Applied and Environmental Soil Science

Soil Management for Sustainable Agriculture 2013

Guest Editors: Philip J. White, John W. Crawford, María Cruz Díaz Álvarez, and Rosario García Moreno

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Editorial Board

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Editorial

Soil Management for Sustainable Agriculture 2013

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Agricultural sustainability can be defined as the ability of a system to maintain stable levels of production and quality in the long term without compromising economic profitability or the environment. The conservation of soil quality is fundamental to agricultural sustainability. The soil provides, amongst other things, a substrate for plant anchorage, a buffered supply of essential mineral elements and water, a repository for carbon, a reservoir of functional biodiversity, and a filter for reducing the pollution of air and water by agrochemicals.

This is the second special issue on soil management for sustainable agriculture. It comprises ten papers describing (1) the preservation of soil organic matter and the phytoavailability of essential mineral elements in soils through the recycling of organic residues to agricultural land, (2) the effects of agricultural management on the accumulation of potentially toxic mineral elements in soils and plants, (3) agricultural practices that reduce losses of organic carbon and nitrogen from soils, restrict soil erosion, and maintain agricultural productivity, and (4) agronomic strategies to manipulate soil chemistry to reduce the abundance of problematical weeds.

Better soil quality is generally associated with greater concentrations of soil organic matter (SOM) and a plentiful supply of essential mineral elements. Thus, the recycling of organic matter and mineral elements from crop residues to soil often benefits agricultural sustainability. R. de Mello Prado et al. review the use of by-products of the production of sugar and alcohol from sugar cane as soil improvers and substitutes for mineral fertilizers. They report that the recycling of filter cake and vinasse can increase SOM, the phytoavailability of mineral elements, and crop yields. However, they caution that these crop residues must be applied judiciously to avoid possible environmental damage. Similarly, R. García Moreno et al. discuss the opportunities for managing the phytoavailability of selenium, which is not thought to be required by plants but is essential for animal health, through the recycling of organic matter to soils. They observe that the application of chemically recovered selenium to crops is nonsustainable. Nevertheless, animal manures and sewage sludge often contain significant amounts of selenium, and increasing SOM prevents selenium leaching to deeper soil horizons. Thus, the application of organic residues to agricultural land can increase soil selenium content and retention, increase selenium concentrations in edible produce, and, thereby, benefit human health.

Composts and manures also contain appreciable quantities of other essential mineral elements, including the micronutrients iron, copper, zinc, and manganese. However, these elements are potentially toxic to both plants and animals if they accumulate to excessive concentrations. In this special issue G. C. G. dos Santos et al. report that the concentrations and phytoavailabilities of copper and zinc are greater in the acidic vineyard soils of the state of São Paulo, Brazil, than in nonacidic natural soils from the same area, although they do not reach toxic concentrations. They attribute the accumulation of these elements to the application of copper-based fungicides and zinc-based agrochemicals and to management practices leading to soil acidification.

Anthropogenic contamination of agricultural land is not just restricted to the application of manures or agrochemicals, but can also be a consequence of dumping industrial wastes. To return agricultural soil to crop production, F. A. Gabos et al. have evaluated the potential for ameliorating soils polluted with automobile scrap by diluting them with uncontaminated soil and liming. Unfortunately this strategy was not successful in reducing the phytoavailability of potentially toxic elements in the soils they studied or in preventing their phytotoxicity to maize.

Soil microbes influence crop production and agricultural sustainability both through their direct and indirect interactions with plant roots and their effects on the biogeochemistry of carbon compounds and mineral elements in the soil. In this special issue, S. P. Val-Moraes et al. describe the contrasting fungal communities of native forest soil and soils cultivated with tomatoes or vegetable crops along the Taquara Branca river basin in Brazil. They speculate that the prevalent fungal community is related, in part, to SOM, tillage, and soil fertility. The fungal communities are also, of course, influenced by the application of fungicides.

The cultivation of grasslands causes a rapid loss of carbon and nitrogen from the soil, which results in both a decline in soil quality and an increase in the emission of greenhouse gasses (GHG). In this special issue, L. A. Milesi Delaye et al. assess the effects of agriculture on soil organic carbon (SOC) and soil organic nitrogen (SON) in grasslands of the Argentine Rolling Pampa over a 140-year period. They combine data from land surveys and experimental trials to develop a simple model simulating changes in SOC and SON in the Rolling Pampa following altered tillage practices. They report an "active" pool of SOM, representing about 50% of SOC and SON in the native prairie soil, with mean residency times of 9 years when soils were tilled and 13 years without tillage. Both SOC and SON could be increased by incorporating organic residues to the soil. Increased cultivation has similarly reduced SOC in tropical soils. In this special issue, W. Mekuria and A. Noble review the impacts of agriculture on SOC in the tropics, concluding that, although improved agronomic practices such as no till, crop rotation, growing cover crops, and the use of mulches, composts, and manures can increase SOC and agricultural productivity, this increase is often short lived. However, they suggest that the production and management of biochar, in both local and global contexts, might be used to increase carbon sequestration in agricultural soils, improve their quality and productivity, and reduce GHG emissions from agriculture in the long term.

Soil erosion is a serious problem in many areas of the world. In principle, it can be reduced by conservation tillage systems that maintain crop residues on the soil surface. The results of a 24-year study on the effects of three conservation tillage systems on SOC and crop yields in Southern Illinois, USA, are presented by K. R. Olson et al. These authors report that a no-till system preserved more SOC than ploughing with a mouldboard, which in turn preserved more SOC than chisel ploughing, over the 24-year period. Commercial yields of maize and soybean from all three systems were similar. The susceptibility of the soils of the Haean catchment in South Korea to erosion was studied by M. Ruidisch et al. in the context of the sustainability of current practices for vegetable production. In this region, soil depth is maintained by spreading sandy material on fields and crops are cultivated in ridges using plastic mulches. This practice results in poor soils with low SOM that are highly susceptible to erosion during the monsoon. They conclude that a more sustainable agricultural system is urgently required.

In the final paper of this special issue, B. Kone et al. have investigated whether the management of soil chemistry might be used to control problematical weeds in West African rice producing areas. It has long been known that soil chemistry can influence plant species' assemblages and this study observed that the abundance of speargrass (*Imperata cylindrica* L.) was positively correlated with soil potassium concentration and negatively correlated with soil calcium and iron concentrations, whereas the abundance of *Cyperus* spp. was positively correlated with both potassium : magnesium and calcium : magnesium ratios in the soil. The authors suggest fertiliser management strategies to exploit these phenomena to control the abundance of these weeds.

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Review Article

Managing the Selenium Content in Soils in Semiarid Environments through the Recycling of Organic Matter

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Around 30% of the world's population suffers from either a lack of one or more essential micronutrients, or the overconsumption of these minerals, which causes toxicity. Selenium (Se) is a particularly important micronutrient component of the diet with a well-documented and wide-ranging role in maintaining health. However, this important micronutrient can be lacking because soil and crop management are focused on high yields to the detriment of the quality of crops required to ensure a healthy human diet. Currently around 15% of the global population has selenium deficiency. This paper focuses on Se availability in semiarid soils and how micronutrients can be effectively managed through the recycling of organic matter. Because many mineral reserves are being exploited unsustainably, we review the advantages of using organic by-products for the management of the biofortification of Se in crops. This type of practice is particularly useful in arid and semiarid environments because organic matter acts as a reservoir for Se, preventing bioaccumulation and leaching. There are also potential local economic benefits from using organic by-products, such as manures and sewage sludge.

1. Introduction

At least 60% of the world's population either lacks one or more essential mineral elements or consumes food containing high amounts of toxic mineral elements [1]. Mineral malnutrition is a widespread problem in both developing and developed countries. This situation is particularly serious for some micronutrients, such as Fe, Zn, I, Se, Ca, Mg, and Cu [2, 3]. In the specific case of Se, 15% of the world's population is already Se deficient [2].

Gupta et al. [4] stated that, in addition to the lack of studies on the ability of plants to uptake minerals, there are insufficient analyses of soil that determine the total nutrient contents. Similarly, there are no studies of the impact of different soil management practices on the concentration and distribution of micronutrient concentrations in the different edible parts of crop plants.

The micronutrient status of a plant can be measured from the leaves because leaves contain the highest amounts of micronutrients. Micronutrient deficiency is easily detected in younger leaves, whereas toxicity can be detected in later stages of development in older leaves [5]. Several factors control the lack of Se content in plants including the genetic variety, soil management, soil type, and climate. The lack of micronutrient content in plants is common in humid temperate and tropical regions due to intense soil leaching caused by the high number of rain events.

Ekholm et al. [6] studied the trends in the mineral and trace element contents in fruits, vegetables, and cereals in Finland over the last 30 years. They found that the content of most minerals has decreased in all crops. Interestingly, the only exception is Se, the content of which has increased as a result of the use of selenium-supplemented inorganic fertilisers over the last 20 years. Tennant et al. [3] found

the same pattern of decline in UK crops and noted that analogous trends have occurred in different countries that share very similar historical farming management strategies, based mainly on the adoption of modern genetic varieties of crops and agronomic practices related to the acceleration of the growth rates of plants. These practices include growth in higher temperatures, increased light intensity, increased CO_2 concentrations, and higher irrigation rates.

Micronutrient cycling in soils is closely related to the organic matter content and crop residue management [7]. Therefore, soil and crop mismanagement that leads to the loss of organic matter leads to a reduction in the mineral content of soils and consequently the mineral content of plants. Biofortification can be achieved either through the use of genetically improved crops for mineral uptake into the edible parts of the plant or through the use of specific fertilisers that increase the phytoavailability of some minerals to specific crops [2]. However, inorganic fertilisers are increasingly expensive to manufacture, distribute, and apply. These fertilizers also have environmental impacts, including an increase in greenhouse gas emission, the unsustainable exploitation of mineral resources, and the mineral enrichment of the environment leading to soil contamination. Biofortification is mainly dependent on the specific chemical forms of micronutrients in soils and the subsequent uptake by plants [8]. To reinforce this strategy, it is necessary to know the forms of the mineral elements that are available to plants, as well as the limitations and the phytoavailability of these elements in the rhizospheres [9]. In the specific case of selenium, the plant roots will obtain this element through the uptake of selenate, selenite, or organoselenium compounds by the plant roots [3]. Agronomic biofortification strategies to increase the mineral concentrations in the edible parts of plants generally rely on the application of mineral fertilisers and the improvement of the solubilisation and mobilisation of soil micronutrients. In the case of selenium, the application of soil and foliar Se fertilisers has been shown to have beneficial effects on animal health and human nutrition. Soil applications are suggested for cropping under late-season moisture and heat stress [3, 5, 6].

The consumption of many key minerals is unsustainable according to Hueso et al. [10], with current rates of consumption leading to the depletion of global mineral reserves in the next 50 years. According to the US Geological Survey [10], almost all of the selenium produced worldwide is currently recovered from anode slimes during Cu electrolysis and to a lesser extent during Ni and Zn electrolysis. According to this same source, the global Se reserves are 172,000 t Se, which is based on Cu deposits. Thus, if one-third of the world's arable land (500 Mha) is fertilised with 10 g Se/ha, 5000 t Se/yr will be consumed, and the global Se reserve would be depleted in less than 40 years. Thus, the use of minerals as fertilisers has to be prioritised to ensure that the nutritional demands are achieved or other strategies must be implemented to avoid the exhaustion of mineral reserves. To these ends it is also important to obtain more information on the geographical distribution of micronutrients in relation to nutrient sampling in crops and the relationship with epidemiological studies to evaluate the relationship between animal and human diseases and the geochemical environment and soil and plant management related to nutrition crops [5].

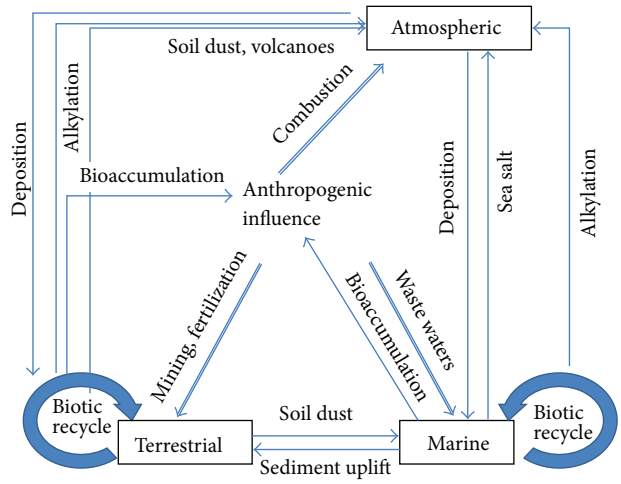

Figure 1: Global Se cycle considering the anthropogenic influence (extracted from [11]).

2. Importance of Selenium in the Human Diet

Se was discovered in 1817 by Berzelius; however, it was not until 140 years later that its nutritional requirement was determined [12]. The Se cycle is represented in Figure 1. Although Se is not essential for plant growth, this element has beneficial effects that promote the growth of plants and it is essential in a healthy diet for humans and other mammals [11]. In general, micronutrients, such as Se, are required as cofactors for enzymes or as part of the protein structure involved in DNA synthesis and repair, the prevention of oxidative damage to DNA, and the maintenance of the methylation of DNA [13]. Because of these functional roles, Se deficiency in mammals can result in several physiological disorders, such as cardiomyopathy (Keshan) and osteoarthritis diseases (Kashin-Beck), pancreatitis, asthma, inflammatory response syndrome, malfunctioning of immune system, decreased response to viral infections, and decreased fertility and thyroid functioning [13].

The individual human Se intake ranges from 3 to 7000 μg Se/day worldwide, with most cases at the lower end of the range [14]. For beneficial effects, the US Government recently recommended dietary Se allowances of 55 and 70 μg/day for women and men, respectively [12] and the current standards designated by the Department of Health (1991) in the UK set the upper safe limit to 400 μg Se/day/person. Broadley et al. [15] noted that the Se intake in the UK has declined from 60 μg Se/d to 29–39 μg Se/d by the end of the 90s, and in other EU countries, the intakes are even lower at 30 and 38 μg Se/d for females and males, respectively, based on the results of blood and serum testing.

Most of the researches conducted on Se and human health report a beneficial effect of this element in the prevention of cancer and cardiovascular disease [15–22]. Against this, Wu et al. [23] did not find any beneficial effects in human

Australian males who consumed a supplementary Se diet with biofortified wheat (193 μm/L). In these individuals, the beneficial effects were tested through biomarkers of cancer and cardiovascular diseases. However, as the authors noted, any beneficial effects may have been related to specific genotypes, and further studies are needed to confirm the conclusions. Se deficiency has been associated with liver, muscle, and heart disease in animals [24]. As mentioned, Se has one of the narrowest ranges in humans between dietary deficiency and toxic levels: less than 40 μg day^{-1} to more than 400 μg day^{-1} [25]. Thus, although global Se toxicity in humans is far less widespread than Se deficiency [26], it is still important to understand the biophysicochemical processes that regulate its bioavailability in nutrition [27]. Furthermore, Se is chemically similar to sulphur in plants and it is therefore metabolised through many of the same pathways, with many plants preferentially uptaking Se over S. Above a critical leaf dry matter concentration in the range of 10 to 100 $\times$ 10^{-3} mg Se/kg plant dry weight, selenium toxicity begins to limit growth in most plants. Se toxicity in crops occurs mainly on seleniferous soils, and only plants that exhibit genetic tolerance to this type of soil can be successfully grown [2, 7].

The selenium level in most soils is generally less than 1 mg Se/kg soil; however, the selenium content in seleniferous soils can be as high as 4 to 100 mg Se/kg soil. The selenium content of plants in most soils is less than 1 mg/kg plant dry weight, whereas most plants grown in seleniferous soils show selenium levels in the range of 1 to 10 mg/kg plant dry weight. In the case of Se-hyperaccumulator plants, this can increase to between 1000 to 15,000 mg/kg [7]. These differences in concentration can be visualized in Figure 2, which shows potential areas where livestock may be at risk for selenium deficiency or toxicity in Australia. The major species of Se in plants include selenate, which is translocated directly from the soil and is less readily bound to soil components than selenite, and selenomethionine (SeMet) and selenocysteine (SelCys), both of which are biosynthesised by plants [15, 28]. The Se content in wheat and other cereals is in the form of SeMet with lower amounts of SelCys and selenate. Se-enriched crops exhibit a higher Se content than the corresponding natural plants; nevertheless, the treatment of crops must be performed with caution to reduce the risk of toxicity [29].

The absorption of Se in humans is not affected by the nutritional human status and approximately 80% of the absorbed selenium originates from food. The studies that have compared the bioavailability of different forms of Se in humans concluded that organic forms are more bioavailable than selenate and selenite [24, 30]. In fact Se-methylselenocysteine and its γ-glutamyl-derivative, which are found in a number of edible plants of the *Allium* and *Brassica* families, have been studied for their potent anticancer effects. These selenoproteins have very high antioxidant properties and are highly beneficial in counteracting diseases related to oxidative stress. As well as the benefits from selenoproteins, the Se obtained in the diet can be metabolised to small-molecular-weight species that are believed to exhibit antitumour effects [30].

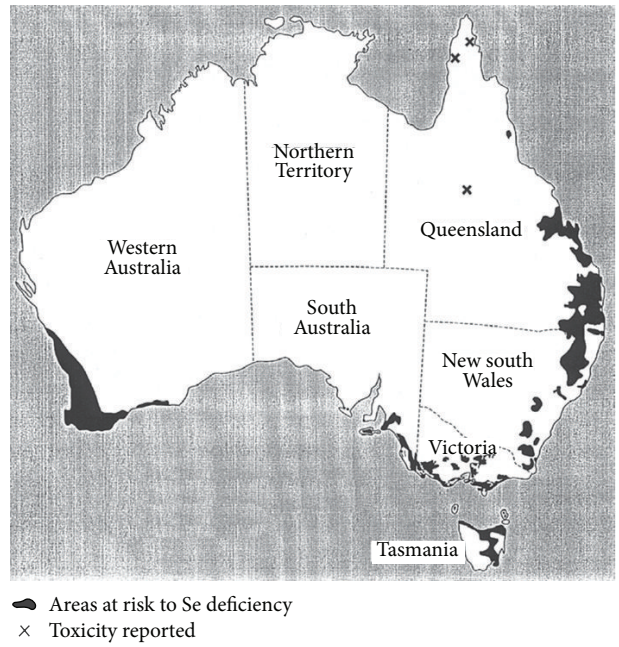

Figure 2: Map of Australia showing potential areas where livestock may be at risk for selenium deficiency or toxicity (extracted from [34]).

At sufficiently high doses, the Se metabolites can also induce toxicity in animals and humans. The effects of the Se toxicity are highly dependent on the form of Se. Se compounds can easily form an anion that generates superoxide in the presence of thiols, such as glutathione, which results in redox cycling. Studies have shown that the toxic effects of Se are due to this oxidative-stress mechanism [31, 32]. In fact, superoxide has been shown to be generated from selenite and diselenides, such as selenocysteine, but not from selenite, in the presence of reduced glutathione [31, 32]. As a result of their inability to generate superoxide, SeMet nor Se-methyl-selenocysteine has a relatively low toxicity to cells in culture or to animals or humans. Nakamuro et al. [33] found that selenodiglutathione, which is an intermediate chemical species in the formation of superoxide from selenite and glutathione, is more toxic than selenite itself. Hasegawa et al. [34] found that another mechanism of Se toxicity includes the inhibition of Se methylation, which represents the major detoxification pathway for Se; the inhibition of this pathway results in the accumulation of selenide hepatotoxic compounds. Although studies on Se toxicity suggest that the organic forms may be more toxic than the inorganic forms after long-term consumption because the organic forms are more easily incorporated into tissues, there is no conclusive evidence that proves this hypothesis [34].

Finally, as noted by Rayman [29], it is difficult to define the optimal intake of Se at the individual level because its concentration in the body is dependent on a large number of factors, such as which functions of Se are most relevant for a certain stage of a disease, which species of Se is predominant in the Se source, the health conditions in the receptor, the adequacy of intake of other nutrients and their interferences,

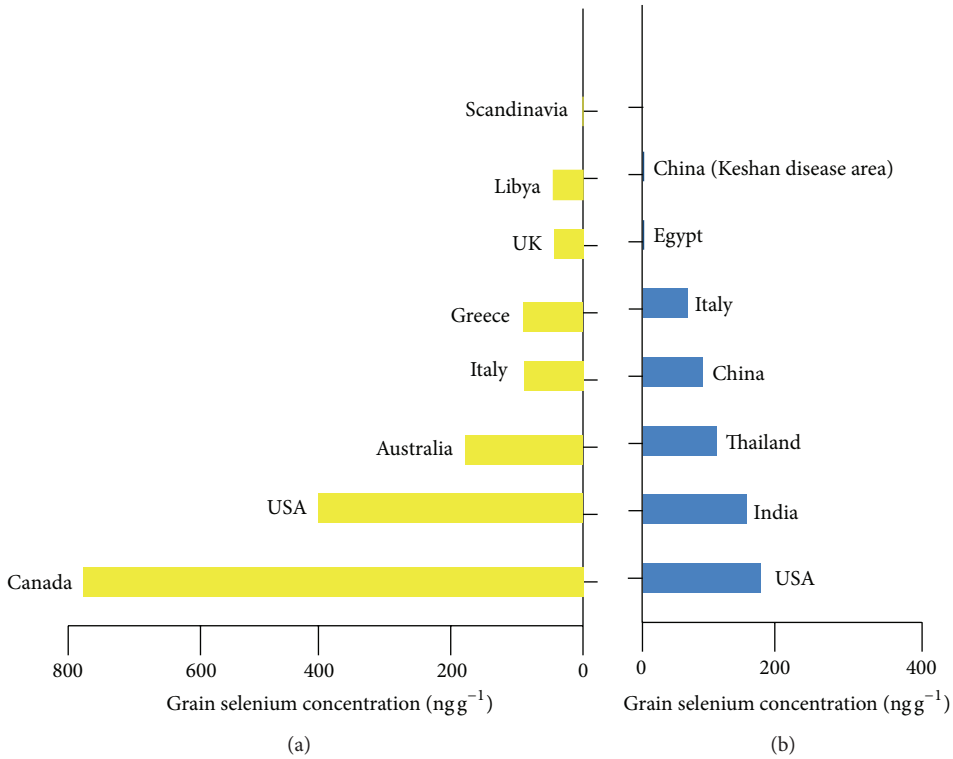

Figure 3: Comparison of Se levels in wheat (a) and rice grains (b) in different countries over the last 40 years (extracted from Zhu et al. [35]).

the presence of additional stressors, and the ability to produce selenoproteins.

3. The Role of Soil Fortification

According to Levander and Burk [21], wheat (*Triticum aestivum* L.) represents the major dietary source of Se worldwide and therefore the decrease in Se intake has been related to changes in the Se content of cereal grains and to the decrease of Se in soils. This hypothesis is supported by decreases in intake and the trend over time in the UK to consume a larger proportion of grain grown in the UK that has a lower Se content compared with imported grain grown in North America, where the soils contain higher amounts of Se [15]. Zhu et al. [35] made a comparison of the Se content in rice and wheat between different countries and crops over the last 40 years, as shown in Figure 3.

Lyons et al. [31] proved that the fertilisation of wheat crops in Australia with Se fertilisers is a cost-effective method for the improvement of the concentration of organic Se in grain, which results in an incremental uptake of Se in animal and human diets. As mentioned above, the important issue associated with the management of Se fertilisation is the control of the amount of Se added to avoid toxicity. The authors added Se in the form of selenate at fertilising rates of up to 120 g/ha in field trials and 500 g/ha in pilot trials in soil and added 330 g/ha of foliar Se applied with low S concentrations (2–5 mg S/kg soil). These researchers did not observe any symptoms of toxicity in the crop even if the application is 20 times higher that safest applications. A soil application of 10 g Se/ha is found to be safe for raising Se content of crops in Finland.

In the case of Se applied as selenite, they observed a critical amount of 70 mg/L required to cause growth inhibition, whereas selenate did not affect the crops in a solution concentration of 150 mg/L. They recommended using application rates of 200 g selenate/ha to avoid toxicity in wheat and to obtain tissue levels of Se below any toxic concentration. In later studies, Lyons et al. [36] found that the concentrations of Se in diverse germplasms did not vary in different cultivars and was in the range of 5 to 720 μg/kg, regardless of the genotypic variation.

Finland has conducted fortification of crops since 1981 and has obtained excellent results: only the Se content exhibited an increasing trend in different crops compared to the decreasing trend in the concentrations of other micronutrients of up to 10-fold in most crops [6]. Eurola et al. [37] measured the Se content in 125 food items before and after fortification in Finland and found that the Se content had increased in all cases. The total intake was distributed across cereals (26%), meat (29%), dairy products (20%), eggs (10%), and fish (9%). In addition, only those diets with a very exceptional composition provide less than 0.05 mg or more that 0.2 mg of Se per 10 MJ (Mega Joules). In the case of cereals, of which wheat is the most important, their contribution to the total intake of Se almost tripled from 1971 to 1991. The biofortification of pastures and forages has been shown to increase the Se content in the diet by increasing the Se content

in livestock [4, 5]. The last authors demonstrated that Se content in pastures and forages prevents disorders amongst grazing livestock, such as muscular dystrophy disorders.

Broadley et al. [38] used selenate fertiliser in wheat crops and found that the crop total recovery, including grain and straw, ranged from 20% to 35%. These researchers added up to 10 g Se/ha to the crop, and, if the straw is removed, approximately 6.5–8 g Se/ha is not recovered. For this reason, to ensure the long-term sustainability, the fate of Se in soils and in the food chain must be known before any biofortification strategy is widely implemented. The residual Se may be leached, volatilised, retained in the soil, strongly absorbed by iron or aluminium oxides, or retained in the soil in nonsoluble elemental forms.

Eurola et al. [37, 39] concluded that Se fertilisation significantly affects the Se content of cereals and other crops. However, the same authors also noted that the Se content varies considerably on an annual basis and between different locations mainly due to the specificity of the fertilising rates and the different soil and climatic conditions.

It is clear that there are individuals and populations that would benefit from a higher Se intake level. However, it is important to be aware of the specific geochemical environment and the baseline intake in any specific country or region because necessary additional intake in one region or country might be excessive in another [18]. Beside these health-related considerations, other elements that should be considered are the cost-effectiveness of adding Se to food sources, such as through biofortification or the recycling of organic by-products, and the environmental effects of the fertiliser and soil management strategies. For example, if the Se fertilisers are economically and environmentally expensive, other sources of recycling, as well as the management of different soils to conserve and retain the surplus of Se in soils to avoid their lost through leaching, evaporation, and absorption, must be considered.

4. Se Management for Crop Fertilisation in Semiarid Environmental Conditions

In the case of semiarid and arid environments, the lack of micronutrients and macronutrients in crops is mainly due to high crop yield, insufficient return of crop residues to soil, low organic matter, and immobilisation of most micronutrients in the soil [3]. This is the situation in most Australian soils used to produce cereals [14], especially those used to produce cereals in the southern regions, which are mainly alkaline and particularly calcareous or sodic. These conditions drive chemical constraints for agricultural production associated with the alkaline soil environment and the dry land climate, which include macronutrient and micronutrient deficiencies and some toxicity related to high sodicity and salinity. More generally, alkaline soils represent an important proportion of world soils that sustain crop production [3, 14, 40]. Most of these soil conditions have led to desertification in some parts due to an increase in the soil erosion and decreases in the soil fertility due to the depletion of nutrients related to the loss of organic matter and the biological diversification of soils [41]. Bowker et al. [41] noted that most of the problems related to desertification in arid and semiarid environments originate from anthropogenic disturbances that change the organic matter and biological properties of soil crusts. This is especially true for arid regions, where desertification is closely related to either a net loss in the soil fertility or a redistribution of the soil nutrients [42–44]. Bowker et al. [41] found that the micronutrient soil content is highly correlated to the biological activity and specifically to the presence of moss and lichen species in semiarid conditions. The distribution of these biological species is highly correlated to the moisture, organic matter content, and higher availability of micronutrients. The high degradation observed in arid lands can therefore be resolved by improving the biological diversity of soil through the management of the organic matter.

From this point of view, biological diversity and the management of the organic matter become important factors for the improvement of micronutrient availability in degraded lands. In most cases, the response of plant growth to the addition of macronutrients and micronutrients in semiarid and arid soils is highly positive [43]. In fact, the response to the addition of a heterogeneous nutrient supply must be optimised in each case by understanding the plant response and the bioavailability of each nutrient [43]. To monitor the addition of different concentrations of nutrients and their effect on plant growth, we need to understand how the nutrient concentrations in the plant respond to changes in nutrient supply. The effects of nutrients on plants can be easily determined by the ability of plants to translocate nutrients and to store pools in different parts of the plant. Thus, the ideal management of the micronutrients will require knowledge on how the different nutrients are specifically taken up by different plants and how the nutrients are stored and translocated inside the different plant parts, particularly the edible portions [27].

Another important issue associated with the availability of different nutrients in soil is the speciation, quantity, and distribution of the nutrient in different soils, as well as the effects of different chemical species on root growth and grain yield [27]. Modern agricultural techniques used to obtain higher yields worldwide are accelerating the depletion of nutrients and leading to an increase in the application of fertilisers to maintain production [45]. Li et al. [46] found that the micronutrient status in soils and crops is affected by fertilisations practices. Specific cases must be studied to determine how fertilisation practices can help improve the soil micronutrient and macronutrient states in order to manage the ideal rates of fertiliser application for in different crops. Research on cereal crops showed that it is possible to obtain higher yields with the application of organic fertilisers because these improve the soil organic matter and thus provide available micronutrients for crops. However, low yields of winter wheat were obtained when only the micronutrient contents were improved because these were highly concentrated in the plant tissues and grains [46]. Sustainable crop production needs to maintain the soil fertility on a long-term basis, and it is essential that the organic matter and nutrients removed during harvest

are replenished through external application on a regular basis. Some authors recommend the maintenance of the soil organic matter at a threshold level, which will depend on the soil and climatic factors, to ensure the physical, chemical, and biological integrity of soil to achieve sustainable agricultural and environmental functions [47–51].

In semiarid and arid environments, some studies concluded that the presence of Se in plants has a protective effect that helps maintain the water status in plants exposed to drought [25]. In this case, selenium is hypothesised to participate in the regulation of the water status of plants and in maintaining the content of water in the tissues at a sufficiently high level [25]. The selenium-supplemented fertilisation of wheat crops in semiarid conditions is a cost-effective method if inorganic fertilisers are used to ensure the ideal concentration of organic Se in grain as a result of dietary needs. Based on the research studies conducted on Se fertilisation as selenate (more mobile form of Se than selenite [52]) at different rates (4 to 200 g/ha), wheat does not express any phytotoxicity (critical tissue level of 325 mg/kg) compared with other crops (tobacco, soybean, and rice), and the crop exhibited an excellent increase in the grain Se content for human consumption. The results noted the possibility of the use of sodium selenate for the biofortification of wheat in Australia [20, 53, 54].

The incorporation of organic by-products as soil conditioners and fertilisers has the advantage of recycling the macronutrients and micronutrients, enhancing the soil conditions, helping establish a sustainable vegetative cover, avoiding erosion, maximising crop yield when applied with best management practices, and monitoring potential hazards to soils and crops [30, 55].

5. Use of Organic Fertilisers to Improve Se Content in Crops

Organic matter is able to increase the sorption of selenate in arid conditions and to act as a reservoir for crops to avoid the leaching, evaporation, and precipitation of this species to deeper soil layers [56]. Thus, it is recommended in the management of Se fertilisation to avoid the consumption of expensive and unsustainable inorganic forms. Organic matter plays a very important role in selenium immobilisation and the availability of selenium to plants. This effect depends on the compounds because organic matter includes highly heterogeneous compounds and the interactions are not very well understood. In this particular case, fulvic and humic acids appear to have an important role on the metalloid regulation through immobilisation and slow release of organic forms of Se [56].

According to Park et al. [57] biosolids and especially poultry and livestock manure are a good source of Se for crops. These organic amendments contain bioavailable forms of this nutrient and are a useful form of amendment since in most cases they are applied to the land as a form of reutilisation of an increasing "waste" product. The addition of manure and organic amendments to agricultural soils is the major source of most micronutrients including Se and sewage sludge has the same Se forms as manure [12].

According to Øgaard et al. [58], the addition of cattle manure to a loam soil in combination with selenite and selenate decreased the adsorption and immobilisation of both anions because the organic acids from the manure compete with selenium for the sorption sites. Organic fertilisers provide greater micronutrient content to plants not only because of the higher concentration of these but also due to their slower release from the plant [12, 25, 59].

In the case of recycling crop residues, such as straw, much of the added Se, that is, as much as 70–75%, remains in the rest of the plant, particularly in leaves, which are a highly concentrated source of this element. This is also true for animal manures because most of the Se is not absorbed by the animal and because farmed animals are fed feedstuffs rich in Se, when animals are fed with forage supplements or are raised on Se-rich soils. Thus, organic fertilisers provide a diverse, albeit unpredictable, source of Se.

Se in organic amendments has been proved to have several advantages compared with inorganic Se fertilizers. For example, Se is bioavailable through several microbial and chemical processes including immobilization, reduction, volatilization, and rhizosphere modification (Figures 4 and 5). The bioavailability depends on several factors, the most important of which is pH. In most of the case this availability is assured by the treatment of organic amendments, where bioavailability is increased by transforming Se from solid to the soil solution phase, improving the mobilisation of the metalloid [41] and increasing the pH buffering capacity.

Organic amendments to fertilise crop with Se offers an additional advantage in arid and semiarid environments since the removal of Se in topsoil is mostly due to volatilization [60, 61]. Indeed, according to Flury et al. [62], the elimination of Se from topsoil mostly happens due to volatilization and leaching, Figure 5. These authors investigated Se removal from organic amendments and summarised that when an abundance of organic C was available in the soil, microbial biodegradation of Se is activated through volatilisation. In general, leaching dominates in wet and cold conditions, whereas volatilization prevails in dry and warm conditions.

6. Conclusions

Recent studies on human health have shown that the appropriate amounts of certain micronutrients in the diet are important for maintaining a healthy society. The evidence for this is especially true in the case of selenium (Se), where 15% of the global population has an insufficiency. The deficiency of this element in the human and animal diets is related to some cancers and numerous physiological disorders. Many countries have implemented Se-supplemented fertilisation strategies, mainly for the production of cereals, because wheat is the most widely used food for improving the amounts of Se in the diet. The issues of Se availability is especially crucial in arid and semiarid environments, where one of the main benefits of the micronutrient to crop production is an increase in the drought resistance, and where many of the soils that are low in selenium are located.

There are constraints that must be taken into account regarding the application of Se-supplemented fertilisers.

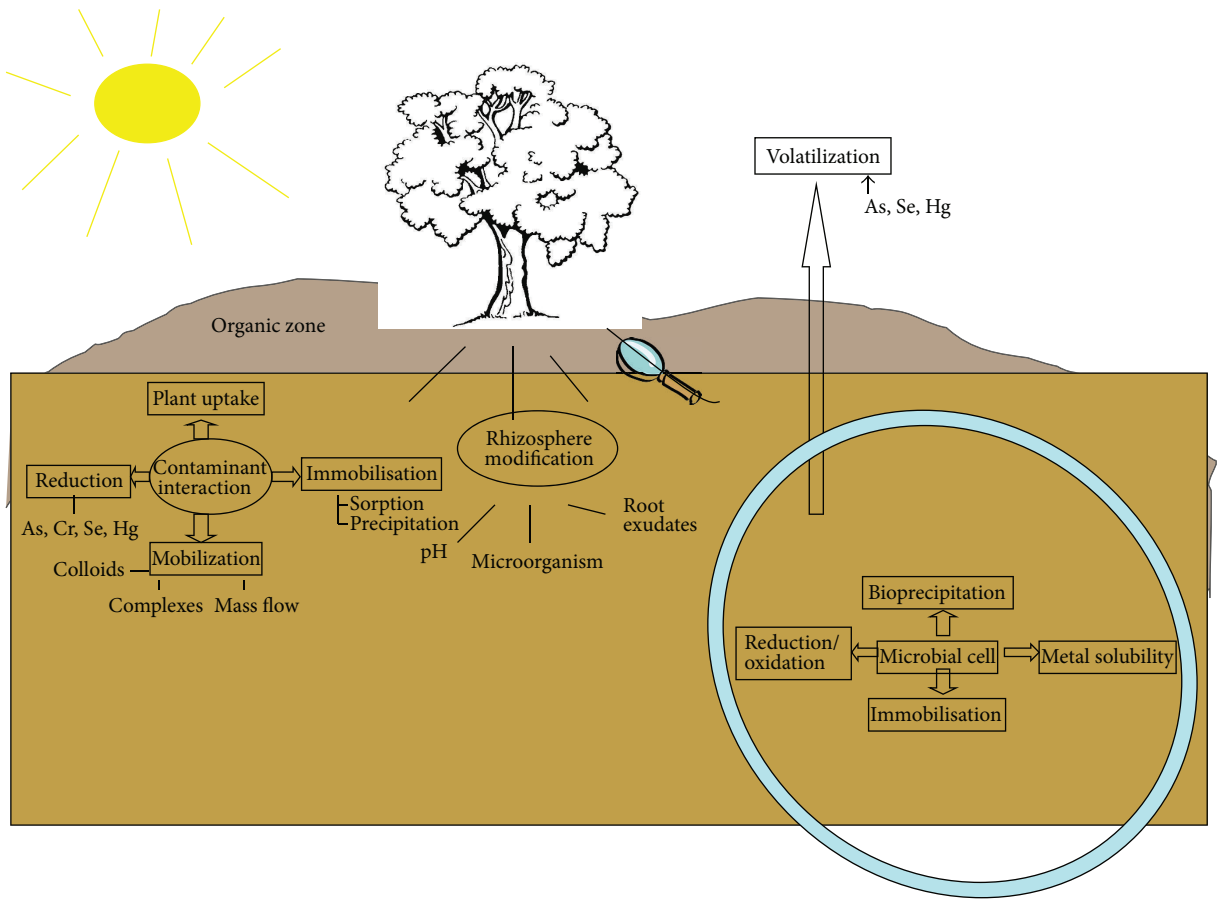

Figure 4: The role of organic amendments in regulating various bioremediation processes (extracted from [57]).

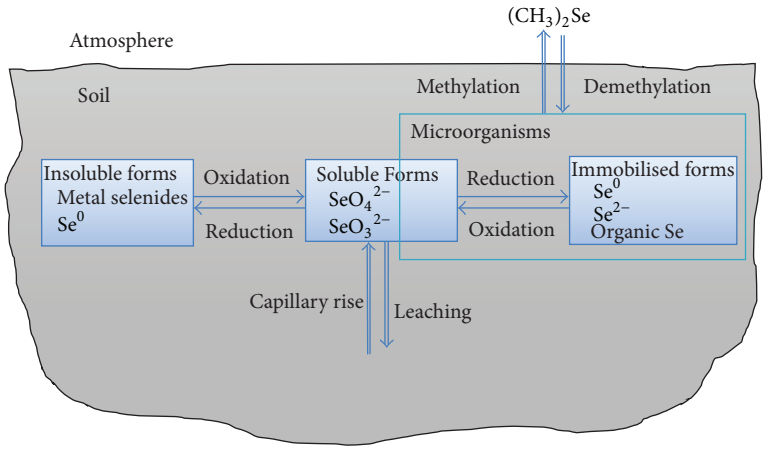

Figure 5: Cycle of Se in soil. Double arrows show preferred pattern for biodegradation (extracted from [62]).

Mineral biofortification has been proven to be effective; however, this strategy is limited by the availability of mineral resources and its cost [34]. Sustainable biofortification depends on the use of organic fertilisers and conditioners to improve micronutrient fertilisation, particularly Se fertilisation. Thus, as well as providing other better-known soil benefits, the addition of organic matter could become an important consideration to ensure a healthy Se content in wheat produced in semiarid conditions.

We have reviewed research conducted in this field and found that further studies must be performed to compare the performance of different sources of organic matter as a fertiliser including biosolids and especially poultry and livestock manure, straw, or any organic by-product, to ensure

the appropriate levels of available Se, as well as other micronutrients, in the fertilisation of wheat to improve the micronutrition of the human diet. More research must be conducted to understand the speciation and release of Se from organic amendments, to improve the use of organic by-products, and to avoid the limitations related to the use of inorganic fertilisers. Finally, research must be focused on the need of each specific land location and crop to provide optimised Se contents for animal and plant intake, avoiding the immobilisation of this metal in soils. Therefore, specific recommendations must be done for specific organic amendments and agricultural uses to optimise uptake and avoid toxicity.

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Research Article

Is Ridge Cultivation Sustainable? A Case Study from the Haean Catchment, South Korea

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Non-sustainable agricultural practices can alter the quality of soil and water. A sustainable soil management requires detailed understanding of how tillage affects soil quality, erosion, and leaching processes. Agricultural soils in the Haean catchment (South Korea) are susceptible to erosion by water during the monsoon. For years, erosion-induced losses have been compensated by spreading allochthonous sandy material on the fields. These anthropogenically modified soils are used for vegetable production, and crops are cultivated in ridges using plastic mulches. To evaluate whether the current practice of ridge cultivation is sustainable with regard to soil quality and soil and water conservation, we (i) analysed soil properties of topsoils and (ii) carried out dye tracer experiments. Our results show that the sandy topsoils have a very low soil organic matter content and a poor structure and lack soil burrowers. The artificial layering induced by spreading sandy material supported lateral downhill water flow. Ridge tillage and plastic mulching strongly increased surface runoff and soil erosion. We conclude that for this region a comprehensive management plan, which aims at long-term sustainable agriculture by protecting topsoils, increasing soil organic matter, and minimizing runoff and soil erosion, is mandatory for the future.

1. Introduction

Ecosystem services and agriculture are closely related and affect each other. On the one hand, ecosystems used for agriculture produce food, reduce hunger, and improve public health—services that become more and more important in view of a growing world population. On the other hand, agricultural mismanagement can reduce the ability of ecosystems to provide these goods and services [1, 2].

Soils play a key role in providing supporting and regulating services such as soil fertility, soil retention, nutrient cycling, and carbon sequestration [3]. Appropriately managed soils in agricultural ecosystems can contribute to soil and water conservation [4], while poorly managed systems may deteriorate ecosystem services by high nutrient and sediment losses from agricultural fields. Possible consequences are soil degradation, declining water quality, water pollution, and increasing costs for water purification [5, 6]. The major goal in agriculture is therefore a sustainable management that minimizes the risk of soil and environmental degradation [7] and at the same time ensures improved yields and ecosystem services [2].

Agricultural production in South Korea faces an enormous pressure due to its limited arable land of about 22% of the total area [8]. To increase yields, forested areas on hillslopes have been converted to agricultural land and the application of chemical fertilisers has increased from 230 kg ha^{-1} year^{-1} in 1980 to 450 kg ha^{-1} year^{-1} in 1994 [9]. These high fertiliser rates in combination with heavy rainfall events during the East Asian summer monsoon are critical in relation to water pollution and eutrophication. Actually, eutrophication of water reservoirs has become a widely recognized problem in South Korea. Especially the transport of applied phosphorus with sediments in surface runoff during monsoon events considerably affects the water resources [9–11]. Therefore, in monsoon regions, an appropriate agricultural management to decrease soil and environmental degradation is particularly important.

To determine the pathways of agricultural pollutants and sediments, we have to identify the impact of agricultural practices on water flow on the soil surface as well as in the soils. In general, there are quite different flow phenomena in the soils. Water can percolate slowly through the soil matrix (uniform flow) or it can move rapidly through preferred pathways and bypass a fraction of the porous soil matrix. This preferential flow can occur in root channels, earthworm burrows, fissures or cracks (macropore flow), or along textural boundaries (funnel flow) [12]. Preferential flow is responsible for a rapid water movement and solute transport to greater soil depths or groundwater [13–15]. Its occurrence in soils depends on soil texture, soil structure, topography, surface microrelief, and management as well as on the initial soil water content and the intensity and duration of rainfall [16, 17].

In South Korea, the distribution of allochthonous soil material on dryland fields has become a widespread method to compensate the erosion-induced soil loss. Although this method has recently been prohibited by the government, the artificial layering induced by this practice still persists in the soil profiles. To our knowledge, the influence of this management practice on the water flow in soils has never been investigated. On most of these anthropogenically modified dryland fields, crops are cultivated in ridge tillage systems using plastic mulch. Ridge tillage and plastic mulching were found to have positive effects on crop yield and weed control [18]. However, their effects on water flow, solute, and sediment transport have rarely been investigated.

The aim of our study is to evaluate whether the current practice of ridge cultivation in the Haean catchment in South Korea is sustainable. We focus on soil quality and soil and water conservation. Therefore, we (i) analysed the soil properties of the anthropogenically modified topsoils from various dryland fields distributed over the Haean catchment. Additionally, to (ii) qualitatively describe the effects of tillage on flow patterns and to (iii) quantify surface runoff and soil erosion, we carried out four dye tracer experiments under flat conventional tillage, ridge tillage, ridge tillage with plastic mulch, and ridge tillage with plastic mulch cropped with potato plants.

2. Materials and Methods

2.1. Study Site

2.1.1. General Description. The Haean-myun catchment (128°1′33.101″E, 38°28′6.231″N), also called "the Punchbowl," is located in the mountainous northeastern part of South Korea and has a total area of approximately 64 km^2. The characteristic bowl-shaped topography subdivides the catchment into three major land use zones. The steep hillslopes are mostly forested (58%), moderate slopes at the forest edges are dominated by dryland farming (22%), and rice paddies (8%) are characteristic for the flat central area of the catchment. The remainder is occupied by residential areas, grassland, field margins, and farm roads.

The annual precipitation in the Haean catchment equals 1599 mm (13-year average from 1999 to 2011) with more than 60% of the annual rainfall occurring during the monsoon season from June to August. The annual temperature averages 8.5°, ranging from −6.8° in January to 21.5° in July (13-year monthly averages from 1999 to 2011).

The bedrock in the catchment is made up mainly of granite which is strongly weathered due to the high precipitation rates. It constitutes the parent material for Cambisols—the most widely spread soil type in the study area.

2.1.2. Agricultural Practice on Dryland Fields. The dominant agricultural practice for row crops on Korean dryland fields is ridge tillage with polyethylene covers (plastic mulch) (Figure SF4 in the Supplementary Material available online at http://dx.doi.org/10.1155/2013/679467). The black plastic cover helps to control weeds and to induce an earlier plant emergence due to higher temperature underneath. Additionally, the cultivation in ridges facilitates harvesting.

At the beginning of the growing season, between April and May (depending on the crop type), a granulated mineral fertiliser is applied, fields are ploughed, and the fertiliser is mixed into the top soil. Subsequently, ridges (approximately 15 cm high and 30 cm wide) are created primarily perpendicular to the main slope direction with approximately 70 cm spacing. The ridges are covered with black polyethylene sheets perforated with 25–30 cm spaced planting holes (5 cm diameter), while furrows between ridges remain uncovered. After ridges and furrows are created, depending on the crop type, seeds are sown or juvenile plants are planted into the planting holes. Several times during the growing season, herbicides and pesticides are applied, and mineral fertilisers are spread a second time on the fields, depending on the crop type. Finally, harvesting begins usually between August and September.

