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Release of As, Ba, Cd, Cu, Pb, and Sr under pre-definite redox conditions in different rice paddy soils originating from the U.S.A. and Asia

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ABSTRACT

The release dynamics of dissolved arsenic (As), barium (Ba), cadmium (Cd), copper (Cu), lead (Pb), and strontium (Sr) was determined in seven different paddy soils under controlled-redox conditions by using an automated biogeochemical microcosm apparatus. Seven surface soils were collected from five major rice-cultivating states in the United States (Arkansas, California, Louisiana, Mississippi, and Texas), and from two Asian regions: Hangzhou (China) and Java (Indonesia). The impact of redox potential (E_H), pH, dissolved organic carbon (DOC), iron (Fe), manganese (Mn), and sulfur (S) on the release dynamics of the elements was quantified. The experiment was conducted stepwise from reducing (−270 mV) to oxidizing (+676 mV) soil conditions. Soil pH increased with decreasing soil E_H. Concentrations of DOC and dissolved As, Fe, Mn were increased under reducing conditions as compared to oxidizing conditions. In opposite — the release of Ba, Cd, Cu, and Sr to soil solution increased under oxidizing conditions as compared to reducing conditions. The decrease of Ba, Cd, Cu, and Sr concentrations under reducing conditions could be caused by the relatively high pH and/or metal-sulfide precipitation. Lead showed an inconsistent trend with E_H in the studied soils (All Soils). Factor analysis demonstrates that As, Fe, Mn, and DOC were associated in one group, while Ba, Sr, Cd, Cu, and E_H were banded together in one cluster. These results indicate that the chemistry of DOC, Fe, and Mn might be stronger linked to the dynamics of As than to the dynamics of Ba, Cd, Cu, Pb, and Sr in these soils.
The canonical discrimination analysis explained 85% of the variability of the geochemical behavior of the different soils and showed that the individual soils can clearly differentiate from each other. However, the Arkansas and Louisiana soils were relatively similar in their geochemical behavior, and the Indonesian and Texas soils were close, while and the California soil showed a different geochemical behavior. The behavior of Sr, Ba, S, DOC, and E_H, respectively, was mainly responsible for the discrimination of the soils. In particular, our findings suggest that aerobic conditions can lead to a release of Ba, Cd, Cu, Pb, and Sr while a release of As under anaerobic conditions was observed. These results provide critical information on the potential risk of toxic elements for the sustainable management of paddy rice soils.

1. Introduction

Wetland rice ecosystems have, both spatially and temporally, a unique aerobic and anaerobic soil environment (Reddy and DeLaune, 2008).Rice soils are characterized by a highly dynamic and variable hydrological regime, which have considerable impacts on the release dynamics and mobilization of soil potentially toxic elements (PTEs) (Reddy and DeLaune, 2008). Dynamics of redox-sensitive processes is of large importance for temporarily flooded soil such as rice soils as the location of the oxic–anoxic interface is subject to change due to fluctuating water table levels (Rinklebe et al., 2007; DeLaune and Seo, 2011; Rinklebe and Laing, 2011). The intensity of soil reduction can be rapidly characterized by soil oxidation–reduction (redox) potential (E_H), which may help to allow the prediction of the stability and dynamics of various nutrients and PTEs in soils and sediments (Frohne et al., 2011, 2014, 2015; Rinklebe et al., 2016a,b).

Redox-sensitive processes can affect the dynamics of PTEs directly via changes in their speciation or indirectly through related changes in pH, dissolved organic carbon (DOC), and the redox chemistry of iron (Fe), manganese (Mn), and sulfur (S) (Frohne et al., 2011, 2014, 2015 Shaheen et al., 2014a,b,c). Thus, we hypothesized that different flooding/drainage regimes in rice soils could affect the solubilization dynamics of the redox-dependent pollutants arsenic (As), barium (Ba), cadmium (Cd), copper (Cu), lead (Pb), and strontium (Sr) due to changes of E_H/pH-values, DOC, Fe, Mn, and S. Arsenic and Cu are widespread redox-sensitive contaminants. The degrees of As mobilization and toxicity

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in soils depend on its oxidation state and its sorption on soil and sediment components (Frohne et al., 2011; Rinklebe et al., 2016a,b; Rinklebe and Laing, 2011; Shaheen et al., 2014b).

The release kinetics of Ba, Pb, and Sr in rice soils have rarely been studied, regardless of the potential toxicity of these elements (Ohgami et al., 2012). Recent studies are dealing with the geochemical behavior of Ba which mainly focus on marine environments (Henkel et al., 2012; Santos et al., 2011). Studies referring to the geochemical behavior of Sr in soils often concentrate on radioactive isotopes rather than stable forms (Wang and Staunton, 2005). Recently, Frohne et al. (2015) studied the impact of systematic change of redox potential on the dynamics of Ba and Sr in a riverine grassland soil. Assessing the release dynamics of As, Ba, Cd, Cu, Pb, and Sr in different rice soils is needed to be able to investigate factors affecting their potential leaching from paddy soils into water and further to plants. This knowledge is essential for an adequate risk assessment of contaminated sites. Additionally, rice paddy management has been a public concern since the daily ingestion of high As, Cd, and Pb from rice productions can be the main cause of chronic and acute diseases (Ok et al., 2011a,b,c). Therefore, detailed knowledge about the behavior of PTEs in paddy soils from different parts of the world is required to understand the mobilization of PTEs. The gained knowledge will enable a more accurate prediction of PTEs release into surface waters in response to changing redox conditions. Thus, we aimed i) to assess the impact of pre-definite E_H on the release dynamics and mobilization of As, Ba, Cd, Cu, Pb, and Sr as governed by pH, DOC, Fe, Mn, and S in seven soils which originated from five major rice-cultivating states in the U.S.A. and from two regions in Asia (China and Indonesia) using an automated biogeochemical microcosm system, and ii) to discriminate the different soils according to the geochemical behavior of the studied parameters.

2. Material and methods

2.1. Soil sampling and characterization

Seven soils (surface 20 cm) were collected from five major rice-cultivating states in the U.S.A. (Arkansas, California, Louisiana, Mississippi, and Texas), and two Asian regions: Hangzhou (China), and Java (Indonesia). The soils were air dried, sieved (<1-mm), thoroughly mixed, and stored at room temperature (20 °C) before the experiment. Soil characterization was done as described in Yu and Patrick (2004) and Yu et al. (2007).

Most soils were dominated by silt, except in the California, and Texas soils were dominated by clay. The soils were weakly acidic to neural and showed pH values between 5.1 and 7.3. The soils contain relatively low concentrations of organic matter (1.4–4.6%). Major soil properties are published in Yu and Patrick (2004) and Yu et al. (2007).

2.2. Automated biogeochemical microcosm experiment

An automated biogeochemical microcosm system was used to simulate flooding of the soils in the laboratory. Controlling soil redox conditions in a constantly stirred microcosm setup has several advantages over static incubations. Redox conditions are reproducible and defined, and can be rapidly changed. Furthermore, the effect of E_H can be studied independently from other soil parameters. More technical details of the system are provided in Yu and Rinklebe (2011). This system was successfully employed in previous studies for the determination of the dynamics of PTEs (Frohne et al., 2011, 2014, 2015; Rinklebe et al., 2016a,b; Rupp et al., 2010; Shaheen et al., 2014a). In addition, this system was used for the investigation of trace gases (Yu et al., 2007), for the quantification of mercury emissions (Rinklebe et al., 2010), and mercury methylation (Frohne et al., 2012). The details used in this experiment are published in Yu et al. (2007).

Briefly, in total, 12 microcosm systems (MCs) were used, allowing for two replicates of each soil except for the Louisiana and Chinese soils (not replicated due to limited amounts of soil sample). The MCs were filled with 200 g air-dried soil mixed with 1600 mL deionized water. A 5 g rice straw was added for each microcosm as an additional source for organic matter. The achieved slurry was continuously stirred to reach homogeneous conditions. As a result, levels of E_H decreased, and this process was accelerated by continuously flushing the MCs with N_2. After that, E_H-values were increased by adding synthetic air and/or oxygen. Controlled redox potential was kept within different E_H-windows by automated supply of O_2 or N_2. The E_H was maintained for approximately 24 h for each E_H pre-set window before moving to next E_H window. Redox potential, pH, and temperature in each MC were automatically recorded at every ten minutes. The slurry was sampled (50 mL) approximately 24 h after reaching each new E_H-window. The soil/water ratio remained the same during the experiment. The total incubation period was 105 days at room temperature (Yu et al., 2007).

