Journal of Environmental Management 234 (2019) 440–447

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Research article

Biowastes alone and combined with sulfur affect the phytoavailability of Cu and Zn to barnyard grass and sorghum in a fluvial alkaline soil under dry and wet conditions

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ARTICLE INFO

Keywords:
Trace elements
Wetlands
Degraded soils
Biowastes
Biomass
Phytomanagement

ABSTRACT

Management of degraded soils (i.e., metal contaminated soils, salt affected soils, and soils with low organic matter content) by applying biowastes (e.g., biosolids and compost) and inorganic soil amendments such as sulfur is of great agro-environmental concern. Because Cu and Zn chemical behaviour may be altered with these additions, we aimed at studying the impact of mono- and co-application of different rates (1.25% and 2.5%) of biosolids, compost, and sulfur on the mobilization of Cu and Zn and their uptake in a fluvial soil contains low and high metal concentrations and under two distinct moisture regimes (wet, where we grew barnyard grass; dry, with sorghum). We measured metal fractions and potential availability, along with soil pH, as well as plant yield and metal content in both plants, in an attempt to identify differences in metal behaviour. We found that organic matter (OM) (increased with biosolids and compost application) and soil pH (dramatically reduced with added sulfur) highly affected Cu and Zn mobility. Plant yield increased with increasing soil OM content and decreased with decreasing soil pH, particularly in the 2.5% sulfur treatment. However, Cu absorption was different in the two studied moisture regimes, as it was higher in the wet soil (Cu-DOC complexes, encouraged under wet conditions, may explain this), while it was lower in the dry soil. The biosolid-added Cu was significantly more bioavailable to sorghum plants than the spiked Cu. Co-application of sulfur and biosolids showed significantly higher sorghum uptake of Cu than application of sulfur to the spiked soil with Cu. Zinc uptake decreased in the high compost application rate (2.5%). This behaviour can be explained with the altered geochemical metal fractionation: added metals were distributed mainly in the oxides and organic fraction, but in the wet soil the percentage was higher compared to the dry, possibly due to metal-DOC associations. Also the residual fraction was lower in the wet, denoting higher metal mobility. We conclude that the observed differences between wet and dry soil concerning the metal geochemical behaviour, as were induced by added OM (with biosolids and compost) and reduced pH (with sulfur), are mainly responsible for the markedly different metal uptake patterns. These results may be an aid for effective phyto-management of alkaline fluvial soils with low and high content of Cu and Zn under paddy- and upland cultivation systems.

1. Introduction

Degraded soils (i.e., toxic metal-contaminated and salt-affected soils) are of great concern related to agricultural reduced productivity and adverse environmental impact. Large areas of soils worldwide, in particular in arid zones (such as those in north of Nile Delta, Egypt), suffer from low content of organic matter, high alkalinity, and often contain high concentrations of trace elements such as copper (Cu) and zinc (Zn). Management of such soils may be done by applying biowastes (e.g., biosolids and compost) and inorganic soil amendments such as

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https://doi.org/10.1016/j.jenvman.2018.12.106
Received 29 September 2018; Received in revised form 10 December 2018; Accepted 26 December 2018

0301-4797/ Published by Elsevier Ltd.

sulfur (S). Indeed, the use of organic amendments and acidic inorganic amendments (e.g., sulfur) for reclamation of such soils is widely used (Cui et al., 2004; Shaheen et al., 2017a,b). However, the mono- and/or co-application of these amendments in such soils can alter the geochemical distribution of these elements and affect their bioavailability under wet and dry conditions; such effects have not been well studied and thus are worth investigating.

It is likely that different sources of Cu and Zn originating from either biosolids or inorganic amendments would result in differences concerning metal distribution among their geochemical fractions. Organic matter-borne Cu is rather expected to enhance the organic-bound Cu fraction of soil after biosolids application. This may also be the case with Zn, although this metal is known to be more readily soluble (Ahumada et al., 2009). On the other hand, application of a radically acidifying material to soil such as sulfate will likely dramatically decrease Cu and Zn retention onto carbonate phases (a major contribution to the overall metal retention capacity of soils—Elbana et al., 2018); this may increase the contribution of other fractions that become more important in lower pH (Wisniowska and Wlodarczyk-Makula, 2018). The effect that added amendments of different nature would have on a wetland crop (such as barnyard grass) as compared to an upland crop (such as sorghum) with respect to Cu and Zn solubility and phytoavailability is not well-known. Therefore, the aim of our study was to investigate the impact of mono- and co-application of biosolids, compost, and sulfur on the fractionation, mobilization, and phytoavailability of Cu and Zn to sorghum (dry soil) and barnyard grass (wet soil) in a contaminated and uncontaminated fluvial soil.

2. Materials and methods

2.1. Sampling and characterization of the soil and amendments

A composite surface (0–20 cm) fluvial soil was collected from the Farm of the University of Kafrelsheikh, Sakha, Egypt. Also we collected a sample of anaerobically-digested biosolids derived from domestic and industrial inputs from the Damanhur wastewater treatment plant (Egypt). The compost was prepared by thoroughly mixing postharvest rice, cotton and maize left-overs (at 60%), farmyard manure (at 35%), and inorganic soil (at 5%). Further details are reported elsewhere (Shaheen et al., 2017a). All collected samples (soil, biosolids and compost) were air-dried, and sieved through a 2-mm sieve. Elemental sulfur (> 95% pure) was obtained commercially. The soil was analysed according to Sparks et al. (1996). The studied soil, biosolid, compost, and sulfur samples were digested in a microwave system (Milestone MLS 1200 Mega, Germany) for pseudo-total element concentrations (US EPA 3051a, 2007). The elements were measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Ultima 2, Horiba Jobin Yvon, Unterhaching, Germany). Details on extraction protocols and analytical instrumentation are given by Shaheen et al. (2017a) and in the Supplementary Material (Appendix A).

