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Black carbon and black nitrogen storage under long-term paddy and non-paddy management in major reference soil groups

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Abstract

Crop-residue burning and frequent paddy-soil flooding can lead to a substantial accumulation of black carbon (BC), thus contributing to long-term C sequestration. There is evidence that the turnover of BC in soils also depends on the soil mineral assembly. We studied the effects of paddy and non-paddy soil management and different major reference soil groups on BC storage. We hypothesized that overall BC storage in soil relates to paddy management and the abundance of reactive mineral phases such as Fe and Al oxides, and clay-sized minerals. Parallel to BC, black nitrogen (BN) should accumulate in soil. Paddy and non-paddy soils were sampled in three different climate zones (tropical, subtropical, and temperate). The soil profiles comprised six replicates of Andosols, Alisols and Vertisols from Java (Indonesia), and Alisols and Cambisols from China, as well as one Fluvisol and Gleysol from Northern Italy. Samples were taken by horizon down to N1 m depth and analyzed for soil organic carbon (SOC) and BC. The latter was analyzed by oxidation to benzene polycarboxylic acids. Abundance of BN (as aromatic N) was estimated by X-ray photoelectron spectroscopic analyses of selected topsoil horizons. In topsoils BC vs. SOC accumulation was affected by management for Andosol, Alisols in China, and Vertisols. However, both flooding and crop-residue management seemed to control this. BC contents relative to SOC also differed between the reference soil groups, independent of management (p b 0.0001), yet were surprisingly con-stant within replicates. We conclude that BC co-accumulated with SOC in all soils. However, the overall storage of BC (1 m depth) was affected by a combination of soil group and management. Vertisols contained the largest BC stocks (17–19 t ha^{-1} in non-paddy and paddy fields), followed by Andosols and Alisols (6–10 t BC ha^{-1} under paddy management; 3–8 t ha^{-1} under non-paddy management). The Gleysol and Fluvisol had the smallest BC stocks, independent of soil use (3–4 t ha^{-1}). Aromatic N proportions increased to 50% of total N after combustion of rice straw. However, aromatic N was barely, or not detectable in soil, and there was no correlation to BC. We conclude that burned crop residues were not a major source for aromatic N in soil. BC and aromatic N showed no distinct relations to soil properties, such as the abundance of clay-sized minerals, and Al and Fe oxides. Differences in BC stocks between the soils were most pronounced in the subsoils, likely caused by physical processes, such as swelling and shrinking of clays and/or translocation by leaching. Climate and regional soil-adjusted management also affected BC accumulation, but this first snapshot indicates that global BC maps may be linked to global soil maps.

1. Introduction

Rice cultivation feeds about half of the human population (Maclean et al., 2002). Burning rice straw on the fields might significantly affect the carbon cycle. Gaddé et al. (2009) calculated for Asian countries (where most rice cultivation takes place) that 23 to 95% of rice straw residues are burned. This may contribute to atmospheric CO_2 and global warming, but residues of biomass combustion (black carbon, BC) may also contribute to relatively persistent C in soil (e.g., Seiler and Crutzen, 1980).

We previously showed that long-term paddy management on marsh sediments in China resulted in equilibrium BC accumulation and degradation. These Cambisols stored ~ 13 t BC ha^{-1} after 300 years of paddy management. Adjacent non-paddy systems had only 7 t BC ha^{-1} (Lehndorff et al., 2014).

However, little is known about BC storage in other paddy soils, particularly if BC storage might systematically change in well-developed soils of different origins and mineral compositions.

Black carbon is recalcitrant in nature (e.g., Seiler and Crutzen, 1980). It comprises a range of incompletely burned organic matter (OM) characterized by fuel and combustion conditions (temperature and oxygen supply) (Czimczik et al., 2002; Keiluweit et al., 2010). Mean residence time (MRT) estimates in soil ranges from decades to millennia (e.g., Fang et al., 2014; Kuzyakov et al., 2014; Singh et al., 2012a). Differences in BC stability have been mainly related to the degree of aromatic condensation, which increases as burning temperature increases and depends on the fuel used (e.g., Singh et al., 2012b). On-field burning of rice straw or other crop residues yields BC equivalent to that of grass burned at about 300–400 °C (Lehndorff et al., 2014; Wolf et al., 2013).

Once incorporated into soil, the turnover of soil BC might additionally be controlled by interactions with minerals (Cheng et al., 2006; Cusack et al., 2012). For example, BC stocks in a weathering sequence of volcanic soils were closely related to the contents of reactive, short-range order minerals (Cusack et al., 2012). Incubation experiments also hinted that minerals may have a dominant role in BC turnover: BC in Ferralsols with high (crystalline) Fe oxide concentration had longer MRT (235–106 years) than BC in clay mineral-rich Vertisols (218–44 years for incubation temperatures of 20° and 40 °C, respectively) (Fang et al., 2014). The authors concluded that variably charged oxide minerals stabilized BC better than the permanently charged smectites in the Vertisol. However, the authors also admitted that MRTs might differ dramatically under field conditions, due to other factors such as variations in climate conditions.

BC might also stabilize by occlusion by soil minerals (e.g., Brodowski et al., 2006). In paddy soils, changing redox conditions may lead to BC stabilization by reaction with, or occlusion in, frequently precipitated short-range order Fe oxides. Effects may vanish by reductive dissolution of Fe oxide-OM associations (e.g., Kirk, 2004; Winkler et al., 2016). In clay-rich soils, BC may be physically protected in deeper soil horizons upon swelling and shrinking (self-plowing due to deep cracks that develop in dry seasons, which allow fresh OM to directly enter the subsoil). These effects may alter the residence time of BC to an unknown extent. In contrast, Fang et al.'s (2014) incubation study implied that Vertisols contain less BC than Ferralsols, and at a more advanced stage of degradation. In any case, it seems reasonable to assume that the storage of BC in soil relates to its mineral assembly.

Amounts and composition of BC in soil can be estimated by a variety of methods, but each has limitations. These limitations are mainly due to large differences in the BC materials. Previous studies showed that oxidation of BC to benzene polycarboxylic acids (BPCAs) recovered at least 70% of BC as BPCA in soil (Hammes et al., 2007; Roth et al., 2012). The relative amounts of five- to six-times carboxylated BPCAs relate to the degree of aromatic condensation of BC in soil (McBeath et al., 2011; Schneider et al., 2010). This is a result of the variation in BC surface/in-terior ratios. In other words, the less the proportion of six-times carboxylated BPCA (mellitic acid; B6CA), the larger the surface of BC (Glaser et al., 1998). The composition of BPCAs may be related to the source of BC, indicating if it stems from biomass, such as rice straw burning, or in-dustrial combustion processes (Lehndorff et al., 2015; Wolf et al., 2013). Additionally, it was assumed that BC degradation leads to large, oxidized, negatively charged surfaces that react with the soil matrix, thereby conserving BC (Brodowski et al., 2005a; Cheng et al., 2006). This effect may differ for aerobic (non-paddy) and anaerobic (paddy) management conditions. BC accumulation, especially in subsoil, may be ac-companied by a relative loss of mellitic acid due to decondensation (Rodionov et al., 2010). Singh et al. (2012a) reported that BC characterized by smaller proportions of mellitic acid was more prone to stabilization processes than condensed counterparts. In this line, both preferential stabilization of decondensed BC and intrinsic stability may contribute to its long residence time in soil (e.g., Singh et al., 2012a).

Burning OM also produces BN, but its role in N storage and cycling is not yet understood (de la Rosa and Knicker, 2011; Knicker, 2007). In previous studies, we found that at least 50% of paddy soil N was abundant in unidentified forms, or not bound to microbial residues (Roth et al., 2011) and proteinaceous amino acid N (unpublished data). X-ray photoelectron spectroscopy (XPS) may reveal if straw burning in paddy management leads to accumulation of N in heterocyclic, aromatic forms as previously detected in other soils (Abe et al., 2005; Mikutta et al., 2009). For example, Ding et al. (2014) related the aromatic N peak in the XPS N 1s spectra to BN in water samples and found a coupling between dissolved BN and BC. We tested if the method is applicable to rice char and soil, and if there is a correlation of BC to aromatic N.

The main objectives of this study were to elucidate the possible effects of paddy versus non-paddy management, and different major reference soil groups on the storage of BC. We sampled pairs of paddy and adjacent non-paddy soil depth profiles from different major soil groups of the world (IUSS Working Group, 2014), analyzed them for BC, and compared this to pedogenic oxide contents and soil texture (see also Winkler et al., 2016). This inevitably included a sampling from different climatic and land-use regions, since soil mineralogical settings were specific to geographic regions and parent material. Since the accumulation of aromatic N in soil due to inputs of BN is not yet well understood, we aimed to detect parallels in soil BC and BN contents. Sampling was done for well-developed soils that were under permanent paddy and non-paddy management during at least the last century.

2. Materials and methods

2.1. Sampling

Three tropical paddy and corresponding non-paddy soils formed on volcanic and clay-rich geological substrates were sampled in Java, Indonesia. To account for regional factors relevant to soil formation, we compared their properties to two subtropical paddy/non-paddy soils from China, and a temperate paddy/non-paddy soil in Mediterranean Italy, where there was no on-field rice straw burning (Fig. 1). Soil classification was done according to the World Reference Base for Soil Resources (IUSS Working Group, 2014) (Table 1). At each site, six profiles were dug into three independent paddy and three non-paddy fields (one main and two subsites per soil and management type). However, only one profile per management was sampled in Italy (Table 1). The profiles were sampled according to horizons to at least a 100 cm soil depth. BC and BN analyses were done for selected horizons, and only the main sites were investigated in full-depth resolution (see Tables 2a, b, and 3). The sampled soils under non-paddy management were classified as Andosols (Indonesia), Alisols (Indonesia and China), Vertisols (Indonesia), Cambisols (China), and Fluvisol (Italy). Upon long-term paddy management, Anthrosols formed from these soils (except for Italian paddy soil, classified as Gleysol). All sites had been continu-ously cropped for generations, according to local farmers. To account for the specific properties of the soils under study, we simplified the nomenclature and referred to the parent Andosol, Alisol, Cambisol, and Vertisol for both paddy and non-paddy managed sites (except for the Fluvisol/Gleysol pair at the Italian site). Soil details are described next.