2.3. Chemical analysis and quality control

Concentrations of Ba, Fe, Mn, S, and Sr in the soil solution were analyzed directly on ICP-mass spectrometry using an ELAN 5000 (PerkinElmer, Wellesley, MA). Concentrations of As, Cd, Cu, and Pb in the soil solution were measured by graphite furnace atomic absorption spectrometry (GF-AAS). Analyses of multi-element standards (CertiPur, Merck) were routinely included into the quality control. The maximum allowable relative standard deviation between replicates was 5%. Dissolved organic C was analyzed after combustion of the finely sprayed solution with a micro N/C analyzer (Analytik Jena AG, Jena, Germany).

2.4. Calculations and statistical analysis

Soil E_H was adjusted to the standard H_2 electrode by adding 210 mV (correction factor for the Ag–AgCl electrode) to the recorded instrument reading. All E_H data were reported as their corresponding values at pH 7 that were calculated according to the inverse relationship of E_H and pH as described by the Nernst equation. Redox potential change per pH unit may vary from 59 to 177 mV, depending on redox couples and kinetics of the reaction (Bohn, 1971). Since E_H values represent mixed potentials, a simple correction of 59 mV per pH unit (assuming equal numbers of protons and electrons involved in the reactions) was used. Origin Pro 7.5G (OriginLab Corporation, Northampton, USA) was used for calculating regressions equations, coefficients of determination (R^2), and for creating the graphical E_H/pH relationships. Simple correlation (r) and multiple regression analysis (Adjusted R^2), were performed stepwise to assess the combined impact of E_H, pH, DOC, Fe, Mn, and S on the dynamics of dissolved As, Ba, Cd, Cu, Pb, and Sr. For this purpose, IBM SPSS Statistics, Version 22 was used. The most significant results of the correlation coefficient and the multiple regression analysis were selected for further interpretation. According to Fowler et al. (2006), the strength of the correlations were categorized in our study as follows: $r < 0.20$ represent very weak correlations; r between 0.20 and 0.39 weak correlations; r between 0.4 and 0.69 modest correlations; and $r > 0.69$ strong correlations.

IBM SPSS Statistics, Version 22 was also exploited for conducting factor analysis and canonical discriminant analysis. For these both statistical procedures, the whole dataset of the entire experiment was used.

The factor analysis (FA) is an advanced multivariate statistical method used to describe variability among observed, correlated variables in terms of a potentially lower number of unobserved variables called factors. Factor analysis is related to principal component analysis and has been widely used in geochemistry and soil and groundwater quality management (Love et al., 2004; Maiz et al., 2000; Shaheen et al., 2014b, c; Rinklebe et al., 2016a,b). The factor analysis was carried out as Principal Component Analysis, used for factor extraction to determine the associations between the measured parameters and to identify complex cause-and-effect interrelationships. A Varimax rotation was chosen to make components easier to interpret. The number of interaction calculations was limited to 25.

The canonical discriminant analysis (CDA) is a multivariate statistical technique to analyze differences between groups, such as soils, and to evaluate the parameters that are accountable for the differentiation of these groups. The groups are defined a priori of the calculations. The discriminant functions explain a maximum part of the variance and are calculated by linear combinations. The standardized canonical correlation coefficients are used to determine the factor, which has the highest influence on the discriminant function ignoring the sign before the value (Backhaus et al., 2011; Rinklebe, 2004).

3. Results and discussion

3.1. Soil E_H and pH

The E_H values at sampling times ranged from −270 to +676 mV (Table 1), a typical E_H range that occurs in wetland soils under natural conditions. In soils where the O_2–H_2O redox couple functions, the E_H range is usually between −300 and +700 mV (Yu et al., 2007). The values of pH fluctuated with changes in E_H conditions and ranged between 5.02 in the Mississippi soil and 7.91 in the Louisiana soil (Table 1).

Dynamics of E_H and pH in the entire experiment period showed a significant negative relation in the studied soil groups (All Soils) (Yu et al., 2007). Statistical analysis for E_H and pH values at sampling times also showed a significant negative relation between the E_H and pH in All Soils at sampling points ($R^2 = 0.36$; $P < 0.0001$; n = 76). This relation was negative in the single soil groups (except the Mississippi soil) (Table 2).

An increase of soil pH with the decline in E_H is commonly observed in acidic waterlogged soils. The increasing of pH might be produced by the consumption of protons required for the reduction of NO_3^-, Mn,

Table 1
Variations of E_H, pH, Fe, Mn, S, and DOC in soil solution.

Parameter	Soil	Unit	Minimum	Maximum	Mean	Standard deviation	n
E_H	Arkansas	mV	−158	676	281	285.6	13
	Mississippi		−268	552	201	289.6	15
	California		−270	617	273	272.4	16
	Louisiana		−247	470	173	259.0	7
	Texas		−122	554	231	258.8	8
	China		−159	559	241	252.1	7
	Indonesia		−153	647	198	271.6	15
	All Soils		−270	676	231	266.16	81
pH	Arkansas		5.45	7.40	6.47	0.65	13
	Mississippi		5.02	7.62	6.69	0.82	13
	California		5.71	7.22	6.45	0.48	14
	Louisiana		6.56	7.91	7.25	0.52	7
	Texas		5.14	6.92	6.31	0.74	8
	China		5.48	6.75	5.96	0.52	7
	Indonesia		5.09	7.14	6.12	0.72	15
	All Soils		5.02	7.91	6.44	0.71	77
Fe	Arkansas	mg L^{-1}	0.063	2.78	1.38	1.08	13
	Mississippi		0.063	2.30	0.42	0.68	16
	California		0.063	16.29	2.18	5.17	16
	Louisiana		0.063	2.63	1.02	1.14	7
	Texas		1.337	28.90	16.06	11.11	7
	China		0.063	18.68	5.26	7.65	7
	Indonesia		0.063	9.06	3.52	3.67	15
	All Soils		0.063	28.90	3.31	6.24	81
Mn	Arkansas	mg L^{-1}	0.250	10.77	4.76	3.62	13
	Mississippi		0.063	4.81	0.97	1.56	16
	California		0.063	5.15	2.26	1.92	16
	Louisiana		0.063	2.47	1.22	1.13	7
	Texas		0.063	1.93	1.22	0.79	8
	China		0.063	4.67	2.29	1.85	7
	Indonesia		0.063	10.27	6.01	2.96	15
	All Soils		0.063	10.77	2.90	2.95	82
S	Arkansas	mg L^{-1}	2.63	4.11	3.53	0.39	13
	Mississippi		0.013	4.44	1.77	1.21	16
	California		1.79	12.42	6.18	2.78	16
	Louisiana		2.52	4.26	3.10	0.56	7
	Texas		5.55	7.81	6.57	0.92	8
	China		8.51	13.63	10.46	1.59	7
	Indonesia		10.82	14.42	12.12	1.09	15
	All Soils		0.013	14.42	6.13	4.02	82
DOC	Arkansas	mg L^{-1}	13.0	94.5	44.02	29.24	13
	Mississippi		9.4	48.3	23.22	14.42	16
	California		8.8	182.3	40.75	53.85	16
	Louisiana		23.2	105.5	53.14	34.92	7
	Texas		8.3	53.8	32.95	19.87	8
	China		66.5	230.0	131.95	67.45	7
	Indonesia		10.8	67.7	32.67	20.58	15
	All Soils		8.3	230.0	44.45	45.11	82

Table 2
Exponential regression analysis of As, Ba, Cd, Cu, Fe, Mn, Pb, S, Sr, DOC, pH and soil redox potential (E_H) in a microcosm incubation study in the soils studied.

