

Characterization of soil heavy metal pools in paddy fields in Taiwan: chemical extraction and solid-solution partitioning

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Abstract

Background, aim, and scope Ongoing industrialization has resulted in an accumulation of metals like Cd, Cu, Cr, Ni, Zn, and Pb in paddy fields across Southeast Asia. Risks of metals in soils depend on soil properties and the availability of metals in soil. At present, however, limited information is available on how to measure or predict the directly available fraction of metals in paddy soils. Here, the distribution of Cd, Cu, Cr, Ni, Zn, and Pb in 19 paddy fields among the total, reactive, and directly available pools was measured using recently developed concepts for aerated soils. Solid-solution partitioning models have been derived to predict the directly available metal pool. Such models are proven to be useful for risk assessment and to derive soil quality standards for aerated soils.

Material and methods Soil samples (0–25 cm) were taken from 19 paddy fields from five different communities in Taiwan in 2005 and 2006. Each field was subdivided into 60 to 108 plots resulting in a database of approximately 3,200 individual soil samples. Total (Aqua Regia (AR)), reactive (0.43 M HNO₃, 0.1 M HCl, and 0.05 M EDTA), and directly available metal pools (0.01 M CaCl₂) were determined. Solid-solution partitioning models were derived by multiple linear regressions using an extended Freundlich equation using the reactive metal pool, pH, and the cation exchange capacity (CEC). The influence of Zn

on metal partitioning and differences between both sampling events (May/November) were evaluated.

Results Total metals contents range from background levels to levels in excess of current soil quality standards for arable land. Between 3% (Cr) and 30% (Cd) of all samples exceed present soil quality standards based on extraction with AR. Total metal levels decreased with an increasing distance from the irrigation water inlet. The reactive metal pool relative to the total metal content is increased in the order Cr << Ni = Zn < Pb < Cu < Cd and ranged from less than 10% for Cr to more than 70% for Cd. Despite frequent redox cycles, Cd, Pb, and Cu appear to remain rather reactive. The methods to determine the reactive metal pool in soils yield comparable results, although the 0.43 M HNO₃ extraction is slightly stronger than HCl and EDTA. The close correlation between these methods suggests that they release similar fractions from soils, probably those reversibly sorbed to soil organic matter (SOM) and clay. The average directly available pool ranged from less than 1% for Cu, Pb, and Cr to 10% for Ni, Zn, and Cd when compared to the reactive metal pool. For Cd, Ni, Zn, and to a lesser extent for Cu and Pb, solid-solution partitioning models were able to explain up to 93% (Cd) of the observed variation in the directly available metal pool. CaCl₂ extractable Zn increased the directly available pool for Ni, Cd, and Cu but not that of Pb and Cr. In the polluted soils, the directly available pool was higher in November compared to that in May. Differences in temperature, rainfall, and changes in soil properties such as pH are likely to contribute to the differences observed within the year. The solid-solution partitioning model failed to explain the variation in the directly available Cr pool, probably because Cr is present in precipitates rather than being adsorbed onto SOM and clay. Despite obvious differences in parent material, source of pollution, climate, and land

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use, solid-solution partitioning of Cd in paddy fields studied here was similar to that in soils from Belgium and the Netherlands.

Discussion To assess risks of metals in soils, both analytical procedures as well as models are needed. The three methods tested here to determine the reactive metal pool are highly correlated and either of these can be used. The directly available pool was predicted most accurately by the 0.43 M HNO₃ method. The similarity of metal partitioning in paddy soils compared to well-drained soils suggests that changing redox conditions in paddy fields have a limited effect on the geochemical behavior of metals like Cd, Ni, and Zn. Small but significant differences in the directly available metal pool during the year suggest that redox cycles as well as differences in rainfall and temperature affect the size of the directly available metal pool. The large observed spatial heterogeneity of contaminant levels requires ample attention in the setup of soil monitoring programs.

Conclusions The directly available pool (0.01 M CaCl₂) of Cd, Zn, and Ni in paddy fields can be described well by an extended Freundlich model. For Cu and Pb, more information on dissolved organic carbon is needed to obtain a more accurate estimate of the directly available pool.

Recommendations and perspectives Soil testing protocols and models used in risk assessment consider the availability of pollutants rather than the total metal content. Results from extensive testing indicate that approaches developed for nontropical regions can be applied in paddy fields as well for metals like Cd, Ni, and Zn. This study shows that the chemical behavior under drained conditions in paddy fields is comparable to that observed in soils across the European Union, which allows regions with large scale soil pollution including Taiwan to apply such concepts to derive meaningful experimental protocols and models to assess risks of metals in soils.

Keywords Availability · Contamination · Extraction methods · Heavy metals · Paddy fields · Risk assessment · Soil quality standards · Solid-solution partitioning models

1 Background, aim, and scope

Metal contents in soils in and around industrialized areas throughout the world have increased, and metals like Cd, Pb, Ni, Zn, Cr, and Cu have reached levels at which they pose risks for human health and the ecosystem (Dudka and Miller 1999). Human beings are exposed to heavy metals by, among other things, consumption of food grown on polluted soils (Fu et al. 2008; Franz et al. 2008), and consumption of rice is a major source of the total daily Cd intake in Asia (Watanabe et al. 2000; Tsukahara et al. 2002). In Taiwan, emission from industry and the use of untreated waste water from cities has caused widespread pollution of paddy fields with metals across the western plains (Chen 1991; Lu et al. 2007). Risk assessment tools are, therefore, needed to evaluate if soils can be used safely for food production. Soil quality standards in most countries including Taiwan are based on the total metal content in soil (EPA, 2006), although the availability and uptake by crops is not related to the total metal content alone. To improve soil quality standards, a conceptual framework has been developed which distinguishes between the total, reactive, and directly available pools of metals in soil (Fig. 1; after Peijnenburg et al. 2007). The aim of this framework is to enable the identification of metal pools related to biological effects and to exclude those which are not. The *total* metal content can be measured by extraction with aqua regia (AR) or hydrofluoric acid or by techniques like X-ray fluorescence