2.1.1. Java, Indonesia

The substrate at Java is mainly of volcanic andesitic origin, consisting of silicate minerals rich in Al and Fe, which form reactive, pedogenic oxides during pedogenesis. Rates of weathering and pedogenesis are generally high due to the tropical monsoon climate. The climate is more humid in West Java (Sukabumi and Jasinga) than in East Java (Ngawi), which has pronounced interchanges of dry and humid weather (Table 1, Fig. 1). Soils at Sukabumi were Andosols under vegetable-maize (non-paddy) cropping and Al-rich Anthrosols under paddy-paddy-pak choi rotation (Table 1). At Jasinga, Fe oxide-rich Alisols formed on andesite, which are now under agroforestry (non-paddy). The respective Hydragric Anthrosol was under rice-rice-maize rotation (Table 1). Local farmers said that on-site burning of straw residues and waste frequently occurred, except for the non-paddy site at Sukabumi (Table 1).

The soils at Ngawi formed on fluvial clay deposits in a broad, shallow valley and were characterized as Vertisols (under sugar-cane monocropping) and as Hydragric Anthrosols under annual paddy-paddy-tobacco rotation. Swelling and shrinking caused formation of thick, deep cracks during the dry period. This allowed for translocation of topsoil material, including charcoal, to deeper soil layers. The non-paddy cropping system had intensive burning, while rice straw was partly harvested for livestock.

2.1.2. China

At the Red Soil Research Station (Yingtan), soil formation into limnic and fluvial sediments under subtropical climate conditions resulted in Fe-rich Alisols under non-paddy and Anthrosols under paddy-paddy-fallow management. Paddy management involved cultivating clover to increase soil N

stocks approximately every five years. Both the paddy and non-paddy cropping systems had frequent on-site burning of straw residues for about 300 years.

Cambisols were sampled in the Yangtze River Delta in the Bay of Hangzhou. The soils developed on deltaic sediments after land embank-ment under paddy and non-paddy management, respectively. Paddy and non-paddy soils had undergone 700 years of crop management and frequent burning of straw residues. Buried topsoil horizons found in two subsoils were excluded from BC stock calculation (see Lehndorff et al., 2014).

2.1.3. Italy

At Zeme, Italy (Rice Research Centre of Ente Nazionale Risi), paddy management was established about 30 years ago in the flood plain of the Po River. Soils forming under temperate climates with seasonally high groundwater levels were Endogleyic Fluvisols under maize monocropping and Haplic Gleysols under paddy management with one rice harvest per year. Crop management did not include puddling and straw burning. Both soils were fallow during winter.

2.1.4. Soil properties (pedogenic oxide contents, texture, and structure)

The soils under study had varying physical and chemical properties. The Andosols had 24–61 g kg^{-1} oxalate-extractable Al (Al_o, likely from allophane), and 8–16 g kg^{-1} oxalate-extractable Fe (Fe_o, short-range order Fe oxides) in their topsoil. All other topsoils had b4 g kg^{-1} Al_o. The Indonesian Alisols were characterized by 3.2–10.5 g kg^{-1} Fe_o, while the Chinese Alisols had 1.0–1.9 g kg^{-1} Fe_o. The Vertisols had 3.3–4.9 g kg^{-1} Fe_o in the topsoil horizons. Chinese Cambisols had 1.3–4.6 g kg^{-1} Fe_o (Kölbl et al., 2014). The Gleysol/Fluvisol soil pair had 1.4–3.5 g kg^{-1} Fe_o (details of Fe and Al analysis in Winkler et al., 2016).

The abundance of clay was estimated by grain-size analysis (Winkler et al., 2016). The Indonesian Andosols were of silt loam, and Alisols had 15/45/40% sand/silt/clay (clayey Alisols). The Chinese Alisols (sandy Alisols) and the Gleysol/Fluvisol soil pair from Italy had N50% sand-sized particles. Vertisols had 50 to 70% percent clay-sized particles in the topsoil. The Chinese Cambisol had about 70% silt and 25% clay. Soil structure was subangular-blocky for all soils except for the Vertisols, which had wedge-shaped aggregates. The Gleysol/Fluvisol pair had a massive structure in the subsoil.

2.2. Analyses

2.2.1. Bulk density (BD) and sample pre-treatment

Undisturbed soil cores (100 cm^3, in triplicate) were taken from each horizon under field-moist conditions to determine the BD (Black and Blake, 1965). In addition, composite samples were taken for each hori-zon from different parts of the profile pit and air-dried. All soil samples were sieved to b2.0 mm and ground in a ball mill prior to BC analysis.

2.2.2. Carbon, organic carbon, and nitrogen

Total carbon and nitrogen of each sample were determined by dry combustion at 950 °C using a Vario Max elemental analyzer (Elementar Analysensysteme, Hanau, Germany). The inorganic carbon content was determined by dissolution of carbonates with phosphoric acid and sub-sequently detecting the evolving CO_2 (C-MAT 550, Ströhlein GmbH, Viersen, Germany). For this purpose, ground samples were placed into gas-tight reaction vessels, 42% phosphoric acid was added, and the sus-pension was stirred. A steady flow of N_2 transports the evolving CO_2 into an infrared detector. All analyses were carried out in duplicate. Concen-trations of soil organic carbon (SOC) were calculated by subtracting in-organic carbon from total carbon.

2.2.3. Oxidation of black carbon to benzene polycarboxylic acids (BPCA)

The amount of BC in soil can be estimated by oxidation to BPCAs (Glaser et al., 1998). The BPCA

oxidation was performed according to a modified method (Brodowski et al., 2005b). Sample aliquots, equivalent to a maximum of 5 mg OC (Kappenberg et al., 2016), were hydrolyzed with trifluoro-acetic acid for metal elimination (105 °C, 4 h). The residue was oxidized with 65% HNO_3 (170 °C, 8 h). BPCAs were then pu-rified on a cation exchange column (Dowex 50 W × 8, 200–400 mesh, Fluka, Steinheim, Germany). The individual BPCAs were then converted to trimethylsilyl derivatives, separated by gas chromatography on an Optima-5 column (30 m × 0.25 mm i.d., 0.25 μm film thickness; Macherey-Nagel, Düren, Germany), and detected via flame ionization (Agilent 6890 gas-chromatograph). Citric acid was used as the first internal standard for BPCA quantification and added immediately before the cation exchange step. Biphenylene-dicarboxylic acid was used as a second internal standard to quantify the recovery of citric acid, which was 70–100%. The sum of two- to six-times carboxyl'ated BPCAs was corrected for CO_2 loss and insufficient conversion of BC to BPCAs by a factor of 2.27 (Glaser et al., 1998), representing a conservative mini-mum estimate of BC (Brodowski et al., 2005b).

Information on the degree of aromatic condensation of BC was achieved by relating the percentage of 4- and 5-times carboxylated acids (B4CAs = sum of prehnitic, mellophanic, and pyromellitic acid, B5CAs = benzenepentacarboxylic acid) to six-times carboxylated acids (B6CAs = mellitic acid). BC stocks [t ha^{-1}] were calculated from BD and horizon thickness for topsoil and down to 1 m depth for total BC stocks.

2.2.4. Black nitrogen (BN) analysis by X-ray photoelectron spectroscopy (XPS)

Straw, burned straw, and topsoil horizons (0 to a max. 15 cm) were analyzed for their bulk chemical surface composition using a Kratos Axis Ultra DLD instrument (Kratos Analytical Ltd., Manchester, UK). As most C and N in soil are enriched on particle surfaces, this analysis was done to detect even small contributions of BN. To also identify BN located within small aggregates otherwise not accessible by XPS, we analyzed homogenized samples over a large spatial area, which gave us information about average N species in a given soil sample. Homogenized powders of source materials, deposited onto adhesive copper-nickel tape, were analyzed for survey and N 1s detail spectra at three positions using monochromated AlKα radiation with excitation energy of 1486.6 eV. Spectra were recorded in hybrid lens mode, with photoelec-trons collected from an area of each 300 × 700 μm. Acquisition param-eters for survey spectra were: Pass energy, 160 eV; step size, 1 eV; three sweeps. Parameters for N 1s spectra: Pass energy, 20 eV; step size, 0.1 eV; three sweeps. After charge correction (survey C peak set to 285 eV), the N 1s peak was deconvoluted into three subpeaks representing different N oxidation states by using the Unifit 2010 soft-ware package (Hesse et al., 2003). The background was fitted together with the three subpeaks to obtain best-fit results. The following N types were distinguished (Mikutta et al., 2010): N bonded in aromatic structures (398.8 ± 0.4 eV), including imine, heterocyclic C_N, and ar-omatic amines; N in peptide bonds (400.5 ± 0.2 eV), including pyrrole and secondary and tertiary amines, and imides; and primary amine N, including protonated amines (402.4 ± 0.1 eV) (see Fig. S1). Fitting was accomplished by a Lorentzian-Gaussian mixing ratio of 0.2 and constraining the full-width-at-half-maximum values between 0.5 and 2.5. Atomic% element concentrations were converted into mass-based concentrations by taking into account the molar weight of each element (Gerin et al., 2003).

