frontiers in Ecology and Evolution

ORIGINAL RESEARCH
published: 04 September 2018
doi: 10.3389/fevo.2018.00123

Phytomanagement and Remediation of Cu-Contaminated Soils by High Yielding Crops at a Former Wood Preservation Site: Sunflower Biomass and Ionome

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Specialty section:
This article was submitted to Agroecology and Ecosystem Services, a section of the journal Frontiers in Ecology and Evolution

Received: 21 March 2018
Accepted: 31 July 2018
Published: 04 September 2018

Citation:
Mench MJ, Dellise M, Bes CM, Marchand L, Kolbas A, Le Coustumer P and Oustrière N (2018) Phytomanagement and Remediation of Cu-Contaminated Soils by High Yielding Crops at a Former Wood Preservation Site: Sunflower Biomass and Ionome. Front. Ecol. Evol. 6:123. doi: 10.3389/fevo.2018.00123

This long-term field trial aimed at remediating a Cu-contaminated soil to promote crop production and soil functions at a former wood preservation site. Twenty-eight field plots with total topsoil Cu in the 198–1,169 mg kg^{-1} range were assessed. Twenty-four plots (OMDL) were amended in 2008 with a compost (made of pine bark chips and poultry manure, OM, 5% w/w) and dolomitic limestone (DL, 0.2%), and thereafter annually phytomanaged with a sunflower—tobacco crop rotation. In 2013, one untreated plot (UNT) was amended with a green waste compost (GW, 5%) whereas 12 former OMDL plots received a second compost dressing using this green waste compost (OM2DL, 5%). In 2011, one plot was amended with the Carmeuse basic slag (CAR, 1%) and another plot with a P-spiked Linz-Donawitz basic slag (PLD, 1%). Thus six soil treatments, i.e., UNT, OMDL, OM2DL, GW, CAR, and PLD, were cultivated in 2016 with sunflower (*Helianthus annuus* L. cv Ethic). Shoots were harvested and their ionome analyzed. At high soil Cu contamination, the 1M NH_4NO_3-extractable vs. total soil Cu ratio ranked in decreasing order: Unt (2.35) > CAR (1.02), PLD (0.83) > GW (0.58), OMDL (0.44), OM2DL (0.37), indicating a lower Cu extractability in the compost-amended plots. All amendments improved the soil nutrient status and the soil pH, which was slightly acidic in the UNT soil. Total organic C and N and extractable P contents peaked in the OM2DL soils. Both OMDL and OM2DL treatments led to higher shoot DW yields and Cu removals than the GW, CAR, and PLD treatments. Shoot DW yields decreased as total topsoil Cu rose in the OMDL plots, on the contrary to the OM2DL plots, demonstrating the benefits to repeat compost application after 5 years. Shoot Cu concentrations notably of OMDL and OM2DL plants fitted into their common range and can be used by biomass processing technologies and oilseeds as well. In overall, there is a net gain in soil physico-chemical properties and underlying soil functions.

HIGHLIGHTS

- Compost incorporated into Cu-contaminated soils improves the sunflower growth.
- Soil organic matter increases in compost-amended soils.
- Extractable soil Cu decreases in compost-amended soils.
- Shoot Cu removal by sunflower reaches 26–88 g Cu ha^{-1} $year^{-1}$.

Keywords: basic slag, compost, carbon sequestration, *Helianthus annuus* L., marginal land, organic matter, phytoextraction, phytoremediation

INTRODUCTION

An estimate of local, anthropogenic soil contamination to the whole of Europe has totaled 2.5 million of potentially contaminated sites, a considerable fraction having real or perceived contamination problems (Panagos et al., 2013; Science Communication Unit University of the West of England, 2013). With an estimated area of 2 ha per site and knowing that 37.3% of the total contamination is caused by metal(loid)s, roughly 1.86 million ha would be contaminated by these ones (Evangelou et al., 2012; Van Liedekerke et al., 2014). Three hundred forty thousand contaminated sites would require a remediation (Van Liedekerke et al., 2014). Similarly, the US EPA tracks nearly 9 million ha of possibly contaminated land (USEPA, 2013) and 1,438 abandoned, worst hazardous waste sites on its National Priority List (USEPA, 2016). Contaminated soils in China would reach 10 million ha and 10–17% of the farmland (more than 20 million ha) would be metal(loid)-contaminated based on food survey (Yao et al., 2012; Zhang et al., 2015). Many impacted sites have been remediated to productive use, but numerous large sites remain derelict or underutilized because their remediation is uneconomic or unsustainable using conventional methods (Le Corfec, 2011; ADEME, 2014; Van Liedekerke et al., 2014; JRC, 2015; Cundy et al., 2016). The 7th Environment Action Programme of the EU however aims that by 2020 "soil is adequately protected and the remediation of contaminated sites is well underway" (Official Journal of the European Union, 2013).

The long-term combination of gentle remediation options (GRO) with profitable crop production and/or green technologies, i.e., phytomanagement, can be applied as part of integrated, mixed, site risk management solutions for the return of low-level risk sites to productive usage and can gradually provide a range of economic and other benefits (Mench et al., 2010; Cundy et al., 2015, 2016; Kidd et al., 2015). Demonstrating the wider benefits of undertaking soil remediation is crucial for several questions, notably: how long it will take for the solutions to reduce pollutant linkages, are the solutions sustainable, and how much it will cost? (Bardos et al., 2016; Cundy et al., 2016; Gerhardt et al., 2017).

The harvested biomass can be used by various biomass processing technologies and sectors, and appropriate biomass cultivation can improve soil functions and underlying ecosystem services, e.g., storage and supply of nutrients, plant and microbe biodiversity, regulation of water supply and quality, erosion control, recycling of raw materials, reduced greenhouse gas emissions and waste generation, landscaping medium, etc. (Carrier et al., 2011; Delplanque et al., 2013; Bourgeois et al., 2015; Evangelou et al., 2015; Strezov and Evans, 2015; Cundy et al., 2016; Gonsalvesh et al., 2016; Asad et al., 2017; Bauddh et al., 2017; Bert et al., 2017a; Ciadamidaro et al., 2017; Clifton-Brown et al., 2017; Šimek et al., 2017; Schröder et al., 2018).

A number of perceived or actual barriers or impediments related to technical issues and stakeholder perceptions is limiting on site phytomanagement application (Cundy et al., 2015; Bert et al., 2017b; Montpetit and Lachapelle, 2017). For overcoming such barriers, several sets of field trials have been either implemented or developed in Europe, notably for metal(loid)-contaminated sites with funding from European projects, i.e., Greenland, PhytoSUDOE, Intense, and Miscomar, and national environment agencies, e.g., Ademe in France (Mench et al., 2010; Kidd et al., 2015; Nsanganwimana et al., 2016; Bert et al., 2017a,b; Friesl-Hanl et al., 2017; Krzyzak et al., 2017; Quintela-Sabarís et al., 2017; ADEME, 2018). Here the purpose was to assess the long-term efficiency and limits of phytomanagement options at a wood preservation site with sandy Cu-contaminated soils.

Copper ranks 5th out of the 10 most frequent contaminants detected on French contaminated sites (singly and in combination; 6% in term of occurrence of soil and water contamination; potentially present at 1,413 sites) after hydrocarbons, Pb, Cr, and polycyclic aromatic hydrocarbons (BASOL, 2017), notably due to smelting, metallurgy and wood preservation, without accounting for vineyard, orchard and horticultural soils contaminated by Cu-based fungicides (at least 1 million ha) and historically sludge-amended soils (Godin, 1983; Hedde et al., 2013). The European wood preserving industry produce around 6.5 million m^3 $year^{-1}$ of pressure treated wood, 71% of this wood being treated with water-borne products (Salminen et al., 2014).

Copper excess in soils at wood preservation sites, often associated with As, Cr(VI), B, Hg, and xenobiotics such as creosote-derived PAH, contributes to impact soil ecological functions, e.g., microbial communities, biogeochemical cycles of organic matter (OM) (U. S. Congress, 1995; Dumestre et al., 1999; Buchireddy et al., 2009; Lagomarsino et al., 2011; OECD, 2013). Soil structure and texture are also altered, notably through the OM cycle, resulting in low water and nutrient retention (Mench and Bes, 2009; Asensio et al., 2013) and in less plant resilience to drought and low fertility (Wong, 2003).

Here, the remediation solution and soil amendments were selected after risk assessment and option appraisal (Bes and Mench, 2008; Mench and Bes, 2009; Negim et al., 2012). As soil pH, OM and Al, Fe, and Mn oxyhydroxides are key-players mutually driving Cu precipitation, reactions with soil fractions, and operational mobility, plots amended with either a combination of compost and dolomitic limestone or basic slags were implemented on site (Kolbas et al., 2011; Le Forestier et al., 2017).

Out of potential Cu-tolerant crops (e.g., willows, poplars, pines, Miscanthus, vetiver, tobacco, sorghum, etc.), sunflower is an annual high yielding plant species and a secondary metal accumulator in shoots, relatively tolerant to metal(loid) excess and suitable for cultivation on derelict areas (Marchiol et al., 2007; Fässler et al., 2010; Mench et al., 2010). It can be used to phytoextract bioavailable metal (Cd, Zn, and Cu) fraction in contaminated soils and provide financial returns from the biomass processing (Mench et al., 2010; Kolbas et al., 2011; Herzig et al., 2014; Kidd et al., 2015). Due to its high biomass, sugar, protein and oil production, sunflower shoots and oilseed are relevant raw feedstock for several biomass processing technologies and various sectors: e.g., insulation material, hydrothermal processing which converts raw materials such as lignocellulosic materials into bioenergy and high added-value chemicals (Ruiz et al., 2013), fatty acids for supporting microbes, oil, production of bioethanol, fermentation and biogas (Alaru et al., 2013; Camargo and Sene, 2014; Hesami et al., 2015), fibers to reinforce plastic products (Malkapuram et al., 2009; Strezov and Evans, 2015; Mati-Baouche et al., 2016; Liu et al., 2017), etc. As water supply and its distribution during the crop cycle is one limiting factor for crop production in SW France, sunflower ability to resist to more frequent heatwaves and long droughts due to the climate change is an advantage (Kidd et al., 2015). A crop rotation however is mandatory in France to avoid fungi diseases related to sunflower cultivation (CETIOM, 2011).