The main row crops cultivated on dryland fields are cabbage, radish, potato, and beans [19, 20]. Because of their low ground cover, especially in early growth stages, fields with row crops are more susceptible to soil erosion by water than other fields [21]. Therefore, as a consequence of extreme rainfall events during the summer monsoon, many dryland field soils in the Haean catchment have been highly degraded. In order to compensate these erosion losses, farmers used to distribute sandy material from nearby mountain slopes on their fields [22] (Figure SF5 in the online Supplementary Material). The distribution of allochthonous material in the past and repeated ploughing generated irregular artificially layered soil profiles on many dryland fields. Thus, frequently, the topsoil and the subsoil have distinct physical and chemical properties.

2.2. Field Work

2.2.1. Sampling of Topsoils on Agricultural and Forest Sites. In 2009, we took samples of topsoils on 32 dryland fields and on 16 forest sites in the Haean catchment. The dryland fields included the four major crops cultivated in the catchment, namely, cabbage, radish, potato, and bean fields. At each agricultural site, five samples (from the four corners and the center of the field) were taken and mixed together. After

Table 1: Soil physical properties of the experimental sites.

	Horizon (WRB)	Depth[a] (cm)	Clay (%)	Silt (%)	Sand (%)	Soil texture class	Bulk density (g cm^{-3})
Site 1	Ap	0–25	3.2	16.4	80.3	Loamy sand	1.43
	2Apb[b]	25–50	20.2	53.4	26.4	Silt loam	1.45
	Bwb	50–100	24.8	46.6	28.6	Loam	1.38
Site 2	Ap1	0–35	1.9	14.5	83.6	Loamy sand	1.41
	Ap2	35–45	8.1	28.9	63.0	Sandy loam	1.66
	Ap3	45–55	7.6	27.9	64.5	Sandy loam	1.61
	2Apb	55–70	20.9	58.2	20.9	Silt loam	1.28
	2Bwb	70–100	13.6	38.9	47.5	Loam	1.56

[a]Approximate depth, [b]horizon continuous in the second experiment (RT) only.

sampling, soil texture, C, N and soil organic matter (SOM) were analysed in the laboratory.

2.2.2. Dye Tracer Experiments. In 2010, we carried out four irrigation experiments at two potato fields (*Solanum tuberosum* L.) on hillslopes. Field site 1 (128°6′32.625″E, 38°18′4.148″N) was located in a distance of approximately 830 m from field site 2 (128°6′54.803″E, 38°17′43.254″N). Both soils can be characterized as anthropogenically modified Cambisols with eroded A-horizons. Allochthonous sandy soil material was spread several times on top of the fields. The soils were classified as a Terric Cambisol and a Terric Anthrosol over Haplic Cambisol [23] with a slope of 8° and 6° on field sites 1 and 2, respectively. We selected these fields because their slope degrees and soil physical properties were comparable (Table 1).

We carried out the first two experiments on field site 1 and the last two on field site 2. The first experiment (CT) took place after ploughing and before ridges were created, so that the soil surface was flat and represented conventional tillage. The second one (RT) was carried out after the creation of ridges. At field site 2, potato crops were planted in ridges covered with black plastic mulch, and we conducted the third experiment (RT_{pm}) in the early season when the potatoes were just sown. Finally, the last irrigation experiment ($RT_{pm+crops}$) was carried out at the same field site as the experiment RT_{pm} but later in the growing season, when potato crops and their root systems were already well developed. In the following we use CT, RT, RT_{pm}, and $RT_{pm+crops}$ to refer to the corresponding experiments, plots, or tillage.

Before irrigation, we installed FDR soil moisture sensors (Decagon devices, Inc., Pullman, WA 99163, USA) to monitor the volumetric water content θ_V. On CT, they were placed in 5 and 20 cm depth from the flat soil surface. In experiments RT and RT_{pm}, two sensors were situated in furrows in 5 and 20 cm depth from the furrow surface and another two in ridges in 5 and 20 cm depth from the ridge surface. Due to technical problems, the fourth experiment was carried out without soil moisture sensors. We recorded the values of soil moisture in a 2-minute interval on a data logger (Decagon devices, Inc., Pullman, WA 99163, USA).

We irrigated a surface of 2 m^2 with a tracer solution containing 5 g L^{-1} of Brilliant Blue FCF using an automated sprinkler. Because this tracer can be retarded compared to the infiltrating water [24], we added 5 g L^{-1} potassium iodide on plots CT and RT_{pm} as a reference tracer. To measure the amount of surface runoff and the sediment load, the irrigation area was equipped with an infiltration frame. It channelled the surface runoff and the sediments via internal tubes into buckets outside of the frame. After the experiment we measured the water level in the buckets. We took homogenized samples of water with sediment, dried them in a drying oven, and weighed the sediment. The total time and amount of irrigation varied among experiments due to technical problems with blocked sprinkler jets. However, the experiments were still comparable (Table 3).

One day after the irrigation we excavated 8–10 soil profiles of 1×2 m spaced by 10 cm on each plot. For visualization of the iodide tracer, an indicator solution with iron(III) nitrate and starch was prepared [25] and sprayed onto the excavated soil profiles. All profiles were equipped with a metallic frame of 2 m^2 and a Kodak color scale and photographed with a digital single lens reflex camera (Canon EOS 1000D). Only the parts of the profiles surrounded by the frame were analysed.

The soil profiles were sampled to determine soil physical properties. We carefully scraped soil material from different profiles and analysed the texture in a laser particle size analyzer (Mastersizer S "MAM 5044," Malvern instruments GmbH, Herrenberg, Germany). Additionally, we took undisturbed samples with small soil core rings (diameter 2.8 cm, height 1 cm) in different horizons. They were weighed, dried for 24 hours at 105°C in a drying oven, and weighed again to calculate the bulk density.

2.3. Data Analysis

2.3.1. Image Processing. We corrected the images for perspective and radial distortion such that they corresponded to pictures taken by an ideal camera looking perpendicularly onto the profiles. The transformation was calculated by

$$\vec{v} = \frac{1}{1 + \kappa \cdot \langle \vec{u}, \vec{u} \rangle} \cdot \vec{u}, \tag{1}$$

where the parameter κ is the magnitude of the radial distortion, $\vec{u}$ are coordinates of a point in the original image, $\vec{v}$ are coordinates in the corrected one, and the brackets $\langle\rangle$ indicate the inner product. If κ is negative, the distortion is barrel

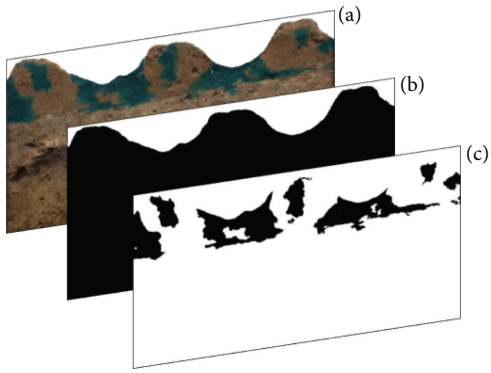

Figure 1: Processing of images of dye-stained soil profiles: (a) rectified dye tracer image, (b) background image with the soil coded black and the background between ridges white, and (c) final binary image used to calculate image indices with dye-stained pixels coded black and nonstained ones coded white.

shaped, while for positive κ it is pincushion shaped [26]. The parameter κ is obtained in a camera calibration procedure with a special calibration plate.

Subsequently, we transformed the images from RGB to HSI (hue, saturation, intensity) color space and classified the pixels into Brilliant Blue stained (black) and nonstained (white) ones to obtain binary images. The transformation is necessary because the HSI color space is more suitable for color-based segmentations of images taken under varying illumination. More details on image transformation and classification are given in Bogner et al. [13].

For the experiments RT, RT_{pm}, and $RT_{pm+crops}$ we additionally produced a second binary background image, where the soil was coded black and the background between ridges white (Figure 1). The correction of distortion and color segmentation were done in Halcon ver. 10.0 (MVTec Software GmbH, Munich, Germany).

2.3.2. Image Index Functions. We used the binary images to assess differences between the tillage management systems. The first two experiments (CT and RT) show the influence of soil surface topography on flow patterns in general. By comparing the experiments RT and RT_{pm}, we can infer the effect of plastic mulch. Finally, we can extract information about the impact of the potato canopy and root system on flow patterns by comparing the images of RT_{pm} with those of $RT_{pm+crops}$.

To effectively analyse the flow patterns in binary images, we calculated image index functions or simply indices. An index is a real-valued function of a binary vector $\vec{r}$ of size m (i.e., a row in a binary image of width m) [27]. These functions are constructed such that they are independent of the size of the image and confined to the interval $[0, 1]$. They extract different features of a binary image row by row. Actually, because the vertical direction is the primary direction of water movement in the vadose zone, these functions summarize the horizontal and emphasize the vertical configuration of patterns. For a detailed mathematical description see Trancón y Widemann and Bogner [27] who we follow closely in the description of image index functions stated below. In the following, we identify stained pixels with the integer 1 and nonstained with 0. The online Supplementary Material contains an example calculation of image indices (Section 1.1).

The *dye coverage* is a well-known index in dye tracer studies. It shows the proportion of stained pixels:

$$I_{\mathrm{D}}(\vec{r}) = \frac{1}{m}\sum_i r_i, \tag{2}$$

with r_i being the ith pixel in the row $\vec{r}$. We call (maximal) contiguous subvectors of equal values "runs." The runs of 1s represent the stained objects and their number is called the *Euler number*. Normalizing by the maximum number of possible runs (i.e., $m/2$) gives:

$$I_{\mathrm{E}}(\vec{r}) = \frac{\left|\mathscr{R}_1(\vec{r})\right|}{\lceil m/2 \rceil}, \tag{3}$$

where $\mathscr{R}_1$ is a function that calculates the sequence of run lengths and the brackets $\lceil\rceil$ are the ceiling function that rounds up to the nearest integer. $I_{\mathrm{E}}(\vec{r})$ is small if the patterns contain only few stained objects and attains its maximum of 1 for a regular sequence of alternating stained and nonstained pixels.

The distribution of run lengths can be summarized in a robust manner by their 5%, 50%, and 95% quantiles. In our experiments, however, we only used the 95% quantile, that we call the *maximum run length*, because it was more suitable than the other quantiles to distinguish between the different tillage managements:

$$I_{\mathrm{Q}\,0.95} = \frac{1}{m}\mathrm{Q}_{0.95}\left(\mathscr{R}_1(\vec{r})\right), \tag{4}$$

where the function Q_p calculates the pth quantile. Furthermore, we can measure how *fragmented* the runs are by defining

$$I_{\mathrm{F}}(\vec{r}) = 1 - \frac{\left\langle \mathscr{R}_1(\vec{r}), \mathscr{R}_1(\vec{r})\right\rangle}{\left(\sum_i r_i\right)^2}. \tag{5}$$

The indeterminate case where there are no stained pixels in a row and $I_{\mathrm{F}} = 1 - 0/0$ is set to 0. I_{F} equals 0 for completely stained and nonstained image rows. Additionally, given two rows with the same amount of staining (i.e., equal I_{D}) I_{F} will be smaller for patterns with larger maximum run length $I_{\mathrm{Q}\,0.95}$. The online Supplementary Material shows the variation of the fragmentation I_{F} for different dye coverages I_{D} and maximum widths of stained objects $I_{\mathrm{Q}\,0.95}$ (see Section 1.2 in Supplementary Material).

Last but not least, we want to evaluate the information contained in an image row $\vec{r}$ via the metric entropy, a version of Shannon's entropy. Shannon [28] defined the information content of an outcome x of a discrete random variable as $h(x) = -\log_2 p(x)$, $p(x)$ being the probability of occurrence of the outcome x. It is measured in bits. The average information content (i.e., Shannon's entropy) is defined as

$$H(X) = -\sum_{x\in X} p(x)\cdot\log_2 p(x) \tag{6}$$

for a set of events X with probability of occurrence $p(x_1)$, $p(x_2), \ldots, p(x_n)$. Among all distributions with n possible events, H attains its maximum of $\log_2 n$ for the uniform distribution. This is intuitively clear for the average information content is equivalent to our uncertainty about which event will occur. In other words, Shannon's entropy measures how much information is "produced" by the random variable. For an event that will certainly occur H is equal to 0.

To apply (6) to binary vectors, we consider individual bits as realisations of a binary random variable (i.e., possible outcomes are "stained" or "nonstained"). In this case H is called the binary entropy function and attains its maximum for $p(1) = p(0) = 0.5$. We replace the theoretical probabilities by empirical frequencies, $p(0)$ and $p(1)$, and calculate Shannon's entropy as

$$H(\vec{r}) = -\left(p(0) \cdot \log_2 p(0) + p(1) \cdot \log_2 p(1)\right). \quad (7)$$

More detailed structures can be captured by considering words of length L of a binary vector. Then, Shannon's entropy is calculated based on the frequencies of these words. A normalization by L yields the metric entropy

$$I_{\mathrm{ME}\,L}(\vec{r}) = \frac{1}{L} \cdot H\left(\mathscr{W}_L(\vec{r})\right), \quad (8)$$

where H is the generalisation of Shannon's entropy in (7) for words of length L. Particularly, the random variable X from (6) is defined to pick an arbitrary word of length L from $\vec{r}$. $\mathscr{W}_L$ is a sliding window function that moves through the image row $\vec{r}$ to produce the different words. The metric entropy gives useful values only if $m \gg L$. For our images we chose $L = 8$. Compared to Shannon's entropy in (6), the metric entropy allows for assessing the correlation structure inside words. Indeed, metric entropy attains its maximum when single pixels in the words are uncorrelated and decrease for correlated pixels. For binary sequences $I_{\mathrm{ME}\,L}$ is confined to the interval $[0, 1]$.

Special care should be taken when calculating image index functions for soils with an uneven soil surface. Actually, pixels not belonging to the soil should be excluded from the analysis. Therefore, to differentiate between soil and nonsoil on the ridged surface of RT, $\mathrm{RT_{pm}}$, and $\mathrm{RT_{pm+crops}}$, we used the background binary images (Figure 1(b)). Areas identified as nonsoil were omitted. Additionally, we discarded the first and the last profiles completely because of edge effects and used 8 images for CT, RT, and $\mathrm{RT_{pm}}$ and 5 images for $\mathrm{RT_{pm+crops}}$. The image indices were calculated in R [29]. Figure SF3 in the online Supplementary Material shows a profile from $\mathrm{RT_{pm}}$ with three different image indices.

3. Results

3.1. Properties of the Topsoils. The analysis of the topsoils revealed large differences between soils in the forest and on dryland fields (Table 2). Indeed, we found larger contents of C, N, and SOM (by a factor of 10) in the forest than in agricultural topsoils. Additionally, the clay fraction was more abundant and clay and silt together made up more than 50% of the soil fine fraction in the forest versus less than 30% on the dryland fields. We consider the forest soils as essentially anthropogenically unaffected. Therefore, these differences underpin the strong anthropogenic transformation of agricultural soils in the former forested catchment.

Table 2: The average topsoil properties of 32 dryland fields and 16 forest sites in the Haean catchment.

Parameter	Dryland sites		Forest sites	
	Mean (%)	Std. dev. (%)	Mean (%)	Std. dev. (%)
N	0.06	0.02	0.41	0.17
C	0.53	0.30	5.77	2.47
SOM[a]	0.98	0.53	9.92	4.25
Clay	5.43	2.98	12.27	4.87
Silt	22.32	7.10	38.81	9.79
Sand	72.26	9.97	48.91	14.01

[a]Soil organic matter; note that SOM of forest sites was estimated by multiplying C by 1.72.

These changes are also evident when comparing topsoil and subsoil properties of the experimental sites (Table 1). The allochthonous nature of these topsoils is reflected in the remarkable jump in texture. Indeed, the clay content increases from 2–8% up to approximately 21% from the topsoil (Ap and Ap1–Ap3) to the subsoil (2Apb).

3.2. Dye Tracer Experiments

3.2.1. Processes on Soil Surface and Soil Water Content. We observed the largest infiltration and the smallest runoff on CT (Table 3). However, the sediment load measured in runoff and the overall erosion were relatively high. The surface topography under RT decreased the amount of infiltrated water and increased the surface runoff. Concurrently, the erosion decreased compared to CT due to the barrier effect of the ridges. On $\mathrm{RT_{pm}}$ the surface topography and plastic mulching of the ridges led to the largest surface runoff and soil erosion. Actually, approximately 50% of the irrigated water contributed to the runoff, and the erosion rate more than doubled compared to CT. Although the plastic mulching protected the soil in the ridges, the soil in the furrows was more susceptible to erosion due to the high runoff energy. By contrast, on $\mathrm{RT_{pm+crops}}$ the infiltration increased again and the surface runoff decreased to 31% probably due to the crop canopy. Indeed, the interception and the throughfall of irrigated water might have reduced the formation of surface runoff as well as the erosion potential.

At the beginning of the dye tracer experiment on CT the water content in 5 cm depth was lower compared to 20 cm depth (Figure 2). Approximately 15 minutes after the start of irrigation, the sensors placed in 5 cm depth registered an increase of water content, while the rise in 20 cm depth was delayed. Although the soil surface was even, the whole plot was inclined which explains larger soil moisture values measured by the FDRs situated downslope (FDR 2 and FDR 4).

On plots RT and $\mathrm{RT_{pm}}$ we found larger water contents in furrows at the beginning of irrigation. This was probably caused by previously preferentially infiltrated water due to

Table 3: Total amount of irrigation, infiltration, surface runoff, sediment load, and erosion during the dye tracer experiments.

Experiment	Total amount of irrigated water (L)	Infiltration		Runoff		Sediment load (g)	Erosion (g m^{-2})
		(L)	(%)	(L)	(%)		
CT[a]	87	69	79	18	21	151.41	75.71
RT[b]	74	46	62	28	38	66.59	33.30
RT_{pm}[c]	81	41	50	41	50	322.45	161.23
$RT_{pm+crops}$[d]	91	63	69	28	31	54.02	27.01

[a]Conventional flat tillage, [b]ridge tillage, [c]ridge tillage with plastic mulch, [d]ridge tillage with plastic mulch and potato crops.

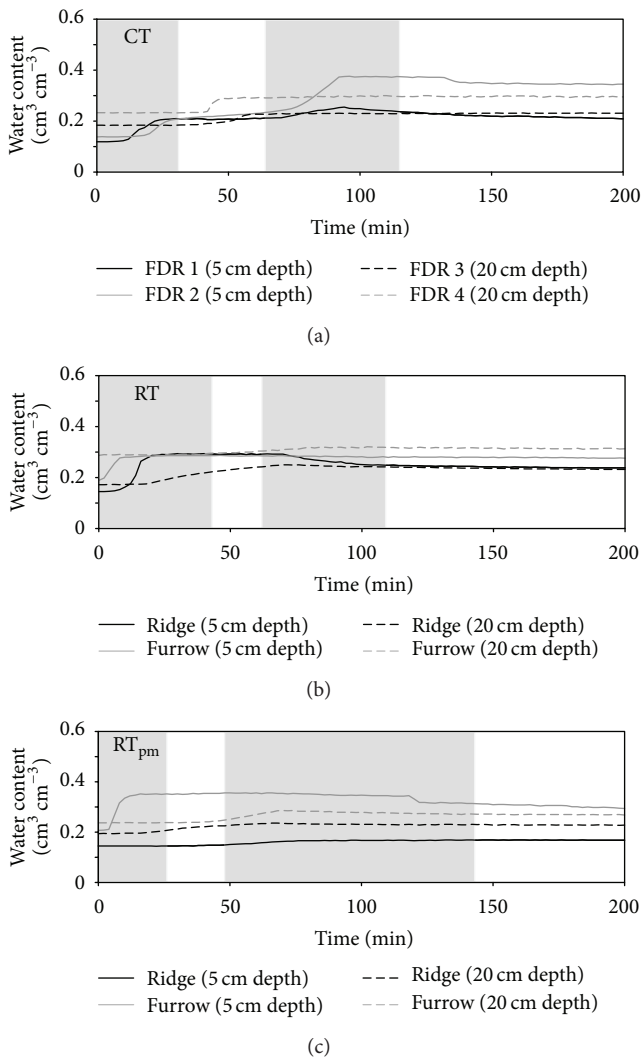

Figure 2: The dynamics of water content in different depths during the dye tracer experiments CT, RT, and RT_{pm}. The grey area indicates the time of irrigation.

topography effects. In 5 cm depth on RT the water content rose first in furrows, since the runoff from the ridges accumulated there and then in ridges. It increased only slightly in 20 cm depth.

During the irrigation on RT_{pm} the dynamics of water content was comparable to RT except on ridges that were covered with plastic mulch. There, it increased slightly only in 20 cm depth probably due to water which infiltrated primarily in the furrows and was subsequently funnelled laterally to the ridges.

3.2.2. Analysis of Flow Patterns. The dye tracer experiments revealed that firstly, tillage produced zones of preferential infiltration, namely, furrows and planting holes, and zones of no infiltration, namely, plastic mulched ridges (Figure 3). Therefore, the patchiness of the patterns and the occurrence of preferential flow are the result of the soil surface topography.

Secondly, the layer boundary between the spread topsoil and the subsoil was the most important feature for water movement in these agricultural soils. This was clearly shown by the decrease of all indices to zero in approximately 25–35 cm depth (i.e., between the horizons Ap and Bwb on site 1 and between the horizons Ap1 and Ap2 on site 2, resp.) (Figure 4).

Thirdly, the shape of the index curves showed that in our experiments water flow occurred in the topsoil and was funnelled preferentially above the layer boundary. Actually, the vertical propagation to the deeper soil horizons via macropores, fissures, and cracks was absent. This was also confirmed by comparing the Brilliant Blue stained patterns to the iodide patterns. The propagation of the iodide tracer solution was similar to that of Brilliant Blue FCF.

The effect of the *ridge topography* can be best seen when comparing the indices I_F and $I_{Q\,0.95}$ on CT and RT. While the topsoil on CT was homogeneously stained, the patterns on RT consisted of alternating stained furrows, unstained parts on the sides of the ridges, and stained inner parts due to infiltration in planting holes (Figure 3). This was well reflected by a larger I_F (max = 0.87 on RT versus max = 0.73 on CT) and a smaller $I_{Q\,0.95}$ (max = 0.72 on RT versus max = 1.00 on CT) that indicated more fractioned patterns with smaller stained objects on RT. The dye coverage I_D was large on both plots with its maximum being on the top of the soil profile. Due to the height of the ridges, I_D decreased slower on RT than on CT. Additionally, we calculated the smallest values of metric entropy I_{ME8} near the soil surface because this part of the profile was homogeneously stained and the correlation between pixels inside the different words was large. Finally, in all four experiments I_E was approximately 0.1, which is quite small and reflected the few stained objects.

The effect of the *plastic mulch* can be best extracted by comparing I_D and $I_{Q\,0.95}$ on RT and RT_{pm}. On RT, I_D was largest (max = 1.00) on the soil surface as a result of

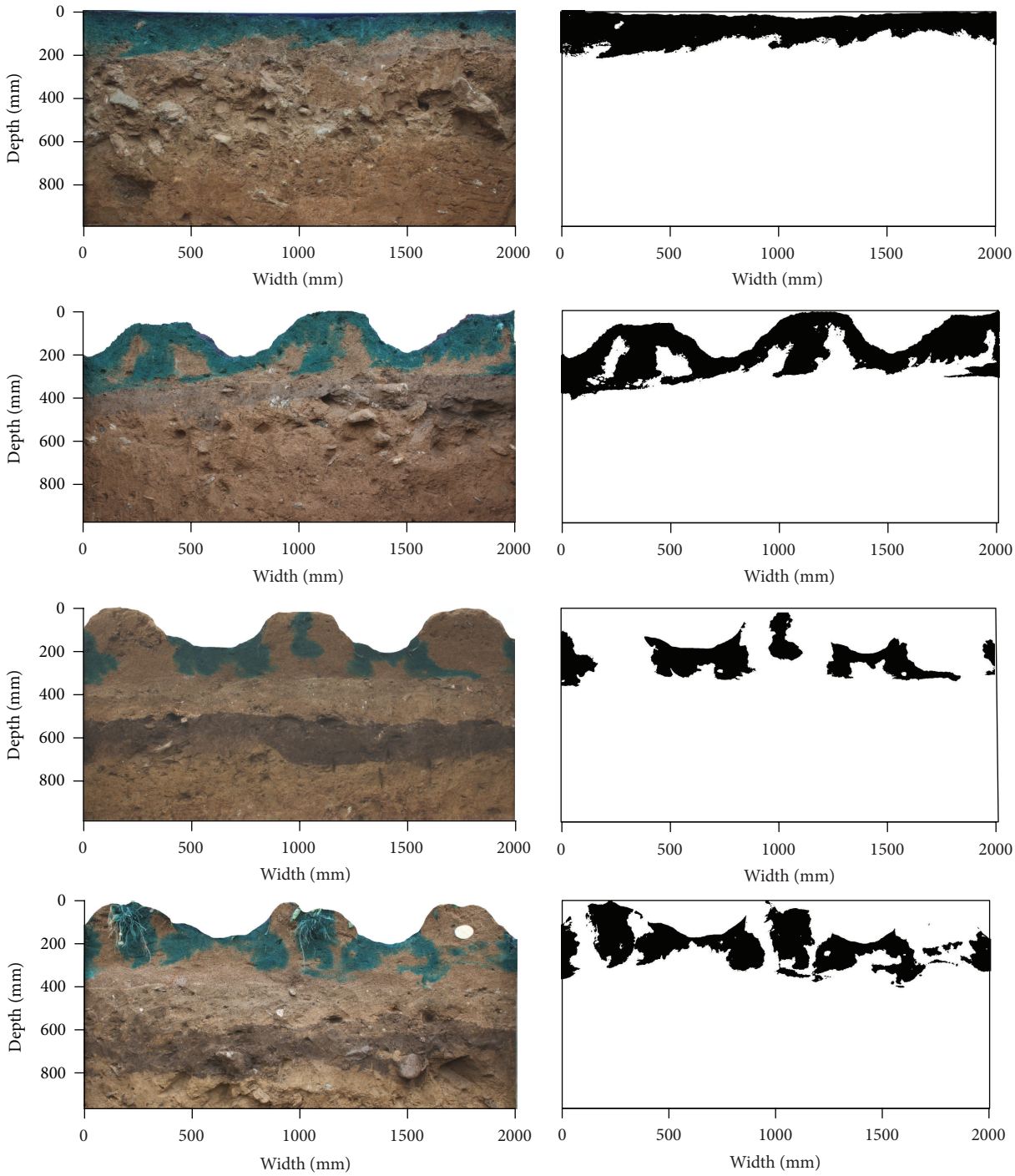

Figure 3: Example images of excavated soil profiles and their binary images. From top to bottom: CT, RT, RT_{pm}, and $RT_{pm+crops}$. Note that the slope orientation differs between field site 1 (CT and RT, slope oriented to the left) and field site 2 (RT_{pm} and $RT_{pm+crops}$, slope oriented to the right). In the colour image of $RT_{pm+crops}$, the white object on the right hand ridge is a potato cut in half.

a homogeneous infiltration. In contrast, I_D on RT_{pm} increased to a maximum of 0.53 in 20 cm depth indicating the large surface runoff from the plastic mulched ridges into furrows where most of the irrigated water infiltrated preferentially. Additionally, because the tracer could not infiltrate into the plastic covered ridges, the stained objects on RT_{pm} were smaller as indicated by a decrease in $I_{Q\,0.95}$. In fact, the homogeneous matrix flow on RT at the soil surface was reflected by a large $I_{Q\,0.95}$ (max = 0.72), whereas the largest $I_{Q\,0.95}$ (max = 0.21) on RT_{pm} marked the depth of the furrows and the laterally funnelled water above the layer boundary.

The effect of the *root system* on dye patterns was only slightly apparent in larger I_D in approximately 20 cm soil depth on $RT_{pm+crops}$ compared to RT_{pm}. The stem flow water

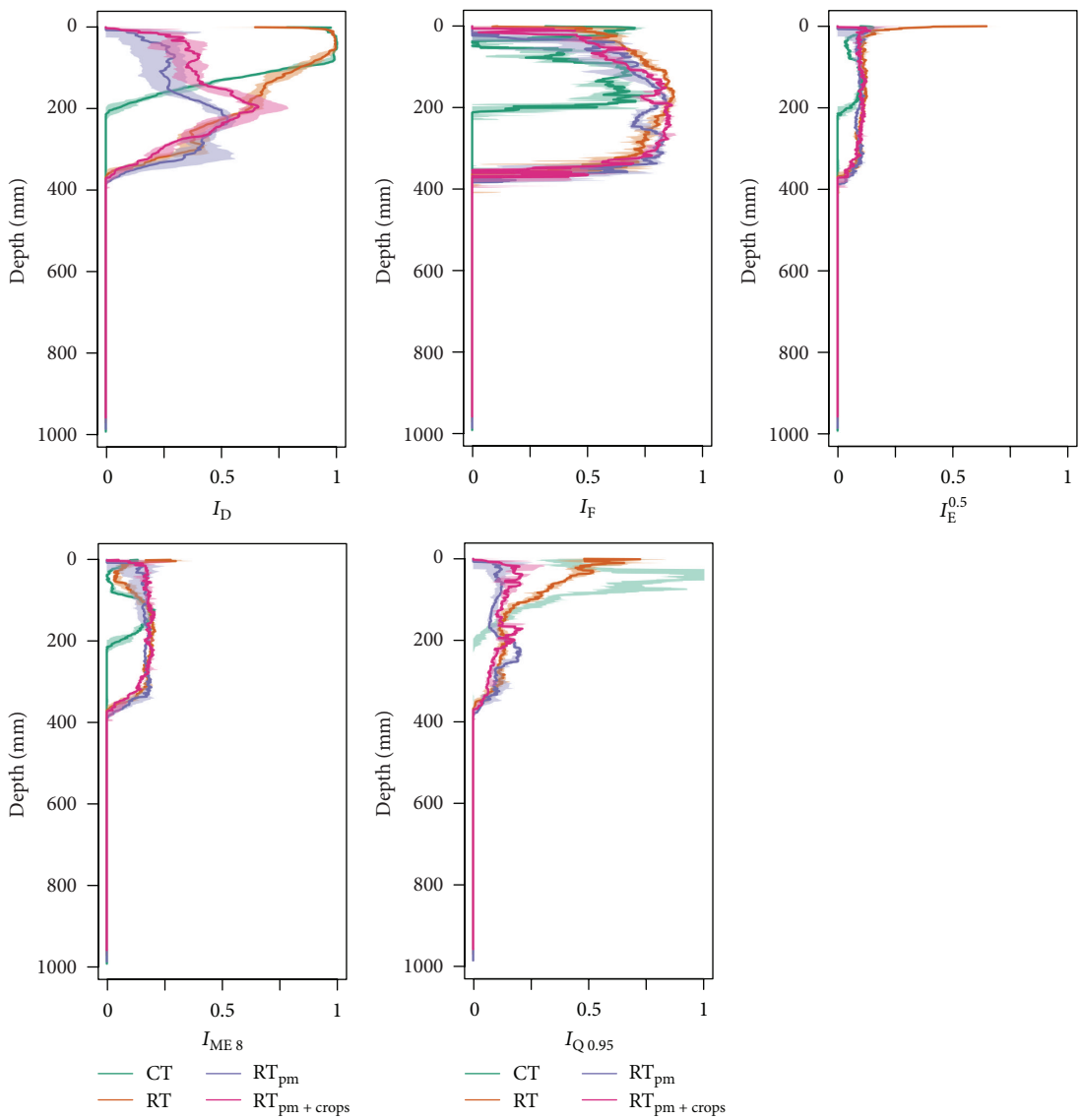

Figure 4: Image index functions and their 25% and 75% quantiles (colored areas): dye coverage I_D, fragmentation I_F, Euler number I_E, metric entropy I_{ME}, and maximum run length $I_{Q\,0.95}$. The Euler number I_E was scaled to enhance the details. The large values of I_E on RT near the soil surface are an artefact of the image processing.

primarily ponded in the planting holes. After infiltration the tracer solution flew preferentially along roots, which resulted in a maximum of I_D (0.66) in the root zone depth. In contrast, the maximum of I_D on RT_{pm} without crop roots occurred in the depth of the furrows (0.53) and a less pronounced increase was visible in the depth of the layer boundary (in approximately 30 cm depth). Similarly, the largest $I_{Q\,0.95}$ reflected the infiltration in the furrows and the funnel flow above the layer boundary on RT_{pm} (0.22) and the highly stained root zone on $RT_{pm+crops}$ (0.25), respectively. Moreover, we observed another important factor which was best visible in the profile pictures (Figure 3). On $RT_{pm+crops}$ water movement in slope direction was no longer pronounced compared to RT_{pm}. Instead, water was primarily redirected upslope from furrows to ridges. We attributed this lateral flow to the hydraulic gradient between ridges and furrows. A similar situation was described by Ruidisch et al. [30] who found the lowest pressure heads in the inner part of the plastic mulched ridges due to root water uptake.

4. Discussion

4.1. The Effect of Tillage Management on Flow Processes. Ridge tillage and plastic mulching created typical infiltration zones (i.e., furrows and planting holes) and noninfiltration zones (i.e., plastic covered ridges) resulting in soil moisture differences between furrows and ridges. Our results agree well with Saffigna et al. [31] who investigated nonuniform infiltration patterns caused by hilling and potato canopy. They observed a higher soil moisture in furrows due to runoff from

ridges. The runoff from ridges to furrows was also reported by Leistra and Boesten [32].

Additionally, we could show that ridge tillage and plastic mulching increased surface runoff and soil erosion substantially in the early growing season. The largest surface runoff and soil erosion under RT_{pm} were confirmed by Arnhold et al. [33]. They combined field measurements with runoff collectors and a process-based modelling study using EROSION 3D to analyse the influence of ridge tillage and plastic mulch on soil erosion on two potato fields in the Haean catchment. These authors reported that in the later season the developed potato canopy could decrease surface runoff due to interception and throughfall. Moreover, a developed root system had the potential to interrupt the subsurface funnel flow above the layer boundary between the sandy topsoil, and the subsoil. Ruidisch et al. [30], for example, found in their combined tensiometer and modelling study that the coverage of the ridges and the root water uptake induced a pressure head gradient that forced the water to flow from wetter furrows to drier ridges. However, the potential for interrupting the lateral subsurface flow above the layer boundary depends presumably on the intensity and amount of rainfall. In our study we can relate the occurrence of the flow from furrows to ridges only to the irrigation rates which equalled moderate rain events of 37–45 mm.

We want to highlight the former practice (that still takes place today occasionally) to distribute sandy soil material on agricultural fields prior to planting and the subsequent ploughing. Indeed, the distribution of sandy soil material to counterbalance erosion loss in the Haean catchment strongly influences the flow processes. This management practice created an artificial layering with different soil physical properties. A cohesive, denser, and finer textured subsoil is overlain by a topsoil consisting of a noncohesive and coarse material. As a result, an important textural boundary is created between the horizons. These structural differences between the topsoil and the subsoil are responsible for the funnel flow above the layer boundary. This was also reported by Petersen et al. [34] who found horizontal flow patterns due to soil layering with abrupt changes in soil structure induced by tillage.

Several authors reported that fissures, cracks, and earthworm burrows could act as preferential flow paths especially in fine textured subsoils [16, 35]. Although ploughing activities lead to a discontinuity of macropores between topsoil and subsoil [36], macropores in the deeper subsoil can still conduct water [37]. In our experiments, we could not detect any macropore flow neither in the topsoil nor in the subsoil. This can be related to the fact that the noncohesive sandy toplayer lacks macropores even before ploughing. Moreover, we did not find any macropores like fissures or cracks, which could initiate preferential flow, in the denser and finer-textured subsoil. Neither did we observe any soil burrowers on our sites, which could build a network of macropores.

4.2. Ecological Implications of the Agricultural Practice. Our results demonstrate that the risk of a vertical propagation of agrochemicals to groundwater is generally relatively low because of lack of macropores in the sandy soils. However, the lateral downhill water flow above the layer boundary between the anthropogenically modified topsoil and the subsoil seems to be ecologically relevant. Especially during the East Asian summer monsoon, when rainfall can reach more than 100 mm per day [22], the lateral flow through a coarse textured topsoil downhill may play a key role in the transport of agrochemicals. Thus, the field sites located next to the river system may represent locations for pollutants entering the water bodies.

We have shown that surface runoff, soil erosion, and subsurface water flow are reduced in the adult stage of the crop development. This also means that the leaching and erosion risk are especially high at the beginning of the growing season when the plants are juvenile and the fertilisers are recently applied. This is supported by Kettering et al. [38] who found the highest amounts of leached nitrate in a plastic mulched radish cultivation in the Haean catchment at the beginning of the growing season due to low interception and root water uptake.

However, in our experiments, the runoff still constituted one-third of the total irrigation even in the later season, when the crop canopy was well developed. We assume that the widespread usage of plastic mulching in combination with heavy monsoon events is partly responsible for higher phosphorus leaching in the Haean catchment because phosphorus is predominately transported via surface runoff. Kim et al. [9], for instance, reported that eutrophication and deterioration of water quality in downstream reservoirs in South Korea are associated with the discharge of phosphorus from agricultural dryland fields.

There are several options to reduce the risk of surface runoff and soil erosion. Arnhold et al. [33], for example, suggested reducing the herbicide application into furrows to allow for weed growth. This would increase surface roughness and, thus, enhance infiltration in furrows. The usage of perforated plastic mulch would be another conceivable option to reduce the runoff [30]. Wallace [39] recommended precision agriculture like better placement of fertiliser and a better timing of its application. Moreover, an adapted levelling, draining, and contouring could, in his opinion, lead to economic and environmental benefits. In a follow-up study Ruidisch et al. [40] simulated different scenarios of best management practices in a plastic mulched ridge cultivation system. They could show that fertiliser placement only in ridges as well as a better timing could considerably reduce the risk of nitrate leaching.

Finally, soil management in terms of a sustainable agriculture should improve the soil quality. This includes, for example, the enhancement of soil fertility and soil structure, soil carbon sequestration and the support of soil biota and bioturbation [5]. Our soil analysis showed that the spread sandy topsoils have a poor structure and a very low SOM content. Spreading of allochthonous soil material resulted in an unsustainable short-term agricultural management that still affects today's agriculture because additional large inputs of fertilisers are necessary to counterbalance the low SOM content of the soils.

Hence, agricultural practices in the Haean catchment should aim now at long-term sustainable improvement of the degraded soils. This can be achieved by soil amendments like, for example, crop residues [5], biochar [41], and/or winter cover crops. These management practices could have several advantages. Biochar, for example, was proposed to enhance plant growth as well as to bind agrochemicals, which reduces phosphate and nitrate pollution of streams and groundwater. A notable retention of N on permeable soils under rainy conditions was pointed out as a further benefit of using biochar. Additionally, the amendment of biochar is assumed to support intensive sustainable agriculture and may thus reduce the necessity of further forest clearance [41]. Winter cover crops such as legumes could increase SOM in the topsoils, protect the field sites from soil erosion after harvest, and improve the nutrient status in the soils for the following season [42]. Thus, the cultivation of adequate winter cover crops can have multiple benefits in relation to soil and water quality.

5. Conclusions

A sustainable agriculture aims at both, increasing crop yield and minimizing the impact on natural resources. Therefore, to improve or at least to maintain the quality of water and soil is of great importance. When focusing on soil and water conservation, agricultural management practices should minimize runoff, control erosion and reduce nonpoint source pollution [5]. It is difficult to decide whether an agricultural practice is indeed sustainable because it has to fulfil several different criteria. However, it is easy to decide that it is nonsustainable if it fails to fulfil one of them. A repeated distribution of infertile sandy soil on agricultural fields in order to compensate soil loss is obviously a short-term nonsustainable practice. Even though this management is nowadays only occasionally practised, the resulting anthropogenic soils should be protected from further degradation.

In our study we found that the impact of ridge cultivation with or without plastic mulch on the subsurface water flow is relatively low compared to the increase in surface runoff. Therefore, to reduce it, we suggest (i) to encourage crop production in ridge cultivation with perforated biodegradable plastic mulch and (ii) to enhance infiltration in furrows by either minimizing herbicide input into furrows or by protecting the furrows with crop residues. These practices will diminish the risk of erosion and leaching of agrochemicals, especially in the early season when crops are juvenile. Perforated plastic mulch can still maintain a positive effect on crop yield by increasing the temperature in the root zone and by weed control.

Furthermore, a particular attention should be paid to the risk of lateral downhill leaching of agrochemicals and fertilisers induced by artificial layering, especially on field sites located directly next to the stream network. Thus, we propose (iii) to promote the establishment of riparian buffer zones between dryland farming fields and the rivers.

Moreover, a sustainable long-term development of fertile topsoils by protection from erosion and return of organic material is necessary. Therefore, we suggest further research (iv) to identify the potential of soil amendments such as biochar to improve the soil carbon stock in sandy soils under monsoonal conditions and (v) to identify appropriate species of winter cover crops that could increase the SOM content of topsoils and protect the bare soil from erosion and leaching after the harvest in the autumn and winter season.

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Research Article

Assessment of Copper and Zinc in Soils of a Vineyard Region in the State of São Paulo, Brazil

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This soil acidification may increase the bioavailability of copper (Cu) and zinc (Zn) in soils. The objective of this study was to verify the concentrations of Cu and Zn in soils of a vineyard region, including sample acidification, to simulate acid rain. The study was developed in an area of vineyard cultivation, with an adjacent land having other crops grown, in the state of São Paulo, Brazil. Soil samples were collected and GPS located under different uses and coverings. The extracted solutions used to determine the available Cu and Zn forms were diethylenetriaminepentaacetic acid (DTPA), pH 7.3, and calcium chloride 0.01 M. The total forms were obtained by HNO_3 digestion. The amounts of Cu and Zn extracted using DTPA were considered high in most of the samples and were greater in the areas cultivated with vineyards that had received fungicide applications for several decades. The total forms were higher in vineyard soils. The amounts of Cu and Zn extracted using $CaCl_2$ did not have good correlation with vineyards or with other metals' forms. The results confirmed that the soil was enriched with Cu and Zn due to the management of the vineyards with chemicals for several decades.

1. Introduction

Soil conservation is fundamental for the sustainable development and preservation of ecosystems and biodiversity. The soil is exposed to contamination through several anthropic activities, mainly agriculture. The contamination of soil by heavy metals results in a high risk of its productive capacity and of the balance of the ecosystems [1].

Soil has a diverse heavy-metal concentration that is dependent on the parent material from which it is formed, the formation processes, and the composition and proportion of the components of the solid phase [2]. This concentration may be affected by several anthropic activities, including irrigation, fertilizer and chemical applications, and industrial or urban sewage incorporation [3, 4]. Moreover, the concentration, distribution, and bioavailability of heavy metals in the environment are influenced by the soil type, topography, geology, and erosive processes [5].

Cultivation may cause soil contamination by heavy metals, specifically copper in vineyard areas [1, 6, 7]. The intensive use of agrochemicals with Cu and Zn in their composition may pollute the soil [8–10]. Historical and current applications have resulted in Cu accumulation in the soil, and total Cu quantities have been measured in vineyards worldwide. High concentrations of fungicide-derived copper in orchard and vineyard soils have been reported from around the world, for example, Brazil, 36–3,215 mg kg^{-1} [11]; Champagne/France, 100–1,500 mg kg^{-1} [12]; India, 29–131 mg kg^{-1} [13]; and Australia, 1–223 mg kg^{-1} [14]. It has been suggested that areas with greater humidity and precipitation, such as Brazil or Champagne, France, exhibit higher Cu concentrations than dry environments, due to higher Cu use [10].

The acidification of soil and surface water is a serious concern in society today [15–17]. The acid rain and resulting soil acidification are a real problem in São Paulo state due to

Table 1: Descriptive statistics of soil attributes in the vineyard and other uses in the region studied.

Variable	Unit	Vineyard				Other uses			
		Minimum	Maximum	Average	STD	Minimum	Maximum	Average	STD
Organic matter	$g\,L^{-1}$	17.0	55.0	34.4	10.9	13.0	82.0	33.0	14.2
CEC	$cmolc\,L^{-1}$	6.07	31.2	12.2	6.49	4.55	15.1	8.05	2.64
Base saturation	%	37.0	95.0	67.5	16.8	10.0	93.0	42.9	21.0
Clay	$g\,kg^{-1}$	150	313	223	41.8	125	450	254	66.9
Silt	$g\,kg^{-1}$	75.0	226	142	38.7	74.0	243	154	41.7
Sand	$g\,kg^{-1}$	562	729	635	41.9	346	788	591	82.9
CuT	$mg\,kg^{-1}$	10.0	40.5	20.7	8.41	4.65	80.3	13.4	11.7
ZnT	$mg\,kg^{-1}$	14.3	243	53.4	43.0	6.48	225	45.7	40.2
pH $CaCl_2$		4.20	6.50	5.16	0.62	3.70	6.40	4.70	0.63
pH $CaCl_2$ after acidified		3.63	6.97	4.96	0.92	3.33	6.60	4.31	0.70
CuDTPA	$mg\,kg^{-1}$	2.80	15.5	6.79	3.27	1.30	15.4	2.69	2.18
CuDTPA after acidified	$mg\,kg^{-1}$	2.59	22.1	9.11	4.89	1.26	20.0	3.47	2.82
ZnDTPA	$mg\,kg^{-1}$	4.80	25.0	11.8	5.63	1.40	24.8	5.39	4.75
ZnDTPA after acidified	$mg\,kg^{-1}$	5.02	29.9	13.7	6.47	0.97	28.0	5.64	5.37
CuCaCl	$mg\,kg^{-1}$	0.01	0.12	0.08	0.03	0.01	0.61	0.06	0.10
CuCaCl after acidified	$mg\,kg^{-1}$	0.03	0.08	0.05	0.01	0.02	1.23	0.07	0.19
ZnCaCl	$mg\,kg^{-1}$	0.01	2.58	0.73	0.73	0.01	8.97	1.17	1.67
ZnCaCl after acidified	$mg\,kg^{-1}$	0.01	3.11	1.37	1.11	0.03	4.54	1.09	1.05

STD: standard deviation.

the intense industrialization [18], and the soils in the region studied here are considered the most sensitive to acidification in Brazil [19].

Statistical and geostatistical techniques can assist in the interpretation of research in soil pollution by heavy metals [1, 20, 21].

The objective of this study was to verify the concentrations of Cu and Zn in the soils of a vineyard region, including the acidification of the samples, with the objective of simulating acid rain.

2. Materials and Methods

The study was performed in a 59.8 ha catchment area in Jundiaí, São Paulo state, Brazil (23°11′ S, 46°53′ W), which is occupied by 2.9 ha vineyard (Figure 1) that is ten to sixty years old, has natural vegetation, pastures, and other types of orchards in the vicinity, and is 672–755 m altitude. The landscape is rolling and hilly in a geomorphological province that is dominated by a "half-orange" type of relief. The soil types in the area are inceptisols, ultisols, and oxisols [22], and the main original rock is the schist. The descriptive statistics of soil attributes are presented in Table 1.

The spatial data were uniform made and were GPS located based on satellite images with high-spatial resolution. An interpretation of land use and cover was made with detailed field checking based on an IKONOS II mosaic (orbital point 159539, on July 4, 2001, at 13:19 PM and on November 08, 2001, at 13:24 PM). The land use/land cover map and the topographic data were utilized to plan the soil sampling, ultimately establishing a total of one hundred sample points. These points were georeferenced and integrated in a vectorial format in the geographic information system (GIS).