2.3. Statistics

Differences in SOC contents, BC amount, and composition (topsoil and total BC stocks [t ha^{-1}] and B5CA/B6CA ratio) were tested between soils (ANOVA) and for the combined effect of paddy and non-paddy management in the different soils from major reference soil groups (Andosols, Alisols [Indonesia], Alisols [China], Vertisols, Cambisols, Fluvisol/Gleysol n = 6; MANOVA). Normal distribution, tested by a Shapiro-Wilk-Test, was just reached (n = 36 and W = 0.942 and 0.940, respectively). Post-hoc Tukey HSD tests highlighted individual differences between management forms and/or soil groups (Table S1). These analyses were done with STATISTICA 8.0 (StatSoft, Inc.). Linear re-gression was tested for BC [g C kg $C^{-}_{org}{}^{1}$] versus aromatic N [%], clay-sized fraction [%], and Fe_o [g kg^{-1}] using SigmaPlot 11 (Systat Software, Inc.).

3. Results

3.1. Soil organic carbon (SOC)

The largest SOC concentrations were found in Andosol topsoils, and the smallest concentrations were found in the Fluvisol/Gleysol pair (Table 2, Fig. 2). These two soil groups contributed the greatest share of the difference between all topsoils, which was significant at the p b 0.0001 level (Table S1). Mean SOC concentration of two topsoil ho-rizons (in non-paddy soils), three topsoil horizons (in paddy soils, including plow pan), and three field replicates were 39.7 ± 4.3 g kg^{-1} in paddy (P) and 35.9 ± 1.9 g kg^{-1} in non-paddy (NP) Andosols, follow-ed by Alisols (Indonesia P: 17.1 ± 3.7, NP: 22.5 ± 2.0 g kg^{-1}; China P: 17.8 ± 11.8, NP: 7.1 ± 0.1 g kg^{-1}), Cambisols (P: 16.6 ± 1.4 and NP: 9.1 ± 1.9 g kg^{-1}), Vertisols (P: 11.7 ± 3.3, NP: 14.4 ± 1.0 g kg^{-1}), and the Gleysol/Fluvisol pair (P: 9.9 ± 3.2, NP: 7.2 ± 0.5 g kg^{-1}). Man-agement affected SOC contents at a p b 0.0001 level, and a post-hoc analysis highlighted the difference between Alisols and Cambisols from China (p b 0.0002; Table S1). The SOC concentrations decreased with soil depth in all profiles. Subsoil OC contents ranged between 24.6 g kg^{-1} in Andosol subsoils under paddy management and 0.5 g kg^{-1} in Fluvisol subsoil under non-paddy management (Table 2). The depth gradient of SOC was most pronounced in Andosols, Alisols and Cambisols, but less developed in the Vertisols and the Gleysol/Fluvisol pair (Fig. 2). A management effect (paddy versus non-paddy) on the depth distribution of SOC was not observed.

3.2. Black carbon (BC)

Average BC concentrations in topsoil horizons ranged from 2.6 ± 0.3 to 0.4 g BC kg^{-1} soil, with the largest values in Andosols under paddy management and in Vertisols (Table 2). Paddy management affected topsoil BC concentrations in Andosols, Alisols (China) and Cambisols to-ward larger BC contents in paddy soils (p b 0.002) and toward smaller BC contents in Vertisols under paddy management (p b 0.006; Tables 2 and S1). Differences related to soil group were significant (p b 0.0001), which was especially driven by the Vertisols and the Fluvisol/Gleysol pair, since these soils had both contrasting BC contents and little variation between management forms (Tables 2 and S1). The BC concentrations decreased with depth in all profiles and varied be-tween 0.1 and 1.7 g BC kg^{-1} in N90 cm depth.

The variation in BC relative to SOC for topsoils was 189 ± 57 to 27.9 ± 2.4 g BC kg^{-1} SOC, with the largest BC portions in the topsoil layers of the Vertisols (Fig. 2). In the Andosols and Alisols, BC tended to decrease with depth relative to SOC, while in Vertisols, paddy-managed Cambisols and the Gleysol/Fluvisol pair, BC accumulated rela-tive to SOC at larger soil depth. Maximum relative BC enrichment was found in the subsoils of the paddy Cambisols and Vertisols, amounting to N30% of SOC, which was almost double the portion found in the re-spective topsoils (Fig. 2; buried topsoil horizons in Cambisols excluded). Andosols, Vertisols, and Alisols (China) indicated differences in BC en-richment relative to SOC upon paddy management (p b 0.04). However, paddy management for the Vertisols led to significantly lower BC pro-portions (p b 0.0005; Fig. 2 and Table S1). Differences between soils were sustained at the p b 0.0001 level for BC/SOC. However, Alisols (China and Indonesia) did not differ significantly from Cambisols.

Total BC storage differed for the soils under study (stocks for 1 m depth, p b 0.0001, Table S1). Vertisols had the largest total BC stocks of 17 and 19 t C ha^{-1}, followed by Cambisols with 13 t ha^{-1} (Fig. 3). These two soils contributed the most to the difference between soils (post-hoc test, Table S1). Andosols under long-term paddy manage-ment accumulated a total of 8 t BC; Alisols had 6–10 t BC ha^{-1}. Non-paddy soils and paddy soils without rice straw burning (non-paddy Andosols and the Gleysol/Fluvisol pair) only had 3–4 t BC ha^{-1} (Fig. 3). A significant effect of paddy management on total BC stocks, i.e. affecting the soil profile down to 1 m, was only found in Cambisols from China (p b 0.0001). For topsoils, management significantly affected BC stocks in Andosols and Cambisols (p b 0.001, Table S1). The Vertisols showed no significant effect of management, but total BC stocks differed from all other soils (p b 0.03–0.0004, Table S1). Composition of individual BPCAs was dominated by benzenepentacarboxylic acid (B5CA) and four-times carboxylated acids (B4CAs). The relative share decreased in order: B5CA (24–100, av-erage 36%) N B4CA (0–70, average 33%) N B6CA (0–42, average 31%) N B3CA (0–7, average 4%). B5CA dominated in all topsoils, except for the

topsoils of Alisols and paddy Cambisols in China, which were dominated by B6CA (B5CA/B6CA ratio b 1, Fig. 2, p b 0.0001). Topsoil BPCA composition was not affected by management practice (p N 0.5). Variable contributions of BPCAs were observed with soil depth, but were small (B5CA/B6CA ratio in Fig. 2) and not specific for soil groups or management practices (p N 0.5). The Gleysol/Fluvisol pair had in-creasing proportions of B5CA in the subsoils, increasing to 100% (Table 2). However, the absolute amount of B5CA was only about one-fifth of that observed in the other soils (data not shown), so most of the other BPCAs were likely below the detection limit.

In summary, when compiling information from both SOC and BC data, we found effects of both management and soil-group. Manage-ment effects specially affected absolute concentrations of BC in topsoil (of Andosols, Vertisols, Chinese Alisols, and Cambisols). Detection of soil-specific differences was improved by looking at relative contribu-tions of BC to SOC in topsoils and complete profile stocks (Table S1).

3.3. Nitrogen and black nitrogen (aromatic N)

The XPS-derived N concentrations in rice straw represented N con-centrations at particle surfaces and were higher than those determined by bulk element analysis (10 g kg^{-1} and 3.8 g kg^{-1}; Table 3). In soil samples, XPS-N was 2.3–13.7 g kg^{-1}, while element analysis yielded 0.7–4.2 g N kg^{-1}. A moderate correlation was observed between N con-tents obtained by the two methods (r^2 0.52; Table 3). Black N was de-tected as aromatic N at ~399 eV. Aromatic N represented 5% of total N in rice straw and was enriched to 57% in rice char (Fig. S1). In soils, aro-matic N contributed only up to 8% to total XPS-derived N. Although var-iability in the XPS signal was high ("noise", Fig. S1), Abe et al. (2005) were able to show by complementary ^{15}N CPMAS NMR analysis that under similar analytical conditions at least 5% aromatic N from soil can be detected. The highest aromatic N proportions occurred in the Italian soils. Surprisingly, these soils had the lowest total N and BC contents.

4. Discussion

Biomass input and turnover controlled accumulation of SOC in top-soils. Paddy management led to almost double the amount of SOC stocks in topsoils of Cambisols compared to non-paddy cropped soils, which was likely related to reduced turnover of SOC under anaerobic condi-tions in paddy fields (Kalbitz et al., 2013). The Chinese Alisols in our study also showed significant increases in SOC concentration under paddy management (p b 0.0001) (Winkler et al., 2016), while Indonesian soil samples showed no significant response of topsoil SOC to paddy management.

Paddy management typically produces a very dense plow pan, po-tentially leading to a reduced translocation of SOC into the subsoil (Kögel-Knabner et al., 2010), as observed in Chinese Cambisols in a pre-vious study (Kalbitz et al., 2013). Here, depth profiles of SOC indicated that OM input into subsoils was reduced by paddy management for Andosols and Chinese sandy Alisols, but not for Indonesian clayey Alisols, Vertisols, and the Fluvisol/Gleysol pair (Fig. 2). This fits to other observations, such as that the paddy plow pan did not limit C in-puts into the subsoil in young coarse-textured soils (Said-Pullicino et al., 2015). In contrast, a layer of cemented Fe oxides likely restricted the transport of SOC down to the 40 to 50 cm depth in paddy-managed Andosols (own observation).

Stabilization and accumulation of SOC in Andosols have been attrib-uted to binding to aluminosilicates (allophones), gibbsite, and Fe oxides (de Junet et al., 2013). Winkler et al. (2016) showed that Fe oxide, phyllosilicates, clay minerals, and allophanes did not directly affect SOC in paddy managed soils. Leaching these potential OC accumulators from paddy-managed topsoils did not reduce SOC. The authors assumed that differences in crop residue input between paddy and non-paddy soils were more relevant. The following section will discuss if and to what extent BC accumulation was driven by the soil mineral assembly in paddy managed soils and by other soil specific properties, such as soil texture.