Element	Equation	R^2	P[a]	n
Arkansas soil				
As	Y = 6.48202 − 0.00933 X	0.43	<0.05	13
Ba	Y = 396.71298 + 0.48985 X	0.52	<0.001	13
Sr	Y = 288.4884 + 0.1408 X	0.36	<0.05	13
Mn	Y = 7560.6238 − 9.95496 X	0.62	<0.005	13
DOC	Y = 70.39629 − 0.09365 X	0.84	<0.0001	13
pH	Y = 6.87368 − 0.0014 X	0.37	<0.05	13
Mississippi soil				
As	Y = 12.78306 − 0.01996 X	0.40	<0.05	15
Ba	Y = 530.0275 + 0.97621 X	0.31	<0.05	15
Cu	Y = 17.64334 + 0.03625 X	0.23	<0.05	15
Sr	Y = 438.15093 + 0.73491 X	0.52	<0.0005	14
Fe	Y = 770.21714 − 1.62865 X	0.45	<0.01	15
DOC	Y = 33.5728 − 0.04691 X	0.89	<0.0001	15
California soil				
As	Y = 18.74728 − 0.04302 X	0.66	<0.0005	16
Ba	Y = 395.69032 + 0.36564 X	0.58	<0.0005	16
Cd	Y = 0.36782 + 4.12993E-4 X	0.22	<0.05	16
Cu	Y = 6.771 + 0.04445 X	0.29	<0.05	16
Pb	Y = 30.30854 + 0.06702 X	0.34	<0.05	15
Fe	Y = 6095.32931 − 14.34457 X	0.57	<0.0005	16
Mn	Y = 4054.69509 − 6.57989 X	0.87	<0.0001	16
S	Y = 4057.2697 + 5.61506 X	0.37	<0.05	15
DOC	Y = 87.52273 − 0.17125 X	0.75	<0.0001	16
pH	Y = 6.72917 − 0.0012 X	0.47	<0.005	14
Louisiana soil				
Mn	Y = 1856.47008 − 3.65497 X	0.70	<0.05	7
DOC	Y = 74.54256 − 0.12329 X	0.84	<0.005	7
pH	Y = 7.54298 − 0.00165 X	0.66	<0.05	7
Texas Soil				
As	Y = 9.01275 − 0.01071 X	0.70	0.018	7
DOC	Y = 46.05552 − 0.05667 X	0.54	<0.05	8
pH	Y = 6.81518 − 0.00216 X	0.58	<0.05	8
Chinese soil				
As	Y = 21.46055 − 0.04596 X	0.65	<0.05	7
Cd	Y = 0.32473 + 5.97905E-4 X	0.53	<0.05	7
Cu	Y = 13.16689 + 0.02858 X	0.68	<0.05	7
Fe	Y = 11,639.21847 − 26.51694 X	0.76	<0.05	7
Mn	Y = 3872.78553 − 6.56799 X	0.80	<0.005	7
DOC	Y = 191.66977 − 0.24821 X	0.86	<0.005	7
pH	Y = 6.31562 − 0.00147 X	0.62	<0.05	7
Indonesian soil				
As	Y = 1.85543 − 0.00528 X	0.59	<0.005	13
Ba	Y = 243.38873 + 0.2046 X	0.31	<0.05	15
Cd	Y = 0.28414 + 5.88125E-4 X	0.43	<0.005	15
Cu	Y = 9.86552 + 0.0211 X	0.29	<0.05	15
Fe	Y = 5634.05033 − 10.69087 X	0.62	<0.0005	15
Mn	Y = 7075.76407 − 5.38962 X	0.25	<0.05	15
S	Y = 12,601.20274 − 2.41859 X	0.36	<0.05	15
DOC	Y = 45.49788 − 0.06473 X	0.73	<0.0001	15
pH	Y = 6.62946 − 0.00256 X	0.92	<0.0001	13

[a] Significant relations are given only.

and Fe as reported by Zarate-Valdez et al. (2006); Frohne et al. (2011, 2012), and Rinklebe et al. (2015a).

3.2. Release of DOC, Fe, Mn, and S in relation to the changes of E_H/pH

The concentrations of DOC in All Soils varied from 8.3 to 230 mg L^{-1} (Table 1). The Texas and California soils showed the lowest values, while the Chinese soil showed the highest concentration (Table 1). In All Soils, the highest concentrations of DOC were observed under reducing conditions, while the lowest were detected under oxidizing conditions (Fig. 1). Therefore, the DOC showed a significant negative relation with E_H in All Soils (Fig. 1). However, the relation between DOC and E_H was negative in each single soil (Table 2). In addition, the relation between the DOC and pH was significantly positive in All Soils (Table 3).

The increase of DOC under reducing conditions has been observed by various authors and is considered to be a response of the release of OM bound to reductively dissolved Fe and Mn oxyhydroxides and/or production of dissolved organic metabolites by reducing bacteria (e.g., Antic-Mladenovic et al., 2011; Frohne et al., 2014; Grybos et al., 2009; Rinklebe et al., 2016a,b; Shaheen et al., 2014a).

Concentrations of Fe and Mn in All Soils varied from 0.063 to 28.9 mg L^{-1} for Fe and from 0.063 to 10.77 mg L^{-1} for Mn. The Texas soil showed the highest concentration of Fe while the Arkansas and the Indonesian soils showed the highest Mn concentration (Table 1). The solubility of Fe and Mn was negatively related to soil E_H in All Soils (Fig. 1). The relation between Fe and E_H was negative in the Mississippi, Indonesian, California, and Chinese soil and non-significant in the Arkansas, Texas, and Louisiana soils (Table 2). The relation between Mn and E_H was negative in the single soil groups (except the Mississippi and Texas soils) (Table 2). The relation between dissolved Fe and pH was positive in All Soils (Table 3).

Table 3
Exponential regression analysis of As, Ba, Cd, Cu, Pb, Sr and their controlling factors (pH, DOC, Fe, Mn, and S) in a microcosm incubation study in the soils studied.

Element	Equation	R^2	P[a]	n
pH				
As	Y = −17.74539 + 3.66529 X	0.08	<0.05	77
Ba	Y = 913.2552 − 76.54017 X	0.06	<0.05	76
Cd	Y = 1.22792 − 0.12184 X	0.09	<0.01	77
Fe	Y = −11,404.56739 + 2343.38254 X	0.07	<0.05	77
S	Y = 18,519.58509 − 1893.27951 X	0.11	<0.005	77
DOC	Y = −77.14634 + 19.18921 X	0.09	<0.01	77
Fe				
As	Y = 3.64445 + 5.8076E-4 X	0.17	<0.001	82
Ba	Y = 521.72251 − 0.01616 X	0.13	<0.005	82
Sr	Y = 471.57382 − 0.00932 X	0.05	<0.05	79
S	Y = 5648.79191 + 0.13794 X	0.05	<0.05	82
DOC	Y = 33.5433 + 0.00313 X	0.20	<0.0001	82
DOC				
As	Y = −0.60074 + 0.14109 X	0.50	<0.0001	82
Ba	Y = 578.11452 − 2.53694 X	0.15	<0.005	82
Cd	Y = 0.51422 − 0.00157 X	0.06	<0.005	82
Sr	Y = 558.47913 − 2.83635 X	0.20	<0.0001	79
Mn	Y = 2102.55007 + 17.97352 X	0.08	<0.05	82
S	Y = 5294.14942 + 18.8066 X	0.04	<0.05	82
Mn				
Cu	Y = 22.67348 − 0.00142 X	0.07	<0.05	82
Sr	Y = 515.71777 − 0.02622 X	0.09	<0.01	79
S	Y = 4796.77044 + 0.45956 X	0.11	<0.005	82
S				
Ba	Y = 701.05798 − 0.03845 X	0.28	<0.0001	82
Sr	Y = 610.35873 − 0.02758 X	0.18	<0.0001	79

[a] Significant relations are given only.

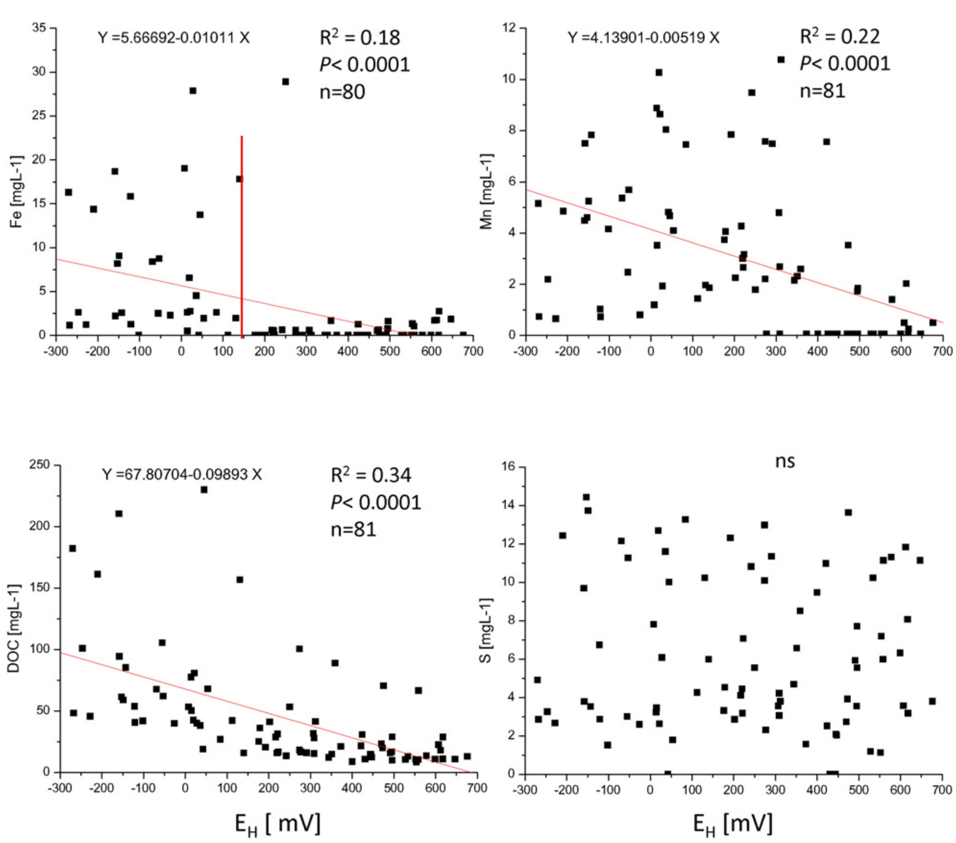

Fig. 1. Relationship between E_H vs. concentrations of DOC, Fe, Mn, and S in the soil solution of All Soils.