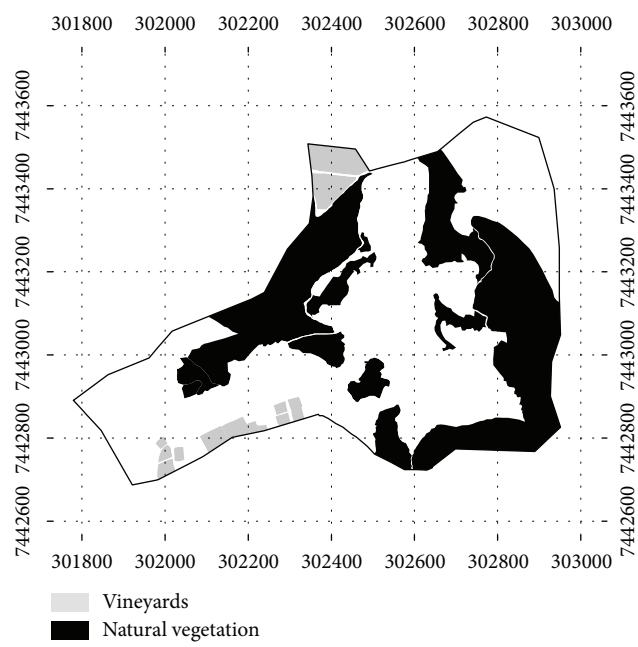


Figure 1: Area of study in a vineyard region of São Paulo state, Brazil.

At this stage, the area was traversed. With the help of an auger, 67 georeferenced perturbed soil samples at 0–0.15 m depth were collected, including 37 from the vineyard and 30 from the land under other crops grown. The samples were air dried, crushed, and passed through a 2 mm sieve.

The 67 soil samples (100 g each), after being dried and sieved, were assembled in glass percolation columns and treated with 20 mL of HNO_3 0.1 mol L^{-1} and 100 mL of

deionized water to eliminate the H+ excess and alter their pH, as described by Camargo and Raij [23]. The samples were incubated for 15 days for a complete acidification reaction and were then dried, sieved, and chemically analyzed for the bioavailability of Cu and Zn. The CuT and ZnT concentrations were determined using HNO_3 according to the procedure described in the U.S. EPA 3051 method [24]; the available form was determined using DTPA pH 7.3 (CuDTPA and ZnDTPA) [25] and $CaCl_2$ 0.01 mol L^{-1} (CuCaCl and ZnCaCl) [6, 26] extractions. The Cu and Zn levels in the digestion extracts were determined by ICP-OES.

A descriptive statistical analysis was used for calculation. The discriminate analysis (DA) is a method of dependence analysis and is a special case of canonical correlation. In this study, the DA was first used to reveal whether the land use patterns differed significantly in terms of Cu and Zn concentrations. To analyze the spatial variability, the geostatistical analysis [27, 28] was used through the elaboration and adjustment of semivariograms and data interpolation by kriging for mapping.

3. Results and Discussion

3.1. General Soil Characteristics. The physicochemical characteristics and element contents are summarized in Table 1. The selected soils were naturally acidic to slightly acidic (1 M $CaCl_2$ pH range 3.7–6.5), with an average value of 5.1, with textures that varied from loam (common in soils developed from schist or slate) to sandy loam (typical for granite soils). The soil samples taken in this region had large sand contents (346–788 g kg^{-1}), and the loam or sandy loam textures that are typical of soils were developed over granites.

Cation exchange capacities (CEC) ranged from 6.07 to 31.2 $cmol_c L^{-1}$ (Table 1). The highest values of CEC were found in vineyard soil.

Soil organic matter contents were generally high but varied widely, ranging from 13 to 82 g L^{-1} (Table 1). The soil organic matter content is useful to give an idea of the texture of the soil, with values up to 15 g L^{-1} for sandy soils, between 16 and 30 g L^{-1} for medium texture and 31–60 g L^{-1} for clay soils. Values above 60 g L^{-1} indicate the accumulation of organic matter in the soil, generally by poor drainage or high acidity. The highest values of organic matter were found in forest soils (82 g L^{-1}) and vineyard soils (55 g L^{-1}).

3.2. Total Cu and Zn Concentrations. The total Cu content in the vineyard and in soil under other uses in the region varied between 10 and 40.5 mg kg^{-1} and between 4.7 and 80.3 mg kg^{-1}, respectively (Table 1).

The total Cu values are generally higher than or similar to those reported by Kabata-Pendias and Pendias [29] for natural soils, whose typical values ranged from 13 to 24 mg kg^{-1}, depending on the soil type. On the other hand, the total Cu values are generally lower than or similar to those reported by Brun et al. [26] in Southern France (30 to 250 mg kg^{-1}) and by Fernández-Calviño et al. [7] in the Northwest Iberian Peninsula (25 to 666 mg kg^{-1}). The differences could reflect different application rates as well as different physical and chemical parameters in the soils, but we do not have enough information to discern diverse possibilities.

The total Zn content in the vineyard and in soil under other uses in the region varied between 14.3 and 243 mg kg^{-1} and between 6.48 and 225 mg kg^{-1}, respectively (Table 1). The total Zn values are generally higher than or similar to those reported by Alloway [30] for natural soils, whose typical values ranged from 10 to 300 mg kg^{-1}, depending on the soil type. Only 25% of samples exceeded the average Zn concentrations reported by Alloway [30] for soils (50 mg kg^{-1}). The total Zn values are generally higher than or similar to those reported by Fernández-Calviño et al. [31] in vineyard soils (60 to 149 mg kg^{-1}).

The total concentrations of Cu and Zn in the area compared to the soil reference values (mg kg^{-1}) from São Paulo state range from 35 to 60 mg kg^{-1} and from 60 to 300 mg kg^{-1} [32], respectively. It was observed that only three topsoil samples (3%) had a concentration higher than the reference value for Cu and that only one sample presented a concentration higher than the prevention values. The higher total Cu concentrations were observed in soils under vineyard, palm, and *Typha*. The area with palm had previously been cultivated with vineyards for decades, and the soil under *Typha* vegetation represents a wetland that is in a lower altitude position of the study area, which most likely received contaminated sediments from the higher parts of the landscape. These results clearly demonstrate the risk of contaminating the adjacent areas and the power of Cu permanency in the soil.

Because many vineyards are located on steep slopes, intensive erosion furtherly influences Cu mobility in these soils and thus increases the risks associated with groundwater contamination.

The effect of landscape on copper levels in soils is unclear. Sediments in Galicia (Spain) river valley were found to have higher copper levels than nearby vineyard soils [33]. Rusjan et al. [34] found that amongst plains, plateaus, and terraces, copper levels were highest on terraces.

The copper content in vineyard soils is attributed to factors such as frequency of pesticide application and local climatic conditions. Studies from France and Italy demonstrate that vineyard soils in wet regions contain more copper than in dry regions [26, 35]. Deluisa et al. [35] attributed this effect to differences in soil type and precipitation, the latter encouraging greater use of copper. However, Pietrzak and McPhail [36] did not see a difference in copper application between humid regions and drier regions. The vineyards situated in the region where humid climate dominates (Gippsland region) generally do not receive greater annual application of copper-based fungicides than vineyards located in subhumid conditions (Rutherhglan region). The local factors of each vineyard (e.g., slope, exposure, amount of sun received, surrounded vegetation, and wind breakers) play important roles in controlling any outbreaks of diseases and at the same time influence the use of fungicides. Other authors have suggested that erosion, leaching, and plowing are the main determinants [37].

For the Zn total concentration, 14 topsoil samples (21%) presented concentrations higher than the reference values in both vineyard and soil used to grow pears. These results indicate that agricultural management contributed to soil contamination with Cu and Zn.

3.3. Available Cu and Zn Concentrations and Soil Attributes. Although the total Cu and Zn soil concentrations are a fair indication of availability, including deficiency or oversupply, they do not provide conclusive information about the environmental impact of this availability. The Cu and Zn availability to the biota, when used as nutrients or toxic elements, and their mobility are important factors to consider when investigating the effect of these metals on the environment. In this context, the available concentrations of Cu and Zn seem to be the best indicator to make inferences about the potential environment impacts of these elements.

The concentrations of Cu and Zn extracted using DTPA may provide information about the elements' availability for plant nutrition [38] and their potential to pollute the soil [39]. The Cu concentration in topsoil varied from 1.3 to 15.5 $mg\,kg^{-1}$, with a mean of 4.3 $mg\,kg^{-1}$ (CuDTPA), and from 0.01 to 0.61 $mg\,kg^{-1}$, with a mean of 0.06 $mg\,kg^{-1}$ (CuCaCl) (Table 1). The highest concentrations of Cu extracted using DTPA occurred in soils under the same use as that used to obtain the total Cu. However, for Cu extraction with $CaCl_2$, the highest Cu concentration which occurred in soils under experimental vineyards differs from the highest total and DTPA Cu concentrations which occurred in experimental and commercial vineyards.

The Zn concentration in topsoil varied from 1.4 to 25.0 $mg\,kg^{-1}$, with a mean of 8.1 $mg\,kg^{-1}$ (ZnDTPA), and from 0.01 to 8.97 $mg\,kg^{-1}$, with a mean of 1.0 $mg\,kg^{-1}$ (ZnCaCl) (Table 1). The higher concentration of available Zn occurred in soils under vineyards and natural vegetation, indicating that the high available Zn concentration may be explained by anthropogenic pollution. Despite the application of agrochemicals, the same finding was observed for the total Zn, that is, the natural concentration of the element once it also occurs in some natural vegetation land uses (Table 1).

According to Student's t-test ($P < 0.05$), topsoils in vineyards had higher concentrations of the total form of Cu as well as that extracted by DTPA and $CaCl_2$ than did the other land uses. The same result was observed for Zn extracted by DTPA but not for Zn extracted by $CaCl_2$ or for its total form. These results show a reasonable soil contamination in vineyard areas by Cu and a probable elevation in the available Zn concentration.

The average concentrations of available forms of Cu and Zn in vineyard soils tend to be higher than the concentrations observed in soils under other uses, with exception of $CaCl_2$-extractable Cu and Zn, where the higher mean concentrations (1.23 and 4.54 $mg\,kg^{-1}$) were observed in soils under natural vegetation (Table 1).

Generally, the vineyard soils have higher pH and CEC than what is observed in soils under other uses. High CEC encourages metals to bind with soil aggregates, depending on the organic matter and the clay content of the soil. High pH enhances the dissociation of organic acids and, therefore, the formation of complexes with metals, altering metal speciation and reducing bioavailability [40].

3.4. Available Forms of Cu and Zn after Acidification. Considering all of the surface samples acidified (Table 1), there is a slight increase in Cu content in the soil, which ranged from 1.26 to 22.1 $mg\,kg^{-1}$, with a mean of 5.7 $mg\,kg^{-1}$ (CuDTPA), and from 0.02 to 1.23 $mg\,kg^{-1}$, with a mean of 0.06 $mg\,kg^{-1}$ (CuCaCl). As observed in the natural, nonacid samples, the maximum values of Cu were found in areas that were occupied by vineyards and *Typha*.

The soil acidification revealed higher concentrations of DTPA-extractable Cu and Zn, which were not observed for $CaCl_2$-extractable Cu and Zn. These results indicate that the DTPA method was more sensitive to soil acidification for simulating acid rain than was $CaCl_2$. These results disagree with those obtained by Brun et al. [26] that indicated the $CaCl_2$ extractant as the best for the available forms of Cu in vineyard soils. Such disagreement is probably due to differences between the original pHs of these soil regions.

The statistical method used to compare the Cu and Zn concentrations extracted both with and without acidification was linear regression ($Y = b0 + b1X$), as suggested by J. C. Miller and J. N. Miller [41]. The null hypotheses were that the declivity ($b1$) would not be different from one (1) and that the intercept ($b0$) would not be different from zero (0). These hypotheses were tested by calculating the confidence limits at 95% for both coefficients. The results were also submitted to an analysis of variance (F-test) and to correlation.

According to the regression analyses of Cu and Zn extracted by DTPA, the intercept is equal to zero (0), and the angular coefficient is higher than the unit (1). These results indicate that the acidification promoted more metal extraction (Table 2). Then, the soil acidification increased the availability of Cu and Zn, thus increasing the risk of environmental contamination. Moreover, in Jundiai, an undulated relief is predominant [22, 42], and the soil erosion potential is high which is reflected by the slope and, in some cases, the texture gradient of the ultisols. In this landscape, erosion may thus transport sediments that have been contaminated with Cu to the lower regions, thus increasing the environmental impact of Cu contamination. Excessive amounts of hydrogen ions, introduced into the soil by acid rain or fertilization, can release Cu through cation exchange. The metal mobilized in the soil can thus eventually enter aquatic systems through rainwater or can enter groundwater, rivers, and lakes. Rivers draining cultivated areas with high soil Cu concentrations can also have high Cu concentrations [43]. In the case of vineyard soils, which are the most easily eroded cultivated soils [44], applied Cu can reach water bodies not only in water-soluble forms but also, due to erosion, in colloid-bound forms that can accumulate below the water body in sediments. In vine growing areas, evaluating the risk of water quality that is posed by the use of copper-based fungicides therefore requires determining the Cu levels and the distribution of Cu among its more and less bioavailable forms in both vineyard soils and the sediments of local water bodies.

Table 2: Regression coefficients for the available forms of Cu and Zn extracted by DTPA and $CaCl_2$; natural (independent variable) and acidified (dependent variable) samples.

Element/method	r^2	Intercept			P	Angular coefficient			P
		Min.	Average	Max.		Min.	Average	Max.	
CuDTPA	0.95	−0.61	−0.18	0.24	0.39	1.29	1.37	1.44	<0.01
ZnDTPA	0.94	−0.88	−0.17	0.53	0.62	1.06	1.13	1.20	<0.01
CuCaCl	0,15	0.028	0.033	0.038	<0.01	0.053	0.126	0.200	<0.01
ZnCaCl	0.59	0.401	0.611	0.820	<0.01	0.480	0.605	0.730	<0.01

Table 3: Correlation coefficients between forms of Cu and Zn and other soil attributes.

	CuT	ZnT	CuDTPA acidified	ZnDTPA acidified	CuCaCl acidified	ZnCaCl acidified
Organic matter	0.49*	0.15	0.27	0.57*	0.12	−0.28
pH	0.37*	−0.09	0.33	−0.25	−0.01	−0.87*
CEC	0.52*	0.08	0.22	−0.01	0.10	−0.60*
Bases saturation	0.45*	−0.05	0.35	−0.06	0.00	−0.88*
CuDTPA	0.72*	0.52*	0.97*	0.44*	0.14	−0.18
ZnDTPA	0.49*	0.63*	0.47*	0.94*	0.06	0.25
CuCaCl	0.00	−0.01	−0.49*	0.12	0.20	0.25
ZnCaCl	−0.16	0.22	−0.25	0.37	0.11	0.88*
CuT	1.00	0.54*	0.70*	0.44*	0.20	−0.29
ZnT		1.00	0.47*	0.63*	−0.01	0.21
CuDTPA acidified			1.00	0.33	0.11	−0.27
ZnDTPA acidified				1.00	0.06	0.23
CuCaCl acidified					1.00	−0.02
Clay			0.45*	−0.17	−0.24	−0.18
Silt			−0.30	0.01	0.26	0.20
Sand			−0.17	0.16	−0.01	−0.01

* $P < 0.05$.

The regression analyses of Cu and Zn extracted by $CaCl_2$ show that the intercepts are higher than zero (0) and that the angular coefficients are lower than one (1). These results indicate a dual behavior in the samples. Conversely, in samples with low metal concentrations, the acidification increases the concentration of the metals, and in samples with high concentrations, the acidification promoted less extraction.

The Cu concentration extracted by $CaCl_2$ was compared to soils under either vineyard or other land uses, using Student's t-test. For both acidified and nonacidified soils, the $CuCaCl_2$ concentration was higher in vineyard soils, though the difference was greater among the nonacidified soils, with a mean of 0.076 mg kg^{-1} in vineyard soils and a mean of 0.041 mg kg^{-1} in soil under other uses. For the acidified soils, the mean in vineyard soils was 0.046 mg kg^{-1}, and it was 0.037 mg kg^{-1} for soil under other uses; the results were significant at the 0.05 level. For Zn extracted by $CaCl_2$, the results showed no difference between soils under vineyard or other uses. These results indicate that the $CaCl_2$ method could not efficiently show Zn contamination by agricultural management: the higher concentrations of Zn extracted by $CaCl_2$ occurred in soils under natural vegetation, which differ from the Zn concentrations determined by total Zn and Zn extracted by DTPA.

3.5. Relationship between Cu and Zn and Soil Attributes. Table 3 presents the correlation coefficients obtained between the Cu and Zn total and acidified forms and for the other soil properties in 27 samples of vineyard topsoil. The total Cu was correlated with soil organic matter ($r = 0.49$), pH ($r = 0.37$), cation exchange capacity (CEC) ($r = 0.52$), base saturation ($r = 0.45$), CuDTPA ($r = 0.72$), ZnDTPA ($r = 0.49$), and total Zn ($r = 0.54$), whereas total Zn was correlated only with CuDTPA ($r = 0.52$) and ZnDTPA ($r = 0.63$).

Brun et al. [26], comparing various soil extractors, observed that Cu extracted by 0.01 mol L^{-1} $CaCl_2$ was correlated well with the soil pH (i.e., it was decreased with increasing

Table 4: Confusion matrix of land use classifications based on discriminant analysis.

Land use	To natural vegetation	To nonvineyard	To vineyard	Sum
From natural vegetation	3	2	0	5
	60%	40%	0.00%	100%
From nonvineyard	0	32	2	34
	0%	94%	6%	100%
From vineyard	0	2	25	27
	0.00%	7%	93%	100%
Sum	3	36	27	66

soil pH), which is an important property controlling the bioavailability of Cu. However, Cu extracted by DTPA at pH 7.3 was correlated only with the CEC.

High positive correlation between CuDTPA and ZnDTPA content, pH, organic matter, and base saturation was found in the same area by Valladares et al. [45] (i.e., the Cu content increases with increasing pH, organic matter, and base saturation).

Copper in soils is strongly immobilized by the composition of the soil sorption complex [10, 46] (i.e., organic matter, Fe-, Mn-oxyhydroxides, and nature of the humic substances). Soluble humic and fulvic acids may increase the solubility and mobility of the elements; once in a neutral to alkaline reaction environment, they form stable complexes with the carboxyl, hydroxyl, and amino groups of these compounds [46, 47].

The acidified forms of Cu and Zn extracted by DTPA were highly correlated with total Cu and Zn, whereas Zn DTPA showed a higher correlation with soil organic matter than did Cu. These results differ from those observed in the literature [46, 47], which correlates Cu with soil organic matter. The acidified Cu DTPA was correlated with clay content.

Unlike the Cu and Zn forms extracted by DTPA, the behaviors of the acidified forms of Cu and Zn that were extracted by $CaCl_2$ were very different. The acidified Cu extracted by $CaCl_2$ was not correlated with other soil attributes; this result should reflect the Cu forms that were released by the weathering of shale because the soils are poorly developed in the vineyards (inceptisols). No correlation between acidified and nonacidified Cu extracted by $CaCl_2$ was observed. The acidified and nonacidified Zn extracted by $CaCl_2$ had good intercorrelation and were high-negatively correlated with pH, CEC, and base saturation.

In order to determine whether the three different land uses, native vegetation, vineyard, and other agriculture activities, differed significantly in terms of Cu and Zn soil concentrations before and after acidification, discriminate analysis was used. In this way, the three land uses were entered in the calculations as the grouping variables and the soil Cu and Zn concentration forms were entered as the independent variables.

The discriminate analysis results are displayed in Figure 2, which present the groups of land uses formed according to the Cu and Zn concentrations in soil. The obtained results indicate that the three land uses had different levels of Cu and Zn concentrations in the top layer of soil, both before and after acidification. For each extracted element concentration, a high degree of between-groups variation exists, with canonical correlation values varying between 0.63 and 0.88. The Wilks' lambda statistics indicate that the difference among the land uses is significant at $P = 0.05$. The statistically significant results also show a very high percentage of correct classification, ranging from 60% to 94% (Table 4). The analysis of Mahalanobis distances indicates a

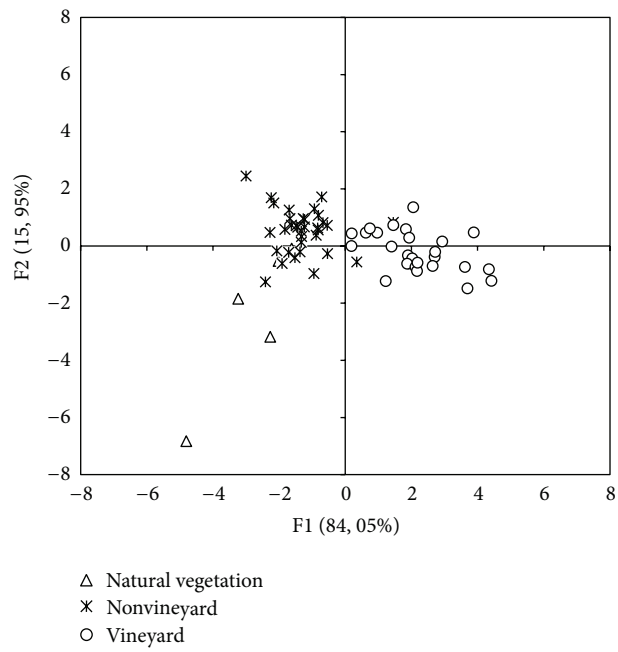


Figure 2: Factors of discriminant analysis showing land use groups formed according to Cu and Zn concentrations in soil.

Table 5: Factor loadings generated by discriminant analysis.

Variable	F_1	F_2
CuDTPA	0.798	−0.206
ZnDTPA	0.510	−0.642
CuCaCl	0.427	−0.242
ZnCaCl	−0.301	−0.853
CuT	0.661	−0.087
ZnT	0.124	0.172
CuDTPA acidified	0.768	−0.209
ZnDTPA acidified	0.559	−0.586
$CuCaCl_2$ acidified	0.369	−0.083
$ZnCaCl_2$ acidified	0.057	−0.621

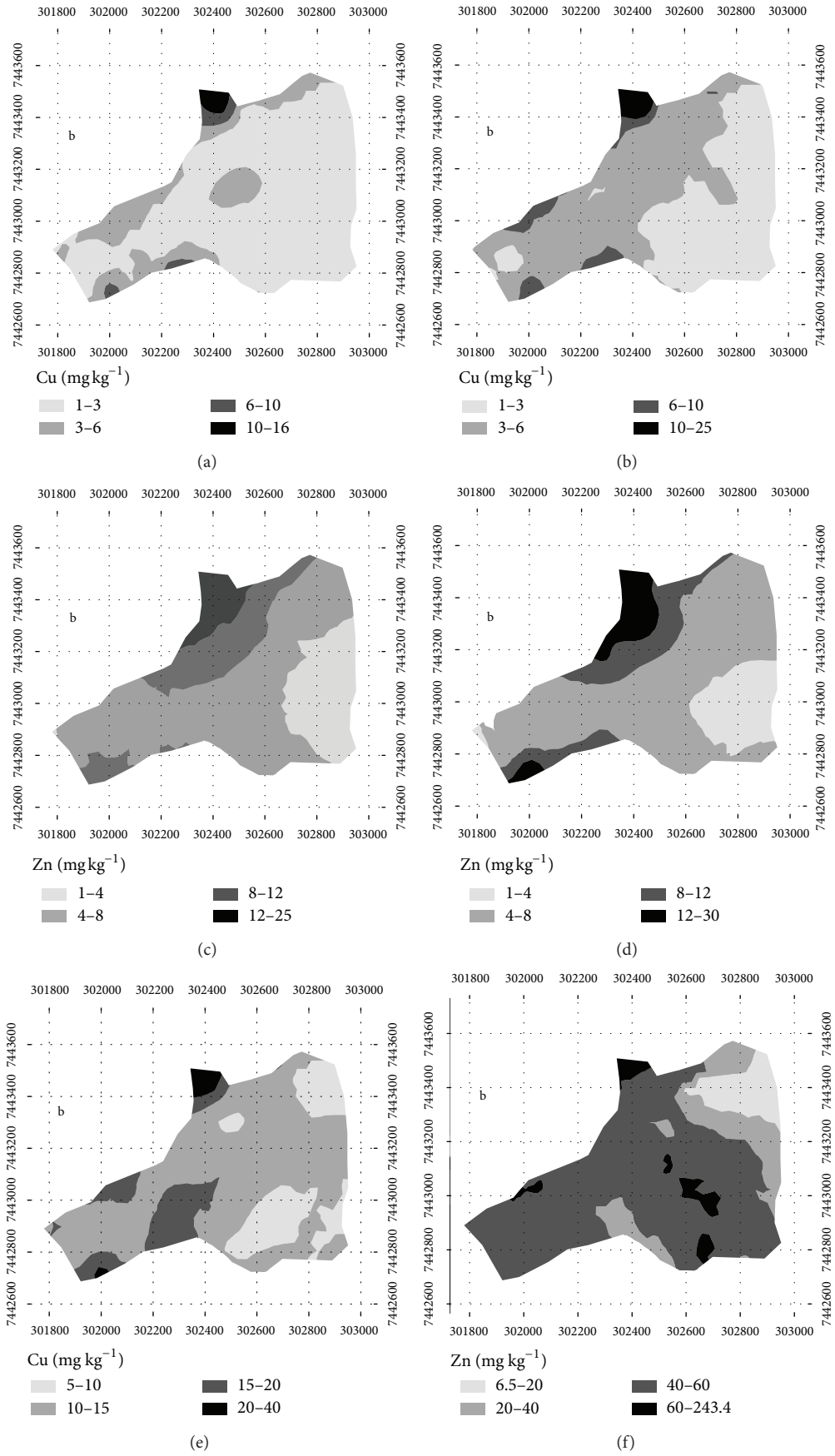
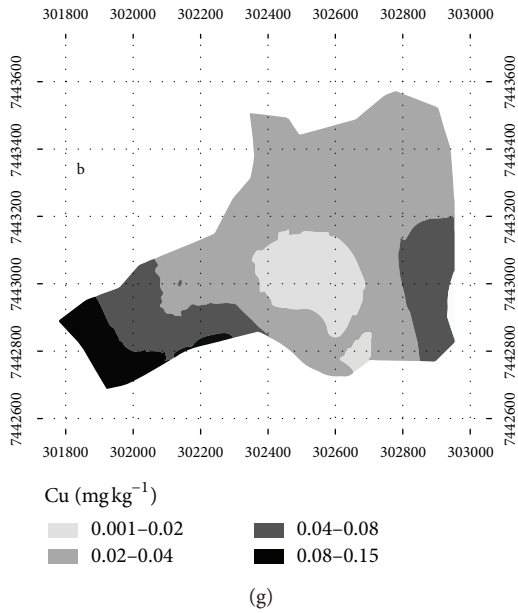


Figure 3: Continued.



(g)

Figure 3: Spatial distributions of the Cu and Zn extracted by DTPA and $CaCl_2$ in natural and acidified samples and the total content of Cu and Zn in natural soil samples. (a) and (c) Cu and Zn extracted by DTPA in natural samples; (b) and (d) Cu and Zn extracted by DTPA in acidified soil samples; (e) and (f) total content of Cu and Zn in soil; (g) Cu extracted by $CaCl_2$ in natural samples.

Table 6: Semivariograms parameters for spatial distributions of Cu and Zn in soils from a vineyard region of São Paulo state: nugget effect (C_0), sill (C), range (A), and dependency degree (GD).

Variable	C_0	C	A (m)	GD (%)	Model
CuDTPA	0.94	6.85	125.8	86	Spherical
CuDTPA acidified	2.36	12.80	125.6	82	Spherical
ZnDTPA	22.00	59.34	966.0	63	Gaussian
ZnDTPA acidified	29.70	107.40	1204.0	72	Exponential
CuT	51.66	102.18	290.5	49	Spherical
ZnT	890.00	5890.00	1666.0	85	Gaussian
CuCaCl	0.0008	0.0026	854.0	69	Spherical
CuCaCl acidified	0.0002	0.0002	—	—	Nugget effect
ZnCaCl	0.64	0.64	—	—	Nugget effect
ZnCaCl acidified	0.13	0.13	—	—	Nugget effect

highly significant probability of differences among the land uses, varying from 0.0001 to 0.003, though vineyard differed from the other land uses more significantly.

Eigenvalues explained 84.05% of variance in the first factor (Figure 2). Factor loadings generated by the discriminate analysis are presented in Table 5, which shows the groups formed by the metals' forms, indicating correlation among them. The first group with high values for factor 1 is formed by the two forms of Cu extracted by DTPA and by the total Cu. A second group is formed by the two forms of Zn extracted by DTPA. These groups indicate the high contaminations of Cu and Zn in the vineyard soils. Other forms of the metals did not have good correlations and may thus describe natural high concentrations of these metals. These results confirm the low correlation between the acidified and nonacidified forms of Cu and Zn extracted by $CaCl_2$.

Discriminate analysis shows strong differences between the Cu and Zn concentrations in the investigated land uses and that the behaviors of the forms are variable.

3.6. Spatial Distribution of Cu and Zn. Copper and Zinc concentrations extracted by DTPA, which was obtained from 67 topsoil georeferenced samples, both natural and acidified, were analyzed to determine their spatial dependence using geostatistical and semivariograms analyses (Table 6), kriging interpolation of data, and map building isolines. The spatial dependence of the samples was strong for Cu and moderate for Zn, according to the ratio of spatial dependence (GD) (Table 6). Spherical model for Cu had a good adjustment, with a nugget effect near 0 (zero). For Zn, the nonacidified soil had the best adjustment using the Gaussian model, and the acidified soil had better adjustment in the exponential model.

A change occurred in the spatial behavior of the Cu and Zn concentrations, extracted by DTPA, in natural and acidified samples (Figures 3(a), 3(b), 3(c), and 3(d)), indicating that an occurrence of acid rain or an acid fertilizer reaction would increase the amount of copper available in the area. This effect is even more pronounced in the vineyard

soils, where an increased Cu concentration (Figure 1) was observed.

High total Cu concentration coincides with the areas under vines (Figures 1 and 3(e)). Thus, a risk of contamination may be occurring in these areas. Considering such factors as high Cu concentrations in vineyard soils, soil acidification, and slope, erosion effects may contaminate the lower lands in the landscape. The total Zn concentration coincides with vineyards and natural vegetation, indicating a natural high concentration and contamination in the vineyard (Figure 3(f)).

Analyzing spatial dependence of Cu and Zn extracted by $CaCl_2$, only nonacidified Cu had moderate dependence and displayed good adjustment to the spherical model (Figure 3(g)). Acidified extraction of the Cu and Zn forms did not show spatial dependence and had verified the "nugget effect." The forms extracted by $CaCl_2$ did not have a spatial correlation with the DTPA and total forms and instead showed different behaviors. These results suggest that $CaCl_2$ extraction was less efficient than DTPA in representing the bioavailability of Cu and Zn.

4. Conclusions

The results confirmed the enrichment of the soil with Cu and Zn due to the use and management of the vineyards with chemicals for several decades.

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Research Article

Effect of Continuous Agriculture of Grassland Soils of the Argentine Rolling Pampa on Soil Organic Carbon and Nitrogen

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Long-term soil organic carbon (SOC) and soil organic nitrogen (SON) following cultivation of grassland soils (100/120-year tillage (T) + 20/30-year no tillage (NT)) of the Rolling Pampa were studied calibrating the simple AMG model coupled with the natural ^{13}C abundance measurements issued from long-term experiments and validating it on a data set obtained by a farmer survey and by long-term NT experiments. The multisite survey and NT trials permitted coverage of the history of the 140 years with agriculture. The decrease in SOC and SON storage that occurred during the first twenty years by a loss through biological activity was 27% for SOC and 32% for SON. The calibrated model described the SOC storage evolution very well and permitted an accurate simultaneous estimation of their three parameters. The validated model simulated well SOC and SON evolution. Overall, the results analyzed separately for the T and NT period indicated that the active pool has a rapid turnover (MRT ~9 and 13 years, resp.) which represents 50% of SOC in the native prairie soil and 20% of SOC at equilibrium after NT period. NT implementation on soils with the highest soil organic matter reserves will continue to decrease (17%) for three decades later under current annual addition.

1. Introduction

It is well established that grassland soils, particularly Mollisols, originally rich in soil organic matter (SOM), rapidly lose important quantities of carbon (C) and nitrogen (N) after cultivation [1–10]. Long-term cultivation effects on soil organic carbon (SOC) and soil organic nitrogen (SON) provide necessary information to evaluate the sustainability of cropping systems and their effects on the environment. Assessment of SOM is a valuable step towards identifying the overall quality of a soil [11–13].

The agriculture of the Argentine Rolling Pampa consists of a sequence of arable crops for 100 to 120 years followed by two or three decades of cropping under no tillage (NT). Before the 1970s, maize (*Zea mays* L.), wheat (*Triticum aestivum* L.), and flax (*Linun usitatisinum* L.) were alternated with pastures for beef production. Since the 1970s, largely due to economic reasons, there has been an important increase in the area under arable crops, with the cropped area increasing relative to the pasture area at an annual rate of 4% [14]. This resulted in an increase in tillage intensities. Furthermore, soybean was often double cropped with wheat (W/S) in the same year. Fertilizer use was relatively restricted until 1992 (<5 kg N ha^{-1}año^{-1}) [7, 15–17], and liming is not practiced by farmers. Conservation tillage, based on chisel plow as primary tillage and no-tillage (NT) practices, was first introduced in the middle of the 1970s to provide several environmental benefits such as reduction of soil erosion, improvement of the soil structure and infiltration, and conservation of soil water. Until 1988, the agricultural area under NT was only 0.02% of the total national agricultural surface. After that NT has continued to develop and evolve, and the Rolling Pampa has become one of the world's fastest growing areas of NT adoption. Currently, the agriculture surface under NT represents 78.5% of the national agricultural area [18]. In the 1990s, the agricultural intensification advanced towards simplified production schemes under NT, with spring-summer species, especially soybean (70% of the agricultural surface) and, secondarily, maize (15% of the agricultural area) and wheat preceding soybean some years, or otherwise, the soil

remaining fallow between the two summer crops. About 80% of soybean, 61% of wheat and 72% of maize are cultivated under continuous NT [19]. This general adoption of NT occurred together with a high dependence on broad spectrum herbicides and increasing mineral nitrogen fertilization rates related to maize and wheat production [17]. These deep modifications of production systems seem to be the origin of the notable decrease in SOM in different zones of this region. In fact, Michelena et al. [20] documented reductions of 21, 56, and 10–84% in SOC, SON, and extractable phosphorus (P), respectively, of half unit in pH values, of 40–60% in stability structure, and of 54–73% in the infiltration rate, following cultivation. This evolution is generally considered to cause water erosion. On the other hand, the soils under NT with dominance of soybean also present a progressive decrease in their physical, chemical, and biological fertility [21]. The main causes of such decrease include the long periods of fall-winter fallow, the low annual C input to the soil, and the enhancement of the mineralization of SOM by products of the biological fixation of N. In addition, NT presents little soil coverage and low structure stability, tends to compaction, reduces the infiltration rate due to the presence of a laminar structure, and produces a significant contribution of N to the groundwater and surface waters [22–26].

SOM changes are likely to be slower in more temperate than in tropical climates [5, 27, 28]. Burke et al. [5] showed that SOC loss under cultivation increases with precipitation. The climate of the Rolling Pampa, with high annual rainfall and a soil temperature that infrequently reaches 0°C, favors a higher organic decomposition than North American or European climates. Among pedoclimatic characteristics, the amount and nature of clay and calcium carbonates participate in protecting SOM from decomposition by adsorption and aggregation, thus slowing turnover and effectively increasing SOM. Particularly, it was shown that montmorillonite presents a higher protecting role than kaolinite [29]. In the soils of the Rolling Pampa, the predominant mineral of the clay fraction is illite. Since calcium carbonates are removed from the overlying horizons, physical protection of the two latter components would be very low. The silt fraction (2–50 μm) of the Pampean soils has a high amount of phytolites (to 50% from 2–20 μm) [30]. This particularity leads to envisage an interaction between SOM and phytolites. Some authors proposed explaining SOM stability of grassland soils by a physical-chemical protection intervening preferentially adsorption mechanisms [31, 32].

During the first years of cultivation, decomposition of easily decomposable roots and crown tissue, soluble fractions, and prehumic substances, in which their production is much greater for native grasses than for cultivated crops, accounts for high initial SOM losses [27, 33–35]. SOM reduction upon cultivation is sensitive to organic management, and the difference relative to general trends depends on the farming practices, especially those involving crop residue utilization, animal manures, crop rotation, fertilizers, and tillage. Several mechanisms have been proposed for the organic matter losses following cultivation of prairie soils: mechanical disruption of previously unavailable organic matter available as substrates for microorganisms, a decrease in the amount and changes in the type of residue applied [36], dilution with subsoil having less SOM [37], and soil erosion [3, 38].

To estimate and predict the evolution of soil fertility to cover the entire period of time since the beginning of agriculture in the Rolling Pampa, we need a model of long-term SOM evolution such as CENTURY, Roth-C, DAISY, or CN-SIM [39]. These models differ by the number of pools taken into account, the initialization and the size of such pools, and the number of parameters considered and their estimation. When we have minimal data input, it is necessary to abandon the explicit part of elementary processes and replace them by gross simulations indicating the average trends [40–42]. In a work on the Rolling Pampa, Andriulo et al. [43] modified the Hénin-Dupuis model [44] in combination with natural ^{13}C abundance and applied it on a soil following cultivation and on a soil with a long cropping history both in medium-term studies (13 years). This model, which they named the AMG model, allowed them to obtain a very good prediction of the evolution of C from old and young SOC with an accurate simultaneous estimation of only three model parameters (humification coefficient, k_1, mineralization coefficient, k, and stable carbon, C_s). AMG, a simple model designed to simulate SOC evolution, is embedded in the soil-plant simulation model STICS [45]. The model runs on an annual time step and assumes that fresh organic matter is either decomposed or humified in the soil after one-year decay. Three compartments are considered: crop residues and stable and active SOM [46].

In the Rolling Pampa, there are no long-term experiments with which we can systematically follow SOM stocks and residue inputs after cultivation and later NT of grassland soils. Since evolution is still relatively recent in Argentine and cultivation of natural grassland soils has developed progressively, there are fields with a different number of years under continuous agriculture since the beginning of the agriculture. Information regarding crop rotations, cultivation systems and yields, which can be obtained from each field by means of a survey, would compose a data set simulating the results of a long-term experiment. This approach has been used by Boiffin et al. [47].

Our objectives were (a) to calibrate the AMG model on the Pergamino soil series of the Rolling Pampa by applying the natural ^{13}C abundance technique during two periods: a long crop cultivation (T) of native grassland and a more recent one under NT and (b) to validate it on other soils series of the same region by using the performing model version over the environmental functions proposed by Saffih-Hdadi and Mary [46], with some differences, in the same two mentioned periods where it was possible to reconstruct the agricultural history through survey and to obtain long-term information from NT experiments, respectively.

2. Materials and Methods

2.1. Description of the Study Area. This work was carried out in the Argentine Rolling Pampa (Figure 1). The soils are developed on deep loess sediment. The study area is located between 32° and 35°S and 58° and 63°W. Soils, formed

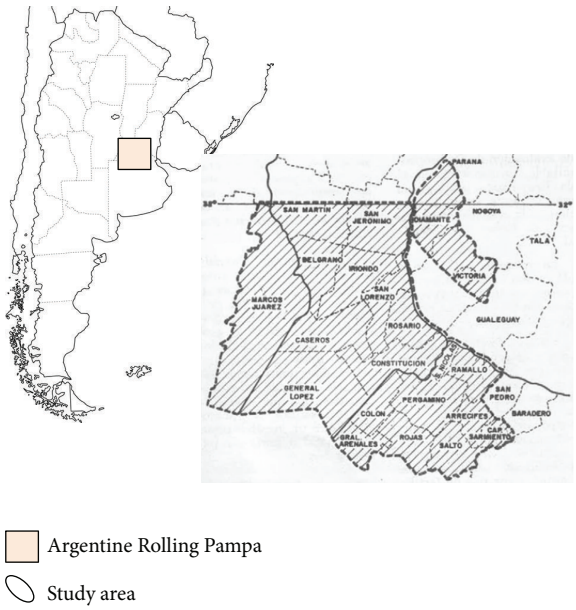

Figure 1: Argentine Rolling Pampa and study area.

from loess, are Typic, Vertic, and Aquic Argiudolls (US Soil Taxonomy) and are deep, relatively well drained, slightly acidic, originally well supplied with SOM, and very fertile. They usually have a silty-loam A horizon (19–26% clay, 55–74% silt, and 4–24% fine and very fine sand) followed by a silty-clay Bt horizon (30–55% in the Bt). Thickness of the Bt horizon is ~60 cm. The climate can be defined as temperate humid without a dry season and with a very hot summer [7]. Monthly mean temperatures range from 9°C in July to 24°C in February. Minimal soil temperature never reaches 0°C; therefore, soils do not freeze, and biological activity is never severely depressed. Rainfall varies from 900 to 1000 mm year^{-1}, 70–75% of which occurs in spring and summer, when monthly rainfall erosivity is greatest. The relief is moderately undulating, with slopes of up to 3%. The combination between the degree of slopes and their length results in some water erosion susceptibility.

2.2. Selection of Study Sites. The data used to calibrate the model, applying the natural ^{13}C abundance technique, came from two sites (sites A and B). Site A consisted of a long-term soybean monoculture experiment, carried out at the Pergamino Experimental Station of the National Institute of Agricultural Technology (INTA) (33°01′S; 61°10′W), Buenos Aires province, Argentina, for 33 years, (1980–2012), where the soil is plowed with moldboard plow/double disk at a depth of 15 cm and disk and teeth harrowed at a depth of 10 cm. The experiment started from a known situation taken as a reference of the native prairie (adjacent to the former). Site B (33°58′S; 60°34′W), with 22 years under NT (16S + 2W/S + 2 M), started after 80 years of cultivation (1991–2012). Both sites are developed on a fine, illitic, thermic Typic Argiudoll (US Soil Taxonomy), Luvic Phaeozem (WRB) of the Pergamino series without water erosion phases (soil slope < 0.3%). The texture of the A horizon is silty loam with 25% and 64% clay and silt, respectively. The mean annual temperature is 16.7°C, and the mean annual rainfall for the 1910–2012 period was 965 mm (agroclimatological network database, INTA).

To validate the model during the T period, we used a survey, which consisted in selecting different sites in which time of continuous cultivation since natural grassland and crop successions were known. We opened profiles to start Bt2 horizon depth in the highest site of the landscape of each field. We considered mainly the pedological profiles of Argiudolls. Only two fields classified as Argialbolls were included because their A2 horizon was very thin. Hence, we excluded the surface horizons with a clay content lower than 19%, the clay soils truncated by erosion and without A horizon, and flooding soils. The soil series or soil phases as well as the soil slope of each site studied were identified by INTA soil survey maps [48–53]. Three sites (Pergamino, Correa, and Urquiza soil series) were selected to determine the time zero of the T period for SOC and SON (Table 1).

To validate the model during the NT period we used information issued during three long-term tillage systems experiments developed on the Pergamino series: a 34-year-old (1979–2012) doubled cropped wheat/soybean-maize (W/S-M) and a 25-year-old (1987–2012) soybean (SS) and maize monocultures (MM), both carried out at the Pergamino Experimental Station. We used only the NT systems from three long-term experiments. Each experiment presented a completely randomized block design. W/S-M started after a long alternating pasture/agriculture period, and the monocultures started 9 years after and were cultivated majorly with soybean conventionally tilled. The main plot was 45 m long by 14 m wide, and the tillage systems were randomized in the main plots. Weeds were chemically controlled, and no previous old plowed soil was recorded under the plow depth. Wheat and maize were fertilized with 90 and 100 kg N ha^{-1}, respectively, as well as with 12 kg P ha^{-1}.

2.3. Sampling and Analysis. For the calibration model, three composed soil samples were taken from three 2 m wide pits of sites A in 1990, 1993, 2003, 2007, 2010, and 2012 and of site B in 1990, 2000, 2010, and 2012. These soil samples were taken from at least two soil depths of the full A horizon and then C, N, and natural ^{13}C abundance were determined (except for ^{13}C in 2000). For the validation during the T period, soil samples were taken from a 2 m wide pit by site in 1990 for all sites (Table 1). Ten measurements of horizon thickness were obtained. Soils were collected in A11/Ap, A12, and A3/BA horizons. Ten 1 kg simple samples were sampled in each horizon to compose one soil sample. For the validation model during the NT period, in June, before carrying out the tillage previous to maize in W/S-M, SS, and MM (2004, 2008, and 2012), soil samples were taken at three depths: 0–5, 5–10, and 10–20 cm. Three sites were chosen at random for subsampling in each of the treatments, avoiding visible wheel tracks. In the selected sampling years, we covered the full A horizon thickness.

Table 1: Description of study sites used for the validation model during T and NT periods.