4.1. Black carbon sources

Burning of crop residues for paddy- and non-paddy managed sites was the major source of BC, except for the non-paddy Andosols and the Italian site, where no burning was reported. The amount of

burned rice straw likely varies. We received information that crop yields dif-fered from 6 to 12 t ha^{-1} and year, and were highest at the Vertisol sites. However, at this site rice straw is rather used for livestock breeding (as fodder and litter) than for on-field burning, which likely reduces the effect of higher yields on BC input. Although information about crop yields and burning practices are vague, enhanced BC input was reflected by elevated BC concentrations in soils at sites subject to in-tensive burning of crop residues. For example, the Andosols with rice-straw burning had absolute and relative BC contents exceeding those of the unburned, non-paddy Andosols by a factor of N2 (p b 0.0001; Table 2a, b). The unburned Gleysol/Fluvisol soil pair had only about one-fourth the absolute BC concentrations found in the other soils. Nev-ertheless, the unburned sites (non-paddy Andosol and the Gleysol/ Fluvisol pair) also had BC in the soil, likely from atmospheric deposition.

The composition of BPCAs in topsoil may indicate the source of BC. It differed between Indonesian topsoils and the Chinese and Italian site (B5CA/B6CA ratio Fig. 2; p b 0.0001). For the Indonesian sites the ratios ~1.1 were comparable to that found for burned straw in previous stud-ies (Lehndorff et al., 2014; Roth et al., 2012; Schneider et al., 2010). The Chinese Alisols and Cambisols had B5CA/B6CA ratios b0.9 (Fig. 2). That ratio value indicates that about 10% of the BC was likely from burned fossil fuel, which produces high shares of mellitic acid (B6CA; calcula-tion based on assumption that BC stemmed from diesel combustion with a B5CA/B6CA ratio ~ 0.15) (Roth et al., 2012). However, most of the BC at all sites was from crop-residue burning.

4.2. Management and soil specific effects on BC storage

4.2.1. Black carbon in Andosols

Indonesian Andosols were predicted to have the greatest potential for BC storage, since they had high concentrations of Al and Fe oxides and thixotropic properties. The latter indicated the presence of reactive nano-sized minerals such as allophanes and ferrihydrite. Allophane-type minerals and Fe oxides are known for their large sorption of OM (Batjes, 1996; Yamaguchi and Okazaki, 2002). Absolute amounts of SOC and BC were largest in the Andosols, indicating strong accumula-tion and probably stabilization of SOC, including BC. In Andosols from intermediate to felsic parent material, 70% of the SOC was found in organo-mineral complexes, half of that bound to alumosilicates, and only small proportions associated with Fe oxides (de Junet et al., 2013). In Andosols formed from basaltic parent material, accumulation and stabilization of OM was mainly due to short-range order Fe oxides or ferrihydrite; aromatic compounds, likely from vegetation fires, oc-curred in mineral-organic associations (Mikutta et al., 2009). Cusack et al. (2012) also found a large, concomitant accumulation of BC and SOC in Andosols, suggesting that BC was co-stabilized with SOC by reac-tive mineral phases.

Andosol subsoils were characterized by Fe oxide-cemented layers at the 40–50 cm depth, restricting OM translocation. This was indicated by strongly decreasing SOC concentrations (Fig. 2). The BC concentrations decreased (Table 2) even more strongly than did SOC (Fig. 2), pointing at differences in BC and SOC translocation. SOC might have been transported in soil water through small pores in the Fe pan and along the surfaces of Lahar fragments (volcanic debris flow), while BC was barely transportable with water in other soil profiles (e.g., Major et al., 2010). While OM maybe transported with water in dissolved form in the soil column and associated to nanoparticles (e.g. Kaiser et al., 1996; Gottselig et al., 2014), little is known about leaching of BC through soil in nanoparticulate forms.

Research has frequently discussed BC degradation in soil. A control by biotic (e.g., Kuzyakov et al., 2014; Singh et al., 2012a; Zimmermann et al., 2012) and abiotic processes (e.g., Ward et al., 2014) was discussed in incubation studies. Field observations showed a trend to less-condensed BC forms (loss of B6CA) in depth profiles of grassland soils. This may be related to BC degradation (Rodionov et al., 2010), e.g., highly condensed BC particles degrade to less condensed, smaller aromatic particles. Here, B4CA, representing the surface portion of BC, relatively increased from the 50 cm depth downward at the expense of B5CA and B6CA (representing the interior portion; Table 2a), supporting this degradation concept. However, it is also possible that old BC deposited with the Lahar led to the observed differences in BC composition.

We assumed a paddy-management effect on SOC and BC stocks in the Andosols due to: A larger input of BC at the paddy fields, since non-paddy fields were not burned; anaerobic conditions that

slowed down SOC and BC turnover (Kalbitz et al., 2013; Lehndorff et al., 2014); and changing redox conditions in the paddy fields, leading to en-hanced interactions of SOC and BC, with hydrous Fe oxides freshly forming during oxic phases. Although BC accumulation was significant-ly higher in paddy-managed soils than in those under non-paddy man-agement, this was related to the missing input in the non-paddy counterparts (see discussion above) rather than an effect of paddy-associated changes in redox conditions on organo-mineral complexes. This conclusion is supported by the lack of differences for SOC contents (Table 2) and a missing correlation between BC and Al, and Fe oxides (Fig. 4).

4.2.2. Black carbon in Alisols

We assumed that SOC and BC stabilization in Alisols would also be due to bonding to, or inclusion in Al and Fe oxides (Fang et al., 2014; Kaiser et al., 1996). For example, low pH values in Alisols contributed to formation of strong organo-mineral associations through ligand-exchange reactions (e.g., Fang et al., 2014). In an incubation study employing four different soils, those soils richest in Fe oxides (Ferralsol) stabilized most of the applied biochar (Fang et al., 2014). Concentrations of SOC and BC in the topsoils of the studied Alisols were large and sim-ilar, except for the non-paddy-managed soil from China (p N 0.07). However, a weak correlation of BC enrichment relative to SOC and Fe_o was observed for the Indonesian Alisols (r^2 0.16, p b 0.03; Fig. 4). Still, the SOC in Alisols was more enriched in BC than that of Andosols. There-fore, other mechanisms than mere association to Fe oxides determine the amount of BC found in soil, such as differences in BC input or soil texture. Depth profiles of SOC in the Indonesian and Chinese Alisols were less steep than in the Andosols. This can be related to a more homogeneous and non-cemented matrix, allowing for better vertical transport of sub-stances, together with the probably small retention capacity of topsoils (due to high shares of crystalline oxides), which promotes deeper movement of OM. The more sandy texture of the Chinese Alisols likely contributed to the low SOC contents in the subsoil, which in turn elevat-ed the overall contribution of BC to SOC. Nevertheless, the overall contribution of BC to SOC also decreased with depth. This indicated a lack of BC input to the subsoil, as discussed for the Andosol above, and does not support the general idea of selective preservation of BC during SOC mineralization. In the non-paddy subsoil, BC contents were even close to the detection limit. Mellitic acid (B6CA) in particular was some-times not detectable (Table 2, Fig. 2). One peculiarity about BPCA com-position of the Chinese Alisols and the Cambisols discussed above was the B5CA/B6CA ratio values b1, indicating the presence of some BC from fossil fuel combustion. We may take advantage of that contribu-tion and conclude from the abrupt change at the plow layer that BC was not significantly translocated deeper than 20 cm into the subsoil. This agrees with a biochar study in an Oxisol, which showed that BC leaching occurred only at the 30 cm depth (Major et al., 2010).

In summary, paddy management only affected BC contents of Alisols in China. Region-specific differences in management, such as straw burning, seem to be the controlling factor of BC in Alisols, as this was also practiced on the non-paddy Alisols in Indonesia. An effect of paddy-specific changes in redox conditions on BC storage in Alisols could not be found.

4.2.3. Black carbon in Vertisols

Vertisols showed the typical morphological features of soils rich in expandable clays, such as large cracks and bumpy surfaces (beside the agricultural plots) and large wedge-shaped aggregates formed due to soil swelling and shrinking with changing moisture. This strong peloturbation can cause OM incorporation into deeper soil horizons (Hulugalle and Entwistle, 1997). However, SOC concentrations in Vertisols were low, possibly due to the lack of biomass return, the low sorption capacity of smectites toward organic anions, and possibly more effective mineralization of OM in the dry period along desiccation cracks (Bundt et al., 2001). The lack of SOC accumulation may also ex-plain extremely high proportions of BC in these soils, as it was selective-ly preserved (Brodowski et al., 2007). Residual biomass was frequently burned in sugar cane fields, and its BC was incorporated almost homo-geneously into at least the 115 cm soil depth (Table 2a, b; Fig. 2). Al-though we were told that rice straw was traditionally used as fodder in this region of Indonesia, BC contents were also elevated in the paddy soils (but to a smaller degree; p b 0.005). This management effect became

insignificant when looking at total and topsoil BC stocks. Peloturbation seemed to lead to a notably larger BC accumulation in Vertisol subsoils than in other soils (Fig. 2).

The incubation study by Fang et al. (2014) showed that the MRT of BC in a Vertisol was the shortest of the four tested soils (young soils to weathered Ferralsols and Vertisols). Again, BC storage in the field contradicted laboratory findings. Possible reasons might be the BC input into the soil via peloturbation, which cannot be accounted for in laboratory studies, stabilization by physical enclosure in aggregates or sealed cracks, and site-specific differences in climate or burning practices during the last decades. In any case, BC degradation rates and related mechanisms derived from laboratory experiments do not allow for proper estimation of BC contents in the field. Indicators of BC degradation were lacking. In other words, the BPCA composition remained stable throughout the paddy and non-paddy Vertisol profiles, with dominance of B5CA (35–40%). Also there was no effect of paddy management on BC contents. However, the non-paddy fields were monocropped with sugar cane. The type of land use involves intensive burning of crop residues as well.