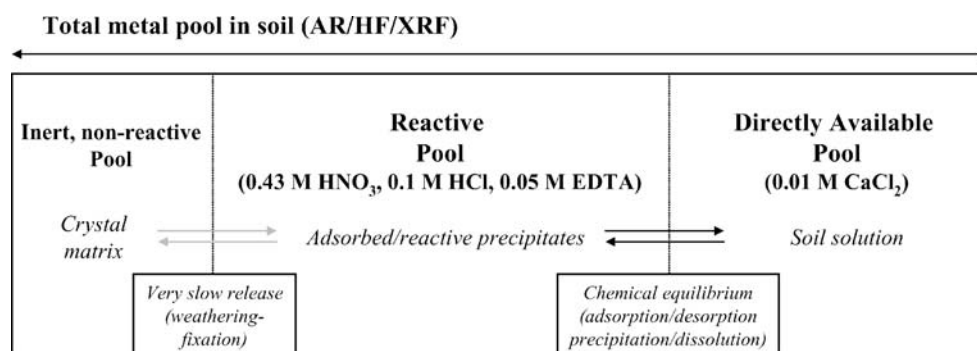


Fig. 1 Conceptual framework to describe metal pools in soil according to their availability. The size of the individual pools is not according to scale and may differ depending on the metal of interest. A rather fast (h/day) equilibrium is assumed to exist between the reactive metal pool and the directly available pool. The release of metals from the inert fraction, on the other hand, is very slow (year)

and is mainly due to weathering of soil minerals. Total metal content can be measured by extraction of soil with Aqua Regia (AR) or hydrofluoric acid (HF) or by X-ray fluorescence (XRF). Reactive metal pool can be determined by extraction of soil with 0.43 M HNO₃, 0.1 M HCl, or 0.05 M EDTA, whereas the directly available metal pool can be determined by extraction with 0.01 M CaCl₂

(Houba et al. 1997). The *reactive* fraction represents sorbed metals reacting with binding sites located on surfaces of soil organic matter (SOM), amorphous metal oxides, and clay and is believed to control the metal concentration in the soil solution (Weng et al. 2001; Tipping et al. 2003). Adsorption–desorption equilibria between the reactive metal pool in the soil–solid phase and the metal concentration in soil solution have been described with empirical solid-solution partitioning models in which pH and cation exchange capacity (CEC) were included to account for differences between soils (Römken et al. 2004; Ingwersen and Streck 2006; Meers et al. 2007; Koopmans et al. 2008a). Various extracts are used to determine the size of the reactive metal pools including dilute acids like 0.43 M HNO₃ (Houba et al. 1997; Weng et al. 2001; Tipping et al. 2003), 0.1 M HCl (Colombo and van den Berg 1998), and EDTA (Clayton and Tiller 1979). The total pool is usually larger than the reactive pool, and the difference between both is considered to be nonreactive or inert, at least on a time scale of years to decades. The *directly available pool* can be related to uptake of metals by soil organisms and plants (Saxe et al. 2001; Lofts et al. 2004, Hough et al. 2005; Peijnenburg et al. 2007; Koopmans et al. 2008a). Both the total dissolved concentration and the free metal ion activity in solution have been used as a measure of the directly available pool (Saxe et al. 2001; Lofts et al. 2004, Hough et al. 2005; Peijnenburg et al. 2007). Since it is difficult to obtain real soil solution samples, soil extracts such as a 1:10 w/v soil-solution extract using 0.01 M CaCl₂ (Houba et al. 2000) are believed to represent the directly available pool in soil (Degryse et al. 2003). Indeed, a clear relationship between the CaCl₂ extractable metal content and accumulation of Cd in rice was observed (Kikuchi et al. 2008; Li et al. 2008; Simmons et al. 2008; Brus et al. 2009).

The first aim of our paper is to characterize metal pools in paddy fields in Taiwan to validate the applicability of the conceptual framework as presented in Fig. 1. Furthermore, limited information is available on how the use of polluted irrigation water affects the distribution of metals between the total and reactive fractions in soils from paddy fields in tropical areas. For nontropical soils, metals from polluted irrigation water or sewage sludge have been demonstrated to remain in an available form decades after application (Rattan et al. 2005; McBride et al. 2006). Our second aim is to compare the effectiveness of the 0.43 M HNO₃ soil test, which is used widely in the European Union (EU), with tests like 0.1 M HCl or 0.05 M EDTA method used in Taiwan. Using empirical solid-solution partitioning models and the reactive metal pool as input, the size of the directly available metal pools measured by dilute salt extracts like 0.01 M CaCl₂ can be predicted (Houba et al. 2000). Hence, our third aim is to derive solid-solution partitioning models for metals based on the 0.01 M CaCl₂ extracts. Dilute salt

extracts and soil-solution partitioning models are used as practical tools in risk assessment studies in well-aerated soils (Peijnenburg et al. 1999; Pueyo et al. 2004; Schröder et al. 2005; Meers et al. 2007), but it is unclear if they are applicable for predicting the directly available metal pools in paddy fields as well which are characterized by a frequent shift from aerobic to anaerobic conditions during the growing season. Shifting redox conditions can lead to a change in the directly available pool and our fourth aim, therefore, is to compare the size of the directly available pool at the two harvest times.

2 Materials and methods

2.1 Location of sampling plots

In 2005 and 2006, soil samples were taken from 19 different existing paddy fields. The fields are located in Chang-Hua (CH, three fields), Ho-Mei (HM, three fields), Lu-Kang (LK, two fields), Hsin-Chu (HC, three fields), and Pa-Deh (PD, eight fields) as shown in Fig. 2. The soils are mostly developed in unconsolidated river sediments in flat to undulating areas. At each field, 12 cultivars of Indica and Japonica rice species were planted on plots with five to nine replicates for each cultivar (depending on the size of the field) to account for the high spatial variability of the metal levels in soil across the paddy field. The total number of plots per field therefore ranged from 60 (i.e., five replicates times 12 cultivars) to 108 (i.e., nine replicates times 12 cultivars). The fields are different in size and shape and the size of the individual plots ranged from 1 to 2 m (width) by 9 to 11 m (length), depending on the total size of the field. Each plot was sampled twice during the year in May (harvest 1) and November (harvest 2). In 2005, the CH, LK, and HM fields were sampled while the HC and PD fields were sampled in 2006, which resulted in a database containing 3265 individual sampling data. Soil samples were taken from the topsoil (0–25 cm) from each plot using a hand auger at the time of harvest when the paddy field was drained. Within each plot, up to 25 soil samples were taken at random across the plot and mixed manually resulting in a composite sample of approximately 3 to 4 kg of field-moist soil.

