil was within the range commonly found in soils of 1–20 mg As/kg (Schachtschabel et al., 1998) (Table 1). In 2006, one field had a considerably higher As content (35.7 mg/kg). Reasons for this are not known. Furthermore, some fields with higher plant available P content were observed in 2006. The range and mean of all other characteristics were similar in both years. The Na-acetate extracted silicic acid content was only weakly related to the plant Si content (Fig. 1). This might be the reason that Na-acetate extracted Si was not significantly influencing the As concentration in straw and polished rice when it was included to the multiple linear regression analysis. However, the plant Si content was significantly negatively related to the As concentration in straw and polished rice (Fig. 2 A and B). The As concentration in polished rice ranged from 50 to 322 µg/kg with mean As concentration of 149 µg/kg (Fig. 3). The relationship between the As concentration in straw and polished rice was fairly close in both years (Fig. 3).

Simple linear regression between the determined soil characteristics and As concentration in straw or grain gave no indication for a significantly influencing factor. As the soil of field samples differed in several characteristics potentially affecting As dynamics, data were subjected to a multiple linear regression analysis. The multiple linear regression analysis revealed that the $As_{(aqua\ regia)}$ content,

Table 1
Soil characteristics of sampled soils during the surveys in 2004 and 2006.

	2004		2006	
	Mean	Range	Mean	Range
Total $As_{(aqua\ regia)}$ [mg/kg]	8.3	3.2–16.4	10.1	2.6–35.7
pH	5.7	5.0–6.4	5.8	5.1–7.4
Clay [%]	17	5–28	18.8	5.1–37.1
Silt [%]	40	16–66	41.6	17.0–70.6
Sand [%]	43	13–67	39.7	7.2–77.0
Total C [%]	1.19	0.69–1.81	–	–
Plant available $P_{(CAL)}$ [mg/kg]	43	12–79	51.1	7.3–137.8
Poorly crystalline $Fe_{(oxal.)}$ [g/kg]	4.8	1.3–9.0	5.8	1.9–11.6
$Si_{(Na\text{-}acetate)}$ [mg/kg]	35	7–95	31.9	6.6–79.0
Number of fields	33		35	

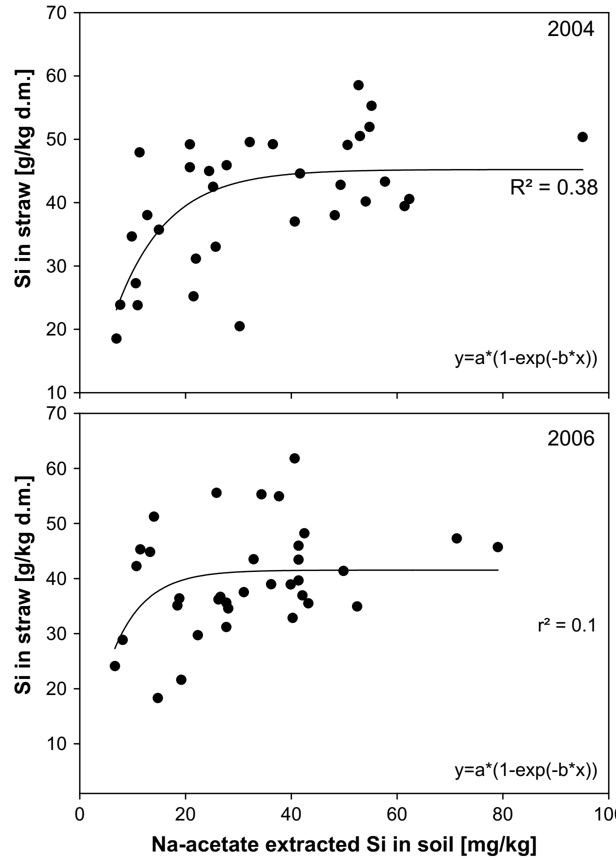

Fig. 1. Relationship between Na-acetate-extractable Si content in soil and Si concentration in straw during field survey 2004 and 2006.

poorly crystalline $Fe_{(oxal.)}$ and plant available $P_{(CAL)}$ content of the soil significantly influenced the As content in polished rice and in straw in 2004 and 2006 (Table 2). In 2006, the contribution of the soil parameters to explain the As concentration in polished rice as well as in straw was considerably lower than in 2004. For visualisation, the data calculated by multiple linear regression model in 2004 and 2006 were related to the observed As concentration in polished rice and straw in both years (Fig. 4). In order to demonstrate the effect of soil parameter variation the model of the year 2004 was used to calculate the As concentration in polished rice influenced by the total $As_{(aqua\ regia)}$ content of the soil, the poorly crystalline $Fe_{(oxal.)}$ and plant available $P_{(CAL)}$ content of the soil (Fig. 5A and B). The soil values used for these calculations are within the range of values found in the field survey 2004. An increase of total $As_{(aqua\ regia)}$ from 4 to 14 mg/kg soil resulted in an increase of 86 µg A/kg d.m. in polished rice. An increase of poorly crystalline $Fe_{(oxal.)}$ content from 2 to 8 g/kg soil decreased As content of polished rice by 104 µg A/kg (Fig. 5A), whereas the increase of plant available $P_{(CAL)}$ enhanced the As concentration in polished rice (Fig. 5B). Within the sampled soils high total $As_{(aqua\ regia)}$, low poorly crystalline $Fe_{(oxal.)}$ and high plant available $P_{(CAL)}$ did not occur in one soil at the same time.

4. Discussion

4.1. Silicic acid in the soil and the Si and As content of the plant

To evaluate the plant availability of silicic acid the Na-acetate buffer method was chosen, since Ma and Takahashi (2002) found a close linear relationship between Si content in rice straw and Si extracted by this method up to 100 mg Si/kg soil.