

Biosolids Soil Application: Agronomic and Environmental Implications 2013

Guest Editors: Silvana I. Torri, Rodrigo Studart Corrêa, Giancarlo Renella, Alejandro Valdecantos, and Leonid Perelomov





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Applied and Environmental Soil Science

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Contents

Biosolids Soil Application: Agronomic and Environmental Implications 2013, Silvana I. Torri, Rodrigo Studart Corrêa, Giancarlo Renella, Alejandro Valdecantos, and Leonid Perelomov
Volume 2014, Article ID 314730, 3 pages

Sediment, Nutrient, and Bacterial Runoff from Biosolids and Mineral Fertilizer Applied to a Mixed Cool- and Native Warm-Season Grassland in the Ozark Mountains, Cody B. Wallace, Michael G. Burton, Steven G. Hefner, and Thomas A. DeWitt
Volume 2014, Article ID 147818, 7 pages

Soil Carbon Sequestration Resulting from Biosolids Application, Silvana I. Torri, Rodrigo Studart Corrêa, and Giancarlo Renella
Volume 2014, Article ID 821768, 9 pages

Characterisation of Organomineral Fertilisers Derived from Nutrient-Enriched Biosolids Granules, Diogenes L. Antille, Ruben Sakrabani, Sean F. Tyrrel, Minh S. Le, and Richard J. Godwin
Volume 2013, Article ID 694597, 11 pages

Field-Scale Evaluation of Biosolids-Derived Organomineral Fertilisers Applied to Ryegrass (*Lolium perenne* L.) in England, Diogenes L. Antille, Ruben Sakrabani, and Richard J. Godwin
Volume 2013, Article ID 960629, 9 pages

Availability and Plant Uptake of Biosolid-Borne Metals, Bon-Jun Koo, Andrew C. Chang, David E. Crowley, Al L. Page, and Alexandria Taylor
Volume 2013, Article ID 892036, 10 pages

Nursery Growing Media: Agronomic and Environmental Quality Assessment of Sewage Sludge-Based Compost, Barbara De Lucia, Giuseppe Cristiano, Lorenzo Vecchiatti, Elvira Rea, and Giovanni Russo
Volume 2013, Article ID 565139, 10 pages

Establishment of Native Grasses with Biosolids on Abandoned Croplands in Chihuahua, Mexico, Pedro Jurado-Guerra, J. Santos Sierra-Tristán, Carlos Lara-Macias, Ruben Saucedo-Teran, and Carlos Morales-Nieto
Volume 2013, Article ID 573808, 7 pages

Temperature Effects on Phosphorus Release from a Biosolids-Amended Soil, Maria L. Silveira and George A. O'Connor
Volume 2013, Article ID 981715, 8 pages

Residual Effects of Biosolids Application on Forage Production of Semiarid Grassland in Jalisco, Mexico, Pedro Jurado-Guerra, Miguel Luna-Luna, Ernesto Flores-Ancira, and Ruben Saucedo-Teran
Volume 2013, Article ID 835960, 5 pages

Monometal and Competitive Adsorption of Cd, Ni, and Zn in Soil Treated with Different Contents of Cow Manure, Mostafa Chorom, Rahim Mohammadzadeh Karkaragh, Babak Kaviani, and Yusef Kianpoor Kalkhajeh
Volume 2013, Article ID 510278, 8 pages

Editorial

Biosolids Soil Application: Agronomic and Environmental Implications 2013

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World production of biosolids is ever increasing due to global population rise and social progress, particularly in emerging countries. While technologies to reduce, transform, or reuse biosolids are under continuous development, their safe use in agriculture is still considered the main feasible option. Land application of biosolids can significantly reduce sludge disposal costs and provide varying amounts of nitrogen and phosphorus to crops. The use of biosolids as a source of organic matter improves the physical and chemical properties of agricultural soils, resulting in an increase in crop yields. An explanation to this is that, by its nature, agriculture has a negative balance in terms of organic matter and soil nutrients content which leads, on the term, to soil physical degradation and reduced chemical and biochemical fertility.

Agriculture use of biosolids still has a large consensus, being both a cost effective practice and a way to close the nutrient loop in agriculture and remediated degraded soils. The consensus is even increasing in the sight of the possible advantages of biosolids soil incorporation as a feasible way to balance anthropogenic greenhouse emissions. However, the complexity of both biosolids and soil systems, the rapid and large impact on the biogeochemical cycles, and the scale of agriculture still pose risks and uncertainties to predict their

effects on the long term and global change scenario. This special issue aims to fill the current gaps in the knowledge of this specific field, although more research is surely needed in a near future.

An aspect gaining worldwide attention is biosolids management in terms of global C budget. Many experiments indicate that application of biosolids to land or opencast mines resulted in an increase in carbon reserves of soils from different regions and under different management practices. The potential of the main mechanisms controlling C sequestration in soils amended with biosolids was discussed in the review article by S. Torri et al. The paper represents a revision of the latest knowledge on this topic, highlighting the role of the quality of the organic C (both from the soil and from the biosolids), soil biological components, soil properties, and the particular case of opencast mine sites.

C. Wallace et al. simulated rainfall conditions on mixed (cool and native warm season) grasslands on sloping, rocky soils to estimate nutrient and bacteria levels in runoff from biosolids and mineral fertilizer. The ability of narrow vegetated filter strips to reduce losses was evaluated. No significant differences were detected among mean fecal coliform levels despite large differences in magnitude. Losses of ammonia

and phosphorous were greater for biosolids application at the lower rate with no vegetated filter strips (LBU) than biosolids applied to the upslope half of the plot with the downslope half serving as a vegetated filter strip (LBF). Results of this study suggest that even a small vegetated filter strip can potentially reduce nutrient levels in runoff.

P. Jurado-Guerra et al. contribute to this special issue with an interesting study dealing with the length of the effects of increasing rates of biosolid applications on forage production in semiarid grasslands. Although the positive effect on grass productivity decreases with time, five years after single applications of biosolids, the amended plots still produce larger amounts of forage than the unamended ones. However, these authors also address some constraints that hinder the generalization of this practice in grasslands.

The paper titled "*Establishment of native grasses with biosolids on abandoned croplands in Chihuahua Mexico*" by Jurado-Guerra et al. illustrates how an appropriate use and land application of biosolids may help the establishment of forage production on degraded grassland soils. Their results showed that the use of biosolids apparently affected the growth parameters and yields of green sprangletop and blue grama crops, with the greater plant morphological modifications and crop yield increases observed for the green sprangletop. Authors concluded that biosolids application at 10 and 20 Mg ha⁻¹ rates had positive effects on the establishment and forage production of native grasses.

M. Chorom et al. assessed a monometal and competitive adsorption of Cd, Ni and Zn in soils incubated with different contents of decayed cow manure. Most sorption isotherms were well described by the Freundlich equation and the monometal and competitive adsorption isotherms of Zn, Cd and Ni followed the L-curve type. Results showed that the mono- and multimetal sorption amounts increased with an increase in organic amendment content. This increasing was consistent with the CEC and particularly pH for the three soils. The metal binding sites in the organic matter were more selective for Zn and Ni than Cd. Competition significantly reduced metal potential mobility, especially for Cd and Ni.

In the paper titled "*Characterisation of organomineral fertilisers derived from nutrient-enriched biosolids granules*" by D. L. Antille et al., the authors compared two biosolids-based organomineral fertilizers, urea and raw biosolids application in grassland and arable crops. Results showed that OMFs were twice as efficient as biosolids and 5–10% less efficient than urea to produce ryegrass (*Lolium perenne* L.). OMFs optimum application rates remained within 10% difference compared to urea and consistently lower than biosolids. Differently to the biosolids, the application of OMFs at rates which do not exceed the optimum N rate for the grass crop has not induced significant changes in soil P Index. Therefore, the wastewater industry may convert sludge into balanced fertilizers with a better economic strength and safer environmental perspectives with regard to the cost of field spreading and N and P load on the environment.

In the paper titled "*Field-scale evaluation of biosolids-derived organomineral fertilisers applied to ryegrass (Lolium Perenne L.) in England*" by D. L. Antille et al., the authors

studied organomineral fertilizers derived from nutrient-enriched biosolids granules. The fertilizers were produced by coating biosolids granules with urea and potash. Routine fertilizer analyses were conducted on four batches of organomineral fertilizers and biosolids granules and compared with a sample of urea to determine key physical and chemical properties of the materials which affect handling and spreading, soil behavior, and fertiliser value. The research utilizes a novel technology to improve the fertilizer value of biosolids, reduce disposal costs and deliver a range of environmental benefits associated with recycling.

B-J Koo et al. have set an experiment to evaluate how organic acids in root exudates affect the absorption of biosolid-borne metals by plants. Results showed that the concentrations of metals in the plant tissue grown on biosolids-treated medium were always higher than that from the standard medium, irrespective of species and cultivar. The amount of metal transferred from the biosolids-treated medium to the plant varied with the metal element, following the order: Cd > Ni = Zn > Cu > Pb > Cr. Interspecies and cultivar differences in metal uptake were trivial compared to differences induced by the treatment. Metal uptake decreased with the growth period and the kinetics of metal uptake and essentially followed a first order during the initial four weeks of growth, especially Cd and Zn.

The study of M. L. Silveira and G. A. O'Connor was designed to evaluate the effects of temperature on the potential leachable P pool and distribution of chemical P forms in a biosolids-amended soil. A P-deficient Spodosol was incubated with biosolids and inorganic P fertilizer at different temperatures. Cumulative P mass leached during the 90-d study for any P-source was low, but greater cumulative P mass was released from the biological P removal and composted biosolids than from the heat-dried materials. Increasing temperature (20 to 32°C) generally decreased cumulative P mass leached, suggesting greater soil affinity to retain P at higher temperature. In a static incubation experiment (no leaching), soil water-extractable P concentrations were reduced over time, but no temperature effect was observed. P distribution among the various fractions was not affected by temperature. The relatively great ability of the soil to sorb P masked differences in biosolids properties and the potential impacts of temperature on P lability.

The potentials of use of biosolids in a specific agricultural field such as the plant nursery were evaluated by B. De Lucia et al. This article sheds light on the specific agricultural activity of plant nursery for ornamental plant which produces high income for farmers of various productive districts in Europe and other World areas but relies on the use of peat and other no renewable substances for the preparation of the plant growth substrates and is one of the agricultural practices with the higher environmental impacts. In fact, the annual amount of peat used every year in the European Union for the production of ornamental plants and horticulture is in the order of 29 million m³, with a high impact on peatlands' stability. It is estimated that field cultivation of ornamental plants may cause annual soil loss in the order of millions of cubic meters (m³). The authors reported how the use of

compost from municipal sewage sludge in the plant growth substrates reduced the overall environmental impact of the plant nursery chain and did not affect the plant quality.

We hope that you find the special issue interesting and useful and that it will act as a precursor for more studies to come in the agronomic and environmental implications of biosolids soil application.

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Research Article

Sediment, Nutrient, and Bacterial Runoff from Biosolids and Mineral Fertilizer Applied to a Mixed Cool- and Native Warm-Season Grassland in the Ozark Mountains

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Rainfall simulations were conducted within mixed (cool- and native warm-season) grasslands in the sloping, rocky soils typical of the Ozark Mountains region to estimate nutrient and bacteria levels in runoff from biosolids and mineral fertilizer (MF). The ability of narrow (1 m) vegetated filter strips (VFS) to reduce losses was evaluated. Experiment 1 included an untreated control (C); 37 kg plant available nitrogen (PAN) ha⁻¹ from biosolids applied to the upslope half of the plot with the downslope half serving as a VFS (LBF); 74 kg PAN ha⁻¹ from biosolids, with VFS (HBF); and a uniform biosolids application at the lower rate and no VFS (LBU). Experiment 2 examined runoff from MF applied at 89 kg ammoniacal nitrogen (NH₄-N) ha⁻¹ and 147 kg phosphorous (P) ha⁻¹ over the whole plot (MFW) or only on the upslope half (with VFS) (MFF). No significant differences were detected among mean fecal coliform levels despite large differences in magnitude. Losses of NH₄-N and P were greater for LBU than for LBF. Although only marginally significant ($P = 0.058$), total phosphorous contained in runoff was nearly three times higher in MFW than in MFF. Results of this study suggest that even a small VFS can potentially reduce nutrient levels in runoff.

1. Introduction

An estimated 226,800 dry tonnes of biosolids are produced each year in Missouri where 60% of the sludge is incinerated and 30% is applied to agricultural land [1]. However, nearly all biosolids produced by the city of Springfield, Missouri, are applied to agricultural land. Many benefits and concerns associated with biosolids application to agricultural lands were recently reviewed by Torri et al. [2] and Lu et al. [3]. Among the benefits, biosolids provide recycled nutrients to soils and can serve as an alternative or a substitute to costly mineral fertilizers (MF). In addition to providing nutrients, biosolids provide organic matter to soil [4, 5], increase infiltration [6], potentially improve soil quality [5, 7, 8], and increase agronomic productivity [5, 7, 9–12]. Using biosolids as a substitute for MF also helps reduce energy use which would have been associated with production and transportation of MF.

A considerable body of research has confirmed the potential for losses of nutrients such as nitrogen (N) and phosphorus (P) from agricultural fertilizers applied to fields [13–17] while less data are available for hay and grazing lands [18, 19]. Nitrogen levels are often a limiting factor for application; however, in a 2003 national biosolids survey, Shober and Sims [20] determined that about one half of the states in the USA have established regulations, guidelines, or legislation that can be used to limit land application of biosolids based on a measure of soil P or biosolids P. Therefore, data for both N and P could be required to conform to regulations. Federal (USA) and Missouri state regulations require that biosolids application rates do not exceed plant available nitrogen (PAN) levels that can be immobilized by the crop [21, 22]. Regulation of land application of manures or biosolids on the basis of P is not yet required in Missouri. Sediment and fecal bacteria are other pollutants that contribute to the degradation of water sources. Biosolids

and animal manures may increase sediment loads and can contain high amounts of coliform bacteria that are often carried in surface runoff from agricultural fields [23, 24].

Management practices that can potentially influence non-point source pollution levels and water quality include a shift in fertilizer time of application and the use of vegetated filter strips (VFS) to reduce contaminant content. In central and southern Missouri nearly two-thirds of cool-season forage production occurs in spring. Consequently, some producers have shifted fertilizer, manure, or biosolids application to late summer in an effort to increase autumn production either for hay harvest or winter grazing (M. Green and M. Kennedy, pers. comm.). VFS have proven effective in reducing sediment [23–26] and nutrient levels [27–29], but the magnitude of the reduction in nutrient loads often depends on the nutrient and its form [25]. For example, Daniels and Gilliam [25] observed that runoff collected at field edges and various locations in vegetated buffers showed that VFS reduced total phosphorus (TP) load by 50%, but as much as 80% of the soluble $\text{PO}_4\text{-P}$ passed through filters. VFS are not highly efficient in trapping fecal bacteria from surface runoff; several studies have shown significant yet still unacceptable reductions in fecal coliform counts [23, 27, 30, 31].

The following two experiments were conducted to provide additional data on fertilization management and VFS efficacy on grassland typical of the Ozarks region (i.e., sloping, rocky soils). The biosolids experiment evaluated and compared sediment, nutrient, and bacteria levels found in runoff from biosolids applications with or without a VFS. Biosolids were applied at PAN levels typically applied to native warm-season grasses. The mineral fertilizer experiment investigated the efficacy of a narrow VFS in reducing sediment, nutrient, and bacteria pollutant loads.

2. Materials and Methods

2.1. Site Conditions and Rainfall Simulation. Rainfall simulations were conducted from August 2009 to October 2009 on field plots with a Nixa very gravelly silt loam (loamy-skeletal, siliceous, active, mesic Glossic Fragiudults) in Lawrence County, Missouri. Vegetation in plots consisted of a mixture of cool- (especially *Lolium arundinaceum* (Schreb.) Darbysh.) and native warm-season grasses (e.g., *Sorghastrum nutans* (L.) Nash and *Andropogon gerardii* Vitman). The study site has been hayed, rather than grazed, since 2006.

Surface runoff plots 1.50×2.00 m (long axis oriented downslope) had metal borders 5 cm above and below ground level in order to isolate runoff. Each experiment was conducted with four replicates. The plots were mowed to a height of 10 cm 7 to 10 days prior to rainfall simulations and had similar vegetative cover conditions. A full replication of each experiment was carried out on each of 4 days (Table 1). Plots were selected for replications to optimize uniformity of slope. Slopes of plots used in the experiment ranged from 3 to 6%.

Portable rainfall simulators [32] fitted with plastic tarps to provide a wind screen were used to apply rainfall to plots (3 rainfall simulators were employed twice each day). The rainfall simulators were equipped with a single Spraying Systems

TABLE 1: Mean volumetric soil moisture, percent vegetative cover, and mean runoff volume from each of the four blocks used in this study.

Date	% Volumetric soil moisture	% Vegetative cover	Mean runoff volume (L)
Aug. 20, 2009	39.1	84.4	57.1
Aug. 27, 2009	19.6	93.8	25.4
Sep. 03, 2009	24.3	88.8	14.6
Oct. 13, 2009	46.7	97.2	80.2

Fulljet HH50WSQ (brand name is included for specificity, not as an official endorsement of a particular product) nozzle at a height of 3 m, were centered over plots, and had an operating nozzle pressure of 28 kPa to yield a rainfall intensity of 70 mm h^{-1} [32] with droplet size and velocity similar to natural rainfall. Rainfall occurring at this intensity for 0.5 h duration has an approximate probability of occurring once every two years in southwest Missouri and imitated an imprudent scenario in which fertilizer application occurred immediately before a heavy thunderstorm. Deionized water ($>50 \text{ k Ohm}$ resistance), provided by cation and anion exchange columns, was used as the water source for the simulators. Additional filtration was provided by an inline filter located on each simulator upstream of the pressure regulator to prevent foreign particles from clogging the regulator and nozzle. The rainfall intensity was applied until 30 min of runoff was collected. Surface runoff was collected in metal gutters at the downslope edge of each plot and pumped from the collector bucket to a 190 L plastic barrel, which was lined with a clean plastic liner. During simulated rainfall, runoff collection gutters were covered to exclude water that had not fallen on the plot surface first. Total surface runoff was then measured, and the bulk solution was agitated so that a subsample (1900 mL) could be collected for laboratory analyses. Tubing and pumps used in sample collection were cleaned before each use by flushing with a 0.5% sodium hypochlorite solution for two minutes followed by thoroughly rinsing with deionized water.

Samples were labeled with a randomly assigned reference number, stored in ice water, and delivered to the Southwest Water Treatment Plant in Springfield, Missouri, within 7 h of collection for stabilization and analyses. Analyses were completed for total suspended solids (TSS), total Kjeldahl nitrogen (TKN), dissolved total Kjeldahl nitrogen (DTKN), $\text{NH}_4\text{-N}$, dissolved ammoniacal nitrogen ($\text{DNH}_4\text{-N}$), nitrate nitrogen ($\text{NO}_3\text{-N}$), TP, dissolved phosphorus (DP), and fecal coliform colony-forming units (CFUs) levels. TSS, $\text{NH}_4\text{-N}$, and CFUs were determined according to standard biosolids protocols [33]. TKN was determined by semiautomated colorimetry [34] and TP was determined by automated colorimetry [35]. $\text{NO}_3\text{-N}$ and DP were determined by ion chromatography [36].

Gutters in plots were sealed with a bentonite/soil mixture and were washed of free soil and clay before the rainfall simulations were initiated. Percent ground cover was measured by the line-transect method (3 transects and 10 observations per transect in each plot), and mean volumetric soil moisture

TABLE 2: Plant available nitrogen (PAN) and total phosphorus (TP) included in mineral fertilizer and biosolids treatments.