2.2 Soil pretreatment and chemical analyses

After collection of field-moist samples, soil samples were air-dried in air-conditioned rooms with a dehumidifier during 96 h at 25°C to 30°C. Dried soil samples were passed through a 2-mm sieve. After drying, the remaining moisture content was measured at 105°C to calculate the dry matter content. Total metal pools in air-dried samples



Fig. 2 Map of Taiwan and the location of the communities where the paddy fields used in this study are located (*PD* Pa-Deh city, Tao-Yuan county; *HC* Hsin-Chu city, Hsin-Chu county; *CH* Chang-Hua city; *HM* Ho-Mei city; *LK* Lu-Kang city; the latter three communities are all located in Chang-Hua county)

were determined by extraction with AR using a microwave digestion device (Lamothe et al. 1986). After destruction, extracts were filtered through a filter with a pore size of 2.5 μm (Whatman no. 42) and analyzed for Cd, Cr, Cu, Ni, Pb, and Zn by an inductively coupled plasma-atomic emission spectrometer (ICP-AES). The reactive metal pool was measured by three reagents: (1) 0.43 M HNO_3 (Houba et al. 1997), (2) 0.1 M HCl (Nelson et al. 1959), and (3) 0.05 M EDTA in the Na form ($\text{Na}_2\text{-EDTA}\cdot 2\text{H}_2\text{O}$; Tiwari and Kumar 1982). All extractions were performed at a soil to solution ratio of 1:10 (*w/v*) for 1 h. After shaking, all extracts were filtered (Whatman no. 42), and metal concentrations were measured by ICP-AES. The directly available metal pool was measured by extraction with 0.01 M CaCl_2 according to Houba et al. (2000). After shaking for 2 h on a tabletop shaker, extracts were filtered (Whatman No. 42 filters), and metal concentrations were measured by ICP-AES. The pH was measured directly in CaCl_2 extracts prior to filtration. SOM was determined by loss-on-ignition after heating to 400°C for 8 h (US-EPA,

2002). CEC was determined using 1 M NH_4OAc buffered at pH 7.0 (USDA 1996). Clay content was measured by laser spectroscopy (Xu 2000). SOM, pH, and CEC were analyzed in all soil samples, but clay content was only measured on a limited number of samples from each field.

2.3 Statistical analysis

Multiple linear regression analysis was performed to derive solid-solution partition models. All data were log-transformed (except for pH) prior to regression. An extended Freundlich equation was used to relate the directly available metal pool to the reactive metal pool, pH, and CEC (Römken et al. 2004; Ingwersen and Streck 2006; Meers et al. 2007; Koopmans et al. 2008a):

$$\log[\text{Me} - \text{CaCl}_2] = \text{intercept} + a \cdot \text{pH} + b \cdot \log[\text{CEC}] + c \cdot \log[\text{Me} - \text{reactive pool}] \quad (1)$$

With

[Me- CaCl_2]	directly available metal pool extracted with 0.01 M CaCl_2 in mg kg^{-1}
pH	pH in the 0.01 M CaCl_2 extracts
[CEC]	cation exchange capacity in $\text{cmol}(+) \text{kg}^{-1}$
[Me-reactive pool]	reactive soil metal content determined by extraction with HCl , HNO_3 , or EDTA in mg kg^{-1}

SOM was not included in Eq. 1 because its contribution to the regression in addition to CEC appeared to be insignificant.

All regression analyses and further statistical tests were carried out using Genstat (version 11.1)

3 Results and discussion

3.1 Soil properties across the paddy fields

Data on soil properties from individual fields are shown in Table 1. Soil texture ranges from sand (LK1) to heavy clay (HM fields and CH fields). Most soils are slightly acidic with pH values ranging from 5 to 6 but 25% of the samples have a pH value below 5.1. SOM levels are fairly comparable and range from less than 3% in the LK1 and HC3 plot to almost 9% in the PDH plot. CEC levels are grouped into two classes, one class has a CEC of approximately 5 $\text{cmol}(+) \text{kg}^{-1}$ (HC and LK1 plots), while the second class has CEC values around 15 $\text{cmol}(+) \text{kg}^{-1}$. Differences in CEC were related to the variation in clay and SOM content. The range in SOM, clay, and CEC within each field is limited as is indicated by the low standard deviation (Table 1). Ranges in soil properties measured here are comparable to those

Table 1 Soil properties from the fields included in this study (average values from all individual plots within a field; data from all harvests combined)

Field	Parameter (<i>n</i>)	Clay (%)		SOM (%)		pH		CEC (cmol[+] kg ⁻¹)	
		Mean	SD	Mean	SD	Mean	SD	Mean	SD
CH6	216	70.7	5.0	6.7	0.5	4.7	0.4	16.9	1.5
CH7	215	59.1	9.1	4.6	0.5	6.1	0.5	11.1	1.4
CH8	217	75.0	3.2	6.3	0.5	6.3	0.3	19.0	2.1
HC3	138	15.7	4.7 ^a	2.7	0.4	5.4	0.2	5.5	1.1
HC4	115	15.7	4.7 ^a	4.5	0.5	5.6	0.2	8.7	1.5
HC5	184	15.7	4.7 ^a	3.5	0.4	5.1	0.3	6.9	1.3
HM3	215	70.1	3.0	7.5	0.6	6.2	0.4	19.1	1.8
HM4	215	69.7	2.8	6.2	0.6	5.9	0.4	16.2	1.6
HM5	215	66.6	3.0	5.9	0.5	5.3	0.3	15.1	1.4
LK1	216	3.8	0.4	2.7	0.7	5.3	0.4	5.9	1.9
Lk2	216	51.9	9.3	4.4	0.5	5.8	0.3	10.6	1.5
PDA	229	33.9	1.6 ^a	7.1	0.4	5.3	0.2	13.1	1.5
PDB	230	33.9	1.6 ^a	7.5	0.4	5.2	0.2	14.4	1.9
PDC	92	33.9	1.6 ^a	6.8	0.4	5.2	0.2	13.3	1.7
PDD	92	33.9	1.6 ^a	7.8	0.4	5.0	0.2	14.6	1.3
PDE	115	33.9	1.6 ^a	7.5	0.6	5.1	0.2	14.1	1.5
PDF	92	33.9	1.6 ^a	7.8	0.4	5.2	0.2	15.2	1.7
PDG	92	33.9	1.6 ^a	7.7	0.4	5.1	0.1	14.9	1.7
PDH	161	33.9	1.6 ^a	8.7	0.5	5.0	0.1	16.4	1.9

^a The clay content in the HC and PD fields was measured in 69 (PD) and 12 (HC) individual samples taken from the PDA field through the PDH field and from the HC3 field through the HC5 field, respectively, but no distinction between fields was made

measured by others in rice paddy fields (He et al. 2006; Simmons et al. 2008)