4.2.4. Black carbon in Gleysols/Fluvisols

The Gleysol/Fluvisol pair in Italy was sampled as a reference site with no straw burning. The BC contents suggested that atmospheric BC inputs formed a background of at least 0.5 g BC kg^{-1} soil, which is about 20% of what was accumulated in the burned soils and 50% of that in the unburned Andosols (Table 2a, b). Although sampled in an in-dustrial region, this background was smaller than that in other soils in remote areas in Europe (~1 g kg^{-1} BC; Nam et al., 2008). Overall, the small background BC contents indicated that straw burning elevates BC levels in soil much more than atmospheric inputs.

Gleysols are often enriched in SOC due to input of dissolved OM in the oxidized horizon mobilized under anoxic conditions in adjacent set-tings and the slowed decomposition of OM under water-saturated con-ditions. Indeed, SOC concentrations were higher in the paddy-managed Gleysols, likely due to both the groundwater input and the seasonally water-saturated topsoil. Riedel et al. (2014) and Said-Pullicino et al. (2015) showed that reductive dissolution of Fe and Mn oxides in a gleyic Fluvisol caused preferential release of aromatic carbon forms sim-ilar to BC. This process, together with vertical fluxes of DOC into the sub-soil in these coarse-textured soils might favor BC enrichment at a 20–42 cm depth (Fig. 2) (Said-Pullicino et al., 2015). Overall, BC con-tents in the Gleysol/Fluvisol pair were low, and detection limits for BPCAs were even reached for subsoils (Table 2).

4.2.5. Black carbon in Cambisols

The BC accumulation in Cambisols under paddy and non-paddy management was previously discussed in detail (Lehndorff et al., 2014). Burning was practiced at all sites, leading to a BC contribution to SOC of about 10% in the topsoil horizons (Table 2). Compared to other soil groups, topsoil BC concentrations ranged second together with the Indonesian Alisol (Fig. 2). Clay and Fe oxides contents were comparable to Chinese Alisols (Fig. 4a, b). The main differences were pH, which was almost neutral, and the silty texture (75% silt) (Kölbl et al., 2014). However, a prominent factor for BC stabilization could not be shown. The subsoils of these Cambisols had BC contents even larger than those of the Vertisols (Fig. 2), likely due to burial of former topsoil horizons (Lehndorff et al., 2014). We considered BC enrichment in Cambisol subsoils as an exceptional case, partly independent from soil properties.

4.3. Mineralogical controls on BC storage

Overall, total BC storage was soil-specific ($p < 0.0001$), but this depended on multiple factors. For Andosols and Alisols, we expected a control of redox-processes on BC storage. In other words, we expected to find elevated BC contents in paddy soils that greatly depend on fre-quent changes in aerobic/anaerobic conditions. Although elevated stocks in paddy-managed topsoil were found for Andosols (Fig. 3), other parameters, such as BC input, were responsible for this accrual. We showed that Vertisols and Cambisols exhibited significantly differ-ent and greater BC storage potential compared to other soils (Fig. 3). Large BC stocks in Vertisols could be related to effective translocation

of BC into the subsoil by peloturbation. The BC stocks of the tested Cambisols were affected by buried topsoil horizons, so may not be rep-resentative for this soil group. Surprisingly, subsoil BC accumulation greatly varied and was mainly responsible for the differences in total BC stocks between the soil groups under study (Fig. 3). Rodionov et al. (2010) found a range of 15–35 t BC ha^{-1} in depth profiles of grassland chernozemic soils, which also had the largest shares of BC stored in the subsoil. Topsoil BC stocks differed less. Burned Vertisol, Andosol, and Alisol stocks were statistically not different and ranged from 3.6–5.3 t BC ha^{-1} (Fig. 3).

In line with this sequence of BC storage, the abundance of clay-sized minerals in all soils had the highest correlation with BC enrichment (BC in g C kg^{-1} SOC, r^2 0.5, p b 0.0001; Fig. 4a). However, this was mainly due to Vertisol horizons. In contrast, in subsoils of the Indonesian Alisol, where clay contents were also high, BC proportions were low. The cor-relation with BC and Fe oxides for all soils was reciprocal (Fig. 4b). A cor-relation was only found for top- and subsoil horizons for Vertisols (less BC/more Fe oxides in the topsoil) and on paddy- or non-paddy-managed Andosols (less BC/more Fe oxides in the non-paddy cropping system; Fig. 4b). A few other studies showed that Fe and BC dynamics are coupled, especially with varying water saturation (Riedel et al., 2014). Nevertheless, we found only a weak positive correlation of BC to Fe oxides for the non-paddy-managed Alisols (Indonesia) (r^2 0.55; Fig. 4b). Again, this contrasts with Fang et al.'s (2014) laboratory find-ings that high Fe contents would promote BC enrichment. Possibly Fe oxides may rather promote overall SOC enrichment, thus, diluting the overall contribution of BC to SOC. It became obvious in our study that BC input may strongly control BC storage. How this masked the effects of Fe oxides on BC storage in paddy soils should be clarified in future studies.

4.4. Black nitrogen formation and accumulation in soil

Accumulation of aromatic N forms in soil has been related to inputs of burned OM (Knicker, 2007). We found that combustion of rice straw increased the proportion of aromatic N by a factor of approximately 10 to N50% relative to amide and primary N, while total N yields were halved (Table 3; Fig. S1). It seems reasonable to assume that input of such rice char would increase aromatic N in soil, as it also increased BC. However, we found no systematic correlation between BC and aro-matic N. Instead, soils with low BC/SOC contents and low N contents (Andosols, Gleysol/Fluvisol) were relatively enriched in aromatic N (see Andosol in Fig. S1). Although a high signal to noise ratio in the XPS spectra may have affected aromatic N quantification (Fig. S1), a lacking clear shoulder in the spectra at 399 eV suggests low aromatic N contents. We hypothesize that aromatic N is rather a product of age-ing of OM in soil (Schulten and Schnitzer, 1997). This is further support-ed by observations made for the Vertisols, which showed the highest BC/SOC contents but no detectable N forms (Fig. S1). We discussed that this soil accumulated fresh OM via the peloturbation typical of that soil. This fresh OM likely completely diluted total and aged aromatic N contents. It remains open what happened to the aromatic N from rice char. Some studies suggest that BN degrades significantly quicker than does BC (Hilscher and Knicker, 2011). The soil mineral as-sembly was also unlikely to control the storage of aromatic N, since soils with the most (Andosols) and least reactive phases (Fluvisol/Gleysol) seemed to have the highest aromatic N portions (Table 3). Consequent-ly, we suggest that aromatic N forms in soil may have different sources, properties, and turnover than BC.

5. Conclusion

We found that crop-residue burning significantly increased BC stocks in arable top- and subsoils, leading to a maximum accumulation of 19 t BC ha^{-1} in Vertisols. Unburned sites had the smallest BC stock levels (b4 t ha^{-1}). The BC stocks varied within soil groups, from Vertisols N Andosols N Alisols N Gleysols/Fluvisols. The BC accumulation in the subsoil was more specific for individual soil groups than that in the topsoil. Vertisols had the highest BC stocks, mainly due to effective incorporation of BC into the subsoil by peloturbation in combination with larger input. Thixotropic Andosols and Alisols likely bound BC in mineral-organic complexes. However, we could not find a direct corre-lation between Al and Fe oxide concentrations and BC. A positive effect of paddy management on BC stocks was found only in unburned soil, likely due to a masking by high input of burned waste and crop residue at the other non-paddy sites under study.

We detected aromatic N in rice char and some soils, but found no hint of BN accumulation via burned crop residues. Our observations in-stead suggested that aromatic N in soil forms from other sources, such as during ageing of organic N.

Overall, we conclude that in these systems differences in BC input and physical effects (such as soil texture, dense plow layers, and cemen-tation by Fe oxides) control BC storage along soil-depth profiles more than do chemical processes.

Supplementary Material

We provide XPS spectra, including fittings for aromatic N (N1), amide N (N2), and primary N (N3) exemplarily for rice straw, rice char, the Andosol under paddy management and the Vertisol under non-paddy management, as Fig. S1 in the supplementary. Table S1 in-cludes a summary of the statistic tests on SOC and BC concentrations, and BC/SOC and BC stocks, as well as on BPCA composition (ANOVA, MANOVA and Tukey HSD tests). Supplementary data associated with this article can be found in the online version, at doi: http://dx.doi.org/ 10.1016/j.geoderma.2016.08.026.

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Table 1
Soil and sampling site descriptions for Indonesia, China and Italy, including management-specific information, such as on crop rotation and burning.