Constituent	LB [†]	HB Kg ha ⁻¹	MF
PAN [‡]	36.8	73.6	89.3
TP	58.3	116.6	146.9

[†]LB: low rate of biosolids; HB: high rate of biosolids; MF: mineral fertilizer.

[‡]For MF, PAN is equal to ammoniacal nitrogen (NH₄-N) content.

(θ) was determined (Table 1) using a capacitance sensor (Theta probe, Delta-T Devices (brand name is included for specificity, not as an official endorsement of a particular product), Cambridge, UK) at four locations within a plot. Biosolids or MF were then spread manually to each plot with careful attention to uniformity and the treatment assigned.

2.2. Biosolids Experiment Details. The four treatments included untreated control (C); 1664 kg ha⁻¹ low rate of biosolids with a 1 m vegetative filter (LBF); 1664 kg ha⁻¹ low rate of biosolids, unfiltered (LBU); 3328 kg ha⁻¹ high rate of biosolids with a 1 m vegetative filter (HBF). PAN and TP values for these treatments are given in Table 2. Filtered treatments received a uniform application of biosolids only on the upslope half of the plot (upper 1 m section) with the downslope half of the plot (lower 1 m section) acting as an untreated VFS. Biosolids were only spread on the downslope half of the unfiltered treatments (lower 1 m section) (i.e., no VFS). Therefore, the LBF and LBU treatments had the same plot size, treated area, and mass of biosolids applied.

The anaerobically digested, dewatered municipal biosolids used in this study were Class B biosolids [37] and were obtained from the Southwest Water Treatment Plant in Springfield, Missouri. Application rates for biosolids treatments were based on the plant available nitrogen (PAN) content of the biosolids, which was calculated by multiplying the organic N fraction of the biosolids (i.e., TKN - (NH₄-N + NO₃-N)) by the first year-mineralization rates (i.e., 0.2) [21] and then adding 0.7 * NH₄-N (to adjust for volatilization losses) [22] and NO₃-N (Table 2).

2.3. Mineral Fertilizer Experiment Details. A blend of triple superphosphate and diammonium phosphate served as the MF in the second experiment. Plots received no amendment (untreated control; C), 89.3 kg ammoniacal nitrogen (NH₄-N) ha⁻¹ and 146.9 kg P ha⁻¹ as a blend of MF applied to upslope half (1 m) of the plot which was “filtered” by the downslope 1 m of the plot which served as a vegetative filter strip (MFF), or an identical rate of blended mineral fertilizer spread over the whole plot (MFW). Therefore, the plots were equal in total area, but the MFW treatment received twice as much fertilizer on a plot area basis. With this design we intended for the MFF treatment to simulate grassland bordered by a narrow span of vegetation that could serve as a buffer to a protected water body, slope change, or area of concentrated flow, whereas the MFW treatment would

TABLE 3: Concentration and total fecal coliform colony-forming units (CFUs) in runoff.

Treatment [†]	Mean CFUs in 100 mL	Mean total CFUs [‡]
LBU	35,720	10,965,563
LBF	7,080	1,348,587
HBF	4,880	367,700
C	117	90,130

[†]LBU: low rate of biosolids, unfiltered; LBF: low rate of biosolids, filtered by a 1 m grass strip; HBF: high rate of biosolids, filtered by a 1 m grass strip; C: untreated control.

[‡]Mean CFUs are given, but no differences among treatments were detected using preplanned orthogonal contrasts on raw, square-root, or log₁₀ transformed data.

represent a landscape that received uniform fertilization up to the edge of an unprotected (no VFS) critical area.

2.4. Statistical Analyses. Because structured treatment levels (i.e., high rate of biosolids treatment was double that of low rate of biosolids treatment) violate an assumption of analysis of variance (ANOVA), the C and biosolids treatment effects from the biosolids experiment were assessed by curve-fitting [38] and orthogonal contrasts (1 df) with the REG and GLM procedures [39]. For the mineral fertilizer experiment, ANOVA was performed on square-root transformed data which were then subjected to protected least significant difference (LSD) tests ($\alpha = 0.05$) and preplanned orthogonal contrasts as a randomized complete block design for the C, MFF, and MFW treatments.

3. Results and Discussion

3.1. Biosolids Experiment. Mean fecal coliform CFUs concentrations ranged from about 100 (C) to nearly 36,000 (LBU) CFUs per 100 mL (Table 3). Plotting the data (Figure 1) helped us to visualize the poor relationship ($r^2 = 0.44$) in runoff CFUs levels among filtered biosolids treatments. Still, it is important to observe that filtered treatments (LBF and HBF) had approximately one-fifth the CFU concentration observed in LBU runoff (Figure 1). Treatment means (\pm s.d.) for CFUs per 100 mL for C, LBF, HBF, and LBU were 116 ± 159 , $7080 \pm 11,195$, 4880 ± 8159 , and $35,720 \pm 61731$, respectively. Large variability in bacterial concentration has been reported by others [23, 30, 40] and feral animal or accidental introductions of fecal material to the plot areas may have contributed to variability; however, the contributions of such introductions would logically be small relative to contributions from biosolids treatments. The relatively low fecal coliform counts observed in runoff from C plots support this perspective. In studies by Coyne et al. [23, 30], comparisons of various sizes of poultry litter amended plots with different VFS lengths did not meet water quality goals for control of fecal coliforms in primary contact water. In this study, CFUs per 100 mL from the biosolids treatments (Table 3) greatly exceeded the maximum amount allowed in Missouri for whole body contact recreation (max. of 206 CFUs/100 mL) [41]. High levels of CFUs were expected

TABLE 4: Untransformed treatment means for all analyzed biosolids nutrients in runoff from Experiment 1 simulated rainfall plots. Note: values have been extrapolated to kg ha^{-1} basis.

Contaminant	C	LBF	LBU	HBF
		Kg ha^{-1}		
TSS [†]	15.7	12.0	37.0	10.3
TKN	1.10	0.67	3.33	9.00
DTKN	0.33	0.77	1.67	8.67
NH ₄ -N	0.07	0.47	2.07	0.93
DNH ₄ -N	0.07	0.47	2.10	0.87
NO ₃ -N	0.03	0.02	0.07	0.03
TP	0.10	0.13	0.33	0.23
DP	0.07	0.10	0.23	0.13

[†]TSS: total suspended solids; TKN: total Kjeldahl nitrogen; DTKN: dissolved total Kjeldahl nitrogen; NH₄-N: ammoniacal nitrogen; DNH₄-N: dissolved ammoniacal nitrogen; NO₃-N: nitrate nitrogen; TP: total phosphorus; DP: dissolved phosphorus.

because a narrow VFS was employed rather than the much wider buffer that is required for biosolids applications in Missouri [22]. Furthermore, bacteria introduced from biosolids into soils have been shown to decline rapidly and have a limited survival time [13, 42]. Large variability in fecal CFU levels has limited our ability to identify differences among treatments in another similarly constructed experiment [40].

Preplanned orthogonal contrasts and linear regression were used to compare and isolate aspects of this study. No differences could be declared among biosolids treatments for TSS in runoff. This result could be expected if biosolids are relatively rainfast and have a relatively low impact on altering sediment runoff levels. However, Harris-Pierce et al. [24] showed that increasing sludge rate can increase sediment levels. TSS content in runoff was numerically highest from LBU and C treatments (Table 4), but the slope of the regression was not significant for the C, LBF, and HBF treatments ($P = 0.14$). Previous research, using much longer VFS, indicated reductions in TSS from surface runoff when VFS are employed [23, 29]. Increasing biosolids rate showed a strong linear relationship for DP ($r^2 = 1.00$, slope $P < 0.001$) in surface runoff (Figure 2). This result is logically supported because DP losses from control plots would only include residual P, whereas losses from the biosolids treatments would be comprised of soil P and DP from the biosolids amendment. An orthogonal contrast of LBF versus LBU indicated that losses of TP ($P = 0.013$) and DP ($P = 0.043$) from LBF were half of the quantities lost from LBU. A strong linear relationship was observed for NH₄-N ($r^2 = 0.99$, slope $P = 0.030$) and DNH₄-N ($r^2 = 1.00$, slope $P = 0.004$) indicating increased losses as PAN rate was doubled (Figure 3). An LBF and LBU contrast indicated differences for NH₄-N ($P = 0.005$) and DNH₄-N ($P = 0.005$), showing the efficacy of the VFS in reducing nutrient losses. TKN and DTKN data are not well described by linear regression; therefore orthogonal contrasts were used to compare the C to LBF and C to HBF. No differences were detected.

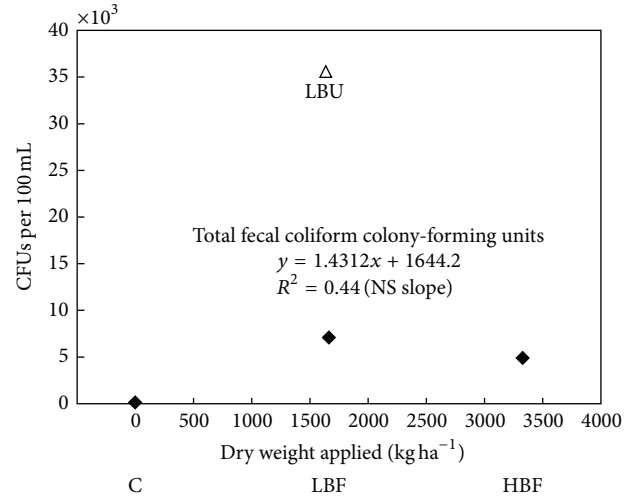


FIGURE 1: Mean fecal coliform colony-forming units (CFUs) concentrations in runoff from control (C); low rate of biosolids, filtered by a 1 m grass strip (LBF); low rate of biosolids, unfiltered (LBU); and high rate of biosolids, filtered by a 1 m grass strip (HBF). CFU level in runoff was not well described by application rate (slope $P = 0.53$); however, mean CFU level of the unfiltered treatment was much greater. LBU mean is included for reference.

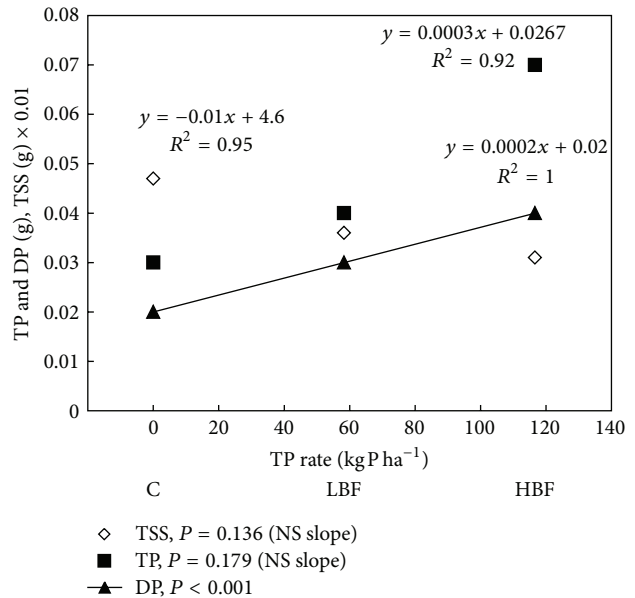


FIGURE 2: Total suspended solids (TSS), total phosphorus (TP), and dissolved phosphorus (DP) loading in response to TP application rate for C, LBF, and HBF.

3.2. Mineral Fertilizer Experiment. In a separate analysis, C was compared to total nutrient runoff from the MF treatments. MFF loading did not differ from MFW for any factor according to the protected LSD mean separation procedure ($\alpha = 0.05$). However, according to an orthogonal contrast (1 df), TP was marginally significant ($P = 0.058$) with MFW having nearly triple the amount of MFF TP loading (18.9

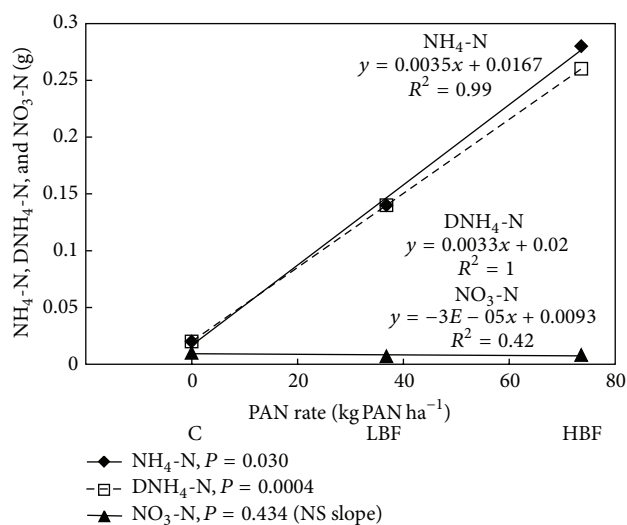


FIGURE 3: Total ammoniacal nitrogen ($\text{NH}_4\text{-N}$), dissolved ammoniacal nitrogen ($\text{DNH}_4\text{-N}$), and nitrate nitrogen ($\text{NO}_3\text{-N}$) loading in response to plant available nitrogen (PAN) application rate for C, LBF, and HBF.

TABLE 5: Untransformed treatment means for all analyzed mineral fertilizer nutrients in runoff from Experiment 2 simulated rainfall plots. Note: values have been extrapolated to a kg ha^{-1} basis.

Contaminant	C [†]	MFF Kg ha^{-1}	MFW
TSS	15.6 ^{a‡}	17.6 ^a	5.7 ^a
TKN	1.1 ^b	5.9 ^{ab}	16.7 ^a
DTKN	0.33 ^b	5.4 ^{ab}	16.4 ^a
$\text{NH}_4\text{-N}$	0.067 ^b	5.4 ^{ab}	15.7 ^a
$\text{DNH}_4\text{-N}$	0.067 ^b	5.4 ^{ab}	15.6 ^a
$\text{NO}_3\text{-N}$	0.033 ^b	0.2 ^{ab}	0.4 ^a
TP	0.10 ^b	5.4 ^{ab}	18.9 ^a
DP [§]	0.07 ^a	1.5 ^a	13.9 ^a

[†] C: untreated control; MFF: fertilizer, filtered by a 1.0 m grass strip; MFW: fertilizer applied to whole plot.

[‡] Values within a row followed by different letters are significantly different according to a protected LSD test ($\alpha = 0.05$).

[§] Three DP samples were lost due to a laboratory error. The consequent loss of statistical power may have contributed to a failed *F*-test ($P = 0.147$) for the protected LSD procedure.

versus 5.4 kg ha^{-1}) (Table 5). MFW runoff content of $\text{NH}_4\text{-N}$ numerically (but not statistically) exceeded that of the MFF plot by a factor of nearly three also. A higher level of nutrient runoff in the MFW plot was, of course, expected because double the amount of fertilizer was applied to the same total plot area and the closer proximity of half of the fertilizer to the collection gutter. However, the narrow VFS of mixed cool-season grasses employed in this experiment were inadequate to significantly reduce nutritive loading. The high water solubility of MF allows a large amount of contaminants to be readily carried off in surface runoff when a sufficient rainfall storm occurs; therefore, wider VFS (e.g., 9.1 m to 45.7 m) are recommended to reduce losses to surface

waters. No differences were observed for TSS among the C and fertilizer treatments according to the protected LSD test ($\alpha = 0.05$) (Table 5). According to the same test, TKN, DTKN, $\text{NH}_4\text{-N}$, $\text{DNH}_4\text{-N}$, $\text{NO}_3\text{-N}$, and TP were lower in runoff from the C than MFW.

These results suggest that even an undersized VFS can reduce certain nutrients when compared to fertilizer applications made without any VFS. DTKN and $\text{DNH}_4\text{-N}$ were dominant components of TKN and total $\text{NH}_4\text{-N}$ values in runoff among all treatments. This result was expected from soluble mineral fertilizer salts and resulted in nearly identical trends among these parameters.

4. Conclusions

Statistical analysis of fecal coliform in runoff was obscured by variability and perhaps made worse by historical or accidental contamination of plots. However, that the biosolids treatment LBU numerically had the highest mean concentration and total runoff of coliform is noteworthy. In the LBF versus LBU contrast, differences suggest that even a small VFS is capable of decreasing biosolids nutrient levels in runoff when compared to unfiltered runoff. Biosolids applications in the state of Missouri, however, require much wider buffer areas (15.2 to 91.4 m) than those used in these experiments [22].

MFF and MFW did not differ in any of the orthogonal contrasts. However, it is important to notice that, except for TSS, MFW always differed from the C according to a protected LSD test ($\alpha = 0.05$), while MFF did not differ from the C. Although VFS are recommended when applying mineral fertilizers, they are not required in Missouri. These data indicate that lack of VFS where mineral fertilizers are applied could result in large nutrient content being delivered to surface water.

Abbreviations

MF:	Mineral fertilizer
CFUs:	Colony-forming units
$\text{DNH}_4\text{-N}$:	Dissolved ammoniacal nitrogen
DP:	Dissolved phosphorus
DTKN:	Dissolved total Kjeldahl nitrogen
$\text{NH}_4\text{-N}$:	Ammoniacal nitrogen (total)
$\text{NO}_3\text{-N}$:	Nitrate nitrogen
PAN:	Plant available nitrogen
TKN:	Total Kjeldahl nitrogen
TP:	Total phosphorus
TSS:	Total suspended solids.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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Review Article

Soil Carbon Sequestration Resulting from Biosolids Application

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Carbon (C) sequestration in soils through the increase of the soil organic carbon (SOC) pool has generated broad interest to mitigate the effects of climate change. Biosolids soil application may represent a persistent increase in the SOC pool. While a vast literature is available on the value of biosolids as a soil conditioner or nutrient source in agricultural systems, there is still limited knowledge on soil sequestration mechanisms of biosolids-borne C or the main factors influencing this capacity. The emerging challenges posed by global environmental changes and the stringent needs to enhance C storage call for more research on the potential of soil biosolids incorporation as a sustainable C storage practice. This review addresses the potential of C sequestration of agricultural soils and opencast mines amended with biosolids and its biological regulation.

1. Introduction

Increasing concern about global climate change has led to growing interest in developing feasible methods to reduce the atmospheric levels of greenhouse gases (GHGs) [1]. Among GHGs, atmospheric carbon dioxide (CO₂) accounts for 60% of the global warming [2]. The atmospheric concentration of CO₂ increased from 280 parts per million (ppm) in the preindustrial era to the present 395 ppm [3]. This increase is attributed to combustion of carbon based fuels, cement manufacturing, deforestation, burning of biomass, and land-use conversion, including soil tillage and animal husbandry. Soil C capture and storage is gaining global attention because of its role as a long-term C reservoir, low cost, and environmentally friendly means to minimize climate change.

Soil C pool is the largest terrestrial C pool, constituting approximately two-thirds of the total C in ecosystems [4]. It is estimated at 2500 Pg to 1-m depth, with the biotic pool estimated at 560 Pg and characterized by fast turnover rates as compared to other natural compartments. The oceanic and geological pools are estimated at 39000 Pg and 5000–10000 Pg, respectively, whereas the atmospheric pool is estimated at 780 Pg [5]. Therefore, total soil C pool is about 4, 1 times the biotic pool and 3 times the atmospheric pool.