3.2 Total metal content

Total metal levels vary considerably between and within fields, and they range from background levels to levels beyond current soil quality standards used in Taiwan (EPA 2006; Table 2). For the metals studied here, the number of soil samples with total metal contents in excess of the present soil monitoring values for cropped soils increases from 2.9% for Cr, 6.3% for Zn, 10.1% for Ni, 13.0% for Pb, 13.3% for Cu to 26.7% for Cd. Not all fields are equally polluted: total Cd and Pb contents are especially high in the PD fields whereas total Ni and Zn contents in the HM and LK fields exceed those of the other locations. Aside from the differences between fields, a broad range in the total metal content was observed within each field. In the HC3 field, for example, the total soil Cd content decreases from 7 to below 0.2 mg kg⁻¹ within 50 m from the inlet. Likewise, the total Cd contents in the PDD and PDB fields, which range from 4.0 to 21.6 and from 6.2 to 29.4 mg kg⁻¹, respectively, are highly variable. This is illustrated in Fig. 3, which shows the maps of HCl extractable Cd in the HC3 and HM3 fields. Cd levels are highest close to the inlet and gradually decrease across the field depending on the topography (elevation). In contrast to the HM and HC fields, total Cd levels in the PDF, PDG,

LK1, and CH6 fields are less variable. In the CH, HM, and LK fields, total Cu contents are highly variable, reflecting the apparently specific Cu emission of different industries. In the CH fields, Cu and Ni are highly correlated, although the Cu/Ni ratio is distinctly different in the three individual CH fields, suggesting that the source for these metals is not the same (data not shown). In general, total metal levels for Cd, Cu, Pb, and Zn in individual samples were highly correlated with correlation coefficients ranging from 0.6 to 0.9 (data not shown). Similar trends of metal levels in soil in paddy fields have been observed by Simmons et al. (2005), and the distance within a paddy field to the main inlet of irrigation water is crucial in relation to the metal levels observed in soil. These examples indicate that soil monitoring programs have to consider the heterogeneous nature of metal distribution between and within paddy fields in order to be able to accurately assess human health and ecosystem risks related to metals in soil in industrialized areas like those in the western plains of Taiwan.

3.3 Reactive metal pools

Amounts of metals extracted by HNO₃, HCl, and EDTA are markedly smaller than those extracted by AR (see Table 2). Figure 4 shows the median ratio of the reactive metal pool extracted with HNO₃, HCl, or EDTA relative to the total metal content. The size of the reactive metal pool relative to the total metal content decreases in the order Cd>Cu>Pb>

Table 2 Overview of the total, reactive and directly available metal pools in all 19 fields as measured by extraction with Aqua Regia (AR; total metal content), 0.1 M HCl, 0.43 M HNO₃, 0.05 M EDTA (reactive metal pool), and 0.01 M CaCl₂ (directly available pool)

Metal	Extract	Parameter (<i>n</i>)	Soil tests (mgkg ⁻¹)								Soil quality standard ^b (mg kg ⁻¹)
			Min.	5%	25%	50%	Mean ^a	75%	95%	Max.	
Cd	AR	3265	0.06	0.21	0.39	0.64	3.8	5.3	14.9	29.4	5.0
	HCl	3250	0.01	0.11	0.22	0.41	3.0	4.3	12.1	25.7	
	HNO ₃	3266	0.08	0.13	0.22	0.41	3.1	4.6	12.3	20.6	
	EDTA	3265	0.05	0.11	0.21	0.39	2.3	3.6	9.1	16.4	
	CaCl ₂	3255	0.001	0.004	0.01	0.04	0.29	0.46	1.3	3.2	
Cr	AR	3265	38.9	47.2	54.8	80.0	94.4	112.4	203.9	483.0	250
	HCl	2560	0.01	0.13	0.89	2.1	2.9	3.5	9.1	31.6	
	HNO ₃	3265	0.93	1.8	2.6	4.9	7.2	8.3	22.2	82.4	
	EDTA	2072	0.004	0.1	0.63	1.1	1.5	1.9	4.0	9.2	
	CaCl ₂	2567	<0.001	0.002	0.01	0.02	0.02	0.02	0.04	0.2	
Cu	AR	3265	22.9	29.9	55.0	101.5	123.9	150.4	312.1	903.5	200
	HCl	3265	6.7	11.3	22.6	50.9	64.7	73.3	180.9	640.3	
	HNO ₃	3265	9.8	14.5	27.8	60.3	74.4	86.5	199.8	635.8	
	EDTA	3265	5.0	12.9	24.0	56.4	70.5	86.5	193.2	539.3	
	CaCl ₂	2776	<0.001	0.008	0.03	0.07	0.18	0.18	0.73	9.2	
Ni	AR	3265	16.8	26.1	32.5	72.9	97.9	147.1	245.6	461.4	200
	HCl	3265	0.83	2.1	3.9	23.9	23.9	39.5	59.4	101.7	
	HNO ₃	3265	1.7	2.7	4.9	27.3	26.8	44.7	64.8	102.2	
	EDTA	3265	0.80	2.1	4.1	22.7	23.9	40.1	60.3	89.1	
	CaCl ₂	3185	0.002	0.082	0.257	0.954	3.1	4.8	12.0	29.4	
Pb	AR	3265	10.8	21.2	30.9	48.8	164.4	194.1	665.5	1171.4	500
	HCl	3262	0.30	4.7	7.8	13.6	84.6	83.7	389.1	821.7	
	HNO ₃	3265	6.7	12.0	17.5	26.2	110.4	127.3	476.7	755.6	
	EDTA	3265	2.0	7.8	11.9	19.8	92.3	109.0	400.7	624.9	
	CaCl ₂	2197	<0.001	0.01	0.06	0.15	0.20	0.309	0.543	1.05	
Zn	AR	3265	63.1	99.1	197.1	277.2	311.7	386.3	666.5	1225.3	600
	HCl	3265	11.9	22.8	41.7	60.8	77.7	97.0	179.5	537.3	
	HNO ₃	3265	17.3	25.7	49.8	70.8	90.4	111.8	209.5	574.2	
	EDTA	3265	10.7	20.1	36.0	54.5	68.6	86.4	160.6	383.6	
	CaCl ₂	3244	0.009	0.13	1.9	5.5	8.0	10.5	25.0	96.9	