Country, City	Manage-ment	Soil	Parent material	Annual precipitation [mm] / climate	Crop rotation		Burning & site information	Elevation [m a.s.l.]	Coordinates
Indonesia, Sukabumi [a]	paddy	Hydragric Anthrosol (Andic, Dystric, Escalic, Loamic)	andesitic pyroclastics (lahar of Gede volcano)	2300-6700 / tropical (21°C)	Oryza sativa (rice), Oryza sativa, Brassica rapa chinensis (pak choi)	main site	Rice straw burnt and spread over the field	870	S 06°52.802‘ / E 106°56.457
						sub site 1	Next terrace above main	871	S 06°52.800‘ / E 106°56.463‘
						sub site 2	Two terraces above main	871	S 06°52.796‘ / E 106°56.465‘
	non-paddy	Dystric Silandic Andosol (Loamic, Thixotropic)	andesitic pyroclastics (lahar of Gede volcano)	2300-6700 / tropical (21°C)	Manihot esculenta (cassava), Zea mays (maize)	main site	No burning	981	S 06°52.029‘ / E 106°56.725‘
						sub site 1	10 m from main	972	S 06°52.034‘ / E 106°56.725‘
						sub site 2	30 m from main	969	S 06°52.046‘ / E 106°56.714‘
Indonesia, Jasinga [a]	paddy	Hydragric Anthrosol (Alic, Clayic, Dystric, Escalic)	andesitic tuffs	1900-4700 / tropical (26°C)	Oryza sativa (rice), Oryza sativa, Zea mays (maize)	main site	Rice straw burnt and spread over the field	248	S 06°32.205‘ / E 106°31.062‘
						sub site 1	One terrace below main site	240	S 06°32.209‘ / E 106°31.062‘
						sub site 2	Two terraces below main site	238	S 06°32.218‘ / E 106°31.059‘
	non-paddy	Chromic Abruptic Alisol (Pantoclayic, Humic, Hyperalic)	andesitic tuffs	1900-4700 / tropical (26°C)	Manihot esculenta (cassava), Musa sp. (banana), Leucaena leucocephala (mimosa)	main site	Burning, nearby village (waste?)	238	S 06°32.158‘ / E 106°31.030‘
						sub site 1	110 m from main	236	S 06°32.212‘ / E 106°31.033‘
						sub site 2	140 m from main	238	S 06°32.239‘ / E 106°31.027‘
Indonesia, Ngawi [a]	paddy	Hydragric Anthrosol (Protocalcic, Pantoclayic, Hypereutric, Vertic)	alluvial-volcanic material	2500-6700 / tropical (22-31°C)	Oryza sativa (rice), Oryza sativa, Nicotiana sp. (tobacco)	main site	Rice straw burnt and spread over the field	79	S 07°26.878‘ / E 111°36.599‘
						sub site 1	200 m from main	78	S 07°26.819 / E 111°36.515‘
						sub site 2	500 m from main	77	S 07°27.095‘ / E 111°36.576‘
	non-paddy	Pellic Vertisol (Protocalcic, Grumic, Hypereutric, Humic, Mollic)	alluvial-volcanic material	2500-6700 / tropical (22-31°C)	Saccharum officinarum (sugar cane)	main site	Rice straw burnt and spread over the field	80	S 07°26.691‘ / E 111°36.667‘
						sub site 1	30 m from main	78	S 07°26.719‘ / E 111°36.672‘
						sub site 2	80 m from main	80	S 07°26.640‘ / E 111°36.530‘
China, Yingtan [a]	paddy	Hydragric Anthrosol (Alic, Endoclayic, Dystric, Escalic, Amphiloamic)	red Cretaceous sandstones with some basalt	1625 / sub-tropical (18°C)	Oryza sativa (rice), Oryza sativa, Trifolium sp. (clover)	main site	Burning	45	N 28°14.020´ / E 116°53.866´
						sub site 1	30 m from main	40	N 28°14.034´/ E 116°53.865´
						sub site 2	100 m from main	45	N 28°14.048´/ E 116°53.860´
	non-paddy	Chromic Alisol (Aric, Cutanic, Hyperalic, Pantoloamic)	red Cretaceous sandstones with some basalt	1625 / sub-tropical (18°C)	Arachis hypogaea (peanuts), Sesamum indicum (sesame), Ipomoea batatas (sweet potatoes)	main site	burning, pollution	nd	N 28°14.035´ / E 116°53.784´
						sub site 1	Ca. 30 m down hill	57	N 28°14.035´ / E 116°53.784´
						sub site 2	Ca. 60 m down hill	50	N 28°14.029´/ E 116°53.830´
China, Cixi [b]	paddy	Endogleyic Hydragric Anthrosol (Hyposodic, Siltic, Thaptomollic)	marine sediments	1325 / subtropical (16°C)	Oryza sativa (rice), Triticum sp.(wheat), oilseed rape, barley, broad bean, vegetables	main site	Rice straw burnt and spread over the field	6	N 30°10.408´ / E 121°09.180´
						sub site 1	N 50 m from main	6	N 30°10.416´ / E 121°09.169´
						sub site 2	N 50 m from main	6	N 30°10.426´ / E 121°09.153´
	non-paddy	Haplic Cambisol (Eutric, Siltic)	marine sediments	1325 / subtropical (16°C)	Triticum sp.(wheat), oilseed rape, barley, broad bean, vegetables	main site	Residual plant material is burnt	5	N 30°10.967´ / E 121°08.706´
						sub site 1	N 50 m from main	5	N 30°10.969´ / E 121°08.724´
						sub site 2	N 50 m from main	5	N 30°10.989´ / E 121°08.724´
Italy, Zeme	paddy	Haplic Gleysol (Eutric, Arenic, Densic)	alluvial sediment	700-1000 / temperate (13 °C)	Oryza sativa (rice), fallow	main site	No burning	79	N 45°11.536´ / E 08°40.078´
	non-paddy	Endogleyic Fluvisol (Eutric, Arenic)	alluvial sediment	700-1000 / temperate (13 °C)	Zea mays (maize), fallow	main site	No burning, high groundwater level	80	N 45°11.555´ / E 08°40.104´

[a] soil, parent material and climate from Winkler et al. (2016)
[b] soil, parent material and climate from Kölbl et al. (2014), information on burning from Lehndorff et al. (2014)

Table 2

Concentration of Black Carbon derived C (BC-C) and single benzenepolycarboxylic acid (BPCA) proportions on total BC in a) paddy soils and b) non-paddy soils. At Indonesian and Chinese sites, all horizons from three replicated soil pits; in Italy no independent replicates existed (B3CAs = Σ tricarboxylic acids, B4CAs = Σ tetracarboxylic acids, B5CA = pentacarboxylic acid, B6CA = mellitic acid; bdl = below detection limit).