When the soil slurry reached strongly reducing conditions, soil redox-active species were transformed into their reduced forms, Fe^{3+} and Mn^{4+} to Fe^{2+} and Mn^{2+}, respectively, resulting in higher dissolved Fe and Mn concentrations. During oxidation, Fe and Mn can be mostly immobilized via precipitation as Fe and Mn oxyhydroxides (e.g., Reddy and Delaune, 2008; Rinklebe and Laing, 2011). Concentrations of Fe and Mn were dropped sharply at E_H ≥150 mV and 400 mV, respectively (Fig. 1). Thus, an increase of E_H from reducing to oxidizing conditions generated a reverse order of Fe and Mn immobilization (Fe earlier than Mn: Fig. 1) compared to when soil conditions were changed from oxidizing to reducing conditions (Shaheen et al., 2014a). In addition, an increase of Fe and Mn solubility under neutral conditions indicate that E_H might have had a stronger impact on the variability of Fe and Mn concentrations in the solution than soil pH.

Concentrations of S in All Soils varied from 0.013 to 14.4 mg L^{-1}. The Mississippi soil showed the lowest concentration, while the Indonesian soil showed the highest concentration (Table 1). In All Soils, concentrations of dissolved S showed non-significant relations with E_H (Fig. 1). However, the relation between S and E_H in the single soil groups was negative in the Indonesian soil, positive in the California soil, and non-significant in the other soils (Table 2).

An inconsistent trend between releases of S with E_H was observed in All Soils (Fig. 1). The most common form of dissolved S is sulfate and sulfide in oxic and anoxic soils, respectively. The sulfur E_H–pH diagram indicates that sulfate is the dominant form of sulfur in most environments (Takeno, 2005). We assume the formation of sulfate under oxic conditions and sulfides under the lowest E_H values in our experiment (−270 mV) since sulfate reduction to sulfide requires E_H value around −100 to −150 mV at pH 7 (Takeno, 2005). In this respect, Reddy and DeLaune (2008) indicated that reducing solutions generally contain H_2S at neutral to weakly acidic conditions (the pH values under reducing conditions in our experiment ranged from 6.7 to 7.9), and an important S-containing ion in an oxidizing solution is SO_4^{2-}. Thereafter, under oxic conditions in our experiment the formed sulfide might be oxidized to sulfate. Therefore, dissolved S showed high concentrations under a wide range of E_H in All Soils (Fig. 1). In the Indonesian soil, the solubility of S increased under reducing conditions and thus showed a negative relation with E_H, while this relation was positive in the California soil (Table 2). This might mean that reducing conditions accelerated the leachate of S in the Indonesian soil, while the opposite trend was found in the California soil.

The relation between S on one hand and Fe and DOC, on the other hand was positive but weak in All Soils (Table 3). The positive relation between S and Fe might indicate that the iron sulfides couple the S cycling with the Fe^{3+}–Fe^{2+} redox wheel what has been supported by the processes and fluxes occurring in the geochemical Fe sulfide cycle (Reddy and DeLaune, 2008; Rickard and Luther, 2007). Additionally, Du Laing et al. (2009b) and Shaheen et al. (2014a,b,c) mentioned that total SO_4^{2-} concentration is often a poor indicator of SO_4^{2-} reduction rates due to rapid internal cycling of S in wetlands. The positive relation between S and DOC might be because a certain part of S in wetland soils occurs in an organic form (Reddy and DeLaune, 2008).

3.3. Release of as, Ba, Cd, Cu, Pb, Sr as affected by E_H/pH, DOC, Fe, Mn, and S

Concentrations of dissolved As, Ba, Cd, Cu, Pb, and Sr in the studied soils under different reducing-oxidizing conditions varied widely depending on the type of soil and element (Table 4). Barium showed the highest concentrations (12.5–1475.0 μg L^{-1}), followed by Sr (144.1–986.0 μg L^{-1}), Pb (2.2–262 μg L^{-1}), Cu (0.9–90.7 μg L^{-1}), As (0.04–42.8 μg L^{-1}), and Cd (0.05–1.6 μg L^{-1}). The Mississippi soil showed the highest concentrations of soluble Ba, California (As, Sr, and Cu), China (Pb), and Texas (Cd) (Table 4).

Reducing conditions caused a significant decrease in concentrations of Ba, Cd, Cu, and Sr as compared to the oxidizing conditions in All Soils (Fig. 2). However, concentrations of As were higher under reducing conditions than oxidizing conditions while dynamics of Pb showed an irregular trend with E_H. Therefore, E_H showed a significant positive relation with dissolved Ba, Cd, Cu, Sr, negative with As, while the relation was non-significant with Pb in All Soils (Fig. 2).

Table 4
Variations of As, Ba, Cd, Cu, Pb, and Sr concentrations (μg L^{-1}) in soil solution in the soils studied.

Element	Soil	Minimum	Maximum	Mean	Standard deviation	n
As	Arkansas	0.04	10.44	3.85	4.05	13
	Mississippi	1.95	30.50	8.37	9.01	16
	California	0.04	42.80	6.99	14.37	16
	Louisiana	0.86	10.30	3.80	3.75	7
	Texas	0.04	10.70	5.60	3.97	8
	China	0.38	32.80	10.40	14.36	7
	Indonesia	0.04	5.10	1.64	1.91	15
	All Soils	0.04	42.80	5.67	9.03	82
Ba	Arkansas	279.5	965.0	534.6	193.9	13
	Mississippi	12.5	1475.0	724.4	487.4	16
	California	231.5	745.0	495.5	131.0	16
	Louisiana	370.5	690.0	513.5	101.4	7
	Texas	126.5	394.0	275.7	97.0	8
	China	206.3	280.1	232.3	31.7	7
	Indonesia	123.6	447.1	283.9	100.6	15
	All Soils	12.5	1475.0	465.3	291.3	82
Cd	Arkansas	0.17	0.93	0.35	0.19	13
	Mississippi	0.20	1.07	0.44	0.29	16
	California	0.09	1.02	0.45	0.26	16
	Louisiana	0.05	1.39	0.39	0.45	7
	Texas	0.14	1.59	0.66	0.44	8
	China	0.16	0.79	0.46	0.20	7
	Indonesia	0.10	1.03	0.40	0.24	15
	All Soils	0.05	1.59	0.44	0.29	82
Cu	Arkansas	4.6	31.8	17.3	7.7	13
	Mississippi	3.5	83.8	24.2	21.0	16
	California	0.9	90.7	18.9	22.6	16
	Louisiana	4.9	40.1	18.8	11.4	7
	Texas	8.0	31.7	15.3	8.2	8
	China	6.8	31.8	20.0	8.7	7
	Indonesia	4.7	42.0	14.0	10.5	15
	All Soils	0.9	90.7	18.5	15.4	82
Pb	Arkansas	10.1	80.8	32.2	19.1	13
	Mississippi	6.7	98.5	37.2	24.6	16
	California	6.5	115.0	45.0	31.7	16
	Louisiana	14.4	211.0	60.4	68.3	7
	Texas	9.3	147.0	56.8	40.3	8
	China	6.6	262.0	97.9	102.0	7
	Indonesia	2.2	136.0	54.7	38.6	15
	All Soils	2.2	262.0	50.4	46.9	82
Sr	Arkansas	252.6	473.9	328.1	67.1	13
	Mississippi	206.9	978.0	602.5	281.3	15
	California	639.0	986.0	826.2	99.2	14
	Louisiana	264.7	340.8	303.8	28.5	7
	Texas	268.8	478.4	381.4	87.1	8
	China	144.1	196.0	162.7	21.4	7
	Indonesia	181.1	341.3	245.6	47.6	15
	All Soils	144.1	986.0	441.4	260.4	79

Release of As was negatively related to E_H in the soil groups except for the Louisiana soil. Soluble Ba showed positive relations with E_H in the Arkansas, Mississippi, Indonesian, and California soils. Dissolved Cd and Cu showed positive relations with E_H in the Indonesian, California, and Chinese soils. Dissolved Sr was negative related to E_H in the Arkansas and Mississippi soils. Dissolved Pb was negatively related to E_H in the California soil (Table 2).

Additionally, we have conducted a factor analysis to determine the associations between the measured parameters in All Soils and to identify complex cause-and-effect interrelationships (Fig. 3). The total explained variance in All Soils is 57.9 (30.3 Component No. 1, 16.3 Component No. 2, and 11.3 Component No. 3).