This field trial aimed at assessing the long-term efficiency of phytomanagement options based on various soil amendments and a crop rotation with high yielding plants relatively Cu-tolerant (sunflower and tobacco) to remediate a Cu-contaminated soil at a former wood preservation site. The hypotheses were (1) to initially reduce the phytoavailable soil Cu, through soil amendment, for allowing a better crop production, usable by biomass processing technologies and the bioeconomy, and then (2) to annually strip a part of the phytoavailable soil Cu corresponding to shoot Cu removal, leading progressively to ameliorate soil functions. Regarding soil amendments, we compared (1) a single dressing of compost combined with dolomitic limestone, (2) a compost dressing renewed 5 years after the first incorporation of compost and dolomitic limestone into the soil, and (3) a single addition of basic slags.

Potential processes behind these soil amendments were: (1) Cu sorption by the compost-derived OM, liming effect for enhancing Cu sorption on soil bearing phases, promotion of soil microbial communities, and nutrient (N, P, K, Ca, and Mg) supply for biomass production and better cellular homeostasis; (2) liming effect and Cu reaction with Fe/Mn oxides, carbonates and phosphates (Bes and Mench, 2008; Kumpiene et al., 2008). Changes in soil physico-chemical properties, shoot dry weight (DW) yield, ionome, and Cu removal of sunflower plants grown in year 9 were reported. Changes in available soil Cu and other soil physico-chemical parameters in line with sunflower parameters were discussed and potential biomass processing as well.

MATERIALS AND METHODS

The field trial was set up in 2008 at a wood preservation site (10 ha) located in Saint-Médard-d'Eyrans, Gironde, SW France (44°43.353′N, 000°30.938′ W—France, Kolbas et al., 2011). The soil developed on an alluvial soil in terrace containing alluvial materials from the Garonne River combined with wind deposits (Fluvisol—Eutric Gleysols, World Reference Base for soil resources) (Mench and Bes, 2009). Its texture is sandy, i.e., 85.8% sand, 5.9% clay, 8.3% silt, 1.6% OM, C/N 17.2, and neutral pH (7.1 ± 0.3), with a low CEC (3.5 $\text{cmol}^{+}\ \text{kg}^{-1}$).

Industrial activity dates back to 1846 with the construction of a railway line and a facility for wood preservation (Mench and Bes, 2009). Copper sulfate (from 1913 to 1980), chromated copper arsenate type C (from 1980 to 2006), Cu hydroxycarbonates (17.3%) with benzylalkonium chloride (4.8%) and Tanalith E (Cu carbonate 16.4%, Tebuconazole 0.18%, and propiconazole 0.18 % w/w) were successively used. No preserved wood was stored on the field trial area since at least 2003. Soil contamination was mainly due to wood washing, Cu being the main contaminant (**Table 3**) and total soil Cu decreasing rapidly in the soil profile. Plant communities were previously characterized (Bes et al., 2010). Soil quality and risks were assessed on site, revealing topsoil ecotoxicity with diffuse contamination generating pollutant linkages (Mench and Bes, 2009; Kolbas et al., 2011; Marchand et al., 2011).

Field Trial

Originally, the site was divided into 15 sub-sites according to past and present activities (Bes et al., 2010). The field trial is located at the P1-3 sub-site (10 m × 11 m) and started in March 2008 (Kolbas et al., 2011). It consists in four blocks (2 m × 10 m) of 10 plots (1 m × 2 m), defined according to total soil Cu (**Figure 1**), i.e., block B1: plots #1 to #10 (198–381 mg Cu kg^{-1}), block B2: plots #11 to #20 (257–556 mg Cu kg^{-1}), block B3: plots #21 to #30 and block B4: plots #UNT, #CAR, #PLD, #GW (719–1,169 mg Cu kg^{-1}) (Kolbas et al., 2011). Six soil treatments were tested on site: OMDL, OM2DL, UNT, GW, CAR, and PLD (**Table 1**). Soil amendments were carefully mixed in the topsoil (0–0.25 m) with a stainless-steel spade. The amendment composition is detailed in **Table 2**. Hereafter plots from the same block and with the same soil treatments were labeled as followed: (block:treatment) (e.g., B2: OMDL). Since 2008, a crop rotation has been annually carried out with sunflower and tobacco (Kolbas et al., 2011; Kolbas, 2012).

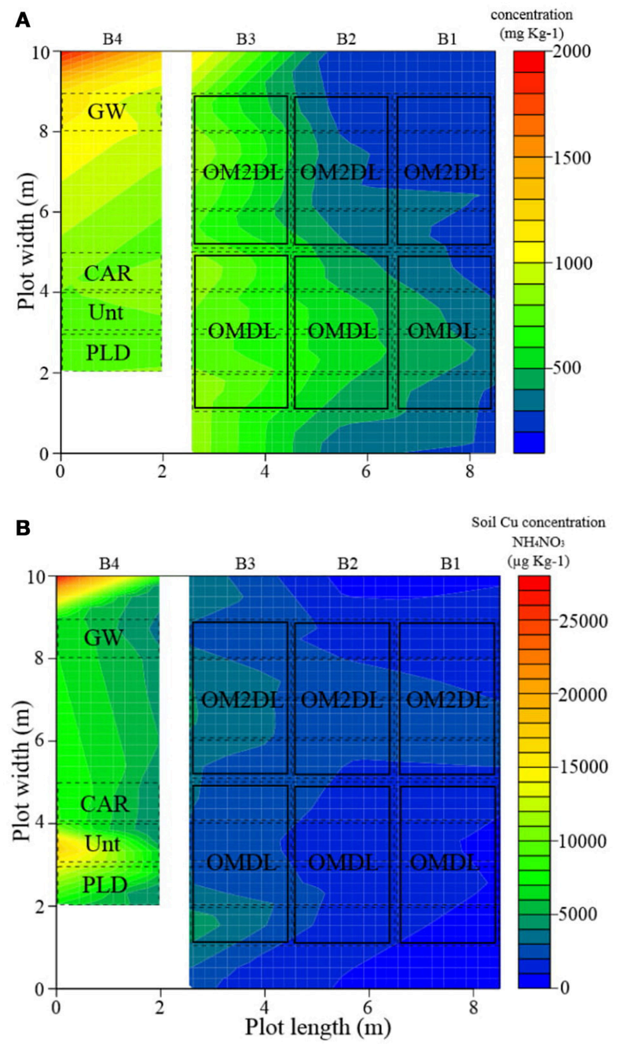

FIGURE 1 | Spatial variability of **(A)** total topsoil Cu (mg Cu kg^{-1} DW) and **(B)** 1M NH_4NO_3-extractable topsoil Cu (µg Cu kg^{-1} DW) (0–0.11 m depth layer) within the field trial. B1: block #1, B2: block #2, B3: block #3, and B4: block #4.

Soil Sampling

In February 2017 (year 10), four soil samples per plot were collected in the topsoil layer (0–11 cm) with a sampling cylinder (ø 3.6 cm × 11.5 cm – 0.39 L) and in the subsoil layer (11–30 cm) with a soil auger. In overall, 28 plots × 4 replicates × 2 soil layers were collected. Fresh topsoil replicates were weighed to determine their bulk density (mean value = 0.9 g.cm^{-3}). Thereafter all fresh soil samples were sieved at 4 mm, paying attention to aggregates and to avoid any loss of compost particles. Soil samples were then weighed, air-dried and weighed again to determine their moisture content. Replicates were further combined to make a composite soil sample (∼ 1 kg soil fresh weight), sieved at 2 mm (nylon mesh) and manually homogenized. After pooling replicates from one plot, we had 28 samples per layer including the 6 treatments. Soil texture and physico-chemical parameters were determined with standard methods and a quality scheme by INRA LAS (2014), Arras, France, e.g inductively coupled plasma/atomic emission spectroscopy (ICP-AES) for metals after wet digestion in HF and $HClO_4$, and hydride-generation for As after wet digestion in H_2SO_4/HNO_3 (2/1) with V_2O_5 at 100°C (3 h). Two certified reference materials, i.e., BCR No. 141 (calcareous loam soil) and BCR No. 142 (light sandy soil) from the Bureau Communautaire de Référence, were used by INRA LAS in the quality scheme. To avoid making this paper too cumbersome, only the topsoil data are presented here and the subsoil data are included in the (**Table S1**).