Soil series	Symbol	Soil type	Agriculture time	Slope	Sampling date	Location	Fait
			years	%	year		
				T period			
Pergamino	Pe	Typic Argiudoll	0	<1.0	1990	34°10′S|60°40′W	Calibration/validation
Correa	Cr	Typic Argiudoll	0	<1.0	1990	32°49′S|61°20′W	Validation
Urquiza	Ur	Typic Argiudoll	0	<1.0	1990	33°55′S|60°25′W	Validation
Rojas	Ro	Typic Argiudoll	2	<1.0	1990	33°56′S|60°55′W	Validation
Peyrano	Py	Vertic Argiudoll	5	1.5–3	1990	33°31′S|60°25′W	Validation
Rojas 5	Ro5	Typic Argiudoll	8	<1.0	1990	33°55′S|60°50′W	Validation
Pergamino	Pe	Typic Argiudoll	10	<1.0	1990	33°57′51.35″S|60°34′39,34″W	Calibration
Pergamino	Pe	Typic Argiudoll	13	<1.0	1993	33°57′51.35″S|60°34′39,34″W	Calibration
Pergamino	Pe	Typic Argiudoll	23	<1.0	2004	33°57′51.35″S|60°34′39,34″W	Calibration
Pergamino	Pe	Typic Argiudoll	27	<1.0	2008	33°57′51.35″S|60°34′39,34″W	Calibration
Pergamino	Pe	Typic Argiudoll	31	<1.0	2010	33°57′51.35″S|60°34′39,34″W	Calibration
Pergamino	Pe	Typic Argiudoll	33	<1.0	2012	33°57′51.35″S|60°34′39,34″W	Calibration
Las gamas	LG	Aeric Argialboll	34	<1.0	1990	33°44′S|60°48′W	Validation
Rojas	Ro	Typic Argiudoll	35	<1.0	1990	34°02′S|60°47′W	Validation
Pergamino 6 o Peyrano 2x	Pe6 o Py2x	Typic Argiudoll	40	1.5–3	1990	33°39′S|60°42′W	Validation
Villa Eloisa	Ve2	Typic Argiudoll	55	1.5–3	1990	33°00′S|61°10′W	Validation
Las gamas	LG	Aeric Argialboll	60	<1.0	1990	33°45′S|60°50′W	Validation
Arroyo dulce 2	AD2	Typic Argiudoll	64	<1.0	1990	34°08′S|60°22′W	Validation
Arroyo dulce 2	AD2	Typic Argiudoll	70	<1.0	1990	34°15′S|60°17′W	Validation
Urquiza	Ur	Typic Argiudoll	72	<1.0	1990	33°55′S|60°25′W	Validation
Arrecifes 2	Ar2	Typic Argiudoll	72	1–1.5	1990	33°52′S|60°17′W	Validation
Correa 1	Cr1	Typic Argiudoll	75	1–1.5	1990	32°49′S|61°20′W	Validation
Pergamino	Pe	Typic Argiudoll	80	<1.0	1990	33°46′S|60°38′W	Calibration/validation
Rojas 4	Ro4	Typic Argiudoll	80	1–1.5	1990	34°14′S|60°35′W	Validation
Arroyo dulce 2	AD2	Typic Argiudoll	83	<1.0	1990	34°10′S|60°30′W	Validation
Peyrano	Py	Vertic Argiudoll	84	<1.0	1990	33°22′S|60°47′W	Validation
Peyrano 1 o Peyrano 2x	Py1 ó Py2x	Vertic Argiudoll	87	1–1.5	1990	33°32′S|60°46′W	Validation
Pergamino	Pe	Typic Argiudoll	100	<1.0	2010	33°46′S|60°38′W	Calibration
Pergamino	Pe	Typic Argiudoll	102	<1.0	2012	33°46′S|60°38′W	Calibration
Peyrano 2x	Py2x	Vertic Argiudoll	112	1.5–3	1990	33°35′S|60°48′W	Validation
Casilda 1	Ca1	Vertic Argiudoll	113	1–1.5	1990	33°07′S|61°20′W	Validation
				NT period			
Pergamino	Pe	Typic Argiudoll	0	<0.3	1979	33°57′36,26″S|60°33′50,25″W	Validation
Pergamino	Pe	Typic Argiudoll	0	<0.3	1987	33°57′32,06″S|60°33′41,58″W	Validation
Pergamino	Pe	Typic Argiudoll	0	<0.3	1987	33°57′31,54″S|60°33′44,85″W	Validation
Pergamino	Pe	Typic Argiudoll	17	<0.3	2004	33°57′32,06″S|60°33′41,58″W	Validation
Pergamino	Pe	Typic Argiudoll	17	<0.3	2004	33°57′31,54″S|60°33′44,85″W	Validation
Pergamino	Pe	Typic Argiudoll	21	<0.3	2008	33°57′32,06″S|60°33′41,58″W	Validation
Pergamino	Pe	Typic Argiudoll	21	<0.3	2008	33°57′31,54″S|60°33′44,85″W	Validation
Pergamino	Pe	Typic Argiudoll	25	<0.3	2004	33°57′36,26″S|60°33′50,25″W	Validation
Pergamino	Pe	Typic Argiudoll	25	<0.3	2012	33°57′32,06″S|60°33′41,58″W	Validation
Pergamino	Pe	Typic Argiudoll	25	<0.3	2012	33°57′31,54″S|60°33′44,85″W	Validation
Pergamino	Pe	Typic Argiudoll	29	<0.3	2008	33°57′36,26″S|60°33′50,25″W	Validation
Pergamino	Pe	Typic Argiudoll	33	<0.3	2012	33°57′36,26″S|60°33′50,25″W	Validation

T: tillage; NT: no tillage.

Samples were dried and sieved finer than 2 mm. Organic matter more coarse than 2 mm was taken into account in this study. Particle size was measured according to the pipette method [54]. C, N, and ^{13}C contents were determined by dry combustion with a mass spectrometer (Fisons/Isochrom) coupled with a CN analyzer (Carlo Erba NA 1500). Soil bulk density (BD) measurements were used to transform mass-based measurements into volume-based ones. BD was determined by the cylinder method [55]. During the first period of validation, BD was measured with 50 or 200 cm^{-3} cylinders, and four replications were sampled in each soil horizon. In the experiments, in a place adjacent to the disturbed sample, a small pit of 0–30 cm depth was opened, and a cylinder was extracted at each depth. The cylinder (58.9 cm^3) was placed vertically at 0–5 cm and horizontally at the other two soil depths. All the samples were dried in an oven at 105°C to constant weight. A mass of 2500 Mg ha^{-1} was chosen to calculate SOC and SON stocks.

2.4. Estimation of Organic Additions. In order to estimate organic additions, culture succession, crop yield, residue removal by burning, and nitrogen fertilization were retained in each field. Before 1947, we used an average yield from typical maize-wheat or maize-linseed sequences in a proportion of 2 or 3 maize crops for each wheat or linseed, depending on the geographical zone and farmer declaration on the proportion. Values for the crop residue additions were based on measured straw [56] as well as on inputs from stem bases and roots calculated as follows: (1) straw harvest index (crop yield/total air dry matter) before 1947 were 0.20, 0.20, and 0.10 for maize, wheat, and linseed, respectively, between 1948 and 1990 were 0.40, 0.36, 0.23, 0.40, 0.36, 0.38, and 0.30 for maize, wheat, soybean, sunflower, sorghum, oat, pea, and lentil, respectively, and after 1990 were 0.50, 0.42, and 0.38 for maize, wheat, and soybean; (2) below-ground C biomass, including roots and rhizodeposits, was considered 0.30 of the total air dry matter for all crops [57]; (3) after harvest, aerial crop residue biomass was reduced to 15% of total aerial crop residue due to burning of maize, linseed, and wheat straws from start of cultivation to mechanical harvest and from W/S during the 1970s. This biomass was considered as black carbon; (4) the C/N ratios before 1990 were 87 for maize, 96 for wheat, 44 for soybean, 24 for sorghum, 12 for prairies, 55 for linseed, 74 for clover, 49 for sunflower, 7 for carrot, 17 for lentil, 29 for pea, 23 for vetch, and 67 for black carbon, whereas those after 1990 were 57 and 64 for maize and wheat, respectively, due to an increase in mineral nitrogen fertilization rate; (5) the C content of straw and below-ground biomass was assumed to be 40% of the total dry matter; and (6) the C biomass from weeds was assumed as 1 Mg ha^{-1} $year^{-1}$ before mechanical weed control was replaced by chemical control (~1990).

In the experiments, annual yields and aerial biomass were used to estimate organic additions and the straw harvest index, below-ground C biomass, and C/N ratios found after 1990 were used. The C content was also 40% of the total dry matter, and no C biomass from weeds was considered.

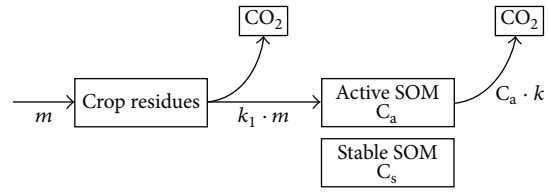

Figure 2: Diagram of AMG model.

2.5. Three-Compartment Model. The basic equations of AMG model (Figure 2) are the following [43]:

$$C = C_s + C_a,$$
$$\frac{dC_a}{dt} = m \cdot k_1 - k \cdot C_a, \quad (1)$$

where C is the SOC amount (Mg ha^{-1}), C_s is the stable C amount (Mg ha^{-1}), C_a is the active C amount (Mg ha^{-1}), m is the mass of annual C input (represents the total mass of organic carbon returned to soil through all crop residues (straw, stubble, roots, and rhizodeposits, in Mg ha^{-1} $year^{-1}$), k_1 is the humification coefficient (unitless), and k is the mineralization coefficient of the active pool (yr^{-1}).

These equations can be integrated if m is considered constant every year. Then, the evolution of the carbon reserve may be described by the following equation:

$$C = C_s + C_{a_0} \cdot e^{-kt} + \frac{m \cdot k_1}{k} \cdot \left(1 - e^{-kt}\right), \quad (2)$$

$$C_{a_0} = C_0 - C_s, \quad (3)$$

where C_0 is the initial SOC amount (Mg ha^{-1}). In (2), the second term on the right side represents the decomposition of the "old carbon" (i.e., existing at time 0), while the third term represents the (net) newly humified carbon which reaches an asymptote:

$$C_{max} = \frac{m \cdot k_1}{k},$$
$$C_{eq} = C_{a_\infty} + C_s, \quad (4)$$

where C_{a_∞} is the maximum quantity of soil C originated from crop sequences (Mg ha^{-1}) and C_{eq} is the total quantity of soil C at equilibrium (Mg ha^{-1}).

This model is traditionally used to describe the turnover of SOC. Here we also use it to simulate the turnover of soil total SON stock

$$N = N_s + NN_{a_0} \cdot e^{-kt} + \frac{m_N \cdot k_1}{k} \cdot \left(1 - e^{-kt}\right), \quad (5)$$

where N_s is the amount of stable N (Mg ha^{-1}), N_{a_0} is the amount of initial active N (Mg ha^{-1}), N_0 is the amount of initial total N (Mg ha^{-1}), m_N is the amount of N from crop residues annually added to soil (Mg ha^{-1} $year^{-1}$), k_1 is the humification coefficient (unitless), and k is the mineralization coefficient of the active fraction ($year^{-1}$).

2.6. Calibration Procedure. As stated previously, the data set obtained from two long-term experiments (sites A and B) was used to calibrate the AMG model. The second and third terms of (2) were determined separately by using the ^{13}C natural abundance technique which allows obtaining a unique evaluation of the parameters k, k_1, and C_s in long-term experiments [43, 58].

Since we needed measurements of natural $\delta^{13}C$ abundance to establish the origin of the SOM in each site, we used the technique developed by Cerri et al. [59] and Balesdent et al. [60]. The proportion of soil C derived from C3 crops (α) was calculated as

$$\alpha\,(\%) = \frac{(\delta_m - \delta_1)}{(\delta_2 - \delta_1)} \cdot 100, \tag{6}$$

where δ_m is the isotopic abundance of ^{13}C in the soil at time t (‰), δ_1 is the isotopic abundance of ^{13}C in the soil at time $t = 0$ (‰) taken at the reference, and δ_2 is the isotopic abundance of ^{13}C of the crop in the crop sequence (‰). These last values were −26.3 and −24.98‰ for A and B sites A and B, respectively [43].

When α is known, the young and old carbon contents can be calculated. The C contents (g kg^{-1} soil) derived from crop sequence residues (C_{DC}) and native prairie or after long-term cultivation period (C_{DP}) in our case were calculated as

$$\begin{aligned} \text{young C}: C_{DC} &= \alpha \cdot C_m = \frac{m \cdot k_1}{k} \cdot \left(1 - e^{-kt}\right), \\ \text{old C}: C_{DP} &= (1-\alpha) \cdot C_m = C_s + C_{a_0} \cdot e^{-kt}, \end{aligned} \tag{7}$$

where C_m represents the total C content of bulk soil (g kg^{-1} soil).

The SOC stocks (total, originated from crop sequences and native prairie, in Mg ha^{-1}) were calculated using the following equation:

$$\text{SOC} = C_x \cdot d \cdot \text{BD} \cdot 10, \tag{8}$$

where C_x represents C_m, C_{DC}, or C_{DP}, d is the depth (m), and BD is the bulk density (Mg m^{-3}) of the corresponding soil depth. SON stocks were also calculated at 2500 Mg soil ha^{-1}.

We tried to fit the two C models (young and old) at the same time, that is, by minimizing the sums of the square of deviations from the model for the variables C_{DC} and C_{DP}. While optimizing, we took account of the variance of the data by weighting the sums of squares of deviations. The following quantity was minimized as follows:

$$\text{SSQ} = \frac{\text{SSQ}_{DC}}{S^2_{DC}} + \frac{\text{SSQ}_{DP}}{S^2_{DC}}, \tag{9}$$

where SSQ_{DC} and SSQ_{DP} are the sums of squares of deviations (observed, simulated) of the variables C_{DC} and C_{DP}, respectively; S^2_{DC} and S^2_{DP} are the mean experimental variances obtained for the variables C_{DC} and C_{DP}. Fitting was performed by fixing C_0 and m and optimizing three parameters: C_s, k_1, and k.

In the case of N, k, k_1, and N_s were treated as follow.

(a) k values were optimized and fixed in T and NT period, respectively, and in this last period the same value estimated in SOC simulation was used; (b) $k_1 = 1$ in the cultivation period and optimized in the NT period; (c) N_s values were optimized in both tillage periods.

The k_1 values to simulate SON evolution are different from those used to simulate SOC evolution. The value $k_1 = 1$ adopted for SON simulation for all residues during the cultivation period means that N harvest residue addition is completely humified. This hypothesis is supported by ^{15}N-labeled harvest residue incubations mixed with the soil [61].

To judge the goodness of fit of the SOC and SON models, we used the absolute root mean square error (RMSE), in Mg ha^{-1}, defined as follows:

$$\text{RMSE}\,(j) = \sqrt{\frac{1}{n_j}\sum_{i=1}^{n} \Sigma\left(X_{ij} - \widehat{X}_{ij}\right)^2}, \tag{10}$$

where n_j is the number of observations of each data set j, and X_{ij} and $\widehat{X}_{ij}$ are the observed and simulated values of SOC (SON), respectively. The optimization was conducted using the Newton's method of Excel solver.

2.7. Validation Procedure. The proportions of stable pool to total SOC at the beginning of the simulations, estimated from the model calibration in the Pergamino soil series for sites A and B were applied in the soil series included in the T and NT validation periods. The proposed default value of the $C_s/\text{SOC}_{\text{reference}}$ relationship (0.65) was not used because it can vary along the agriculture period and can be smaller in the native grassland [62]. The $\text{SOC}_{\text{reference}}$ (native grassland) used for the sites included in the cultivation period were obtained from Michelena et al. [20]. The k_1 values obtained by calibration were only applied for soybean culture. The k_1 values used for the other crops were taken from international references, according to the evolution of different residue management practices (stubble burning, mineral N and P fertilization, tillage system, and weed control). As normally accepted, the value of k is highly dependent on the pedoclimatic conditions and tillage systems. Thus, we used the environmental functions proposed by Saffih-Hdadi and Mary [46] with the introduction of a third environmental factor (rainfall index) during the cultivation period. The k value obtained from NT calibration was used for the NT period.

The mineralization rate k depends particularly on soil temperature (Te), clay content (A), and a simple rainfall index (RI):

$$k = k_0 f_1\,(\text{Te})\, f_2\,(A)\, f_3\,(\text{RI}), \tag{11}$$

where k_0 is the potential mineralization rate (year^{-1}) in reference conditions and f_1 (Te), f_2 (C), and f_3 (RI) are the temperature, clay, and rainfall functions, equal to 1 in reference conditions. The reference conditions are defined here as 15°C soil temperature, zero clay content, and 900 mm

annual rain. The effect of clay content on mineralization of SOC is described by an exponential law:

$$f_2(A) = e^{-aA}, \quad (12)$$

where A is the clay content (g g^{-1} soil) and a is a constant (g soil g^{-1} clay) with a value of 2.72. The effect of temperature (Te, °C) on mineralization of humified organic matter is assumed to obey a logistic law:

$$f_1(T) = \begin{cases} \dfrac{c}{1 + (c-1)\, e^{-k(T-T_{\text{ref}})}} & \text{if Te} \geq 0, \\ 0 & \text{if Te} < 0. \end{cases} \quad (13)$$

The effect of water content on mineralization of SOM and residues was based on a very simple macroclimatic index since soil water data were not available. We assume the following relationship between mean annual precipitation (P) and annual potential evapotranspiration calculated by Thornwhite method (PET), both expressed in mm, considering P and PET from the 1910–2012 period 965 mm and 870 mm, respectively (INTA, soil data network) (Table 2).

In the model, the humification coefficient k_1 was only dependent on the quality of the residues. The k_1 values of all crops included in crop sequences extracted from published values are shown in Table 3.

The values assumed for the $C_{\text{stable}}/N_{\text{stable}}$ ratio were very close to those obtained during the model calibration. Besides, k_1 values were fixed considering that all N additions are completely humified regardless of the type of tillage [61]. The initial $SON_{\text{reference}}$ for T sites was estimated using a C/N ratio = 11 (we averaged SOC/NOC contents of the three sites without agriculture history of this paper (Table 1) and those reported by Michelena et al. [20].

Finally, to obtain the goodness of fit of the AMG model simulated versus observed SOC and SON values were compared separately for the T and NT periods.

3. Results and Discussion

3.1. Model Calibration. Figure 3 shows the evolution of the average ^{13}C values and their depth distribution for the two study sites. The effect of C incorporation issued from C3 species in the SOM was recorded by decreasing ^{13}C values in time. These results allowed progress in monitoring the young and old SOC compartments. In site B, where maize crops occupied half of the cropping history, the previous agricultural period enriched the δ^{13}SOC (−18.3‰ at 0–14 cm soil depth) which had started from mixed C3/C4 grasslands (−19.6‰ at 0–14 cm soil depth).

The model fit to data using the C_s, k_1, and k values issued from ^{13}C measurements in sites A and B is presented in Figure 4. The parameter settings used worked very well, and the model described the general trends in the soil carbon data well (RMSE 1.13 and 0.94 Mg SOC ha^{-1} for sites A and B resp.) despite the small available number ^{13}C measurements to obtain the parameter values during the NT period.

The C_s values found were very similar in both sites, both in a situation of recent agriculture and in one of old agriculture (Table 4). Hence, the size of this pool can be considered as a valid indicator for the full period of the Pergamino soil series under agriculture. The SOC content of the A horizon was 12.5–13.0 mg SOC g^{-1}. A similar result had been previously obtained in soils of this region [43]. This value represents 47% at the beginning of agriculture and 67% at the beginning of NT, 80 years after cultivation. These values are in agreement with previous reports in different countries [46, 62, 63]. The rate constant of mineralization k was 0.108 and 0.078 year^{-1} and in agreement with the climate and soil conditions previously set, indicating a rapid transition to a new equilibrium under cultivation (mean residence time—MRT—of the active fraction ~9 years) and a significant decrease under NT (MRT ~13 years), respectively. In site A, the k_1 value was the same as that been previously obtained [64] and higher than that obtained for cereal crop (0.21) combining the AMG model with the ^{13}C technique [65]. Soybean residue decomposes relatively faster than cereal residues and stimulates the mineralization of SOM [66]. However, as it has higher lignin content, its soil stabilization is favored when it is incorporated into the soil [56]. The k_1 value under NT was markedly smaller than under cultivation and slightly higher than that obtained by other authors [65, 66].

Table 2

P/PET	RI
[0.5; 0.6)	0.5
[0.6; 0.7)	0.6
[0.7; 0.8)	0.7
[0.8; 0.9)	0.8
[0.9; 1.0)	0.9
≥1	1

The estimated annual C addition in crop sequences of sites A and B, with a very high proportion of soybean, is characteristic in the Rolling Pampa [68]. In both sites, the technology was unable to maintain existing SOC stocks. Novelli et al. [69] found that the SOC storage was negatively associated with the soybean cropping frequency in the cropping sequences. After the introduction of agriculture in site A, there was a rapid loss of SOC (25%) during the first ten years, followed by a period with a lower loss (15%) in 23 years. In site B, NT implementation after a long history of continuous cultivation led to a loss of SOC of 15%. At the equilibrium, the active fraction would represent 23 and 19% in sites A and B, respectively.

The same general trends were observed for the soil nitrogen data which were well described by the model: RMSE 0.04 and 0.05 Mg SON ha^{-1} for sites A and B, respectively (Figure 5). The two crop sequences had similar N additions. However, the size of N_s was smaller in site B than in site A (Table 4). This difference can be explained by the previous agriculture history. In site B, the long cultivation period without N fertilization, where maize culture occupied half of the total crop sequence and the other crops such as wheat and linseed with high C/N ratios before the NT period, led to a poor N resistant pool (C_s/N_s = 12.7). In contrast, soybean

Table 3: Crop k_1 values used in the validation procedure as a function of the predominant soil residue management.

Culture	k_1				
	Default	Stubble burning from aerial|root biomass	Mineral N/P fertilization	Mechanicall weed control	NT
Maize	0.35[a]	0.5|0.3[c]	0.21[d]		0.13[e]
Leenseed		0.5|0.3			
Wheat	0.3[ab]	0.5|0.3	0.21		0.13
Soybean	0.3				
Sunflower	0.3				
Sorghum	0.35[a]		0.21		
Carrot	0.3				
Oat	0.3				
Pea	0.3				
Lentil	0.3				
Vetch	0.3				
Weed				0.21	

Taken from: [a][43]; [b][29, 47]; [c][67]; [d][46]; [e][65].
NT: no tillage.

monoculture, implemented after a pristine prairie, showed a relatively high stable N pool ($C_s/N_s = 10$). Besides, since under NT part of the crop residues are not in contact with the soil, the k_1 value under NT was smaller than that in tilled soils. As a consequence, a similar m_N addition tended to higher N_{eq} in site A than in site B.

In site A, N_{a_0} was 3.2 Mg ha^{-1}. Then, the nitrogen mineralized during the first period of cultivation was large enough for crop requirements and the nonused mineral nitrogen was likely leached out of the rooting zone and into subterranean water reserves. The optimized k values and the proportion of the stable fraction were close for SOC and SON. Similar results have been informed by Mary and Guérif [70] for the Rothamsted trials.

3.2. Model Validation. Mean SOC and SON contents and BD values of the sites surveyed and clay content at 2500 Mg soil ha^{-1} are shown in Table 5. Low variability of soil texture is observed among the study sites. Besides, some of the sites sampled during the T period did not meet the requirement of soil mass that is to have an A horizon with 2500 Mg ha^{-1}.

The AMG model was able to provide satisfactory simulation of the evolution of SOC and SON stocks in the sites that satisfied soil mass requirement in the cultivation period (Figure 6).

Figure 7 shows the evolution of SOC and SON stocks of all the sites surveyed during the T period. Some variability was observed in the data set partly due to the nature of this study (i.e., survey). A part of the mentioned variation can be attributed to the vertical and horizontal spatial variation of surface deposits. This was confirmed by considering the three virgin sites which showed values of 65, 68, and 76 Mg SOC ha^{-1}. These three values are in the content range reported for the virgin soils of the study area [20, 71]. These reports showed SOC contents which translated in storage values ranging from 60 to 80 Mg SOC ha^{-1} for a soil mass of 2500 Mg ha^{-1}. So, we are confident that the current soil C storage of virgin soils corresponds to the C storage present in the last century. Also, certain cultivated sites with less than 40 Mg SOC ha^{-1} belong to soil series with high C contents in virgin state (Table 1 and Figure 7(a)). Therefore, variations in the observed SOC stocks cannot be completely explained by natural variability.

Water erosion can also explain part of the data variability, since it has been previously mentioned as a very important cause of losses in zones with high slopes [71]. Data showed that several sites older than 40 years are in slopes higher than 1% (Table 1). Six of these sites showed SOC stocks lower ($\leq$40 Mg SOC ha^{-1}) than the average stock of all T sites (Figure 7(a)). On the other hand, one of the sites with five years of tillage and a slope higher than 1.5% showed a SOC stock lower than that of the other young sites (Table 1 and Figure 7(a)). Furthermore, a decrease in the A horizon mass was observed in the soils located in slopes higher than 1% (Table 1). On the other hand, soil survey maps classify the soils with slopes higher than 1% as eroded phases [48–53]. We are therefore confident that some of the losses for the sites with slopes higher than 1% are due to erosion. The sites with an A horizon soil mass smaller than 2500 Mg ha^{-1} were not taken into account in the validation (Table 5).

On average, during the first twenty years of cultivation, the SOC storage varied from 70 to 51 Mg ha^{-1} and SON storage varied from 6.6 to 4.5 Mg ha^{-1}; this represents losses of 27 and 32% for SOC and SON, respectively (Figure 7). After the first twenty years, when water erosion was present (>1% slope), SOC and SON loss increased with the years of tillage. For instance, a soil with a slope higher than 1% had about 47

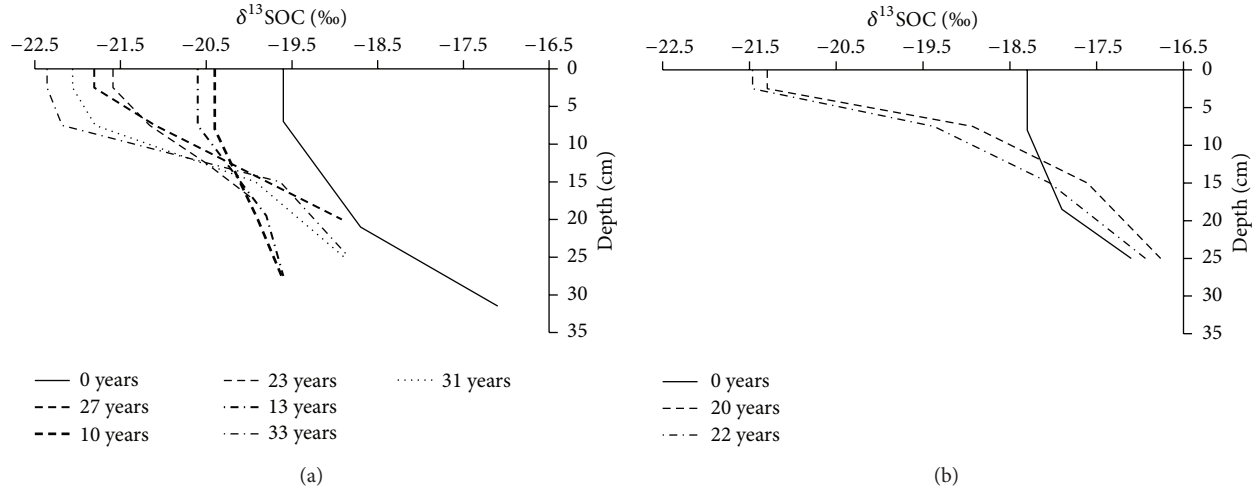

Figure 3: Distribution of mean 13COS values with depth and their evolution in sites A (a) and B (b).

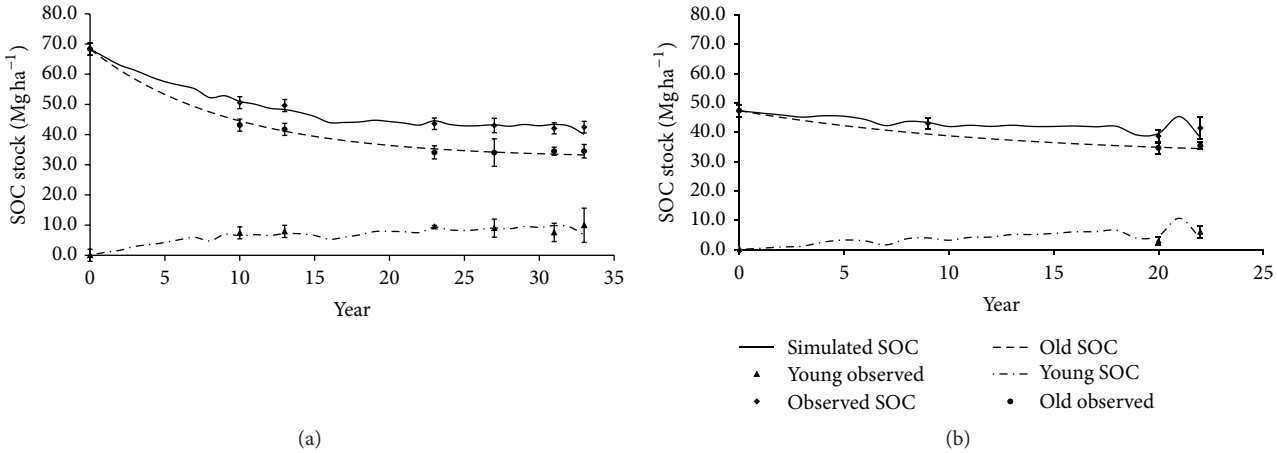

Figure 4: Observed and simulated total, young, and old carbon evolution in sites A (a) and B (b).

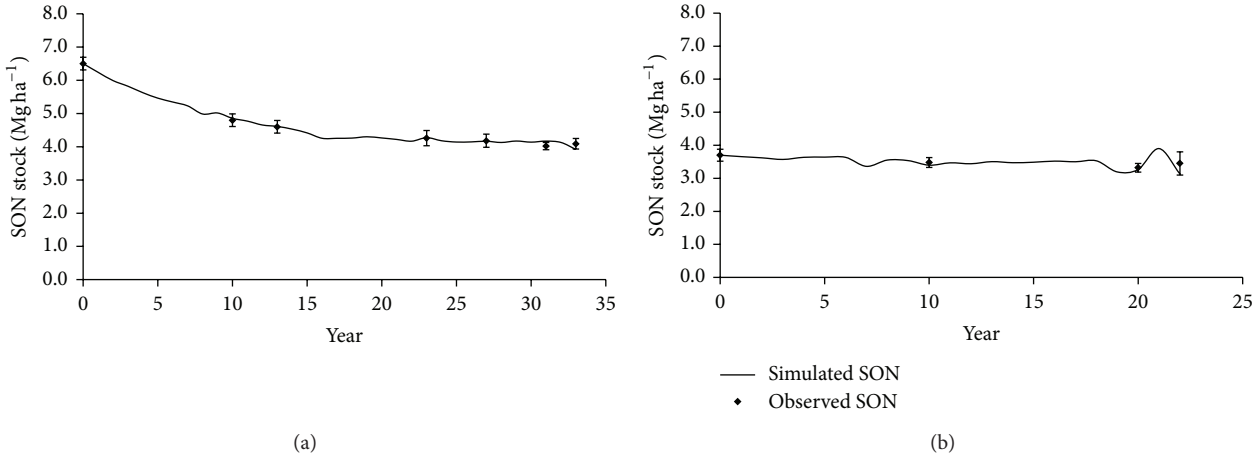

Figure 5: Observed and simulated SON evolution in sites A (a) and B (b).

Table 4: Values of model parameters (C_s, k, and k_1) obtained with the AMG model in sites A and B.

Site	Fixed parameters				Optimized parameters			Predicted values at equilibrium	
	C_0	m	k	k_1	C_s	k	k_1	$C_{a\ max}$	C_{eq}
	Mg ha^{-1}	Mg ha^{-1} year^{-1}	year^{-1}		Mg ha^{-1}	year^{-1}		Mg ha^{-1}	
A	68.3	3.6	—	—	32.2	0.108	0.288	9.6	41.8
B	47.3	3.5	—	—	31.7	0.079	0.167	7.3	40.4
	N_0	m_N	k	k_1	N_s	k	k_1	$N_{a\ max}$	N_{eq}
	Mg ha^{-1}	Mg ha^{-1} year^{-1}	year^{-1}		Mg ha^{-1}	year^{-1}		Mg ha^{-1}	
A	6.5	0.079	—	1	3.3	0.113	—	0.7	4
B	3.7	0.082	0.079	—	2.5	—	0.827	1	3.4

and 57% SOC and SON losses, respectively, after 40 years of tillage. A site located in the same soil series but after 112 years of tillage had 63 and 72% SOC and SON losses, respectively (dotted line). When erosion was not a factor, for instance the Pergamino soil series, SOC and SON losses were 30 and 43%, respectively. After 80 years of tillage, losses in the Pergamino soil series were in agreement with those in the other sites. This suggests that SOC and SON changes obtained by survey were the same as those obtained from long-term experiment evolution.

Average C_s, k, and k_1 validated values were 32.9 ± 2.6 Mg ha^{-1}, 0.102 ± 0.003 year^{-1}, and 0.41 ± 0.02, respectively, whereas average C_0 and m values were 70.0 ± 5.6 Mg ha^{-1} and 4.0 ± 1.1 Mg ha^{-1} year^{-1}, respectively (solid line of Figure 7(a)). The average crop residue C input was necessary to maintain the equilibrium C level in 48 Mg ha^{-1} (19 mg C kg^{-1} soil). The active fraction changed from 37 Mg ha^{-1} at the beginning to 15 Mg C ha^{-1} at equilibrium. Average N_s and k validated values were 2.9 ± 0.6 Mg ha^{-1} and 0.102 ± 0.003 year^{-1}, respectively, whereas average N_0 and m_N values were 6.6 ± 0.6 Mg ha^{-1} and 0.074 ± 0.02 Mg ha^{-1} year^{-1} (solid line of Figure 7(b)).

The k value obtained using the Saffih-Hdadi and Mary approximation was very close to the optimized value (0.106) and can be recommended to use under conventional tillage conditions. Overall, the MRT of the active compartment would be included in 9 years. This is twice the MRT of the North American prairie [72]. This model clearly shows that equilibrium is reached after the first 20 years following cultivation of grassland. The annual mineralization coefficient (k) from the three-compartment model can be compared with the annual mineralization coefficient (k_2) from the single-compartment model using the following relation:

$$k_2 = k \cdot \frac{C_a}{C_a + C_s} \tag{14}$$

k_2 values varied with tillage time, from 0.056 year^{-1} at the beginning to 0.03 year^{-1} at equilibrium. The k value from the active fraction was 2- to 3-fold higher than the k_2 values. Our k_2 values are intermediate between the Australian values (from 0.065 to 1.22 year^{-1}) obtained by Dalal and Mayer [73] and the British value (0.008 year^{-1}) obtained by Mary and Guérif [70] or French values (from 0.008 [74] to 0.03 year^{-1} [75]). Australian studies were carried out in a subtropical climate with average temperatures from 18.5 to 20.5°C, while British and French studies were carried out in a temperate climate with average temperatures from 9 to 13.5°C. In our study, the average temperature was 17°C.

The inclusion of the RI factor caused no changes in the estimated k value: the Saffih-Hdadi and Mary approximation without inclusion of the RI factor gave a mean value of 0.106 ± 0.002. As expected, the only model parameter that showed a difference with the value obtained for soybean in the calibrated model was k_1 due to the inclusion of residue management recorded by the survey. The crop history of the cultivation period showed similar crop sequences in all the sites in the last twenty years (1970–1990s) (data not shown). In general, organic additions were greater than those in the preceding period (Figure 8).

Before the 1960s, typical crop rotations were maize wheat or maize linseed, sometimes sunflower, with a ratio 2-3 years of maize to 1 year of wheat or linseed or sunflower. Residue burning was a common practice until 1950 and the oldest farmers declared that crop yields were much lower before 1960. After 1960, there was important technical progress (fall tillage, improvement of the drilling technique, better selection of soils, advances in crop protection, better harvesting efficiency, and genetic progress), which resulted in significant yield improvements [7]. Hence, in the older sites, it is probable that crop additions and SOC contents progressively decreased with time (1960–1970s). At that moment, INTA reported that SOC contents under annual crops had decreased from 28.0 to 13.5 mg g^{-1}, that is, about 30 Mg SOC ha^{-1} after 70 years of crop cultivation [71]. Moreover, soybean introduction double cropped with wheat and the significant decrease of straw burning probably contributed to the increase in C additions into the soil. Thus, the decrease suffered by SOC and SON stocks observed in 1990 may have been higher before than after the 1960–1970s.

In general, the losses observed in our study are greater than those observed in other climatic regions with the same initial vegetation (grassland) [76]. Several reasons can explain these apparent faster losses in the soils of the Rolling Pampa.

One possible explanation is that the sites with less than twenty years of tillage (1970–1990s), as opposed to the oldest sites, have been, in general, cropped in soybean monoculture or soybean double cropped with wheat with many tillage

Table 5: Soil organic carbon and nitrogen contents (mg g^{-1}) and bulk density (Mg m^{-3}) of the different soil depths and A horizon clay content (mg g^{-1}) at 2500 Mg soil ha^{-1} used in all the sites analyzed.

Symbol	Soil type	Agriculture time years	Depth cm			Bulk density Mg m^{-3}			Carbon			Nitrogen g Kg^{-1}			Clay	Requirement 2500 Mg ha^{-1}
						T period										
Pe	Typic Argiudoll	0	14	14	7	1.07	1.1	1.25	30.1	23.2	20.2	2.9	2.2	2.0	25.2	Pass
Cr	Typic Argiudoll	0	30		7	1.19		1.26	26.2		16.0	2.5		1.4	26.3	Pass
Ur	Typic Argiudoll	0	28		8	1.07		1.25	30.5		19.8	2.8		1.6	24.6	Pass
Ro	Typic Argiudoll	2	13	12	8	1.1	1.18	1.27	24.9	23.7	14.6	2.2	1.9	1.2	23.9	Pass
Py	Vertic Argiudoll	5	16	10	7	1.07	1.22	1.25	24.3	18.1	10.6	2.1	1.6	0.9	24.1	Pass
Ro5	Typic Argiudoll	8	22			1.17			23			1.9		0.0	23.9	Pass
LG	Aeric Argialboll	34	11	11	3	1.18	1.18	1.22	20	21.1	18.2	1.7	1.9	1.5	23.3	Pass
Ro	Typic Argiudoll	35	15	10	8	1.1	1.22	1.3	19.1	18.9	11.8	1.6	1.6	1.0	21.4	Pass
Pe6 o Py2x	Typic Argiudoll	40	18		4	1.19		1.31	15.2		12.9	1.2		1.0	19.0	Fail
Ve2	Typic Argiudoll	55	15		8	1.22		1.24	15.1		13.8	1.3		1.2	23.0	Fail
LG	Aeric Argialboll	60	16	5	8	1.23	1.28	1.3	19.1	19.4	11.2	1.4	1.8	0.8	24.7	Pass
AD2	Typic Argiudoll	64	20			1.25			18			1.4			22.1	Pass
AD2	Typic Argiudoll	70	16	5	7	1.23	1.41	1.35	16.1	15.9	14	1.3	1.1	1.1	21.2	Pass
Ur	Typic Argiudoll	72	12	6	5	1.15	1.36	1.38	18.7	18.5	16.7	1.4	1.5	1.2	20.8	Pass
Ar2	Typic Argiudoll	72	20			1.25			15.2			1.1			19.7	Fail
Cr1	Typic Argiudoll	75	16		8	1.19		1.3	19.4		17.3	1.5		1.4	24.1	Fail
Pe	Typic Argiudoll	80	16	5	7	1.25	1.32	1.28	19	18.4	18.5	1.5	1.4	1.5	21.5	Pass
Ro4	Typic Argiudoll	80	15			1.25			18.9			1.5			19.7	Fail
AD2	Typic Argiudoll	83	20		5	1.26		1.35	19.7		20.7	1.4		1.9	23.5	Pass
Py	Vertic Argiudoll	84	15	8	7	1.22	1.38	1.28	19.4	18.6	18.2	1.6	1.5	1.4	22.0	Pass
Py1 ó Py2x	Vertic Argiudoll	87	15		5	1.28		1.29	19.8		20.5	1.5		1.9	21.6	Fail
Py2x	Vertic Argiudoll	112	13			1.22			16.3			1.2			21.2	Fail
Ca1	Vertic Argiudoll	113	20		6	1.24		1.3	12.7		12.2	1.0		0.9	23.2	Fail
						NT period										
Pe	Typic Argiudoll	0	10	10		1.2	1.34		20	16.4		1.9	1.6			Pass
Pe	Typic Argiudoll	0	10	10		1.22	1.35		16.8	15.7		1.5	1.4			Pass
Pe	Typic Argiudoll	0	10	10		1.22	1.34		17.1	16		1.7	1.6			Pass
Pe	Typic Argiudoll	17	5	5	10	1.16	1.3	1.33	17.2	14.3	14.0	1.4	1.2	1.0	22.6	Pass
Pe	Typic Argiudoll	17	5	5	10	1.14	1.27	1.33	21.1	16.2	14.9	1.9	1.4	1.2	22.7	Pass
Pe	Typic Argiudoll	21	5	5	10	1.16	1.33	1.34	17.6	14.2	13.8	1.5	1.3	1.3		Pass
Pe	Typic Argiudoll	21	5	5	10	1.27	1.39	1.38	19.8	14.9	14.0	2.0	1.6	1.5		Pass
Pe	Typic Argiudoll	25	5	5	10	1.20	1.39	1.38	23.6	16.5	14.9	1.6	1.4	2.3	22.4	Pass
Pe	Typic Argiudoll	25	5	5	10	1.15	1.33	1.36	19.1	14.1	13.4					Pass
Pe	Typic Argiudoll	25	5	5	10	1.19	1.31	1.38	21.1	15.2	14.2					Pass
Pe	Typic Argiudoll	29	5	5	10	1.16	1.32	1.37	22.1	16.3	15.2	2.2	1.6	1.4		Pass
Pe	Typic Argiudoll	33	5	5	10	1.02	1.33	1.36	21.6	15.9	14.9					Pass

T: tillage; NT: no tillage.

operations per year, including mechanical weed control, and sometimes carried out under conditions, which favored mineralization. Besides, we have previously suggested that soybean accelerates SOM decomposition [77]. The comparison of the SOC stocks between soybean monoculture (site A) and crop rotations (T period) 33 years after the introduction of agriculture showed a smaller SOC stock with soybean monoculture than with crop rotation (Figure 7(a)).

Another factor which could explain the changes in SOC storage after grassland cultivation is the decrease in the amounts of crop residue additions. Our calculations show that under native vegetation, organic additions are as important as under cultivation, that is, about 3-4 Mg C ha^{-1} year^{-1}. Aboveground production is presently substantially greater than the estimated production of native grassland. Hence, apparently, this factor cannot explain the differences observed.

SON losses were more important than SOC losses, except in the case of soybean monoculture of the site A (Figure 7(b)), where the C/N ratio increased with time of cultivation

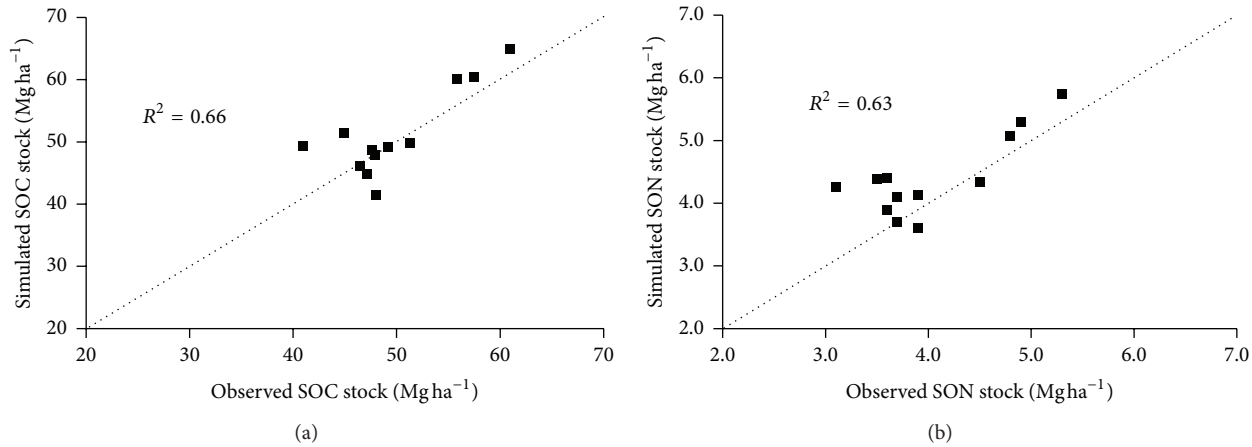

Figure 6: Comparison of observed and simulated SOC (a) and SON (b) in the T period.

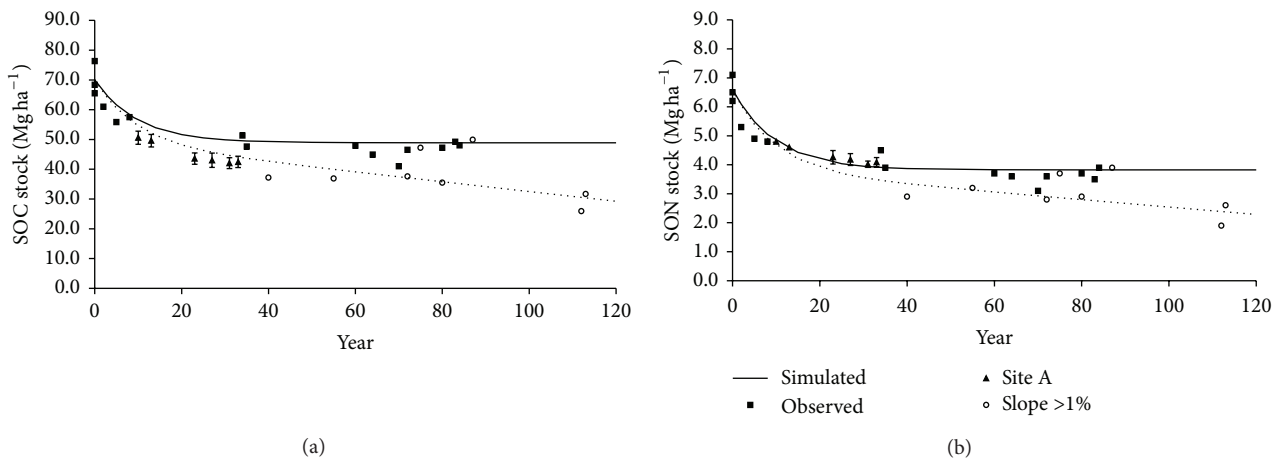

Figure 7: SOC (a) and SON (b) mean evolution during the T period of sites at 2500 Mg soil ha^{-1} (solid line) and <2500 Mg soil ha^{-1} (dotted line).

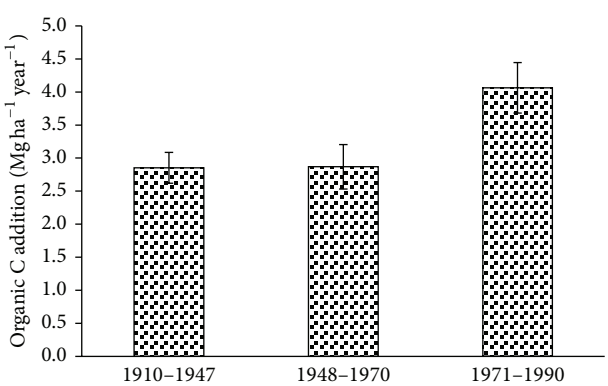

Figure 8: Organic C addition (Mg ha^{-1} year^{-1}) from three phases: manual harvest and stubble burning (1910–1947), mechanical weed control (1948–1970), and improved crop management (1971–1990).

(from 10-11 to 12–14), indicating the presence of physically protected SOM, with a low C/N ratio and a labile pool in the virgin soil with a faster mineralization rate than the rest of SOM during cultivation. Apparently, in uncultivated soils, macroaggregation plays an important role in N protection [78–80]. Opposed trends in C/N have been reported in other studies where N fertilizers are regularly applied [2, 28]. We can assume that resistant organic fractions increased with time. Soils with a long period of cultivation would have a residual SOM that would mineralize less N. On the other hand, C/N ratios from sites with slopes >1% are not systematically greater than those from sites with slopes <1%. Therefore, we conclude that losses of N with the time under tillage were not due to erosion.

Farmer surveys not only have the advantage of their low cost but also provide the required information on equilibrium values of SOC and SON. The principal problem is that they mix sites with a different crop history. Despite the measure of the true Rolling Pampa crop history in the oldest sites, there is not the same history in the youngest sites.