a) site	depth	horizon	bulk density	SOC	BC-C		B3CAs	B4CAs	B5CA	B6CA
	[cm]		[g cm^{-3}]	[g C kg-1]	[g C kg-1]	[g C kg-1 SOC]		%		
Andosol	0-9±1	Alp1	0.67±0.07	42.01±2.34	2.39±0.25	56.91±4.48	4.05±0.23	22.93±0.54	40.56±0.89	32.46±0.34
paddy	9-22±1	Alp2	0.76±0.05	42.28±2.53	2.25±0.10	53.26±1.22	4.08±0.11	22.82±0.28	40.42±0.48	32.67±0.50
	22-31±3	Aldp	0.75±0.02	34.77±7.05	1.97±0.11	57.95±9.68	4.75±0.32	24.48±1.09	37.88±0.45	32.89±0.98
	29-35	Bl	0.93±0.08	24.64	1.36	55.28	4.78	28.06	36.54	30.61
	35-50	Bgc1	0.82±0.08	16.38	0.99	60.68	3.92	25.90	40.47	29.71
	50-75	Bgc2	0.77±0.06	9.97	0.35±0.11	46.87±5.92	4.76±3.51	46.59±3.84	23.69±2.34	24.96±2.01
	75-105	Bw	0.72±0.04	6.20	0.18	29.63	2.77	44.26	23.61	29.36
Alisol (I)	0-7±0	Alp1	0.88±0.05	20.04±1.29	1.91±0.28	95.48±13.57	5.43±1.78	26.63±2.84	37.80±5.52	30.14±0.90
paddy	7-16±0	Alp2	0.97±0.03	18.20±0.83	1.66±0.22	91.51±15.68	6.85±1.78	28.69±1.12	34.52±3.80	29.93±1.73
	16-23±3	Alcdp	1.13±0.08	12.95±0.77	1.42±0.11	109.94±2.52	4.75±0.23	27.25±0.25	38.55±0.33	29.45±0.28
	25-48	B(t)gc1	0.97±0.01	10.96	0.89	81.48	4.85	24.24	37.15	33.76
	48-75	B(t)gc2	0.93±0.01	9.90	0.80±0.21	92.90±10.25	5.91±0.51	33.74±3.35	32.95±1.77	27.40±2.88
	75-95+	B(t)gc3	0.88±0.03	6.98	0.43	61.34	3.37	27.40	32.39	36.84
Vertisol	0-8±1	Alp1	0.92±0.92	14.93±1.26	2.08±0.14	140.73±20.70	5.71±0.20	28.32±0.54	35.12±0.58	30.86±0.13
paddy	8-18±2	Alp2	1.04±1.04	11.99±2.09	2.07±0.07	176.58±33.93	5.55±0.28	27.96±0.72	35.29±0.78	31.21±0.39
	18-26±1	Aidp	1.03±1.03	8.25±2.00	2.04±0.26	252.00±28.98	3.81±0.21	25.94±0.16	39.98±0.70	30.28±0.70
	27-47	Bwi	1.00±1.00	5.16	1.65	319.00	4.27	26.94	39.88	28.92
	47-90	Bigc	1.01±1.01	4.76	1.76±0.18	322.24±23.64	4.77±0.09	27.03±0.45	38.50±0.28	29.71±0.33
	90-115+	Bikgc	0.99±0.99	4.64	1.38	296.70	4.55	26.54	40.38	28.53
Cambisol	0-10	Alp1	1.06±0.02	23.20±1.90	1.98±0.25	84.77±14.34	6.75±2.33	29.11±3.84	29.57±2.52	34.57±2.43
paddy	10-16	Alp2	1.20±0.02	18.00±1.80	1.87±0.37	99.48±15.09	12.20±12.89	28.97±5.53	27.72±5.95	31.11±5.92
	16-22	Ardp	1.46±0.03	8.60±0.50	1.15±0.15	133.69±18.57	7.28±3.97	28.82±3.82	30.99±2.93	32.91±4.80
	22-45	Bg	1.49±0.01	4.10±0.60	0.96±0.24	225.19±62.96	10.42±3.83	31.62±3.62	31.07±2.96	26.89±3.21
	45-69	2Ahgb	1.53±0.04	5.30±0.60	1.62±0.58	369.87±169.58	6.44±4.39	28.88±3.22	32.90±3.27	31.78±3.71
	69-106	2Blg1	1.45±0.01	3.30±0.40	1.25±0.60	321.10±108.50	9.40±4.38	29.15±3.96	30.79±2.22	30.66±4.88
	106-116	3Ahlgb	1.50±0.05	6.00±0.90	3.05±0.09	433.80±13.39	5.88±1.65	31.23±5.12	32.44±5.02	30.45±1.92
Alisol (C)	0-9±1	Alp1	0.81	26.2±0.22	1.62±0.13	67.99±1.85	3.09±0.13	24.74±0.13	33.40±0.68	38.77±1.07
paddy	15-20	Ardp	1.59	9.4	0.85	89.97	4.09	22.89	35.14	37.89
	20-28	Bl	1.39	5.8	0.53	92.37	3.59	27.25	37.39	31.76
	28-42	Bg1	1.42	3.5	0.38	108.52	4.24	34.83	33.14	27.79
	60-95+	Bg3	1.21	3.1	0.22	71.91	2.83	49.02	25.20	22.95
Gleysol	0-13	Arp1	1.42	11.67	0.52	44.77	4.13	34.15	32.87	28.86
paddy	13-25	Arp2	1.49	11.75	0.53	44.91	3.58	31.95	35.40	29.07
	25-34	Ardp	1.82	6.20	0.41	66.96	3.43	37.31	31.00	28.25
	34-43	Brd	1.93	3.23	0.23	71.04	3.84	64.67	31.49	bdl
	43-53	Bg1	1.74	2.39	0.18	75.85	1.51	67.77	30.72	bdl
	53-80	Bg2	1.64	2.44	0.16	64.58	0.52	58.11	41.36	bdl
	80-90	2CBw	1.61	2.16	0.08	37.97	bdl	34.94	65.06	bdl
	90-110+	3C	1.46	1.82	0.08	41.34	bdl	bdl	100.00	bdl
b) site	depth	horizon	bulk density	SOC	BC-C		B3CAs	B4CAs	B5CA	B6CA
	[cm]		[g cm-3]	[g C kg-1]	[g C kg-1]	[g C kg-1 SOC]	%			
Andosol	0-10±3	Ah1	0.67±0.05	37.27±3.13	0.98±0.09	26.24±2.57	3.57±0.29	22.28±0.97	39.55±1.57	34.60±0.66
non-paddy	10-20±3	Ah2	0.65±0.04	34.59±1.48	1.03±0.15	29.56±3.36	3.55±0.40	22.13±0.90	39.36±1.80	34.96±0.99
	16-28±8	BwAh	0.51±0.05	17.43	0.38±0.38	21.56±7.56	2.94±0.08	35.82±2.99	28.85±2.50	32.40±1.08
	28-56	Bw1	0.53±0.06	13.54	0.26	19.16	2.00	33.08	29.89	35.03
	56-78	Bw2	0.63±0.11	13.77	0.30±0.30	32.55±10.29	2.21±0.06	46.72±0.98	25.47±0.48	25.59±1.32
	78-100+	Bw3	0.63±0.17	8.80	0.29	15.45	3.72	23.04	39.08	34.16
Alisol (I)	0-9±2	Ah1	0.83±0.17	23.86±3.35	1.89±0.11	80.73±15.78	5.14±0.48	26.72±0.39	35.67±0.86	32.48±1.56
non-paddy	9-16±2	Ah2	0.88±0.15	21.08±2.97	1.94±0.24	93.74±22.35	4.82±0.27	26.61±0.35	35.68±0.55	32.89±0.94
	16-22	B(t)o1	0.94±0.16	17.20	1.61±0.10	92.56±2.86	5.00±0.43	26.72±0.41	36.41±0.40	31.87±0.46
	22-46	B(t)o2	0.89±0.08	9.43	0.70	73.87	4.52	27.51	35.32	32.64
	46-63	B(t)o3	0.92±0.03	7.79	0.57±0.17	61.53±11.90	4.09±0.31	31.49±0.55	32.80±0.55	31.62±0.58
	63-83	B(t)o4	0.87±0.06	6.78	0.36	53.76	2.32	40.56	29.46	27.66
	83-100+	B(t)o5	1.11±0.00	4.24	0.32	76.32	1.60	31.88	24.21	42.31
Vertisol	0-10±0	Ah1	0.82±0.11	15.11±1.49	2.84±0.43	187.57±9.93	4.81±0.64	26.39±0.75	37.92±3.00	30.88±1.60
non-paddy	10-21±2	Ah2	0.94±0.15	13.63±0.53	2.37±0.07	173.65±4.50	5.69±0.42	27.43±1.24	34.59±1.31	32.29±0.48
	23-29	Bw	0.96±0.05	8.98	2.55±0.36	229.38±20.74	4.21±0.18	25.44±1.06	39.94±1.03	30.41±2.18
	29-55	Bwi1	0.97±0.05	7.14	1.88	262.82	4.39	26.28	39.90	29.43
	55-100	Bwi2	1.02±0.03	5.76	1.57±0.22	275.11±37.07	4.70±0.11	26.99±0.22	38.46±0.12	29.86±0.22
	100-120 +	Bwi3	0.99±0.06	4.78	1.67	349.73	4.58	30.57	39.53	25.32
Cambisol	0-12	Ap1	1.25±0.06	10.83±2.73	1.08±0.33	99.95±22.17	5.09±0.75	28.26±3.46	35.20±4.97	31.44±4.97
non-paddy	12-17	Ap2	1.32±0.03	7.53±2.87	0.84±0.17	119.83±34.44	5.48±1.11	33.64±6.73	32.59±4.98	28.29±3.59
	17-23	Bw1	1.38±0.01	4.75±1.02	0.52±0.14	113.11±31.11	5.00±1.18	36.34±4.63	30.98±2.68	27.68±4.09
	23-45	Bw2	1.39±0.03	5.19±0.54	0.43±0.21	80.59±28.27	5.01±1.09	41.07±3.67	28.04±3.26	25.88±2.59
	45-70	Bwl1	1.42±0.02	4.81±0.15	0.37±0.08	76.57±15.85	4.45±1.05	43.55±4.98	27.30±2.56	24.70±3.63
	70-100	Bwl2	1.42±0.01	3.29±1.60	0.43±0.14	91.24±30.36	3.84±1.01	44.41±3.55	25.27±3.52	26.48±1.67
Alisol (C)	0-10±3	Alp1	1.13	7.13±0.06	0.78	109.22	3.35	30.58	30.33	35.73
non-paddy	20-28	Bl	1.34	2.8	0.23	83.68	2.45	29.25	37.11	31.20
	28-42	Bg1	1.23	1.5	0.11	78.18	1.28	69.66	29.05	bdl
	60-95+	Bg3	1.37	1.4	0.12	86.56	2.41	40.93	41.16	15.50

(continued on next page)

Table 2 (continued)

a) site	depth	horizon	bulk density	SOC	BC-C		B3CAs	B4CAs	B5CA	B6CA
	[cm]		[g cm^{-3}]	[g C kg-1]	[g C kg-1]	[g C kg-1 SOC]			%	
Fluvisol	0-15	Ap1	1.48	6.87	0.38	55.63	2.50	40.29	28.00	29.21
non-paddy	15-30	Ap2	1.66	7.56	0.40	52.94	3.56	36.51	30.13	29.81
	30-70	Bgw	1.55	2.26	0.07	31.56	bdl	bdl	100	bdl
	70-85	2Bgw	1.51	1.51	0.10	68.93	bdl	bdl	100	bdl
	85-110+	3C	1.49	0.46	0.04	85.89	bdl	bdl	100	bdl

Table 3
N forms in rice, rice char, and paddy and non-paddy topsoils, main sites only (n = 3, na: not analyzed, nd: not detectable).

Site, sample info	Management	Depth	Horizon	N (EA)	N 1s (XPS)	Aromatic N ~ 399 eV	Amide N ~ 400 eV	Primary N ~ 402 eV
		[cm]		[g kg^{-1}]	[g kg^{-1}]	[%]	[%]	[%]
Rice straw				3.8	10 ± 1	5 ± 3	87 ± 7	3 ± 6
Rice char					6 ± 1	57 ± 24	40 ± 22	3 ± 4
Andosol	Paddy	0–8	Alp1	4.2	11 ± 2	6 ± 3	83 ± 13	12 ± 13
Alisol (I)	Paddy	0–7	Alp1	1.9	3 ± 1	nd	64	36
Vertisol	Paddy	0–8	Alp1	1.5		na		
Cambisol	Paddy					na		
Alisol (C)	Paddy	0–8	Alp1	2.6	14 ± 2	3 ± 4	81 ± 8	16 ± 10
Gleysol	Paddy	0–13	Arp1	1.1	8 ± 0	8 ± 8	75 ± 13	18 ± 6
Andosol	Non-paddy	0–7	Ah1	3.5	13 ± 3	1 ± 1	91 ± 3	8 ± 4
Alisol (I)	Non-paddy	0–7	Ah1	1.8	3 ± 1	0 ± 0	80 ± 2	20 ± 2
Vertisol	Non-paddy	0–10	Ah1	1.2	2 ± 2	nd		
Cambisol	Non-paddy					na		
Alisol (C)	Non-paddy	0–12	Alp1	0.7	4 ± 2	nd		
Fluvisol	Non-paddy	0–15	Ap1	0.8	5 ± 1	7 ± 3.3	72 ± 7	21 ± 6

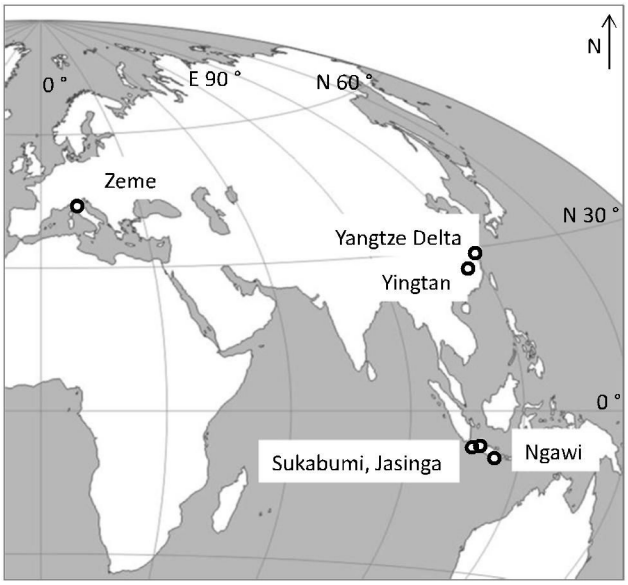

Fig. 1. Locations of the six paddy and non-paddy soil sites under study.