Sunflower Cultivation and Analysis

In April 2016 (year 9), face to a severe spring drought, sunflower seeds (cv. LG545010 ES Ethic) were firstly sowed in plastic pots (6.5 cm × 6.5 cm × 6.5 cm) filled with a plant growth substrate (compost 33%, soil 33%, and perlite 33%) and then placed in a greenhouse during 1 month. In early May, plantlets were transplanted in field plots in three rows (0.33 m between rows, 0.28 m between plants, 21 plants per plot, and 105,000 plants ha^{-1}). The soils were fertilized twice, i.e., before and 2 months after transplantation, with NPK fertilizer [Blaukorn classic, 12-8-16 (3–25)] at 40 kg N (58% NH_4, 42% NO_3), 26.7 kg P_2O_5, 53 kg K_2O, 10 kg MgO, 83 kg SO_3, 0.06 kg B, 0.2 kg Fe, and 0.04 kg Zn per ha. Plant shoots were harvested in September 2016. Stem bottoms were carefully brushed to remove soil particles, shoots cut and placed in paper bags, and oven-dried at 50°C until constant weight. The shoot dry weight (DW) yields were determined (including stem, leaves and flower heads). Flower heads were separated and shoots ground in an universal cutting mill (<1.0 mm particle size, Fritsch Pulverisette 19). Weighed aliquots (0.5 g DW) were wet-digested under microwaves (CEM Marsxpress 1200 W) with 5 mL suprapure 14 M HNO_3 and 2 mL 30% (v/v) H_2O_2 not stabilized by phosphates and 1 mL MilliQ water. Certified reference material (BIPEA maize V463) and blank reagents were included in all series. Mineral composition (As, Ca, Cu, Cr, Fe, K, Mg, Mn, Na, Ni, P, and Zn) in digests was determined by ICP-MS (Thermo X series 200, INRA USRAVE laboratory, Villenave d'Ornon, France). All elements were recovered (>95%) according to the standard values and standard deviation for replicates was <5%. All element concentrations in plant parts are expressed in mg or g DW kg^{-1}. The shoot Cu removal was calculated as follows: Cu (µg plant^{-1}) = shoot DW yield (g plant^{-1}) x shoot Cu concentration (µg g^{-1}), assuming similar Cu concentration in shoots and flower heads as reported by Kolbas (2012).

Statistical Analyses

Influence of soil treatments in the B3 and B4 plots on shoot DW yields, shoot ionome and Cu removal of sunflower plants were tested using one-way analyses of variance (ANOVA). When significant differences occurred between treatments, multiple comparisons of mean values were made using *post-hoc* Tukey HSD tests. When assumptions were not met, Wilcoxon pairwise tests adjusted with a Bonferroni correction were used (i.e., shoot Mg concentration). Differences between OMDL and OM2DL, in the B1 and B2 plots for these same plant parameters were tested

TABLE 1 | Soil treatments.

Soil treatments	Block: plots	Set-up	Amendments	References
Unt	B4: #31	March 2008	None (untreated)	Kolbas et al., 2011 Kumpiene et al., 2011 Quintela-Sabarís et al., 2017
OMDL	B1: #2 to 5 B2: #12 to 15 B3: #22 to 25	March 2008	Single dressing of a compost of pine bark chips and poultry manure (OM, 5% w/w) and dolomitic limestone (DL, 0.2% w/w),	Kolbas et al., 2011 Kumpiene et al., 2011 Quintela-Sabarís et al., 2017
OM2DL	B1: #6 to 9 B2: #16 to 19 B3: #26 to 29	March 2008	2008: one dressing of compost and dolomitic limestone as for OMDL; 2013: one dressing of green waste compost (GW, 5% w/w)	Jones et al., 2016 Oustriere et al., 2016
GW	B4: #GW	March 2013	One dressing of green waste compost (GW, 5% w/w)	Jones et al., 2016 Oustriere et al., 2016
CAR	B4: #CAR	March 2011	One single dressing of Carmeuse basic slag (1% w/w)	Le Forestier et al., 2017
PLD	B4: #PLD	March 2011	One single dressing of P-spiked Linz-Donawitz basic slag (1% w/w)	Negim et al., 2012; Le Forestier et al., 2017

using a Student test (T-test). Normality and homoscedasticity of residuals were met for all tests. Differences were considered statistically significant at $p < 0.05$. Changes in shoot Cu concentration, Cu removal and shoot DW yield of sunflower plants depending on soil treatments (i.e., OMDL and OM2DL), total topsoil Cu and their interaction were analyzed using an ANCOVA for the B1, B2, and B3 plots. The mapping of total topsoil Cu and organic C was carried out using the surface trends analysis technic, with the Lattice and Akima packages of the R software (**Figure 1** and **Figure S1**). All statistical analyses were performed using R software (version 3.0.3, Foundation for Statistical computing, Vienna, Austria).

RESULTS

Soil Physico-Chemical Parameters (Topsoil, 0–11 cm, Table 3)

Total topsoil Cu (mg Cu kg^{-1}) in year 10 varied from 237 (B1: OM2DL) to 1169 (GW) and exceeded its pedogeochemical background and screening values (**Table 3**). Mapping of total soil Cu showed its higher values in the B3 and B4 plots (**Figure 1A**). Total topsoil Cu was similar for the OMDL and OM2DL treatments in the B1 and B3 plots. The corresponding mean values for the B2 block differed, however, being significantly higher in the OMDL plots than in the OM2DL ones. For total topsoil As, Cd, Cr, Co, Ni, Pb, and Zn, values were generally at the background levels (**Table 3**). Total topsoil Zn increased in compost-amended plots, notably in the OM2DL and GW ones, as compared to the untreated and basic slag-amended soils. As expected, total topsoil Fe, Mn, and in a lesser extent Cr were enhanced in the basic slag-amended plots. Across all plots, extractable topsoil Cu ranged from 0.71 (B1:OMDL) to 17.9 (Unt) mg Cu kg^{-1} soil (mean values varied between 0.89 and 17.9, **Table 3**; **Figure 1B**). The values were normalized based on total topsoil Cu, and the ratio (R_L) varied between 0.24 (B1:OMDL) and 2.35 (Unt) (**Figure 2A**). This ratio was significantly (p-value $1.63e^{-07***}$) lower in the OMDL soils, i.e., 0.31 ± 0.10 and 0.32 ± 0.07, than in the OM2DL soils, i.e., 0.8 ± 0.08 and 0.65 ± 0.05, for the B1 and B2 plots, respectively. This indicated a higher NH_4NO_3-extractable Cu fraction in the OM2DL topsoils of these plots. In contrast, the extractable vs. total soil Cu ratio was similar in the OMDL and OM2DL soils for the B3 plots. In this last one, this ratio ranked in decreasing order: Unt (2.35) > CAR (1.02), PLD (0.83) > GW (0.58), OMDL (0.44 ± 0.09), OM2DL (0.37 ± 0.10), indicating a lower Cu extractability in the compost-amended plots. Considering all OM2DL plots, the extractable soil Cu fraction decreased as total topsoil Cu rose, and fitted well a quadratic function (**Figure 2B**). For the OMDL plots, this Cu fraction matched less with a quadratic function, with an opposite trend as total topsoil Cu decreased.

The UNT topsoil pH was slightly acidic (6.3) and rose in all amended soils from 7.0 (OMDL in B1 and B2) to 7.7 (PLD and CAR in B4) (**Table 3**). The topsoil CEC increased in all amended soils in the 4–15.5 $cmol^{+}$ kg^{-1} range as compared to the UNT soil (3.1 $cmol^{+}$ kg^{-1}), and notably peaked in all plots amended with the green waste compost in year 6. For comparison, its value was 16 $cmol^{+}$ kg^{-1} for an uncontaminated soil of the same soil series (**Table 3**). The soil moisture, and total soil organic N and C were higher in the compost-amended soils than in the UNT and basic slag-amended soils. The soil organic matter (SOM) peaked in the topsoils amended with the green waste in year 6, but the C/N ratio (in the 14–15 range) was similar in all plots and matched with its value for the uncontaminated soil, slightly exceeding that reported for French sandy soils (10). Soil available P (Olsen method) ranged (mg kg^{-1}) from 73 (UNT) to 96 (B2:OM2DL), being higher in all soils amended with the green waste, albeit differences were significant between OMDL and OM2DL treatments in the B1 and B2 plots. Soil $CaCO_3$ concentration was low, in relation with neutral pH, and ranged (g kg^{-1}) from ≤1 (UNT and PLD in B4) to 4 (GW). Total topsoil K, Mg, Na and P were similar in all plots, ranging from 7 to 8 g K kg^{-1}, 0.8 to 1 g Mg kg^{-1}, 1.9 to 2.1 g Na kg^{-1}, and 0.7 to 1 g P kg^{-1}, respectively. Total soil Fe and Mn increased in the PLD- and CAR-amended soils as compared to the UNT soil. Total soil Ca (g kg^{-1}) was higher in all amended soils than in the UNT soil (0.9), raising from 1.3 (B1:OMDL) to 6.1 (GW).

TABLE 2 | Composition and main physico-chemical properties of soil amendments.

	OM	GW	DL	CAR	PLD
pH	6.94 ± 0.08	7.53	–	12.7	11.6
EC (µS cm^{-1})	–	–	–	10,700	2,100
SiO_2 (g kg^{-1})	–	–	–	111	146
Al_2O_3 (g kg^{-1})	–	–	–	14	56
Fe_2O_3 (g kg^{-1})	–	–	–	366	214
TiO_2 (g kg^{-1})					10.9
CaO (g kg^{-1})	47.1	–	300	448	307
MgO (g kg^{-1})	4.7	–	200	64	95
K_2O (g kg^{-1})	10.9	–	–	–	–
Na_2O (g kg^{-1})	1.4	–	–	2	–
MnO (g kg^{-1})	–	–	–	42	25
P_2O_5 (g kg^{-1})	17.7	–	–	12	140
SO_3 (g kg^{-1})	4.9	–	–	–	–
CEC (cmol kg^{-1})	–	26.7	–	–	–
Major elements					
Total *N* (% DW)	–	0.69	–	–	–
Organic C (g kg^{-1})	321	109	–	–	–
C/N	19.4	15.8	–	–	–
Nutrients (g kg^{-1})					
Ca	–	22.5	–	–	–
K	–	5.4	–	–	–
Mg	–	1.9	–	–	–
Na	–	–	–	–	–
P	–	0.374	–	–	–
Trace elements (mg kg^{-1})					
Al	–	12,700	–	–	
As	0.8	4.47	–	–	<5
Cd	0.5	<0.5	–	–	–
Cr	<0.5	21	–	–	–
Cu	32.1	85.8	–	139	<5
Mn	–	–	–	–	11,300
Fe	–	6,830	–	–	–
Hg	0.2	<0.1	–	–	–
Ni	1.8	7.98	–	–	<10
Pb	9	51.5	–	–	<20
Zn	131	174	–	–	24

OM, compost of poultry manure and pine bark chips; GW, compost of green wastes; DL, dolomitic limestone; CAR, Carmeuse basic slag; PLD, P-spiked Linz-Donawitz slag.