Overall, the results in the Rolling Pampa after 120 years of tillage indicate that the SOM is composed of two pools: an active pool with a rapid turnover (MRT ~9 years) which represents 50% of SOC (SON) in the native prairie soil and

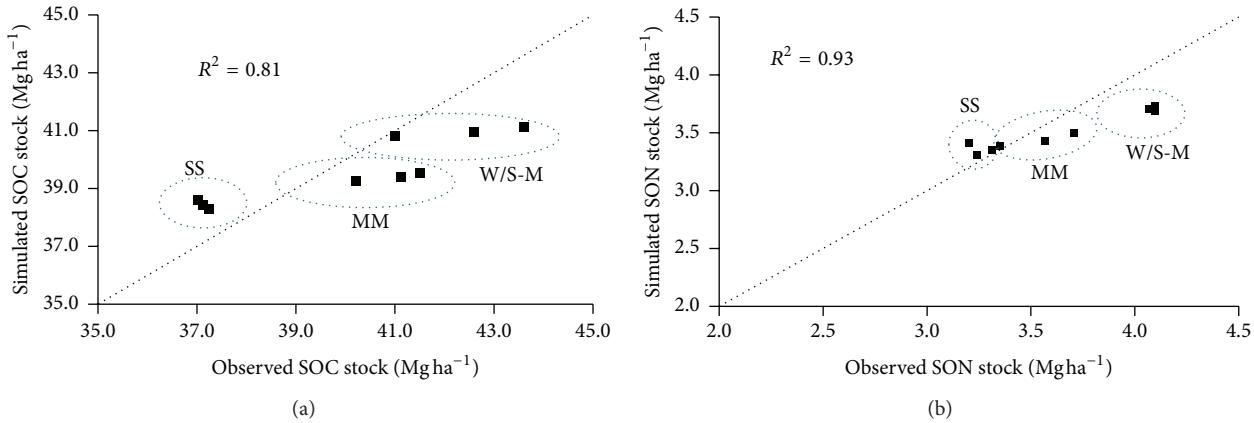

Figure 9: Comparison of observed and simulated SOC (a) and SON (b) in NT period. SS: soybean monoculture; MM: maize monoculture; W/S-M: doubled-cropped wheat/soybean maize.

a stable pool. SOM storage after 120 years of tillage is probably a result of an important decrease in the active fraction of a native soil, which would not be compensated by the inputs from the crops. At equilibrium, the active fraction would represent only 30% of the SOC and 20% of the SON.

In the NT period, the AMG model showed a better simulation of SOC and SON evolution than in the cultivation period (Figure 9). In this period, both the site used for calibration and that used for validation belonged to the same soil series and were implemented in similar times (1980–2012s). We could have done the calibration of this period using the long-term trials, even without sufficient information on ^{13}C measurements, but decided not to use them because there is no accurate information from the previous agricultural history cycles, corresponding to alternated agriculture and pasture cycles.

Despite the high R^2 value obtained for SOC, the model tended to underestimate them in M-W/S and MM sequences and overestimate them in SS. This fate is correlated with the quantity of annual C addition: 2.9, 4.2, and 4.8 Mg ha^{-1} year^{-1} in SS, MM, and M-W/S sequences, respectively (Table 6). The crop sequences with more C addition tended to have higher observed SOC stocks, although observed SOC stocks in M-W/S and MM had a higher variation among years than simulated stocks. Another factor causing high variability was the size of the stable pool, C_s. The size of this pool was fixed for all the sequences evaluated (32 Mg SOC ha^{-1}). However, it is likely that the size under NT tended to be a little higher in MM and M-W/S and relatively lower in SS. A C_s of 33.9, 32.6 and 30.4 Mg ha^{-1} increases the R^2 value to 0.92. In general, a similar behaviour was observed for SON simulations among the different crop sequences, although with better quality adjustment than with SOC. The k_1 value was fixed at 0.83 for the three sequences. It is likely that in M-W/S the humification of N is higher than in SS and MM. Stemmer et al. [81] found that the mineralization of maize was delayed when straw was left on the surface and attributed it to the low contact of the residue with the soil. In MM, part of the maize stalks would be incorporated very slowly because they remain standing after the harvest and because their nature and morphology offer a contact surface with the soil of about half of that of wheat stubble [82]. However, in M-W/S, during the W/S period, the fall of soybean leaves with annual frequency from the R6/R7 stage, which have very low C/N relationships, stimulates the breakdown of residues and becomes a nitrogen fertilization of low dose (around 25 kg N ha^{-1}) [83] that leads to the formation of labile fractions very processed by fungal activity [84]. The k_1 values of 1 and 0.63 for M-W/S and MM increased the R^2 value to 0.95.

The SOC stocks at the beginning of the MM and SS (Table 6) were smaller than SOC stocks found at equilibrium of the T period (Figure 7(a)), whereas the SON stocks showed the opposite pattern (Table 6 and Figure 7(b)). Soybean conventionally tilled before to the start of monocultures probably decreased the SOC stocks but not the SON stocks as happened in the same Figure 7 at the site A.

All sequences tended to decrease the SOC and SON stocks by 5–9% and 25–27% (Table 6). The higher initial organic stocks increased further losses.

The C_a varied from 8.0, 9.0, and 13.3 Mg ha^{-1} at the beginning to 7.2, 7.0, and 9.2 at equilibrium for SS, MM and M-W/S, respectively. When equilibrium is reached, this fraction would represent 18, 18, and 22% of SOC. It would be necessary to increase the annual C addition by 40–45% to maintain the C_0 value in SS and M-W/S, respectively.

The active fraction N_a varied from 1.38, 1.43, and 1.50 Mg ha^{-1} at the beginning to 0.63, 0.78, and 0.85 at equilibrium for SS, MM, and M-W/S, respectively. When equilibrium is reached, this fraction would represent 19, 22, and 23% of SON.

Overall, the results indicate that although the NT implementation in the rich SOM soils of the Rolling Pampa after a century of continuous agriculture contributed to a decrease in the SOM mineralization rate (overall MRT of active SOM compartment would be included in 13 years), the system also implies a low humification from harvest crop residues addition. The active fraction continued to decrease even in cases of high C and N input rates. At equilibrium, this fraction would represent between 20 and 25% of the overall SOM,

Table 6: Measured C_0 (N_0), annual C (N) additions, m (m_N), C_{max} (N_{max}), and C_{eq} (N_{eq}) at equilibrium.

Crop sequence	C_0 Mg ha^{-1}	m Mg ha^{-1} year^{-1}	C_{max} Mg ha^{-1}	C_{eq}
SS	40.5 (2)	2.8 (0.6)	0.47	37.9
MM	41.0 (2)	4.2 (1.8)	0.55	38.9
W/S-M	45.3 (0.8)	4.8 (0.8)	0.67	40.4
	N_0 Mg ha^{-1}	m_N Mg ha^{-1} year^{-1}	N_{max} Mg ha^{-1}	N_{eq}
SS	4.05 (0.2)	0.068 (0.01)	0.057	3.3
MM	4.20 (0.2)	0.074 (0.03)	0.061	3.55
W/S-M	4.33 (0.1)	0.090 (0.01)	0.076	3.71

C_0 (N_0): initial soil C (N) stock; m (m_N): annual C (N) addition; C_{max} (N_{max}): maximum humified C (N) stock; C_{eq} (N_{eq}): soil C (N) stock at equilibrium. SS: soybean monoculture; MM: maize monoculture; W/S-M: doubled-cropped wheat/soybean maize.

corresponding to very high and low soybean frequency in crop sequences, respectively.

In 2010, we sampled fourteen new sites of Pergamino soils with a long time of continuous agriculture and at least five years under NT to obtain the SOC and NOC stocks at time zero of the future independent validation sites. The SOC and NOC values were 42.8 ± 3.3 and 3.6 ± 0.2 (data not shown). The AMG model previsions for the next 30 years are 15 and 20% in SOM loss in the sites where organic reserves are highest and annual C additions are 2.8 and 4.8 Mg ha^{-1} year^{-1}, respectively; meanwhile, SOM will remain steady and will tend to go up slightly for the same inputs in the sites where organic reserves are smallest. Using the Century model for the same region, Caride et al. [85] predicted a decrease of 15% in SOM for the next 60 years, in agreement with our results.

A strategy to balance the decreasing tendency in SOM reserves is to increase the residue addition to the soil by means of intensification of sequences, including the use of cover crops [86].

4. Conclusions

The approach used to reconstitute the overall continuous agriculture history (T + NT periods) from grassland soils of the rolling Pampa was successful. During the cultivation period, the decrease in SOC and SON storage was due to two causes: a loss through biological activity and a loss through erosion. The samples were stratified (according to landscape position), allowing the selection of situations where biotransformation processes are dominant. The simple AMG model adequately simulated the evolution of SOC and SON stocks both during the T period and in the NT period when the erosion was not a major factor regarding N and C losses. The stable pool represented near 50% of total SOC and SON before cultivation and its proportion increased with the increase in agriculture time. The active fraction presented a rapid turnover during the T period (MRT = 9 years), which slowed down during the NT period (MRT = 13 years). The environmental functions used over the active mineralization rate worked very well in tillage soils, and the values found were very close to those obtained with ^{13}C measurements. During the first twenty years, there was a loss of 27% for SOC and 32% for SON, and after that the equilibrium was apparently reached. The soils remained rich in SOM reserves. The NT applied in these conditions reduced not only the active mineralization rate but also the humification coefficient. In consequence, a slow new loss was produced: SOM storage after 140 years of continuous agriculture is probably the result of an important decrease in the active fraction, which would not be compensated by the inputs from the crops. A reduction of 20% or no reduction of the SOM reserves is expected in this region for the next 30 years with the average C (3.8 Mg C ha^{-1} year^{-1}) and N (0.08 Mg N ha^{-1} year^{-1}) annual addition, in the sites with the current highest (85.2 Mg SOM ha^{-1} year^{-1}) and the smallest (66.7 Mg SOM ha^{-1} year^{-1}) SOM, respectively.

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Review Article

The Role of Biochar in Ameliorating Disturbed Soils and Sequestering Soil Carbon in Tropical Agricultural Production Systems

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Agricultural soils in the tropics have undergone significant declines in their native carbon stock through the long-term use of extractive farming practices. However, these soils have significant capacity to sequester CO_2 through the implementation of improved land management practices. This paper reviews the published and grey literature related to the influence of improved land management practices on soil carbon stock in the tropics. The review suggests that the implementation of improved land management practices such as crop rotation, no-till, cover crops, mulches, compost, or manure can be effective in enhancing soil organic carbon pool and agricultural productivity in the tropics. The benefits of such amendments were, however, often short-lived, and the added organic matters were usually mineralized to CO_2 within a few cropping seasons leading to large-scale leakage. We found that management of black carbon (C), increasingly referred to as biochar, may overcome some of those limitations and provide an additional soil management option. Under present circumstances, recommended crop and land management practices are inappropriate for the vast majority of resource constrained smallholder farmers and farming systems. We argue that expanding the use of biochar in agricultural lands would be important for sequestering atmospheric CO_2 and mitigating climate change, while implementing the recommended crop and land management practices in selected areas where the smallholder farmers are not resource constrained.

1. Introduction

Evidence from the Intergovernmental Panel on Climate Change [1] is now overwhelmingly convincing that climate change is real, that it will intensify, and that the poorest and most vulnerable will be disproportionately affected by these changes. Climate change and variability, drought, and other climate-related extremes have a direct influence on the quantity and quality of agricultural production and, in many cases, adversely affect it. In particular, the influences of climate change on agricultural production are severe in developing countries because the technology generation, innovation, and adoption are too slow to counteract the adverse effects of varying and changing environmental conditions [2].

Agricultural intensification invariably has several negative impacts on the environment [3]. One of the major consequences of agricultural intensification is a transfer of carbon (C) to the atmosphere in the form of carbon dioxide (CO_2), thereby reducing ecosystem C pools. Agriculture contributes 10–12% of the total global anthropogenic greenhouse gas emissions [4, 5]. Tropical agricultural soils in particular have undergone significant depletion of their native carbon stocks but have considerable potential to act as CO_2 sinks through improved management practices [6, 7]. To this end, locally appropriate adaptation and mitigation strategies to increasing climate variability and climate change are urgently needed especially in vulnerable regions where food and fiber production are most sensitive to climatic fluctuations [2].

The implementation of improved land management practices to build up carbon stocks in terrestrial ecosystems is a proven technology in reducing the concentration of CO_2 in the atmosphere and lowering atmospheric CO_2 [8].

As a result, soil organic carbon sequestration in agricultural lands has recently drawn attention in mitigating increases in atmospheric CO_2 concentrations [5, 9].

Management practices to build up soil carbon must increase the input of organic matter to soil and/or decrease soil organic matter decomposition rate. At this point, it is worth to mention that the most appropriate management practices to increase soil carbon vary regionally, depending on both environmental and socioeconomic factors. In the tropics, increasing carbon inputs through improving the fertility and productivity of crop land and pasture is essential because climate change has negative influence on the livelihood of the vast majority smallholder farmers. In extensive systems with vegetative fallow period, planted fallows and cover crops can increase carbon levels over the cropping cycle [10]. Uses of no-till, green manures, and agroforestry are other beneficial practices to sequester soil C. Overall, improving the productivity and sustainability of existing agricultural lands is crucial to reduce the rate of new land clearing and the amounts of CO_2 emitted to the atmosphere.

Carbon sequestration in agricultural soils is frequently promoted as a practical solution to slow down the rate of increase of CO_2 in the atmosphere. To date, the bulk of research into agricultural production systems being net carbon sinks has been based on temperate based production systems that are quite different to those in the tropics. There is a need to improve our understanding on how land management practices affect exchange processes that lead to net removal of atmospheric CO_2 in the tropics. Therefore, we reviewed and analyzed the impacts of different land management practices such as agronomic practices, tillage, organic input management (i.e., addition of compost, manure, biochar, and other clay materials), and agroforestry as a means to increase carbon sequestration in agricultural soils of the tropics. Moreover, we reviewed the opportunities and constraints to adapt mitigation and adaptation options in the tropics with the goal of developing a possible framework for smallholder farmers to benefit from carbon markets.

2. Overview of Tropical Production Systems

In the tropics, farming systems have undergone major changes from hunting and gathering through fallowing to stationary cultivation systems during the course of history [11]. The changes in farming systems were mainly driven by the increase in human population and agricultural mechanization (e.g., [12]), the quality and availability of land resources (e.g., [13]), and access to markets (e.g., [12]). The decision-making environment in tropical agricultural systems is complex. The first factor that controls farmer's decision-making is the physical environment (e.g., [14]). The second can be called household characteristics (e.g., [15]), where uniform producers react in a uniform and rational manner during decision-making processes. The third factor that determine farmers' choice of production systems is the politico/economical frame conditions (e.g., [16, 17]).

Furthermore, farming systems may be differentiated into subtypes that continue to evolve along different pathways. For example, in systems under population and market pressure, some farms could successfully intensify and even specialize to produce for the market, whereas others could regress to low-input/low-output systems [17]. Moreover, in any one location within a farming system, different farms are likely to be at different stages of evolution because of differentiated resource bases, household goals, capacity to bear risk, and degree of market access, among others [15]. It is the sum of all farmers' decisions that will determine the quality of the future land resources in the tropics as there is a feedback mechanism between farmer's decisions and the quality of the natural resource base. The chain of linkages among population pressure, agricultural intensification, economic growth, societal well-being, and technical changes in agriculture and their subsequent environmental consequences are thus very complex in nature and causation and as a result are often difficult to analyze and understand.

3. Tropical Agricultural Production Systems and Soil Carbon

The key problem of tropical agriculture is the steady decline in soil fertility, which is due primarily to soil erosion and the loss of soil organic matter. Some soils in tropical agricultural systems are estimated to have lost as much as 20 to 80 t C ha^{-1}, most of which has been released into the atmosphere [3, 18]. The low soil organic carbon content is due to the low shoot and root growth of crops and natural vegetation, the rapid turnover rates of organic material as a result of high soil temperatures and fauna activity particularly termites, and the low soil clay content [19]. In addition, soil erosion and the long-term cultivation using conventional tillage practices reduce soil carbon levels, and over time the soils have become degraded, often resulting in land abandonment [6, 20, 21]. For instance, a study in west African agro-ecosystem revealed that there is a tremendous SOC loss in agricultural lands due to soil erosion (ranging from 65 to 1801 kg ha^{-1} yr^{-1}) compared to the loss of SOC (ranging from 6 to 13 kg ha^{-1} yr^{-1}) in undisturbed ecosystems [19]. The loss of SOC could range from 9 to 65% depending on severity of soil erosion and soil types.

Furthermore, the burning of biomass or vegetation as a conventional land preparation method and the use of crop residues and cow dung as a source of energy have a net negative impact on the soil organic carbon and on the environment through the release of CO_2. For instance, in Ghana, Parker et al. [22] documented a 21% reduction in soil organic carbon because of biomass burning that resulted in the release of 1.4 t CO_2 ha^{-1} to the atmosphere. A study in southern Asia also demonstrated that burning of 5–7 t ha^{-1} of rice residues causes air pollution through releasing 13 t CO_2 ha^{-1} [23].

In the tropical agricultural systems, the removal of crop residues for or by livestock, either through grazing or cut and carry, is a common practice, which conflicts the use of crop residues and cover crops for soil improvement [24]. Smith et al. [5] showed that it was more likely to observe an effect of straw removal on SOC: (i) in the less fertile soils,

(ii) when greater quantities of residues were removed, and (iii) over longer periods. In line with this negative effect of residue removal on soil carbon, Nandwa [25] demonstrated that residue removal for off-farm use should consider only amounts that can be harvested without decreasing SOC levels. However, livestock are an important part of production in mixed farming systems and in the absence of alternative feed sources; farmers are usually unwilling to abandon this critically important one [25].

There is a consensus among the literature that most of the tropical agricultural systems lead to the depletion of organic matter due to the long-term extractive agricultural practices and reduced organic inputs, which consequently make most of the agricultural systems unsustainable. Due to this, there is an urgent need to improve the management of organic inputs and soil organic matter dynamics in tropical land use systems. One desirable goal is the ability to be able to manipulate soil organic matter dynamics via management practices so as to promote soil conservation, to ensure the sustainable productivity of agroecosystems, and to increase the capacity of tropical soils to act as a sink for, rather than a source of, atmospheric carbon.

4. Land and Crop Management Practices for Soil C Sequestration

In the last two to three decades, several land and crop management practices have been advocated to restore soil organic carbon and reduce net emissions of CO_2 from the agricultural systems in the tropics [5, 26, 27]. Among others, practices that restore soil organic carbon and reduce net emissions of CO_2 include crop rotation, avoiding use of bare fallow, conservation tillage, management of organic inputs such as manure and crop residues, restoration of degraded agricultural lands, water management, and agroforestry (e.g., [28–34]).

Studies demonstrated that smallholder farmers can reduce greenhouse gas emissions and maintain carbon stocks in soil and vegetation at relatively low cost by implementing crop and land management practices (e.g., [27, 35–37]). However, a review by Giller et al. [38] and Sanchez, 2000 [39], identified a number of constraints that include a low degree of mechanization within the smallholder system, lack of appropriate implements, problem of weed control under no-till system, and lack of appropriate technical information that hinders large-scale adoption of the practices by the smallholder farmers. Woodfine [27] added that a key bottleneck to realizing the adoption of many mitigation practices is the availability of financing to catalyze initial change. Operationally, improved crop and land management practices may require more manual labor than conventional agricultural practices [40]. Optimizing these advantages and disadvantages can be a complex task which is in itself a disadvantage where there is a scarcity of trained personnel and extension workers to provide information and advice to farmers.

Furthermore, the temporal pattern of influence in mitigating the increase in CO_2 varies among practices and, in most cases, CO_2 emissions reduction resulted from the advocated practices are temporary [5]. For example, a study in Kenya documented that the residual effect of manure applied for four years only lasted another seven or eight years when assessed by yield, SOC, and Olsen P [41]. Effect of no-till practices are also easily reversed and lead to the release of CO_2 to the atmosphere as soon as the system started to be disturbed.

In sum, under present circumstances, recommended crop and land management practices are inappropriate for the vast majority of resource constrained smallholder farmers and farming systems [38]. However, this does not mean that mitigation practices advocated in the last two to three decades could not be one option that can offer substantial benefits for smallholder farmers in the tropics who are not constrained by resources and in certain locations where political, economical, and institutional frame conditions are relatively efficient. Identification of the situations when mitigation practices can offer major benefits is a challenge that demands active research [38].

5. Biochar as a Climate Change Mitigation Option

Biochar is a charcoal produced under high temperatures (300 to 500°C) through the process of pyrolysis using crop residues, animal manure, or any type of organic waste material [42]. The two main methods of pyrolysis are "fast" pyrolysis and "slow" pyrolysis. Fast pyrolysis yields 60% bio-oil, 20% biochar, and 20% syngas and can be done in seconds, whereas slow pyrolysis can be optimized to produce substantially more char (~50%), but takes on the order of hours to complete [43]. Depending on the feedstock, biochar may look similar to potting soil or to a charred substance. The combined production and use of biochar are considered a carbon-negative process, meaning that it removes carbon from the atmosphere [42, 44]. Studies suggest that biochar sequester approximately 50–80% of the carbon available within the biomass feedstock being pyrolyzed depending upon the feedstock type [45, 46].

6. Can We Produce Biochar Using Locally Available Technologies?

Biochar can be produced using locally made technologies, which can be affordable to the local farmers and easily adopted and used. One of such easy technologies is the use of biochar chamber made of stainless steel (Figure 1). This kind of technology only costs about $ 70 US per chamber (based on the amount of money invested to produce a chamber at Laos PDR), and the system operation and maintenance are quite easy and can be managed by the smallholder farmers in the tropics. We have also measured that it has the capacity to produce 83.3 (±4.2) kg of biochar from a rice husk with conversion efficiency of 48.1 (±2.1) % per 14.5 (±1.0) hours of burning. Other methods used to produce biochar in small quantity for use by the small-scale farmers that are described in http://www.biochar.info/ include carbon zero

Biochar chamber made of stainless steel | The chamber covered with rice husk and burning | Biochar produced after 14–18 hours of burning

Figure 1: The process of biochar production using biochar chamber made of stainless steel from a rice husk (photo by Wolde Mekuria).

experimental biochar kiln, simple two-barrel biochar retort, and simple two barrel biochar retort with afterburner.

In addition, in The Netherlands, a "Twin-retort" carbonization process has been developed to address charcoal production efficiency and emission problems [47]. The traditional charcoal production systems used in the past such as charcoal production in open pits, earthen kilns, and traditional charcoal mounds, as carried out in rural areas, are inefficient. In most cases, weight efficiency of the traditional charcoal production systems carried out in rural areas ranged from 10 to 15% indicating that seven to ten kilograms of wood are required to produce one kilogram of charcoal [47]. Reumerman and Frederiks [47] documented that the efficiency of "Twin-retort" carbonization process is more than double compared to the tradition charcoaling processes. This indicates the possibility to reduce emissions with at least a factor of two.

We argue that the possibility to produce biochar using simple and locally available technologies speeds up the adoption of biochar production systems and its use as a climate change mitigation measure and improving agricultural productivity provided that obstacles that may halt rapid adoption of biochar production systems include technology costs, system operation, and maintenance [42]. Although biochar research and development are in their early stage, interest in biochar as a tool to mitigate the increase in CO_2 and improve agricultural productivity is growing at a rapid pace across the tropics.

7. Biochar, Soil C, Soil Fertility, and Productivity

Soil amendment with biochar has been proposed as a means to sequester C (Table 1) and improve soil fertility. Application of charcoal to soils is hypothesized to increase bioavailable water, build soil organic matter, enhance nutrient cycling, lower bulk density, act as a liming agent, and reduce leaching of pesticides and nutrients to surface and ground water [48–51]. Leach et al. [52] also documented that application of biochar to the soil enabling increases in agricultural productivity without, or with much reduced, applications of inorganic fertilizer. Furthermore, Harley [53] indicted that biochar is a promising amendment for ameliorating drastically disturbed soils due to its microchemical, nutrient, and biological properties (Table 2). Biochar-based strategies are thus being seen to offer valuable routes to building sustainable agricultural futures, particularly for resource poor farmers for whom soil fertility and water availability are seen as key constraints on crop production and food security [52].

The extent of the effect of biochar on crop productivity and soil carbon sequestration is, however, variable due mainly to the different biophysical interactions and processes that occur when biochar is applied to soil, which are not yet fully understood [59]. For instance, in nitrogen limited soils, application of high rates of biochar may affect growth negatively due to immobilization effect [46]. Moreover, feedstock and pyrolysis conditions (temperature, holding time, etc.) may affect both stability and nutrient content and availability of biochar [59–61]. Given how inconsistent biochar impacts on yields and soil carbon sequestration are and how little is known about their longer-term impacts, farmers who are to use biochar on their fields are taking considerable risks such as a possible reductions in crop yield during the early cropping seasons.

Thus, we argue that care should be taken on the amount and type of biochar added to the soil for restoring degraded soils. In addition, it is crucial to detect the consequent soil organic carbon accumulation and increase in crop yields under different soil and climatic conditions. Long-term studies on biochar in field trials are also required to better understand biochar effects and to investigate its behavior in soils, thereby reducing the associated risks.

Table 1: Effects of biochar sourced from different biomass on soil C.

Country	Soil type	Treatment	Application rate	Changes in soil C*	Source	Remark
Philippines	Gleysols	Rice husk biochar	41.3 t ha^{-1}	12.9 g kg^{-1}	[54]	After 3 years
Philippines	Nitosols	Rice husk biochar	41.3 t ha^{-1}	12.4 g kg^{-1}	[54]	After 3 years
Thailand	Acrisols	Rice husk biochar	41.3 t ha^{-1}	0.51 g kg^{-1}	[54]	After 3 years
Ethiopia	Nitosols	Maize stalk biochar	5 t ha^{-1}	0.71%	[55]	Incubation trial
Ethiopia	Nitosols	Maize stalk	10 t ha^{-1}	0.77%	[55]	Incubation trial
South Africa	Acidic sandy soils	Pinewood sawmill biochar	10 t ha^{-1}	8.11%	[56]	Pot trial
India	Vertic ustropept	*Prosopis* biochar	5% of the incubated soil	4.5 g kg^{-1}	[57]	After 90 days of incubation
Kenya	Ferrasol	Acacia tree biochar	50 t ha^{-1}	0.7%	[58]	Greenhouse experiment

*Changes in soil C refers to the increase in C due to addition of biochar against the control plots.

8. Potential of Biochar to Mitigate the Increase in CO_2

Studies have shown that cover crops, mulches, compost, or manure can be effective in enhancing soil organic carbon pool and agricultural productivity in the tropics (e.g., [29, 34, 62]). The benefits of such amendments are, however, often short-lived, especially in the tropics, since decomposition rates are high, and the added organic matters are usually mineralized to CO_2 within only a few cropping seasons. Organic amendments therefore have to be applied intermittently to sustain soil productivity. In case of agricultural lands converted to no-tillage systems, stored carbon can be released once we convert no-tillage back to conventional tillage. Therefore, carbon sequestered by these crop and soil management practices is generally considered only temporarily sequestered from the atmosphere and associated with a high risk of rapid or large-scale leakage [44].

Management of black carbon (C), increasingly referred to as biochar, may overcome some of those limitations and provide an additional soil management option. Once biochar is incorporated into soil, it is difficult to imagine any incident or change in practice that would cause a sudden loss of stored carbon indicating that biochar is a lower-risk strategy than other sequestration options [44]. Thus, biochar could be a potentially a powerful tool for mitigating anthropogenic climate change as the carbon in biochar, it is claimed, resists degradation and can sequester carbon in soils for hundreds to thousands of years [26, 44, 54, 63, 64]. The half-life of C in soil charcoal is in excess of 1000 yr [65]. Laird et al. [49] presented an interesting graph that compares the stability of organic input added as residue biomass and biochar (Figure 2).

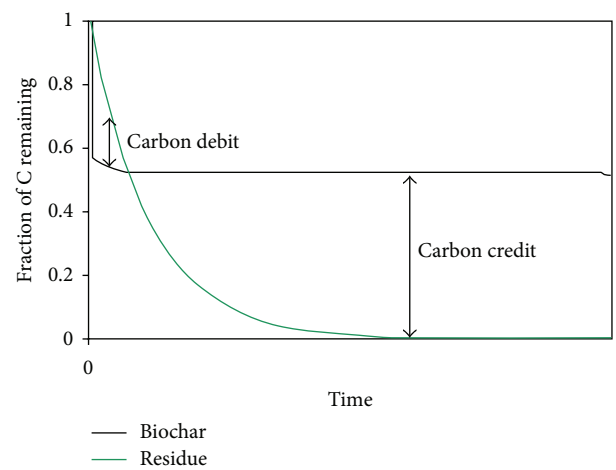

Figure 2: Impact of biomass pyrolysis with soil application of biochar on the amount of original biomass C remaining in the soil relative to the amount of C remaining in the soil if the same biomass is returned to the soil as a biological residue (source: Laird et al., 2009 [49]).

> According to Laird et al. [49] (Figure 2) "For the Biochar example, about 40% of the C is lost at time 0 when the biomass is pyrolyzed, 10% of the total C is lost to mineralization over a few months, and the remaining 50% of the total C is stable for millennia. For the Residue example, the half-life of the residue C is assumed to be 6 months and 99% of the C is lost to mineralization after 4 years. The biochar scenario results in a C debit for the first 6 months and a C credit thereafter relative to the residue scenario". This indicates that biochar is a highly stable form of carbon and as such has the potential to form an effective C sink, therefore sequestering atmospheric CO_2 [59].

Current analyses suggest that there is global potential for annual sequestration of atmospheric CO_2 at the billion-tone scale (109 t yr^{-1}) within 30 years [59]. Woolf et al. [66] also indicated that annual net emissions of carbon dioxide (CO_2) could be reduced by a maximum of 1.8 Pg CO_2-C equivalent (CO_2-C e) per year (12% of current anthropogenic CO_2-C e emissions; 1 Pg = 1 Gt) and total net emissions over the course of a century by 130 Pg CO_2-C e, without endangering food security, habitat, or soil conservation. In addition, Gaunt and Lehmann [67] documented that emission reductions can be 12–84% greater if biochar is put back into the soil instead of being burned to offset fossil fuel use. Furthermore, the application of biochar once in every ten years to the estimated 15×10^9 ha of cropland worldwide would

Table 2: Role of biochar in ameliorating drastically disturbed soils [53].

Limiting factor	Variable	Problem	Short-term treatment	Long-term treatment	Role of biochar
Physical	Soil structure	Soil too compact	Rip or scarify	Vegetation	Decreased soil bulk density, increased infiltration, and decreased erodibility
	Soil erosion	High erodibility	Mulch	Regrade vegetation	
	Soil moisture	Too wet	Drain	Wetland construction	
		Too dry	Organic mulch	Tolerant species	Increased water retention due to surface area and charge characteristics
Nutritional	Macronutrients	Nitrogen deficiency	Fertilizer	Nitrogen fixing plants, for example, leguminous trees or shrubs	Yield increases Slow nutrient release Soil organic matter stabilization Retention of released nutrients Increased microbial activity Habitat for mychorrhizal fungi hyphae
		Other deficiencies	Fertilizer	Fertilizer, amendments, tolerant species	
Toxicity	pH	Acid soils (<4.5)	Lime	Tolerant species	Designed for alkaline surface charge
		Alkaline soils (>7.8)	Pyritic waste, organic matter	Weathering, tolerant species	High CEC for Na retention
	Heavy metals	High concentration	Organic matter, tolerant cultivar	Inert covering, tolerant species	High surface area and cation exchange capacity allows for metal retention
	Salinity	EC > 4 ds/m pH < 8.5, SAR < 13	Gypsum, irrigation	Weathering, tolerant species	Mixed with gypsum to reduce soil structural issues
	Sodicity	EC < 4 ds/m, pH > 8.5, SAR ≥ 13	Gypsum, irrigation	Weathering, tolerant species	Nutritional values as described High CEC for Na retention

result in a CO_2-equivalent gain of 0.65 Gt C yr^{-1} [68, 69]. These in turn indicate that biochar sequestration could be one option to change bioenergy into a carbon-negative industry [44].

9. Opportunities and Constraints for Mitigating Carbon Emissions in Tropical Agricultural Production Systems

In the tropics, soil organic carbon in the agricultural landscape has been depleted through the long-term use of extractive farming practices [18, 70, 71]. Most agricultural soils have lost 30 to 40 t C ha^{-1}, and their current reserves of soil organic carbon are much lower than their potential capacity indicating that there is great technical potential to increase soil carbon in agricultural soils and reduce greenhouse gas emissions. According to Lal [71], most soils have a technical or maximum sink capacity from 20 to 50 t C ha^{-1} that can be sequestered over a 20-to-50-year period. The greatest potential for sequestration is in the soils of those regions that have lost the most soil carbon. These are the regions where soils are severely degraded and have been used with extractive farming practices for a long time. Among developing countries, these regions include Sub-Saharan Africa, South and Central Asia, the Caribbean, Central America, and the Andean regions [71]. Among others, converting degraded soils into restorative land and adopting practices such as no-till, organic C input management such as additions of manure, compost, biochar, and agroforestry are practices that can increase the soil carbon pool in the tropics [71].

The literature reveals that in the last two to three decades that enabling and encouraging broader adoption of mitigation options were advocated through market-based mechanisms. This could create the catalyst necessary to elevate agriculture's role as a key part of a global approach to mitigating climate change. However, soil C sequestration through the advocated crop and soil management practices currently does not fit under emission trading (ET), the clean development mechanism (CDM), or joint implementation (JI), and neither Article 3.3 nor 3.4 of the Kyoto Protocol specifically include soil carbon as an option [72]. According to Lehmann [44], some of the reasons why soil C sequestration through crop and soil management practices is not allowed into trading markets under current agreements include (1) the net withdrawal of CO_2 through the advocated crop and soil management practices is usually short-lived, (2) accountability of the process of C sequestration is not straightforward, and monitoring and certifying the changes in C stocks are difficult and costly, and (3) the processes of C sequestration also associated with rapid or large-scale leakages. Sohi and Shackley [26] also pointed out that decomposition rate may increase with climate change making soil carbon stores vulnerable to "feedback." Only a small proportion of added organic matter stabilized for longer time, and accumulation rate diminishes with time resulting in inefficient use of organic resource after equilibration.

Yet, considering soil carbon as a commodity and creating another income stream for resource poor and small size land holders are essential prerequisite to widespread adoption of recommended management practices in the developing countries where the problems of food insecurity and soil/environmental degradation are extremely severe. Realizing these incomes would necessitate substantially greater policy support and investment in sustainable land uses than is currently the case [73]. Furthermore, while soil and crop management practices that enhance soil carbon pool in general clearly offer economic and ecological advantages, the development of robust systems compliant with stakeholder needs and requirements is constrained by our limited understanding of the tradeoffs between subsistence requirements, acceptable risks, and the costs involved [74].

10. Can We Integrate Biochar into Trading Markets under Current Agreements?

Funding from carbon trading is argued to be essential to finance the research and development necessary to discover and exploit the full potential of crop and soil management practices to contribute to climate change mitigation and to enable wider adoption of the practices to sequester carbon at globally significant levels [52]. When it comes to including biochar in emission-trading schemes, the issues of permanence, land tenure, leakage, and additionality are less significant for biochar projects than for projects that sequester C in biomass or soil through management of plant productivity [44]. This is because biochar carbon sequestration might avoid difficulties such as accurate monitoring of soil carbon, which are the main barriers to inclusion of agricultural soil management in emissions trading [44, 75]. In addition, no complex predictive models or analytical tools are required, as is the case with other soil sequestration approaches. The source of biochar additions can easily be identified by soil analyses, if desired for verification under carbon-trading schemes.

We argue that there is a great potential to allow the associated emission reductions through using biochar into trading markets under current agreements, because emission reduction units obtained due to the use of biochar can easily be accounted, monitored, and verified. In addition, climate change is real that it will intensify, and there is an urgency not only to identify but also to implement solutions. Biochar sequestration does not require a fundamental scientific advance, and the underlying production technology is robust and simple, making it appropriate for many regions of the world [44]. Furthermore, the possibility to produce biochar using locally available technologies (Figure 1) even makes it more appropriate for the resource poor smallholder farmers living throughout the tropics.

11. Considerations in Upscaling Biochar

Recognizing that biochar technology is in its early stages of development, there are many concerns about the applicability of the technology in the tropics. Three issues are feedstock availability, biochar handling, and biochar system deployment. To date, feedstock for biochar has consisted mostly

of plant and crop residues, a primary source of energy and livestock feed for the smallholder farmers in the tropics. Thus, there is still sustainability concerns related to supplying feedstock for large-scale biochar production. The ideal time to apply biochar and how to ensure that it remains in place once applied and does not cause a risk to human health or degrade air quality is also a concern. Furthermore, developing a "one size fits all" biochar system would also be a challenge as biochar systems are designed on the feedstock to be decomposed and the energy needs of an operation [42].

The literature indicates that biochar can be effective in improving soil organic C, nutrient cycling, and crop yield (e.g., [49]). However, biochar production involves removal of crop residues from agricultural lands and would increase risk of accelerated erosion. Thus, determination of sustainable crop residue removal rates and implementation of additional conservation practices such as contour cropping, conservation tillage, and cover crops in agricultural lands are crucial. Furthermore, competition with food production and induced land use change would diminish the carbon sequestration potential even for a strategy as promising as biochar [75]. As biochar carbon sequestration depends on revenues from carbon trading, it is important to ensure that large-scale biochar application on agricultural lands will not lead to depleting the terrestrial carbon stock as it reduces the economic viability of biochar.

We argue that it is important to consider issues such as feedstock availability while promoting biochar as climate change mitigation option in the tropics as the farming system in the tropics is dominated by mixed crop-livestock production systems. Under such system there is always a competition in the use of crop residues for soil amendments or for livestock feed. However, this conflicting issue can be resolved by arranging alternative feedstocks to feed the livestock.

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Research Article

Fertility Evaluation of Limed Brazilian Soil Polluted with Scrap Metal Residue

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The aim of this work was to characterize the main inorganic contaminants and evaluate the effect of lime addition, combined with soil dilution with uncontaminated soil, as a strategy for mitigation of these contaminants present in a soil polluted with auto scrap. The experiment was performed in a greenhouse at Campinas (São Paulo State, Brazil) in plastic pots (3 dm^{-3}). Five soil mixtures, obtained by mixing an uncontaminated soil sample with contaminated soil (0, 25, 50, 75, and 100% contaminated soil), were evaluated for soil fertility, availability of inorganic contaminants, and corn development. In addition to the expected changes in soil chemistry due to the addition of lime, only the availability of Fe and Mn in the soil mixtures was affected, while the available contents of Cu, Zn, Cd, Cr, Ni, and Pb increased to some extent in the soil mixtures with higher proportion of contaminated soil. Liming of 10 t ha^{-1} followed by soil dilution at any proportion studied was not successful for mitigation of the inorganic contaminants to a desired level of soil fertility, as demonstrated by the available amounts extracted by the DTPA method (Zn, Pb, Cu, Ni, Cr, Cd) and hot water (B) still present in the soil. This fact was also proved by the phytotoxicity observed and caused by high amounts of B and Zn accumulating in the plant tissue.

1. Introduction

In many parts of the world, soil is still considered as an option for waste disposal, acting simultaneously as a filter that protects the groundwater and as a bioreactor in which many pollutants may be degraded or stored [1]. Thus, inorganic chemical elements accumulate in soil as a result of human activities.

The monitoring and remediation of contaminated soil are relatively new processes in Brazil, introduced less than 20 years ago. The environmental agency of São Paulo State (CETESB) is a pioneer in the country and has identified more than 4,131 contaminated areas in that state, of which at least 13% are contaminated exclusively by the addition of heavy metals to the soil [2].

Soil contamination by heavy metals requires an effective and affordable solution due to their potential toxicity and high persistence [3]. Among the so-called heavy metals, elements such as Cu (copper), Pb (lead), and Zn (zinc) are important contaminants because high quantities of these elements can decrease crop production and due to the risk of biomagnification and bioaccumulation in the food chain [4, 5]. Other inorganic contaminants that are not as frequently considered, such as B (boron) and Ba (barium), can be extremely toxic to some plants at concentrations only slightly higher than levels that are optimum for others [6].

The boron requirement of plants is small, with a narrow concentration range from deficiency to toxicity. In arid and semiarid areas, B toxicity results from high levels of B in soils and from the addition of B via irrigation [7–9]. Considerable research has shown the potential toxicity of Ba in plants, but such studies were short-term and performed in nutrient solutions [10, 11].

Although a number of techniques have been developed to remove inorganic contaminants from soils, many sites remain untreated due to high economic costs, and mitigation must be considered. Mitigation can be used to reduce further undesirable impacts on chemical and physical soil degradation,

to immobilize contaminants and to enable plant growth in contaminated areas to protect the soil from erosion [12–14]. Liming and the addition of organic materials are considered the most promising mitigation techniques for reducing the availability of heavy metals in soil [15–17].

The aim of this work was to characterize the main contaminants and evaluate the effect of lime addition, combined with soil dilution with uncontaminated soil, as a strategy for mitigation of inorganic contaminants present in a soil polluted with auto scrap residue.

2. Materials and Methods

2.1. Site Description. The studied soil samples were collected from a polluted area located in Piracicaba, São Paulo State, Brazil (22°42′30″S; 47°38′01″W), which was cultivated with sugarcane before the contamination event, which occurred in 2005. The soil studied is a eutrofic technic leptosol in association with an endodystric leptic cambisol. This soil is intensively cultivated with either sugarcane or pastures in the Piracicaba city region (more than 300,000 ha). The climate is classified as Cwa (tropical moist), according to Köppen, with rainy summers and dry winters. June, July, and August are the driest months, the average temperature of the warmest month is higher than 22°C, and the temperature drops below 16°C in the coldest month. The annual average temperature is 21.5°C, and the precipitation is 1,270 mm [18].

Scrap metal residue was discarded on arable land and incorporated unevenly into the soil. After local environmental agency (CETESB) intervention, 10 t ha^{-1} of dolomitic limestone was applied (April 2005) in an attempt to increase the pH and to precipitate the metals.

The total inorganic contaminant content of the waste and the soil samples was extracted using the nitric acid-microwave oven digestion method EPA-3051, with determination by inductively coupled plasma-optical emission spectrometry (ICP-OES) [19].

The chemical composition of the waste (dry weight basis) was P = 0.6, K = 0.8, Ca = 10.9, Mg = 12.3, and S = 1.5 g kg^{-1}, and Al = 7,449, B = 170, Ba = 919, Cd = 7.4, Pb = 775, Cu = 2,497, Fe = 101,603, Mn = 1,115, Ni = 153, Cr = 178, and Zn = 8,157 mg kg^{-1}.

Due to heterogeneity in the disposal, for all of the research developed within this area, the region was divided into twelve subareas of approximately 2,450 m^2 each for chemical analysis. Soil samples were taken from the 0 to 20 cm depth layer, dried at room temperature and sieved to 2.0 mm, and the total heavy metal content was analyzed (Table 1). The soil from subarea number four was selected for the experiment because its composition was close to the average for most of the elements found in the sub-areas considered. One uncontaminated soil sample (SC) was obtained in the vicinity of the contaminated area, at the same depth.

2.2. Greenhouse Experiment. The experiment was performed in a greenhouse at Campinas (São Paulo State, Brazil) in plastic pots (3 dm^3). Four soil mixtures, obtained by mixing the uncontaminated soil sample (SC) and contaminated soil from subarea 4 (CA4) to create a gradient of contamination, were evaluated for soil fertility, chemical contaminant availability, and corn development.

The experimental design used randomized complete blocks with five proportions (0, 25, 50, 75, and 100%) of contaminated soil, with five replicates. The soil mixtures were carefully homogenized and incubated at room temperature for 10 days, with the soil moisture maintained at 70% of the soil's water holding capacity (WHC).

After incubation, the soil samples were collected, air dried, and sieved through a 2 mm mesh screen and then submitted to chemical characterizations for soil fertility and available metal content as explained in the site description (Table 3).

The corn cultivar cv. Al Bandeirantes-CATI was seeded at a rate of ten seeds per pot. Seedlings were thinned to five per pot after emergence. During the cultivation, the soil moisture was maintained at 70% field capacity by watering regularly for water loss. The only nutrient added to the pots was nitrogen, as ammonium nitrate, in four applications of 50, 100, 250, and 250 mg pot^{-1}, respectively at 7, 14, 21, and 28 days after emergence.

The plants were harvested 45 days after emergence. The shoots were selected to evaluate the metal phytoavailability.

2.3. Soil Fertility Analyses. Soil fertility attributes were determined by São Paulo State official methods developed at Instituto Agronomico [20] and consisted, briefly, of soil pH measured in a 0.01 mol L^{-1} calcium chloride solution ($pHCaCl_2$) with a soil solution ratio of 1 : 2.5; H+Al extracted by the SMP buffer; phosphorus (P), potassium (K), calcium (Ca), and magnesium (Mg) extracted by the mixed ion-exchange resin method with cation determination by AAS and P-determination spectrophotometry using the blue molibdate method; organic matter (OM) oxidized with potassium dichromate and determined by photometry; cation exchange capacity (CEC) and base saturation (SB) obtained by calculation; sulfate (S) extracted by calcium phosphate and determined by turbidimetry; available Zn, Cu, Fe, Mn, Cd, Cr, Ni, and Pb contents extracted with DTPA-TEA solution at pH 7.3 and determined by ICP-AES; and B contents extracted with hot water and determined photometrically with azomethine-H.

2.4. Plant Analyses. After harvesting, the plant material was rinsed thoroughly with tap water, followed by 1% HCl solution and then deionized water. After the excess water flowed off, each sample was placed in a paper bag and dried in a forced air oven at 70°C until a constant weight was achieved; the samples were then weighed and ground in a *Wiley*-type grinder. Each sample was submitted to oven digestion (incineration) according to Bataglia et al. [21], and the extracts were analyzed for P, K, Ca, Mg, S, B, Cu, Mn, Zn, Fe, Cd, Cr, Ni, and Pb by induced coupled plasma emission spectrometry (ICP-OES) (Varian, Vista MPX, Australia). Nitrogen contents were determined using a sulfuric digestion extract using the steam distillation method [22].

Table 1: Heavy metal concentrations of the twelve subareas analyzed.

Subarea	Ba	Cd	Pb	Cu	Cr	Ni	Zn
				Total content[a]			
				mg kg^{-1}			
SA1[b]	311	3.6	332	198	110	52	1,811
SA2[b]	696	8.8	632	150	15	39	3,225
SA3[b]	322	3.2	357	250	118	48	3,371
SA4[b]	**619**	**6.4**	**254**	**172**	**105**	**55**	**2,223**
SA5[b]	327	4.0	238	147	99	32	1,890
SA6[b]	306	13.5	198	265	130	30	1,985
SA7[b]	263	2.1	178	199	102	41	1,411
SA8[b]	314	2.2	211	131	114	49	1,678
SA9[b]	881	12.6	438	115	198	52	2,102
SA10[b]	365	4.0	167	201	85	102	1,721
SA11[b]	487	14.2	451	389	190	61	2,930
SA12[b]	291	7.0	244	108	112	51	2,014
Mean	**432**	**6.8**	**308**	**194**	**115**	**51**	2,197
SC[c]	**109**	**<0.1**	**13**	**7**	**34**	**2.0**	20

[a]SW-846 3051 method [19].
[b]Contaminated soil sample.
[c]Uncontaminated soil sample.

2.5. Data Analysis. The results of the soil and plant analyses were submitted to an analysis of variance ($P < 0.05$). When significant, the results obtained were also examined using regression analysis (linear and quadratic models). The software used was SISVAR 4.0 [23] and XLSTAT Pro 7.0.