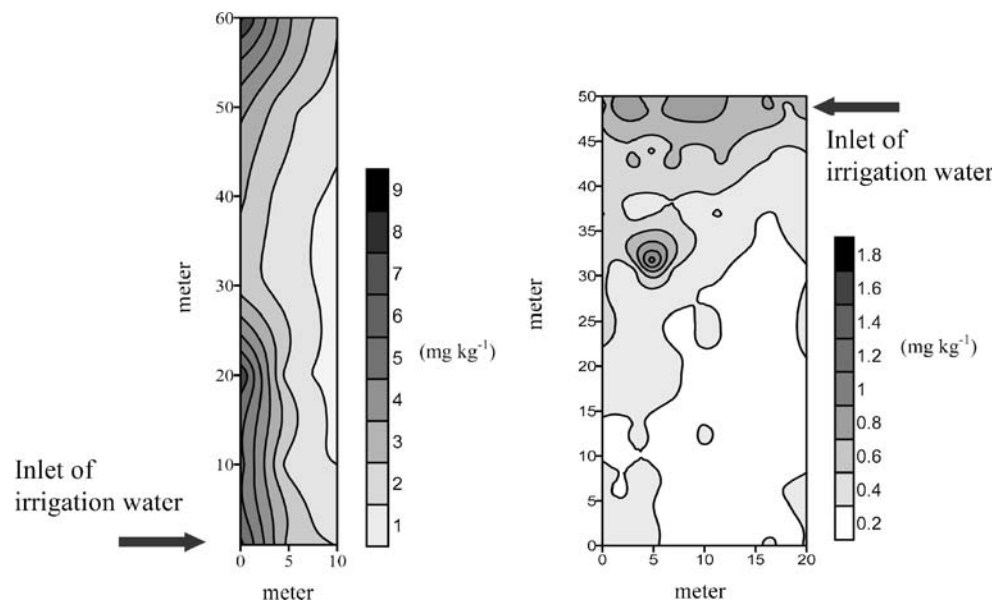
^a All elements have a log-normal distribution, which results in a large difference between the median and the average value

^b Soil monitoring value for cropped soils used at present in Taiwan (EPA 2006)

Zn≈Ni>>Cr. Amounts extracted with HNO₃ are slightly ($p<0.001$) larger than those extracted with HCl for Cd, Zn, and Ni. For Pb, HNO₃ extracts almost twice the amount extracted with HCl. Apparently, HNO₃ mobilizes a specific soil component (e.g., amorphous Fe) that binds Pb which is not mobilized with HCl. EDTA usually extracts less metals from soil compared to HCl and HNO₃ except for Cu and Pb. This difference may reflect the amount of Cu and Pb sorbed to SOM which can be released by EDTA but not by HCl. Both Cu and Pb are known for their high affinity binding to SOM (Weng et al. 2001; Qin et al. 2006). For Cr, only 12% of the total metal pool could be released by HNO₃, which suggests that Cr in paddy soils is present in rather immobile and chemically inert fractions. In contrast

to Cr, the median reactive pool of Pb, which is considered a rather immobile metal (Tipping et al. 2006), equals 61% of the total metal pool. This is higher than the reactive to total ratio for Zn (23%) and Ni (21%) which often are considered to be more reactive than Pb. Apparently, Zn and also Ni in the samples from this study are mostly present in rather immobile and chemically inert fraction forms which supports observations that Zn and Ni can become immobile due to fixation and surface precipitation onto oxyhydroxides (Singhal and Gupta 1978; Bruemmer et al. 1981; Elzinga and Sparks 1999; Buekers 2007). In contrast to Cr, Ni, and Zn, Cd remains highly reactive which is in agreement with data from soils for moderate climate zones (McBride et al. 2006). For both HNO₃ and

Fig. 3 Spatial distribution of Cd as measured by extraction with 0.1 M HCl in the soil across field HC3 (left) and HM3 fields (right). The inlets for irrigation water are marked with an arrow. The scale is different in both fields. Spatial distribution patterns were obtained by kriging of the observed data



HCl, the median reactive to total ratio exceeds 70%, and in 5% of all soil samples, this ratio increases to more than 90%. Hence, Cd in these soils remains potentially available for uptake by rice plants. The median reactive (measured by HNO₃) to total ratios for Cd, Pb, Zn, Cu, and Ni are in close agreement with data from nonpolluted soils from the Netherlands and Belgium (Römkens et al. 2004; Meers et al. 2007). This suggests that the chemical processes controlling the reactivity or binding of Cd to the soil–solid phase are comparable regardless of the obvious differences between well-drained soils from moderate climate zones and paddy field soils from Taiwan.

3.4 Directly available metal pools and solid-solution partitioning models

For all metals, the average directly available metal pool is only a minor fraction of the reactive or total metal content in soil (Table 2). The average ratio of the CaCl₂-extractable

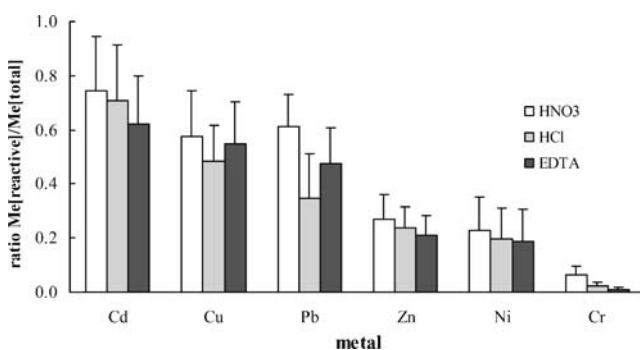


Fig. 4 Mean median ratio of reactive metal pool relative to the total metal content as found for 0.43 M HNO₃, 0.1 M HCl, and 0.05 M EDTA. The error bars represent the standard deviation

pool relative to the HNO₃ pools increases from less than 0.3% for Cu, Cr, and Pb to approximately 10% for Cd, Ni, and Zn (Table 3). However, for the latter metals, the directly available pool can be as high as 70% of the total reactive (HNO₃) pool, which reflects the relatively high availability of these elements compared to Cu, Pb, and Cr.

Table 4 shows the results of the multiple regression analysis according to Eq. 1 using the reactive metal pool (HNO₃), pH, and CEC. For Cd, Zn, and Ni, between 80% and 93% of the observed variation in the directly available metal pool (CaCl₂) can be explained by these parameters as is shown in Fig. 5. For Cr, Cu, and Pb, between 9.9% (Cr) and 59% (Cu) of the variation in the directly available metal pool was explained by the reactive metal pool, pH, and CEC. Apparently, the parameters included here are not the only ones controlling the solid-solution partitioning of Cu, Pb, and especially of Cr. To predict the solubility of Cu and Pb, dissolved organic carbon (DOC) is crucial (Römkens and Dolging 1998; Römkens et al. 1999; Weng et al., 2001; Koopmans et al. 2008b). In this study, however, DOC was not measured, which partly explains the rather low variability of the directly available Cu and Pb pools. For Cr, the model as such is not an appropriate one since Cr behaves rather different, being an anion and prone to precipitation and dissolution processes even at low concentrations. Neither the reverse effect of pH on the solid-solution partitioning for anions compared to cations nor the precipitation phenomena are accounted for in the Freundlich equation (Eq. 1).