Shoot DW Yield of Sunflower Plants (Table 4)

In year 9, sunflower plants did not display visible phytotoxicity symptoms on their shoots for all plots. Survival rate was roughly 100% in all compost-amended plots. In the UNT and basic slag-amended plots, with high Cu exposure, plants had a lower maximum stem length, more brittle, leading to lower shoot DW yield (**Table 4**). At high total soil Cu (B3 and B4 plots), the shoot DW yield in year 9 was significantly higher for plants grown in all compost and dolomitic limestone-amended soils than in the UNT soil and peaked for the OM2DL plants. In contrast no significant difference occurred between plants from the basic slag- and GW-amended plots and the UNT plot. At intermediate soil Cu contamination (B1 and B2 plots), the shoot DW yields of OMDL and OM2DL plants did not differ (g DW plant^{-1}: 48 ± 20 and 43 ± 16 in B1 and 45 ± 17 and 51 ± 22 in B2, respectively). These values were similar to those for the B3:OM2DL plants, but higher than for the B3:OMDL ones. Based on ANCOVA analyses, the shoot DW yield decreased in the OMDL plots as total and extractable soil Cu increased whereas it remained steady in the OM2DL plots (**Figure 3**; **Table S2**; **Figure S2**), underlining the slight benefit to repeat the compost addition in year 6.

Shoot Ionome and Shoot Cu Removal of Sunflower Plants (Table 4)

The shoot Cu concentration decreased significantly for all plants from the amended plots as compared to the UNT one (i.e., 48 ± 10 mg Cu kg^{-1}). In the amended soils, it varied between 10 ± 2 (B1 and B2:OM2DL) and 31 ± 4 (PLD) mg Cu kg^{-1}, this upper value slightly exceeding common values for sunflower. In the B1 and B2 plots, shoot Cu concentration was higher in the OMDL plants than in the OM2DL ones, despite a higher extractable Cu fraction in the OM2DL soils (**Tables 3**, **4**; **Figure 4**). Shoot Cu concentration increased more in the OMDL shoots than in OM2DL ones with total soil Cu, and significantly differed between both treatments at high total soil Cu (B3 plots) (**Table 4**; **Figure S3**). Shoot Cu concentration also increased with extractable soil Cu for both OMDL and OM2DL plants and, on the whole extractable Cu range, Cu concentration was higher in the OMDL shoots than in the OM2DL ones (**Figure 4**). Based on ANCOVA analysis, shoot Cu concentration in OMDL sunflower plants can exceed the upper critical threshold value (20 mg Cu kg^{-1} DW) at NH_4NO_3-extractable soil Cu over 2.7 mg Cu kg^{-1} soil (**Figure 4**, **Table S2**).

Shoot Cu removal (g Cu ha^{-1}) increased significantly for plants grown in amended soils from 42 ± 26 (PLD) to 88 ± 55 (B3:OM2DL) as compared to the UNT plants (19 ± 8), except for the GW and CAR plants (respectively, 26 ± 14 and 39 ± 25). Shoot Cu removal significantly differed between OMDL and OM2DL plants in the B1 and B2 plots but this difference was bridged as total and extractable soil Cu increased (**Table 4**, **Table S2**; **Figure 5** and **Figure S4**). Compared to the extractable topsoil Cu, annual shoot Cu removal corresponded respectively for the OMDL and OM2DL treatments to 9 ± 3.9% and 2.8 ± 1.4% in the B1 plots, 5.4 ± 3.4% and 3.0 ± 1.5% in the B2 plots, and 2.6 ± 1% and 2.8 ± 1.7% in the B3 plots.

Shoot Ca, K, and P concentrations were significantly higher for plants grown in all amended soils than for the UNT plants, whereas the shoot Zn and Mg concentrations only significantly increased for plants grown in compost-amended soils (**Table 4**). Changes in NH_4NO_3-extractable soil Zn from 0.023 to 1.2 mg kg^{-1} did not induce clear changes in shoot Zn concentration, which varied between 41 and 89 mg kg^{-1} under the influences of soil pH and total soil Zn and Cu. Shoot Mn concentration was significantly higher for the OMDL plants than for the UNT ones. In contrast, the shoot Fe concentration (mg Fe kg^{-1} DW) decreased for all amended soils from 239 ± 63 (UNT) to the 64 ± 22 (B3:OM2DL) −109 ± 25 (B1:OMDL) range as the shoot DW yield rose (exponential relationship, R^2: 0.51). For the B1 and B2 plots, shoot Ca, P, and Na concentrations did not differ between the OMDL and OM2DL plants. Shoot Fe and Mn concentrations

TABLE 3 | Main soil properties and physico-chemical parameters in the 0–10 cm soil layer.

Treatments	Block 3 and 4						Block 2		Block 1		Year 1[c]	Background levels		
	UNT	GW	OMDL	OM2DL	PLD	CAR	OMDL	OM2DL	OMDL	OM2DL		French sandy soils[a]	Control soil (same soil series)[b]	French agricultural soils[a]
pH KCl	5.5	7.1	6.5 ± 0.3	6.6 ± 0.3	7.1	7.2	6.4 ± 0.1	6.6 ± 0.1	6.4 ± 0.1	6.8 ± 0.1			7–8	
pH water	6.3	7.5	7.4 ± 0.2	7.1 ± 0.2	7.7	7.7	7.0 ± 0.1	7.1 ± 0.1	7.0 ± 0.03	7.2 ± 0.1	5.9 – 7.4			
Moisture (g kg^{-1})	3.8	12	13 ± 7	17 ± 8.1	3.9	4.1	7.3 ± 0.3	8.4 ± 0.5	6.6 ± 0.9	10 ± 0.6				
CEC (cmol$^+$ kg^{-1})	3.1	15.5	7.0 ± 3.3b	11 ± 2.3a	4.5	5.1	6.4 ± 0.2b	11 ± 0.5a	6.0 ± 1.1b	10 ± 1.1a	3.5		16.1	
P-Olsen (mg kg^{-1})	73	89	78 ± 10ab	85 ± 4.9a	82	79	72 ± 6b	96 ± 10a	75 ± 4b	92 ± 7a				
$CaCO_3$ (g kg^{-1})	<1	4.0	1.5 ± 0.7	1.7 ± 0.6	<1	1.0	1 ± 0.0	1.5 ± 0.6	1 ± 0.0	2.5 ± 0.6				
OM (g kg^{-1})	17	72	33 ± 14ab	43 ± 12.5a	17	16	25 ± 1.2b	42 ± 3a	24 ± 2.9b	40 ± 2a	16		69.9	
Organic C (g kg^{-1})	10	2	19 ± 8ab	25 ± 7.2a	10	9	15 ± 0.7b	24 ± 1.5a	14 ± 1.7b	23 ± 1.2a		14.5	40.4	
Total N (g kg^{-1})	0.7	2.9	1.4 ± 0.6ab	1.8 ± 0.5a	0.7	0.7	1.1 ± 0.02b	1.7 ± 0.1a	1.0 ± 0.1b	1.6 ± 0.1a			2.94	
C/N	14	15	14 ± 0.3	14 ± 0.1	15	14	14 ± 0.4	14 ± 0.5	14 ± 0.4	14 ± 0.3	17.2	10.0	13.8	
Texture (g kg^{-1})														
Sand	837	821	844 ± 13	839 ± 14	832	846	838 ± 3	833 ± 5	836 ± 5	829 ± 5		≥650	665	
Silt	109	107	96 ± 8	96 ± 7	107	97	99 ± 2	97 ± 3	101 ± 3	101 ± 5		≤350	155	
Clay	54	72	60 ± 6	66 ± 8	1	57	63 ± 0.8	70 ± 4	64 ± 4	70 ± 3		≤180	180	
Elements (mg kg^{-1})														
As	6.2	5.4	4.6 ± 0.5	3.8 ± 0.2	5.6	5.7	5.2 ± 0.3	5.0 ± 0.7	5.1 ± 0.2	4.5 ± 0.7		1–25	3.6	
Cd	0.12													
Cu	**760**	**1169**	**842 ± 69c**	**807 ± 81c**	**794**	**796**	**514 ± 48b**	**316 ± 52a**	**307 ± 60a**	**237 ± 41a**	163–1,170	3.2–8.4	21.5	7.1–28
Cr	14	16	11 ± 1.4	11 ± 1.5	19	22	12 ± 1	14 ± 2	13 ± 0.7	13 ± 1.5		14–40	17.9	16.7–69.4
Co	1.73	1.94	1.75 ± 0.11	1.77 ± 0.17	1.64	1.66	1.73 ± 0.05	1.89 ± 0.07	1.81 ± 0.01	1.82 ± 0.03				
Mn	173	179	171 ± 12	173 ± 9	359	412	191 ± 6	191 ± 4	184 ± 3.3	192 ± 6		72–376	189	
Pb	27													
Ni	5.0	6.3	5.3 ± 0.4	5.5 ± 0.9	4.9	4.7	5.0 ± 0.2	5.7 ± 0.2	5.1 ± 0.2	6.8 ± 2.6		4.2–14.5	7.46	9.1–41.8
Zn	29	**93**	45 ± 18ab	**59 ± 18ab**	30	31	43 ± 9b	**58 ± 5a**	**53 ± 12ab**	**68 ± 2a**	35–98	17–48	50.9	31.1–102
Extractable Cu[d]	17.9	6.78	3.40 ± 0.88a	3.53 ± 0.68a	6.65	8.17	1.54 ± 0.21*b*	2.02 ± 0.27*b*	0.89 ± 0.16*c*	1.90 ± 0.32b				
Nutrients (g kg^{-1})														
Ca	0.9	6.1	2.3 ± 1.7ab	3.4 ± 1.4a	1.9	1.9	1.6 ± 0.1*b*	3.3 ± 0.2a	1.3 ± 0.2*b*	3.3 ± 0.4a			1.04 ± 0.05	
Fe	6.6	6.5	6.4 ± 0.3	6.3 ± 0.2	7.8	7.7	6.5 ± 0.3	6.4 ± 0.1	6.3 ± 0.02	6.4 ± 0.1		6–14.3	6.55	
K	7.9	7.0	7.6 ± 0.3	7.4 ± 0.2	7.6	7.8	7.8 ± 0.1	7.5 ± 0.2	8.0 ± 0.03	7.4 ± 0.1			1.9 ± 0.2	
Mg	0.8	0.9	0.9 ± 0.1	0.9 ± 0.03	1.0	1.0	0.9 ± 0.03	0.9 ± 0.03	0.8 ± 0.02	0.8 ± 0.05			0.012 ± 0.01	
Na	2.0	1.9	1.9 ± 0.05	2.0 ± 0.09	1.9	2.0	2.1 ± 0.03	1.9 ± 0.09	2.1 ± 0.03	2.0 ± 0.05				
P	0.8	1.1	0.9 ± 0.04	0.9 ± 0.1	1.0	0.8	1.0 ± 0.06	0.7 ± 0.4	0.9 ± 0.04	0.9 ± 0.1				