Fig. 3 demonstrates that As, Fe, Mn, and DOC was associated in one group what indicates a close relation between those parameters. The Pb was relatively close to this group while sulfur was separated. Moreover, Ba, Sr, Cd, Cu, and E_H were banded together in one cluster. This

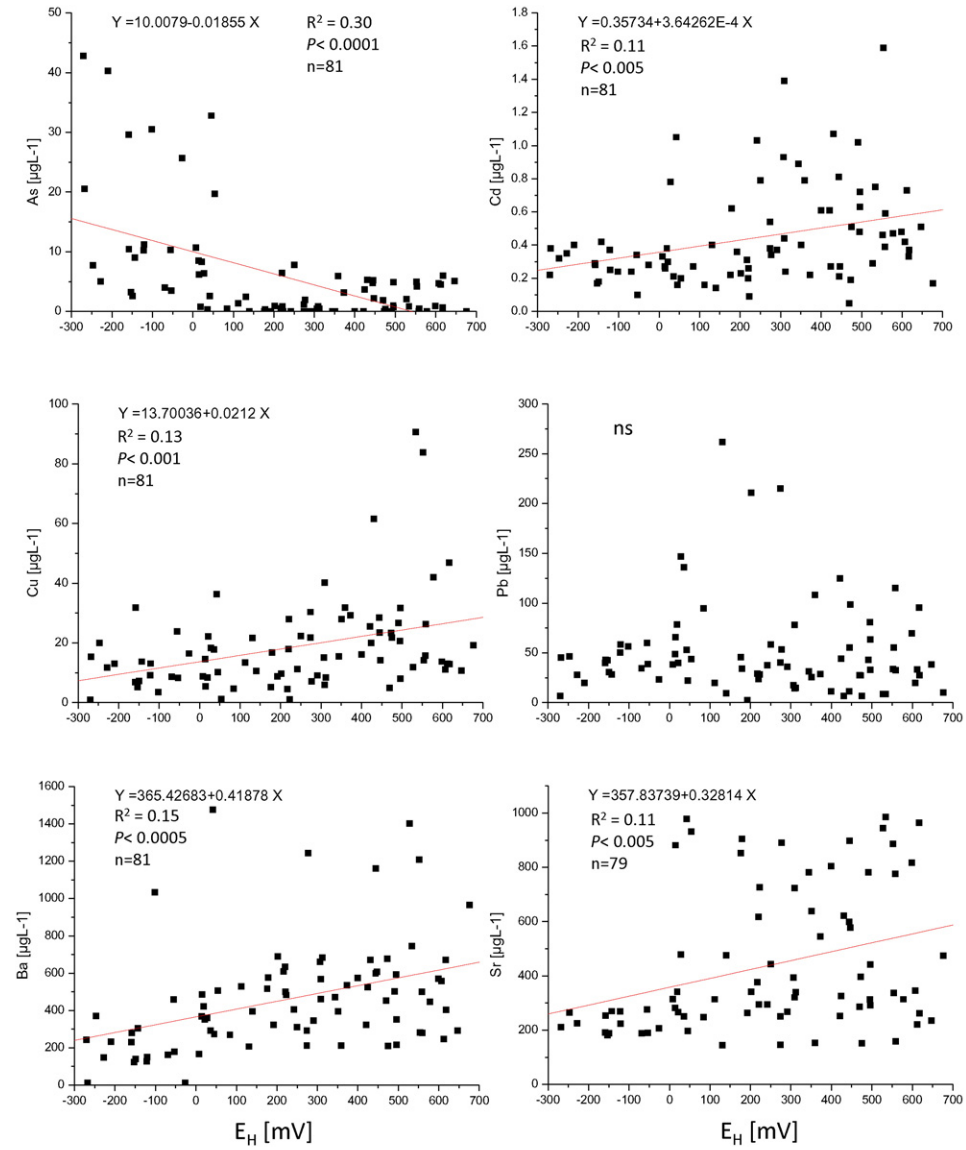

Fig. 2. Relationships between E_H vs. concentrations of As, Ba, Cd, Cu, Pb, and Sr in the soil solution of All Soils.

might support the interpretation that Ba, Sr, Cd, and Cu show a similar fate in response to the changes of soil E_H. The pH was separated (Fig. 3). The different behavior of the elements in the studied soils might be explained by indirect effects of E_H via the changes of pH, and the chemistry of Fe, Mn, S, and DOC.

3.3.1. Impact of soil E_H

Several ions are reduced/oxidized under anaerobic/aerobic conditions which can lead to changing solubility of these elements. For example, increasing the solubility of As under reducing conditions might be due to the direct reduction from As (V) to As (III) which might increase its solubility under reducing conditions as compared to oxidizing conditions (Du Laing et al., 2009a; Majumder et al., 2014; Shaheen et al., 2014b).

Decreasing of Cu solubility under reducing conditions can be attributed to the reducing of Cu^{2+} to Cu^{1+} under reducing conditions with the help of electron donors (e.g., Fe (II)) and bacteria. Our results extended beyond the findings of Frohne et al. (2011); Rinklebe et al., 2016a,b; Schulz-Zunkel et al. (2013, 2015); Shaheen and Rinklebe (2014) and Shaheen et al. (2014c) whose reported an increase in dissolved amounts of Cu during periods with high E_H. They reported that Cu which occurs as Cu^{2+} in oxidizing conditions may be reduced as Cu^{1+} or even as Cu^0 in reducing environments. Furthermore, changes to anoxic conditions may cause a microbial formation of reduced metal (e.g., Cu^0) colloids (Weber et al., 2009a).

However, Cd, Ba, Pb, and Sr ions are rarely reduced or oxidized; thus, changes of the valence state of these elements as a consequence of E_H changes have not been observed in natural sediments and soils (Du Laing et al., 2009c; Frohne et al., 2011, 2014; Menzie et al., 2008; Rinklebe and Shaheen, 2014). Under our experimental conditions, we expect Ba^{2+}, Cd^{2+}, Pb^{2+}, and Sr^{2+} ions to occur under a wide range E_H and pH as shown in Fig. 2 and in the E_H–pH diagrams (Takeno, 2005).

3.3.2. Impact of the chemistry of Fe and Mn

Iron-Mn (hydr)oxides are assumed to be important binding agents for trace elements under oxic conditions. Thus, element concentrations should decrease with rising E_H and decreasing Fe and Mn concentrations since they co-precipitate with Fe (hydr)oxides (e.g., Borch et al., 2010; Du Laing et al., 2009c; Shaheen et al., 2014a). In our study, dissolved As in All Soils and the single soil groups seem to follow this mechanism. However, Ba, Cd, Cu, Sr, and Pb in All Soils did not decrease when Fe concentrations decreased at increasing E_H (Figs. 1 & 2). Therefore, the factor analysis demonstrated that As, Fe, and Mn were clustered in one group (Fig. 3). However, Ba, Cd, Cu, Pb, and Sr were

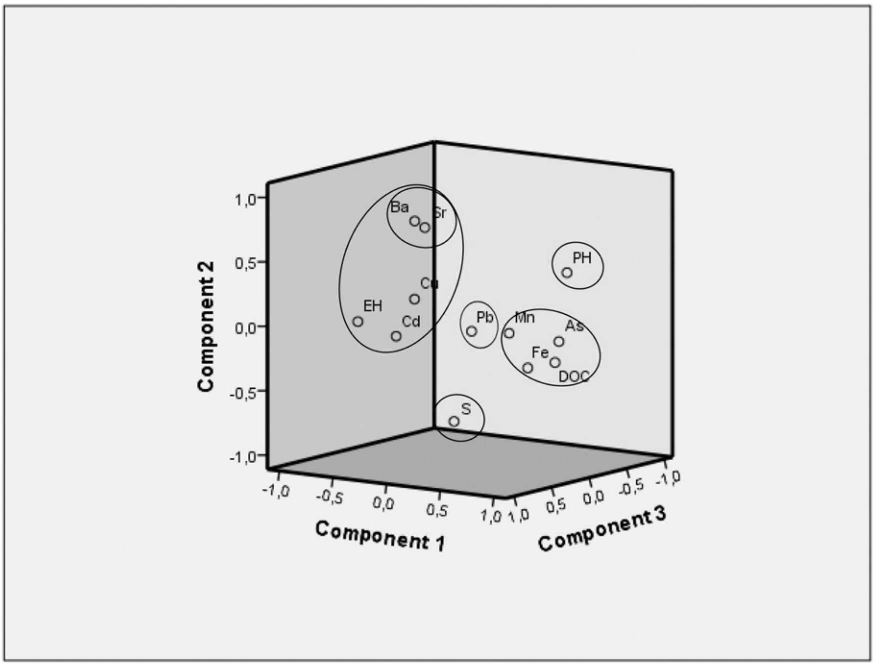

Fig. 3. Factor analysis to determine the relationships between the measured parameters and to identify complex cause-and-effect interrelationships.

Table 5
Correlation coefficients (Pearson) between the studied elements and relevant parameters.