2.2. Mixing the soil with biosolids, compost, and sulfur, soil spiking, and the pot experiment

The soil was treated with biosolids, compost, and sulfur (Table 1). The rate of application of biosolids to soil was 25 g DM (dry matter) kg^{-1} soil (equivalent to 50 ton ha^{-1}). Added biosolid was not expected to surpass US Environmental Protection Agency (USEPA, 2002) biosolids-borne heavy metal loads. Also this rate is not unusual in similar studies (e.g., Shaheen et al., 2018). The un-amended and biosolids (BS)-amended soils were mixed thoroughly with compost and sulfur at two rates. Also, we spiked the soil with Cu and Zn and to this soil we added two rates of compost (thereafter "C1" and "C2") and sulfur (thereafter "S1" and "S2," Table 1). The soil was spiked individually with sulfate salts of Cu as $CuSO_4.5H_2O$ and Zn as $ZnSO_4.7H_2O$ at concentrations of 200 mg Cu kg^{-1} soil and 400 mg Zn kg^{-1} soil. Spiking solutions and rationale are included in the Supplementary Material (Appendix A) and similar spiking procedure is thoroughly mentioned and explained in a work reporting results of Cd and Ni from the same experiment (Shaheen et al., 2017a). The experimental design is further explained in Table 1.

The mixtures were placed in pots and cultivated with *Sorghum bicolor* (sorghum) and *Echinochloa crusgalli* L. (barnyard grass). Pots with sorghum were minimally irrigated and are thereafter referred to as "dry soil", while plants of barnyard grass were submerged (thereafter "wet soil"). The treatments were replicated 3 times and the experiment lasted for 15 weeks. Further details on the setup of the pot experiment are included in the Supplementary Material (Appendix A).

2.3. Preparation and analyses of plant and soil samples

At the end of the experiment, plant aerial biomass was harvested, dried at 70 °C until no further weight loss, and, after dry mass was recorded, ground to fine powder. Subsequently 1 g of it was dry-ashed at 450 °C and extracted with 20% HCl (Jones et al., 1991). After plant harvest, soil samples were collected from each pot, and analysed for soil pH, soil organic matter, and the potentially available form of Cu and Zn. The potentially available form of Cu and Zn in both the dry and wet soils was extracted according to Soltanpour and Schwab (1977). The non-residual chemical fractions of Cu and Zn in selected treatments (i.e., control soil, mono-BS-treated soil, BS-C2-treated soil, BS-S2-treated soil, spiked soil, spiked C2-treated soil, and spiked S2-treated soil) were sequentially extracted based on the work of Tessier et al. (1979). The four steps categorize metals into (a) soluble plus exchangeable (F1), (b) sorbed and bound onto carbonate (F2), (c) occluded and bound to Fe and Mn oxides (F3), and (d) organically bound (F4). Copper and Zn were measured by graphite furnace atomic absorption spectroscopy (GBC Avanta E, Victoria, Australia). Further details on sample handling, sequential extractions, analytical instruments, and quality control are in the Supplementary Material (Appendix A) and also provided by Shaheen et al. (2017a). Variable means were analysed with one-way ANOVA, and Duncan's multiple range test was employed at $p < 0.05$, using the IBM SPSS Statistics 23 (NY, USA) package. Figures were created with OriginPro 9.1 b215 (OriginLab Corporation, Northampton, USA).

3. Results and discussion

3.1. Soil pH and organic matter

The pH value of the control "dry" soil was 7.62 and that of the "wet" 8.55 (Fig. 1). Increased pH with flooding might be due to proton consumption required for the reduction of elements such as NO_3^-, Mn^{4+} and Fe^{3+} (Frohne et al., 2011; El-Naggar et al., 2018).

Soil pH decreased significantly with biosolids application to the wet soil compare to the unamended wet, while biosolids did not affect pH in the dry soil (Fig. 1). Decreasing soil pH in the biosolids-treated wet soil is likely connected to the low biosolids pH of 6.43. This is in agreement with previous works (e.g., Shaheen and Tsadilas, 2010, 2013). Also this pH reduction may be ascribed to the production of humic acids as biosolids-borne organic carbon biodegrades (Shaheen et al., 2014a). Added compost (high compost rate; C2) increased soil pH in the dry soil as compared to the dry control, but did not affect the wet soil, although there was an increasing trend. Compost was slightly alkaline (pH 7.2; Appendix A) and this may have caused the increasing pH trend. Sulfur application decreased significantly soil pH to 5.1 when added at 1.25% and to 4.2 at 2.5% in the dry soil, and such was also the case in the wet soil. The co-application of biosolids and compost increased significantly soil pH in the dry soil at BS + C1, but did not increase it further at BS + C2, while the co-application of biosolids and sulfur decreased significantly soil pH as compared to the mono-application of biosolids (Fig. 1).

Added Cu decreased significantly soil pH by *ca*. one unit in the dry

Table 1

Treatments of the pot experiment.

No.	Treatments in three replicates	Code	Description
1	Soil	Soil	5 kg soil without any treatments
2	Soil + Biosolids	Soil + BS	5 kg soil + 125 g biosolids
3	Soil + Compost 1	Soil + C1	5 kg soil + 62.5 g compost
4	Soil + Compost 2	Soil + C2	5 kg soil + 125 g compost
5	Soil + Sulfur 1	Soil + S1	5 kg soil + 62.5 g sulfur
6	Soil + Sulfur 2	Soil + S2	5 kg soil + 125 g sulfur
7	Soil + Biosolids + Compost 1	Soil + BS + C1	5 kg soil + 125 g biosolids + 62.5 g compost
8	Soil + Biosolids + Compost 2	Soil + BS + C2	5 kg soil + 125 g biosolids + 125 g compost
9	Soil + Biosolids + Sulfur 1	Soil + BS + S1	5 kg soil + 125 g biosolids + 62.5 g sulfur
10	Soil + Biosolids + Sulfur 2	Soil + BS + S1	5 kg soil + 125 g biosolids + 125 g sulfur
11	Spiked Soil with Cu	Soil + Cu	5 kg soil spiked with 200 mg kg^{-1} Cu
12	Spiked Soil + Compost 1	Soil + Cu + C1	5 kg spiked soil + 62.5 g compost
13	Spiked Soil + Compost 2	Soil + Cu + C2	5 kg spiked soil + 125 g compost
14	Spiked Soil + Sulfur 1	Soil + Cu + S1	5 kg spiked soil + 62.5 g sulfur
15	Spiked Soil + Sulfur 2	Soil + Cu + S2	5 kg spiked soil + 125 g sulfur
16	Spiked Soil with Zn	Soil + Zn	5 kg soil spiked with 400 mg kg^{-1} Zn
17	Spiked Soil + Compost 1	Soil + Zn + C1	5 kg spiked soil + 62.5 g compost
18	Spiked Soil + Compost 2	Soil + Zn + C2	5 kg spiked soil + 125 g compost
19	Spiked Soil + Sulfur 1	Soil + Zn + S1	5 kg spiked soil + 62.5 g sulfur
20	Spiked Soil + Sulfur 2	Soil + Zn + S2	5 kg spiked soil + 125 g sulfur