Mean values ± standard deviation (n = 1 for UNT, CAR, GW, and PLD; n = 4 for OMDL and OM2DL in each block); mean values followed by the same letter did not differ; no letter in a row indicates no significant difference. <1 = below detection limit. Numbers in bold exceed background values in French sandy soils. OM, organic matter.

[a] *Frequent values in French sandy topsoils (Baize, 2009; Mench and Bes, 2009; Saby et al., 2009).*

[b] *Uncontaminated soil Eutric gleysol from a kitchen garden nearby (12 km) the site, Gironde, France.*

[c] *Kolbas et al. (2011).*

[d] *1M NH_4NO_3-extractable soil Cu.*

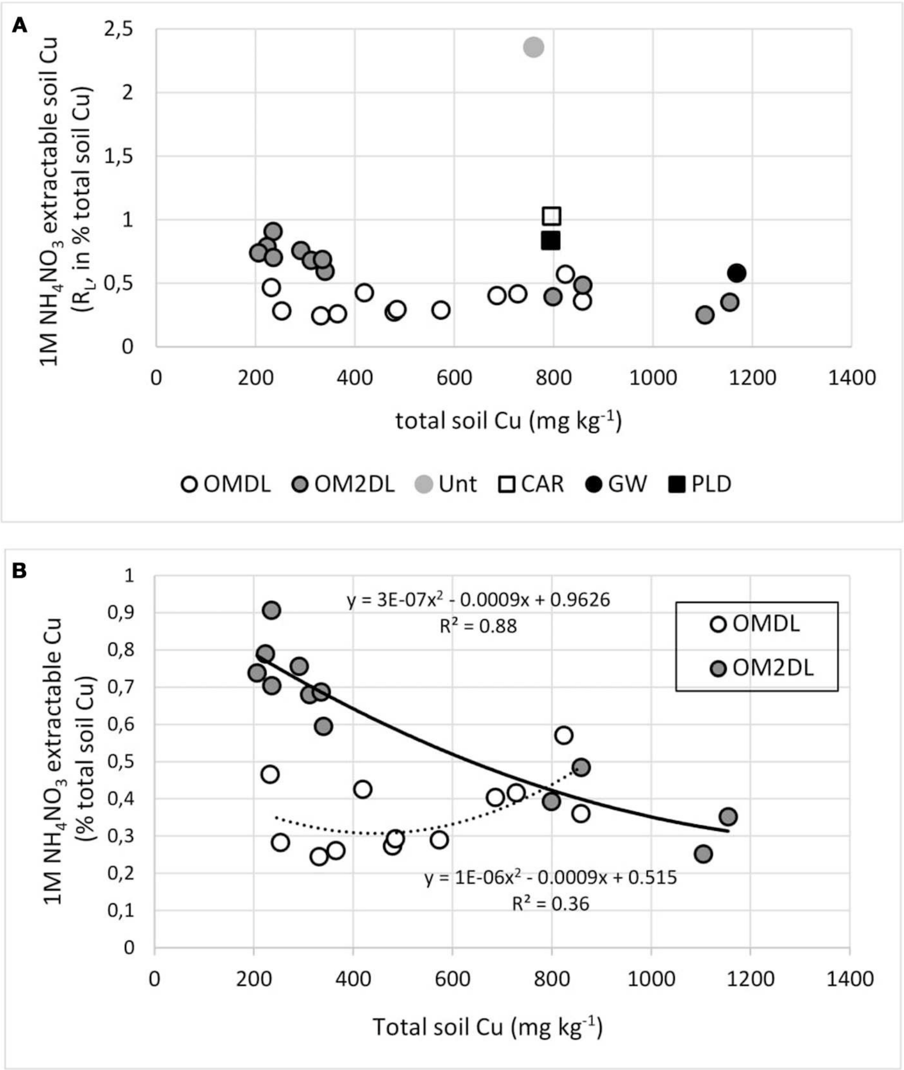

FIGURE 2 | (A) 1M NH_4NO_3-extractable soil Cu (expressed in % of total soil Cu, R_L) depending on total soil Cu in the topsoil (0–0.11 m) and soil treatments; **(B)** modeling for the OMDL and OM2DL topsoils.

in the B1 plots and shoot Mg concentration in the B2 plots peaked for the OMDL plants, whereas shoot K and Zn concentrations were higher for the B2:OM2DL plants.

In all plots, shoot Ca and Mg concentrations were similar to common values for sunflowers (respectively 19–24 and 3–6.5 mg kg^{-1}), but with a lowest value for the UNT plants. For all amended plots, shoot Fe, Mn, and Zn concentrations were slightly higher than common values for sunflowers but remained in the common ranges for aboveground plant parts. Shoot P and K concentrations were lower than their common values for sunflowers.

DISCUSSION

Compared to year 1 (Kolbas et al., 2011), mean values of total topsoil Cu in year 10 (**Table 1**) slightly decreased in the B1 and B3 plots (i.e., by 7–21 and 13%, respectively) but these decreases were not significant as well as in the B2 plots (**Figure S5**). The potential cumulative effects of annual shoot Cu removal and Cu leaching for decreasing total topsoil Cu were not statistically evidenced in year 10. Total topsoil Cu still exceeded the pedogeochemical Cu background and screening values, notably for French sandy soil (**Table 3**; Saby et al., 2009). Spatial variability of total topsoil Cu, such as the "hot spot" at the edge of the GW plot, was mainly attributed to variability in cumulative wood washings resulting from long-term storage of preserved wood. Based on its composition (**Table 2**; Oustriere et al., 2016) and addition rate, Cu inputs by the green waste compost was negligible (4.3 mg Cu kg^{-1} soil, 1.9 g Cu $plot^{-1}$) regarding total topsoil Cu (0.4%). The ratio of total topsoil Cu vs. total subsoil Cu was in the 0.99–1.09 range for all plots, except for the B3:OM2DL plots where its value decreased to 0.82. This raises

TABLE 4 | Shoot DW yield, ionome, and Cu removal of sunflowers.