Soil organic carbon (SOC) includes plant, animal, and microbial residues in all stages of decomposition. SOC represents a balance between inputs, mostly via primary productivity or organic amendments, and outputs via decomposition [6]. Land application of organic amendments is a management practice that enhances SOC in the short term [7, 8]. In the last decades, the production of organic urban wastes such as biosolids has worldwide increased, and its accumulation, storage, and disposal pose growing environmental and socioeconomical problems. The safe disposal of biosolids has been a challenge for municipal wastewater treatment companies [9, 10]. In most countries, landfilling and land application have been the main disposal practices since they are the most economic outlet [11, 12]. However, sludge is a biodegradable material and releases CO₂, CH₄, and other gases when disposed in landfills [13]. Biosolids are a valuable source of organic matter and plant nutrients, especially nitrogen (N) and phosphorus (P) [14]. Recycling biosolids to agricultural land completes natural nutrient cycles. Besides, repeated land application of biosolids provides long-term benefits by increasing soil organic matter which, in turn, improves soil chemical and biological fertility [15–17]. Land application of biosolids may also result in

a decrease in bulk density, increase in pore size, soil aeration, root penetrability, soil water holding capacity, and biological activity, all of which may be reflected in an increase in crop yields [18]. One of the main disadvantages of land application of biosolids is the fact that it may contain human pathogens and trace elements, including arsenic, cadmium, zinc, copper, chromium, lead, mercury, nickel, and selenium [19–21]. The concentration of these compounds and concerns about nitrate leaching or losses to the atmosphere may limit biosolids land application [22, 23].

Soil C sequestration is defined as any persistent increase in SOC originated from removing CO₂ from the atmosphere. Increases in soil carbon storage may be accomplished by the production of more biomass. In this way, there is a net transfer of atmospheric CO₂ into the soil C pool through the humification of crop residues, resulting in net carbon sequestration [24]. Powlson et al. [25] postulated that whether SOC increases produced by applying organic residues constitute C sequestration entirely depend on the alternative fate of this material. For example, biosolids soil application represents additional carbon retention in soil if the alternative disposal method is landfilling. On the contrary, if organic wastes are regularly land applied, increases in SOC resulting from biosolids application cannot be regarded as a waste management practice to mitigate climate change. Although many studies have examined the potential value of biosolids to increase soil productivity, relatively limited work has examined its effect on soil C sequestration [8, 26, 27].

2. Biosolids-Borne C Sequestration Capacity of Soils

2.1. Agricultural Soils. Soil C sequestration capacity reflects soil aptitude to retain and stabilize C. In the light of global change scenario, soil humification mechanisms have acquired renewed interest. Traditionally, the stability of organic compounds has been regarded as the main process controlling SOC retention, but recent analytical and experimental advances have demonstrated that molecular structure alone does not explain SOM stability [28]. The amount of SOC accumulated does not only depend on the quantity and quality of the organic inputs, but on the physicochemical and biological influence of the environment as well [28, 29]. Various mechanisms of SOM stabilization have been proposed [27]. Physical protection by incorporation into soil aggregates or by occlusion in micropores inaccessible to soil microorganisms or chemical protection through interaction with mineral surfaces is considered important mechanisms to reduce the bioavailability and accessibility of SOM for soil microorganisms or hydrolytic soil enzymes [30]. Another mechanism of SOC stabilization is assumed to be biochemical protection. Biotic organic C is biologically transformed by the action of microbial populations (i.e., bacteria, fungi) and invertebrates, resulting in acquired chemical stability [31]. Therefore, the residence time of organic compounds in soils is directly related to intrinsic or developed resistance to further microbiological degradation.

Biosolids are typically made up of 40–70% organic matter, with organic C content ranging from 20–50%, total nitrogen

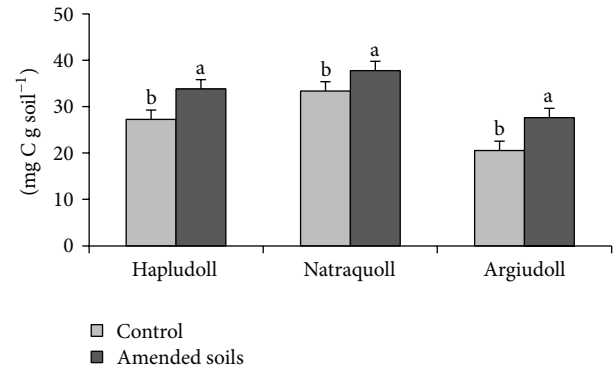


FIGURE 1: Storage capacity of biosolids-borne C of typical soils of the Pampas region, Argentina, 360 days after biosolids application (application rate of 150 dry t/ha). Different letters for the same soil indicate significant differences at the 0.05 probability level ($n = 4$). (Adapted from Torri et al. [34]).

(N) ranging from 2–5%, and a C/N ratio of about 10–20 [32, 33]. Biosolids' organic matter has usually undergone some degree of stabilization through anaerobic or aerobic digestion before being land applied. Long- and short- term observations have demonstrated that biosolids amended soils accumulate a significantly higher amount of organic C compared to mineral fertilized soils. Over a 34-year reclamation experiment, Tian et al. [8] reported that soil C sequestration capacity in agricultural soils under conventional tillage was significantly correlated with biosolids application rate. In the short term, Torri et al. [34] reported soil C accumulation in three pristine representative soils of the Pampas region, Argentina, amended with high biosolids rate. These soils had different particle size distribution, although the clay fraction had the same origin and mineralogical composition. During the 30 days following biosolids incorporation, decomposition mechanisms associated with an intense biological activity originated a rapid CO₂-C release [35]. After 150 days, the three pristine amended soils appeared to reach a new equilibrium, with C contents being significantly higher than the respective controls. Total C content did not change significantly between days 150 and 360 in the three studied soils, showing the potential of these soils to store biosolids-borne C (Figure 1).

Many mathematical models have been proposed to describe the decomposition process of land applied organic materials, ranging from one to multicompartiment models [29, 36, 37]. In the study made by Torri et al. [34], a first-order exponential model provided the best fit to C mineralization data for the three soils (1):

$$\%C_B [t] = C_{RB} + C_{LB}e^{-kt}, \quad (1)$$

where %C_B is the percent residual C from biosolids in soil; %C_{LB} the initial percent of biosolids borne-C in the labile pool; %C_{RB} the percent of biosolids borne-C in the resistant pool; k is the first order rate constant (day⁻¹); t is the time after biosolids application (days).

According to this model, organic C added through biosolids consisted of two fractions of different degree of biodegradability: a labile fraction (53–71%) that was quickly

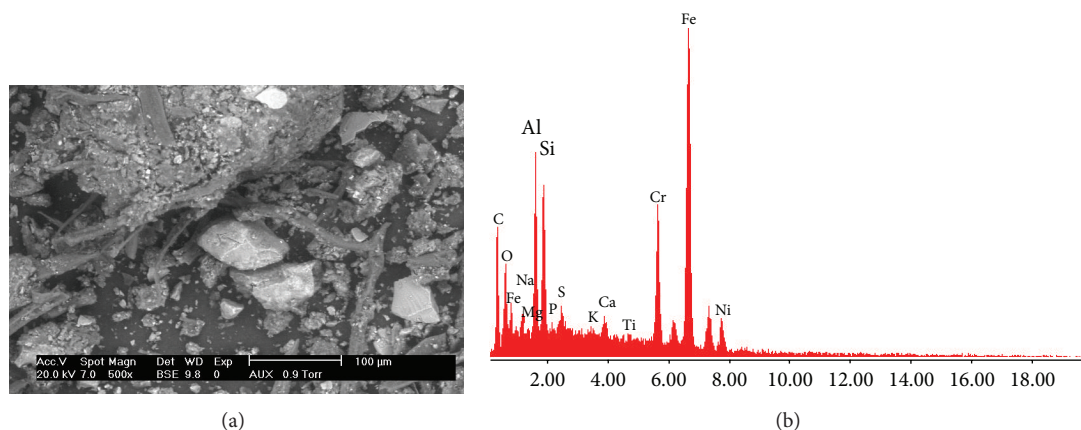


FIGURE 2: Scanning electron microscopy with X-ray microanalysis (SEM-EDS) image of biosolids (a) and X-ray diffraction (XRD) patterns of biosolids (b).

mineralized at a constant rate (k) and a recalcitrant fraction (28.5–45.4%), not available or resistant to soil microorganisms that remained in the soils one year after biosolids application [34]. Organic compounds of the recalcitrant fraction are mainly stable cholestane-based sterols [38] which may have a turnover rate in the order of hundreds of years [39]. The labile organic fraction has often been found to be largely dependent on the degree of biosolids stabilization [40].

In general, C mineralization rates of freshly added organic sources have been found to be more rapid in soils with low than with high clay content [41]. An explanation to this could be that residual substrate and decomposition products become stabilized by sorption onto mineral clay particles, by incorporation into pores that are too small for bacteria or fungi to penetrate. Consequently, they are physically inaccessible to microbial turnover [42, 43]. Furthermore, organic matter may be protected against decomposition as a result of being inside large aggregates that become partially anaerobic because of slow O_2 diffusion through the small intra-aggregate pores [44].

Despite the protection provided by clay particles, many studies reported that mineralization rates of biosolids-borne C were not related to soil texture [34]. Strong et al. [45] indicated that clay protects the organic matter which had time to become entangled in the soil matrix, although this may not happen if a great volume of fresh material is added. Moreover, the turnover of organic matter in soils of different texture was better explained by other soil parameters, such as temperature, moisture, pH, redox condition, and nutrient availability [46–50]. In the study of Torri et al. [34], the water content of the three studied soils was periodically adjusted according to water holding capacity and did not limit microbial activity. In this case, soil pH was the dominant variable on soil decomposition of biosolids. Most studies reported that acidic pH delayed the decomposition of soil organic matter because of its profound influence on biomass, activity, and composition of the soil microbial community [51, 52]. The higher pH of the Natraquoll stimulated microbial activity, increasing carbon mineralization of incorporated biosolids, whereas slightly acidic soils retained more biosolids-borne C (Figure 1).

In turn, the effects of microbes on composition and recalcitrance of SOC have been shown to be as important as climatic and edaphic characteristics [53]. Soil aggregates are held together by mucilages and by fungal hyphae, roots, and polysaccharides. Increased amounts of any of these agents would promote the formation of macroaggregates, which, after further decomposition, form the stable and more resistant core of microaggregates [54, 55].

X-ray fluorescence analysis of dried sludge indicated that oxides of Si, Al, and Fe were the three main inorganic constituents of biosolids [7, 56]. X-ray diffraction analysis of biosolids performed by a number of researchers also indicated the presence of quartz, feldspars, kaolinite, mica, and expandable clays [57, 58]. In Figure 2(a), the scanning electron microscopy with X-ray microanalysis (SEM-EDS) image of a biosolids sample showed the presence of both organic and inorganic phases [7]. The inorganic phase included silica, Fe, Al, and calcium compounds (Figure 2(b)). Taking into account that soil organic matter carries negative charges, whereas Fe oxides have positive ones, under certain conditions both of them may be intimately associated [59]. Biosolids-borne amorphous iron and aluminum oxides would promote SOM stabilization after biosolids application [60, 61]. Amorphous Fe and Al oxides are very reactive due to their small size and high surface area. These reactive surfaces are often presumed to account for sorption and stabilization of OM [62]. More recent research has suggested that stabilization mechanisms include ternary C - Fe oxide - clay associations [63] and the formation of unidentified chemical bonds [64]. Lines of evidences that the association of organic matter with secondary hydrous Fe and Al phases would prevent SOC degradation have been published [65, 66]. Taking into account that biosolids are rich in amorphous Fe/Al oxides [60, 67], long-term biosolids application could increase soil amorphous Fe/Al, leading to increased SOM stability.

Some authors indicated that “the capacity of terrestrial ecosystems to store carbon is finite and the current sequestration potential primarily reflects depletion due to past land use” [68]. However, recalcitrant organic carbon and amorphous Fe/Al oxides are land applied through biosolids amendments. The presence of Fe/Al oxides has been shown

to stabilize soil organic matter and, likely, biosolids borne organic matter [66]. Moreover, Kögel-Knabner et al. [69] suggested that one possible reason for soil C immobilization in these soil amendments could be its adsorption or complexation by Fe and Al cations. These results may indicate that, with time, biosolids amended soils would be able to store more carbon than the one depleted due to past land use. Nevertheless, this hypothesis requires further investigation.

2.2. Opencast Mine Sites. In recent years, there has been growing evidence that biosolids may be used to restore mine spoils or tailings. Rehabilitation of rocky materials exposed by mining typically involves physical amelioration and organic matter incorporation. The use of biosolids in such operations represents an opportunity to couple biosolids application with soil C sequestration. In several cases, this practice has led to high soil C accumulation, edaphic improvement, and an effective vegetation cover establishment [70, 71]. Furthermore, organic matter inputs and revegetation lead to humus accumulation and pedogenesis, including soil profile development [70, 72–74]. As the system evolved, grasses progressively dominated and represented the most important source of SOC in biosolids amended soils [72]. After a decade of biosolids incorporation, SOC reached concentrations comparable to those found in hydromorphic soils and about twice those of undisturbed mineral soils under primary forests [70].

Mined spoils in tropical regions present factors that can accelerate C flow, such as high temperatures, acidity, and low charges surfaces, and factors that may retard it, like clay texture, overburden materials, and anaerobic conditions due to waterlogging. Carbon accumulation in revegetated mining spoils suggests that retarding factors have prevailed under stripped soil situation. Common inorganic components present in mining spoils include aluminosilicates (allophone and imogolite) and Fe-(oxy) hydroxides (like ferrihydrite). Both of them have been reported to stabilize soil C [75, 76]. Since vegetation coverage is usually established on low-permeable rocky material in mining sites, roots are usually subjected to waterlogging, leading to SOC accumulation [77]. Several hypotheses about deleterious effects on soil microbial activity by compounds formed under anaerobiosis, such as volatile fatty acids, H_2S , and toxic concentrations of NH_3 , Al, Fe, and other elements, have been postulated [78].

Although mining spoils are not a suitable environment for plant development, the incorporation of biosolids has promoted plant colonization and unprecedented organic-C accumulation was reported in temperate and tropical regions [70, 79]. Depending on site management, Shrestha and Lal [80] estimated that C sequestration rates for reclaimed mine soils could be in the order of 0.1–3.1 and 0.7–4 $Mg\ ha^{-1}\ y^{-1}$. Scaling up such figures, mining site restoration could account for $\approx 16\ Tg\ CO_2$ per year [80].

3. Biological Regulation of C Storage in Biosolids Amended Soils

Soil organic C dynamic depends on microbial activity, community composition, and soil enzyme activity [81]. While

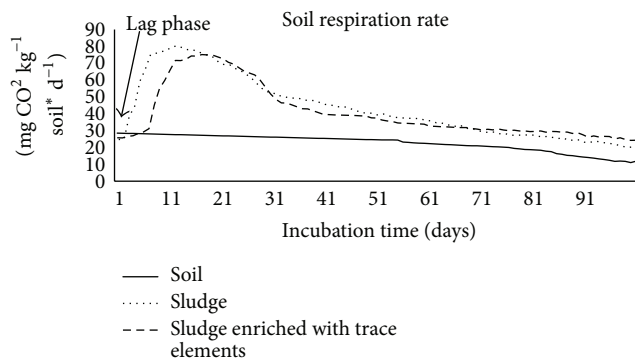


FIGURE 3: Typical respiration trends of soils amended with sewage sludge enriched or not with trace elements ($Cd\ 12\ mg\ kg^{-1}$, $Zn\ 300\ mg\ kg^{-1}$). A lag phase can be observed before the onset of the C flush for metal spiked sludge.

incorporation rates and quality are relevant factors controlling soil organic C inputs, land application of biosolids may change the activity and diversity of soil microbial communities [82, 83]. Consequently, the use of biosolids as a soil amendment may have variable effects on soil C retention.

3.1. Microbial Activity. Most of the existing information on soil microbial responses due to biosolids incorporation is related to the use of sewage sludge [84–86]. Contrasting responses—from stimulation to inhibition—have been reported. These results reflect the large variability of sludge chemical composition and the level of resolution of the biological studies (i.e., biochemical or biomolecular) [87–89].

In most soils, microbial activity and proliferation is typically C-limited whereas N limitation hardly occurs [90]. Biosolids application modifies soil main regulating parameters, particularly the nutrient stoichiometry. Sludge incorporation into soils provides labile C that produces a large initial C- CO_2 flush due to rapid labile organic matter decomposition and microbial growth. This respiratory response is known as the “C dominated phase” (Figure 3) and is invariably bell-shaped. The shape of the curve is generally related to N availability, the quality of biosolids’ organic matter, and the release of trace elements or organic pollutants through biosolids decomposition [87]. On the contrary, soil application of composted or thermally dried sludge may reduce soil microorganisms decomposition rates due to the higher proportion of recalcitrant C added [89].

Before the onset of CO_2 release, an increase in the lag time may be observed in sludge amended soils [91]. The lag phase allows the adaptation required for bacterial cells to begin to exploit new environmental conditions [92] and has been suggested to be a sensitive microbial indicator of soil metal pollution [93]. Sludges with high content of trace elements may result in a longer “lag phase,” as depicted in Figure 3. However, this may not be a universal microbial response [94].

There is still considerable controversy about the effects of biosolids applications on the native SOC pool [95]. Some authors reported that the strong microbial activity induced by the application of biosolids with high contents of labile

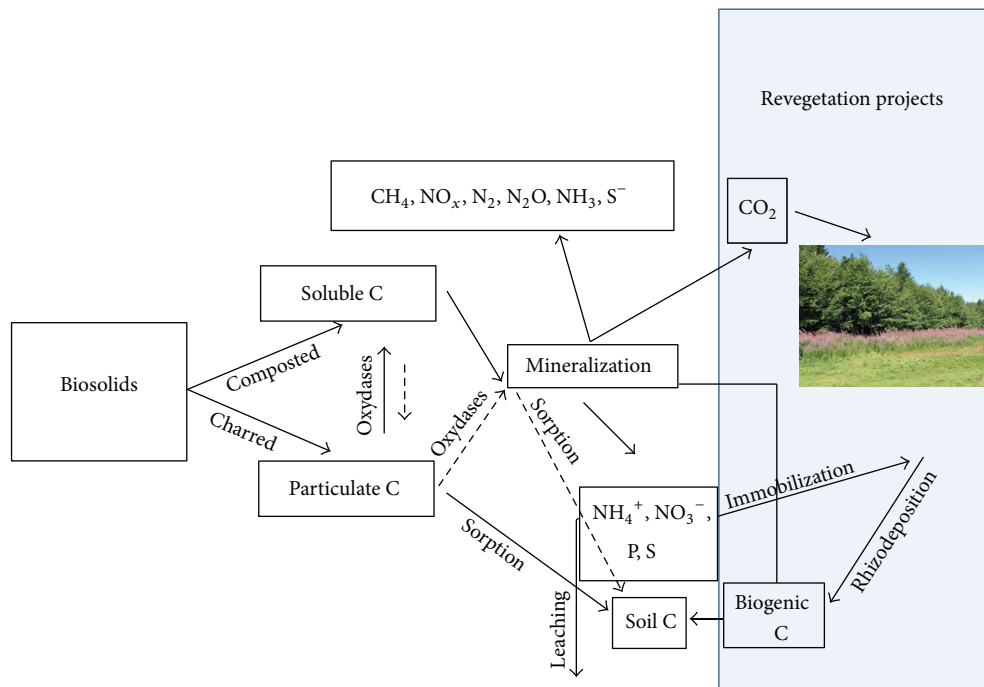


FIGURE 4: Schematic contribution of biosolids-borne C to SOC fractions and to soil nutrient fluxes, in addition to biogenic extra C inputs in mine spoils revegetation projects. The dotted lines indicate the still poorly understood effect of oxydases on particulate C mineralization or the stabilization of mineralized soil C by chemisorption.

organic substances would mineralize native SOC [96]. This effect was mainly noticed when biosolids were applied to soils containing high initial levels of SOC, a phenomenon known as *priming effect* [97]. Conversely, the application of the same amount and type of biosolids in soils with low levels of initial SOC contributed, in general, to an increase in the short-term SOC pool. An explanation to this was the low density of microbial communities in soils with low organic matter content. Although positive and negative priming effects have been reported, the latter does not always result in reduced soil C storage capacity. In general, the amount of added organic amendment entirely compensates the priming-induced C loss [97]. Soil microorganisms can be triggered into activity by the availability of water and nutrients such as those present in the root exudates [98], and therefore these factors are important covariates to be accounted for assessing the biological control of biosolids soil C storage. Theoretically, C storage is achievable when the metabolic energy required to decompose biosolids-borne organic substrates is larger than the energy obtained by catabolism within microbial cells.