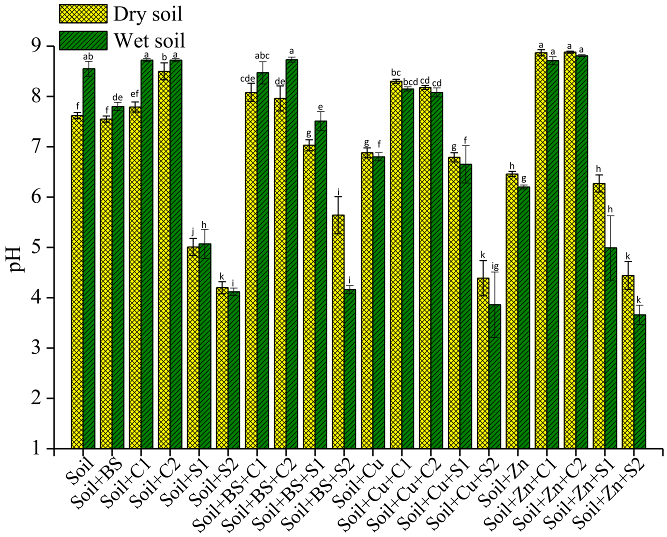

Fig. 1. Impact of mono- and co-application of biosolids, sulfur, and compost on soil pH in the dry and wet soil. Values accompanied by different letters are significantly different within columns at the level ($P < 0.05$).

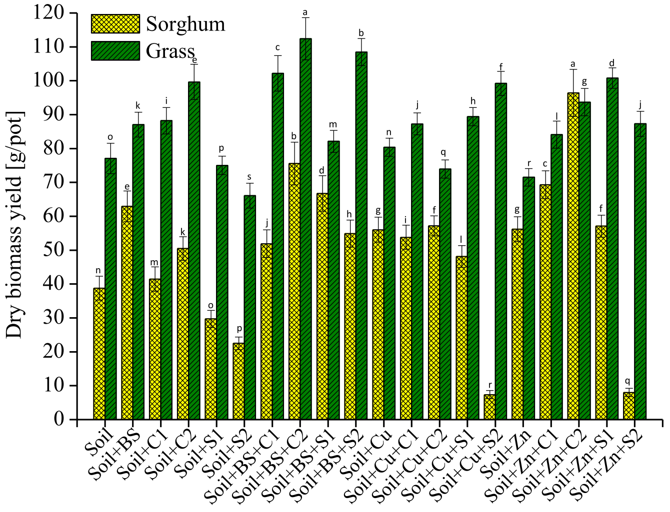

Fig. 2. Impact of mono- and co-application of biosolids, sulfur, and compost on the dry biomass yield of sorghum and barnyard grass. Values accompanied by different letters are significantly different within columns at the level ($P < 0.05$).

soil and two units in the wet soil (Fig. 1), and similar also was case with Zn; decreased pH might be due to the sulfate anions added with metal salts. Added compost in the Cu-spiked soil increased pH significantly compared to the unamended Cu-spiked soil in both dry and wet conditions; however, compost in the Zn-spiked soil increased pH to a greater extent. As for added sulfur, it decreased pH significantly in both Cu- and Zn-added soils (Fig. 1).

Soil OM was increased from 3.7% (control) to 5.3% in the biosolids- and to 5.9% in the compost-treated soils (at soil + C2). Soil OM in the highest rate of co-applied compost and biosolids increased further to 6.87% (Appendix A; Fig. S1), exhibiting thus the beneficial effects of such organic wastes to soil quality.

3.2. Dry biomass yield

Biosolids application increased significantly the yield of sorghum and grass by 38% and 12%, respectively, as compared to the untreated soils (Fig. 2; please note that comparisons are conducted only within plant species). Compost at C2 increased significantly plant yield by 23% compared to the untreated soils in both plants. Yield increased with compost probably because of the soil supply with compost-borne nutrients such as carbon and nitrogen (note the low C/N ratio of 17). Contrary to that, sulfur application, in particular at high rate, decreased significantly the yield of sorghum by 70% and of grass by 17% compared to their control. The negative impact of sulfur was more dramatic under the dry conditions, a probable consequence of the highly acidic pH recorded in this treatment (Shaheen et al., 2017a). Biosolids and compost co-application, especially in the high compost rate, improved significantly sorghum growth (increased by 49%) and grass (by 31%) as compared to the mono-application of either of them, as it also increased plant yield compared to the untreated soil; this is linked to enhanced soil fertility due to added N, as well as to improved plant growth conditions related to increased soil macro-porosity and reduced bulk density (Oleszczuk and Hollert, 2011). The co-application of biosolids and sulfur improved significantly plant growth of sorghum and grass as compared to the mono-application of either material exhibiting an increase up to 42%.

Spiking with Cu and Zn increased significantly sorghum yield by 30–31% compared to the un-spiked soil, but did not affect grass yield. The increased sorghum yield with spiking may be attributed to added sulfate that accompanied the Cu and Zn salts. Compost, especially at 2.5%, increased significantly the biomass of the two plants in both the wet and dry Zn-spiked soils as compared to the unamended spiked soil, while it did not affect plant growth in the Cu-spiked soils.