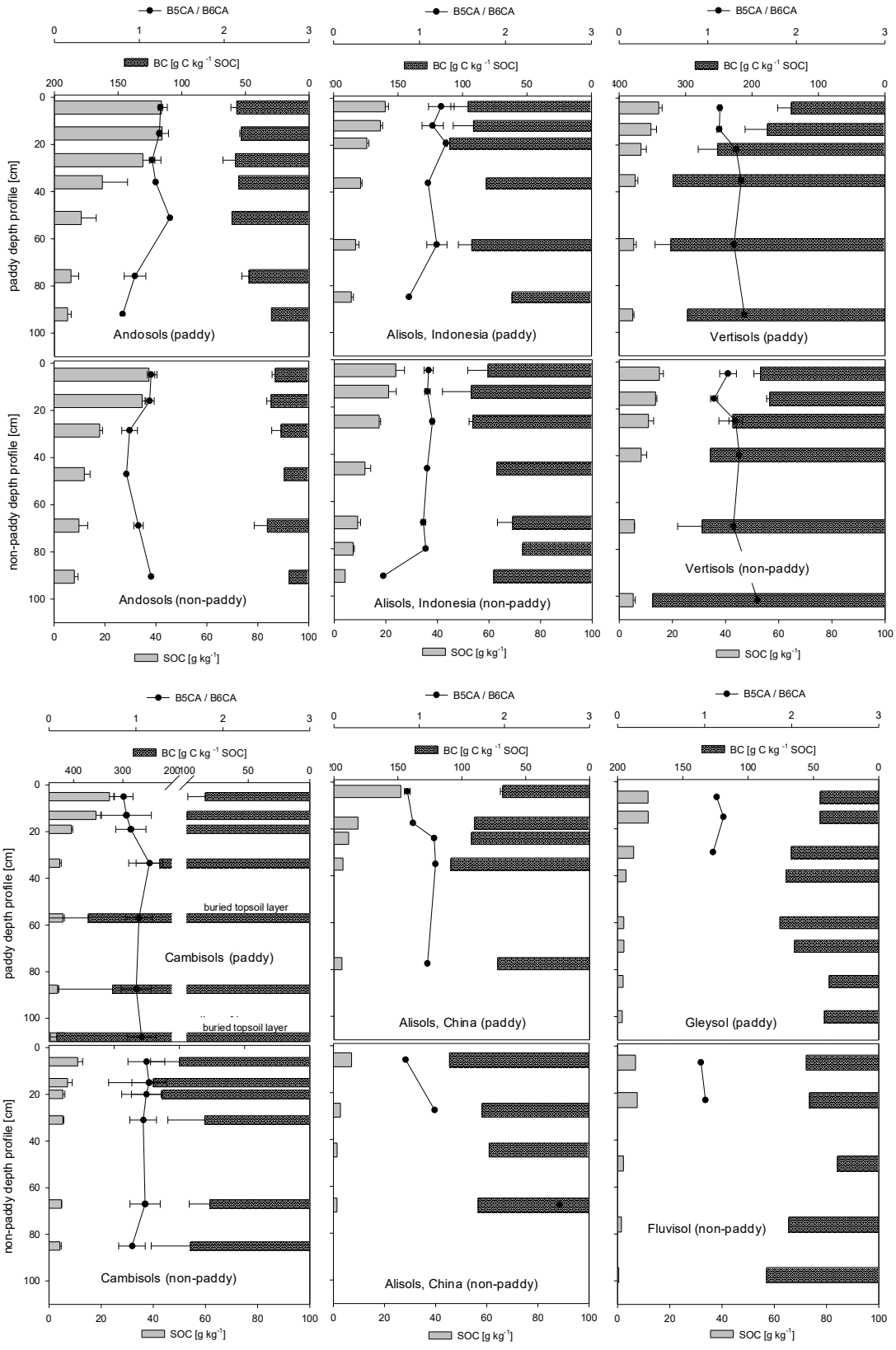

Fig. 2. Soil organic carbon concentrations (SOC) (left), black carbon (BC-C) (right), and the ratio of pentacarboxylic to mellitic acid (B5CA/B6CA) in depth profiles of different paddy and non-paddy soils (averaged across field replicates, for subsoils only one horizon was replicated, for Chinese Alisols only topsoil horizons were replicated; Gleysol/Fluvisol was sampled from one site only, error bars indicate SD; BC calculated from Σ BPCA ∗ 2.27).

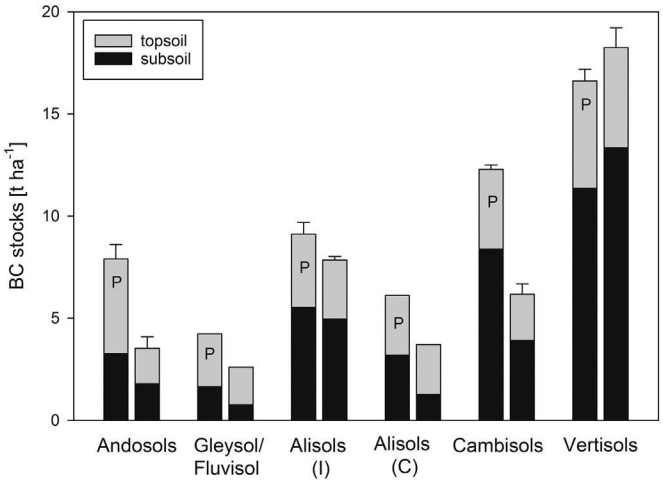

Fig. 3. Total and topsoil BC stocks of different soil groups under paddy (P) and non-paddy management. The stocks were estimated from oxidation of soil BC to benzene polycarboxylic acids from three field replicates per site (except for Chinese Alisols and the Gleysol/Fluvisol pair; C = China, I = Indonesia; BC calculated from Σ BPCA ∗ 2.27).

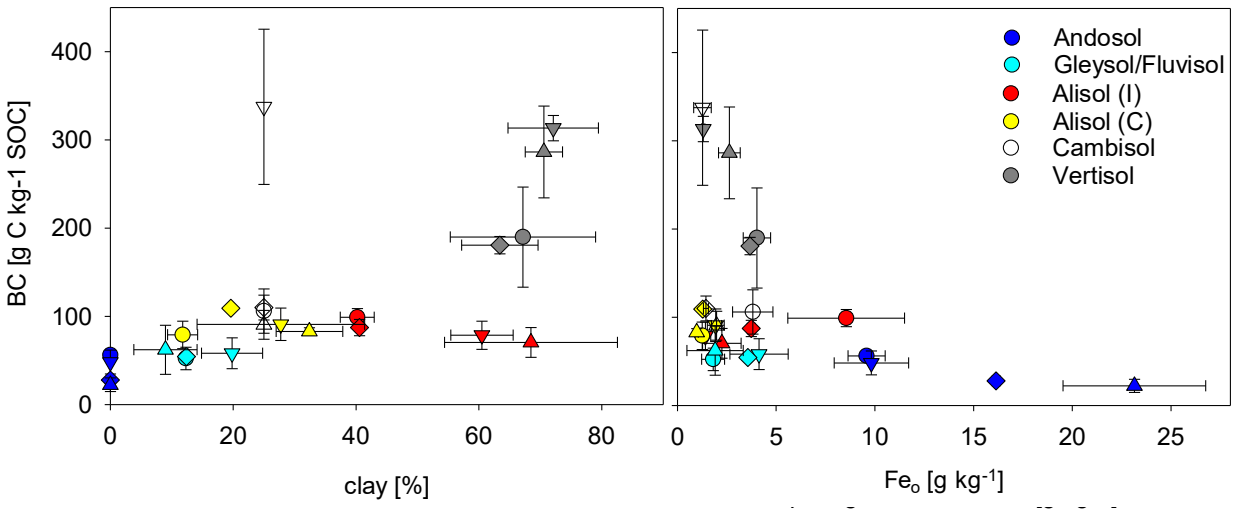

Fig. 4. Relative soil BC content vs. a) clay-size fraction, and b) oxalate-extractable Fe. Dots and diamonds represent the average for paddy and non-paddy topsoil horizons. Triangles facing down and up indicate paddy and non-paddy subsoil, respectively (average of three field replicates and different soil horizons, except for Chinese Alisols and the Gleysol/Fluvisol pair; clay-size fraction analyzed for one profile per site only, C = China, I = Indonesia; BC calculated from Σ BPCA ∗ 2.27).