Soil management practices may influence soil C storage after biosolids amendment. It has been widely reported that intensity of mineralization processes is much higher in soil surface layers than in deepest soil horizons [99]. However, root exudates or decomposition of root litter in subsurface horizons may induce priming effects that may, in turn, enhance the decomposition of biosolids-borne organic C. Low molecular weight organic compounds present in root exudates support large microbial biomass in the rhizosphere and induce SOM mineralization [99, 100]. Therefore, the current information on the priming effects on native SOM

cannot be extended to biosolid amended soils. The reason for this is that the overall effects will not only depend on soil's characteristics and basal microbial activity, but on the nature of nutrient inputs as well. Therefore, the biosolid-borne C storage capacity of soils will depend on the site specific equilibrium between C inputs and outputs, regulated by mineralization processes. Nevertheless, it is undisputable that, on the long term, biosolids amended soils retain more C than soils under conventional agricultural regime in different tillage, fertilization, and rotational schemes [101]. The same applies for marginal and degraded soils [102].

3.2. Soil Enzyme Activity. Soil enzyme activity is responsible for most of the soil functionality, as it promotes the decomposition of organic matter and release nutrients in forms available to plants and microorganisms. Soil enzymes are actively released by proliferating soil microorganisms, plant roots, and soil fauna or passively released by dead microorganisms and root cell sloughing. A large fraction of the enzymes released in the extra- or pericellular space are stabilized by stable soil organic and inorganic phases [103], which protect them from soil proteolytic activity [104]. Biosolids amendments play a dual role on soil enzyme activity: biosolids may increase the stabilization of extracellular enzymes through their solid phase surface properties or they may provide substrates (i.e., proteins and peptides) for soils enzymes, leading to microbial proliferation and the increase of enzymatic activity. This aspect is important for the long term of biosolids-borne C storage in soils because the presence of active enzymes reduces energy barrier to the decomposition of complex organic substrates thus facilitating the

biosolids matrix mineralization without new and metabolically expensive synthesis of extracellular enzymes [105]. This may produce a long-term positive feedback effect on soil microbial activity after amendment (Figure 4).

In any case, the presence of soil stabilized “enzymatic background” makes soil’s decomposition capacity only partially related to the actual levels of microbial activity in biosolids amended soils. As it is currently impossible to estimate the ratio between intra- and extracellular enzyme activity, it is not possible to precisely determine the actual contribution of active microorganisms to biosolids degradation.

4. Conclusions

In the light of global change scenario, increasing soil organic matter stocks has been identified as a feasible way for soil C sequestration. Many experiments indicated that application of biosolids to land or opencast mines resulted in an increase in carbon reserves of soils from different regions and under different management practices. Biosolids are typically made up of 40–70% organic matter, consisting of two fractions of different degree of biodegradability: a labile fraction that is quickly mineralized by soil microorganisms and a recalcitrant fraction, not available or resistant to soil microorganisms, responsible for soil organic carbon accumulation. The amount and proportion of recalcitrant C in biosolids are important attributes to predict the biological control of C storage in soils. It seems to be a direct relationship between C recalcitrance and mineralization: the higher the C recalcitrance in biosolids amended soils, the higher the metabolic energy needed for biosolids mineralization by soil microorganisms. Monitoring microbial communities and soil enzyme activity may be used as ecological indicators of biosolids C stabilization in soil.

Many studies reported that mineralization rates of biosolids-borne C may not depend on soil texture and that slightly acid soils retained more biosolids-borne carbon than soils with a higher pH. Furthermore, amorphous iron and aluminum oxides usually found in biosolids would play an important role in soil organic C accumulation. Therefore, the capacity of soils to sequester biosolids borne C may not be finite. It is important to remark that the benefits associated with the use of biosolids for soil carbon sequestration are in addition to other benefits, like the improvement of soil quality in terms of physical, chemical and biological fertility, although the presence of contaminants may impact soil microbial communities on the long term.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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Research Article

Characterisation of Organomineral Fertilisers Derived from Nutrient-Enriched Biosolids Granules

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Organomineral fertilisers (OMFs) were produced by coating biosolids granules with urea and potash. Two OMF formulations with $N:P_2O_5:K_2O$ compositions: 10:4:4 (OMF₁₀) and 15:4:4 (OMF₁₅) were developed for application in grassland and arable crops. Routine fertiliser analyses were conducted on four batches of OMF and biosolids granules and compared with a sample of urea to determine key physical and chemical properties of the materials which affect handling and spreading, soil behaviour, and fertiliser value. Bulk and particle densities were in the range of 608 to 618 kg m⁻³, and 1297 to 1357 kg m⁻³, respectively. Compression tests showed that OMF particles undergo deformation followed by multiple failures without disintegration of the granules when vertical load was applied. Static particle strength was between 1.18 and 4.33 N mm⁻² depending on the particle diameter. The use of a model for fertiliser particle distribution studies showed that OMF granules should be between 1.10 and 5.50 mm in diameter with about 80% of the particles in the range of 2.25 to 4.40 mm to enable application at 18 m tramline spacing. This research utilises novel technology to improve the fertiliser value of biosolids, reduce disposal costs, and deliver a range of environmental benefits associated with recycling.

1. Introduction

1.1. The Need for Recycling. The production of sewage sludge (biosolids) in England and Wales is estimated to be 1.6 million tonnes (dry solids) per year [1] while this amount exceeds 10 million tonnes (dry solids) per year in the European Union (EU) [2]. Current levels of sludge production are set to increase due to the growth of the population and continuous adoption of improved technologies which are introduced to comply with standards required for the treatment of effluents. The quantity of sewage sludge recycled to agriculture varies considerably between EU member states. The UK and Ireland recycle approximately 70% and 90%, respectively, while Finland, Slovenia, Sweden, Holland, Greece, and Belgium recycle very low quantities or no sewage sludge to agriculture

[3]. Conventional routes for disposal of sewage sludge include landfill and incineration which are considered to be unsustainable and therefore being progressively restricted. In this respect, the EU Landfill Directive 99/31/EC [4] requires reduction of 35% of biodegradable waste by 2020 of that generated in 1995 while the UK Government is committed to cut back CO₂ emission by 20% [5] which narrows the opportunities for increased disposal through incineration. Expanding incineration infrastructure to deal with increased sewage production can be cumbersome due to difficulties arising from approval of planning permissions and because of strong public opposition.

Recycling of biosolids to agricultural land is relatively less expensive compared with other disposal practices, that is, 30% to 40% compared with incineration and landfill per

tonne of raw sludge (dry solids) [6], and it is regarded as the best practicable environmental option in most circumstances [7]. The practice of recycling supports the waste management hierarchy [1] and the principles of sustainable intensification of agriculture [8]. It is envisaged that the use of organic-based fertiliser materials will increase in the near future [9] as a result of technological developments that may enable production of high-quality products, improvements in application techniques for field spreading and specialist equipment, and cost advantages compared with mineral fertilisers.

The expected increase in the global population with the associated rise in demand for food and energy will increase the reliance on fertiliser inputs [10]. The global demand for N, P, and K is forecasted to increase at an average rate of about 2.5% per year to 2020 [11]. Since phosphate reserves are limited [12], there is a need to ensure that phosphorus is recycled to a large extent so that the rate of depletion of phosphate rock is reduced [10, 13]. Dawson and Hilton [10] argued that legislation concerning management of phosphorus in agriculture appears entirely linked to its potential to disturb natural ecosystems with apparently no regulations yet requiring the efficient use and reuse of a finite resource.

In recent years, there has been a progressive increase in the price of mineral fertilisers [11]. This trend is likely to continue driven by the projected increase in fertiliser demand and the cost of energy with special regard to synthetic nitrogen fertilisers [11]. Enhanced quality of organic-based fertiliser materials can provide an opportunity to improve crop profit margins by means of reduced input costs of fertilisers while delivering some of the environmental benefits associated with recycling.

Development of new fertiliser products requires determining key properties of the materials that affect storage and spreading, soil behavior, and agronomic efficiency. The information available describing physical characteristics of organomineral fertiliser products is limited (e.g., [9, 14, 15]), which responds to the lack of legal requirements for their declaration on the label [16]. Conversely, the physical properties of mineral fertilisers have been studied in detail (e.g., [17, 18]). Miller [18] indicated that fertiliser materials which have moderately high crushing strength can resist handling, storage, and spreading without significant shattering, dust formation, or caking. Density properties are related to the volume needed for storage and transport, and are required to calibrate fertiliser spreading equipment [9, 18]. Particle size and size distribution affect uniformity of distribution during field application [19], and it is well documented that uneven spreading of fertilisers can increase nutrient losses to the environment, reduce fertiliser use efficiency and crop profit margins [20].

1.2. Organomineral Fertilisers. The literature abounds with reported experiences in the use of organomineral fertilisers applied to a variety of crops with satisfactory agronomic performances. According to the Working Groups drafting the revised EU Fertiliser Regulations EC2003/2003, organomineral fertiliser is defined as a fertiliser obtained by blending, chemical reaction, granulation, or dissolution in water

of inorganic fertilisers having a declarable content of one or more primary nutrients with organic fertilisers or soil improver [21]. These products have been derived from a range of different organic and inorganic sources (e.g., [22–25]). Zebarth et al. [26] proposed the use of organic-based fertiliser materials to mitigate potential environmental effects associated with the use of mineral fertilisers alone which usually release their nutrients more rapidly following soil application. In such materials, the organic fraction protects the inorganic components by means of binding and absorption, thereby slowing the rate of release of plant nutrients [27]. Tejada et al. [28], however, suggested that the existence of a time lag between soil application and nutrients uptake by the crop can increase the risk of nutrient losses to the environment.

In the UK, some wastewater companies commercialise treated biosolids pellets available in one tonne bags for agricultural use, but they are produced without the addition of mineral fertilisers [29]. This article focuses on the study of physical and chemical characteristics of organomineral fertilisers which are produced by coating biosolids granules with urea and potash. A patent application (US7504035-B2) was assigned to United Utilities Group PLC [30] for the treatment of putrescible cakes for reduction of *Escherichia coli* and odour both of which are required in this product for safe spreading on agricultural land. The use of biosolids-derived organomineral fertilisers can reduce the cost of spreading by about 30% compared with biosolids when these are applied at the optimum N rate in winter cereal crops [6]. Cost savings and differences in working rates become greater when compared with liquid sludges requiring injection [6].

The main aim of this development was to design a product that could satisfy the requirements of modern agricultural practices, maximise the use of biosolids in crop production, particularly, in areas close to production sites, and ultimately, reduce the reliance on mineral fertilisers. The GB Fertiliser Regulations are currently considering renewable sources of phosphorus, but discussions are still in their infancy. The use of biosolids-based organomineral fertilisers addresses an important issue of nutrient cycling between urban and agricultural ecosystems. The use of such products represents a technological advancement compared with ways that sewage sludge has been traditionally recycled in agriculture, and it appears to be in line with the current environmental and regulatory frameworks. The specific objective of this study was to characterise chemical and physical properties required to meet the specifications for organomineral fertilisers (OMFs) derived from nutrient-enriched biosolids granules for application in grassland and arable crops.

2. Materials and Methods

2.1. Description of the Products. The organomineral fertilisers (OMFs) are produced by drying digested sewage sludge cake (25% dry solids) at 80°C in a tumble dryer which produces granules of varying diameter and increases the dry solids content of the sludge to about 80% to 85%. The sludge cake is produced at United Utilities Group PLC wastewater treatment works in Ellesmere Port in the NW

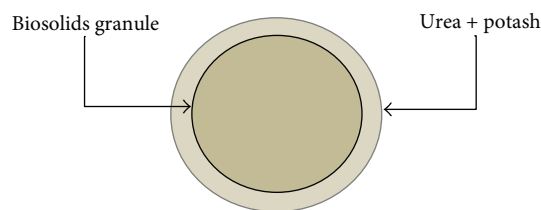


FIGURE 1: Schematic drawing of an organomineral fertiliser (OMF) particle.

of England. The sludge granules are subsequently coated, by means of spraying, with melted urea (46% N) and ground potash (60% K_2O) to raise the concentration of nitrogen and potassium, respectively. The final product is a compound NPK organomineral fertiliser which is shown in Figure 1. The core of the granules (biosolids) releases nutrients more slowly compared with the mineral fraction (urea and potash) [31].

The land application of sewage sludge (biosolids) is regulated by the Sludge (Use in Agriculture) Regulations 1989 S.I. no. 1263 which implements the provisions of the EU Sewage Sludge Directive 86/278/EEC [32] in Great Britain regarding the protection of the environment. The treatment of sewage sludge (biosolids) is a requirement prior to land application [33]. A process known as high rate enzyme hydrolysis is employed to control the pathogens load in biosolids [34]. This process takes place during the anaerobic digestion and it provides up to 99.9999% pathogens destruction [34] enabling compliance with the Safe Sludge Matrix [33].

2.2. Product Formulation. The organomineral fertiliser (OMF) products were suggested for broadcast application in grassland as well as arable cropping. Phosphorus fertilisation in excess of crop requirements may be avoided in soils that have satisfactory soil P Indexes as defined in [35]. Research [36] has shown that about 20% of the soils in Northern England had soil P Index 3 or greater (Olsen's $P \geq 45 \text{ mg L}^{-1}$) which agrees with more recent information supplied by wastewater operators in the NW region of England [37]. High soil P status imposes a restriction to biosolids recycling, and it compromises meeting recycling targets by wastewater companies. It also increases the cost of disposal as biosolids require transportation farther away from wastewater treatment works.

Chemical analyses conducted on samples of biosolids granules [37] reported an average content of 3% N (standard deviation = 0.81), 4.35% P_2O_5 (standard deviation = 1.07), and 0.15% K_2O (standard deviation = 0.062). The relatively low content of nitrogen compared to phosphorus results in low N: P_2O_5 ratios which are often less than 1. This can lead to a progressive build-up in soil P levels if biosolids are regularly applied based on crop nitrogen requirements. Soil P levels above the target Index [35] for the soil and crop system can have undesirable effects if P is subsequently lost to the environment [38]. This required increasing existing N: P_2O_5 ratio in the base biosolids to (1) ensure that both nutrients were supplied to the crop in sufficient quantities for a grain yield of 8 t ha^{-1} considered to be typical of winter wheat crops

in England [35] and (2) reduce the risk of increasing soil P Index when the fertilisation strategy considered routine application of OMF.

Narrow N: P_2O_5 ratios in the product would be suitable for lower P Index soils; for example, less than 3, allowing for corrections to be made overtime towards the target Index [35]. Wider N: P_2O_5 ratios suit situations where soil P Index is higher but where the overall fertility status of the soil is to be maintained. This requires that P fertilisation does not exceed but instead replenishes P offtake by crops. Based on this criterion, the content of phosphorus in OMF remained equivalent to that of the base biosolids granules. Nitrogen concentrations in OMF above the suggested 15% are technically possible, but this has some drawbacks. Firstly, it increases the manufacturing costs due to higher input cost of urea-N. Secondly, the production of more concentrated N products can reduce the total amount of biosolids recycled through agriculture. Equally, if the nitrogen concentration in the product was increased, the land bank for recycling would need to be increased accordingly to meet the same disposal targets compared with biosolids. Estimates [6] suggested that the required land bank for OMF₁₅ would need to be approximately 1.5 times greater than that of OMF₁₀ assuming that OMF-N was applied at a standard rate of 200 kg ha^{-1} and that the price of nitrogen was equivalent to that of urea-N.

For winter wheat crops in soils with P Index below 3, the recommended phosphorus application rates (grain yield: 8 t ha^{-1}) are between 60 and 85 kg ha^{-1} of P_2O_5 [35]. Supplying these rates of phosphorus with biosolids would require between 1400 and 1950 kg of biosolids per hectare resulting in N application rates in the range of 140 to 160 kg ha^{-1} based on the nutrients concentrations of biosolids mentioned earlier [37]. For a standard rate of 200 kg ha^{-1} of N [35], the concentration of N in the biosolids, in percentage terms, should be increased from 3% to about 10% and 15%, respectively. For potassium, the application of the same amount of biosolids would supply approximately 45 to 65 kg ha^{-1} of K_2O less than the recommended quantities for soils with K Index below 3 [35]. Hence, the concentration of potash in biosolids would need to be increased from 0.15% to about 3.5%. From this simple analysis, the formulations of the two OMF products were inferred and the final compositions were approximated to N: P_2O_5 : K_2O ratios: 15:4:4 (OMF₁₅) and 10:4:4 (OMF₁₀).

The application of OMF₁₀ or OMF₁₅ is not restricted to soils with P Indexes below 3; however, crop requirements for P should not be exceeded in soils which are above the target soil P Index. This criterion for P fertilisation is supported by the basic principle for P and K management which is to ensure the maintenance of sufficient nutrient reserves in the soil [39]. The narrower N: P_2O_5 ratio of OMF₁₀ compared with OMF₁₅ makes it more suitable for situations with relatively lower soil P Index and vice versa with OMF₁₅. Mixtures of these materials with other compatible fertiliser sources [40] may be used to match specific soil-crop requirements, but differences in their physical properties must be observed. A distinctive aspect of this product development is that the coating technology used to supplement biosolids

with mineral fertilisers enables overcoming the expected variability in the chemical composition of sludges [41] to provide a consistent product.

2.3. Chemical Composition. Chemical analyses were conducted in compliance with the specifications outlined in the Fertilisers (Sampling and Analysis) Regulations 1991 S.I. no. 973. Total N was determined based on the Dumas technique [42] which converts the N present in the fertiliser sample to N_x gases and gaseous-N by means of combustion. The combustion products are subsequently converted to N_2 and quantified by a Thermal Conductivity Detector (TCD). Total P (% P_2O_5 , w w⁻¹), total K (% K_2O , w w⁻¹), and heavy metals, total cadmium (Cd, mg kg⁻¹), total copper (Cu, mg kg⁻¹) and total zinc (Zn, mg kg⁻¹), were determined by means of digestion in concentrated hydrochloric and nitric acids (collectively known as *aqua regia*) in a microwave unit following the specifications given in [43, 44]. The resulting solution was diluted volumetrically, and the total Cd, Cu, and Zn in the solution were subsequently determined by Atomic Absorption Spectrophotometer (AAS). The P content was determined by measuring the intensity of methylene blue colour formed using a spectrophotometer at 880 nm. Cd was determined due to risk of plant toxicity at low concentrations and potential transfer to the food chain [45]. Cu and Zn are essential elements but can be toxic to plants and microorganisms above certain levels; therefore, maximum permissible levels in soil must be observed [46]. Soluble P (% P_2O_5 , w w⁻¹) was determined based on [43] to provide an indication of the fraction readily available for plant uptake. A sample was treated with 0.5 mol L⁻¹ sodium hydrogen carbonate solution at pH 8.5. The extract was subsequently analysed using a spectrophotometer as explained above. Whilst the final method of detecting P is similar, the difference is in the extraction solution, that is, *aqua regia* and sodium hydrogen carbonate extract representing a more vigorous extract to denote total P and a more gentle extract to denote the plant available fraction, respectively.