A further analysis of the data revealed that Zn had a significant influence on the amounts of Cd, Ni, and Cu extracted with CaCl₂. Since Zn and Cd have similar affinity for sorption sites in soils (McBride 1994), an increase in the available pool of Zn should induce competition between

Table 3 Overview of the ratio of the directly available metal pool as measured by extraction with 0.01 M CaCl₂ relative to the reactive metal pool as measured by extraction with 0.43 M HNO₃

	Ratio directly available metal pool/reactive metal pool (%)					
	Cu	Zn	Cd	Cr	Ni	Pb
Minimum	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Median	0.1	7.9	8.8	0.2	7.1	0.1
Average	0.2	9.3	10.4	0.3	9.4	0.2
Maximum	2.7	75.0	65.8	3.3	77.1	3.8

these metals for sorption leading to higher directly available Cd levels in soil as measured by extraction with CaCl₂. Including Zn in the regression indeed improved the model even further ($R^2=0.95$; $se(Y\text{-est})=0.19$) as is shown for Cd in Eq. 2:

$$\log[Cd - CaCl_2] = 0.83 - 0.29 \cdot pH - 0.50 \cdot \log[CEC] \quad (2)$$

$$+ 0.91 \cdot \log[Cd - HNO_3]$$

$$+ 0.29 \cdot \log[Zn - CaCl_2]$$

With

[Zn-CaCl₂] directly available metal pool extracted with 0.01 M CaCl₂ in mg kg⁻¹

For Ni and Cu, similar improvements were obtained upon inclusion of Zn in the regression (data not shown). For Pb and Cr, however, no effect of Zn was observed. Apparently, Pb and Zn do not compete for the same sorption sites in paddy soils, whereas a strong competition effect was found to exist between Cd, Ni, and to a lesser extent for Cu on the one hand, and for Zn on the other for sorption to the soil solid phase.

In Table 5, results of multiple regression analyses for Cd, Ni, and Zn are presented using all soil tests (i.e., AR, HNO₃, HCl, and EDTA). For Pb and Cr, and to a lesser extent also for Cu, the error of prediction using HNO₃ was high (see Table 4), and the use of AR, HCl, or EDTA in the regression did not improve this (data not shown). The data presented in Table 5 indicate that the use of HCl or HNO₃ and, for Ni even EDTA, result in comparable regression coefficients for the prediction of the directly available metal pool in soil. This is not surprising considering the similarity between these soil tests in extracting metals from soil.

Table 4 Regression coefficients of the Freundlich equation to predict the size of the 0.01 M CaCl₂-extractable metal pool using 0.43 M HNO₃ and soil properties like pH and CEC as input parameters (Eq. 1)

Metal	n	Regression coefficients					R ²	se(Y-est)
		Intercept	a (pH)	b (CEC)	c (HNO ₃)			
Cd	3255	2.64	-0.53	-0.80	0.96	92.9	0.22	
Cu	2776	0.16	-0.38	-1.18	1.17	58.7	0.38	
Cr	2567	-1.12	-0.05	-0.59	0.17	9.9	0.41	
Ni	3185	2.73	-0.58	-0.95	1.22	86.0	0.27	
Pb	2197	-1.69	-0.02	-0.28	0.65	46.7	0.40	
Zn	3244	4.57	-0.88	-1.25	1.16	80.3	0.30	

Results from an all-subset analysis (Genstat 11.1) nevertheless showed that the combination of pH, CEC, and HNO₃ was the most significant model based on three terms. After including Zn as a regression term (Eq. 2), the best model still was the one using the 0.43 M HNO₃ extractable pool. The use of AR results in both a lower R² and a higher standard error of the predicted values, which indicates that the prediction is less accurate. This supports the hypothesis that AR not only extracts the reactive metal pool but also the inert fraction which is not in equilibrium with neither the reactive nor the directly available metal pool. This effect is more pronounced for Ni and Zn for which also the difference between the reactive and total metal content was much larger than for Cd. For Cd, model coefficients based on HNO₃, HCl, or EDTA are comparable to those obtained using AR, which shows that the reactive metal pool is closely related to the total metal content in the soil. Also for Cd, however, the model fit based on AR is less accurate compared to that based on HNO₃, HCl, or EDTA.

For Cd, a comparable regression analysis was performed by Meers et al. (2007) using soils from Belgium. Meers et al. (2007) used the AR extractable Cd content instead of a reactive Cd pool to predict the directly available pool (same units as in Eqs. 1 and 2):

$$\log[Cd - CaCl_2] = 2.91(\pm 0.26) - 0.55(\pm 0.04) \cdot pH - 0.94(\pm 0.14) \cdot \log(CEC) + 1.13(\pm 0.06) \cdot [Cd - AR] \quad (3)$$

All coefficients except the intercept are very similar to the ones listed in Table 5. This suggests that the response