Parameter	Soils	pH	DOC	Fe	Mn	S	As	Ba	Cd	Cu	Pb	Sr	n
	Arkansas	1.0	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	13
	Mississippi	1.0	ns	0.64*	ns	ns	ns	−0.82**	ns	ns	ns	−0.86**	13
	California	1.0	0.70**	0.66**	0.56*	ns	0.69**	−0.59*	ns	ns	ns	ns	14
pH	Louisiana	1.0	ns	ns	ns	0.95*	ns	ns	ns	ns	ns	ns	7
	Texas	1.0	0.87**	0.92**	0.84**	ns	ns	ns	ns	ns	ns	ns	8
	China	1.0	0.93**	0.99**	0.89**	ns	0.95**	ns	ns	−0.88*	ns	0.91*	7
	Indonesia	1.0	0.94**	ns	ns	0.64*	ns	−0.66*	−0.76**	−0.57*	ns	ns	15
	Arkansas	ns	1.0	0.71**	0.76**	ns	0.87**	−0.80**	ns	ns	ns	−0.69**	13
	Mississippi	ns	1.0	0.76**	ns	ns	0.74**	−0.64**	ns	ns	ns	−0.83**	16
	California	ns	1.0	0.97**	0.71**	ns	0.99**	−0.76**	ns	ns	ns	ns	16
DOC	Louisiana	ns	1.0	0.88**	0.79*	ns	0.92**	ns	ns	ns	ns	ns	7
	Texas	0.87**	1.0	ns	ns	ns	0.76*	ns	ns	ns	ns	ns	8
	China	0.93**	1.0	0.89**	0.89**	ns	0.90**	ns	−0.87*	−0.86*	ns	0.80*	7
	Indonesia	0.94**	1.0	0.96**	ns	ns	ns	−0.74**	−0.69**	ns	ns	−0.62*	15
	Arkansas	ns	0.71**	1.0	ns	−0.60*	0.93**	−0.86**	ns	ns	ns	−0.78**	13
	Mississippi	0.64*	0.76**	1.0	ns	ns	0.56*	−0.75**	ns	ns	ns	−0.80**	16
	California	ns	0.97**	1.0	0.58*	ns	0.96**	−0.77**	ns	ns	ns	ns	16
Fe	Louisiana	ns	0.88**	1.0	ns	ns	0.97**	ns	ns	ns	ns	−0.78*	7
	Texas	0.92**	ns	1.0	0.94***	ns	ns	ns	ns	ns	ns	ns	7
	China	0.99**	0.89**	1.0	0.86*	ns	0.96**	ns	ns	−0.89**	ns	0.93**	7
	Indonesia	0.90**	0.96**	1.0	ns	ns	0.53*	−0.70**	−0.64*	−0.52*	ns	−0.57*	15
	Arkansas	ns	0.76**	ns	1.0	ns	ns	ns	ns	ns	ns	ns	13
	Mississippi	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	16
	California	0.56*	0.71**	0.58*	1.0	ns	0.65**	−0.68**	−0.51*	−0.57*	ns	ns	16
Mn	Louisiana	ns	0.79*	ns	1.0	ns	ns	ns	ns	ns	ns	ns	7
	Texas	0.84**	ns	0.94**	1.0	−0.80*	ns	ns	ns	ns	ns	0.79*	7
	China	0.89**	0.89**	0.86*	1.0	ns	0.89**	ns	ns	ns	ns	0.76*	7
	Indonesia	ns	ns	ns	1.0	ns	−0.67*	ns	ns	ns	ns	ns	15
	Arkansas	ns	ns	−0.60*	ns	1.0	ns	ns	ns	ns	ns	0.59*	13
	Mississippi	ns	ns	ns	ns	1.0	ns	ns	−0.77**	ns	ns	ns	16
	California	ns	ns	ns	ns	1.0	ns	ns	ns	0.52*	ns	ns	16
S	Louisiana	0.95*	ns	ns	ns	1.0	ns	ns	ns	ns	ns	ns	7
	Texas	ns	ns	ns	−0.80*	1.0	ns	−0.72*	ns	−0.76*	ns	−0.82*	8
	China	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	7
	Indonesia	0.64*	ns	ns	ns	1.0	ns	−0.54*	−0.54*	ns	ns	ns	15

DOC: dissolved organic carbon; ns: not significant.
* Correlation is significant at the 0.05 level.
** Correlation is significant at the 0.01 level.

separated in different groups (Fig. 3). These results indicate that the chemistry of Fe and Mn might be linked to the dynamics of As more than the dynamics of Ba, Cd, Cu, Pb, and Sr in the soils.

The positive relations between As and Fe was shown using the single regression analysis for All Soils in Table 3 and by using the simple correlation analyses for the single soil groups in Table 5 indicating a passive mobilization of As due to the dissolution of Fe-minerals.

In addition, multiple regression analysis revealed that E_H and Fe together explained 33% of the dynamics of As (Adjusted $R^2 = 0.33$). Moreover, the impact of Fe on As dynamics was stronger in the individual soils than All Soils, since E_H and Fe together explain 70, 91, and 94% of the dynamics of As in the Indonesian, Arkansas, and California soil, respectively. Dissolved Mn has non-significant relation with As in All Soils (Table 3).

These results imply a sorption of As to Fe(hydr)oxides. Therefore, when the oxides are reductively dissolved, associated elements will be released. Under oxidized conditions Fe- and Mn-oxides precipitate, and As is sequestered. Both As(III) and As(V) are known for their high sorption affinity to Fe-mineral surfaces (especially oxides and hydroxides), where they form strong complexes via ligand exchange (Dixit and Hering, 2003; Ona-Nguema et al., 2005; Shaheen et al., 2013). Redox-sensitive components indicated that As was mobilized in moderately reducing conditions. The Fe/Mn oxide-bound As would be released during reductive dissolution of Fe/Mn oxides in reducing conditions (Guo et al., 2014). Therefore, reductive dissolution of Fe/Mn oxides was the major cause for As mobilization in the moderately reducing conditions, which is the most accepted mechanism for high As groundwater in Southeast Asia (Guo et al., 2014; Islam et al., 2004) and in soil solution (Frohne et al., 2011; Rupp et al., 2010; Shaheen et al., 2014b). Recently, Ying et al. (2013) found that As(III) oxidation by birnessite is appreciable in the presence of O_2 only; oxidation of As(III) to As(V) by Mn-oxides under anaerobic conditions might appear as a result of microbially mediated Mn(IV/III) reduction.

Although As was released during reductive dissolution of Fe/Mn oxides, the relation between dissolved As and dissolved Fe was weak ($R^2 = 0.17$) and non-significant with Mn (Table 3). Three plausible reasons would be used to explain the weak relations. One is that both reduced Mn and Fe would be re-sorbed onto residual Fe oxides (Guo et al., 2014; Stüben et al., 2003), due to strong adsorption of Fe(II) on the surface of Fe oxyhydroxide/oxides (Handler et al., 2009). The second one is that adsorbed As(V) would be reduced to As(III) in the presence of indigenous bacteria (Chang et al., 2012), leading to As release due to the weak affinity of As(III) species on Fe/Mn oxide minerals (Guo et al., 2014). The third is that Fe(II) was co-precipitated together with S^{2-} in soil solution being oversaturated with respect to the relatively high S in our soils (Guo et al., 2014).

The correlation, regression, and factor analyses (Fig. 1, Tables 3 and 5) showed that a co-precipitation of Ba, Cd, Cu, Pb, and Sr with Fe-Mn oxides is unlikely in the current study which is in agreement with results reported by several other authors (e.g., Caetano et al., 2003; Cappuyns and Swennen, 2005; Frohne et al., 2011, 2014; Tack et al., 1998). In addition, Menzie et al. (2008) found that Ba ions do not bind strongly to inorganic ligands. Furthermore, adsorption of Ba and Sr on Fe(hydr)oxides can be hindered due to competition with other dissolved cations with a similar ionic radius such as Ca^{2+} und Mg^{2+} (Kamel, 2010; Seliman et al., 2010). This could have happened in the Arkansas, Mississippi, California, Louisiana, and Indonesia soils as well. Also, similar to our results, Cappuyns and Swennen (2005) and Caetano et al. (2003) did not observe a co-precipitation of Cd with Fe (hydr)oxides, whereas Cu was not affected by the dissolution of Fe oxides in the study of Tack et al. (1998).

The relatively low pH (5.02) and relatively high amounts of DOC (8–100 mg L^{-1}) which might contribute to the formation of mobile metal–DOC complexes under oxic conditions in our study might have prevented Ba, Cd, Cu, Sr, and Pb from co-precipitating with or adsorbing to Fe–Mn oxides under these oxic conditions (Frohne et al., 2011; Schulz-Zunkel and Krüger, 2009).