2.4. Physical Properties. Particle size analysis was conducted by sieving samples of the fertiliser materials following the specifications outlined in [47]. Fertiliser samples of 500 g were passed through a series of sieves with apertures in the range of 0.60 to 37 mm. The sieves were placed on a shaker for three minutes, and the fertiliser retained was weighed and expressed as percentage of the total weight of the sample. From the particle size analysis, the mean diameter (d) was obtained. Standard BS EN 1235 [47] also recommends the characterisation of fertiliser materials by providing the values of percentiles d_{16} , d_{50} , and d_{84} . These correspond to particle diameters (mm) below which 16%, 50%, and 84% (by weight) of the material respectively can be collected after sieving [48]. The d_{50} value equates to the median particle diameter [49]. Based on these percentiles, a granulometric spread index (GSI, %) was derived [49]

$$GSI = \frac{d_{84} - d_{16}}{2 \times d_{50}} \times 100. \quad (1)$$

The GSI was used to provide an indication of the likelihood of the materials to undergo segregation during transport, handling, loading, and spreading. Segregation is the re-arrangement of particles as a result of differences in their physical characteristics, particularly, the size ratio of particles [50]. The GSI is more commonly used to characterise blended than complex and compound fertilisers; however, its application to this situation is justified given the relatively wide range of particle sizes encountered in the samples. Based on [9], a uniformity index (U_i , %) was calculated which is the ratio times 100 of the two extreme sizes in the range of particles retained at the 95% (d_{95}) and at the 10% (d_{10}) levels, respectively [51]. A larger U_i value indicates a more uniform granulometric distribution and vice versa.

Untapped bulk density (ρ_b ; kg m⁻³) was determined based on [52] by pouring of a fertiliser sample from a funnel into a measuring cylinder of known volume and weighing the contents and the cylinder. Particle density (ρ_p ; kg m⁻³) was determined by measuring the diameter and calculating the volume of individual fertiliser particles from a sample containing 100 particles and by recording the mass of the particles individually. Particle diameter was measured using a digital vernier calliper in two perpendicular directions to better account for unevenness in the particles' shape. Subsequently, the mean of the two measured diameters was obtained, which was the value used to calculate the volume of the particles; these were regarded as spherical. The porosity of untapped granules (η ; m³ m⁻³) was calculated based on [9]:

$$\eta = 1 - \frac{\rho_b}{\rho_p}. \quad (2)$$

Static particle strength (τ ; N mm⁻²) was determined using an Instron 1122 apparatus [53], previously calibrated [6], which consists of a frame and a moving crosshead. Particles were placed individually between the crosshead and the bottom of the frame. The crosshead (tip rod = 1 mm²) moved downwards at a speed of 95 mm min⁻¹. The device has a load cell that senses the vertical load applied to the particle, and it was connected to a laptop computer which recorded the force applied versus the time. The force required to induce the breaking of the particle [17] or its complete compression, as determined by visual assessment, was recorded. For known crosshead speed, the vertical load versus time plot was converted to vertical load versus displacement [54]. Measurements were conducted for a selected range of particle diameters (from 2.85 to 6.30 mm; except for urea: from 2.85 to 4.75 mm). The total surface area per unit mass (A ; m² kg⁻¹) of a fertiliser sample was estimated from the particle size analyses based on [55]

$$A = \left(\frac{\beta_s W_t}{\beta_v \rho_p} \right) \exp \left[4.5 \times S_{ln}^2 - \ln d_{gw} \right], \quad (3)$$

where β_s ($\approx \pi$) and β_v ($\approx \pi/6$) are the shape factors for calculating surface area and volume of particles, respectively, ρ_p is the particle density (g cm⁻³), S_{ln} ($\approx 2.3 \log[d_{50}/d_{16}]$) is the log-normal geometric standard deviation by mass in natural logarithm, d_{gw} ($\approx d_{50}$) is the geometric mean particle diameter (cm), and W_t is the mass of the sample (g).

TABLE 1: Chemical analyses conducted on OMF₁₅, OMF₁₀, and biosolids granules.

Fertiliser material Determination	<i>n</i>	OMF ₁₅	OMF ₁₀ Mean ± SD	Biosolids granules
Total N (% w w ⁻¹)	4	13.0 ± 2.75	9.0 ± 1.55	4.5 ± 0.73
Total P ₂ O ₅ (% w w ⁻¹)	4	3.8 ± 0.23	4.3 ± 0.52	5.5 ± 0.97
Total K ₂ O (% w w ⁻¹)	4	3.2 ± 0.92	3.0 ± 0.61	0.2 ± 0.07
Total Cd (mg kg ⁻¹ DS)	3	0.98 ± 0.07	0.98 ± 0.15	1.20 ± 0.03
Total Cu (mg kg ⁻¹ DS)	3	268.4 ± 10.7	264.2 ± 11.0	329.3 ± 11.6
Total Zn (mg kg ⁻¹ DS)	3	422.7 ± 3.8	422.2 ± 5.6	493.0 ± 5.1
Soluble P (% w w ⁻¹)	3	<0.10 ± 0.02	<0.10 ± 0.02	0.20 ± 0.05
N : P ₂ O ₅ ratio	4	3.4 ± 0.75	2.1 ± 0.41	0.80 ± 0.29

(The standard deviation (SD) is shown as ± the mean value; DS is dry solids).

2.5. Statistical Analyses. Statistical analyses were undertaken using GenStat 14th Edition [56]. For density properties, untapped porosity and particle strength analyses involved ANOVA and least significant differences to compare the means with a probability level of 5% (LSD 5% level). For particle size distribution, analyses involved *t*-tests (95% confidence level) to compare the mean particle size and *F*-tests ($\alpha = 0.05$; 100 degrees of freedom) to compare the variation in the particle size distribution between fertilisers. *F*-tests used a critical *F*-value of 1.41 [57].

3. Results

3.1. Chemical Composition. The results of the chemical analyses conducted on OMF and biosolids samples are summarised in Table 1.

Figure 2 shows a sample of OMF₁₅ produced after coating biosolids granules with urea and potash.

Heavy metals (Cd, Cu, and Zn) content were below the recommended limit values given in the EC Sewage Sludge Directive 86/278/EEC [32] and therefore in compliance with the Sludge (Use in Agriculture) Regulations 1989 S.I. no. 1263. The Directive suggests the following limit values for heavy metals concentration in sludges intended for use in agriculture: 20 to 40 mg kg⁻¹ DS (Cd), 1000 to 1750 mg kg⁻¹ DS (Cu), and 2500 to 4000 mg kg⁻¹ DS (Zn), [32]. The relatively low concentration of soluble P confirmed that the majority of OMF-P and biosolids-P is not readily available for plant uptake. This responds to the technique used for the removal of P during the wastewater treatment process which is conducted by precipitation with FeCl₃ resulting in the formation of Fe-phosphates. These compounds are largely unavailable for plant uptake following soil application [31]. The phosphorus thereby removed is subsequently incorporated into the sludge [58].

3.2. Physical Properties. The results of the measured physical properties are summarised in Table 2. The particle size and size distribution of OMF and biosolids granules varied between samples due to difficulties encountered during the coating process. Loss of heat occurred during the spraying of melted urea which meant that urea droplets solidified before being attached to the biosolids granules producing



FIGURE 2: A sample of OMF₁₅ with particles in the range of 1.18 to 5.50 mm in diameter.

unbounded urea (fine particles). Due to the relatively high temperatures used in the process (range of 120° to 130°C), fine particles of urea remelted and aggregated to biosolids granules. As a result, the thickness of the coating was not uniform for all granules which resulted in a relatively wide range of particle sizes. Particles ranged between <0.60 mm (up to 3% and 6% in OMF₁₀ and OMF₁₅, resp.) and 25 mm (up to 5% and 2% in OMF₁₀ and OMF₁₅, resp.) in diameter. The two OMF products did not show significant differences in the mean particle diameters, but these were significantly higher (*t*-values > 1.96) compared with biosolids granules and urea. The *F*-tests indicated significant differences (*F*-values > 1.41) between the two OMF products compared with urea for all fertiliser samples.

Overall, there were significant differences in bulk density depending on the fertiliser type ($P = 0.024$). This effect was mainly due to the value encountered for urea which was on average 20% to 30% higher compared with the other fertiliser materials. The measured bulk densities of biosolids granules, OMF₁₀, and OMF₁₅ were not significantly different for an LSD value (5% level) of 110 kg m⁻³. There were significant differences ($P = 0.002$) in particle densities, but the overall effect was due to urea which was on average 6% to 10% higher compared with the other materials. Similarly, biosolids granules, OMF₁₀, and OMF₁₅ were not significantly different in their particle densities for an LSD value (5% level) of 73 kg m⁻³.

TABLE 2: Physical properties determined on OMF₁₅, OMF₁₀, biosolids granules, and urea.

Fertiliser material	<i>n</i>	OMF ₁₅	OMF ₁₀	Biosolids granules	<i>n</i>	Urea
Physical property		Mean \pm SD				Mean (or value) \pm SD
d_{16} (mm)	4	2.52 \pm 1.0	2.40 \pm 0.6	2.74 \pm 3.1	1	2.52
d_{50} (mm)	4	4.60 \pm 2.8	4.45 \pm 2.8	4.87 \pm 5.6	1	3.03
d_{84} (mm)	4	7.24 \pm 4.4	6.91 \pm 5.2	7.08 \pm 7.5	1	3.73
d (mm)	∞	5.42 \pm 2.6	5.28 \pm 2.9	4.97 \pm 5.5	∞	3.10 \pm 0.35
GSI (%)	4	49.3 \pm 14.3	43.6 \pm 16.1	48.9 \pm 7.7	1	20.0
A (m ² kg)	4	20.9 \pm 32.2	13.6 \pm 21.2	7.0 \pm 5.1	1	1.61
U_i (%)	4	15.7 \pm 9.6	22.7 \pm 16.2	24.7 \pm 4.8	1	57.3
ρ_b (kg m ⁻³)	4	603 \pm 73.1	623 \pm 85.5	578 \pm 87.2	3	748 \pm 5.7
ρ_p (kg m ⁻³)	100	1357 \pm 178	1297 \pm 263	1333 \pm 315	100	1432 \pm 255
η (m ³ m ⁻³)	4	0.56 \pm 0.05	0.52 \pm 0.07	0.57 \pm 0.07	3	0.48 \pm 0.01
^a τ (N mm ⁻²)	2	4.10 \pm 0.11	4.33 \pm 0.08	5.85 \pm 0.26	2	4.25 \pm 0.06
^b τ (N mm ⁻²)	2	2.85 \pm 0.09	2.78 \pm 0.11	1.64 \pm 0.04	2	3.11 \pm 0.05
^c τ (N mm ⁻²)	2	2.14 \pm 0.23	2.12 \pm 0.14	2.24 \pm 0.34	2	1.38 \pm 0.02
^d τ (N mm ⁻²)	2	1.25 \pm 0.04	1.18 \pm 0.06	1.23 \pm 0.02	—	—

(For τ , particle size ranges were: ^a2.00–3.35 mm; ^b3.35–4.00 mm; ^c4.00–5.50 mm; ^d5.50–7.10 mm. For urea, particles in the sample were smaller than 5.50 mm in diameter; therefore, τ is not shown for the range of 5.50 to 7.10 mm. The standard deviation (SD) is shown as \pm the mean value, except for $n = 1$).

The calculated values of porosity were not significantly different ($P = 0.14$), but the difference between urea and biosolids granules appears to be significant for an LSD value (5% level) of $0.08 \text{ m}^3 \text{ m}^{-3}$. The relatively lower value of porosity in urea samples was expected given that η was calculated from density properties [9]. Allaire and Parent [16] encountered higher total porosity values in materials with more organic matter content which explains the relatively higher value of η in biosolids compared with the two OMF products.

The surface area of urea was significantly lower compared to the other fertiliser materials which was due to the relatively lower proportion of fine particles ($<1.18 \text{ mm}$) in the sample, and the same holds true when comparing OMF₁₀ and OMF₁₅. Compression tests showed that OMF and biosolids granules undergo deformation followed by multiple fractures without disintegration of the granule when vertical load was applied (Figure 3).

Unlike urea particles, OMF and biosolids granules behaved in a plastic fashion and did not show a characteristic force that induced the breaking of the particle. Deformation started immediately after the tip rod made contact with the granule and the test was allowed to progress until the particles were fully compressed, as recorded by visual assessment. As a result, for OMF and biosolids, the value of τ reported in Table 2 was obtained by dividing the force required to induce full compression of the particle by its cross-sectional area. Depending on the fertiliser material and the particle diameter, full compression was observed when the vertical load applied was approximately in the range of 18 to 44 N. This response of the materials was attributed to the moisture content (range of 10.7% to 17.3% w w^{-1}) and their organic nature. Figure 4 shows a vertical load versus displacement diagram for particles of urea and OMF₁₀. It can be seen that the particle of urea breaks at 33 N whereas the OMF₁₀ granule compresses to a further extent requiring a force of 29 N to

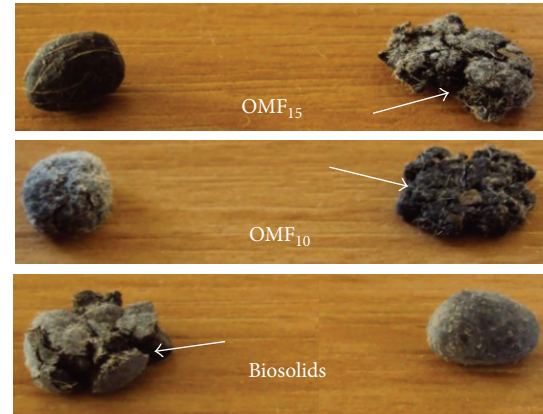


FIGURE 3: OMF₁₅, OMF₁₀ and biosolids granules (range of 3.35 to 4.00 mm). The arrows show the multiple failures produced during the compression tests.

reach full compression, but displacement is approximately double.

Due to the behaviour exhibited by OMF and biosolids granules, the statistical analysis to determine differences in the breaking force was only conducted for particles of urea: particles in the range of 3.35 to 4.00 mm in diameter required a significantly ($P < 0.001$) higher force (32.9 N) compared with those in the range of 2.36 to 3.35 mm (23.8 N) and 4.00 to 5.50 mm (24.4 N), respectively, which were not statistically different for an LSD value (5% level) of 1.26 N.

4. Discussion

OMF₁₀ and OMF₁₅ were not strictly made to specification due to some challenges encountered during the coating

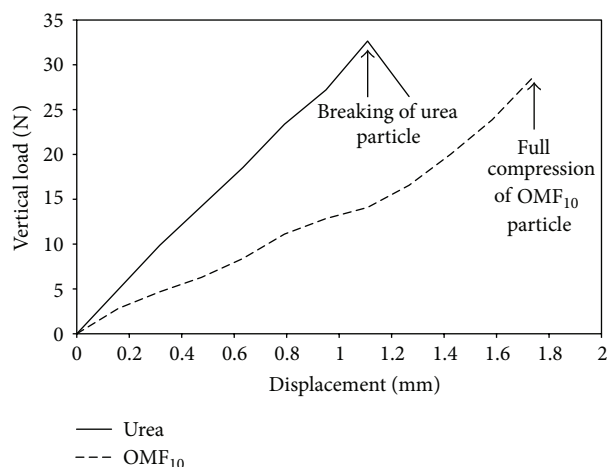


FIGURE 4: Vertical load versus displacement recorded in particles of urea and OMF₁₀ (particle size range: 3.35 to 4.00 mm).

process. On average, the concentrations of nitrogen, phosphate, and potash were slightly lower than the corresponding formulations. Consequently, a recommendation was made to correct nutrient shortfalls for soil application of OMF, so that it could meet the formulation specifications required for crop growth. The difficulties found during the coating process were related to heating urea and spraying it onto biosolids granules which causes urea to volatilise with subsequent loss of nitrogen, thereby affecting the amount added to the formulation. Optimisation of the coating technology involving suitable temperature ranges needs to be carried out to overcome this challenge.

The relatively greater surface area (A) in the two OMF products compared with biosolids granules will enhance contact of particles with soil and soil water following field spreading as observed in the study of Allaire and Parent [16]. Given the relatively low degradability of the organic-N fraction in OMF [31], increased surface area and particle contact with soil will favour the release of nutrients following application to a greater extent compared with biosolids granules. However, the increase in total surface area as result of increased proportion of small particles (<1 mm) should be avoided due to adverse effects upon spreader performance.

Miserque and Pirard [59] indicated that granulometric segregation in bulk blended fertilisers can be minimised at granulometric spread indexes (GSIs) of about 15% or lower while values above 25% will likely produce severe segregation. Segregation can occur with blends as well as complex and compound fertilisers which have relatively wide range of particle sizes [50]. For low-quality compound fertilisers whose particles do not have similar chemical composition, segregation results in uneven distribution of nutrients in the field [50]. When segregation occurs before loading the fertiliser spreader, the spreading width can be affected [60]. This is due to smaller and larger particles coming through in turns during loading and being subsequently delivered at different times during spreading [60]. As a result, the uniformity of distribution both longitudinally and transversely

can be adversely affected [17, 60]. For OMF₁₀ and OMF₁₅, it was found [6] that particle density decreases with increasing particle diameter ($P \leq 0.001$) which will enhance segregation if the materials have a relatively wide particle size range.

On average, the percentage of fine particles (<1.18 mm) in the two OMF products accounted for about 4% (by weight) across all fertiliser samples (range: 0.15% to 16.5% by weight). These particles must be maintained to a minimum since the fraction below 1 mm is greatly responsible for the increase in the coefficient of variation (CV) during broadcast spreading [61]. The values of GSI reported by Miserque and Pirard [59] provide a valuable threshold to compare against those obtained for OMF. Given the relatively wide range of particle sizes encountered, it can be stated that particle segregation is therefore likely to occur affecting distribution uniformity during broadcast spreading.

The compression tests demonstrated that OMF and biosolids granules did not show a characteristics force that induced the fracture of the particles. Instead, OMF and biosolids granules deformed permanently when a relatively small force was applied and behaved in a plastic fashion. An important feature was that OMF and biosolids granules exhibited multiple failures and they did not disintegrate into smaller particles as it was observed with urea when the breaking force was reached. Studies with urea [62] showed that this force must be greater than approximately 15 N to avoid particle fracture during handling. At this equivalent force, OMF₁₀ particles had been compressed to about 50% (Figure 4). Particle deformation influences the aerodynamic properties of the material as a result of changes in the particle shape. Miller [18] indicated that particle shape is related to spreader distribution and metering flow performances as it affects particle motion in the distributor. Since one of the reasons for the relatively low particle strength was the moisture content of the material, it is suggested that this should be maintained at about 10% ($w w^{-1}$). Lower values can significantly increase the cost of energy during the granulation process. The use of plastic packaging for OMF may be recommended to prevent increases in moisture content of the material. Urea particles exhibited breaking forces which are considered to be satisfactory as they were above the lower limit suggested by Hignett [62].

Fertilisers with wide range of particle sizes can suffer from caking due to increased number of contact points and relatively high bond strength per unit mass of the fertiliser [63]. Caking is likely to be enhanced when increased porosity and low particle strength are combined [63] which was observed in OMF and biosolids granules. An increase in the percentage of fine particles results in increased particle-contact area which combined with low particle strength can produce compaction of the material during storage. Allaire and Parent [16] highlighted that particle strength increases with density which agrees with the relatively higher density and strength encountered for particles of urea compared with OMF and biosolids granules. The values of porosity encountered in the two OMF products were relatively lower than those of OMF compounds reported by Paré et al. [9] but of similar magnitude to those obtained by Allaire and Parent [16] for bulk-blended and compound organic-based fertilisers.