3. Results and Discussion

3.1. Soil Analysis. The total contents of Cu—160 mg kg^{-1}, Cr—103 mg kg^{-1}, Ni—47 mg kg^{-1}, Cd—8.2 mg kg^{-1}, Pb—268 mg kg^{-1}, and Zn—2,454 mg kg^{-1} were above the maximum content commonly found in the soils of São Paulo (Table 2). The total metal content reference levels in soils established by CETESB are (in mg kg^{-1}) Cu—35, 60, 200; Pb—17, 72, 180; Zn—60, 300, 450; Cd—<0.5, 1.3, 3.0; Cr—40, 75, 150; Ni—13, 30, 70, and Ba—75, 150, 300, respectively, for quality (Quality Reference Level—the concentration of a substance in soil that defines a ground as clean or of natural quality. This level should be used as a reference in the prevention of soil pollution and the control of contaminated areas.), prevention (Prevention Level—the concentration of a substance above which changes to soil quality may occur. This level should be used to regulate the introduction of substances into a soil. When this level is exceeded, continued activity shall be subject to further evaluation.), and agricultural intervention (Intervention Level—the concentration of a substance in soil above which potential risks, direct or indirect, to human health may occur. For soil, this level is calculated using the risk assessment procedure to human health exposure scenarios for agricultural, residential, and industrial protection. The area is classified as an investigational contaminated area when the presence of contaminants is found in the soil at concentrations above the intervention value, indicating the requirement for action to protect the receptors of risk.) [24].

Considering such values, the amounts of Cu, Cr, and Ni fell between the levels of prevention and agricultural intervention. The amounts of Cd and Pb fell between the levels of agriculture and residential intervention. The most critical value was obtained for Zn, which was 50% higher than the industrial prevention level. No reference values are provided for Mn or B by the local environmental agency. However, considering the limits for Austrian soil (100 mg kg^{-1}), the content of boron in the contaminated soil (62 mg kg^{-1}) can be considered high [25]. The concentration of Ba that was found during soil characterization (241 mg kg^{-1}) is close to the intervention level (300 mg kg^{-1}) [24].

The addition of scrap metal residue and lime to the soil (SA-4) also changed some soil attributes when compared to uncontaminated soil obtained from a neighboring area (Table 2). There was an increase in attributes related both to the lime and to the residue, which were rich in elements such as B, Cu, Zn, Ni, Pb, Cd, Cr, and Ba.

The DTPA method, originally proposed by Lindsay and Norvell [26] to evaluate micronutrient availability for agricultural purposes, can also be helpful in monitoring soil contamination with heavy metals [27]. According to Abreu et al. [28], the available micronutrients in Brazil's soils fall into the following ranges (in mg dm^{-3}): B—0.01–10.6; Cu—0.1–56; Mn—1–325; Pb—0.00–63.9; and Zn—1–453, while the respective average values for São Paulo State were B—0.32; Cu—2.5; Mn—16; Pb—0.85; and Zn-4.8. Higher values are indicative of anthropogenic inputs, either due to excessive application of fertilizers or urban and industrial wastes resulting from industrial or mining activities. Thus, the available levels of B and heavy metals (Table 3) found in

Table 2: Total element content, available content of heavy metals, and fertility evaluation of the original soil samples studied.

Soil	Soil fertility attributes[a]									
	OM	pH	P	K	Ca	Mg	H+Al	CEC[f]	SB[g]	
	g kg^{-1}		mg kg^{-1}			mmol$_c$ kg^{-1}			%	
SC[d]	23.2	5.2	39.0	2.3	90.8	27.6	28.0	149.0	80.6	
SA4[e]	26.6	7.5	25.0	2.8	285.0	66.8	9.0	363.0	97.6	
	S	B	Cu	Fe	Mn	Zn	Cd	Cr	Ni	Pb
	mg kg^{-1}									
SC[d]	6.4	0.23	5.3	55.0	52.3	1.9	0.1	<0.1[c]	0.6	1.5
SA4[e]	56.0	14.9	29.8	47.4	15.6	325.0	0.8	0.1	2.5	18.3
	Total content[b]									
	Cd	Pb	Cu	Cr	Ni	Zn	Ba	B	Mn	Fe
	mg kg^{-1}									g kg^{-1}
SC[d]	2.5	13.2	30.2	18.5	7.0	38.1	107	1.8	544	30
SA4[e]	8.2	268	160	103	47	2450	241	62	498	66

[a]Kabata-Pendias and Pendias 2001 [25].
[b]USEPA 2007 [19].
[c]Lower than detection limit.
[d]SC: uncontaminated soil.
[e]SA4: contaminated soil (subarea 4).
[f]CEC: cation exchange capacity.
[g]SB: base saturation.

the studied area should be of substantial concern due to their high availability to plants and their potential for entering the food chain.

The available contents of Zn, B, Pb, and Cu in the contaminated soil (SA-4) were 171, 75, 12, and 6 times higher, respectively, than the values found in the uncontaminated soil sample (rate 0%) (Table 3). Even at the lowest rate of contaminated soil used in the soil mixtures (rate 25%), the dilution effect with uncontaminated soil did not sufficiently reduce the contamination levels to reach the São Paulo availability reference values. Because micronutrients are needed by plants in only minute quantities, plant toxicity and other detrimental effects occur with excess amounts [29, 30].

Considering the soil mixtures tested, the soil pH increased from 5.2 (no contaminated soil added, rate 0%) to 7.5 (rate 100%) This increase is due to the corrective action of lime, releasing OH^- ions and consuming H^+. The dissolution of limestone also promoted an increase in Ca and Mg in the soil, indirectly increasing the CEC and SB as well, while reducing H+Al acidity (Table 3). Similar effects have been reported for such soil attributes when high pH residues, such as slag, are used as soil correctives [31, 32].

The phosphorus availability, as measured by the ion exchange method, clearly increased up to the 50% proportion of contaminated soil and decreased for mixtures enriched with it, as reflected by the 2nd order polynomial used to describe the phosphorus availability behavior (Table 3). The lower P availability in soil mixtures with more than 50% contaminated soil may be explained by the presence of high contents of Ca and Mg and the pH liming effects, with the formation of insoluble calcium phosphate [33].

Regression models were developed to better understand the effect of lime addition (increase in soil pH); the increase in contamination by heavy metals in the soil mixtures; soil dilution effect on micronutrient availability and mobility to plants; and plant uptake (Table 3 and Figure 1, Table 4 and Figure 2). Since the linear behavior can be related directly to the soil dilution effect, deviations from linearity can be identified and attributed to changes in elements mobility in soil and availability to plants promoted by liming.

Soil pH is the single factor most consistently cited as the parameter controlling metal solubility and plant availability [36–38]. In general, heavy metal cations and micronutrients, such as Cu and Zn, are mobile under acid conditions, and increasing the pH by liming reduces their bioavailability and mobility in soils. The waste contained high levels of Mn (1,115 mg kg^{-1}) and Fe (101,603 mg kg^{-1}) and the availability of Mn to the plants decreased as the soil pH increased, reducing the element mobility in the soil even in the soil mixtures with higher proportion of contaminated soil (Table 3). Such a decrease also correlates well with the soil pH (Figure 1), but no significant correlation was observed for iron. The availability of most metals is highly reduced at pH levels higher than 6.0, due to the formation of hydroxides or precipitation as carbonates or phosphates.

Despite liming, the available contents of Cu, Zn, Cd, Cr, Ni, and Pb increased to some extent in the soil mixtures with higher proportion of contaminated soil (Table 3). However, most elements available content also correlated well with the increase in soil pH (Figure 1). Thus, one can conclude that liming was not sufficient to immobilize all such metals.

Cadmium is usually very mobile in soils, although it can precipitate at pH values higher than 7.0 as carbonate or phosphate compounds [39]. In contrast, Cu is commonly associated with organic and inorganic compounds, displaying limited mobility in soil, which is further reduced at pH levels higher than 7.0 [25]. Liming has already been tested without success as an alternative to reduce Cd mobility in

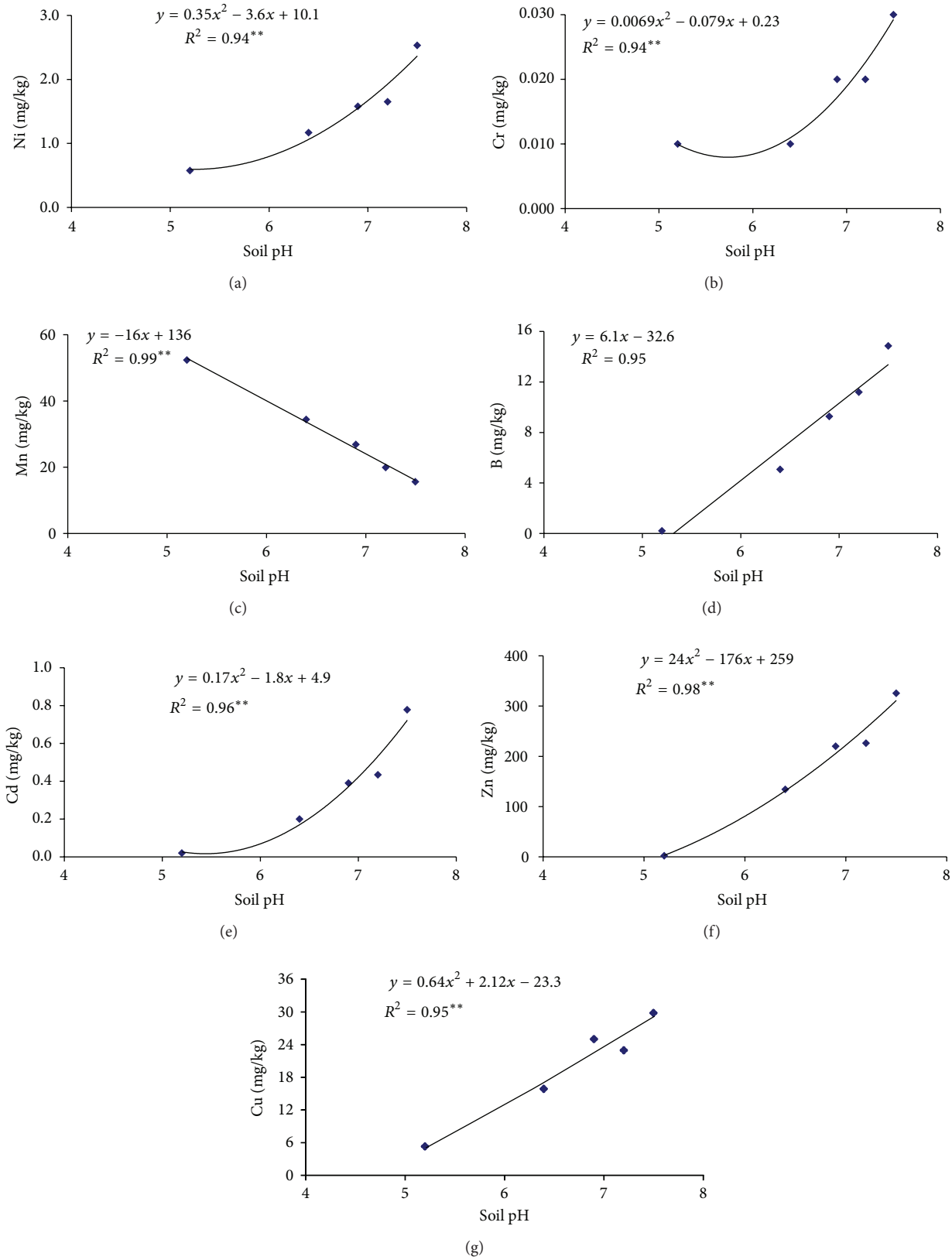

Figure 1: Effect of soil pH on the some elements availability in the soil mixtures tested. **Significant at $P < 0.01$.

Table 3: Soil fertility and available content of heavy metals in the soil mixtures used in the experiment (after incubation).

Attribute	Proportion of contaminated soil (%)					Equation	Regression coefficient[a]
	0	25	50	75	100		R^2
pH $CaCl_2$	5.2	6.4	6.9	7.2	7.5	$y = -2.3E-04x^2 + 4.5E-02x + 5.3$	0.98*
OM (g kg^{-1})	23.2	23.8	25.3	25.6	26.6	$y = -3.2E-05x^2 + 3.8E-02x + 23.13$	0.52*
P (mg kg)	39.0	40.6	48.2	30.0	25.0	$y = 0.3x + 38.7$	0.52*
K (mmol$_c$ kg^{-1})	2.3	2.0	2.7	2.4	2.8	$y = 5.5E-05x^2 + 7.5E-04x + 2.2$	0.27*
Ca (mmol$_c$ kg^{-1})	90.8	193	288	242	285	$y = 4.7x + 95.1$	0.80*
Mg (mmol$_c$ kg^{-1})	27.6	48.6	57.6	61.6	66.8	$y = 0.8x + 28.9$	0.84*
H + Al (mmol$_c$ kg^{-1})	28.0	15.8	12.2	11.4	9.0	$y = 0.003x^2 - 0.4x + 26.9$	0.95*
CEC (mmol$_c$ kg^{-1})[b]	148	259	360	317	363	$y = 5.1x + 153$	0.80*
SB (%)[c]	80.6	93.6	96.6	96.6	97.6	$y = 0.5x + 81.7$	0.89*
S (mg kg^{-1})	2.4	14.4	26.0	45.0	82.2	$y = 6.6E-03x^2 + 0.1x + 4.2$	0.83*
B (mg kg^{-1})	0.2	5.1	9.3	11.2	14.9	$y = -5.5E-04x^2 + 0.20x - 0.36$	0.98*
Cu (mg kg^{-1})	5.3	15.8	25.0	22.9	29.8	$y = 0.4x + 5.9$	0.87*
Fe (mg kg^{-1})	55.0	56.8	58.8	56.2	47.4	$y = 0.2x + 54.3$	0.27*
Mn (mg kg^{-1})	52.3	34.0	26.8	19.9	15.6	$y = 0.003x^2 - 0.7x + 51.4$	0.99*
Zn (mg kg^{-1})	1.9	134	220	226	325	$y = 4.6x + 12.9$	0.92*
Cd (mg kg^{-1})	0.02	0.2	0.4	0.4	0.8	$y = 1.4E-05x^2 + 5.5E-03x + 4.9E-02$	0.91*
Cr (mg kg^{-1})	0.01	0.01	0.02	0.02	0.03	$y = 1.6E-07x^2 + 7.9E-06x + 0.01$	0.69*
Ni (mg kg^{-1})	0.6	1.2	1.6	1.7	2.5	$y = 2.2E-05x^2 + 1.5E-02x + 0.7$	0.89*
Pb (mg kg^{-1})	1.5	12.3	35.3	24.1	18.3	$y = 0.9x - 0.4$	0.41*

[a]Significant at $P < 0.05$ (*).
[b]Cation exchange capacity = $Ca^{2+} + Mg^{2+} + K^+ + H^+ + Al^{3+}$.
[c]Base saturation = $(Ca^{2+} + Mg^{2+} + K^+ + Na^+/CEC) * 100$.

soils [40]. The data presented in Table 3 are consistent with both statements, as the available contents of Cd were poorly affected by the soil pH and a low increase in Cu DTPA was observed above a rate of 50% contaminated soil.

Reduction in Zn mobility is usually associated with its adsorption to Al, Fe, and Mn oxides at pH levels higher than 5.5 [41]. A reduction in Zn availability was observed due to dilution of the contaminated soil, but when compared to the pH effect on Cu availability (Figure 1), Zn seemed to be more affected by the lime addition. This finding may be attributed to the higher Zn content in the soil mixtures because the total content of Zn was approximately 15 times higher than that of Cu.

Boron is usually found in soils in its anionic form, which is highly available from pH 5.0 to 7.0 [42] and which corresponds to the range observed in the pot experiment. According to the literature, B availability can be influenced by soil organic matter content and texture [43, 44]. In the present study, because a small increase was observed in the organic matter content of the soil mixtures and a larger increase was observed for the B concentration in the same situation, there is no evidence of an organic matter effect on B availability (Table 3).

The concentration of both OM and B did not seem to be affected by liming (Table 3). A significant linear regression was obtained for OM and available B with increasing amounts of contaminated soil in the soil mixtures (Table 3). However, in both cases, one can conclude that this is exclusively due to the contribution of the contaminated soil content. A very small deviation was observed when a mass balance of such attributes was performed while considering the contaminated soil proportion in such mixtures.

According to van Raij et al. [34], concentrations of B above 0.6 mg dm^{-3} and of S above 10 mg dm^{-3} in soil are to be considered high for local soils. Values above such limits were observed for all of the proportion tested. In addition, the linear increase in S concentration in the soil mixtures with contaminated soil indicates that changes in pH did not affect the availability of S. A similar effect has been reported in the literature [45].

3.2. Dry Matter Yield and Element Contents in the Corn. Although symptoms of toxicity in plants were observed, this did not affect the dry matter yield. Visual evaluation of the plants 40 days after emergence evidenced purple and brown spotting, suggesting P deficiency in treatments without contaminated soil (0%). The soil analysis showed lower concentrations of available P as the contaminated soil proportion increased in the soil mixtures (Table 3).

The Zn concentrations in the corn shoots varied from 46.1 to 454 mg kg^{-1}, surpassing the level of 100 mg kg^{-1} considered to be adequate [35] for all proportion studied, except for the 0 proportion(uncontaminated soil). The toxic range for zinc in plants is reported as 100–400 mg kg^{-1} [25, 46].

Table 4: Dry matter yield, element concentration, and adequate nutritional range for corn grown in the soil mixtures studied.

Attributes	Proportion of contaminated soil (%)					Adequate range	Equation	Regression coefficient[a]
	0	25	50	75	100			R^2
Dry matter (g pot^{-1})	13.3	12.9	12.4	12.4	13.1		—	NS
N (g kg^{-1})	29.1	27.7	26.9	27.2	26.5	27–35[b]	$y = 2.9E-04x^2 - 5.2E-02x + 28.9$	0.27*
P (g kg^{-1})	1.10	0.90	0.94	1.14	1.13	2.0–4.0[b]	$y = 6.1E-05x^2 - 4.9E-03x + 1.1$	0.28*
K (g kg^{-1})	39.3	47.9	48.1	49.7	49.9	17–35[b]	$y = 0.3x + 40.2$	0.73*
Ca (g kg^{-1})	7.3	8.6	8.9	9.1	9.1	2.5–8.0[b]	$y = -3.1E-04x^2 + 4.8E-02x + 7.4$	0.48*
Mg (g kg^{-1})	3.6	5.1	5.6	5.7	5.8	1.5–5.0[b]	$y = -3.61E-04x^2 + 5.5E-02x + 3.7$	0.76*
S (g kg^{-1})	1.2	1.8	2.0	2.0	2.2	1.5–3.0[b]	$y = -1.1E-04x^2 + 2E-02x + 1.3$	0.75*
B (mg kg^{-1})	25.7	315	572	779	950	10–25[b]	$y = 12.5x + 24.8$	0.91*
Cu (mg kg^{-1})	7.5	8.9	11.6	9.8	13.0	6–20[b]	$y = -1.2E-04x^2 + 5.9E-02x + 7.7$	0.51*
Fe (mg kg^{-1})	66.8	83.4	93.0	86.0	80.5	30–250[b]	—	NS
Mn (mg kg^{-1})	112	43.8	46.0	55.2	67.5	20–200[b]	$y = 0.02x^2 - 2.23x + 104.4$	0.77*
Zn (mg kg^{-1})	46.1	276	328	359	454	15–100[b]	$y = 6.92x + 71.5$	0.81*
Cd (mg kg^{-1})	0.22	0.34	0.32	0.26	0.42	0.1[c]	—	NS
Cr (mg kg^{-1})	0.80	0.56	1.22	0.84	0.30	0.20[c]	—	NS
Ni (mg kg^{-1})	0.60	0.10	2.60	0.10	0.10	0.19[c]	—	NS
Pb (mg kg^{-1})	0.58	0.82	6.32	12.1	0.70	0.02[c]	$y = 0.3x - 1.5$	0.30*

[a]Significant at $P < 0.05$ (*) and not significant (NS).
[b]van Raij et al. [34].
[c]U. C. Gupta and S. C. Gupta [35].

Other symptoms of toxicity and deficiency were observed in the shoots starting at the 25% proportion, such as chlorosis, necrosis, browning, spotting, and death of older leaves. The chlorosis of older leaves with evolution to necrosis has been associated with boron toxicity [42]. Similar symptoms of toxicity in corn due to excess B have also been reported, with toxic effects for most plants in the range of 50–200 mg kg^{-1} [25, 44, 46]. In the present work, the soil available B concentration increased with the addition of contaminated soil to the mixtures tested. This finding indicates that B availability was not affected by soil pH. Plant analysis supported this statement, as B concentrations were found well above the nutritionally adequate range and accumulated in the corn shoots (Table 4, Figure 2).

Gabos et al. [47], in an experiment using the same contaminated soil employed in this study, tested organic matter amendments for the mitigation of contaminants and used sunflowers as the test plants; they also observed high levels of B, Cu, and Zn in the shoots regardless of treatment (385–374 mg kg^{-1} for B; 305–289 mg kg^{-1} for Cu, and 338–473 mg kg^{-1} for Zn). However, the plants showed no symptoms of B, Cu, or Zn toxicity. According to van Raij et al. [34], levels of 100, 100, and 80 mg kg^{-1}, respectively, for B, Cu, and Zn are considered adequate for sunflowers.

Toxicity in plants has been reported in the literature to occur for Cu from 20–100 mg kg^{-1}, for Mn from 300–500 mg kg^{-1}, and for Pb from 30–300 mg kg^{-1} [25, 46]. No accumulation effect above the adequate range was observed for the Cu content in the corn shoots for all soil mixtures (Table 4), despite an increasing trend with an increase in available contents in the soil (Figure 2). Although a liming effect on Mn availability in the soil was clear, liming's nutritional impact on corn did not limit plant development or result in deficiency (Table 4). Lead accumulation in the corn shoots seemed closely related to the available contents of lead in the soil (Tables 3 and 4) but did not reach toxic levels.

Chromium, nickel, and cadmium concentrations in the corn shoots varied from 0.3 to 1.22, 0.1 to 2.6, and 0.22 to 0.42 mg kg^{-1}, respectively, surpassing the level of 0.2 mg kg^{-1} considered as adequate [35]. According to Macnicol and Beckett [48], levels above 8 mg kg^{-1} of Ni, 4 mg kg^{-1} of Cd, 2 mg kg^{-1} of Cr, and 15–30 mg kg^{-1} of Pb [25, 49] may cause toxicity in many plants, reducing their production. Although the available contents of Cd, Cr, and Ni were higher in the soil mixtures containing higher proportion of contaminated soil, such metals were not significantly found in the corn shoots (Table 4).

Nitrogen and iron absorption by the plants was not influenced by the rate of contaminated soil in the soil mixtures or by the soil pH.

The correlation coefficients for the proportion of contaminated soil and the Ca, Mg, S, and K concentrations in the shoots of the corn were significant (Table 4), with Ca, Mg, and S found to be within or close to the adequate nutritional range. The Ca and Mg concentrations in the shoots of the corn varied from 7.3 to 9.1 and 3.6 to 5.8 g kg^{-1}, respectively, barely surpassing the levels of 8.0 and 5.0 g kg^{-1} considered as adequate [35] for all proportion studied except for the 0 rate (uncontaminated soil). The S and Fe concentrations in the shoots of the corn were considered as adequate for all proportion tested [35]. The K concentration in the shoots of the corn varied from 39.3 to 49.9 g kg^{-1}, surpassing the level of

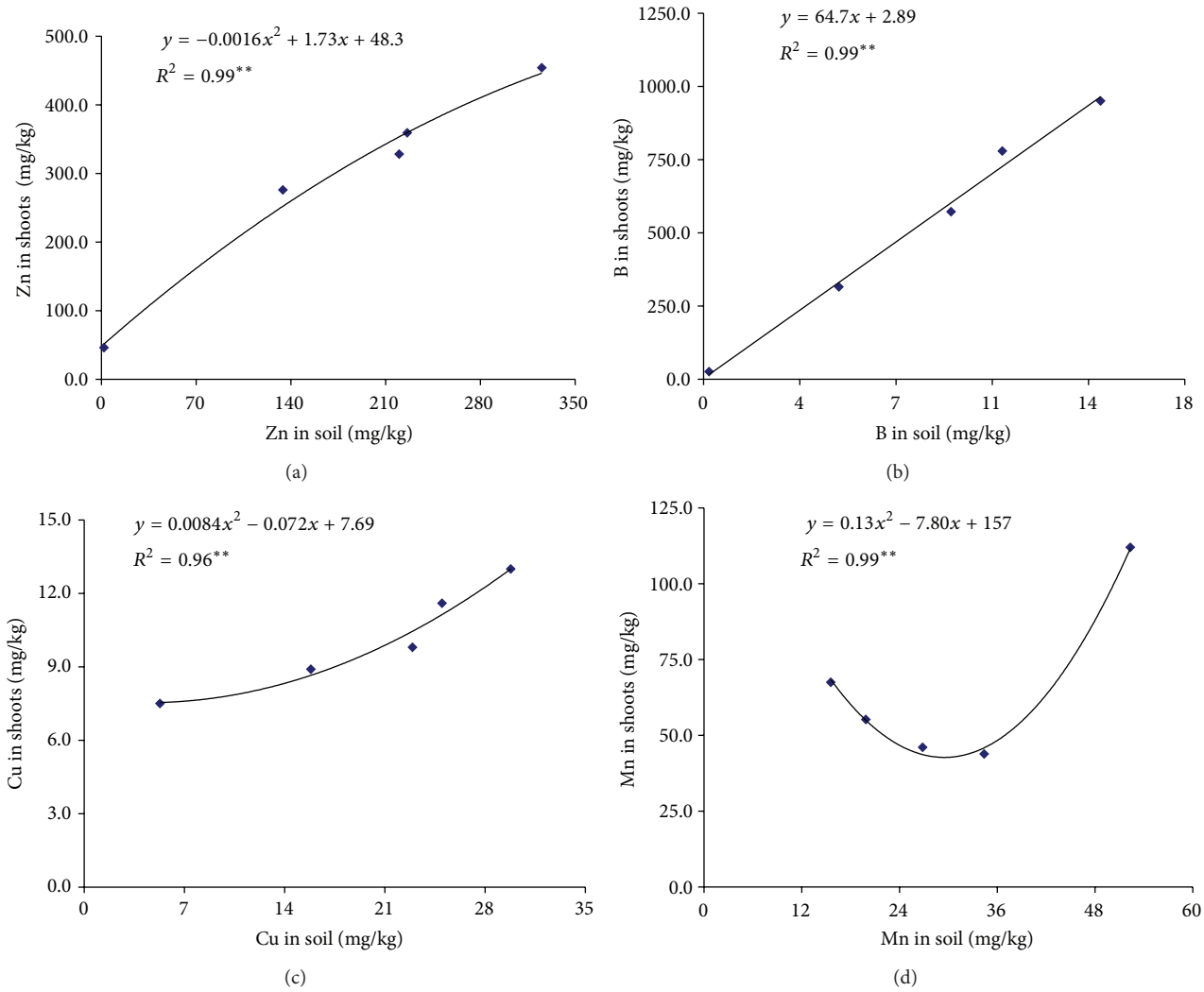

Figure 2: Corn shoots uptake and available content of elements in soil. **Significant at $P < 0.01$.

35 g kg^{-1} considered as adequate [35] for all proportion tested (Table 4).

4. Conclusions

The main contaminants present in the scrap metal residue were Ba, Cu, Cr, Ni, Pb, Zn, and B, which increased total concentrations of these elements in the soil above the maximum content commonly found in the soils of São Paulo. Furthermore, the amounts of Zn, Cd, and Pb were above the intervention levels suggesting that a strategy should be made for soil remediation at this area.

Liming of 10 t ha^{-1} followed by soil dilution at any proportion studied was not successful for mitigation of the inorganic contaminants to a desired level of soil fertility, as demonstrated by the available amounts extracted by the DTPA method (Zn, Pb, Cu, Ni, Cr, Cd) and hot water (B) still present in the soil. This fact was also proved by the phytotoxicity observed and caused by high amounts of B and Zn accumulating in the plant tissue.

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Research Article

Molecular Identification of Fungal Communities in a Soil Cultivated with Vegetables and Soil Suppressiveness to *Rhizoctonia solani*

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Fungi constitute an important part of the soil ecosystem, playing key roles in decomposition, cycling processes, and biotic interactions. Molecular methods have been used to assess fungal communities giving a more realistic view of their diversity. For this purpose, total DNA was extracted from bulk soils cultivated with tomato (STC), vegetables (SHC), and native forest (SMS) from three sites of the Taquara Branca river basin in Sumaré County, São Paulo State, Brazil. This metagenomic DNA was used as a template to amplify fungal 18S rDNA sequences, and libraries were constructed in *Escherichia coli* by cloning PCR products. The plasmid inserts were sequenced and compared to known rDNA sequences in the GenBank database. Of the sequenced clones, 22 were obtained from the SMS sample, 18 from the SHC sample, and 6 from the STC sample. Although most of the clone sequences did not match the sequences present in the database, individual amplified sequences matched with Glomeromycota (SMS), Fungi incertae sedis (SMS), and Neocallimastigomycota (SHC). Most of the sequences from the amplified taxa represent uncultured fungi. The molecular analysis of variance (AMOVA) indicated that fluctuations observed of haplotypes in the composition may be related to herbicide application.

1. Introduction

Despite the importance of soil microbial communities in regulating soil ecosystem-level processes, such as the nutrient cycle and organic matter decomposition, little is known about the structure of these microbial communities and the factors that influence it in soils. This lack of knowledge arises, in part, from the enormous complexity of soil microbial communities, which are estimated to contain more than 4,000 different genomic equivalents in a single gram of soil [1]. Because of their broad ecological range, ready adaptation abilities, and wide spectrum of nutrient sources, filamentous and yeast-like fungi are able to colonize many different niches or substrates [2]. As integral components in the soil ecosystem, fungi play an important role as major decomposers of plant residues, releasing nutrients that sustain and stimulate plant growth [3]. In spite of their importance, there are very few reports on the fungal communities in soil.

Comparative studies have reported that microbial communities can change in response to soil disturbances, and differences have been observed between microbial communities in fields with different histories of soil amendment, irrigation, tillage, and plant community structure [4]. Knowledge of soil microorganisms is expanding with the advent of new methods available for characterizing organisms in nature [5]. Cultivation-independent approaches using rRNA gene sequence analysis have been used to explore the taxonomic diversity of soil microbial communities. Recent technological advances in DNA-based methodologies have allowed rapid and accurate identification of fungal and yeast species from a wide variety of samples [2]. Concerning rDNA genes, the small subunit 16S has been successfully used to

assess bacterial diversity in natural ecosystems, offering the possibility to discover new species [6–9]. This method has been successful for the evaluation of bacterial communities in soil [8] of the region studied in the present paper.

There have been few descriptions of soil fungal diversity based upon ribosomal RNA sequences. The purpose of this paper was to compare fungal communities from samples of a latosol under cultivation of tomatoes and vegetables, and, as undisturbed soil, a native forest; these samples were assessed by the analysis of metagenomic DNA from which 18S sequences from fungi can potentially be rDNA amplified.

2. Materials and Methods

2.1. Soil Samples. The surface horizons (0 to 30 cm) of a red latosol soil were sampled in February 2001 (summer season) from three sites in the Taquara Branca river basin in Sumaré County (22°49′13″S, 47°16′08″W), São Paulo State, Brazil. Mean annual rainfall and mean annual temperature are 1100 mm and 21°C, respectively. The cultivated fields had been managed for more than 10 years using conventional management practices and planted with tomatoes (*Lycopersicon esculentum* Mill) (STC) and vegetables (*Brassica oleracea* variety *botrytis*) (SHC) at the time of soil sampling. The third field had native undisturbed forest soil (SMS) and was characterized as suppressive to mycelial growth of the plant pathogen *Rhizoctonia solani* [10]. Chemical and physical soil properties were determined on air-dried soils according to the IAC soil analysis system [11].

2.2. Cultivable Fungi. Fungal communities were extracted by shaking 10 g of bulk soil samples in 800 mL of 8 μL pyrophosphate solution 0.1% containing penicillin (100 mg·L^{-1}) and streptomycin (100 mg·L^{-1}) at 200 rpm for 30 min at 25°C. After 10-fold serial dilution (100 μL) were spread onto Martin medium [12] containing G penicillin (five millions of unities) and streptomycin (2 grams in 100 mg·L^{-1}) and the plates incubated at 28°C. For enumeration of the fungi, the colonies were counted daily until the tenth day. The serial dilution was carried out in triplicate.

2.3. DNA Procedures. Total microbial community DNA was extracted from the soil using a FastDNA Spin Kit for Soil (Bio 101, catalog # 6560-200) according to the manufacturer's instructions using 1 g of from each soil sample. The primer pairs EF3 (5′-TCCTCTAAATGACCAAGTTTG-3′) and EF4 (5′-GGAAGGG[G/A]TGTATTTATTAG-3′) were used for 18S rDNA amplification [13]. Reactions were again carried out in a thermal cycler (PTC-100 Programmable Thermal Controller, MJ Research, Inc.) and the PCR products were purified by electrophoresis on 1% low melting temperature agarose (Gibco) and inserted into pGEM-T cloning vector (Promega, Madison, WI, USA, catalog # A3600) according to the manufacturers' instructions. Clone libraries were constructed by transforming *E. coli* DH5α. After screening for inserted clones, the recombinant plasmid DNA from the selected clones was isolated, purified, and quantified [14]. Sequencing PCR was carried out in microplates containing 100–150 ng template plasmid DNA, 1 μL BigDye Terminator; 3.2 pmoles of oligonucleotide primer M13/pUC 1211 forward (5′-GTA AAA CGA CGG CCA GT-3′) and buffer 5x (400 mM Tris-HCl pH 9; 10 mM $MgCl_2$) to complete 10 μL of reaction mixture. Reactions were performed with the following cycling parameters: initial denaturation at 96°C for 2 min, then 40 cycles at 96°C for 10 sec, annealing at 52°C for 20 sec, and extension at 60°C for 4 min. The amplicons were sequenced by a Capillary Sequencer model ABI 3700 (Applied Biosystems, Foster City, CA, USA).

2.4. Phylogenetic Analysis of 18S rDNA Sequences. The electropherograms were generated by Sequencing Analysis 3.4 software. The computer program phred (available at http://bozeman.mbt.washington.edu/phrap.docs/phred.html) was used to assign bases to the electropherograms. After eliminating vector sequences, the program phrap (available at http://bozeman.mbt.washington.edu/phrap.docs/phrap.html) was used to analyze the sequences. The ContiGEN.pl program was used to determine only nucleotide sequences above 400 bp in size and phred quality >20 (quality scores are assigned to each base call in automated sequencer traces) was selected [15]. All fragments used in this analysis were sequenced three times in order to confirm the base sequence. Since single base alterations are used to differentiate the groups, this high quality standard is absolutely necessary: any problems regarding quality of the sequences could negatively affect the accuracy of the final result. The program used for comparison was basic local alignment search tools (BLAST) [16] and the sequences were compared with those online at the GenBank; these sequences were identified as uncultured organisms. The 18S rDNA sequences of the representative clones were aligned against the most similar sequence using the Practical Extraction and Reporting Language (Perl) Program implemented by the Laboratory of Biochemistry of Microorganisms and Plants localized in UNESP/FCAV. Sequence alignments were first done using Clustal W (version 1.8) [17] and then adjusted using the BioEdit (version 5.0.9) Program [18]. Phylogenetic relationships were inferred by preferential alignments of the soil fungal sequences obtained from GenBank. This was done using the program MEGA5 (version 2.1) [19]. Bootstrap analysis was performed with 2,000 replicates [20].

2.5. Genetic Diversity. Genetic diversity indexes were calculated using DNA sequences from the three soil samples classified according to the phylogenetic relationships revealed by the preferential alignments.

Genetic distance: values of genetic distance were calculated between groups of fungi from different soils and from the same soil. Estimates of genetic distances were used to evaluate genetic divergence within and between fungal groups [21]. The genetic distance within groups was estimated by the arithmetic mean of all individual pairwise distances between taxa within a group, and the genetic distance between groups was estimated by the arithmetic mean of all pairwise distances between two groups in the intergroup comparisons [22].

2.5.1. Pairwise Fixation Index (F_{ST}) Values, Average Pairwise Differences, and Other Indexes. These values were calculated

Table 1: Chemical and physical characteristics soils cultivated for vegetable (SHC) and tomato (STC) production and of forest soil (SMS).

Parameters	SMS	SHC	STC
pH (in $CaCl_2$)	4.8	5.6	5.9
Organic matter (g $dm^{3(-1)}$)	50	56	24
P (mg $dm^{3(-1)}$)	14	280	200
K ($mmol_c$ $dm^{3(-1)}$)	1.6	5.0	3.9
Ca ($mmol_c$ $dm^{3(-1)}$)	31	83	59
Mg ($mmol_c$ $dm^{3(-1)}$)	12	15	40
H + AL ($mmol_c$ $dm^{3(-1)}$)	52	31	15
CEC ($mmol_c$ $dm^{3(-1)}$)	97	134	118
Textural class	Silty clay	Silte clay	Silte clay

CEC: cation exchange capacity.

to estimate if isolated groups from different soils were structured according their origin and soil farming. Arlequin software [23] was used to estimate genetic structure among groups from different soils and intraspecific genetic diversity. The significance of differences in pairwise fixation index (F_{ST}) values and average pairwise differences between isolated groups were calculated using analysis of molecular variance (AMOVA). The F_{ST} test was used to compare the genetic diversity within each group related to the total combined genetic diversity according to the equation $F_{ST} = (\theta_T - \theta_W)/\theta_T$, where θ_T is the genetic diversity for all samples and θ_W is the genetic diversity for each group [24]. The statistical significance of F_{ST} was calculated by randomly assigning sequences in the populations and for 1000 permutations. Average pairwise differences were estimated from comparisons within a group of different sequences between a given sequence and all other sequences [23]. To estimate genetic diversity within soil fungal groups, some indexes were calculated using a distance method with the p-distance substitution nucleotide model. Average pairwise differences and nucleotide diversity were calculated for each group. In addition, molecular indexes such as number of gene copies and haplotypes, total number of loci, usable loci, polymorphic sites, and nucleotide diversity were calculated for each data set.

3. Results

3.1. Soil Analysis. The organic matter was lowest in soil cultivated with tomatoes. However, soils cultivated with vegetables and suppressive native forest had similar organic matter contents. Soil pH, phosphorus, potassium, calcium, and magnesium were higher in cultivated soils (Table 1) than in uncultivated forest soil, probably reflecting the regular liming and fertilization to support crop productions. An increase in pH was usually accompanied by a decrease in exchangeable al and an increase in cation exchange capacity (CEC) and other cations (K, Ca, and Mg).

3.2. Numbers of Cultivable Fungi. Most probable number method for fungi populations using a microassay technique [25] was deposited 40 μL aliquots on individual selective agar plates is the drop plating method (3 replicates per dilution). The number of cultivable fungi obtained was 1.78×10^5 CFU/g (colony-forming units per gram) for soil cultivated with vegetables, 1.45×10^5 CFU/g for natural forest, and 1.08×10^5 CFU/g for soil planted with tomatoes.

3.3. Phylogenetic Analysis of 18S rDNA Sequences. Of the 576 clones obtained for each soil sample, only 38 were found to have inserts of the expected size and quality, such as 22 for SMS, 18 for SHC, and 06 for STC. The rDNA fragments had about 400 bp of 18S rDNA, which was enough for phylogenetic identification, at least to the taxon level of organisms belonging to groups represented in sequence databases. Most of 0.4 kb fragments of cloned 18S rDNA obtained from both soil samples did not match those in the database. The grouping of the clone sequences with the superior fungal sequences present in GenBank for the three soil samples is shown in Figure 1. Overall, the sequences were associated with Glomeromycota (2 sequences from SMS), Fungi incertae sedis (1 sequence from SMS), and Neocallimastigomycota (1 sequence from SHC) and other sequences with uncultured fungi. Alignment of the sequences resulted in a phylogenetic tree with several clades, some of which contained at least one known sequence. Similarity values ranged from 69 to 97%.

The evolutionary history was inferred by using the maximum likelihood method based on the Jukes-Cantor model [26]. The bootstrap consensus tree inferred from 2000 replicates [27] is taken to represent the evolutionary history of the taxa analyzed [27]. Branches corresponding to partitions reproduced in less than 50% bootstrap replicates are collapsed. The percentage of replicate trees in which the associated taxa clustered together in the bootstrap test (2000 replicates) is shown next to the branches [27]. Initial tree(s) for the heuristic search were obtained automatically by applying Neighbor-Join and BioNJ algorithms to a matrix of pairwise distances estimated using the maximum composite likelihood (MCL) approach, and then selecting the topology with superior log likelihood value. A discrete Gamma distribution was used to model evolutionary rate differences among sites (5 categories (+G, parameter = 25.0042)). The analysis involved 58 nucleotide sequences. Codon positions included were first + second + third + noncoding. All positions with less than 95% site coverage were eliminated. That is, fewer than 5% alignment gaps, missing data, and ambiguous bases were allowed at any position. There were a total of 51 positions in the final dataset. Evolutionary analyses were conducted in MEGA5 [19].

All nucleotide sequences were submitted to NCBI and assigned accession numbers DQ641264, AY613927, AY645193 to AY645205, AY646688 to AY646692, AY646694, AY646-696 to AY646699, AY646701, AY646702, AY646704, AY646-707 to AY646711, DQ641264.1, DQ792517.1, DQ792532.1, DQ792534.1, DQ792535.1, DQ792536.1, DQ792544.1, DQ79-2551.1, DQ792556.1, DQ792559.1, DQ792563.1.

3.4. Genetic Diversity and Pairwise Fixation Index (F_{ST}), Average Pairwise Differences, and Other Indexes. The highest genetic diversity sampled was distributed within the soil groups (98.48%) and a minor portion was sampled among the soil groups (1.52%) (Table 2(a)). The F_{ST} value was the

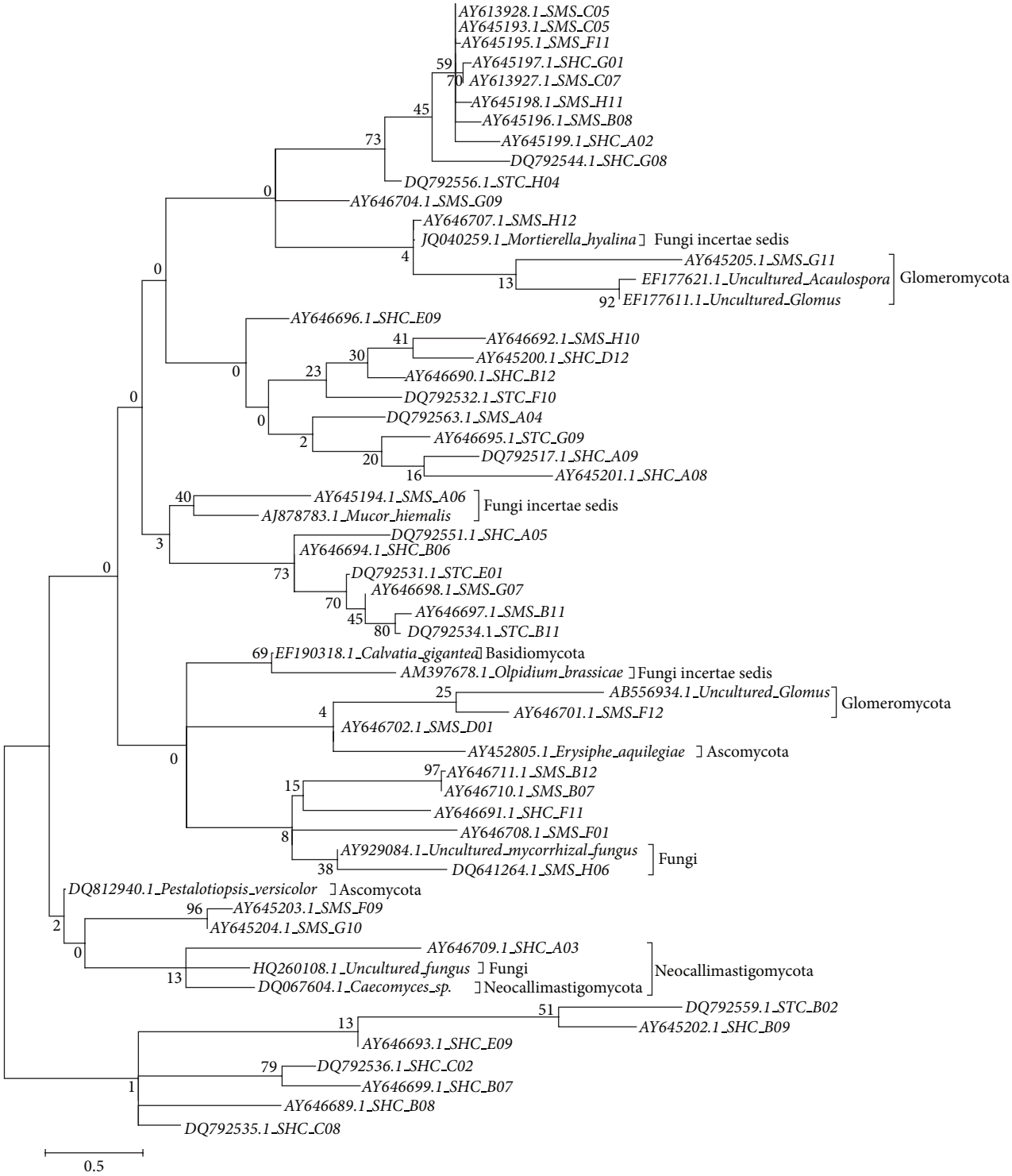

Figure 1: Molecular phylogenetic analysis by maximum likelihood method.

highest for the tomato crop (STC) compared to the native forest (0.01888); the F_{ST} value for SHC and SMS was slightly lower (0.01750) (Table 2(b)). Average pairwise differences and number of polymorphic sites for the STC sample showed the highest values (Table 2(c)). The three soils do not have shared haplotypes.

4. Discussion

The regular liming and fertilization to maintain soil fertility to the crop production probably altered the amount of organic matter in the soil (Table 1). Soil organic matter (SOM) is the most often reported characteristic of long-term experiments

Table 2: Genetic distance between the soil and the values diversity.

(a)

Soils groups	Sum of squares	Percentage of variation
Among populations	1.149	1.52
Within populations	17.167	98.48

(b)

Soils groups	SMS	SHC	STC
SMS	0.00000		
SHC	0.01750	0.00000	
STC	0.01888	0.00000	0.00000
Among all		0.01517	

(c)

Indexes	SMS	SHC	STC
Number of sequences used	22	18	6
Number of haplotypes	17	11	6
Number of shared haplotypes	0	0	0
Total number of sites	3212	3212	3212
Number of polymorphic sites	884	784	1881
Nucleotide diversity	0.9667 ± 0.0301	1.0000 ± 0.0388	1.0000 ± 0.0962
Average pairwise difference	0.443121 ± 0.220213	417.8990900 ± 0.533024	1047.733276 ± 10.551729

and can be identified as a valuable indicator of agroecosystems development within the specific agro ecological conditions and agricultural practice [28]. Although not observed for soil in which tomato was cultivated, changes in soil conditions due to the surface residue accumulation in continuous crops are often characterized by an increase in soil organic matter [29]. Crop residues influence soil organic matter dynamics to the greatest extent by increasing or decreasing decomposition and nutrient availability, thereby sustaining soil fertility and sustainability of agroecosystems [30]. Thus, tillage or soil management can have significant impacts on soil properties and microbial community structure. According to a study conducted for 24 years, the productivity of no-till compared favorably with that of moldboard plow and chisel plow systems [31]. Crop residues can influence soil organic matter dynamics to the greatest extent by increasing or decreasing decomposition and nutrient availability, thereby sustaining fertility of the ground and sustainability of agroecosystems. Thus, tillage or soil management can have significant impacts on soil properties and microbial community structure.