As for sulfur, the high added rate had a negative impact on sorghum growth, while grass growth was slightly but significantly improved in the metal-spiked soils (Fig. 2). Sorghum in the Cu- and Zn-spiked soils was affected by sulfur much more than grass did: it was significantly adversely affected by the higher sulfur rate to a greater extent than by the lower rate. Application of sulfur at 2.5% decreased significantly sorghum biomass yield in both the Cu- and Zn-spiked soils by 8-to-9-fold compared to the unamended spiked soils. This decrease is very likely linked to the dramatic pH decrease from 8.55 to 3.66 with added sulfur, which may have triggered Cu and Zn phytotoxicity, a phenomenon observed particularly under the dry conditions (as also agreed by others, e.g., Cui et al., 2004; Shaheen et al., 2017b).

3.3. Fractionation of Cu and Zn

3.3.1. Unamended/unspiked soil

Both Cu and Zn were mainly distributed in the residual fraction in the studied soil (82% for Cu and 93% for Zn). The dominance of the residual fraction is in agreement with Rinklebe and Shaheen (2017). Among the non-residual fractions (potential mobile fractions PMF = ΣF1-F4), the organic/sulfide fraction (F4) was dominant (9.0–10.0% for Cu, 5.4–7.3% for Zn), followed by the oxides fraction (F3) (7.7–8.6% for Cu and 1.4–2.0% for Zn); the carbonate and soluble + exchangeable fractions were negligible, in particular for Cu (Fig. 3). The dominance of the residual and the organic/sulfide and oxides fractions indicates that clays, oxyhydroxide minerals, along with soil organic matter (SOM) and sulfur compounds, are the predominant sorbents for Cu and Zn (Rinklebe and Shaheen, 2017).

3.3.2. Mono- and co-amended unspiked soil with biosolids alone and combined with compost and sulfur

Biosolids application increased the total content of Cu from 43.6 to 49.1 mg kg^{-1} (non-significant increase) and that of Zn from 88.2 to 107.5 mg kg^{-1} (significant increase; Table 2). Enhanced metal concentrations are not unexpected, given the biosolids metal content (Table 1S). Increasing total content of Cu and Zn as a result of biosolids application is in agreement with other similar studies (e.g., Shaheen et al., 2017b; Sharma et al., 2017).

Biosolids-added Cu was distributed mainly in the oxides and organic fractions, in particular under the wet conditions; while the increase of soluble + exchangeable and carbonate fractions was rather unimportant (Fig. 3). On the other hand, biosolids-added Zn was distributed in all fractions and mainly in the oxides and organic fractions; the increase of all fractions, including the soluble + exchangeable and carbonate, was significant as compared to the control. The increased percentage of the Zn oxides and organic fractions was higher under dry conditions than under wet, while the opposite was observed with the soluble + exchangeable and carbonates fractions (Fig. 3). A large percentage of the biosolids-borne Cu and Zn, in particular Cu, was distributed in the organic fraction, and this may be attributed to the higher stability of organo–Cu complexes when compared with those of Zn (Hansda et al., 2017). The high Cu affinity for SOM and sulfides is well-documented, in particular under wet conditions, which encourage the evolution of dissolved organic carbon (DOC) and the formation of Cu-sulfides species (Zhong et al., 2011). The observed increase of the Cu and Zn oxides fractions as compared to the mobile (F1 and F2) fractions in the biosolids-treated soil might reflect the possibility that a part of the biosolids-borne metals is likely retained onto Fe-Mn oxides; indeed, the high affinity of Cu and Zn for Fe oxides concurs with results obtained by others (e.g., Rinklebe and Shaheen, 2017).

Co-application of compost and biosolids decreased the solubility

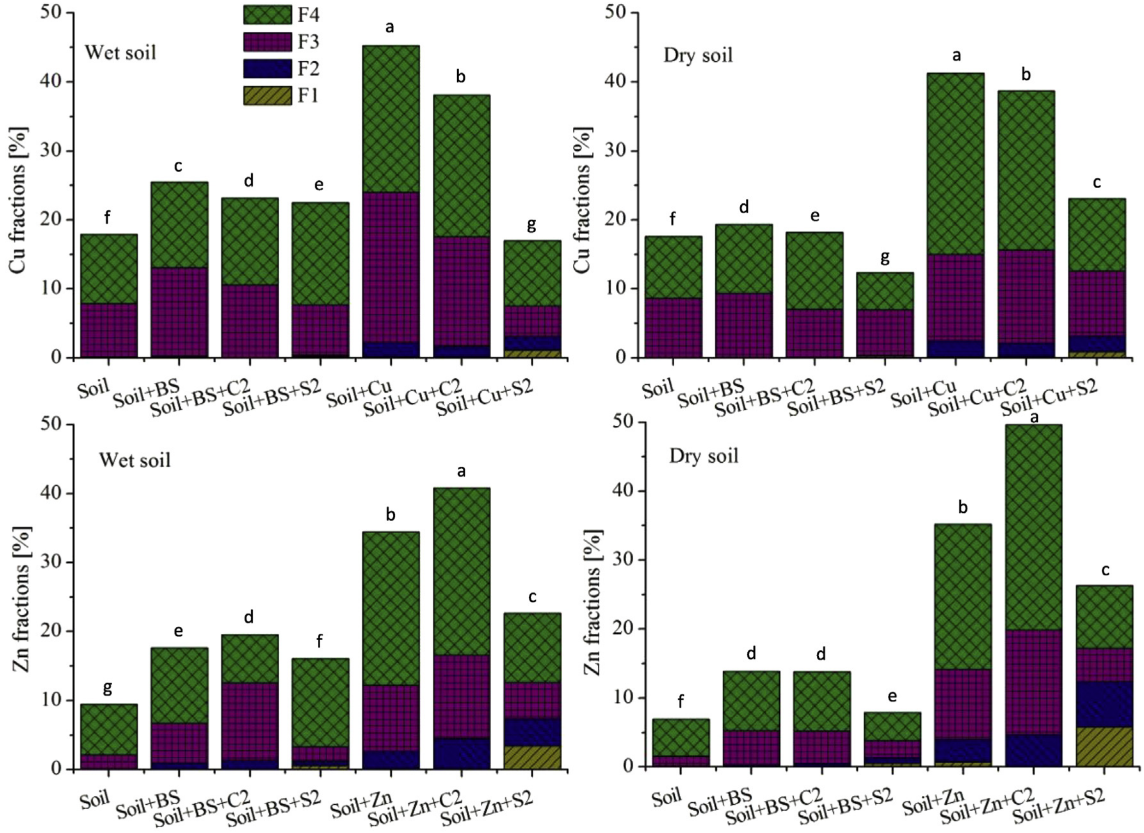

Fig. 3. Impact of mono- and co-application of biosolids, sulfur, and compost on the non-residual fractions (potential mobile fraction; PMF = ΣF1-F4) of Cu and Zn (% of total) in the dry wet soil. Values accompanied by different letters are significantly different within columns at the level ($P < 0.05$).