	Shoot DW yield	Copper			Shoot nutrient concentrations							
		Shoot Cu concentration	Shoot Cu removal		Ca	Mg	K	P	Fe	Mn	Na	Zn
	g plant^{-1}	mg kg^{-1}	mg plant^{-1}	g ha^{-1}	g kg^{-1}				mg kg^{-1}			
Block 3 and 4 (Total Soil Cu: 719–1,169 mg Cu kg^{-1})												
UNT	4 ± 1c	48 ± 10a	0.2 ± 0.1c	19 ± 8c	13 ± 2c	2.5 ± 0.2c	4.4 ± 0.9c	0.8 ± 0.1b	239 ± 63a	41 ± 11bc	155 ± 24c	44 ± 5b
GW	10 ± 4c	24 ± 7**b**	0.3 ± 0.1bc	26 ± 14bc	23 ± 3**b**	3.8 ± 0.6bc	14.7 ± 3.8**a**	1.7 ± 0.4**a**	89 ± 26**bc**	38 ± 6bc	252 ± 15**a**	80 ± 9**a**
OMDL	30 ± 10**b**	26 ± 5**b**	0.7 ± 0.2**a**	77 ± 23**a**	21 ± 2**b**	5.5 ± 0.8**a**	11.4 ± 3.4b	1.7 ± 0.7**a**	91 ± 21b	37 ± 6c	159 ± 35c	70 ± 13**a**
OM2DL	50 ± 21**a**	16 ± 5c	0.8 ± 0.5**a**	88 ± 55**a**	21 ± 3b	5.2 ± 1.5**ab**	10.8 ± 2.4b	1.6 ± 0.7**a**	64 ± 22c	45 ± 14bc	178 ± 33c	82 ± 16**a**
PLD	14 ± 10c	31 ± 4b	0.4 ± 0.2**ab**	42 ± 26**ab**	29 ± 2**a**	3.6 ± 0.2abc	12.4 ± 0.8**ab**	1.7 ± 0.4**a**	99 ± 17b	64 ± 3**a**	180 ± 4bc	41 ± 1b
CAR	14 ± 9c	27 ± 2b	0.4 ± 0.2bc	39 ± 25bc	23 ± 3b	2.6 ± 0.4c	13.3 ± 1.4**ab**	1.7 ± 0.4**a**	93 ± 30b	51 ± 11b	223 ± 57**ab**	43 ± 7b
Block 2 (Total Soil Cu: 257–556 mg Cu kg^{-1})												
OMDL	45 ± 17a	15 ± 6**a**	0.7 ± 0.4**a**	73 ± 42**a**	19 ± 3a	4.9 ± 0.9**a**	7.4 ± 2.3**a**	1.5 ± 0.5a	88 ± 30a	72 ± 24a	164 ± 46a	67 ± 13a
OM2DL	51 ± 22a	10 ± 2b	0.5 ± 0.3b	56 ± 29b	20 ± 3a	3.8 ± 1.1b	13.7 ± 3.9b	1.5 ± 0.6a	73 ± 20a	67 ± 26a	178 ± 38a	78 ± 17b
Block 1 (Total Soil Cu: 198–381 mg Cu kg^{-1})												
OMDL	48 ± 20a	14 ± 4**a**	0.7 ± 0.3**a**	70 ± 31**a**	21 ± 4a	4.2 ± 0.8a	12.5 ± 3.3a	1.7 ± 0.5a	109 ± 25**a**	59 ± 17**a**	190 ± 25a	89 ± 21a
OM2DL	43 ± 16a	10 ± 2b	0.5 ± 0.2b	47 ± 20b	19 ± 3a	4.5 ± 0.8a	11.1 ± 3.6a	1.9 ± 0.4a	72 ± 16b	47 ± 11b	196 ± 44a	80 ± 16a
Common values for sunflower (non-contaminated soils)												
(Kolbas et al., 2014)[a]	–	6	–	–	19.68	3.43	37.84	3	48	22	–	24
Unpublished data	–	10	–	–	24.2	6.5	29.5	4.3	57	37	–	38
(Blum et al., 2012)[b]	–	3–12	–	–	–	–	–	–	50–200	20–400	–	20–100
(De Maria and Rivelli, 2013)[c]	60–64	10 ± 0.5	–	–	–	–	–	–	–	–	–	23 ± 2

Mean value ± SD for each treatment (n = 5 for UNT, CAR, and GW; n = 2 for PLD; n = 20 for OMDL and OM2DL in each block). Block 3 and 4: values with different letters in a column differ significantly (one way ANOVA. p-value <0.05); Mean values followed by letters in bold are significantly higher or lower as compared to the UNT plants. Block 1 and 2: values with different letters in a column differ significantly (t-test, p-value <0.05).

[a] *Values from sunflowers grown in an uncontaminated soil.*

[b] *Common values in aboveground plant parts.*

[c] *Shoot DW yield and foliar Cu and Zn concentrations of sunflowers grown in an uncontaminated soil.*

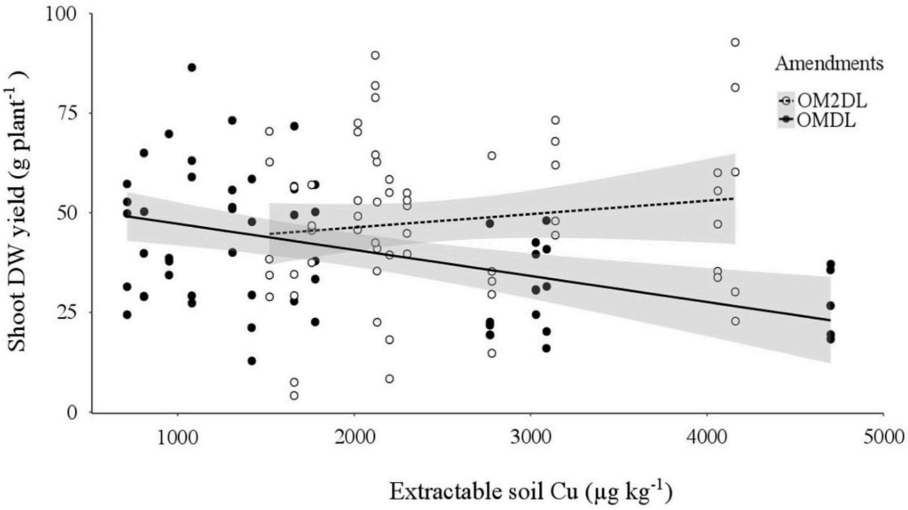

FIGURE 3 | ANCOVA analysis for shoot DW yield (g DW plant^{-1}) of sunflower plants depending on 1M NH_4NO_3-extractable soil Cu (mg Cu kg^{-1}) and soil treatments: OMDL (• and black lines) and OM2DL (○ and dotted lines) (*n* = 20 plants).

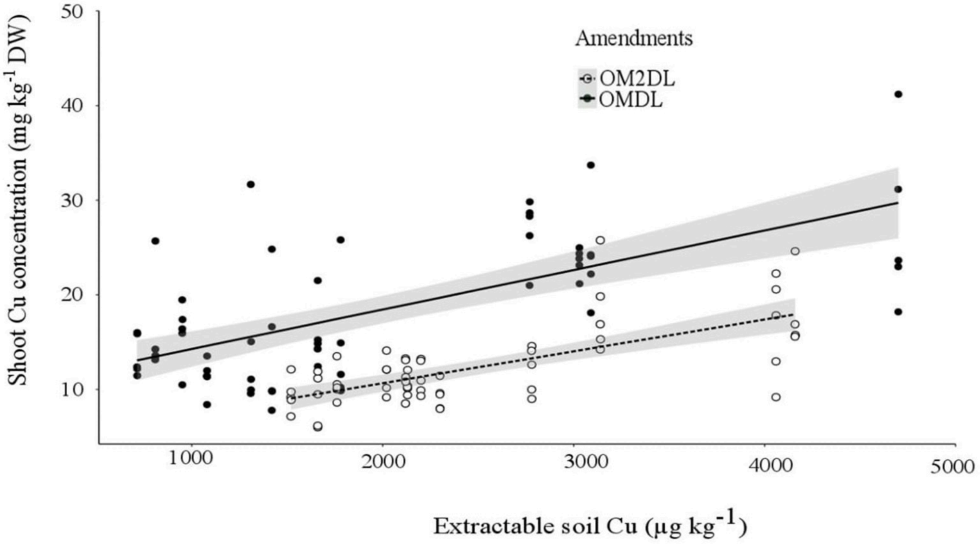

FIGURE 4 | ANCOVA analysis for shoot Cu concentration (mg kg^{-1}) of sunflower plants depending on 1M NH_4NO_3-extractable soil Cu (mg Cu kg^{-1}) and soil treatments: OMDL (• and black lines) and OM2DL (○ and dotted lines) (*n*=20 plants).

a question concerning a possible downward Cu migration with the organic matter, whose content was higher in the B3:OM2DL subsoils (**Table S1**). This may mark the green waste inputs in year 6 as total subsoil Zn was higher in all OM2DL and GW plots than in the OMDL plots (**Table S1**).

Total topsoil concentrations of other assessed metal(loid)s did not exceed their background levels (**Table 3**). Total topsoil Zn in year 10 was higher in all compost-amended plots as compared to the Unt and basic slag-amended plots, in line with the compost composition (**Table 2**), e.g., Zn inputs by the green waste compost in year 6 corresponding to 9% of total topsoil Zn. This was mirrored by increased shoot Zn concentration in plants from all compost-amended plots (**Table 4**), and notably in the B3 plots in contrast with plants from the Unt, CAR and PLD plots, likely also due to better root development and less Zn/Cu antagonism. Nevertheless, in year 1, total topsoil Zn already varied in the 35.2–98.4 mg Cu kg^{-1} range (Kolbas et al., 2011).