The mean values of bulk density for urea corresponded with those reported in the literature [63]; however, the two OMF products had relatively lower values compared with other compound organic-based fertilisers [16]. Fertiliser materials with low bulk density lead to increased cost of transport and spreading [16]. The relatively lower bulk density of biosolids compared with OMF is explained by higher organic matter in the former material compared with the latter.

Mixing of fertilisers may be restricted when differences in the size grade number between the materials are large [64]. Therefore, due to the relatively large differences in particle size, size distribution, and particle density encountered between OMF and urea (Table 2), the bulk mixture of the two fertiliser types may not be recommended. Based on the relationship between flow time and bulk density encountered by Miller [18] for straight N fertilisers and given the differences in density properties that exist between OMF and urea, a mixture of the two materials may result in significant differences in their flow time which will affect spreading uniformity.

Particle density for urea was within the range (from 1250 to 1500 kg m⁻³) reported in the literature [65, 66] which confirmed that the technique used for measuring particle density was adequate. For OMF, mean values of particle density were lower than those reported by Allaire and Parent [16] for bulk-blended and compound organic-based fertilisers (range of 1540 to 2270 kg m⁻³) but within the range (from 900 to 1580 kg m⁻³) of values encountered by Paré et al. [9]. Due to the relatively low particle density of OMF, field application with twin discs fertiliser spreaders at wide tramline spacing (e.g., greater than 18 m apart) may not be possible. Given that OMF granules did not shatter during the compression tests conducted, it may be possible to set the disc of the fertiliser spreader at higher than standard rotational velocities, typically used with mineral fertilisers, to enable application of the material at greater spreading widths (e.g., at 24 m tramline spacing). However, because of greater forces exerted on the particles at higher rotational velocities, deformation of the granules can occur which can affect their aerodynamic properties.

Antille [6] reported satisfactory results from distribution uniformity and machinery calibration field tests conducted with OMF using a pneumatic fertiliser applicator Kuhn 2212. The pneumatic applicator performed well when delivering an application rate equivalent to 455 kg ha⁻¹ of OMF which was uniform both across the working width of the machine and along the tramline. The data reported by Antille [6] showed that there were no significant differences ($P = 0.572$) in the amount of fertiliser collected in three sets of nine trays (dimensions 0.5 × 0.5 × 0.15 m) placed at 10 m intervals along the tramline. The author observed that the variation (CV = 12.4%) in the amount of fertiliser collected in the trays was mainly due to fine particles (<1.18 mm) which originated from disintegration of large aggregates of urea (>5.50 mm) in the hopper and in the boom during fertiliser application. Compression tests showed that these aggregates of urea, which originated during the coating process, break when

a relatively small force (vertical load = 4.43 N) is applied [6]. Despite this, the above results demonstrated the suitability of OMF for application with pneumatic applicators, but further work is required to determine whether this material can be uniformly applied with twin discs spreaders which are the common type in the UK.

In this respect, a model developed for fertiliser particle distribution studies [6, 67] showed that OMF particles should be between 1.10 and 5.50 mm in diameter with about 80% of the particles in the range of 2.25 to 4.40 mm to enable application with twin discs fertiliser spreaders at 18 m tramline spacing. This requires that particles leave the spinning disc with velocities in the range of 20 to 40 m s⁻¹ for discs set at angles between 0° and 10° and at 1 m above the ground level. Therefore, the particle size and size distribution of the two OMF products reported in this study require optimisation to enable broadcast spreading at conventional tramline widths. Field spreading tests (e.g., ASAE [68]) will aid the optimisation of the physical properties of OMF and will verify the information obtained with the above model [6, 67].

5. Conclusions

- (1) The proposed OMF₁₅ and OMF₁₀ formulations were based on relatively high N:P₂O₅ ratios (≥2.5) which will reduce the risk of build-up of soil P in areas near to sewage treatment works allowing for a wider range of land bank to receive organomineral fertilisers.
- (2) The physical properties investigated showed that it may be possible to conduct field application of organomineral fertilisers with standard broadcast fertiliser spreading equipment at 18 m tramline spacing. However, this requires improving the quality control for the physical properties of the products with particular regard to particle size and size distribution which showed some variability in the samples analysed. The coating process of biosolids granules with urea requires optimisation to enable consistency in the product formulations.
- (3) Optimisation of the particle size and size distribution are required for safe spreading on the land to minimise adverse effects on the environment, poor fertiliser use efficiency by crops, and loss of crop productivity. Initial efforts should be made to perfect OMF₁₅ as this product has higher N content and it could better fit the needs of the market in the proximity of wastewater treatment works in the NW region of England.
- (4) The conversion of biosolids into organomineral fertilisers addresses an important issue of nutrient cycling between urban and agricultural ecosystems. A key aspect of this product development is that it will contribute to maximising the use of biosolids in agriculture in areas that are close to production sites. The cost of disposal of sewage sludge can be significantly reduced while enabling wastewater companies meeting recycling targets and securing the

agricultural route for disposal. Farmers may be able to reduce the reliance on mineral fertilisers, which are going up in price, and therefore reduce fertiliser input costs, while maintaining overall soil fertility.

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Research Article

Field-Scale Evaluation of Biosolids-Derived Organomineral Fertilisers Applied to Ryegrass (*Lolium perenne* L.) in England

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A field-scale experiment was conducted to compare the suitability of two organomineral fertiliser (OMF) formulations (OMF₁₀—10 : 4 : 4 and OMF₁₅—15 : 4 : 4) with urea and biosolids granules applied to perennial ryegrass. Results showed a 25% to 30% increase in dry matter yield (DMY) with application of OMF compared with biosolids granules but about 5% lower than urea. For OMF, an average input of $0.8 \times N_{\max}$ yielded $0.98 \times DMY_{\max}$ which was similar to that of urea; whereas, for biosolids, a yield of $0.92 \times DMY_{\max}$ required an input of $0.6 \times N_{\max}$ but DMY was lower ($P < 0.05$). Agronomic efficiencies with OMF were in the range of 26 to 35 kg kg⁻¹, approximately double those of biosolids but about 5% to 10% lower than urea. Soil extractable P levels remained close to constant; therefore, soil P Index was not affected by OMF application. This result supported the reasons for the proposed OMF formulations and demonstrated the advantage of the products compared with biosolids which induced an increase ($P > 0.05$), in soil extractable P. The application of OMF at rates which do not exceed the optimum N rate for the grass crop should not induce significant changes in soil P Index including application to soils with satisfactory P levels. OMF application strategies are discussed which will enable minimising environmental concerns and maximising fertiliser use efficiency.

1. Introduction

In Europe, the gradual implementation of the Urban Waste Water Treatment Directive 91/271/EEC [1] has resulted in increasing amounts of sewage sludge that require safe disposal [2]. Estimates for 2005 indicated that the European community produces approximately 9 million tonnes per year of sewage sludge (dry solids) which represents an increment of about 65% compared with the level recorded in 1992 [2]. The use of tertiary treatment for the removal of nutrients from wastewater is a requirement in sensitive areas before treated water is recycled to the environment [3]. Therefore, further requirements for enhanced treatment of sewage effluents can arise from future designations of sensitive waters under the provision of the Directive [1] which will result in increased sludge production. Edge [4] estimated that phosphorus removal by precipitation increases sludge

production by about 10% to 25% compared with sludge that receives secondary treatment only.

In England, the water industry recognises significant cost advantages in recycling biosolids through agriculture compared with alternative more expensive disposal options such as landfill and incineration. Estimates (Antille [5] with 2007 figures) indicated that agricultural recycling costs wastewater companies approximately 150 GBP per tonne of raw sludge (dry solids) including finance and depreciation and that landfill and incineration are about 35% and 60% more expensive, respectively. The latter two disposal options are regarded as less sustainable practices [6], therefore, being increasingly restricted by environmental legislation [7] such as the EU Landfill Directive 99/31/EC [8]. Specifically for the NW region of England, the disposal strategy of wastewater operators is based upon a dual approach of recycling to

farmland and incineration representing, approximately, 70% and 30% of the total sludge production, respectively [5]. The relatively high reliance on recycling means that the agricultural route for disposal needs to be protected by maintaining, or where possible increasing, existing levels of biosolids uptake by farmers. However, this presents wastewater companies with a number of challenges, such as those indicated in earlier studies for example, [9–11], which combine to restrain the agricultural route as well as the opportunities to increase recycling targets in the longer term. One possible way to increase recycling levels is by improving the quality of biosolids which can significantly minimise environmental concerns, enhance their agronomic performance, and therefore secure the agricultural route [5, 12]. The focus on product quality, needed for increased acceptance of biosolids, requires a cultural shift within wastewater management companies.

The need to increase agricultural production to sustain a growing population requires the development of sustainable technologies to ensure that food supply is not affected [13, 14]. In the UK, some of the challenges associated with food security, sustainability, and health are being addressed following the launch of the Food Strategy 2030 [15]. Dawson and Hilton [16] recognised that increased food production will bring about increased demand for mineral fertilisers. A more stable fertiliser demand may be achieved by improving the efficiency of nutrient management from organic materials recycled to land, combined with increased levels of recycling of these materials. Fischer et al. [17] acknowledged that there is a synergism amongst sustainable technologies which enables achieving not only greater yields but also greater resource efficiency.

Technology is available for the production of organomineral fertilisers (OMF) which can be obtained by coating biosolids granules with urea (46% N) and potash (60% K_2O) to provide a balanced compound fertiliser with suitable physical characteristics [5, 18]. This product concept appears to be a sustainable approach to recycling biosolids to agriculture, and it aims to increase current levels of uptake by farmers by offering an enhanced organic-based fertiliser material. The coating technology used in the production of OMF enables the concentration of nutrients in the granules to be adjusted to meet specific soil-crop requirements [5, 18]. The development of such product requires evaluation at the field-scale to determine if the perceived agronomic, environmental, and economic benefits can be effectively delivered.

The aim of this work was to assess the agronomic efficiency and the effects on selected soil chemical properties, especially those related to potential build-up of soil P, of two organomineral fertilisers (OMF) which were applied to a grass crop (*Lolium perenne* L.) in a field-scale trial during 2009 and 2010. The OMF are referred to as OMF₁₀ and OMF₁₅, and have N:P₂O₅:K₂O compositions 15:4:4 and 10:4:4 respectively, [5, 18]. It was hypothesised that: (1) DMV of the grass crop amended with OMF would be comparable to that of urea but higher than biosolids-treated crop and (2) soil P levels would not change significantly as a result of OMF application and therefore soil P Index would remain close to constant. The results reported in this study

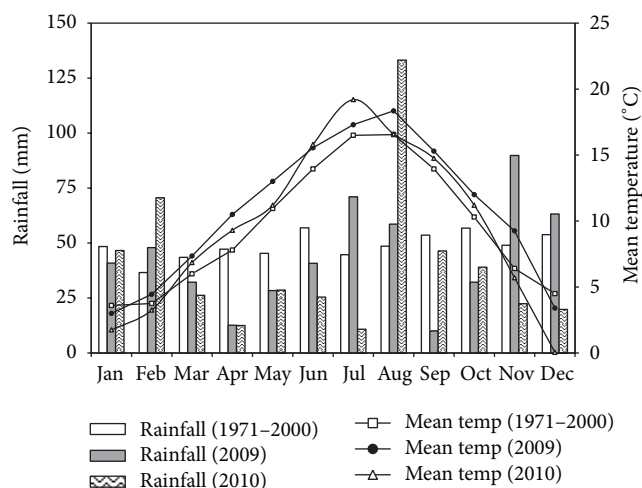


FIGURE 1: Rainfall and temperature records for Silsoe, Bedfordshire, UK [19].

aided the development of a set of practical recommendations concerning the use of OMF in grass crops.

2. Materials and Methods

2.1. Experimental Site. An experimental site was established at Cranfield University, Silsoe (52°00'19" N, 0°25'36" W) located in Bedfordshire, England, in February 2009. The site had been occupied by a first (2006–2007) and a second (2007–2008) winter wheat (*Triticum aestivum* L.) crops prior to the start of the experiment. The meteorological records for the site are shown in Figure 1 [19].

The soil type within the field is a *Cottenham series* sandy loam [20] which has 67% sand, 13% clay, and 20% silt [21]. The soil is well drained with a gentle slope (<1%). Field capacity determined at 0.05 bar reported a moisture content equivalent to 26.6% (w w⁻¹) [21]. The mean annual rainfall recorded for the period 2009 to 2010 was 505 mm, about 15% lower compared to historic records (from 1971 to 2000) [19]. Air temperatures in the spring and summer of 2009 and 2010 were above the historic average. Smith and Trafford [22] reported that Area 28 (Cambridgeshire and Bedfordshire, England) is characterised by a mean excess winter rain of 130 mm which allows the soil to return to field capacity around 10 December. This soil condition ends around 27 March but usually not later than 19 April. Mean soil moisture deficits of up to 85 mm and 103 mm typically occurring at the end of June, and at the end of July respectively [22]. The experimental site was marked out to comprise 60 plots (plot dimensions: 2 m × 5 m) which were georeferenced using a Leica ATX-1230 Smart Rover apparatus to facilitate their repositioning in subsequent years.

2.2. Grass Crop. The grass crop was drilled on March 30, 2009 at a rate of 1.5 kg of seeds per ha and emergence recorded on April 11, 2009. A commercially available grass mix (15% Molisto, 30% Gandalf, 30% Premium, and 25% Fornax) of

perennial ryegrass (*Lolium perenne* L.) was used. Broadleaves weeds were chemically controlled in postemergence with a conventional herbicide following standard farm practices. The grass was harvested manually using a 0.5 m² quadrat which was placed approximately in the center of the plots and the grass was cut at 20 mm above the soil surface three times in 2009 (14 July, 25 August and 21 October) and two times in 2010 (17 April and 20 June). The harvested plant material was oven-dried at 60 degrees Celsius for 48 hours [23] to determine dry matter yield (DMY) which is reported in kg of dry matter (DM) per hectare. After each harvest, the entire experimental site was mechanically cut to about the same height (20 mm) to ensure that the regrowth of the grass sward was uniform both in and between plots.

Yield-to-nitrogen response curves were examined by applying nonlinear regression analyses [24]. Quadratic functions (1) were fitted to the data from which the maximum (2) and the optimum (3) dry matter yields were derived [25]. Consider

$$y = a + bx - cx^2, \quad (1)$$

where a , b , and c are regression coefficients, “ x ” is the nitrogen application rate, and “ y ” is dry matter yield (DMY). Consider

$$\text{DMY}_{\max} \left(\frac{dy}{dx} = 0 \right), \quad (2)$$

$$\text{DMY}_{10} \left(\frac{dy}{dx} = 10 \right), \quad (3)$$

where DMY_{\max} and DMY_{10} are the maximum and the optimum dry matter yields (kg ha⁻¹), respectively. DMY_{\max} is equivalent to the potential harvestable yield given the climatic and soil condition, and subjected to the particular crop and fertiliser management practices [25]. DMY_{10} is the yield at which the response of the grass crop equates to 10 kg of DM per kg of N added. The nitrogen application rates (kg ha⁻¹) required for DMY_{\max} and DMY_{10} are N_{\max} and N_{10} , respectively.

The agronomic efficiency of the N applied with the fertilisers (4) was obtained using the difference method [26, 27]. This parameter was calculated for the optimum dry matter yield (DMY_{10}) and the corresponding N application rate (N_{10}), and it is reported in kg of DM per kg of N. Consider

$$\text{Agronomic efficiency} = \frac{\text{DMY}_{10} - \text{DMY}_{\text{Control}}}{N_{10}}, \quad (4)$$

where $\text{DMY}_{\text{Control}}$ is the mean dry matter yield corresponding to the unfertilised control.

2.3. Fertiliser Treatments. The experiment was subjected to the following treatments: two organomineral fertilisers (OMF), referred to as OMF₁₅ (15 : 4 : 4) and OMF₁₀ (10 : 4 : 4) [5, 18], were compared with a mineral fertiliser (urea, 46% N) and biosolids granules; the latter material had the following N : P₂O₅ : K₂O compositions: 4 : 6.6 : 0.1 and 5.5 : 4.3 : 0.2 for the batches corresponding to 2009 and 2010, respectively

[5, 18]. The fertilisers materials were hand-applied in a single dressing at rates ranging from 0 (control) to 250 kg ha⁻¹ of N at regular increments of 50 kg ha⁻¹ of N. There were two fertiliser applications which were conducted on June 10, 2009 and April 18, 2010, respectively. In 2010, the fertiliser application was conducted after the first cut of the grass to assess residual effects of OMF-N and biosolids-N on DMY up to this cut. This was justified given the relatively slow mineralisation rate of the organic-N fraction contained in OMF and biosolids granules [21]. Under the UK conditions, mineralisation of biosolids-N and organic OMF-N is likely to continue well after the harvest of winter cereal crops when these materials are applied in early spring [21]. Therefore, N carried over into the autumn and winter, if not lost by leaching or gaseous evolution, can influence DMY levels in the first cut the following year which needed to be assessed.

2.4. Soil Analyses. Soil was sampled to a depth of 150 mm [28] and analysed using standard laboratory techniques. Soil sampling was conducted prior to the start of the experiment to determine background levels and routinely thereafter. The following analyses were conducted: total N in soil [29], soil extractable P [30, 31], soil exchangeable K [23] (Method no.: 63), soil pH [23] (Method no.: 32), soil organic matter (SOM) [23] (Method no.: 56), and soil mineral N (SMN) [23] (Method no.: 53). For soil exchangeable K, analyses were conducted for the control (zero fertiliser) and the treatments that received 150 and 250 kg ha⁻¹ of N. Analyses of soil extractable P and exchangeable K enabled examining changes in soil P and K Indexes, respectively, that occurred as a result of the fertiliser treatment. Soil P and K Indexes are defined in DEFRA [28] and analytical values are expressed in mg L⁻¹. A soil bulk density value of 1.34 g cm⁻³ was used to convert from mg L⁻¹ to mg kg⁻¹ [21].

2.5. Statistical Analyses. Statistical analyses were undertaken using GenStat 14th Edition [32]. For dry matter yield (DMY), analyses involved ANOVA and LSD test ($P < 0.05$). For the measured soil chemical properties, analyses involved repeated measurement of analysis of variance ($P < 0.05$) which enabled factoring in the effect of the time. The experiment used a completely randomised design, and all treatments were replicated three times ($n = 3$) except for the controls (zero fertiliser) and the plots treated with 250 kg ha⁻¹ of N which were replicated four ($n = 4$) and two ($n = 2$) times, respectively. This arrangement enabled fitting all plots within the designated experimental area and minimising the interference with the surrounding commercial crop in the field.

3. Results and Discussion

3.1. Dry Matter Yield and Crop Responses. Figure 2 shows dry matter yields (DMY) of the grass crop as affected by fertiliser treatment in 2009 and 2010, respectively. In both years, there were significant differences in total (annual) DMY between the control and the treatments ($P < 0.001$). The differences in DMY were significant with respect to the

fertiliser type and the N application rate (P values < 0.001). The interaction fertiliser type \times N application rate was not significant (P values > 0.05). On average across all treatments, the application of fertiliser increased DMY by about 80% in 2009 and approximately three times in 2010 compared with the controls. There was a positive response of DMY to the concentration of N in the fertiliser material, in particular, the concentration of readily available N. The first cut conducted in 2010 resulted in DMY levels in the range of 680 to 920 kg ha⁻¹ of DM across all treatments which were not significantly different for an LSD value (5% level) of 388 kg ha⁻¹ of DM. These results confirmed that the residual effect of the fertiliser applied in the previous year was relatively small and of similar magnitude across all treatments. Hence, it is possible to suggest that losses of N via leaching or gaseous evolution from fertiliser-treated plots had occurred following the third cut in 2009.