Table 2
The geochemical fractions of Cu and Zn in wet and dry soil after the mono- and co-amendment of biosolids, compost, and sulfur.

Treatments	Geochemical Fractions (mg/kg)											
	Soluble + exchangeable (F1)		Sorbed and bound to carbonate (F2)		Occluded and bounded to Fe–Mn oxides (F3)		Organically bound (F4)		Residual (F5)		Total	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
Copper												
Soil	bdl	0.08	bdl	0.00	3.9	3.4	5.6	6.1	35.8	34.1	45.3	43.6
Soil + BS	bdl	0.07	bdl	0.07	4.0	6.0	4.9	5.8	40.2	34.7	49.1	46.6
Soil + BS + C2	bdl	0.03	bdl	0.00	3.3	5.2	4.9	6.2	38.6	38.0	46.8	49.5
Soil + BS + S2	0.03	0.10	0.02	0.09	2.9	3.2	2.4	6.5	38.4	34.1	43.8	44.1
Soil + Cu	0.25	0.28	5.14	4.50	27.2	46.6	57.4	45.6	128.4	117.4	218.4	214.4
Soil + Cu + C2	0.33	0.29	4.12	3.13	29.0	33.6	49.4	43.4	131.5	130.9	214.3	211.3
Soil + Cu + S2	1.87	2.27	4.81	4.11	19.9	9.0	22.4	19.4	162.6	169.7	211.5	204.5
Zinc												
Soil	0.02	0.02	0.08	0.10	1.3	1.8	4.9	6.5	84.2	79.9	90.5	88.2
Soil + BS	0.04	0.08	0.38	0.91	5.2	6.0	9.2	11.4	92.6	86.0	107.5	104.4
Soil + BS + C2	bdl	0.05	0.59	1.34	4.9	11.6	9.1	7.2	90.8	83.1	105.3	103.3
Soil + BS + S2	0.55	0.58	0.86	0.65	2.5	2.2	4.2	12.9	95.1	85.0	103.3	101.3
Soil + Zn	2.48	0.38	11.52	8.96	35.4	33.6	73.4	78.2	226.0	230.9	348.8	352.0
Soil + Zn + C2	0.34	0.41	15.76	15.04	52.6	41.6	103.0	83.6	174.4	204.0	346.1	344.7
Soil + Zn + S2	19.84	11.68	22.48	13.28	16.6	17.8	31.0	34.2	251.9	262.3	341.8	339.2

bdl = below detection limit.

and potential mobility (PMF) of Cu in the dry and wet soil (Fig. 3). As for Zn, co-application caused redistribution among the organic and oxides fractions in the wet soil, while the impact was non-significant in the dry soil: it increased the oxides fraction and decreased the organic (Fig. 3). These results indicate that the biosolids- and compost-derived Zn under wet conditions may react and be associated with soil Fe-Mn oxides.

Although the application of sulfur along with biosolids increased the solubility (F1) and mobilization (F1 + F2) of Cu and Zn (in particular of Zn), it decreased the potential mobility of the metals in both soils (Fig. 3). These results indicate that sulfur altered the oxides and organic fractions in favour of the residual fraction, by decreasing the non-residual fractions under both dry and wet conditions (Fig. 3). We assume that Cu and Zn formed stable mineral compounds with sulfur that contributed towards the residual pool. Such a shift must also be linked to the significant sulfur-induced soil pH decrease; this would cause the acidic dissolution of the oxides fraction of Cu and Zn, and in turn decrease the oxides metal fraction.

3.3.3. *Spiked soil*

Metal fractions were altered with spiking as compared to the non-spiked soil under the dry and wet conditions (Table 2; Fig. 3). The Cu percentages in the spiked soil distributed in the PMF (45% in the wet soil and 41% in the dry) were higher than those of Zn (34% in the wet soil and 35% in the dry soil; Fig. 3). As for the mobile fractions (MF = ΣF1-F2), they had lower Cu percentages (2.3% in the wet soil and 2.5% in the dry) than those concerning Zn (2.6% in the wet soil and 4.1% in the dry; Fig. 3). Therefore, the Cu *potential* mobilization (reflected by PMF) was higher than that of Zn, while the *easily* mobilized Zn (reflected by MF) was higher than that of Cu. The altered metal solubility between wet and dry soils likely occurs due to metal precipitation with sulfides in the wet soil triggered by the expectedly low redox potential (E_H) found in soils with high moisture regime (e.g., Frohne et al., 2011). On the other hand, Cu previously retained by sulphides, may be released under oxic conditions (typically in dry soils) when sulphides are oxidized to SO_4^{2-} (Rinklebe et al., 2017). Moreover, Fe oxides seem to have an important role in Cu mobilization in our work under the wet conditions: Cu, typically bound onto Fe oxides by sorption or co-precipitation under oxidizing conditions, may be readily released due to Fe and Mn oxides precipitation when soil conditions become anoxic (Shaheen et al., 2014b).