3.3.3. Impact of DOC

Concentrations of As showed strong positive relations with DOC in All Soils (Table 3). In the soil groups (except for the Indonesian soil), As showed strong positive relations with DOC and r values ranged between 0.74 to 0.99 (Table 5). In addition Sr showed strong positive relations with DOC in the Chinese soil. On other hand, Ba, Cd, and Sr showed negative relation with DOC in All Soils (Table 3).

The factor analysis demonstrated that As and DOC were clustered in one group that support the hypothesis of the association between DOC and As (Fig. 3). One might conclude that the behavior of As in All Soils can also be explained by the impact of the chemistry of DOC on the temporal dynamics of this element. Additionally, the association between DOC and As confirmed by the multiple regression where the E_H and DOC together explain 51% of As dynamics in All Soils (adjusted $R^2 = 0.51$). Theses regression relations were stronger in the individual soil than All Soils, where E_H and DOC together explained 50, 55, 86, and 97% of As dynamics in the Mississippi, Indonesian, Arkansas, and California soil, respectively.

These results indicate that As in All Soils might be bound to DOC under oxidizing conditions. Therefore, when the DOC becomes reductively and microbial decomposed, the associated As will be released. Organic matter can strongly influence the solubility of As mainly through redox reactions, competitive sorption, desorption and complexation reactions. Dissolved organic carbon was believed to be the major contributor to reducing conditions. Because degradation of DOC consumed oxidants, including O_2, NO_3^-, Fe(III), As(V) and SO_4^{2-}, and resulted in reducing conditions (Anawar et al., 2013; Guo et al., 2014), there was a strong relation between As concentrations and DOC ($R^2 = 0.50$; Table 3). In this respect, Williams et al. (2011) reported that DOC was the strongest determinant of arsenic solid-solution phase partitioning, which demonstrates the dual importance of organic matter, in terms of enhancing arsenic release from soils.

Dissolved organic carbon and Fe mineral phases are known to influence the mobility of As in groundwater. Arsenic can be associated with colloidal particles containing organic matter and Fe (Majumder et al., 2014). The positive relations between As, DOC, and Fe might indicate the combined impact of DOC and Fe on the release dynamics of As in our soils. The microbially mediated dissolution of As-hosting Fe-minerals is considered as a key mechanism in As mobilization (Neidhardt et al., 2014). Our first hypothesis is that the positive relations between As, Fe, and DOC in soil solution suggest that As mobilization might occur via microbially mediated reductive dissolution of As bearing Fe(III) oxides by organic matter. Arsenic was released during release of DOC in combination with reduction of Fe oxides and formation of As(V) (Anawar et al., 2013; Guo et al., 2014; Lawson et al., 2013; Weiske et al., 2013). In addition, Mladenov et al. (2010, 2015) underscored the importance of natural DOM in the release of As and Fe from aquifers.

Second hypothesis might be that the positive correlations between DOC, Fe and As indicate a close association of As with larger Fe-rich inorganic colloids and highlights the close association of As with smaller organic colloids in our soils. In this respect Majumder et al. (2014) found that As(III) is mainly associated with larger inorganic colloids, whereas, As(V) is associated with smaller organic/organometallic colloids. Majumder et al. (2014) confirmed the association of As with DOC and Fe mineral phases suggesting the formation of dissolved organo-Fe complexes and colloidal organo-Fe oxide phases.

The element/DOC ratio can serve as an indication of the complexation strength of metals with DOC (Frohne et al., 2014). Generally, organic matter molecules contain various functional groups that act as binding sites for metals with different binding strength. At high element/DOC ratios, binding sites with very high affinity for metals will be filled up, and metal binding partly shift to sites with lower binding affinities (Jansen et al., 2002). According to Craven et al. (2012), the ratio of Cu to DOC affects the strength of Cu binding to DOC. They found that at low Cu/DOC ratios, Cu binds to strong ligands such as nitrogen-containing or sulfur functional groups. At high Cu/DOC ratios, Cu might associated with weaker sites such as carboxyl and phenol groups.

We observed low element/DOC ratios at low E_H and vice versa. Therefore, the ratios between Ba, Cd, Cu, Pb, Sr on one hand and DOC, on the other hand, correlated significantly positive with E_H (Fig. 4).

This indicate that Ba, Cd, Cu, Pb, and Sr might preferentially bind to strong binding sites at low E_H, whereas the binding shifts to weaker forms at high E_H in our soils, which is in agreement with Frohne et al. (2014).

3.3.4. Impact of sulfur

With decreasing redox potential, microbial sulfate reduction is initiated, and mobilization of PTEs can be limited by co-precipitation with mixed valence secondary phases and sulfides (Borch et al., 2010; Weber et al., 2009b). However, when sulfate reduction begins some PTEs are also released in colloidal form as element-sulfide colloids, resulting in enhanced mobilization for several days after flooding (Hofacker et al., 2013; Weber et al., 2009a). The extent to which element sulfides are formed is limited by the available sulfate and controlled by the solubility of the corresponding element sulfides (Weber et al., 2009b). When conditions change back from anoxic to oxic, sulfides will be oxidized, releasing PTEs to pore waters, which may (co)precipitate with oxy(hydr)oxides (Du Laing et al., 2009a,b; Frohne et al., 2011, 2014).

As mentioned in Section 3.1, we assume the formation of sulfides under the lowest E_H values in our experiment. Therefore, the low Ba, Cd, Cu, Pb, and Sr concentrations at low E_H in our experiment (Fig. 2) might be caused to a certain extent by sulfide precipitation, as also found by other authors (Du Laing et al., 2009a,b; Frohne et al., 2011, 2015).

Concentrations of Ba and Sr showed negative relations with S in All Soils (Table 4). The factor analysis showed that S was separated far from the Ba and Sr group (Fig. 3). The multiple regression showed that the E_H and S together explain 39 and 25% of Ba and Sr dynamics, respectively in All Soils.

Dissolved Cu correlated negatively with S in the Texas soil (Table 5). Dissolved Cd correlated negatively with S in the Mississippi and the Indonesian soils (Table 5). Nevertheless, a very small amount of sulfides is needed to precipitate most of Cd. This amount may even not be detectable with common titration-based procedures for sulfide determination (Du Laing et al., 2009a). In addition, sulfides will preferentially precipitate with Cd because the solubility of CdS is lower in comparison

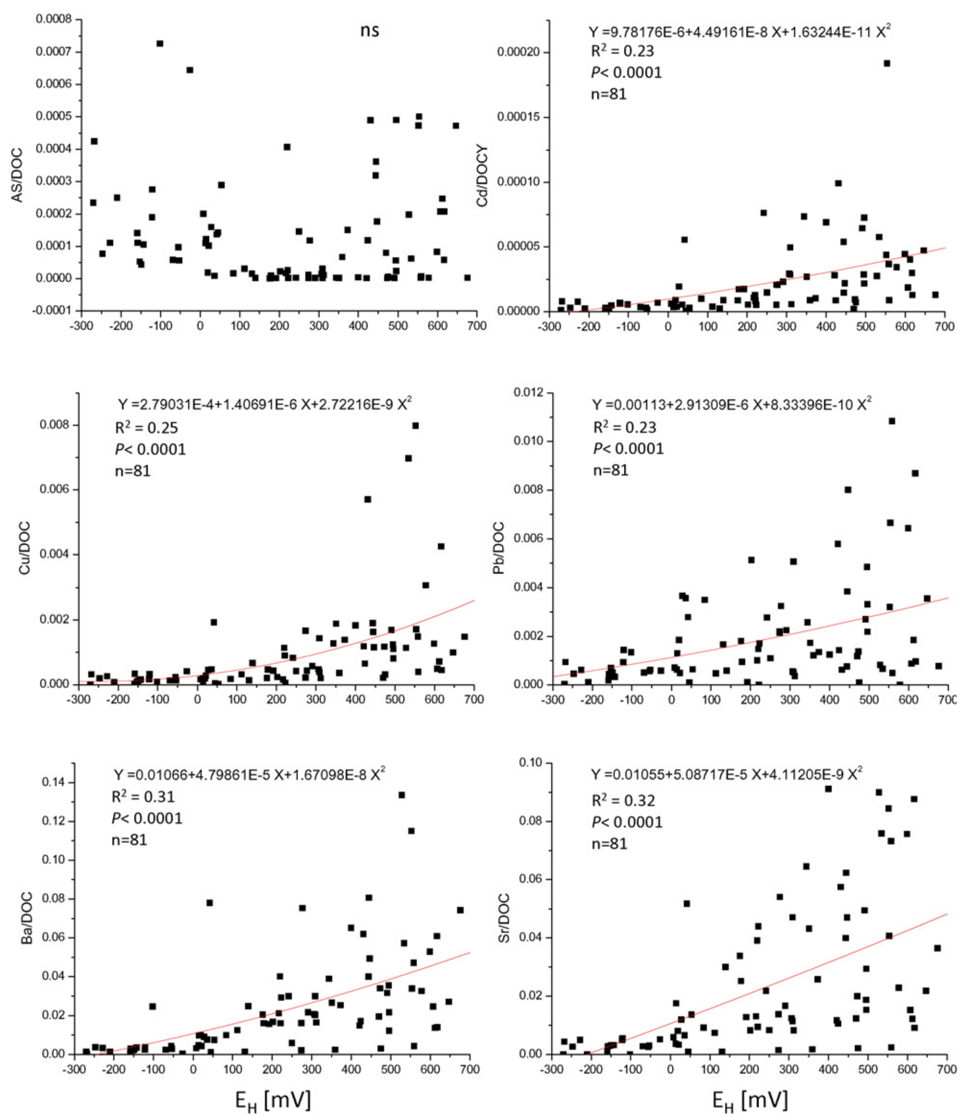

Fig. 4. Relationship between E_H and total metal(loid)/DOC ratios in the soil solution in All Soils.