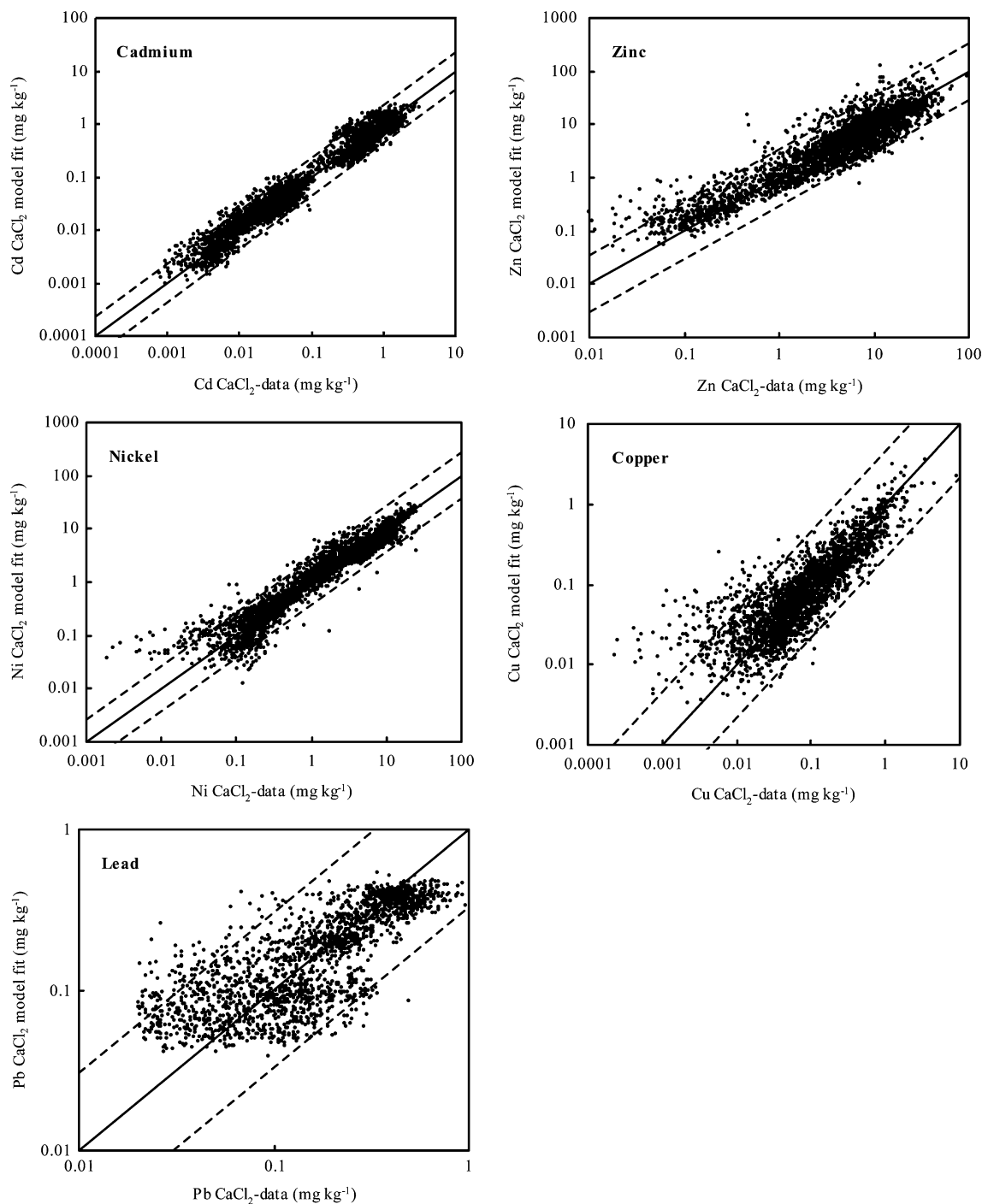


Fig. 5 Measured data of metals in the 0.01 M CaCl_2 extracts versus model fit based on Eq. 1. The *solid line* indicates the 1:1 line, while the *dotted lines* are equal to $Y\text{-est} \pm 2 \cdot \text{se}(Y\text{-est})$, which is approximately equal to the 95% confidence interval of the predicted mean levels

of Cd in the CaCl_2 extracts to changes in pH, CEC, and even the total Cd content is similar in samples from paddy fields and soil samples used by Meers et al. (2007). When applied to data from this study, the higher intercept derived by Meers et al. (2007) results in an average overestimation of the directly available Cd pool by a factor of approximately 2.

3.5 Effect of sampling time on the directly available metal pools and on solid-solution partitioning models

In the PD fields, the directly available metal pools at the second harvest increased between 0.05 (for Pb) and 0.58 log units (for Cu). In the CH, HM, LK, and HC fields, however, the reverse trend was observed and the size of the

Table 5 Regression coefficients of the Freundlich equation to predict the size of the 0.01 M CaCl₂-extractable metal pool based on Aqua Regia (AR), 0.43 M HNO₃, 0.1 M HCl or 0.05 M EDTA, and soil properties like pH and CEC (Eq. 1)

Metal and extract	Regression coefficients					
	Intercept	a (pH)	b (CEC)	c (Reactive metal pool)	R ²	se(Y-est)
Cd						
HNO ₃	2.64	-0.53	-0.80	0.96	92.9	0.22
HCl	2.69	-0.53	-0.83	0.96	92.8	0.23
EDTA	2.81	-0.53	-0.87	1.02	93.0	0.22
AR	2.58	-0.55	-0.79	1.04	91.2	0.25
Zn						
HNO ₃	4.57	-0.88	-1.25	1.16	80.3	0.30
HCl	4.54	-0.87	-1.21	1.16	80.7	0.30
EDTA	4.34	-0.83	-1.18	1.17	82.1	0.29
AR	4.65	-1.01	-1.18	1.12	74.1	0.35
Ni						
HNO ₃	2.73	-0.58	-0.95	1.22	86.0	0.27
HCl	2.88	-0.57	-0.98	1.16	86.2	0.27
EDTA	2.78	-0.55	-0.99	1.17	86.4	0.27
AR	2.01	-0.61	-1.63	1.67	77.3	0.35

directly available metal pools at the first harvest exceeded those extracted at the second harvest, although differences were less pronounced compared to those obtained in the PD fields. Only for Pb, CaCl₂-extractable metal pools at the second harvest exceeded those from the first harvest in all fields. Also, pH levels in all fields were higher at the second harvest compared to the first harvest which partly can explain the larger directly available metal pools in the CH, HM, and LK fields at the first harvest. The higher pH at the second harvest, however, cannot explain the increase in CaCl₂-extractable metals in the PD fields since the size of the directly available metal pool for metals like

Cd, Zn, and Ni usually decreases with an increase in pH (McBride 1994). Other soil properties (CEC) as well as the reactive soil metal pools remained constant in the first and second harvest. Possibly, dynamics in other soil parameters including DOC, salinity, or redox potential, which were not included in this study, play an important role in the temporal variability of the directly available metal pools.

Differences between the size of the directly available metal pool at the first and the second harvest became evident after deriving separate solid-solution partitioning models for the data from these harvests as shown in Table 6.