3.3.4. *Mono- and co-amended spiked soil with compost and sulfur*

The impact of sulfur on metal fractions was stronger than that of compost (Table 2; Fig. 3). Sulfur induced a significant 7.5-fold increase in Cu solubility (F1) in the dry soil and an 8.1-fold increase in the wet soil; as for Zn, the increase in F1 was 8.0-fold (dry soil) and 30.5-fold (wet). Added sulfur increased Cu MF fractions from 2.5% to 3.2% of total Cu (dry soil) and from 2.2 to 3.1% (wet), as well as that of Zn (from 4.1 to 12.4%, dry; from 2.6 to 7.4%, wet soil). The high solubility of Cu and Zn with sulfur addition concurs with the previously observed soil pH decrease (Fig. 1). This is also evident in the correlation between fractions and pH, which indicates that the F1 fractions are negatively associated with pH ($r = -0.92^{**}$ to -0.99^{**} for Cu; $r = -0.96^{**}$ to -0.98^{**} for Zn; data not shown). Thus sulfur added for the purpose of decreasing highly alkaline soil pH triggers metal solubility when toxic metals are present in soil (Cui et al., 2004).

Although compost application decreased the Cu mobile fractions (MF = F1 + F2) from 2.5 to 2.1% (of total Cu) in the dry soil and from 2.3 to 1.6% in the wet soil, it increased the MF of Zn from 4.0 to 4.7% in the dry soil and from 2.6 to 4.5% in the wet soil as compared to the untreated spiked soils. Decreasing Cu mobilization (MF fractions) and potential mobilization (summation of all non-residual fractions) with compost is likely linked to increased soil pH in that treatment (Fig. 1) (as also agreed by Alburquerque et al., 2011). Moreover, increased SOM content with compost by 52% relative to the unamended soil is an additional reason for Cu immobilization and decreased solubility (Al Mamun et al., 2016).

3.4. *Potential availability of Cu and Zn*

3.4.1. *Impact of biosolids, compost, and sulfur on the potential availability of Cu and Zn in the un-spiked soil under dry and wet conditions*

Biosolids increased significantly Cu and Zn availability (Fig. 4). The increase was higher in the dry soil (70% for Cu; 389% for Zn) than that in the wet (Cu 12%; Zn 213%). Biosolids-borne Zn was of much higher concentration than Cu (616.8 vs. Cu 112.3 mg kg^{-1}) and this may explain the more dramatic Zn DTPA-extractability with added biosolids. Compost had a similar effect, with Zn exhibiting a higher rate of increase in solubility than Cu, an effect likely caused due to metal concentrations in compost (462 for Zn vs. 78 mg kg^{-1} for Cu). Copper enhanced solubility with compost (14–125%) was higher than that with biosolids (12–70%), and this may mean that compost-borne Cu was probably more readily available than that of the biosolids-borne. The

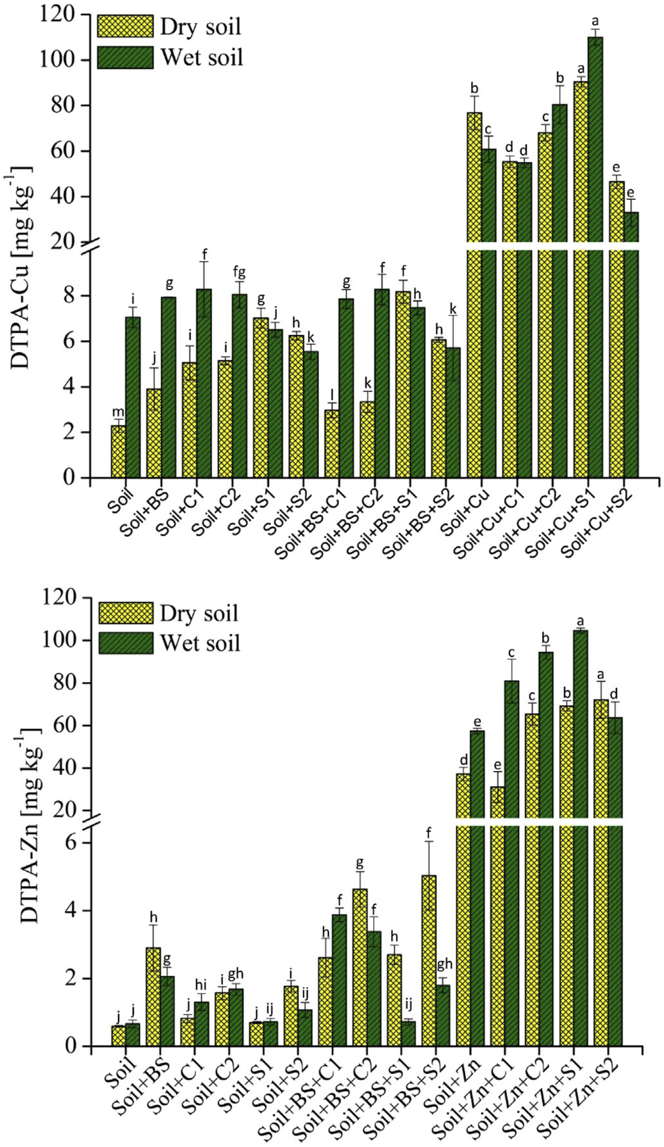

Fig. 4. Impact of mono- and co-application of biosolids, sulfur, and compost on the availability of Cu and Zn (mg/kg) under sorghum (dry soil) and barnyard grass (wet soil) cultivation. Values accompanied by different letters are significantly different within columns at the level ($P < 0.05$).

opposite was the case with Zn: increase with added biosolids (213–389%) was higher than that with compost (38–164%), a finding probably linked again to the Zn content in the added wastes. Similar to biosolids, Cu DTPA-extractability increase with compost was much higher in the dry soil (124%) than in the wet (14%), while the opposite occurred with Zn (98% increase with added compost in the wet and 38% in the dry soil). As for sulfur, it caused a significant decreased in Cu availability in the wet soil (7–21%), and an increase in the dry (172–206%), while it increased Zn availability in both soils (10–199%). Copper decreased extractability with added sulfur is likely connected to the decreased redox potential under flooded conditions and subsequent precipitation of Cu with sulfides; on the other hand, under oxic conditions, soluble Cu-S complexes may be formed, in agreement with other similar works (e.g., Shaheen et al., 2017c; El-Naggar et al., 2018).