with other elements like Fe (Du Laing et al., 2009a,b). Thus, it is commonly known that solubility and bioavailability of Cd in paddy fields decrease when the soil is under waterlogged (reduced) conditions (Shaheen et al., 2014c). The formation of CdS is the expected mechanism of Cd immobilization in reduced paddy soils. Recent investigations using X-ray absorption fine structure (XAFS) spectroscopy determined the presence of CdS and Cd sorbed with multiple soil colloids in an anthropogenically contaminated paddy soil (Hashimoto and Yamaguchi, 2013; Khaokaew et al., 2011).

Elements which are bound to sulfides can be released during the oxidation of the soil due to the oxidation of sulfides to sulfates (Du Laing et al., 2009a,b,c; Frohne et al., 2011; Khaokaew et al., 2011; Shaheen et al., 2014c). This might be one reason for the increasing solubility of Ba, Cd, Cu, Pb and Sr with increasing E_H (Fig. 2).

3.3.5. Impact of soil pH

The increase of Ba, Cd, Cu, Pb and Sr solubility under oxidizing conditions can also be attributed to the decrease of pH caused by changes of E_H conditions as confirmed by the negative relation between pH and dissolved concentrations of these elements (except Pb) in some of the single soil groups (Table 5). In All Soils, dissolved Cd showed a negative relation with pH (Table 3). As reduction of soil chemicals increases over time, soil pH rises and CdS has been shown to be formed (Hashimoto and Yamaguchi, 2013; Khaokaew et al., 2011). And upon drainage of the flooded soil, pH falls and CdS is oxidized rapidly.

Generally, metal cations are released from organic matter and other sorbents such as clay mineral surfaces when pH decreases (e.g., Du Laing et al., 2009b; Frohne et al., 2014).

3.4. Canonical discriminate analysis

Fig. 5 illustrates that the geochemical behavior of the seven soils can clearly be differentiated from each other. The underlying dataset of the entire microcosm experiment was used. A little overlap was observed between Arkansas and Louisiana soils only. Function 1 explained 51.2% of the variability of the geochemical behavior of the seven different soils; Function 2 can explain 33.8% and both function together 85.0%.

In general, the seven soils were discriminated separately according to their geochemical behavior. However, function 1 discriminate the soils to three groups, i.e., the Arkansas, Louisiana, and Chinese soils; the Mississippi, Texas, and Indonesian soils; and the California soil (Fig. 5). Function 2 discriminates the soils to two groups, i.e., the Arkansas, Louisiana, and Mississippi soils; and the Chinese, Indonesian, Texas, and California soils (Fig. 5). Standardized canonical discrimination coefficient showed that Sr, Ba, DOC, and E_H parameters, respectively are mainly responsible for the discrimination of the soils based on function 1, while Ba, S, and E_H, respectively are mainly responsible for the discrimination of the soils based on function 2. Based on both function 1 and function 2, the behavior of the Arkansas and Louisiana soils was relatively similar, while the geochemical behavior of the Indonesian and Texas soils was very close (Fig. 5).

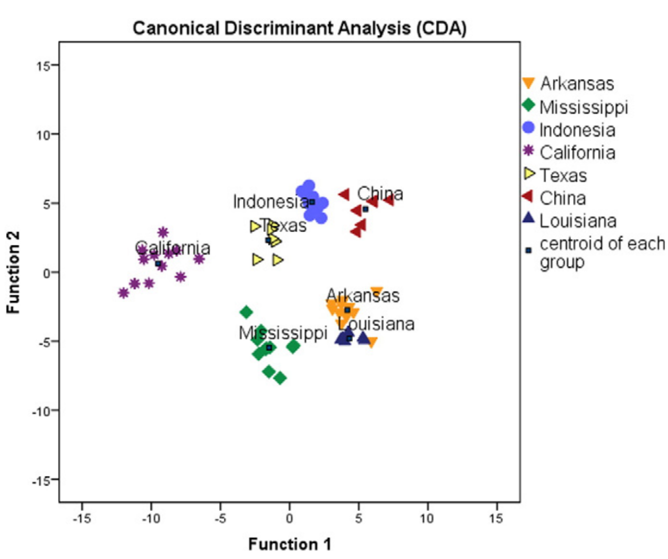

Fig. 5. Canonical discriminant analysis (CDA) illustrates a separation of the seven different soils based on their geochemical behavior.

The similarity in the geochemical behavior in the Indonesian and Texas soils might be explained by the relatively close mean values of E_H, pH, DOC, Ba, Cu, and Pb in both soils (Table 1 and 4) and the relatively similar negative relations between E_H and pH, As, and DOC in both soils (Table 2), as well as the relatively similar negative relations between pH and Fe and DOC in both soils (Table 5).

The similarity in the geochemical behavior in the Arkansas and Louisiana soils might be explained by the relatively close mean values of As, Ba, Cd, Cu, Sr, Fe, S, and DOC in both soils (Table 1 and 4) and the relatively similar negative relations between E_H and Mn and DOC in both soils (Table 2), as well as the relatively similar negative relations between As and Fe and DOC in both soils (Table 5).

The California soil showed different behavior compared to the other soils (Based on Function 1) and this might be due to that this soil showed the highest maximum concentrations of As, Cu, and Sr (Table 4). In addition this soil showed stronger relations between E_H and As, Ba, Cu, Fe, Mn, and S than the other soils, as well as was the only soil which showed a significant relation between E_H and dissolved Pb (Table 2).

4. Conclusions

Wetland soils can be net sinks for pollutants; however, during different flooding-drainage- cycles and the onset of reducing/oxidizing conditions, these soils may act as a source for pollutants. We aimed to determine the impact of a range of reducing and oxidizing conditions of different rice cultivated soils on the dynamics of the redox-dependent pollutants, As, Ba, Cd, Cu, Pb, and Sr as well as the associate changes of pH, DOC, and the chemistry of S, Fe, and Mn. Redox potential is important for metal(loid)s fate in the current study. Arsenic, Fe, Mn, and DOC showed a negative relation with E_H, while the relationships between Ba, Cd, Cu, and Sr versus E_H were positive. Results imply an absorption of As to Fe(hydr)oxides and an interaction with DOC while a co-precipitation of Ba, Cd, Cu, Pb, and Sr with Fe-Mn oxides is unlikely in the current study and particularly their dynamics may be influenced by pH and the chemistry of S.

We observed low metal/DOC ratios at low E_H and vice versa (except for As). These results indicate that Ba, Cd, Cu, Pb, Sr might preferentially bind to strong binding sites of DOC at low E_H, whereas the binding shifts to weaker forms of DOC at high E_H. The geochemical behavior of the different soils differentiated clearly from each other. The geochemical behavior of the Arkansas was close to the Louisiana soil, while the Indonesian soil was close to the Texas soil, and the California soil showed a different behavior. In summary, inundation of the soils favors the mobilization of As while diminishing the mobilization of Ba, Cd, Cu, Pb, and Sr. Dissolved concentrations of As were high under reducing conditions while Ba, Cd, Cu, Pb, and Sr were high under oxidizing conditions. Thus, the solubility of these elements might be of concern in paddy soils and our results might indicate a possible risk with view to the uptake of toxic metal(loid)s i.e., As, Ba, Cd, Cu, Pb, and Sr by rice plants as well as transport via surface waters during different periods of flooding/drainage. This potential risk should be given serious consideration since the ecotoxicology threat of dissolved toxic metal(loid)s in temporarily waterlogged soils could be of a potential threat to food safety in those regions of the world heavily dependent on rice production. In future, a multiscale assessment of the release kinetics and speciation of the studied elements in paddy soils under pre-definite redox conditions should be determined. The speciation of the PTEs in the dissolved and colloidal fraction as well as in soil-sediments of the flooded soils under dynamic redox conditions should be investigated in future. In addition, further studies should elucidate the specific role of DOC and S chemistry on the dynamics of the studied elements.

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