The NH_4NO_3-extractable Cu fraction for years 4, 6, and 10 did not vary in the B3:Unt plot, remaining in the 15–24 mg Cu kg^{-1} soil (**Figure S6**). This fraction was already lower in the B3:OMDL plots in year 4 and remained significantly lower in years 6 and 10 for both the B3:OMDL and OM2DL plots, with no influence of the number of compost dressing. For the B1 and B2 plots, the higher extractable Cu fraction in the OM2DL plots

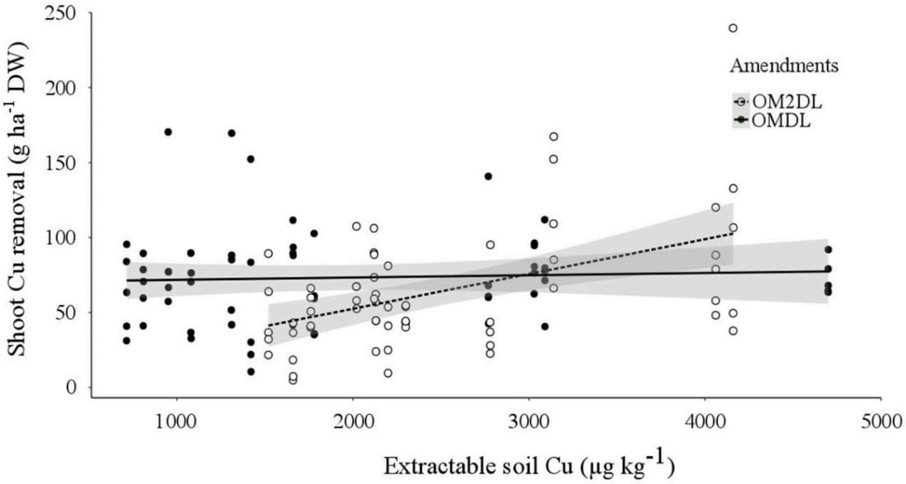

FIGURE 5 | ANCOVA analysis for shoot Cu removal (mg kg^{-1}) of sunflower plants depending on 1M NH_4NO_3-extractable soil Cu (mg Cu kg^{-1}) and soil treatments: OMDL (• and black lines) and OM2DL (○ and dotted lines) (*n*=20 plants).

than in the OMDL ones may be related to the dissolved organic matter (DOM) derived from the second compost dressing and the buffer effect of a higher total soil organic C (**Table 3**), whereas soil pH increase was similar in compost-amended soils, in line with compost pH and application of dolomitic limestone in year 1 (**Table 2**). In the B1 and B2 plots, the extractable vs. total soil Cu ratio was merely driven by the SOM. This might promote downward Cu migration in the OM2DL plots. Higher spatial variability in SOM and higher total soil Cu led to similar extractable Cu fractions in both OMDL and OM2DL topsoils of B3 plots. Increase in the SOM influenced less the extractable vs. total topsoil Cu ratio in the B3 plots (**Table S1**; **Figure 2** and **Figure S6**). Strong complexation of Cu with SOM and DOM is widely claimed (Ruttens et al., 2006; Kumpiene et al., 2008; Beesley et al., 2010; 2011; Karami et al., 2011; Park et al., 2011).

NH_4NO_3-extractable topsoil Cu in total data set (without accounting for soil treatments) was weakly correlated to total topsoil Cu ($R^2 = 0.5$, **Figure 2B**). Based on Hattab-Hambli et al. (2016), total dissolved Cu concentrations (µg L^{-1}) in the soil pore water of these contaminated soils increased with total soil Cu and available Cu concentration was generally low as compared to total soil Cu, i.e., <0.01% in year 3 and <0.007% in year 4. Accounting for spatial variability of total topsoil Cu, for the B1 and B2 plots, NH_4NO_3-extractable Cu was positively correlated to a cluster of soil parameters related to the SOM, i.e., total soil organic C, N, and Ca, clay content, soil CEC and pH, and available P (**Figure S7**); in contrast, at high total topsoil Cu (B3 and B4 plots), it was negatively correlated to total soil organic C, N, and Ca, clay content and available-P and positively to total soil Mn, Fe, and soil pH, showing the buffer effect of the SOM and the influence of basic slags (Le Forestier et al., 2017). In overall, this confirmed SOM, soil pH, and Fe/Mn oxyhydroxides as key players on Cu availability (Kumpiene et al., 2008, 2011; Bolan et al., 2014). The second compost dressing has improved other soil parameters that may enhance plant production, i.e., SOM, total organic N, available P, and soil CEC (**Table 3** and **Table S1**). Compost incorporation into the soil can enhance Cu sorption, microbial biomass, OM cycle, soil CEC, and water holding capacity (Clemente et al., 2005; Chiu et al., 2006; Asensio et al., 2013; Touceda-González et al., 2017).

Regarding C sequestration in the context of climate change, increases in total topsoil organic C varied from 40% (B1:OMDL) up to 150% (B3:OM2DL), respectively 10 and 5 years after the last compost dressing. To repeat compost dressing was beneficial as mentioned in Kidd et al. (2015). Based on soil organic C in years 1 and 10, compost composition and inputs (**Tables 2**, **3**, Kolbas et al., 2011), the apparent remaining rate of C inputs (including the contribution of annual root residues for all plots and winter crops for the OM2DL treatment) was 22% for the OMDL treatment and 55% for the OM2DL one, agreeing with the number of compost dressing. Increase in SOM had a positive effect on soil humidity (+28 to +132%, **Table 3**) and likely the soil structure, which was visually ameliorated in all OM2DL plots. The water holding capacity was positively correlated with the cluster of soil parameters related to SOM (i.e., soil CEC, total soil organic C, and N, etc.) and clay content (**Figure S7**). This is beneficial to face the more frequent heat waves and drought in Aquitaine, France, to promote the soil microbial community, sorption of exchangeable cations (notably in these sandy soils), and to limit soil erosion (Roy et al., 2016). According to Chenu et al. (2000), SOM increase from 1.7 to 4.3% (**Table 3**) would enhance the structural stability from instable to stable. Thus the combination of compost incorporation into the topsoil, winter cropping with clover and crop rotation with sunflower and tobacco can ameliorate the quality of these Cu-contaminated soils and potentially the crop production. Necrosis and chlorosis on leaves and reduced shoot DW yields reported for the B3:OMDL sunflower plants in year 1 (Kolbas et al., 2011) did not occur in year 9.

Basic slags are alkaline by-products of steel mills consisting of Ca, Al, Fe, Mn, and other metal oxides, which are used for soil liming, P fertilization and *in situ* metal immobilization (Mench et al., 1994; Bert et al., 2012; Negim et al., 2012; Le Forestier et al., 2017). The UNT soil was slightly acidic, while the PLD- and CAR-amended soils had higher pH values (**Table 3**) due to the liming effect (Le Forestier et al., 2017). At neutral pH, Cu tends to precipitate with carbonates and hydroxides dissolved from slags rather than adsorbing on the slag surface (Kim et al., 2008). Liming would also increase Cu sorption on native soil compounds. Consequently, the ratio of extractable vs. total topsoil Cu (R_L) decreased by 56% for CAR and 64% for PLD, but less than in the compost-amended soils (**Figure 2A**). This 1% (w/w) addition rate of PLD and CAR slags in the same Cu-contaminated soils increased Cu concentration in the residual fraction, reduced free ionic Cu concentration in the soil pore water and labile Cu pool measured by diffuse gradient in thin film (DGT), and lowered the Cu bioavailability (Le Forestier et al., 2017). In outdoor lysimeters, Cu leaching was lower in the PLD soils than in the OMDL and Unt soils (Marchand et al., 2011). As expected soil CEC and extractable P-Olsen were slightly higher in the PLD and CAR soils than in the UNT soil (**Table 3**), agreeing with previous findings (Bert et al., 2012). Total topsoil K, Mg, Na, and P were similar in all plots (**Table 3**), so amendment influence on those nutrients was not detected, may be due to the annual mineral fertilization. Phosphates might be less phytoavailable due to liming and sorption by Ca, Fe, and Al oxides in basic slag-amended soils, but in fact extractable P (Olsen) remained at least steady in these plots and its values were similar to those for the compost-amended plots (**Table 3**).

Morphological parameters of sunflower depend on several ecological factors including Cu exposure (Kolbas et al., 2014). Mineral and organic amendments, e.g., compost, alkaline materials and phosphate minerals, alone and in combination, can increase plant yields, and reduce plant exposure to Cu and Zn in metal-contaminated soils (Brallier et al., 1996; Su and Wong, 2004; Bes and Mench, 2008; Beesley et al., 2010). The Ethic cultivar used here was selected based on its high oleic acid content and Cu tolerance (Mench et al., 2013). In year 1, the shoot DW yield was in the 0.2–6.6 t ha^{-1} range depending on plots and commercial cultivars, and 4.5 t ha^{-1} in an uncontaminated soil of the same soil series (Kolbas et al., 2011). Here, in year 9, it varied between 0.42 and 5.35 t ha^{-1}, and peaked in compost-amended plots, except the GW one (**Table 4**). This increase ranged from 7- to 12-fold as compared to the Unt plot. Shoot DW yield reached its common ranges for sunflower in both OMDL and OM2DL treatments, except for the B3:OMDL plots (**Table 4**). In addition to nutrient supply, composts improve many soil characteristics, including soil structure and water retention, which can promote crop yields (Andersson-Sköld et al., 2014; Huang et al., 2016; Wiszniewska et al., 2016; Sharma and Nagpal, 2018). Plants grown in the OMDL and OM2DL soils of the B1 and B2 plots were less exposed to Cu than those in the B3 and B4 plots, reflecting both a lower total soil Cu and long-term influence of compost and liming. This confirmed compost amendments improved sunflower growth (**Table 4**; **Figure 3**), mirroring previous findings in pot experiments (Beesley et al., 2010; Jones et al., 2016). Liming influenced positively yields of sunflower biomass in other studies (Barman et al., 2014; Hajduk et al., 2017).

Lower shoot DW yield of sunflower plants in the GW plot (**Table 4**) may be explained by (1) a higher total topsoil and subsoil Cu than in the OMDL and OM2DL plots (**Table 3** and **Table S1**) and (2) a higher SOM and soil CEC that may buffer and resupply Cu in the soil solution, whereas the extractable soil Cu was similar in these plots (**Figure 2A**). In the B3 and B4 plots, shoot DW yield was significantly higher for the OM2DL plants than for the OMDL ones, demonstrating the benefits to repeat compost dressing in year 6 and of the cultivation of white clover as winter crop (**Table 4**). Shoot DW yield of OM2DL plants remained steady as extractable soil Cu increased, whereas it decreased for OMDL plants, suggesting that a regular compost supply would be suitable to produce a high shoot DW yield at high total soil Cu (**Figure 3**). Similar findings were obtained with lettuce cultivated in potted soils sampled in the plots in year 6 (Quintela-Sabarís et al., 2017).