Compost and biosolids co-application (in particular at C2) increased SOM (Fig. S1), decreased Cu availability in the dry soil, while it increased Cu availability in the wet; it also increased Zn availability in both soils as compared to the biosolids mono-application (all significant effects; Fig. 4). These indicate that the interaction of Cu and Zn with SOM differs in the dry soil from that in the wet. Copper behaviour is dependent on the formation of soluble Cu-DOC compounds, with DOC evolution being encouraged at lower redox potential; thus the observed Cu availability increase in the wet soil. The role of DOC in Cu solubility is well-documented, as it affects Cu biogeochemistry and mobility (Craven et al., 2012).

3.4.2. *Effect of compost and sulfur on the potential availability of Cu and Zn in the spiked soil under dry and wet conditions*

Spiking increased significantly Cu concentration from 2.3 to 76.8 mg kg^{-1} (dry soil) and from 7.1 to 60.8 mg kg^{-1} (wet). Soil spiking with Zn caused a significant increase in Zn availability from 0.60 to 37.2 mg kg^{-1} (dry soil) and from 0.70 to 57.4 mg kg^{-1} (wet; Fig. 4).

The low (C1) and high (C2) compost application rates decreased Cu compared to the spiked unamended dry soil (by 11% at C1, 28% at C2), but in the wet soil Cu availability increased at C2 by 32% relative to the spiked unamended soil. Similar was Zn behaviour at C1: it decreased in the dry soil (16%), and increased in the wet (41%, compared to the spiked unamended soil). At C2, Zn availability increased in both dry and wet soils (75% in dry vs. 64% in the wet). Such Zn behaviour is likely associated with added SOM (Wu et al., 2002). As for the fluctuation in metal behaviour, this seems to be dependent on application rates and moisture regime, and is likely a reflection of underlying changes in the MF metal fractions, as discussed earlier (Fig. 3; section 3.3.4).

Copper availability increased significantly with added sulfur in the spiked soils at S1 (low sulfur application), both dry (18%) and wet (81%), while at S2 Cu availability decreased (40% in dry, 46% in wet). We assume that the impact of sulfur on Cu availability is connected to moisture content and soil pH: the latter did not change at S1 (pH *ca.* 6.7) as much as at S2 (pH 3.66–4.4; Fig. 1). The two rates of sulfur increased significantly Zn availability in both soils, with a higher increasing rate in the dry soil (86% at S1 and 94% at S2) than in the wet soil (82% at S1 and 11% at S2). We assume that this is again connected to the dramatically decreased pH with added sulfur (pH 3.6 at S2; Fig. 1). Also, the reducing conditions in the wet soil affect the sulfur chemistry and thus Cu solubility. Copper is expected to be affected to a greater extent than Zn under sulfate-limited conditions, because Cu forms much more stable sulfide complexes than those of Zn (Karimian et al., 2018).

3.5. *Plant concentration of Cu and Zn*

3.5.1. *Biosolids, compost, and sulfur mono- and co-application impact on Cu and Zn plant concentrations in the un-spiked soil under dry and wet conditions*

Biosolids application increased significantly the content of Cu and Zn in sorghum (136% for Cu, 186% for Zn) and grass (20% for Cu, 160% for Zn) relative to the control (Fig. 5). The results indicate that the biosolids-added Cu was more bioavailable under dry conditions than under wet. The increase in plant Cu and Zn in the biosolids–treated soils as compared to the unamended soil might be due to the high metal biosolids content (as also discussed earlier; Appendix A). Also, it may be explained by the lower soil pH in the biosolids–amended soils as compared to the unamended soil, as also agreed by other similar works (Singh and Agrawal, 2010). Also biosolids-added DOC may have had a role in metal mobilization from soil to plant (Mendoza et al., 2006).

Compost application increased significantly the content of Cu and Zn in sorghum (24–30% for Cu and 49–93% for Zn) and grass (127–246% for Cu and 90–91% for Zn) as compared to the control soil. The impact of compost on Cu and Zn in the grass was greater than that on sorghum (Fig. 5). The lower compost rate (C1) caused a higher increase in plant Cu than C2, while the opposite was recorded with Zn (Fig. 5). Sulfur application increased significantly the content of Cu and Zn in sorghum (44–75% for Cu and 78–134% for Zn) and grass