Although CFUs provide only a rough idea of the soil fungal community, the results showed that it seems to be affected by vegetation type and management intensity, being lowest for tomato, where cultivation makes use of a variety of pesticides. Since most colonies on plates stem from fungal spores [32], it is possible that soil from tomato favored few specific spore-producing fungi. The results of this work are partially consistent with previous studies about shifts in microbial community structure versus changes in soil management; with no tillage, the microbial community shifts towards a higher proportion of fungi [33]. In general, high soil fertility and nutrient availability favors the bacterial community and low fertility favor the fungi [34]. This result can be associated with the suppressiveness to mycelia growth of the plant pathogen *R. solani* found in this soil [10]. However, no colony was assayed against *R. solani* in this work. Concerning this, the vast majority of natural soils inhibit germination and growth of fungi to a certain extent, a phenomenon known as soil fungistasis. Furthermore, there is a long list of examples on suppression of soil-born fungal and bacterial root pathogens by mycorrhiza [34]. The STC soil DNA sample amplified few fungal 18S rDNA sequences, though cultivable fungi have been isolated from this soil. This probably reflects the observation that plate count techniques favor the isolation of fast-growing, low-substrate-specific, and spore-producing fungi [35], while molecular methods favor numerically dominate fungi with relatively high amounts of vegetative mycelium.

Some fungal species were favored and/or affected by the soil husbandry, such as vegetable and tomato cultivation, when compared to soil of a native forest. In the context it is important to mention that cultivation of tomato makes use of a variety of pesticides [36], the intensive management of which impacts soil microorganisms in a generally harmful manner, although this is difficult to quantify exactly [37]. In a maize-French bean field trial it was observed that organic fertilizers particularly farm yard manure and plant compost, have impact on the fungal population, its diversity and the physic and chemical properties of the soil than not adding an organic amendment [38]. The structure and operation of the soil microbial community reflect the interaction between many biotic and abiotic factors. Among the most important factors is the quality of organic substrates available [39].

The types of nutritional substrates are different in soils with contrasting quality of organic matter, with direct effects on the nature of microbial communities and active soil fauna. Additionally, organic matter affects the structural properties of the soil such as aggregation and aeration, which can affect the growth of organisms that live in soil [40]. The content of organic substances affect enzymatic activities and the activity of most enzymes as matter content increases reflecting higher microbial communities and further stabilization of enzymes by humic materials [41]. The important justification presented in soil metagenomic studies on the low frequency of sequences belonging to fungi, despite fungi being major constituents of the soil biomass, that this are present in the form of hyphae and because of this fungi DNA extracted fromsoil is approximately 10 times lower than bacterial DNA extracted from soil in bacterial diversity studies [42].

5. Conclusion

Tomato cultivation appeared to reduce the abundance and diversity at compared to vegetable cultivated and native forest soil. However, this conclusion must be with caution since soil sampling was confined to selected experimental plots. There is need for a wider study area for to find of fungal diversity. The occurrence several 18S sequences that have not been grouped to any phylum, suggests the existence of new phyla in the soil studied in this paper.

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Review Article

Filter Cake and Vinasse as Fertilizers Contributing to Conservation Agriculture

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Utilising organic residues in agriculture contributes to the conservation of natural resources by recycling carbon and mineral elements. Organic residues produced by the sugar and alcohol agroindustries have great potential for use in conservation agriculture. The production of sugar and alcohol generates large quantities of byproducts, such as filter cake and vinasse, which can be used as soil improvers and substitutes for inorganic phosphorus and potassium fertilizers. However, the use of these residues in agriculture requires specific recommendations for each pedoclimatic condition to prevent environmental damage.

1. Introduction

Recently, the high cost of fertilizers and concerns about environmental protection have been great incentives to study the recycling of the large quantities of organic residues produced as byproducts of the sugar and alcohol agroindustries in agriculture.

The mechanized harvest of sugar cane, which is used widely in countries producing this crop, leaves about 6–24 t ha^{-1} of residues on the soil surface [1]. The layer of residues protects the soil against erosion, inhibits weed germination, improves water retention, ameliorates physical and biological soil properties, and is a source of plant nutrients. In addition, industrial processing of sugar cane to produce sugar and alcohol also generates residues, such as filter cake and vinasse, which have a great potential for use in agriculture as soil improvers and fertilizers. Commercial uses of industrial residues strengthen the sugar and alcohol agroindustries [2].

Filter cake, a residue from the treatment of sugar cane juice by filtration, is a rich source of phosphorus and organic matter and has a large moisture content. It has been used as a complete or partial substitute for mineral fertilizers in sugar cane cultivation [3, 4], in the cultivation of other crops [5–10], in composting [11], in vermicomposting [12], and as a substrate in the production of seedlings [13, 14].

Vinasse is an aqueous effluent of the distillation unit in the sugar-alcohol industry and a problem to the sector due to the large quantities produced and its potential effects as an environmental pollutant. It is largely composed of water, organic matter, and mineral elements. The environmental damage caused by discarding vinasse into the soil or running waters was an incentive to studies aiming to find alternative, economic applications for this residue. Results from such studies indicate that, properly used, vinasse contributes to improvements in soil quality [15–25] and agricultural productivity [19, 24–30].

Recycling organic residues is a sustainable activity, which is increasingly necessary when dealing with natural resources [31]. It is recognized that the use of filter cake and vinasse, which are low cost materials, can improve soil fertility. Some authors even suggest that their use is beneficial to soil physical attributes, such as stability and average weighted diameter of aggregates [32]. It is possible to estimate the potential contribution of byproducts produced by the sugar-alcohol agroindustry to the annual recycling of nitrogen, phosphorus, and potassium in cultivated land with sugar cane in Brazil (Table 1). These amount to 293 kt N, 99.6 kt P_2O_5, and 197 kt K_2O. It should be noted that nitrogen and phosphorus are present as organic compounds and must be mineralized before becoming readily available to plants [33].

Table 1: Estimates of the potential contribution of byproducts produced by the sugar-alcohol agroindustry to the annual recycling of mineral elements in agriculture (adapted from [33]).

Residues	Nutrients			Volume of residues	Returning nutrients		
	N	P_2O_5	K_2O		N	P_2O_5	K_2O
	(% in dry residue)				($t\,yr^{-1}$)		
Filter cake[1]	1.40	1.94	0.39	2.34 million t dry cake yr^{-1} (Mt dwt)	32800	45400	9130
Straw[2]	0.46	0.11	0.57	34.5 million t dry straw yr^{-1}	158700	37950	196650
	($g\,m^{-3}$ vinasse)						
Vinasse[3]	375	60	2.035	270 billion L yr^{-1}	101250	16200	549450
Total	—	—	—	—	292750	99550	755230

[1]Supposing that the cultivated area in Brazil is 6.9 million hectares and 475 million tons of cane sugar are harvested, of which 223 million tons are utilized for sugar production generating 35 kg of filter cake ton^{-1} of crushed cane; filter cake with 70% moisture content. [2]Generation of 5 t ha^{-1} of dry straw, considering that 100% of the sugar cane cultured area in Brazil is not burnt. [3]Alcohol production: 20.8 billion liters; vinasse generation: 13 L L^{-1} of produced alcohol.

The objective of this review is to evaluate the potential for the agricultural use of filter cake and vinasse and to discuss not only recent advances but also the necessity for further research.

2. Filter Cake

Filter cake is utilized as fertilizer in several countries, including Brazil, India, Australia, Cuba, Pakistan, Taiwan, South Africa, and Argentina. The residue is produced in large volumes (30–40 kg t^{-1} of crushed cane) and it contains a considerable amount of organic matter and mineral elements required for plant nutrition, characteristics that explain its potential for agriculture. It can partially substitute for mineral fertilizers [4], and some suggestions have been made as to the amounts to be applied in the cultivation of sugar cane. In Brazil, the recommended applications of filter cake pre-planting are 80–100 t ha^{-1} if applied to the whole area, 15–30 t ha^{-1} if applied in the planting grooves, or 40–50 t ha^{-1} if applied between the grooves [34].

The chemical composition of filter cake is a function of the variety and maturation of the sugar cane, type of soil, procedure of juice clarification, and various other factors. Table 2 shows chemical composition data from various reports. Of the mineral constituents of filter cake, phosphorus is the most significant as a fertilizer in agriculture and, for this reason, it is intensely studied. Phosphorus is the nutrient mostly commonly applied to tropical soils due to its low natural availability, its high capacity for adsorption to soil colloids, and its joint precipitation with iron and aluminum oxides and hydroxides [35].

The main effects of filter cake on soil chemical properties are increased nitrogen, phosphorus, and calcium concentrations, increased cation exchange capacity (CEC), and reduced concentrations of exchangeable aluminum (Al^{3+}), which is toxic to plants [37]. Beneficial effects on physical and biological soil properties are also observed. Thus, due to its characteristics, filter cake can play a fundamental role in agricultural production, in the maintenance of soil fertility, and as a soil conditioner [33].

Table 2: Concentrations of organic matter (OM) and mineral elements, pH values, and C/N ratios determined in filter cake calculated on dry weight basis. Data are taken from reports of different authors for contrasting pedoclimatic conditions.

Determinations	Filter cake				
	(∗)	[10]	[12]	[36]	Average
OM (%)	29.6	15	—	—	22.3
pH	8.2	—	7.1	—	7.7
N (%)	1.4	4.8	1.6	0.3	2.0
P (%)	1.2	1.8	1.3	0.1	1.1
K (%)	0.2	0.3	0.4	0.4	0.3
Ca (%)	2.7	1.6	2.5	1.7	2.1
Mg (%)	1.1	0.4	—	0.2	0.6
S (%)	0.2	0.3	—	—	0.25
C/N ratio	12	—	25	36	24

∗: Data of the authors. —: Not determined.

3. Effects of Filter Cake Application on the Production and Quality of Various Crops

A report from Egypt [7] showed that the use of filter cake, enriched by rock phosphate in the presence or absence of a biofertilizer, in organic onion culture resulted in improved plant nutrition, growth and crop production, in addition to better export quality.

The productivity of sugar cane crops receiving organic and mineral fertilizers was analyzed in a study conducted in Cuba [38]. It was observed that soil structure was improved when natural and organic fertilizers were used rather than chemical fertilizers. The authors reported that application of 15 t ha^{-1} of filter cake plus 2 t ha^{-1} zeolite, 4 t ha^{-1} of compost and 2 t ha^{-1} of phosphate and calcareous rock had better residual effects on soil properties that were reflected in the agricultural and industrial yield of sugar cane for over three years.

In Swaziland, the destination of filter cake is a problem to the country. It is not widely used as a fertilizer, but one report [6] considers that this organic product should be better studied and used, for example, in the cultivation of

manioc, in a similar manner to maize [39] and sweet potato cultivation [5]. There are indications that addition of filter cake at 60 t ha^{-1} has potential as an organic amendment in manioc production by preventing competition with weeds and increasing productivity by 50% compared to mineral fertilization [6].

Another study in Swaziland [8] reports that the use of filter cake application is of great importance due to limited funds to buy chemical fertilizers in addition to its environmental benefits. The authors studied the application of different amounts of filter cake in maize cultivation (0, 10, 20, 40 t ha^{-1}) and reported that the higher applications increased soil organic matter. Soil phosphorus concentrations increased from 6 mg kg^{-1} (without fertilizer) to 56 mg kg^{-1}, while treatments with mineral fertilizer led to a phosphorus concentration of only 24 mg kg^{-1}. Micronutrient concentrations were also increased, with exception of boron and copper. Maize yields were also increased by the addition of filter cake. Yields of maize crops receiving the largest amounts of filter cake (5,254 kg ha^{-1}) were comparable to those receiving chemical fertilizers (5,046 kg ha^{-1}), and both were much larger than the control treatment (3,732 kg ha^{-1}).

In a study conducted in Indonesia [9], ashes of rice husks and filter cake were applied at two amounts to cabbages and phosphorus availability in soil, phosphorus uptake by plants, and plant growth were determined. The results indicated that phosphorus availability increased 120% and 78%, when rice husk ashes and filter cake were applied, respectively. The treatments increased silicon concentrations, cation exchange capacity, solution pH, and anion concentrations in the soil. The authors also observed that in soils containing high amounts of organic matter, addition of rice ashes and filter cake increased phosphorus uptake 3-fold and 2-fold and increased plant growth by 197% and 231%, respectively. In soils poor in organic matter addition of rice ashes and filter cake increased phosphorus uptake by 1.9-fold and 2.7-fold and increased plant growth by 17% and 11.9%, respectively, compared to untreated soils.

In a report from India [40] the combined application of N (0, 75, 100, and 150 kg ha^{-1}) and filter cake (0, 10, 20, 30 t ha^{-1}, with 80% water content) to sugar cane indicated that 10 t ha^{-1} of filter cake together with 75 kg ha^{-1} N produced equivalent yields to 150 kg ha^{-1} N, resulting in the saving of 75 kg ha^{-1} of chemical N fertilizer.

Assays conducted in a Vertisoil in Sudan [41] indicated that filter cake applications to crops increased soil concentrations of organic matter, organic carbon, total nitrogen, and available phosphorus.

Studies conducted in Brazil [42] evaluated the effects of filter cake in combination with mineral fertilizers (0, 50, and 100% of the recommended dose) in sugar cane production. It was observed that filter cake improved soil fertility, expressed as increased concentrations of macro- and micronutrients, and reduced soil acidity and concentrations of soil aluminum. Sugar cane plants showed a positive response to the addition of filter cake through increased concentrations of phosphorus, potassium, and copper in the aerial parts. The authors concluded that the use of filter cake in combination with mineral fertilizers can maximize productivity and reduce the costs associated with mineral fertilizers.

In another Brazilian experiment [4], the response of vegetative growth and productivity of sugar cane to the application of fertilizers containing filter cake enriched with soluble phosphate was studied. It was verified that phosphorus increased productivity in sugar cane and that the application of filter cake to the planting grooves could substitute for part of the inorganic phosphate fertilizer. The best combination suggested by the authors to optimize the concentration of soluble solids and sugar production was 2.6–2.7 t ha^{-1} of filter cake in combination with 160–190 kg ha^{-1} of P_2O_5.

The yield of lettuce in Brazil [10] showed a linear increase with the application of filter cake from 0 up to 40 t ha^{-1}.

The beneficial effects of filter cake were also demonstrated in Brazil [3] in a field study of ratoon cane where the application of 70 t ha^{-1} of fresh filter cake increased the production of cane sugar internodes.

4. Other Applications of Filter Cake in Agriculture (Composting, Vermicomposting, and Substrate)

Some factors, such as lack of solubility and unbalanced concentrations of nutrients, limit the application of filter cake to soil [12]. The strong disagreeable smell during biological degradation [43], the high temperature of the residue (65°C), and the long period of natural decomposition [44] are additional disadvantages. Reports in the literature mention immobilization of nutrients and phytotoxicity after application of residues that are not composted or otherwise stabilized [45]. Discarding the raw residue is of concern in developing countries, as for example, in India [12].

Vermicomposting is an important technique for the utilization of filter cake. Filter cake has a high potential [12] as a starting material for vermicomposting and results in a biologically stable product that is free of pathogens, as confirmed by coliform counting. In India [46], vermicomposting of filter cake in combination with equine manure accelerated mineralization of nutrients and was adequate for growth and reproduction of earthworms.

Other authors suggest composting as a viable use of filter cake [11]. In countries like Thailand, enhanced performance at composting facilities for organic products needs improvements to preserve nitrogen concentration and produce a stable product in the short term. The C/N ratio in filter cake is around 14 and in sugar cane bagasse, another sugar cane residue, it is 100. Therefore, the filter cake composting could result in considerable ammonia N loss through volatilization due to the low C/N ratio. On the other hand, bagasse composting is only possible with the addition of N due, in this case, to the high C/N ratio. Since composting maturation is highly dependent on the nature of organic residues, investigators in Thailand [11] determined the time required for filter cake to compost to a stable product and considered that composting a mixture of bagasse and filter cake (2 : 1 by weight) would prevent N losses by increasing the C/N ratio. The authors concluded that nitrogen loss was

Table 3: The chemical requirements for oxygen (CRO), biological requirements for oxygen (BRO), electrical conductivity (EC), total dissolved solids (TDS), pH values, sodium and macronutrient concentrations of vinasse according to reports of various authors.

Determinations	Vinasse				
	(∗)	(51)	(17)	(15)	Average
CRO (mg L^{-1})	21.450	26.771	48.860	—	32.360
BRO (mg L^{-1})	10.000	5.000	21.275	—	12.092
EC (dS m^{-1})	14.12	11.5	9.65	3.6	9.72
TDS (mg L^{-1})	7.940	11.352	19.000	—	12.764
pH	4.5	4.4	4.6	5.7	4.8
N (mg L^{-1})	410	—	—	560	485
P (mg L^{-1})	160	—	175	190	175
K (mg L^{-1})	3.100	1.123	1.392	960	1.644
Na (mg L^{-1})	350	113	110	—	191
Ca (mg L^{-1})	640	352	728	280	500
Mg (mg L^{-1})	340	16	29	130	129

∗: Data of the authors. —: Not determined.

reduced by 12–15% and that both products have potential use in agricultural production. They also observed that during the first five days of composting the temperature of the mixture rose to about 55°C but decreased considerably (<40°C) in the next 15–20 days. The time for complete composting took approximately 90 days.

Another application for filter cake is as a substrate for seedling production. Some trials conducted in Brazil have indicated that filter cake mixed with bagasse could be an adequate substrate for the production of eucalyptus [47] and citrus seedlings [14]. Citrus plants cultivated in this substrate were ready for grafting 120 days after transplanting, whilst plants growing in commercial substrate were not ready at this time. The addition of 18 g k^{-1} N to plants growing in substrate containing filter cake resulted in taller plants with more leaves, greater leaf area, and larger aerial dry matter than plants grown in commercial substrate [14].

Evaluation of different substrates in the production of vegetable seedlings [13] verified that composted filter cake enriched with 4 kg m^{-3} of plain superphosphate produced better plant responses than commercial substrates.

5. Vinasse

Alcohol production generates large quantities of agroindustrial residues, the main one being vinasse, an aqueous effluent of the distillation unit in the sugar-alcohol industry [29]. The effluent is troublesome for the sector, not only because large volumes are produced but mainly because it can contribute to pollution.

The quantity of vinasse produced depends on the processing technique employed and also on the wine composition, varying between 10 and 18 liters of vinasse per liter of alcohol produced [48]. It originates from three sugary musts: molasses, mixed must, and juice. Vinasse *in natura* is a dilute solution and its application to soil is made in high quantities, making use difficult in areas distant from the sites of production. However, vinasse can be concentrated by evaporation, resulting in a product with higher economic viability that can be transported to distant locations.

Organic matter, K, N, Ca, and Mg are the main chemical components of vinasse (Table 3), K being the most important mineral element for the agricultural use of the residue. Therefore, vinasse is a source of nutrients, organic matter, and water and its use can contribute to increased productivity of sugar cane [29], with effects on the chemical [15], physical [20], and biological [49] soil attributes.

However, the amount of vinasse applied in agriculture must follow appropriate guidelines, which vary according to soil characteristics. Specific recommendations must be followed for each region to prevent excessive use and consequent mineral lixiviation, for example, of nitrate and potassium, and contamination of subterranean waters. Also, the high content of organic matter in vinasse can contribute to significant pollution.

6. Vinasse as a Pollutant

The use of vinasse in agriculture is an important conservation practice, but its use has been challenged due to its high polluting potential to both soil and subterranean waters [48].

Characteristics of vinasse that contribute to pollution are high CRO (chemical requirements for oxygen) and BRO (biological requirements for oxygen) values, an acidic pH, the elevated temperatures during production, and the consequent corrosive power [49]. Continuous application of high volumes of vinasse leads to increased soil nitrogen and potassium, the main chemical components of this residue [50, 51]. Vinasse also promotes soil alterations, such as improved aggregation, but this culminates in higher water infiltration, lixiviation of mineral elements, and contamination of subterranean waters.

Studies conducted in Mexico [52] studied the influence of the raw material and anaerobically-aerobically treated vinasse (a treatment conducted in the presence and absence of oxygen to remove dissolved organic matter) on soil chemical properties. The authors concluded that untreated vinasse posed a risk of soil salinization and contamination by zinc and manganese. A report from Colombia [53] compared the physicochemical properties of vinasse residues for sugar cane processing with synthetic substrates. The results indicated that the use of both residues affected water quality and had environmental impacts. The authors suggested that the impacts of vinasse could be reduced by biological treatments, such as aerobic and anaerobic technologies that removed organic matter, nitrates, and dissolved solids.

Analysis of ground water quality in areas of sugar cane production fertigated with *in natura* vinasse in volumes of 300 m^3 ha^{-1} soil [50] concluded that the practice minimizes the polluting potential of the residue but still affected the quality of ground water, irrespective of the soil type.

Another report from Brazil [54] relates studies on the effects of vinasse (300 m^3 ha^{-1}) on properties of various soils,

including weakly humic Gley and Cambisol, conducted over 10 years. The authors concluded that the amounts of heavy metals were not changed and there was little risk of soil contamination with these elements.

The effect of *in natura* vinasse applied at 0, 350, and 700 m^3 ha^{-1} on the leaching of mineral elements was studied in three soils [51]. It was shown that cation concentrations in the leachate were less than those in the vinasse, indicating the high cation retention of soils. In a complementary study [55] the physicochemical properties of percolates in soils, which received vinasse applications of 0, 350, and 700 m^3 ha^{-1} for different lengths of time (30 and 60 days), were evaluated and the parameters analyzed (CRO, BRO, EC, TDS, and pH) indicated lack of environmental problems and that the risk of polluting subterranean waters was low.

It is obvious that there is no consensus about the polluting capacity of vinasse. The two main lines of thought indicate, on one side, deleterious effects on ground and surface waters while the other side claims that rational use of the residue does not result in environmental risk. However, it should be emphasized that depending on the amount of vinasse applied it might act as a pollutant or a beneficial soil conditioner. In this context, a review article [48] concludes that a consensus among authors is that the appropriate application of vinasse must consider the soil chemical and physical characteristics, besides aspects like the history of residue application, the intensity of cultivation in the agricultural area, and the proximity of water springs.

7. Effects of Vinasse on the Improvement of Soil Quality

Vinasse is being utilized in irrigation, mainly in sugar cane culture with results indicating improved quality in soil chemical, physical, and biological properties. In Brazil, several studies show the beneficial effects of the use of vinasse on soil chemical and physical properties. Increased concentrations of K, Ca, and Mg, improved soil macroaggregation, and a better development of the radicular system in sugar cane have all been observed following the application of vinasse [15]. The use of vinasse in fertigation increased cation concentrations in the soil, especially potassium [16]. In this context, the effects of application of vinasse to sugar cane in Brazil were evaluated over 10 years [17]. It was concluded that macronutrients were more abundant in the soil profile, but micronutrient availability was reduced.

In a comparative study of different soil types before and after application of vinasse [18], it was observed that the residue increased the pH and potassium concentrations in depths varying according to the type of soil. Another group of investigators [19] also verified increased potassium and organic carbon concentrations when studying the chemical properties of soils treated with vinasse and used for sugar cane production. Therefore, if vinasse is an important source of potassium, its use could reduce the need for inorganic potassium fertilizers.

The effects on soil physicochemical properties after continuous application of vinasse for three years were analyzed in a study conducted in China [20]. The results showed a decrease in soil density, increased capillary porosity and, again, increased concentrations of potassium. It was concluded that continuous application of the residue promotes conditions able to sustain the growth and productivity of sugar cane. Another report from the same country [21] concluded that vinasse used as a fertilizer increases soil fertility in sugar cane production systems.

The populations of microorganisms, bacteria in general, and actinomycetes, in soil cultured with sugar cane fertilized with different organic residues [22] were larger when soils were treated with vinasse and filter cake compared to other residues, implying an improvement in the biological quality of soil when these residues are used.

The beneficial effects and risks of applying vinasse from wine production to the soil over extended periods have been studied in Spain [23]. The treatment resulted in increased soil electrical conductivity and a small decrease in pH. Another study in the same country on vinasse from sugar beets [24] showed increased concentrations of soil organic matter and nitrogen and an increase in soil cation exchange capacity.

Studies in Greece [25] have described the effects of the addition of vinasse on the physicochemical properties of soils used for wheat production. The results indicated that the application of vinasse resulted in increased, but nontoxic, concentrations of potassium, sodium, and manganese in the soil. As a whole, it is possible to conclude that agricultural use of vinasse leads to improvements in soil quality with consequent benefits for crop productivity.

8. Plant Response to Application of Vinasse

The use of vinasse in fertigation systems has advantages because it can contribute substantial amounts of water and mineral nutrients, support soil quality and crop productivity [56], and finally, but no less importantly, can solve the environmental problem of the disposal of this agro-industrial residue.

In China sugar cane treated with vinasse has increased productivity and sucrose yields [26, 27]. In Brazil [19, 28], long-term application of vinasse (150 m^3 ha^{-1} $year^{-1}$) in sugar cane production confirmed positive effects on productivity and increased potassium concentration in soil, as already discussed. Other Brazilian studies [29] involving the application of vinasse and management of the straw cover in sugar cane production also indicated gains in productivity and sugar production. Applications of vinasse of 300–400 m^3 ha^{-1} were considered adequate to increase sugar and alcohol production [30]. In Greece, wheat production was increased by vinasse application, confirming the beneficial effects of the residue in agriculture. In Spain [24], yields of beets and maize were compared after treatments with an organic compound based on vinasse or a mineral fertilizer. Crop production was similar in both treatments indicating that the utilization of vinasse is a viable alternative for mineral fertilizers. Therefore, conservation practices, like the employment of residues in agriculture can contribute to increased agricultural productivity whilst minimizing environmental pollution.

9. Concluding Remarks

Filter cake and vinasse, which are produced in large quantities by sugar-alcohol agroindustries in various countries, have great potential for agricultural use. Filter cake has been utilized with good results, as a substitute for phosphate mineral fertilizers in field crop production, in composting and vermicomposting processes, and as a substrate for the production of seedlings. The use of vinasse in fertigation is increasing in several agricultural areas, substituting for potassium mineral fertilizers and furnishing water, organic matter, and other mineral nutrients in smaller quantities. The use of both filter cake and vinasse should be optimized for each agricultural system and follow recommendations of responsible organisations to prevent environmental damage.

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Research Article

A Case of *Cyperus* spp. and *Imperata cylindrica* Occurrences on Acrisol of the Dahomey Gap in South Benin as Affected by Soil Characteristics: A Strategy for Soil and Weed Management

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Because of the limiting efficacy of common weed control methods on *Cyperus* spp. and *Imperata cylindrica* their occurrences in tropical agroecologies and the effect of soil properties in suppressing these species were investigated in south Benin (Cotonou), a typical ecology of the Dahomey gap. Weeds and soil samples were collected twice early and later in the rainy season in 2009 at four topographic positions (summit, upper slope, middle slope, and foot slope). Sampling was done according to Braun-Blanquet abundance indices (3 and 5) and the absence (0) of *Cyperus* and *Imperata* in a quadrat, respectively. The relationship between their respective abundances and soil parameters (texture, C, N, P, K, Na, Ca, Mg, and Fe) was explored. Weed occurrence was less related to soil texture, and *Imperata* growth was more influenced by soil nutrients (K, Ca, and Fe) than *Cyperus* spp. Soil cation ratios of K : Mg and Ca : Mg were the main factors that could be changed by applying K and/or Mg fertilizers to reduce *Cyperus* and/or *Imperata* occurrence. Maintaining high Fe concentration in soil at hillside positions can also reduce *Imperata* abundance, especially in the Dahomey gap.

1. Introduction

Weeds are notorious yield reducers that are, in many situations, economically more important than insects, fungi, or other pest organisms [1, 2]. The yield loss due to weeds is almost always caused by an assemblage of different weed species, and these can differ substantially in competitive ability [3]. In rice growing agro-ecologies of West Africa, weed species assemblages include nutsedges and speargrass that are perennial and serious threats [4].

Imperata cylindrica (L.) Raeuschel (speargrass) is a common and persistent weed in upland ecology. It reproduces through seeds and rhizomes. This weed is particularly difficult to control, as it is tolerant to fires and shallow cultivation due to its extensive underground network of rhizomes. The weed tends to be abundant where fields are regularly cultivated and burnt, as it recovers rapidly from disturbance, and burning induces flowering. It exerts great competition on crops [5, 6].

In moist to hydromorphic upland areas, some of the most intractable weed problems in rice are due to the perennial sedges *Cyperus rotundus* L. (purple nutsedge) and *Cyperus esculentus* L. (yellow nutsedge). Their tubers and seeds can remain dormant to survive periodic flooding or dry seasons. These species are able to multiply rapidly through tubers which can be greatly accelerated by soil tillage [7]. Because of these characters, *I. cylindrica* and *Cyperus* spp. are typical weeds of intensively cultivated lands and very difficult to control [8].

Some relative successes were observed using chemical methods for the control of *Cyperus* spp. and *I. cylindrica* [9]. But, herbicide is expensive and not always available to

West African smallholder farmers. Moreover, there is a risk of environmental pollution. Therefore, additional knowledge and technology are needed for improving the control of *Cyperus* spp. and *Imperata cylindrica* in Africa, especially in the Dahomey gap (south Benin) where they are seriously threatening livelihoods [10].

Considering that reduced soil fertility often increases weed infestation [11] and the effects of soil parameters in weed occurrence in Nigeria [12], the concept of chemotropism [13] is hypothesized in order to identify soil nutrients (N, P, K, Ca, Mg, and Fe) that influence the occurrence of *Cyperus* spp. and /or *Imperata cylindrical* attention should be paid to topography and soil texture influencing soil organic matter that can change vegetation structure [14].

A nonsite replicated ecological study [15] was initiated during the rainy season of 2009 along a catena of Acrisol in south Benin (West Africa), which is a typical ecology of the Dahomey gap. The implication of soil texture and nutrients (C, N, P, K, Ca, Mg, and Fe) on the occurrence of *Cyperus* spp. and *I. cylindrica* in this upland agro-ecology was explored. The aim was to identify soil parameters that can be used to develop a management strategy for the control of these perennial weeds in continued rice growing agro-ecologies of the Dahomey gap.

2. Materials and Methods

2.1. Site Description. The study was conducted during the 2009 cropping period (June–September) at the Africa Rice Center (ex-WARDA) experimental station in Cotonou (6° 28 N; 2° 21 E, 15 m asl), Benin. The site is a derived savanna zone in the Dahomey gap of West Africa. The rainfall pattern was bimodal with 807 mm during the cropping season of 2009. The soil is locally named "terre de barre." It is a very deep Acrisol (>10 m), with sandy top soil (0–40 cm) and free of constraints (gravels, stones, or hardpan) to plant rooting in the profile. Soil pH_{water} was 5 and C : N, Ca : Mg and K : Mg ratios were about 12, 1.7 : 1 and 1 : 1, respectively. The studied area is continuously cultivated for upland rice production.

2.2. Weed Sampling. Two dominance-abundance indices were considered for *Cyperus* spp. and *Imperata cylindrica* as a proportion of weeds in 1 m^2 quadrats: 3 = covering between 1/4-1/2 of the soil surface and 5 = covering more than 3/4 of the soil surface [16]. Weeds were also sampled where *Cyperus* and *Imperata* were absent, and zero (0) was the corresponding index. Indices 0, 3, and 5 were considered as absent (A), medium density (M), and high density (H), respectively. Three sampling places (A, M, and H) were identified for each of *Cyperus* spp. and *I. cylindrica* in the summit, the upper slope, the middle slope, and the foot slope as described by Ruhe and Walker [17]. Sampling was replicated twice in the studied site: in July (1) and in September (2) at the beginning and the end of the rainy season, respectively. In a quadrat, all the weed species were sampled separately with bellow ground dry matter. Individual identification was done as described by Akobundu and Agyakwa [18] and they were coded according to Braun-Blanquet [16]. The roots were cut off, and weeds were oven dried at 70°C for 24 hours before weighting.

2.3. Soil Sampling and Analysis. Topsoil (0–20 cm depth) was sampled using augur (20 cm × 7 cm) in each quadrat at every time of weed sampling. After sampling weeds, a soil sample was taken from the centre of the quadrat. Twenty-four (24) soil samples (12 at each sampling time) were taken, and sun dried before laboratory analysis. Soil particle sizes were determined by the Robinson pipette method [19] as well as organic-C, total-N, P-available (BrayI), and total-P (Pt). Soil exchangeable K, Ca, Mg, and extractable Fe were also determined. Chemical analyses were performed as described by Page et al. [20].

2.4. Statistical Analysis. Descriptive statistics were used to calculate the frequency of weed species in a specific quadrat. By analysis of variance (ANOVA), mean values of soil particle size and nutrients were determined for each topographic section. Mean values of total weed biomass dry matter were also determined for each placement of quadrat. The mean values were separated by Student-Newman and Keul methods. The relationships between biomass dry matter and soil physical and chemical characteristics were evaluated by Pearson correlation. SAS 10 package was used for these analyses. Soil clay, sand, C, N, Pa, K, Ca, Mg, and Fe concentrations were used to discriminate *Imperata* abundance indices (3 and 5) and absence (0) by canonical function analysis using SPSS 16.

3. Results

3.1. Soil Characteristics. The topsoil (0–20 cm) was sandy, and the middle slope (MS) had a significantly greater proportion of sand than other positions (Table 1). This topographic position also had significant lower contents of clay (11%) and silts (4%). The soil had moderate carbon content throughout the toposequence except in the soil at foot slope (FS) position; where it was significantly higher, similar gradient was observed for total nitrogen-Nt content along the toposequence. Phosphorus (P-available and P-total) contents were moderate in the soils of upper slope (US) and MS while they were higher in the soils at summit (SUM) and FS positions. Soil concentrations of divalent cations (Ca and Mg) were significantly higher at the SUM position with a decreasing trend along the toposequence. Similar result was observed for soil Fe concentration. Meanwhile, monovalent cations (K and Na) concentrations contrasting with these results with an increasing trend from the SUM to the FS.

3.2. Weed Assemblages. Seventeen weed species were most frequently encountered in the quadrats. Other species were also observed in at very low frequencies, and their cumulative frequencies were depressed in the medium and high densities of *Cyperus* spp. and *I. cylindrical,* respectively (Figure 1). However, more diverse communities were observed where *Cyperus* spp. and *I. cylindrica* were recorded in the quadrats compared to places where they were absent. Nevertheless, *Richardia brasiliensis* (Ricbr) was encountered in all quadrats with moderate (9.09%) to high (21.74%) frequency and *Dactyloctenium aegyptium* (Dacae) at a low frequency (2.56%–8.82%), about 14% in 1 m^2 characterized the medium density of *Cyperus* spp. and *I. cylindrica* occurrence, respectively.

Table 1: Mean values of soil particle sizes and nutrient contents (C, Nt, Pa, Pt, Mg, K, Ca, Na, and Fe) along the toposequence in topsoil (0–20 cm).

	Sand (%)	Clay (%)	Silt (%)	C-org (%)	Nt (%)	Pa (ppm)	Pt (ppm)	Mg (cmol kg^{-1})	Ca (cmol kg^{-1})	K (cmol kg^{-1})	Na (cmol kg^{-1})	Fe (ppm)
SUM	82.0^{b}	12.5^{ab}	5.5^{b}	1.19^{b}	0.07^{b}	26.4^{a}	170.8^{b}	2.8^{a}	2.9^{a}	0.2^{c}	0.05^{c}	2800^{a}
US	81.0^{b}	14.0^{a}	5.0^{c}	1.19^{b}	0.06^{c}	12.8^{b}	126.0^{c}	2.5^{b}	2.6^{b}	0.1^{d}	0.10^{c}	1960^{b}
MS	85.0^{a}	11.0^{b}	4.0^{c}	1.09^{b}	0.05^{d}	8.0^{b}	117.0^{c}	2.0^{c}	2.1^{c}	0.3^{b}	0.21^{b}	1924^{b}
FS	74.0^{c}	14.0^{a}	11.5^{a}	1.71^{a}	0.08^{a}	25.2^{a}	241.0^{a}	2.0^{c}	1.9^{d}	0.4^{a}	0.55^{a}	1547^{b}
Pr > F	<0.0001	0.001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001

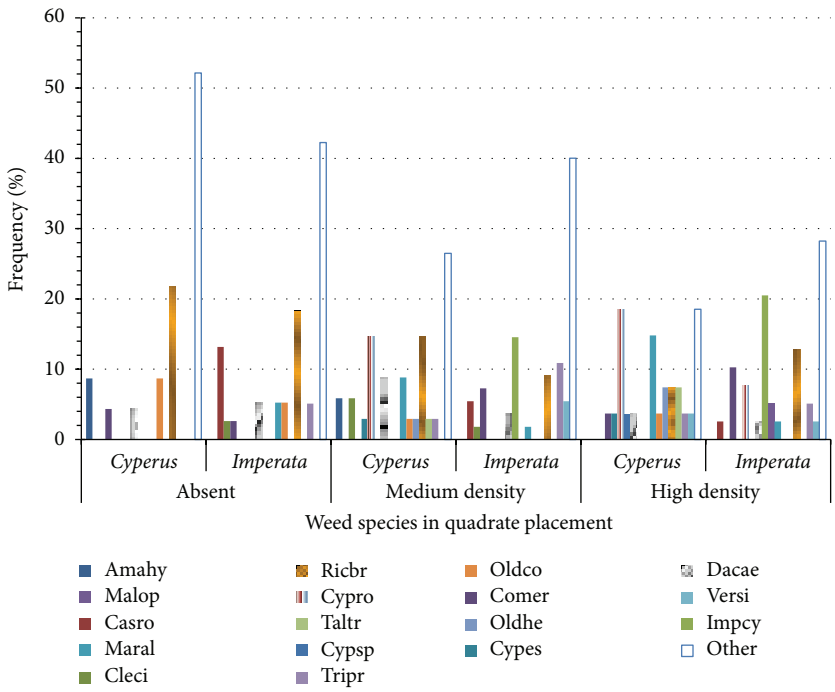

Figure 1: Weed specie average frequency in different placements of the quadrate.

Three species of *Cyperus* including *Cyperus esculentus*, *Cyperus sphacelatus,* and *Cyperus rotundus* were identified. But only *Cyperus rotundus* (Cypro) was encountered for the medium density of *Cyperus* spp. Whenever high densities of *Cyperus* and *Imperata* were observed, they accounted for 25.92% and 20.51%, respectively. *Commelina erecta* (10.26%) and *Richardia brasiliensis* (12.82%) were the most frequent weed species associated with the high density of *Imperata*.

Figure 2 shows the mean values of total weed biomass dry matter for each quadrat according to *Imperata* and *Cyperus* densities. Weed biomass was significantly higher in quadrats with high densities for *Imperata* and *Cyperus,* respectively. Wherever *Cyperus* and *Imperata* were absent, total weed biomass did not differ significantly with that observed for their medium densities.

3.3. Weed and Soil Relations. Table 2 shows the Pearson correlation values (R) between soil characteristics and the biomass of *Cyperus* and *Imperata,* respectively, when high

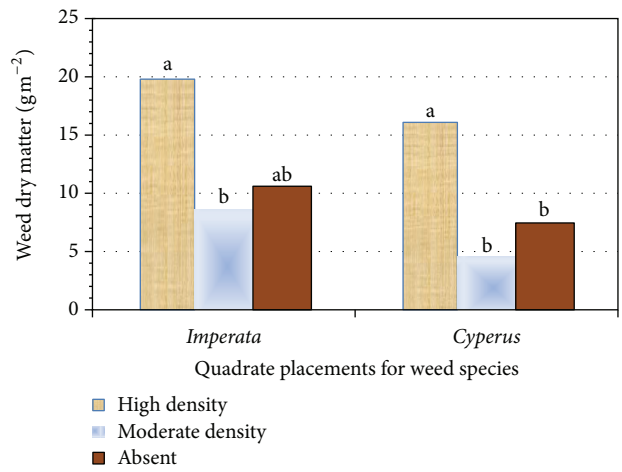

Figure 2: Weed biomass dry matter in quadrate placements for different densities of *Imperata* and *Cyperus* (a and b are indicating mean values that are different significantly).

Table 2: Pearson correlation coefficient values between soil characteristics and the dry matter of *Cyperus* and *Imperata* in their respective high density quadrate placement.

	R	
	Cyperus biomass	*Imperata biomass*
Clay	−0.31	−0.66*
Silt	−0.19	0.62*
Sand	0.22	−0.02
C	−0.34	0.39
N	−0.39	−0.08
Pa	0.55	0.48
Pt	−0.13	−0.13
Mg	−0.11	−0.60
K	0.06	0.73**
Ca	−0.36	−0.84**
Na	−0.29	0.54
Fe	0.03	−0.88**

* significant at 10%; ** significant at 1%.

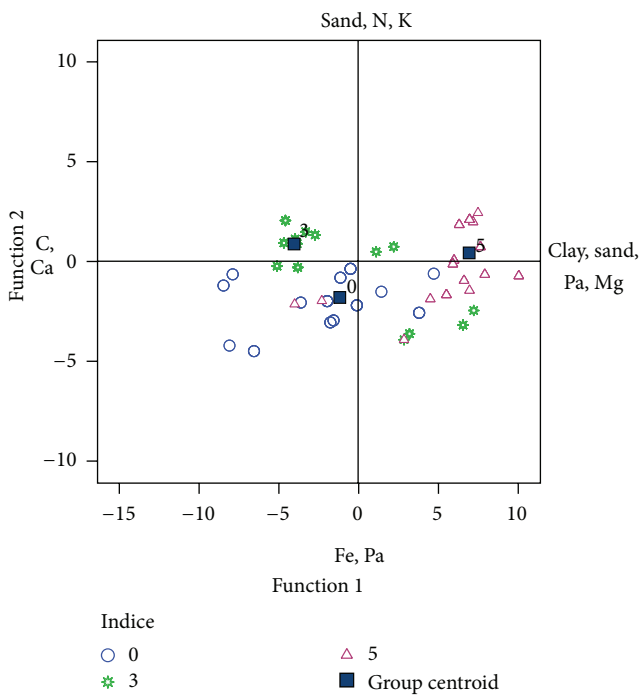

Figure 3: Canonical function discrimination of *Imperata* abundance according to soil parameters.

densities were observed. Carbon-C (−0.34), N (−0.39), Pa (0.55), and Ca (−0.36) had highest correlation values with *Cyperus* biomass, but these results were not significant. Meanwhile, highly significant ($P < 0.01$) correlations were observed between the biomass of *Imperata* and K (0.73), Ca (−0.84), and Fe (−0.88) concentrations in the soil. Moreover, clay (−0.66) and silt (0.62) had significant correlation with *Imperata* biomass at certain level of probability ($P = 0.1$).

Figure 3 shows that group centroids (mean of the discriminant score for a given category of dependant variable) of *Imperata* abundance indices are well separated, attesting the ability of soil parameters (clay, sand, Pa, C, N, K, Ca, Mg, and Fe) to discriminate *Imperata* density: absence was mainly characterized by lower Fe and Pa concentrations in soil, while increasing of soil sand, clay, Pa, and Mg was characterized by abundance (5). The medium (3) density of *Imperata* was observed for low soil C and Ca contents.

Table 3: Mean values of clay, silt, Fe, K, and Ca contents in soil at different topographic positions for different abundance of *Imperata*.

		Clay	Silt	Fe	K	Ca
		%		(ppm)	cmol kg^{-1}	
SUM	A	9^c	5^b	3277.87^b	0.02^b	3.32^a
	M	10^b	6^a	1506.75^c	0.01^c	2.84^b
	H	14^a	6^a	3509.50^a	0.04^a	3.28^a
$P > F$		<0.0001	0.006	<0.0001	<0.0001	<0.0001
US	A	14^b	5^b	2584.94^a	0.05^b	2.87^a
	M	12^a	4^c	654.08^c	0.03^c	2.90^a
	H	13^b	8^a	2330.99^b	0.08^a	2.88^a
$P > F$		<0.0001	<0.0001	<0.0001	<0.0001	0.272
MS	A	10^a	4^b	2366.19^a	0.18^c	2.00^c
	M	7^c	5^a	1018.08^c	0.30^a	2.19^b
	H	9^b	3^c	2046.45^b	0.23^b	2.44^a
$P > F$		<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
FS	A	10^a	9^c	591.65^c	0.36^b	2.87^a
	M	10^a	11^a	4498.86^a	0.41^a	2.02^c
	H	9^b	10^b	1269.39^b	0.21^c	2.25^b
$P > F$		<0.0001	<0.0001	<0.0001	<0.0001	<0.0001

SUM: Summit; US: upper slope; MS: middle slope; FS: foot slope; A: absent; M: moderate density; H: high density; [a,b,c] are indicating mean values that are significantly different.

Table 3 shows variance of these relationships according to topographic positions. In fact, the highest soil clay (14%), Fe (3509.5 ppm), and K (0.04 cmol kg^{-1}) concentrations were associated with the abundance of *Imperata* at the summit. However, the absence of *Imperata* at the US and MS positions was more related to high soil Fe concentration. Highest (US) and lowest (MS) K concentration in soil characterized the highest density and the absence of *Imperata,* respectively, according to topographic positions. Soil calcium concentrations were not significantly different for the absence and the high density of *Imperata* at the SUM and the US. In contrast, the highest (2.44 cmol kg^{-1}) and lowest (2.00 cmol kg^{-1}) soil Ca concentrations were related to high density of *Imperata* at the FS and MS positions, respectively.

4. Discussion

4.1. Extension and Limit of Our Finding. *Cyperus esculentus*, *Cyperus sphacelatus,* and *Cyperus rotundus* were encountered in the studied area. The last species was the most frequent along the toposequence compared to the others. However, the occurrence of *Cyperus sphacelatus* contrasts with observations by Johnson [5] who mentioned the occurrence of *Cyperus difformis* in rice agro-ecosystems rather than

C. sphacelatus. *Dactyloctenium aegyptium* (Dacae), *Richardia brasiliensis* (Ricbr), and *Commelina erecta* (Comer) were the most frequent weed species associated with *Cyperus* and *Imperata* according to our study which differs from previous knowledge of weed community in upland ecology of West Africa [8]. Furthermore, *Andropogon*, *Cymbopogon*, *Hyparrhenia*, *Pennisetum*, and *Setaria* were frequently encountered in the southern guinea savanna including *Brachiaria* spp. instead of *Setaria* identified in the northern guinea savanna of West Africa [21]. Therefore, the studied location in the Dahomey gap differs from the ecologies of north and south guinea savanna of West Africa. Indeed, the studied zone was described as a costal savanna [22] representing a marginal zone of West Africa, which was named the Dahomey gap [23]. Therefore, this particularity could have induced differences in weed assemblages compared to the others savanna ecologies. Hence, our analyses provide additional knowledge of weed occurrence in rice growing agro-ecologies of West Africa.