Shoot DW yields of CAR and PLD plants were similar to that of the UNT plants (**Table 4**). In potted soils collected in year 5, dwarf bean growth was higher in the CAR and PLD soils than in the UNT soil (Le Forestier et al., 2017) confirming other findings (Negim et al., 2012). However, Linz-Donawitz slag incorporation into contaminated soils can reduce the mobility and phytoavailability of Cd, Zn, and Pb without increasing the plant growth (Mench et al., 1994), and total subsoil organic C and N were lower in the CAR and PLD plots than in the compost-amended ones (**Table S1**). Roots in field plots can also colonize the unamended subsoil. Moreover, unlike field trials, potted soils were managed at an optimal soil humidity for the root development, avoiding water stress and making a difference. One additional option to optimize crop production would be to irrigate, although it is somewhat in contradiction with one phytomanagement objective, which is saving resources for a sustainable land management.

Upper critical threshold values of shoot Cu concentration for most plants are (mg Cu kg^{-1}) 15–30 (MacNicol and Beckett, 1985) and 25–40 (Chaney, 1989), while common values for sunflower shoots are in the 6–12 range (**Table 4**). Here, shoot Cu concentrations peaked for the UNT plants (48 ± 10 mg kg^{-1}) and exceeded these upper critical threshold values (**Table 4**) but remained far lower than values required to produce Cu-ecocatalysts (i.e., 1,000 mg kg^{-1}) (Clavé et al., 2016). To detoxify and sequester high metal (Cu) amounts, plants need to spend energy, leaving less resources for growth, reproduction, and other processes (Audet and Charest, 2008; Maestri et al., 2010; Printz et al., 2016). For the UNT sunflower plants, decrease in shoot DW yield would indicate an increase in plant maintenance cost, but also a less developed root system. Nutrient deficiencies (i.e., Ca, Fe, K, Mg, and P) cannot explain this decrease in shoot DW yield as their concentrations in sunflower shoots were within the common ranges (**Table 4**; **Figure S8**), although some differences between the soil amendments were observed. Root and shoot DW yields of 1 month-old sunflower plants grown in our soil series decreased by 10% as total soil Cu respectively reached 252 and 323 mg kg^{-1} (Kolbas et al., 2014), which already occurred in the B1 and B2 plots (**Table 3**). These values were even lower using the fading technique, i.e., 74 and 166 mg Cu kg^{-1} soil (Kolbas et al., 2018).

Shoot Cu concentration generally mirrors root Cu exposure, but it depends on plant species and cultivars (Poschenrieder et al., 2001). All tested amendments significantly reduced shoot Cu concentrations to the common range for sunflower or slightly above (i.e., mg Cu kg^{-1}) from 10 for the OM2DL plants in the B1 and B2 plots to 31 for the PLD plants (**Table 4**). In year 1, shoot Cu concentrations varied from 5 to 68 mg kg^{-1} for the OMDL plants (Kolbas et al., 2011). Lowest shoot Cu concentrations of the OM2DL plants could be related to (1) soil factors, e.g., low Cu availability, high soil CEC, and higher total N, Ca, organic matter and water contents in the OM2DL soils (**Figure 4**, **Table 3**), and (2) plant factors, i.e., Cu dilution into the shoot biomass as for Fe (**Table 4**) and high shoot K, Zn, and Mn concentrations helping likely to regulate ion cellular homeostasis (**Table 4**; **Figure S8**, Malachowska-Jutsz and Gnida, 2015; Printz et al., 2016). For lettuce in year 6, shoot Cu concentration was also lower in the OM2DL plants than in the OMDL and Unt ones (Quintela-Sabarís et al., 2017).

Shoot Cu removal in year 9 (26–88 g Cu ha^{-1}) was higher in all amended plots than in the UNT plot (19 ± 8 g Cu ha^{-1}) due to the lower shoot DW yield of UNT plants (**Table 4**). In year 1, shoot Cu removal varied from 20 to 116 g Cu ha^{-1} (Kolbas et al., 2011). Shoot Cu removal by sunflower in year 9 was similar for both basic slag-amended soils, i.e., PLD 42 ± 26 and CAR 39 ± 25 g Cu ha^{-1} (**Table 4**). In contrast, for dwarf beans cultivated in potted soils collected in year 5, the PLD plants had a shoot Cu removal twice higher than the CAR plants due to their higher leaf biomass (Le Forestier et al., 2017). At high total topsoil Cu, shoot Cu removal peaked in both OMDL and OM2DL plots, as the OM2DL plants had a higher shoot biomass than the OMDL ones, but it was the reverse for shoot Cu concentration (**Table 4**). This reflected a Cu dilution in the sunflower shoots. As both agronomic options were relevant for progressively stripping bioavailable topsoil Cu, the remediation strategy will depend on site manager aims, i.e., to produce biomass and/or to remove Cu from the topsoil without the cost of compost amendment. However a regular compost supply promote many soil processes and underlying soil services.

To phytomanage the Cu-contaminated soils of this wood preservation site, organic matter such as compost should be regularly supplied to ensure the crop production taking advantages of nutrient supply and SOM properties including Cu complexation, amelioration of soil structure and water holding capacity. Even though Cu leaching was reduced after a single compost dressing (Marchand et al., 2011) attention should be paid to the following ones. Investigations on structural and functional diversity of soil microbial communities, micro- and mesofauna are ongoing. In the OMDL soils of the B3 plots collected in year 5, soil microbial biomass and respiration, and enzyme activities were consistently higher than in the Unt soils, with shifts in the bacterial community structure at both the total community and functional group levels (Touceda-González et al., 2017). Other soil functions, e.g., xenobiotic biodegradation, stability of soil aggregates, regulation of water run-off and soil erosion, can be investigated.

By 2020, 20% share of energy resources should be supplied by renewable energy sources to achieve the objectives set by the European Union (Directive, 2009/28/EC). This feedstock may essentially be provided by biomass production through energy crops and by using agricultural by-products and forest logging residues. Faced with the need for arable land to produce food resources, energy crop cultivation on marginal land is an option (Schröder et al., 2018). The biomass processing is a pivotal pillar of the phytomanagement concept. Here, even at high soil Cu exposure, shoot Cu concentrations of sunflower plants did not reach the values required for producing Cu-ecocatalysts used by the biosourced fine organic chemistry (>1,000 mg Cu kg^{-1}, Clavé et al., 2016). Use of mutant lines and plant inoculation with endophytic bacteria were however assessed to promote Cu tolerance and shoot Cu removal by sunflower, and root Cu concentrations of 1-month-old sunflower plants reached up to 2,000 mg Cu kg^{-1}, being suitable for producing Cu-ecocatalysts (Kolbas et al., 2015). Copper did not end up in oil and kernel Cu concentrations of sunflower plants grown in our field trial were in the range of permitted concentrations to feed cattle, so sunflower oil cake can be produced from our crops (Madejón et al., 2003; Kolbas et al., 2011).

Shoots and seed hulls can be merged with other lots and used by various sectors processing non-food crops such as (1) biorefineries for bio-oil (Casoni et al., 2015), biofuel (Ziebell et al., 2013; Zhao et al., 2016) and bioethanol (Dhiman et al., 2017) via the production of fermentable sugars (Ruiz et al., 2013; Liguori et al., 2016; Tavares et al., 2016), (2) bioconversion into branched-chain fatty acids (Dulermo et al., 2016) (3) solid fuel production (Alaru et al., 2013), (4) syngas and biogas production (Zabaniotou et al., 2010; Graß et al., 2013; Hesami et al., 2015), (5) energy production by co-firing with coal (Kułazynski et al., in press), (6) organic fertilizers for marginal land and Cu-deficient soils as compost or biochar amendment (Evangelou et al., 2015; Colantoni et al., 2016; Saleh et al., 2016); and (7) insulation eco-material and biocomposites (Mati-Baouche et al., 2016; Liu et al., 2017; Brouard et al., 2018).

Crop rotation is mandatory for sunflower cultivation in France (CETIOM, 2011). Here, the phytomanagement is based on a sunflower-tobacco crop rotation. Data for tobacco will be reported in a companion paper. Other crop rotations were assessed including energy and biomass sorghum, but both plant species were too sensitive to water stress and Cu excess (Kolbas, 2012).

AUTHOR CONTRIBUTIONS

MM mainly drafted the paper, made the hypotheses, implemented and managed the field trial, and took the measurements. CB contributed to drafting the paper and implementing and managing the field trial. NO carried out the statistical analysis, assisted in taking measurements, and contributed to drafting the paper, implementing and managing the field trial. LM contributed to drafting the paper, the analysis of statistics, the implementation and management of the field trial, and took the measurements. AK and MD contributed to drafting the paper, implementing and managing the field trial, and worked on taking the measurements. PL contributed to drafting the paper and producing the P-spiked basic slags.

FUNDING

This work was supported by the ERA-Net FACCE SURPLUS (project INTENSE; http://faccesurplus.org/research-projects-1st-call/intense/), the ANR project Phytochem (http://www.agence-nationale-recherche.fr/projet-anr/?tx_lwmsuivibilan_pi2%5BCODE%5D=ANR-13-CDII-0005), and the PhytoSUDOE project (Interreg SUDOE SOE1/P5/E0189, http://www.phytosudoe.eu/). The field trial has received supports from ADEME (Phytodemo project), the Aquitaine Region Council and the COST Action 859. NO was granted by ADEME, France. The UMR Biogeco is a member of the INRA Ecotoxicologist network, ECOTOX, and the Labex COTE.

SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fevo.2018.00123/full#supplementary-material

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Conflict of Interest Statement: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.