The functions used to describe the responses of the grass crop to the application of N showed acceptable fits to quadratic models, and the terms derived from these responses produced reasonable solutions (Table 1). Linear relationships were also possible since the estimates of parameters were significant (P values < 0.05) for the linear term in all cases. The responses of the grass crop to the application of biosolids did not produce a significant effect for the square term of the quadratic function which was observed in both years (P values > 0.05). Hence, the dry matter yield-to-nitrogen response curve for biosolids may be better explained by a linear function instead. However, since the coefficients of the square term were negative, there was an indication that, under the prevailing experimental conditions, DMY started to decline above certain level of N fertilisation. Therefore, the use quadratic functions to describe these responses may be justified which also enabled deriving the maximum (DMY_{max}) and the optimum dry matter yields (DMY₁₀) respectively.

The responses to the application of OMF₁₀, OMF₁₅, and urea showed average increments in DM (range of 21 to 31 kg DM kg⁻¹ N) which were within the range (14 to 29 kg DM kg⁻¹ N) reported by Morrison [25] but exceeded those encountered by McFeely and MacCarthy [33] and O'Donovan et al. [34] (range of 5 to 17 kg DM kg⁻¹ N). The responses obtained were related to the concentration of readily available N in the fertiliser. Biosolids showed average increments in DM per additional unit of N which were between 16% and 30% lower than OMF or urea. Differences between fertilisers were smaller in 2010 which responded to the combined effect of drier soil conditions in the early part of the spring (Figure 1) and the surface application of the fertilisers. This effect was observed despite that the timing of fertiliser application matched, approximately, the expected peak of growth of the grass crop which under the UK conditions typically occurs around May [35]. The relatively dry and warm conditions recorded in April 2010 (Figure 1) support the possibility of N losses by volatilisation of NH₃ after the fertiliser application. For urea-containing fertilisers, these losses are enhanced at higher N application rates or with increased temperature (range of 10°C to 30°C) [36].

The values of N_{max} obtained for biosolids granules (Table 1) should be treated with caution as they resulted from extrapolating data that falls outside the range of N application rates used in this study, that is, from 0 to 250 kg ha⁻¹ of N. These N_{max} values however reflect the linearity of the responses of the grass treated with biosolids granules. In 2010, the grass treated with OMF₁₅ marginally outperformed that treated with urea, but differences between the two fertiliser sources were not significant (LSD 5% level = 525 kg ha⁻¹ of DM). The same was observed for the other parameters derived from the response curves as OMF₁₅-treated grass required slightly less N for both maximum (DMY_{max}) and optimum (DMY₁₀) yields. This was due to weather conditions recorded in the early part of the spring in 2010 (Figure 1), especially, the lack of rainfall during April which accounted for a total of 8.2 mm [19].

The N₁₀ values showed in Table 1 indicate the N application rates above which the response of the grass crop is less than 10 kg ha⁻¹ of dry matter. This value is considered to be an adequate lower limit of response from the agronomic and environmental perspectives [25]. For all fertiliser types, the calculated values of N₁₀ were approximately within the range of N application rates recommended for grass (cut) in England [28] in situations with moderate to high soil N supply. These N₁₀ values are also in close agreement with those obtained by Morrison et al. [25] (range of 183 to 300 kg ha⁻¹ of N) for more than 20 experimental sites scattered across England and Wales. In situations where soil N supply is low or where more than three cuts are performed during the main growing season (April to September), the use of a straight N source may be recommended after the second cut. Based on the general guidelines given for England in RB209 [28], N application rates for individual cuts should not exceed 120 kg ha⁻¹. For OMF, this is an important consideration given that it contains urea which is prone to volatilisation at high N application rates [36]. For the first cut, which is typically the one that requires the highest N dressing (e.g., up to 120 kg ha⁻¹ of N), apply about 30% to 40% between the middle of February and early March with the balance in late March to early April allowing a minimum of six weeks before the cut. For subsequent cuts, N should be applied immediately after the previous cut but, because the N rates are usually lower than 120 kg ha⁻¹, the full dressing may be applied. Because of the characteristics patterns of growth of grass swards under the climatic conditions of the UK [35], this fertilisation strategy will maximise the response of the grass to the application of fertiliser-N, including OMF-N, and will minimise the opportunities for N losses to the environment [5, 28]. In 2009, the recommendations regarding the timing of fertiliser application could not be strictly followed because it was the year of grass establishment and emergence was recorded on 11 April.

For OMF₁₀ and OMF₁₅, an average input of about $0.8 \times N_{max}$ yielded $0.98 \times DMY_{max}$ which was similar to that of urea, whereas, for biosolids, a yield of $0.92 \times DMY_{max}$ required an input of $0.6 \times N_{max}$ but DMY was significantly lower ($P < 0.05$). The agronomic efficiencies of the fertilisers applied reflect an improved performance of the grass crop

TABLE 1: Parameters derived from the response of the grass crop to the application of fertiliser-N in 2009 and 2010.

Parameter	Mean DMY	SD	Response	P value	R ²	DMY _{max}	N _{max}	DMY ₁₀	N ₁₀	Agronomic efficiency
Unit	kg ha ⁻¹	kg ha ⁻¹	—	—	—	kg ha ⁻¹	kg ha ⁻¹	kg ha ⁻¹	kg ha ⁻¹	kg kg ⁻¹
Treatment	2009									
Control	6188 ^a	126	—	—	—	—	—	—	—	—
Biosolids	9285 ^b	1389	$y = 6406 + 24.6x - 0.03x^2$	<0.001	0.74	11986	455	11060	270	18.0
OMF ₁₀	11270 ^c	1330	$y = 6576 + 53.8x - 0.12x^2$	<0.001	0.87	12460	219	12255	180	33.7
OMF ₁₅	11958 ^d	1643	$y = 6547 + 56.9x - 0.11x^2$	<0.001	0.94	13798	255	13574	210	35.2
Urea	12230 ^d	1778	$y = 6586 + 60x - 0.12x^2$	<0.001	0.89	14027	248	13820	207	36.9
Treatment	2010									
Control	2192 ^a	204	—	—	—	—	—	—	—	—
Biosolids	5394 ^b	1287	$y = 2435 + 26.6x - 0.04x^2$	<0.001	0.78	7266	364	6581	227	14.1
OMF ₁₀	6624 ^c	1080	$y = 2532 + 46.9x - 0.11x^2$	<0.001	0.90	7651	218	7418	172	25.8
OMF ₁₅	7385 ^d	1266	$y = 2396 + 63.6x - 0.17x^2$	<0.001	0.92	8500	192	8348	162	32.1
Urea	7357 ^d	1240	$y = 2523 + 58.4x - 0.14x^2$	<0.001	0.90	8477	204	8302	170	30.4

Mean DMY is annual dry matter yield across all N application rates, and SD is the standard deviation. For mean DMY, different letters indicate values that are significantly different at a 95% confidence interval.

treated with OMF₁₀, OMF₁₅, and urea relative to that of biosolids granules as well as differences in their relative effectiveness between years. In the drier year (2010), the efficiency of biosolids N was affected by lower microbial activity which reduced the mineralisation rate of organic N in the material. For OMF and urea water shortages translated into greater N losses by volatilisation of NH₃, hence, reduced N availability to the grass crop and reduced N uptake [36] which is reflected in the relatively lower agronomic efficiencies obtained for these materials in the second year.

3.2. Soil Analyses

3.2.1. Nitrogen in Soil. The controls (zero fertiliser) did not show significant differences in total N in soil compared with the treatments at the end of the experiment ($P = 0.06$). However, there were significant differences ($P < 0.001$) both in the control plots and the treatments compared with the initial levels of total N in soil recorded at the start of the experiment (Figure 3). The effects of the fertiliser type or N application rate on total N in soil were not significant (P values > 0.05) which suggested that there was an effect of the grass crop that masked differences between control and treatments.

The increase in total N in the control plots compared with the initial level was attributed to restricted crop growth and therefore reduced N uptake in the absence of N fertilization and the effect of mulching which returned organic matter to the soil after each cut. The soil treated with biosolids reported relatively higher values compared with the control and the other treatments (Figure 3) but the overall effect of the fertiliser type was not significant ($P > 0.05$). However, analytical results suggested that differences in total N in soil between biosolids and the other fertiliser treatments would be greater in the longer term because of the slow mineralisation rate of organic biosolids-N [21]. Therefore, it is suggested that total N in soil is monitored when routine applications of biosolids

are conducted as part of the fertilisation plan as this will affect soil N supply in subsequent years and consequently fertiliser-N recommendations. Sylvester-Bradley [37] suggested that there is scope for reducing N fertilisation if soil N supply could be accurately predicted for the main growing season. However, its estimation based on soil mineral N (SMN) did not appear to be a reliable approach in this study since the overall differences between control and treatments were not significant ($P = 0.21$). There was an effect of the fertiliser type ($P = 0.02$) on SMN levels which was due to marginally higher values recorded in urea-treated plots compared with the other treatments. However, SMN values were generally low across all fertiliser treatments and rarely exceeding 5 mg kg⁻¹ as determined annually before the fertiliser application and after the last cut of the grass crop. The ample period of growth of the grass crop, hence N uptake, combined with a relatively slow mineralisation rate of organic-N in OMF and biosolids [21] explain the results obtained in this set of analyses.

3.2.2. Soil Extractable Phosphorus. The control and the treatments reported a soil P Index 5 which equates to Olsen's P in the range of 71 to 100 mg L⁻¹ [28]. Figure 4 shows that, overall, there were no significant differences in soil extractable P between the control and the treatments ($P = 0.92$) but there was a significant effect of the fertiliser type ($P = 0.01$). This effect was due to the relatively higher soil extractable P value recorded in biosolids-treated plots compared with those treated with OMF₁₀, OMF₁₅, and urea. The application of OMF did not change soil extractable P levels significantly compared with the unfertilised control plots; therefore, soil P Index remained unchanged.

The results showed that continuous application of biosolids granules will tend to build up soil extractable P levels, while the absence of P fertilisation in urea-treated grass will have the opposite effect (Figure 4). On the contrary, the application of OMF₁₀ and OMF₁₅ maintained soil P status

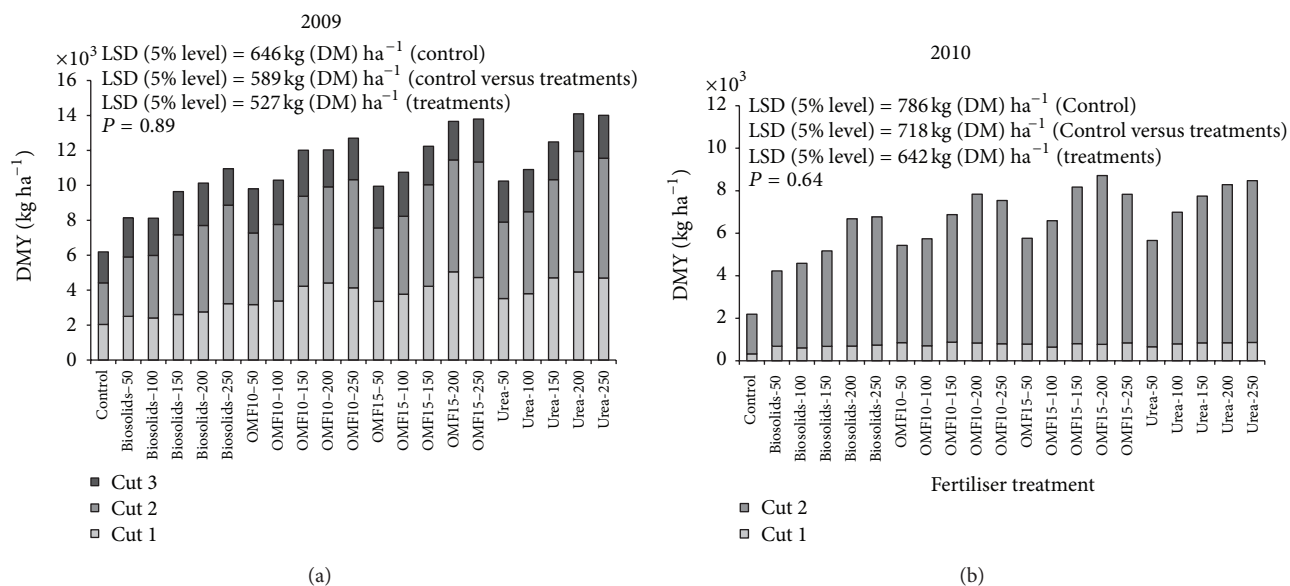


FIGURE 2: Dry matter yield (DMY) of the grass crop as affected by the fertiliser treatment in 2009 (a) and 2010 (b). The x-axis shows the fertiliser type followed by the corresponding N application rate in kg per ha. Use $n = 4$ (control) and $n = 3$ (treatments) except when $N = 250 \text{ kg ha}^{-1}$, $n = 2$.

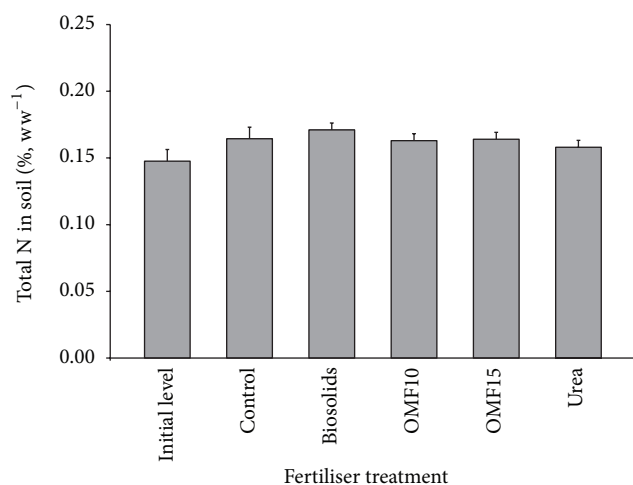


FIGURE 3: Mean total N in soil over the range of fertiliser application rates used in the experiment. The initial level corresponds to the baseline level prior to the start of the experiment. Use $n = 14$ except for initial level and control $n = 3$; $P = 0.06$ (control versus treatments), $P = 0.91$ (treatments). The error bars show the LSD value at 5% level.

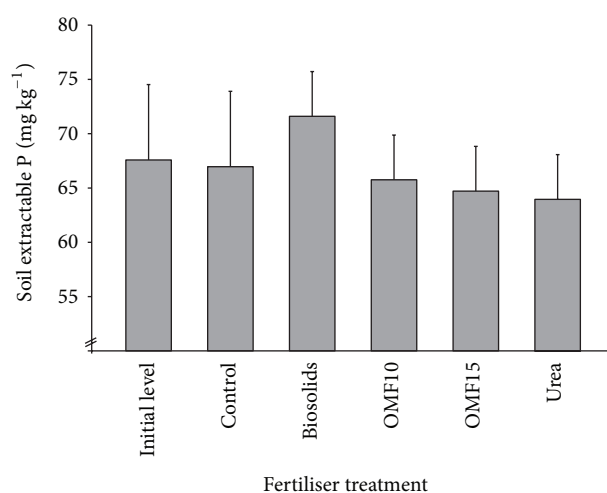


FIGURE 4: Mean soil extractable P over the range of fertiliser application rates used in the experiment. The initial level corresponds to the baseline level prior to the start of the experiment. Use $n = 14$ except for initial level and control $n = 3$; $P = 0.92$ (control versus treatments), $P = 0.01$ (treatments). The error bars show the LSD value at 5% level.

close to constant which therefore supports the reasons for the proposed OMF formulations [5, 18]. The importance of these results strives for the need to ensure that soil extractable P is not increased in those soils which have satisfactory P levels, as defined in DEFRA [28] but that their overall fertility is maintained. The results obtained with biosolids reflected the issue of potential build-up of soil P when materials with low N : P ratio (≈ 1) are applied based on the N requirements of the crop. They also highlight one of the limitations being faced

by wastewater operators in England, especially in the NW region, regarding the application of biosolids in agricultural land which has satisfactory soil P Indexes [28, 38]. The conversion of sludge into balanced organomineral fertilisers has therefore potential to address this issue and increase recycling targets in areas close to production sites.

The small decline in soil extractable P in urea-treated plots also responded to the relatively higher DMY obtained with this fertiliser (Table 1) which resulted in enhanced

P removal. In soils with adequate P and K Indexes [28], avoidance of P and K fertilisation may not affect DMY of grass crops in the short term [39]. However, the long-term experiments at Rothamsted in the UK [40] showed that continuous omission of P and K application causes reduction in crop yield when the available soil P and K reserves have declined below a critical level appropriate for the soil and crop system [39]. Below this level, and due to nutrient interactions, N use efficiency in grassland soils is significantly affected which has adverse effects both from the economic and environmental perspectives [39, 41, 42]. Since the availability of biosolids-N is low [21], DMY and P uptake in biosolids-treated crop were restricted by N supply which contributed to maintaining relatively higher concentrations of P in the soil solution compared with the other treatments.

Application of OMF-N at rates equivalent to N_{10} should not increase soil P Index as the calculated N_{10} rates are lower than the highest N application rate (250 kg ha^{-1} of N) used in this study, which did not result in significant changes in soil P status. On the contrary, the application of OMF at the optimum rate will replenish, approximately, P off-take by the crop thereby maintaining soil P levels close to constant over time. Previous studies with OMF under controlled glasshouse conditions [5] showed that P uptake in OMF-treated grass was greater ($P < 0.05$) than that of biosolids granules. The enhanced uptake of P with the use of a fertiliser material with higher readily available N content was due to the positive interaction that exists between the two plant nutrients [43]. Reduced P uptake in biosolids-treated grass led to a significant change (increase) in soil extractable P after three years [5]. For OMF-treated grass, the same study showed that soil extractable P levels were not modified significantly ($P > 0.05$) which agrees with the results presented in this article. This occurred despite of the relatively low bioavailability of P contained in OMF [21]. The application of P with OMF replenishes the less readily available and the very slowly available soil P pools which overtime are released to the readily available pool and the soil solution, that is, the two fractions measured in routine soil analyses [30, 31, 44]. This process enables restoring soil extractable P levels that had been temporarily diminished as a result of P uptake by the crop.

Analyses of soil pH showed that there were no significant differences between control and treatments and that there was no effect of the fertiliser type, the application rate, or the interaction fertiliser rate \times fertiliser type (P values > 0.05). Therefore, changes in soil extractable P cannot be explained by differences in soil pH between fertiliser treatments. Soil organic matter was also measured but there were no significant differences between control and treatments ($P = 0.82$).

3.2.3. Soil Exchangeable Potassium. Overall, there were significant differences in soil exchangeable K between control and treatments ($P = 0.04$), and there was a significant effect of the fertiliser type ($P = 0.02$). All fertiliser treatments showed a small decline in soil K Index from 3, as recorded for the control at the start of the experiment, to 2+ [28]. The decline

in soil exchangeable K occurred to a greater extent in urea-treated plots which showed a relatively lower value (153 mg kg^{-1}) compared with the control (201 mg kg^{-1}). OMF₁₀ and OMF₁₅ showed intermediate levels of soil exchangeable K (166 and 168 mg kg^{-1} , resp.) between the control and the plots treated with biosolids granules (180 mg kg^{-1}). There was no effect of the fertiliser application rate ($P = 0.06$) but soil exchangeable K decreased approximately 10% more in plots that received 250 kg ha^{-1} of N compared to those at 150 kg ha^{-1} of N. These results explain differences in K uptake by the grass crop as a result of the fertiliser treatment and reflect the positive interaction that exists between nitrogen and potassium [41]. A higher N application rate combined with increased N availability in the fertiliser applied (e.g., urea at 250 kg ha^{-1} of N) enhanced biomass production and K uptake; hence, soil exchangeable K recorded a lower value in the analyses. The above is possible because of the satisfactory soil K Index observed at the start of the experiment.