Table 6 Regression coefficients of the Freundlich equation to predict the size of the 0.01 M CaCl₂-extractable metal pool using 0.43 M HNO₃ and soil properties like pH and CEC as input parameters (Eq. 1) at harvest 1 (H1) and at harvest 2 (H2)

Metal	Regression coefficients					
	Intercept	a (pH)	b (CEC)	c (HNO ₃)	R ²	se(Y-est)
Cd-H1 and H2						
Cd-H1	2.20	-0.47	-0.71	0.88		
Cd-H2	3.17	-0.61	-0.88	1.05		
Zn-H1 and H2						
Zn-H1	3.96	-0.77	-1.28	1.17	80.3	0.30
Zn-H2	5.32	-1.00	-1.20	1.14		
Cu-H1 and H2						
Cu-H1	-1.22	-0.25	-1.26	1.55	58.7	0.38
Cu-H2	1.35	-0.52	-1.23	1.01		
Ni-H1 and H2						
Ni-H1	2.07	-0.50	-0.87	1.31	86.0	0.27
Ni-H2	3.49	-0.67	-1.03	1.13		
Pb-H1 and H2						
Pb-H1	-1.41	-0.07	-0.48	0.73	46.7	0.40
Pb-H2	-1.79	0.00 (ns)	-0.05 ^a	0.55		

^a Not significant

The data were split solely based on the time of sampling, but no further distinction was made between fields. For all metals except Pb, the intercept increased between 0.97 (Cd) and 2.57 (Cu) log units. The ultimate effect of the time of harvest on the solubility of metals appeared to be most pronounced in the more polluted paddy fields where, for all metals except Pb, a clear increase in the size of the directly available pool was observed at the second harvest. This is schematically shown for Cd in Fig. 6 where the ratio of the directly available Cd pool at the second harvest relative to that obtained at the first harvest is plotted. For each combination of the reactive Cd pool and pH, the directly available Cd pool was calculated for both the first and second harvest, and plotted as a function of the reactive Cd pool and pH. This figure illustrates the overall effect of the time of harvest across all fields which is difficult to assess from the data points for each field alone. The increase in the directly available Cd pool at the second harvest is most pronounced in polluted soils with a reactive Cd pool >1 mg kg⁻¹ and a pH <5.5 ; the opposite effect was observed at a higher pH or at a smaller reactive Cd pool.

At present, it remains unclear as to what causes these changes in both pH and CaCl₂-extractable metal levels, but the observations clearly show that the variation in the size of the directly available metal pools in paddy fields throughout the year can be considerable. Obviously, changes from reducing to oxidizing conditions and vice versa can result in long-lasting changes in the directly available pool of metals in soil. Further investigation on the controls of metal solubility under drained and water-logged conditions and its dynamics after changing from the anaerobic state to the aerobic state seems essential and can be the clue to understanding some contrasting results obtained not only here but also by others. Simmons et al. (2008), for example, showed that the availability of Cd in extracts from air-dried soils differed from that from field-moist samples. However, the direction of this change was different and depended on the type of extract used. Dissolved Cd concentrations in a 0.01 M CaCl₂ extract decreased upon drying, but those in

0.05 M CaCl₂ extracts increased upon drying. This shows that the time of sampling, conditions at the time of soil sampling, soil pretreatment, and extraction procedure all affect the amounts of metals extracted by standard soil tests. The usefulness of the directly available fraction of metals in soils in risk assessment is evident, but our field results suggest that underlying mechanisms that control the amount of metals present in such extracts still require ample attention.

4 Conclusions

Total levels of Cd, Pb, Cu, Zn, and Cr in paddy fields in Taiwan exceed current soil quality standards, although the degree of pollution is rather heterogeneous across and between fields. Levels of all metals in 19 fields are usually highest near the inlet of irrigation water and decrease substantially with an increase in distance from the inlet. Despite this large heterogeneity and differences in the source of metals, methods to determine the reactive metal pool used in the EU (HNO₃), Australia (EDTA), and Taiwan (HCl) give comparable results, although HNO₃ consistently extracts more metals from soil compared to HCl or EDTA. As such, all three soil tests can be used to predict the size of the directly available pool of Cd, Zn, and Ni, and to a lesser extent also of Cu and Pb. Regression analyses indicated that the combination of HNO₃-extractable metals with CEC and pH explains most of the observed variation in the directly available metal pool. For Cr, no such relation could be obtained since the solubility of Cr is controlled by other processes compared to cationic metals like Cd or Zn. For Cd, Ni, and Cu, a competition effect of Zn was observed. Despite differences in climate, soil type, and hydrological conditions, the variability in the directly available Cd, Zn, and Ni pools in paddy soils was described well by solid-solution partitioning models similar to those published for permanently drained soils (Römkens et al. 2004; Meers et al. 2007). This suggests that processes that control the variability in the directly available Cd pool are comparable. This is an important finding since it suggests that knowledge and model concepts for metals which have been developed elsewhere can also be of use to predict the availability of metals in paddy fields. In this study, we focused on the prediction of the directly available metal pool under drained, oxidizing conditions since it has been suggested that uptake of metals by rice is controlled largely during the period following the shift from flooded to drained conditions (Simmons et al. 2008). It is known, however, that both solubility and availability of metals decrease under reducing conditions when the soil is water-logged (Kashem and Singh 2004; Contin et al. 2007). The return to oxidizing conditions can lead to an increase in the availability and

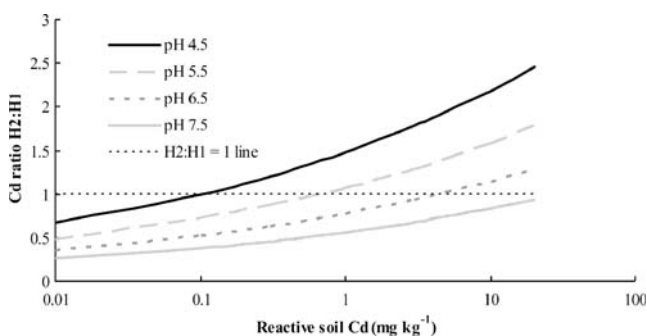


Fig. 6 Ratio of the 0.01 M CaCl₂-extractable Cd pool as measured at harvest 1 (H1) relative to the same pool measured at harvest 2 (H2) at various pH levels between pH 4.5 and pH 7.5

uptake of metals (Daum et al. 2001; Kelderman and Osman 2007), although the degree to which metals are bound or released by sulfides has been shown to be quite variable. Barret and McBride (2007) showed that an increase in the Cd/Zn ratio in soil reduced the metal scavenging effect of sulfides for Cd considerably. Charlatchka and Cambier (1999) even observed an initial increase in the solubility of metals after flooding of a soil due to dissolution of ferric and manganese oxides. These contrasting observations, together with the observed differences in the size of the directly available metal pool between the first and the second harvest, suggest that careful monitoring of soil conditions, metal ratios, and time period of drainage is essential in order to better understand the dynamics of the availability and uptake of metals in paddy soils. The data collected here nevertheless illustrate that the use of a dilute acids like 0.43 M HNO₃ or 0.1 M HCl in combination with generally available soil properties like pH and CEC can be used to obtain a robust estimate of the availability of some of the most critical elements (e.g., Cd) in relation to food safety and environmental effects. To better explain the observed differences in the solubility of Cu and Pb, the influence of DOC needs to be considered.

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