The studied ecology was also characterized by a landscape of a wide plateau with depressions instead of a hydrographic network as described by Raunet [24] on the crystalline basement of West Africa. However, the trends of variation in soil nutrients were the same along the toposequence of *terre de barre* as described elsewhere [25]: divalent cations concentrations decreased from the summit to the foot slope, while soil concentrations of monovalent cations increased. Therefore, the influence of soil parameters on weed species occurrence as revealed in our actual study can be considered for the entire Dahomey gap and the other ecologies of West Africa according to the rule of nonreplicated ecological study [15].

4.2. Weeds Control by Soil Fertility Management. The lowest total weed biomass was observed in the quadrats when *Cyperus* and *Imperata* were absent. This result attested that factors affecting the occurrence of these species can also be considered for the others weeds species. Therefore, our result provides an insight to deeper knowledge of the interactions of divers weed communities with soil. However, exceptions should be considered for *Richardia brasiliensis* (Ricbr) and *Dactyloctenium aegyptium* (Dacae) which were encountered in all the quadrats (Figure 1) indifferently to the density of *Cyperus* and *Imperata*.

No significant relationship was observed between the soil parameters studied and *Cyperus* spp. biomass (Table 2). However, Koné et al. [26] showed a decreased of *Cyperus* abundance with the increasing soil Mg concentration. Indeed, our study revealed some implications of this nutrient (Mg) in *Cyperus* occurrence through the soil balance of K and Mg, excepted in the FS position (Table 4). Application of K fertilizer might be able to increase soil K : Mg ratio and decrease *Cyperus* abundance at the SUM, while supplying Mg might induce the same effect on *Cyperus* occurrence at the US and MS positions by altering the Ca : Mg ratio. Therefore, K or Mg amendments are required for depressing *Cyperus* occurrence according to topographic positions. Indeed, soil balance in K : Mg and Ca : Mg can affect not only K and Ca availability to plant but also P as observed by Yates [27]. Thus, it appears that *Cyperus* occurrence is more related to imbalanced ratio of nutrients in soil rather than the depletion effect of sole nutrient content.

Table 4: Pearson correlation values (R) and its probabilities (P) between *Cyperus* spp. and *Imperata Cylindrica* and soil different ratios in K : Mg and Ca : Mg at each topographic position.

		Correlation (R) and probability value (P)			
		Cyperus spp.		*Imperata Cylindrica*	
		R	P	R	P
K : Mg	SUM	−0.703	0.0002	0.397	0.021
	US	0.853	<0.0001	0.482	0.007
	MS	0.956	<0.0001	−0.338	0.032
	FS	0.273	0.290	0.378	0.034
Ca : Mg	SUM	0.843	<0.0001	−0.231	0.195
	US	0.839	<0.0001	0.066	0.729
	MS	0.822	<0.0001	−0.839	<0.0001
	FS	−0.094	0.719	−0.743	<0.0001

SUM: Summit; US: upper slope; MS: middle slope; FS: foot slope.

I. cylindrica occurrence was significantly influenced by soil Fe, Ca and K concentrations with less importance to soil particle sizes (Table 2). This result restricts the assertion made by Andreasen and Streibig [28] concerning the influence of soil texture on weed occurrence. Furthermore, the influence of soil nutrients was confirmed partially according to topographic positions. Highest soil K concentration was associated with high density of *Imperata* at the uphill position (SUM and US). Instead of reducing soil K concentration for depressing the density of *Imperata*, management strategy must focus on reduction of K : Mg by supplying Mg compound as consequence of Pearson correlation value observed in Table 4. *Imperata* density can also decrease at the downhill position with the decrease or increase of soil Ca concentration at the MS and the foot slope positions, respectively. However, no consistent management of soil Ca can be drawn from our study regarding the contrasts observed in Tables 3 and 4. Further investigations should also focus on K : Ca: Mg or [(Ca + Mg) : K] ratio for improving knowledge of the interaction between Ca and *Imperata*. Up to now, our study has improved knowledge of the effect of soil nutrients balance on weed occurrence as mentioned by the Midwest Organic and stainable Education Service (MOSES) [29].

4.3. Indicators of Soil Degradation in the Environment. The study revealed that highest soil Fe concentrations at the Hillside (US and MS) were also associated with a low density of *Imperata*. Otherwise, Fe leaching as observed in degraded soil [30] may be favorable to *Imperata* occurrence depending on topographic positions. Low soil K (0.03–0.08 cmol kg^{-1}) concentrations observed at the US position reinforced (Table 3) this assertion. Indeed, low K concentrations in soils of Africa occur generally in degraded soils according to Juo and Grimme [31]. Therefore, our finding confirms the fact that *Imperata* is a bioindicator of degraded soil as propounded by Scherr and Yadav [32].

The leaching of soil K and Mg leads to impoverishment of soil in these nutrients, justifying their requirement for

the control of *Cyperus* spp. occurrence, especially by changing soil nutrient balance. Thus, soil chemical degradation can also induce *Cyperus* spp. occurrence and likewise for *Imperata*. In the Philippines, *Imperata cylindrica* and *Cyperus compressus* were observed in strongly weathered soil [33] corroborating our analysis and suggesting that soil organic amendment can reduce the invasion of these species, especially for Cyperus [26]. In the context of land management, we can recommend further study of fallowing or the cultivation of cover crops on *Cyperus* spp. and *Imperata* occurrences on Acrisols. These practices might be able to avoid soil degradation [34], restricting *Cyperus* and *Imperata* invasions.

Most of the knowledge of upland soil chemical degradation processes is related to nutrient depletion [35, 36]. Nutrient ratios have been investigated less frequently. Except for soil C (1.09–1.71%) and N (0.05–0.08%) concentrations and K (0.1 cmol kg^{-1}) concentrations at certain levels of significance, the studied soil had high nutrient concentrations, especially for P (8–26.4 ppm) and Na that reached 0.55 cmol kg^{-1} (Table 1). But rice yield can drop to 0.26 tha^{-1} even for improved varieties with a potential yield of 4-5 tha^{-1}, as a consequence of mineral imbalances, particularly C : N, Ca : Mg and K : Mg [23]. Regarding yield reduction as an indicator of agricultural soil degradation [32], we deduce that unbalanced soil nutrients in the studied area are likely to contribute. These characteristics (nutrient ratios) of soil were also involved in rice P-nutrition in an acid Ferralsol of Nigeria [37]. More investigations for understanding the effects of nutrient ratios in soils are required in tropical ecologies for improvement of agricultural land use, weed management, and restoration of degraded soils.

Our results showed association of high density of *Imperata* to *Commelina erecta* and *Richardia brasiliensis*. Finally, *Imperata*, *Cyperus*, *Commelina,* and *Richardia* can be considered as indicators of degraded Acrisols in the studied environment. The importance of soil exchangeable cation concentrations (Ca, Mg, Fe, and K) and the ratios of Ca : Mg and K : Mg for weeds occurrence in the Dahomey gap, and West African ecosystems by extension, confirms the work done by Udoh et al. [12] citing the importance of soil C, N, Zn, and Mn contents.

5. Conclusion

Soil parameters have influence the occurrence of weeds according to topographic positions, especially for *Cyperus* spp. and *Imperata Cylindrica*. However, the relationship with *Cyperus* spp. was less pronounced than with *Imperata Cylindrica*.

Soil balance, and in particular K : Mg and Ca : Mg ratios, were the main factors affecting the occurrence of these weeds in the studied ecosystem. Applying Mg and/or K fertilizers might be employed to change these soil characteristics to reduce *Imperata* and Cyperus invasions. Soil Fe concentration also influenced *Imperata* occurrence. It is suggested that Cyperus and *Imperata* occurrences prevailed in degraded soil for which they can be used as indicators, along with *Commelina* and *Richardia*. To some extent, our finding can be extended to other West African ecosystems.

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Research Article

Effects of 24 Years of Conservation Tillage Systems on Soil Organic Carbon and Soil Productivity

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The 24-year study was conducted in southern Illinois (USA) on land similar to that being removed from Conservation Reserve Program (CRP) to evaluate the effects of conservation tillage systems on: (1) amount and rates of soil organic carbon (SOC) storage and retention, (2) the long-term corn and soybean yields, and (3) maintenance and restoration of soil productivity of previously eroded soils. The no-till (NT) plots did store and retain 7.8 Mg C ha^{-1} more and chisel plow (CP) −1.6 Mg C ha^{-1} less SOC in the soil than moldboard plow (MP) during the 24 years. However, no SOC sequestration occurred in the sloping and eroding NT, CP, and MP plots since the SOC level of the plot area was greater at the start of the experiment than at the end. The NT plots actually lost a total of −1.2 Mg C ha^{-1}, the CP lost −9.9 Mg C ha^{-1}, and the MP lost −8.2 Mg C ha^{-1} during the 24-year study. The long-term productivity of NT compared favorably with that of MP and CP systems.

1. Introduction

Conservation program was established to take highly erodible lands out of production. In the United States, the Food Security Act of 1985, the 1990, 1995, 2001, 2006, and 2011 Farm bills, and the Illinois T by 2000 Program have resulted in millions of hectares of erodible land previously in row crops being put into the CRP for 15 to 25 years. Any conversion of Conservation Reserve Program (CRP) land back to corn and soybean production could require the use of conservation tillage systems such as NT to meet soil erosion control standards. Evaluations of yield response of these conservation tillage systems over time are needed to assess returning this land to crop production, the effects on SOC storage and retention and crop yields.

Conservation tillage (defined as having 30% residue at the time of planting) can result in an increase in crop yield when compared with that of a moldboard plow system. Lawrence et al. [1] showed in a 4-year study in a semiarid environment in Australia that no-till had a higher crop yield than did reduced till fallow or conventional till fallow. Wilhelm et al. [2] observed a positive linear response between yields of corn and soybean, and amount of residue applied to a no-till system. Lueschen et al. [3], in a corn-soybean rotation in Minnesota, found an increase of 6.30 Mg ha^{-1} in yield of the NT system above the MP system in a dry year. Kapusta et al. [4] studied the effects of tillage systems for 20 years and found equal corn yield for no-till, reduced till, and conventional tillage systems despite the lower plant population in no-till.

Maintaining crop residue on the soil surface [5, 6] can reduce the severity of erosion. At planting with chisel plowing, residue cover has to be 30 percent or more, but often much higher with no-till (usually 50% or more residue) due to minimum soil disturbance [7]. Lueschen et al. [3], for a corn-soybean rotation in Minnesota, observed 69 to 82, 49, and 10 percent of soybean residue cover on the soil surface after corn planting in no-tillage, chisel plow, and moldboard plow system plots, respectively.

The impact of tillage and cover crops on SOC sequestration (net increase) or loss has been the focus of many studies

since this management techniques are thought to contribute to atmospheric C loss or sequestration. SOC sequestration or retention has been shown to retain more SOC with decreasing disturbance or enhanced rotation diversity [8]. Many of the early studies found NT to have significantly higher SOC than MP and CP systems when the soils were only sampled to 15 or 30 cm depth [8, 9]. The NT plots have SOC concentrated in the top 30 cm, but was dispersed to greater depths in tilled plots [9, 10].

Decline of SOC content in agricultural systems and increased awareness of its importance to global C budgets has accelerated evaluations of land management impacts on soil C dynamics and storage [11]. Land use practices that may affect SOC sequestration include a switch to NT [12]. The impact of tillage on SOC sequestration (net increase) or loss has been the focus of many studies since these management techniques contribute to atmospheric C loss or sequestration. SOC sequestration or retention has been shown to occur with decreasing soil disturbance or enhanced crop rotation diversity.

Change in frequency and intensity of tillage practices alter the bulk density and soil organic matter in the soil profile. Mann [13] reported that the reduction in SOC content of soils having an initial content of between 20 and 50 g kg^{-1} was 20 percent less after cultivation. He found that changes in SOC content were most pronounced during the first 20 years of cultivation. Also, changes in SOC storage were more variable in the upper 15 cm of soil than in the upper 30 cm. Varvel and Wilhelm [14] studied the use of conservation tillage systems for corn and soybean production and found soil organic carbon levels were maintained or even increased in all tillage system with the greatest increase obtained in systems with the least amount of soil disturbance which strongly support the adoption and use of conservation tillage systems for soil sustainability.

Franzluebbers and Follett [15] reported that SOC content of timberland and prairie soils declined with cultivation in North America. The rate of decline as a result of cultivation was 22% ± 10% for the northeast; no value was reported for the central, 25% ± 33% for southwest, and 36% ± 29% for southeast. Ismail et al. [16] observed a decrease in SOC in the 0- to 30-cm silt loam layer of soil during the first 5 years, no change in the next 5 years, and an increase in SOC in the last 10 years in both NT and MP in comparison with sod plots. SOC was higher in NT than in MP. Hunt et al. [17] and Angers and Giroux [18] found NT systems increased SOC content, compared with MP and CP systems, in the top 5-cm layer of soils with a range of soil textures, including loamy sand, silt loam, and silty clay loam.

Mulvaney et al. [19] did not find an increase in soil organic matter build-up in response to increased crop residue input as a result of fertilizer N applications when a pretreatment SOC data were collected and used as the baseline to determine SOC change over time in long-term cereal cropping experiments. Khan et al. [20] found that the use of the comparison method with SOC content measurements only taken in the middle and at the end of a variable rate N fertilizer, crop yield, and SOC sequestration studies resulted in an overestimation of the magnitude and rate of SOC sequestration in response to N fertilizer. Comparison studies with one treatment as the baseline or control should not be used to determine SOC sequestration, if soil samples are only collected and tested once during or at the end of study. Only experimental designs with pretreatment SOC measurements (baseline data) made before or at the start of long-term field studies should be used.

Olson [21] found that the SOC content of the MP treatment, used as baseline in comparison method studies, was not at steady state during the 20 yr tillage experiment at Dixon Springs, Illinois. In fact MP plots lost −15.2 Mg C ha^{-1} from the root zone as a result of mixing, intensity of crop rotation, aeration, and eroded SOC rich sediments being transported off the plot area [22]. NT treatment only reduced the magnitude and rate of SOC loss over time. The pair comparison method used by many researchers with MP as baseline suggested +9.1 Mg C ha^{-1} of SOC sequestration occurred during the 20 yr experiment [21]. However, the 1988 pretreatment baseline method did not validate the SOC sequestration value. At this site the sloping and eroding NT plot actually lost −6.8 Mg C ha^{-1} during the 20-year study so no actually SOC sequestration occurred. The assumption that the MP was at a steady state, made by researchers [15, 23–27] using the comparison method with one year of SOC sampling near the end, was incorrect and resulted in an SOC sequestration finding that was invalid. Olson [21] findings suggest a pretreatment SOC baseline is essential in all tillage comparison studies to determine the amount and rate of SOC sequestration, steady state, or loss. A pretreatment SOC baseline was needed in these comparison studies when determining the amount and rate of SOC sequestration, storage, retention, or loss, especially on sloping and eroding soils with more intensive cropping rotations (more row crops and fewer years of forages) during the study than in previous years.

Shorter term tillage studies [28–30] were extended to 24 years with the objective of evaluating long-term tillage systems (NT, CP, and MP) effects on corn and soybean yields and the effects on the SOC storage or retention and the maintenance and restoration of soil productivity of previously eroded soils in southern Illinois. These SOC storage and retention values by tillage treatment at the end of the study will be compared to pretreatment SOC levels to determine the amount and rate of SOC sequestration or loss as a result of the 24 years of tillage treatments. The study was extended to show that NT system can be used instead of MP or CP systems to reduce soil erosion and maintain long-term crop yields.

2. Materials and Methods

A conservation tillage experiment was started in 1989 at the Dixon Springs Agricultural Research Center in southern Illinois. The soil at the study site was a moderately eroded phase of Grantsburg silt loam (fine-silty, mixed, mesic Typic Fragiudalf) [31] with an average depth of 64 ± 6 cm to a root-restricting fragipan. The area had an average slope gradient of 6 percent. Starting with corn in 1989, corn and soybean were grown in alternate years. The experimental design was two Complete Latin Squares and each square has three rows

and three columns [32] which allowed for randomization of the tillage treatments (NT, CP, and MP) both by row (block) and by column. This replication was used to control random variability in both directions. Each tillage treatment was randomized six times in 18 plots with a size of 9 m × 12 m. The columns were initially separated with 6 m buffer strips of sod. Later the buffer strips were planted to NT corn and soybeans to reduce deer damage. An electric fence was later used to protect the crops in the plots. There was a 60 m wide filter strip between the plot area and the drainage way.

The implements used in each tillage system and depth of tillage were as follows: NT (John Deere No-Till planter with wavy coulters), CP (straight-shanked chisel plowed to 15 cm with disking to 5 cm), and MP (moldboard plowed to 15 cm with disking to 5 cm). In the spring of each year the MP and CP plots were moldboard and chisel plowed followed by 2 disking and planting. In odd years corn was planted at the seeding rate of 64,000 seeds ha^{-1} with fertilizers of 218 kg ha^{-1} N, 55 kg ha^{-1} P, and 232 kg ha^{-1} K. The tillage study did not focus on N fertilizer application in corn years since the rate was the same for both conventional (MP) and conservation (NT and CP) tillage systems.

The percentage surface residue was determined after planting by the line-transect method [33]. Plant population for the center 0.001 ha of each plot was determined by counting at 25 days after planting. The crop yield and plant population data from 1989 to 2012 were collected as part of this study. The soil loss rates were not measured directly. They were determined using RUSLE2 [34] and USLE [35] models that have been validated and widely used in USA by USDA, NRCS Soil Conservationists.

2.1. Field and Laboratory Methods. Soil samples were collected in September of 1988 (prior to the establishment of the tillage experiment in spring of 1989), in August of 2000 and in June of 2009, at depths of 0- to 5-, 5- to 15-, 15- to 30-, 30- to 45-, 45- to 60-, and 60- to 75-cm for SOC determination. The sampling depth was limited due to the presence of a root restricting fragipan at a 64 ± 6 cm depth. Previous soil sampling found only trace amounts of SOC present below a 75 cm depth, probably from previous grass roots penetrating the fragipan along the prism faces. Four soil cores (3.2 cm diameter), one from near each of the four corners of the plot (1.5 m from adjacent, above or below plot, and 1.5 m from border strip), were obtained for each depth and composited by crumbling and mixing. The samples were air-dried and pulverized to pass through a 2 mm sieve prior to analysis. The SOC was determined after removal of un-decomposed plant residue using the modified acid-dichromate organic carbon procedure number 6A1 [36]. Field moist core bulk density was determined [36] using a Model 200 soil core sampler (5.6 cm in diameter and 6 cm high) manufactured by Soil Moisture Equipment Corp.

2.2. Statistical Methods. Statistical analysis for all parameters was performed using the procedures from Statistical Analysis System (SAS) computer software [37]. Analysis of variance and least square means of crop yield and SOC content were performed by General Linear Model (GLM) procedures. Analysis of variance and least square means of crop yield and SOC content were performed by General Linear Model (GLM) procedures. An LSD procedure was used at the $P = 0.05$ level to determine, if there were significant SOC differences between tillage treatments for the same date and depth.

3. Results

The NT system maintained a significantly greater amount of residue on the soil surface as compared with that of the CP, and MP systems at planting during each selected year (Table 1). Crop residue on the soil surface was greater with corn as previous crop, compared with that of soybean because of greater residue production from corn and slower rate of decomposition of corn residue [38] than soybean residue. On Grantsburg soil with 5–7 percent slopes, the estimated annual soil loss, determined with USLE and RUSLE2, was 8, 20, and 30 Mg ha^{-1} with the NT, CP, and MP systems, respectively, (Table 1) [34, 35]. The greater the percentage of crop residue (Table 1) on the soil surface with the NT system protected the soil from erosion keeping it below the tolerance level of 8.4 Mg ha^{-1} yr^{-1} [35]. On the other hand, rill erosion was observed with the MP and CP systems as a result of fewer residues on soil surface compared with that of the NT system.

Rainfall data (30-year average growing season rainfall by month for the southeastern Illinois, USA) and 1989–2012 growing seasons are shown in Table 2. The 30-year average cumulative rainfall during April–September in southeastern Illinois was 64.4 cm. Seven years (1991, 1994, 1999, 2004, 2007, 2008, and 2012) could be characterized as dry years with a growing season rainfall of 43.3, 50.7, 47.7, 38.3, 44.4, 45.8, and 37.1 cm, respectively.

From 1989 to 2012, the MP system had greater plant populations than the other tillage systems in 6 of 24 years (Table 3). The NT system had greater plant population than the other tillage systems in 7 of 24 years while CP only had 1 of 24 years with greater plant populations than the other tillage systems. In 1989, 1996, 1998, 2002, and 2006, the NT had fewer plants per plot (Table 3) compared with the other tillage systems which was probably due to insufficient soil-seed contact, lower germination, and greater soil strength in the NT system [28]. During 1990, 1996, 2002, 2006, and 2011 the high April and May rainfalls (Table 2) contributed to less plants per plot with the NT system compared with that of the MP system (Table 3). Better seed-soil contact with the MP system could have increased the germination compared with that of the NT system during 1996, 2002, and 2006 (Table 3). On the other hand, in 1994 and 2000 the plant population was greater with the NT treatment compared with that of the MP treatments, which could have been due to relatively greater water availability in the NT system compared with MP tillage system at planting. Twelve-year average plant population (Table 3) for corn and soybean was not statistically different from NT and MP systems.

In 2004, one of the driest years, the soybean yields were zero for all treatments (Table 4) since all plant available

Table 1: Effect of different tillage treatments on plant residue after planting and soil loss at Dixon Springs. Odd years have soybean residue and even years have corn residue.

Tillage	Residue present from previous crop (% cover)									Soil loss[#]
	1996	1997	1998	1999	2005	2006	2007	2011	2012	(Mg ha^{-1})
No-till	91a[*]	75a	95a	73a	85a	90a	78a	74a	88a	8c
Chisel plow	21b	18b	29b	21b	18b	28b	24b	20b	28b	20b
Moldboard plow	6c	6c	17c	5c	5c	10c	8c	6c	9c	30a

[*]For each year means in a same column followed by the same letter is not significantly different at the $P = 0.05$ probability level.
[#]Soil loss is calculated by Universal Soil Loss Equation (USLE) and Revised Universal Soil Loss Equation (RUSLE2).

Table 2: Rainfall data for 1989–2012 growing season at Dixon Springs in Southern Illinois.

Year	Rainfall (cm)						
	April	May	June	July	August	September	Growing season
1989	6.1	4.1	14.3	12.8	10.0	4.6	51.9
1990	14.5	28.2	4.4	6.4	10.5	8.8	72.8
1991	12.5	8.9	1.8	3.7	4.0	12.4	43.3
1992	6.1	6.7	7.6	13.4	3.9	19.1	56.8
1993	12.3	13.0	17.8	13.4	10.9	19.4	86.8
1994	16.2	1.5	10.2	6.0	9.8	7.0	50.7
1995	17.7	22.0	15.2	7.3	8.2	4.8	75.2
1996	14.8	14.2	9.0	13.1	1.4	14.8	67.3
1997	9.5	14.9	14.5	5.8	7.5	4.0	56.2
1998	15.3	6.5	19.3	10.3	11.8	2.5	65.7
1999	10.3	6.8	16.8	10.0	2.3	1.5	47.7
2000	6.2	15.8	15.1	6.8	3.8	8.3	56.0
2001	6.0	8.4	9.3	15.9	9.8	9.3	58.7
2002	19.0	24.7	3.1	5.1	7.2	18.8	77.9
2003	12.4	32.2	11.9	4.0	13.5	12.6	86.6
2004	6.5	13.5	5.4	8.1	4.8	0.0	38.3
2005	10.0	4.7	6.5	10.8	18.2	6.8	57.0
2006	7.5	10.2	7.0	21.3	7.7	21.3	75.0
2007	8.2	7.3	7.1	9.9	4.5	7.4	44.4
2008	11.6	6.6	5.8	11.6	7.0	3.2	45.8
2009	12.9	20.0	9.9	34.7	9.4	13.2	99.9
2010	8.8	12.2	10.5	6.8	9.2	8.5	55.2
2011	35.3	21.4	20.6	11.1	7.8	16.6	112.6
2012	3.3	1.6	3.0	9.4	6.7	13.2	37.1
1989–2012 average	11.0	12.1	9.8	9.8	7.9	9.5	59.8
30-year average	12.3	13.9	10.3	10.2	8.3	9.4	64.4

water above the fragipan was extracted from all treatments including the NT system. In 1994, another year of low rainfall, the soybean yields were low for all treatments, but NT yield (Table 4) was substantially greater than CP and MP yields. In 1999, the NT corn yield of NT system was significantly greater than CP and MP. The 24-year average rainfall for the April through September period was 59.8 cm which is equal to the 30-year average (Table 2). Years of 1990, 1993, 1995, 2002, 2003, 2006, 2009, and 2011 were considered wet years.

From 1989 to 2012, tillage affected crop yields in only 1989, 1994, 1999, 2001, 2002, 2006, 2009, 2011, and 2012 (Table 4). In 1994, 2002, and 2012, the NT system produced significantly greater soybean yield than with the CP and MP systems partially due to greater plant population. Since 1994 and 2012 were dry years, and 2002 had a dry June to August period, the NT system could have provided more soil water to soybean at planting and later in the season compared with that of the other tillage systems. This enhanced soil water storage could have resulted in an improvement in nutrient availability and played an important role in greater soybean yields in 1994, 2002, and 2012 with the NT system as compared to MP and CP systems. Greater crop yield with the NT system than MP system in a dry year (not a drought) was also noted by Lueschen et al. [3]. Although the differences in soybean yield in 1996 were not significant by tillage treatment, the NT system had 8 and 16 percent greater yield than the MP and CP

Table 3: Effect of different tillage treatments on the corn and soybean populations during 1989–2012 at Dixon Springs.

	Plant population (1000 plants ha^{-1})						
Corn year	1989	1991	1993	1995	1997	1999	
NT	55.3b*	57.9a	51.4a	58.8ab	46.9a	69.2a	
CP	59.2ab	47.4b	54.1a	55.7b	51.9a	64.2ab	
MP	62.9a	52.2ab	52.6a	62.2a	51.9a	62.7b	
Year	2001	2003	2005	2007	2009	2011	12-year average
NT	64.5a	59.5a	70.5b	68.8a	65.0a	75.7a	59.4a
CP	56.5b	61.3a	76.0a	68.5a	65.5a	67.7ab	58.6a
MP	65.9a	60.0a	69.5b	68.3a	64.0a	61.3b	60.2a
Soybean year	1990	1992	1994	1996	1998	2000	
NT	191.0b*	344.0a	303.0a	263.0b	271.0b	422.0a	
CP	247.0a	335.0a	229.0b	277.0b	273.0b	398.0a	
MP	249.0a	343.0a	181.0c	309.0a	294.0a	405.0a	
Year	2002	2004	2006	2008	2010	2012	12-year average
NT	293.0b	240.0a	320.0a	310.0b	294.0a	168.5a	284.4a
CP	393.0a	228.0a	363.0b	390.0a	279.0a	125.6b	296.5a
MP	420.0a	255.0a	388.0c	360.0ab	288.0a	176.0a	297.8a

*For each crop means in a same year followed by the same letter is not significantly different at the $P = 0.05$ probability level.

Table 4: Effect of different tillage treatments on corn and soybean yields during 1989–2012 at Dixon Springs.

Tillage	Crop yield (Mg ha^{-1})						
Corn year	1989	1991	1993	1995	1997	1999	2001
NT	8.99b*	6.57a	11.79a	11.60a	9.87a	8.12a	9.73b
CP	9.99b	6.10a	11.61a	11.55a	9.32a	6.78b	9.60b
MP	11.26a	6.60a	10.98a	10.37a	9.59a	6.98b	10.34a
Year	2003	2005	2007	2009	2011	12-yr ave.	% of MP yield
NT	6.67a	11.40a	6.46a	13.10a	6.13a	9.18a	96
CP	7.33a	11.82a	6.80a	13.60a	6.85b	9.24a	97
MP	7.82a	11.41a	7.33a	14.03b	7.68ab	9.53a	100
Soybean year	1990	1992	1994	1996	1998	2000	2002
NT	2.37a	3.74a	2.87a	2.63a	2.63a	2.32a	2.37a
CP	2.62a	3.46a	1.81b	2.27a	2.63a	2.38a	2.07a
MP	2.62a	3.65a	1.49b	2.43a	2.75a	2.32a	1.98b
Year	2004	2006	2008	2010	2012	12-yr ave.	% of NT yield
NT	0a	3.17ab	2.84a	2.94a	2.65a	2.54a	100
CP	0a	3.37a	2.84a	2.79a	1.96b	2.35a	93
MP	0a	3.10b	3.04a	2.88a	1.82b	2.34a	92

*For each crop means in a same year followed by the same letter is not significantly different at the $P = 0.05$ probability level.

systems, respectively. In 2002, the NT soybean yield (Table 4) was significantly greater than MP when the plant population (Table 3) was significantly less. Year 2002 was considered a wet year; however, the combination of a dry period (between June and August of 2002) and the greater number of plants in MP resulted in less water available per plant. In 2004, there were no measureable soybean yields on any of the tillage treatments. Growing season rainfall totaled 38.3 cm which is 26 cm below the average. In addition, the fall 2003 and winter and spring of 2004 had below average rainfall and the 15 cm water storage capacity of the Grantsburg moderately eroded soils was not full on April 1 which caused the soybean yield to be zero on all treatments.

A tillage study was conducted to determine the amount and rate of SOC storage and retention in NT and CP tillage system when compared to MP system as the comparison baseline. The SOC levels were determined at the end of the 24-year study (Table 5). The MP SOC level (43.1 Mg C ha^{-1} layer^{-1}) was significantly less for the 0–75 cm layer (root zone) than the NT (50.9 Mg C ha^{-1} layer^{-1}) and similar to the CP SOC value (42.0 Mg C ha^{-1} layer^{-1}). The NT plots did store and retain more SOC in the soil (7.8 Mg C ha^{-1}) and the CP plots less (−1.6 Mg C ha^{-1}) than MP. These SOC amounts were retained and stored in the soil and not decomposed and reemitted to the atmosphere as a

Table 5: Paired comparisons using MP as baseline to determine no-till (NT) and chisel plow (CP) effects after 24 years of tillage treatments on the volumetric SOC content change of the Grantsburg soil.

Tillage treatment	Depth cm	June 2012	Comparison method NT or CP versus MP 24 yr total SOC retained above MP Mg C ha^{-1} layer^{-1}	Paired comparison annual SOC retention rate above MP the comparison baseline
NT	0–15	26.3a**	+7.5	+0.31
	15–75	24.6a	+0.3	+0.01
	0–75 (all)	50.9a	+7.8	+0.32
CP	0–15	20.3b**	+1.5	+0.06
	15–75	21.7a	−2.6	−0.11
	0–75 (all)	42.0b	−1.1	−0.05
MP	0–15	18.8b		
	15–75	24.3a		
	0–75 (all)	43.1b		

**Means six replications with the same letter and in the same year and depth with a different tillage treatment are not significantly different at $P = 0.05$.

Table 6: Use of pretillage treatment 1988, 2000, and 2012 SOC during 24 years of tillage treatments.

Tillage treatment	Depth cm	September 1988 (pretreatment baseline)	August 2000 Mg C ha^{-1} layer^{-1}	June 2012
NT	0–15	28.5a**	26.8a**	26.3a**
	15–75	23.6a	20.2a	24.6a
	0–75 (all)	52.1a	47.0a	50.9a
CP	0–15	28.4a	25.0a	20.3b
	15–75	23.5a	18.7ab	21.7a
	0–75 (all)	51.9a	43.7ab	42.0b
MP	0–15	28.3a	19.9b	18.9b
	15–75	23.1a	17.8b	24.3a
	0–75 (all)	51.4a	37.7b	43.1b

**Means six replications with the same letter and in the same year and depth with a different tillage treatment are not significantly different at $P = 0.05$.

result of cultivation or in the transported sediment moved off of the plots.

Since the plot area was on 6% slopes and eroding, the NT plot SOC storage and retention amount and rate benefited from a smaller soil erosion rate of 8 Mg ha^{-1} yr^{-1} versus 20 Mg^{-1} ha^{-1} yr^{-1} for CP and a soil erosion rate of 30 Mg^{-1} ha^{-1} yr^{-1} for the MP plots (Table 1). The erosion rates were calculated using USLE and RUSLE2 [34, 35]. When MP loses SOC rich sediment from the plots and MP is the baseline, it has the effect of crediting NT (using comparison approach) with more SOC storage and retention.

Based on the paired comparison between NT and MP SOC in Table 5, it appears that NT stored and retained 7.8 (50.9–43.1) Mg C ha^{-1} more SOC than the MP plots at the end of the 24-year study. Using the comparison method [15, 23–27] with SOC levels determined in the last year of the study and MP treatment as the baseline, the NT plots at Dixon Springs appear to have sequestered 7.8 Mg C ha^{-1} of SOC in the soil. However, without knowing the SOC content in the plot area prior to or at the start of the tillage experiment (pretreatment SOC baseline), it would not have been possible to determine if SOC sequestration actually occurred and at the annual SOC retention rate (0.32 (7.8/24) Mg C ha^{-1} yr^{-1}) suggested in Table 5. These plots were sampled again and the SOC measured in August of 2000 and June of 2012 (Table 6) are lower than the initial September 1988 values for future NT, CP and MP plots sampled prior to tillage treatments being applied. The tillage plots (NT, CP and MP) lost SOC during the 24-year experiment and no SOC sequestration occurred on any of the tillage treatments. The NT plots actually lost a total of −1.2 Mg C ha^{-1}, the CP lost −9.9 Mg C ha^{-1}, and the MP lost −8.2 Mg C ha^{-1} during the 24-year study (Table 7).

The annual loss in SOC in Mg C ha^{-1} yr^{-1} is shown in Table 8. The NT rate of SOC loss from the root zone during the first 12 years was −0.42 Mg C ha^{-1} yr^{-1} but gained SOC at the rate of +0.33 Mg C ha^{-1} yr^{-1} during the last 12 years with an annual SOC loss rate for the 24 years of the tillage experiment was reduced to −0.05 Mg C ha^{-1} yr^{-1}. The CP rate of SOC loss from the root zone during the first 12 years was −0.68 Mg C ha^{-1} yr^{-1} and the loss rate decreased to −0.14 Mg C ha^{-1} yr^{-1} during the last 12 years with an annual SOC loss rate for the 24 years of the tillage experiment that was −0.41 Mg C ha^{-1} yr^{-1}. The MP rate of SOC loss from the root zone (0–75 cm) during the first 12 years was −1.14 Mg C ha^{-1} yr^{-1} and gained +0.45 Mg C ha^{-1} yr^{-1} during the last 12 years making MP annual loss rate −0.34 Mg C ha^{-1} yr^{-1} for the entire 24-year tillage experiment (Table 8). The higher rate of SOC loss from all tillage treatments during the first 12 years would have been as a result of the land use conversion and cultivation of the 15-year-old sod covered plot area.

4. Discussion

The 12-year average corn yield and the 12-year soybean yields were not affected by tillage (Table 4). Twelve-year average MP soybean yield was 2 and 9% greater than NT and CP

Table 7: Use of pretillage treatment (1988) SOC values (sod) as baseline to determine the total SOC change in the first 12 years and during 24 years of tillage treatments. The 2000 SOC values for each plot were used as baseline to determine the total SOC content change during the last 12 years for the Grantsburg soil.

Tillage treatment (6 replications)	Depth cm	First 12-yr tillage effect on SOC total change by treatment using 1988 baseline	Last 12-yr tillage effect on SOC total change by treatment using 2000 baseline	24 year tillage effect on SOC total change by treatment using 1988 baseline
			Mg C ha^{-1} layer^{-1} (% change)	
NT	0–15	−1.7 (−6)	−0.5 (−2)	−2.2 (−8)
	15–75	−3.4 (−14)	+4.4 (+22)	+1.0 (+4)
	0–75 (all)	−5.1 (−10)	+3.9 (+8)	−1.2 (−2)
CP	0–15	−3.4 (−12)	−4.7 (−19)	−8.1 (−28)
	15–75	−4.8 (−20)	+3.0 (+16)	−1.8 (−8)
	0–75 (all)	−8.2 (−16)	−1.7 (−4)	−9.9 (−19)
MP	0–15	−8.3 (−29)	−1.1 (−5)	−9.5 (−34)
	15–75	−5.3 (−23)	+6.5 (+36)	+1.2 (+5)
	0–75 (all)	−13.6 (−27)	+5.5 (+14)	−8.2 (−16)

Table 8: Use of pretreatment SOC baseline (1988) to determine the rate of SOC change During the first 12 years and for 24 years of tillage. A 2000 baseline was used for the last 12 years on the volumetric SOC content (Mg C ha^{-1} layer^{-1} yr^{-1}) of the Grantsburg soil.

Tillage treatment	Depth cm	1988 to 2000 tillage effect on SOC rate of change by treatment (baseline 1988)	2000 to 2012 tillage effect on SOC rate of change by treatment (baseline 2000)	24-year tillage effect on SOC rate of change by treatment (baseline 1988)
			Mg C ha^{-1} layer^{-1} yr^{-1}	
NT	0–15	−0.14	−0.04	−0.09
	15–75	−0.28	+0.36	+0.04
	0–75 (all)	−0.42	+0.33	−0.05
CP	0–15	−0.28	−0.39	−0.33
	15–75	−0.40	+0.25	−0.08
	0–75 (all)	−0.68	−0.14	−0.41
MP	0–15	−0.70	−0.09	−0.39
	15–75	−0.44	+0.54	+0.05
	0–75 (all)	−1.14	−0.45	−0.34

systems. The MP corn yields were 3% greater than for CP and NT systems as a result of significantly greater yields with MP system when planted into sod. At the beginning of the experiment, the MP system produced 21 and 11 percent higher yield compared with that of the NT and CP systems during 1989. The NT yields were lower in the early years of study but improved with the passage of time. The NT performance relative to MP and CP (Table 4) was better during dry years (1999) or years with extended dry period than wet years (Table 2), which was previously observed by Eckert [38]. The only year that CP treatment had the greatest yield was 2006 when compared to other tillage systems. The growing season rainfall that year was greater (75 cm) than average.

The NT crop yields were lower during the 3 early years (1989 to 1991) of the study but the NT system yielded as well as the MP system during the last 21 years of study. No-till yields were less than MP system in wet years (except 2002 with a dry period from June to August) but were greater in relatively dry years (Tables 2 and 4). The greater yields with the NT system in relatively dry years (1994, 1999, 2002, and 2012) were probably due to the conservation of more soil water than the MP system. Chisel plow yields were less in wet years and greater in dry years as compared to MP system (Table 4).

In the 1860s, the plot area was under private ownership and was intensively cultivated until 1937 with some gully erosion evident in the 1937 air photographs. Land ownership changed from private to public at that time and plot area was then cultivated periodically until 1973 when it was in sod for 15 years. Clearly, the tillage effect on rate of SOC loss slowed or even started to gain over time (Table 6), but the NT, CP, and MP plots were still losing SOC (from pre-tillage treatment baseline) with no SOC being sequestered. Had the tillage experiment been established on a plot area which had been in row crops for the previous 15 years, it would appear that the rate of SOC loss to atmosphere and in transported sediment from MP, CP, and NT would have been reduced (Table 6). Tillage (NT and MP) treatments were starting to gain SOC in the last 12 years of the 24-year tillage study. In the NT, the

SOC additions could be as a result of the annual additions of plant roots in topsoil and subsoil and crop residue being added on the soil surface. In the case of MP, the SOC annual additions included plant roots into the topsoil and subsoil and the incorporation of both roots and plant tops into the topsoil layer.

The SOC content of the MP (comparison baseline) did not appear to be at or reach a steady state during the 24-year experiment since the SOC losses from water erosion, moldboard plow tillage, and mixing, some disturbance during planting and subsequent nitrogen injection in corn years and aeration was greater than any SOC sequestration or net SOC storage gain or mineralization gain in MP plots. Consequently, the SOC storage and retention reported in Table 5 for the NT system could not be verified as SOC sequestration using the pretreatment SOC values measured before during the 24-year tillage experiment and no SOC sequestration occurred on the NT plots. The same is true for the CP and MP plots.

If one were to compare the pretreatment SOC values for the NT, CP and MP (Table 8) with those measured at the end of the 24-years of a tillage experiment, one would find that SOC sequestration did not occur and that the NT lost $-0.05\,\mathrm{Mg\,C\,ha^{-1}\,yr^{-1}}$, the CP $-0.41\,\mathrm{Mg\,C\,ha^{-1}\,yr^{-1}}$, and the MP lost $-0.34\,\mathrm{Mg\,C\,ha^{-1}\,yr^{-1}}$. The NT SOC sequestration rate of $-0.05\,\mathrm{Mg\,C\,ha^{-1}\,yr^{-1}}$ (actually a SOC loss) is inconsistent with the central USA soil carbon sequestration rate of $0.40 \pm 0.61\,\mathrm{Mg\,C\,ha^{-1}\,year^{-1}}$ [23] and the southeast rate of $0.45 \pm 0.04\,\mathrm{Mg\,C\,ha^{-1}\,year^{-1}}$ [26] and inconsistent with a published national rate of 0.50 Mg (or MT) $\mathrm{C\,ha^{-1}\,year^{-1}}$ [27]. No SOC sequestration occurred on the 24 yr tillage study since the SOC levels of NT, CP, and MP were higher before the tillage treatment was applied than at the end of the study. The primary reason for SOC loss was the transport of carbon rich sediment from the plots by water erosion (responsible for 54 to 120% of the SOC storage loss in 24 years), moldboard plow or chisel plowing and mixing, some disturbance even on NT plots during planting and subsequent nitrogen injection in corn years, aeration, and mineralization.

Soil carbon sequestration (SOC) is the process of transferring carbon dioxide from the atmosphere into the soil through plants, plant residues, and other organic solids which are stored or retained as part of the soil organic matter (humus) [22]. The retention time of sequestered carbon in the soil can range from short-term (not immediately released back to atmosphere) to long-term (millennia) storage. The sequestered carbon process should increase the net soil organic carbon storage during and at the end of a study to above pretreatment baseline levels and result in a net reduction in the carbon dioxide levels in atmosphere. Olson [21] amended the definition of SOC sequestration to include meaningful boundaries to be used to measure actual changes in a specific part of a terrestrial (soil) pool. The proposed definition of soil organic carbon sequestration is the "process of transferring CO_2 from the atmosphere into the soil of a land unit through unit plants, plant residues, and other organic solids, which are stored or retained in the unit as part of the soil organic matter (humus)".

Much of the literature [15, 23–27] suggested that paired comparisons between conservation tillage and conventional tillage at the end of a short- or long-term study can be used to determine SOC sequestration rate. Researchers assumed that the conservation and conventional tillage plots have the same SOC level at the start of the tillage experiment, the conventional tillage plots maintained the SOC over time (at steady state), and any increase in SOC of the conservation tillage treatment above the conventional tillage plot at end of study represented the amount of SOC sequestered by the conservation tillage system. However, these studies often lacked or did not report a pretreatment baseline SOC content in the plot areas collected prior to or at the start of the tillage experiment. Without such pretreatment baseline data, the SOC sequestration magnitude and rate findings cannot be verified [21].

If SOC sequestered in conservation tillage plots at the end of the experiment is higher than the initial SOC of the plot area then SOC sequestration would have occurred in the conservation tillage (NT) plots and at the measured rate. Alternatively, if the conservation tillage plots did not have more SOC content at the end of the study than at the start of the experiment (pretreatment baseline), then no SOC content sequestration occurred and the SOC sequestration rate is not correct. This long-term study was conducted on a plot area that was previously in sod for 15 years and on a 6 percent slope. The Grantsburg soils were previously eroded as a result of cropland use between 1860 and 1973. If the comparison approach is used, the projected SOC storage and retention (not sequestration) rate for NT would have been $0.32\,\mathrm{Mg\,C\,ha^{-1}\,yr^{-1}}$ (Table 5) which was less than the published regional SOC sequestration rate averages ($0.40 \pm 0.61\,\mathrm{Mg\,C\,ha^{-1}\,yr^{-1}}$) for the north central USA region [23]. Regional studies included both nearly level (flat) and sloping and eroding plot areas.

Since the SOC content in the Dixon Springs plot area was measured before the establishment of the tillage experiment (pretreatment baseline), it was possible to determine that the NT plots had lost $-1.2\,\mathrm{Mg\,C\,ha^{-1}}$ (or 2%) and the MP and CP plots had loss SOC $-8.3\,\mathrm{Mg\,C\,ha^{-1}}$ (or 16%) and $-9.9\,\mathrm{Mg\,C\,ha^{-1}}$ (or 19%), respectively over the 24 years. Contributing substantially to the above SOC losses from the tillage plots as a result of SOC rich sediment being transport off of the plots for the 24 yr study was $2.4\,\mathrm{Mg\,C\,ha^{-1}}$ for NT, $5.3\,\mathrm{Mg\,C\,ha^{-1}}$ for CP, and $7.2\,\mathrm{Mg\,C\,ha^{-1}}$ for MP. The NT plots did retain more SOC than MP plots; however, they did not sequester SOC. NT treatment only reduced the magnitude and rate of SOC loss over time. It is true that if a farmer had decided to use MP instead of NT the amount of SOC retained in the soil after 24-years of NT treatment would be 7.8 Mg C $\mathrm{ha^{-1}}$ greater than after 24 years of MP treatment and therefore the greenhouse gas emissions from the SOC in the NT plots would be less than from the SOC in the MP plots (but still greater than if the plot area had remained idle or in sod).

5. Conclusions

Using the comparison method with MP as the baseline, the NT plots did store and retain 7.8 Mg C ha^{-1} more SOC in the soil than MP and the CP stored and retain −1.6 Mg C ha^{-1} less SOC in the soil than MP. That SOC amount was retained in the soil and not decomposed and reemitted to the atmosphere as a result of cultivation or in the transported sediment moved off of the plots. However, no SOC sequestration occurred in the NT, CP, and MP plots and SOC was actually lost since the SOC level of the plot area was greater at the start of the experiment than after 24 years of tillage treatments. At the end of the study the NT plots had 2% less SOC than the pretreatment plot area, CP had 19% less SOC, and MP had 16% less SOC.

The comparison tillage study method with MP as baseline and with SOC measured in the last year of a 24 yr study was used to determine the magnitude of SOC storage and retention rate for the conversion of MP tillage system to an NT or CP tillage system. However, the SOC storage and retention rates could not be validated as SOC sequestration since the pretreatment had significantly higher SOC in pretreatment plot area than in the NT, CP, and MP plots after a 24-year tillage study. The use of the tillage comparison method without establishing a pretreatment baseline (the SOC content of the plot areas prior to establishment of the tillage experiment) could in some cases, including this study, overestimate the amount of SOC sequestration, the SOC sequestration rate and underestimate the amount greenhouse gas released to the atmosphere from SOC during the study.

Findings suggest that a pretreatment SOC baseline was needed in this tillage comparison study to determine whether or not the NT and CP SOC storage and retention amount and rate findings actually resulted in SOC sequestration or loss. There was no SOC sequestration in the NT, CP, or MP plots since the SOC level of the plot area was greater at the start of the experiment than at the end of the 24 yr study. Based on 24 years of crop yield measurements (12-year corn and 12-year soybean), the NT system appears to have resulted in similar long-term productivity compared with that of the MP and CP systems. The results of this study should be applicable to similar root-restricting, sloping, and moderately eroded soils in Illinois, Indiana, Missouri, and Kentucky.

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