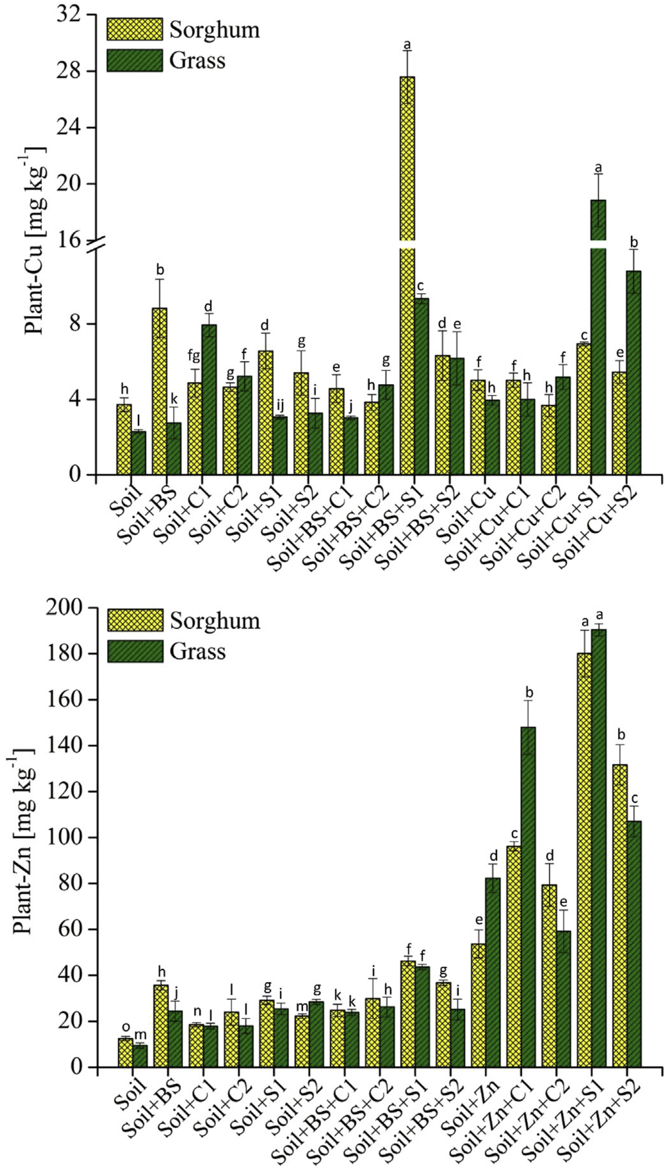

Fig. 5. Impact of mono- and co-application of biosolids, sulfur, and compost on the plant tissues concentrations of Cu and Zn in sorghum and barnyard grass. Values accompanied by different letters are significantly different within columns at the level ($P < 0.05$).

(33–42% for Cu and 170–202% for Zn) as compared to the control soil. Compost increased Cu and Zn content in the grass more than it increased them in sorghum (Fig. 5). The impact of the lower rate (C1) on the plant content of Cu was higher than that in the higher rate (C2), while the opposite trend was recorded with Zn (Fig. 5). Compost application along with biosolids decreased the sorghum content of Cu and Zn, while it increased the grass content of Cu and did not affect Zn as compared to the sole biosolids treatment.

3.5.2. *Impact of spiking and compost and sulfur application on the plant tissue concentrations of Cu and Zn under dry and wet conditions*

Plant Cu in the spiked soil was relatively low; it was 5.02 mg kg^{-1} in the sorghum and 3.95 mg kg^{-1} in the grass. Added compost had no apparent effect on sorghum at C1, while it significantly decreased Cu content at C2. It is interesting to note that the opposite was the case for grass: at C2, Cu content significantly increased. Although plant physiology-related reasons cannot be ruled out, we assume that these trends are connected to the previously discussed Cu chemical behaviour at soil level: compost-eluted DOC, typically triggered under wet conditions, could have caused Cu increased absorption at C2, while at C1 DOC was not of sufficiently high concentration to react with Cu for significant impact. On the other hand, under dry conditions DOC elution is much less likely and thus the decreased Cu absorption by sorghum. With added sulfur at S1, plant Cu increased significantly relative to the spiked unamended treatment, a likely reflection of the enhanced Cu availability as recorded previously (due to mildly but significantly reduced pH at S1). This increase was much more marked for grass than for sorghum: it seems that plant vigour due to better irrigation was impacted in the wet soil, while the dry sorghum had to address the ever present water stress, compressing thus Cu absorption relative to the wet plant. However, at S2 the dramatically reduced soil pH induced toxic effects to plants in both the wet and dry soils, and thus Cu concentration at C2 was lower than that at C1. In agreement with soil Cu chemical behaviour, toxicity could have been induced by Cu itself, although reduced plant vigour (observed in shrunk plant yield at S2) has also had a significant role.

Plant Zn concentration was high in the spiked treatment (53.68 for sorghum, 82.33 for grass, units in mg kg^{-1}), an impressive increase from the un-spiked control in both plants. Compost at C1 caused a considerable increase in both plants (up to 96.22 for sorghum and 148.02 mg kg^{-1} for grass), a likely combination of enhanced plant vigour with compost-added OM and compost-borne Zn. However, in agreement with sorghum Cu, Zn decreased significantly at C2 as compared to C1 in both plants, with grass Zn being even lower at C2 than in the spiked unamended treatment. This shows the protective role of added OM, as was also observed in the case of Cu in dry sorghum (Cu also decreased at C2 relative to C1). Sulfur triggered an impressive Zn increase in both plants (180.20 in sorghum, 190.50 mg kg^{-1} in grass), at levels observed typically in plants grown in polluted soils (Antoniadis et al., 2017). Interestingly, at S2, Zn levels decreased significantly relative to S1 in both plants, as was the case for Cu, although levels did not get anywhere close to the spiked unamended Zn concentrations. This, similar to Cu at S2, is an indication of plant stress induced by the dramatically acidic soil pH at S2.

4. Conclusions

To our arid alkaline soil, the addition of organic wastes, biosolids, and compost, increased significantly SOM, while it did not affect to a considerable extend soil pH. Acidifying elemental sulfur, added to reduce plant growth-restricting alkalinity, decreased soil pH considerably down to the levels of pH *ca.* 4. We suggest that these two amendment-altered soil parameters had the most important role in plant growth and in the chemical behaviour of spiked Cu and Zn in both wet conditions (under which grass was grown) and dry (sorghum). Plant yield increased with added OM and dramatically decreased with sulfur, due to reduced pH. Although added OM enhanced plant vigour, Cu absorption was different in the two studied moisture regimes: it was increased in the wet soil (we assume due to the formation of soluble, easily absorbed Cu-DOC complexes, encouraged by DOC evolution in wet anoxic conditions), while it decreased in the dry (due to the protective role of OM). Zinc uptake was reduced in the high compost application rates. Such differences in metal behaviour between wet and dry conditions were also observed in (and are thus explained by) the geochemical fractionation of Cu and Zn: organic waste-added metals were mainly distributed in the organic fraction; however, in the wet soil the organic fraction percentage was higher than in the dry, possibly due to metal-DOC associations; and at the same time the residual (inert, non-bioavailable) fraction was lower, leading to higher metal mobility in the wet soil. These two findings, inducing significant changes in the underlying soil chemical behaviour of the studied metals under the two moisture regimes, also reflected in metal uptake by the plants, accentuates the novelty of this work.

Acknowledgments

We thank the German Alexander von Humboldt Foundation (Ref 3.4 - EGY - 1185373 - GF-E) for the financial support of the experienced researchers' fellowship of Prof. Dr. Shaheen at the University of Wuppertal, Germany. Technical assistances from the Laboratory of Soil and Water Sciences, Faculty of Agriculture, Kafrelsheikh University and the central laboratory for Environmental Studies in Kafrelsheikh University are acknowledged.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2018.12.106.

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