For OMF-treated grass, the supply of K with the fertiliser offsets, to a greater extent than urea, the decline in soil exchangeable K despite the relatively high DMY levels observed (Table 1). The soil application of K with biosolids was negligible given its low concentration in the material [5, 18]. However, DMY was restricted by the availability of N contained in the biosolids; hence, K uptake was reduced and the levels detected in the soil analyses remained closer to the initial values. The same mechanism of reduced uptake holds true for the unfertilised (control) grass crop. The trends observed in soil exchangeable K levels that resulted from the fertiliser treatment may be monitored in the longer term. Because the efficiency of applied fertiliser N is significantly affected by the availability of soil K, this becomes an important consideration in situations where crop management practices do not include applications of K fertilisers [39].

4. Conclusions

The OMF₁₀ and OMF₁₅ formulations are suitable for application in grass crops. Agronomic efficiency calculations demonstrated the improved performance of the grass crop treated with OMF compared with biosolids granules and showed that they were comparable to those of the grass treated with a straight N source. This means that the efficiency of nutrient uptake from applied OMF is comparable to that of a mineral N fertiliser despite the organic nature of the material. The response curves to the application of OMF-N showed average increments in dry matter which were approximately within the range reported in the literature for straight N fertilisers. The optimum N application rates with OMF were within 10% difference compared with urea and consistently lower than biosolids. This has implications from the economic and environmental perspectives in regards to the cost of field spreading and the N load on the environment.

The suggested fertilisation strategy should not induce significant changes in soil extractable P levels; hence, soil P Index should not be affected. End users such as farmers will find that OMF has a demonstrable advantage compared with biosolids when the materials are applied on soils which have

satisfactory P levels. The wastewater industry will be able to convert sludge into balanced fertilisers that has potential to meet long-term recycling targets in areas close to production. Therefore, the conversion of biosolids into nutrient-balanced organomineral fertilisers offers an opportunity for improved resource efficiency to deliver some of the agronomic, economic, and environmental benefits associated with recycling.

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Research Article

Availability and Plant Uptake of Biosolid-Borne Metals

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Metal uptake by different plant species was quantified in sand media amended with biosolids in a sand-culture hydroponic medium. In a previous paper (Koo et al. 2006), we concluded that total quantities of organic acids were greatest in treatments containing both plants and biosolids, with lesser amounts in treatments with plants alone, biosolids-treated media alone, and a nutrient solution-irrigated blank medium. Biosolids enhanced organic acid production in the rhizosphere. The purpose of this study was to evaluate how organic acids in root exudates affect the absorption of metals by selected plants. We found that the concentrations of metals in the plant tissue grown on biosolids-treated medium were always higher than that from the standard medium, irrespective of species and cultivar. The amount of metal transferred from the biosolids-treated medium to the plant varied with the metal element, following the order: Cd > Ni = Zn > Cu > Pb > Cr. Interspecies and cultivar differences in metal uptake were trivial compared to differences induced by the treatment. The metal uptake decreased with the growth period, and the kinetics of metal uptake, as indicated by accumulation in corn shoots, were essentially a first order during the initial 4 weeks of growth, especially for Cd and Zn.

1. Introduction

The chemical and biological reactions occurring in the soil-root interface play an important role in the availability of metals to plants [1]. Metal uptake by plants depends on both edaphic and plant factors. Edaphic factors include metal concentration in soil, interactions of metal with the soil (solid) surfaces, and the pH at the root-soil interface. Plant roots may change the physical, chemical, and biological conditions of the soil immediately adjacent to the root, commonly referred to as the rhizosphere. The rhizosphere, in comparison to bulk soil, is enriched with organic substances of plant and microbial origin. They include organic acids, sugars, amino acids, lipids, coumarins, flavonoids, proteins, enzymes, aliphatics, aromatics, and carbohydrates [2–6]. Among them, the organic acids are the most abundant and highly chemically reactive with soil constituents. The commonly found organic acids in the rhizosphere are acetic, butyric, citric, fumaric, lactic, malic, malonic, oxalic, propionic, tartaric, and succinic acids [5, 7–9]. In soils, organic acids are involved in biogeochemical processes that release the not-so-readily available

nutrients such as phosphorus, iron, and other micronutrients for plant nutrition [10–12].

Organic acids in the rhizosphere affect the translocation of metal elements in soil [13–15]. They influence the acidification, metal chelation, precipitation, and oxidation-reduction reactions in the rhizosphere. Thus, they influence the solubility and plant uptake of metals, the dynamics of microbial activity, rhizosphere physical properties, and root morphology. There is increasing evidence that root exudates increase the solubility of metals in the rhizosphere. Linehan et al. [16] reported that concentrations of Cu, Zn, Mn, and Co in soil solution increased when plants were present. Morel et al. [17] and Mench et al. [18, 19] showed that corn root exudates, for example, were capable of binding Cd in soil.

In land application of biosolid, metals are added into the soil mainly associated with solid particles. In this case, plant absorption of biosolids-borne metals may take place through root extraction from those present in bulk soil solution via solid-solution phase equilibration or at the rhizosphere and soil interface where root exudates mobilize the solid phase metals. Considering that metal concentrations in the soil

solution are typically low and dissolution kinetics for metals in soils are also commonly slow, metal absorption from the bulk soil solution may not be the most predominant process by which metals are taken up by plants grown in biosolids-treated soils. Accordingly, Eaton [20] reported that plants grown in sand nutrient culture obtained Fe and P from water-insoluble minerals by absorption across the particle-root interface rather than by absorption directly from the culture or soil solution. Mench and Martin [21] found that soil Cd, Cu, Fe, Mn, Ni, and Zn were solubilized and therefore facilitated their uptake by root exudates of *Nicotiana tabacum*, *N. rustica*, and *Zea mays*. They also reported that Cd concentrations in these plant species were proportional to the amounts of Cd extracted from the soil in which they were grown. Likewise, Krishnamurti et al. [22] demonstrated that soil Cd was mobilized by low-molecular-weight organic acids such as acetic, citric, oxalic, fumaric, and succinic acids often found in root exudates. At the same concentration, they found that Cd released from the soil by organic acids followed the order: fumaric > citric > oxalic > acetic > succinic.

As plants develop and roots grow in soil, biogeochemical reactions are dynamically changing. These changes, in turn, may affect the availability of metals in the growth medium and their subsequent uptake by plant. For example, Koo et al. [5] demonstrated that the nature and diversity of organic acids from root exudates were affected by the growth stage of the plant. Since organic acids are known to influence the mobility of metals in soil, the purpose of this study is to elucidate how the length of plant growing period, plant species, and cultivars affect the availability of metals to plants grown on biosolids-treated medium.

2. Materials and Methods

2.1. Culture Medium, Nutrient Solution, and Statistical Analyses. Experiments were conducted in a glasshouse in which corn plants (*Zea mays* L.) were cultured on a sand medium irrigated with a nutrient solution and on biosolids-treated sand media that were irrigated with the same nutrient media minus trace metals (Zn, Cu, Mn, and Ni). Plants were cultivated under septic conditions, and no attempt was made to control the microbial population in the culture media.

Each hydroponic-culture unit consisted of a reservoir containing 100 liters of nutrient solution that supported four 10-liter size plastic pots on the cover plate of the nutrient solution reservoir. Each plastic pot had a standpipe to control the water level and prevent overflow during irrigation and perforations at the bottom for gravity drainage back into the nutrient solution reservoir. Pots in the same treatment level received separate biosolid treatment and were irrigated with the common irrigation solution. A biosolid compost produced by the Metropolitan Wastewater Reclamation District of Greater Chicago in 1975 was air dried and used at a rate equivalent to 20 Mg ha⁻¹ in all experiments. This biosolid has been a reference material for multiple state and year studies in the past [23], and it has considerably higher metal contents than the contemporary biosolids. For the phosphate rock treatment, the amendment in powder form was incorporated at the equivalent rate of 150 kg P ha⁻¹. The total C and N content

of this biosolid was 8.9% and 0.8%, respectively. The concentrations of selected metals (mg kg⁻¹ dw) in this compost are as follows: As, 23 ± 1; Cd, 119 ± 12; Cr, 1, 556 ± 202; Cu, 767 ± 92; Ni, 482 ± 31; Pb, 1, 344 ± 40; Se, 2.8 ± 0.3; and Zn, 4, 390 ± 274. All of the biosolids were air dried and screened to pass a 2 mm sieve prior to use. The added biosolids amendments were mixed with the top two-thirds of the sand in each pot, leaving the bottom one-third as a buffer to prevent the amendments from being washed into the nutrient solution reservoir. An automated watering system was set up so that the nutrient solution was pumped from the reservoir at preset time intervals to irrigate plants growing on the sand medium 5 times per day. After irrigation, excess nutrient solution drained into the reservoir by gravity. The stored nutrient solution was continuously aerated.

A modified Hoagland solution was used as the standard nutrient solution (in mM): 2.0 Ca (NO₃)₂, 2.0 KCl, 0.5 MgSO₄, 0.1 NaCl, 1.0 C₆H₁₃NSO₄ buffer, 0.2 NaH₂PO₄, 0.012 Zn as ZnCl₂, 0.15 Fe as Fe (NO₃)₃, 0.006 Mn as MnCl₂, 0.002 Cu as CuCl₂, 0.0001 Ni, 0.01 H₃BO₃, and 0.0001 Na₂MoO₄ [24, 25]. Amounts of ethylenediaminetetra acetic acid (HEEDTA) were added to match trace element nutrient solution concentrations. For the biosolid treatment, Zn, Mn, Cu, and Ni along with HEEDTA were withheld from the nutrient solution as the biosolids contained significant amounts of trace elements. The pH of the nutrient solution was checked routinely and maintained at pH 6 with HCl and NaOH. During the course of growth, the nutrient levels in the reservoir were checked and replenished biweekly during the first 4 weeks, weekly during the period between 4 and 8 weeks, and twice per week for the remainder of the growing period.

The experiments were set up in blocks. Within each block, it followed the factorial design, with biosolid treatments (nutrient solution versus nutrient solution + biosolids) and plants (blank versus planted) as the factors. The four pots in each treatment combination received separate biosolid treatments and irrigated with the modified Hoagland nutrient solution, from a common reservoir, that represents the controlled condition. These four pots are replicates in terms of the biosolid treatments. For the experiment, each tank was sampled at a given date that represented a treatment level, and the four pots represented four observations made with this treatment level. Student's *t*-tests were used to differentiate the difference between the control and the treatment. When the differences with respect to time were considered at the end of the experiment, the data of each treatment was treated as a one-way analysis of variance (ANOVA) and the time was treated as the incremental treatment levels. Tukey's multiple range test determined whether the treatment, were significantly different from one another. Similar approaches were employed to analyze data of the second experiment in which each biosolid was a separate treatment. The outcomes of each biosolid were compared with the control using Student's *t*-test. Again, the differences with respect to time for each treatment were tested using one-way ANOVA.

2.1.1. Plant Species Used. Depending on the experiment, corn (*Zea mays* L.), durum wheat (*Triticum turgidum* L.), rape (*Brassica napus* L.), Sudan grass (*Sorghum sudanense* L.),

chickpea (*Cicer arietinum* L.), and Swiss chard (*Beta vulgaris* L.) were grown on the three different sand media. Seeds were placed on moist germination towels, rolled up, and incubated in a growth chamber. Following germination, the towels were unwrapped and the root length of each seedling was measured. Seedlings with approximately the same root length were selected for planting; 3–5 day old seedlings were transferred to pots and root exudates were collected at preset times following planting. At each sampling date, plants were removed from the sand culture system for root exudate and plant tissue collection.

2.2. Biomass and Plant Tissue Samples. At the time of harvesting, plants were removed from the pots, separated into shoot and root portion, rinsed with deionized water, dried to constant weight at 65°C for 5 days, and weighed for biomass determination. For metal analysis using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and Atomic Absorption Spectrophotometry (AAS), aliquots of plant tissue were digested in Teflon Parr bombs by a HNO₃ microwave digestion procedure (0.25 g dried tissue with a mixture of 2.0 mL concentrated HNO₃ + 2.0 mL H₂O₂ + 1.0 mL H₂O in a 120 mL Teflon digestion vessel for 15 minutes and with maximum pressure of 1,037 kPa) [26].

3. Results and Discussion

3.1. Plant Uptake of Biosolid-Borne Metals

3.1.1. Metal Uptake by Corn Grown on Biosolid-Treated Medium. When corn plants were grown from seed to maturity on the sand medium without biosolids and biosolids-treated medium, metal concentrations in the root were considerably higher than those in shoot (Table 1). Plants grown on biosolids-treated medium had significantly higher concentrations of metals than those grown on the sand medium without biosolids at all stages of growth. In plant tissue, accumulations of Cd (in shoots and roots) and Ni (in roots) were especially high for plants that received the biosolids treatment. Except for Cd in shoots and roots of plants grown on biosolids-treated medium and Zn in shoots and roots of plants grown on the sand medium without biosolids and in roots of plants grown on biosolids-treated medium, there was a trend for metal concentration in the plant tissue to decrease with the length of growing period (Table 1). This decrease is an indication of mass dilution when metal availability in the nutrient medium did not keep pace with the rate of biomass accumulation. For metals that were either not readily available to the plant (such as Pb or Cr) or present only in limited amounts (such as Cd in the sand medium without biosolids), the amount of metals absorbed appeared to be limited by their supply in the nutrient medium. However, for metals that were in chemical forms readily available to plants and in abundant supply in the nutrient medium (such as Cd in biosolids-treated medium or Zn in both sand medium without biosolids and biosolids-treated medium), the metal concentration of plant tissue either continued to rise with plant growth (such as Zn in shoots of corn grown on both the sand medium

TABLE 1: Metal concentrations (means \pm SD where $n = 4$) of corn tissues grown on sand media amended, without biosolids (Standard) and with biosolids[†].

Plant tissue	Treatment	Time (weeks)	
		0–4	4–16
		mg kg ⁻¹	
Cd			
Shoot	Standard	0.38 (0.04) ^a	0.03 (0.004) ^b
	Biosolids	7.25 (1.27) ^b	9.50 (1.09) ^a
Root	Standard	1.85 (0.31) ^a	0.20 (0.02) ^b
	Biosolids	36.5 (4.06) ^b	60.7 (2.82) ^a
Cr			
Shoot	Standard	1.20 (0.11) ^a	0.83 (0.03) ^b
	Biosolids	2.70 (0.49) ^a	1.43 (0.06) ^b
Root	Standard	1.80 (0.14) ^a	1.17 (0.07) ^b
	Biosolids	13.5 (0.84) ^a	6.00 (1.42) ^b
Cu			
Shoot	Standard	12.0 (0.55) ^a	6.67 (0.13) ^b
	Biosolids	17.0 (0.55) ^a	12.7 (0.80) ^b
Root	Standard	22.0 (1.45) ^a	18.3 (1.20) ^b
	Biosolids	63.5 (6.70) ^a	40.3 (3.97) ^b
Ni			
Shoot	Standard	14.5 (0.90) ^a	9.00 (0.57) ^b
	Biosolids	44.0 (4.65) ^a	23.3 (2.01) ^b
Root	Standard	19.5 (2.15) ^a	12.7 (0.60) ^b
	Biosolids	276 (49.5) ^a	149 (41.7) ^b
Pb			
Shoot	Standard	5.50 (0.65) ^a	3.33 (0.27) ^b
	Biosolids	13.5 (1.01) ^a	9.33 (0.71) ^b
Root	Standard	5.50 (0.65) ^a	2.33 (0.37) ^b
	Biosolids	27.1 (1.95) ^a	11.1 (0.27) ^b
Zn			
Shoot	Standard	30.0 (1.15) ^b	39.3 (0.73) ^a
	Biosolids	161 (9.50) ^b	295 (9.67) ^a
Root	Standard	58.5 (2.00) ^b	120 (5.00) ^a
	Biosolids	211 (15.5) ^a	158 (3.67) ^b

[†]The differences of metal concentrations among the growth periods were tested by one-way ANOVA and Student-Newman-Keuls test. Within a row and between shoot and root, values followed by different letters were significantly different at $P < 0.05$.

without biosolids and biosolids-treated medium and in root of the sand medium without biosolids) or remained at the same level throughout the growing period (such as Zn in root of corn grown on biosolids-treated medium). For example, Zn in shoots and roots of corn grown on the sand medium without biosolids and in the shoot of the biosolids-treated medium increased with time following planting. Zinc concentrations in the roots of corn grown on biosolids-treated medium, however, either remained the same or decreased slightly with time following planting (Table 1).

The amounts of metal transferred from the biosolids-treated medium to the corn varied with the metal elements.

Based on the mass of metals that was present in the plant growth medium and absorbed by corn, the percentage of the biosolids-borne metals in the rhizosphere that was absorbed by corn was calculated (Figure 1). They were indicators of the phytoavailability of biosolids-borne metals and followed the order: $\text{Cd} > \text{Ni} = \text{Zn} > \text{Cu} > \text{Pb} > \text{Cr}$. For corn seedlings grown to maturity on biosolids-treated medium, the amounts of metals absorbed by the plants were 14.2, 0.01, 1.63, 9.77, 1.36, and 8.60% of total Cd, Cr, Cu, Ni, Pb, and Zn in the rhizosphere, respectively. In the root environment, mucigel was reported to be an accumulation site for heavy metals [6, 27]. Mucigel can modify the flux of metal cations to the root. Due to the viscous nature of this compound, diffusion of metals can probably be hindered. Furthermore, because of complexing reactions, diffusion of metals (such as Pb and Cu) having high affinity for the mucilage can decrease in the rhizosphere, while Cd could easily diffuse to the root surface. This way mucigels can act as a selective filter for metals. Morel et al. [27] reported that Pb uptake by corn was minimal despite its high concentration in biosolids-treated soil, compared to Cd. Similarly, Cd and Zn can readily form organometallic complexes with organic acids from root exudates facilitating their diffusion to roots [28].

The how availability of Pb and Cr to corn in biosolids-treated soil can be explained by the formation of relatively stable complexes or chelation that results from the interaction with organic matter and redox reaction in the case of Cr. Certain metals (e.g., Cu and Pb) exhibit high affinities for soil organic matter, where soluble and insoluble complexes between the metals and organic matter may form. Thus, indigenous soil organic matter and the added biosolids can affect the binding ability for metals in biosolids-treated soils. The majority of Pb immobilized by biosolids-treated soils is believed to be associated with organic matter [29]. Then, because of the strong affinity of Pb for organic matter and its generally immobile nature, Pb can be expected to accumulate in the surface layer of biosolids-treated soils and is less phytoavailable. Chang et al. [30] found that in cropped soils treated continuously for 6 years with municipal sewage sludge, >90% of the applied Pb was found in the surface 0 to 15 cm, the zone of application. In contrast to Pb, biosolids treatment in soil resulted in significant increase in uptake of Cd, Ni, and Zn by plant tissues, since biosolids lead to higher acidification of rhizosphere by release of organic acids [5, 21, 31].

The moisture content of soils also influences their retention for metals (e.g., Cr and Mn) through oxidation-reduction reactions. Hexavalent chromium, Cr(VI), is more soluble and mobile in soils and more available to plants than trivalent chromium, Cr(III). While Cr(III) strongly binds with soil particles, Cr(VI) is very weakly adsorbed and therefore readily available for plant uptake [32]. Chromium(VI) can be reduced to Cr(III) in the biosolids-treated soils because of the presence of organic matter acting as an electron donor [33, 34]. Bolan et al. [35] demonstrated that the addition of organic manure enhanced reduction of Cr(VI) to Cr(III) that resulted in higher insoluble fractions and lower plant uptake of the element from soils. Although atypical of arable land condition, elemental concentrations in soil solution extracted similarly from biosolids-treated soil indicated the decreased

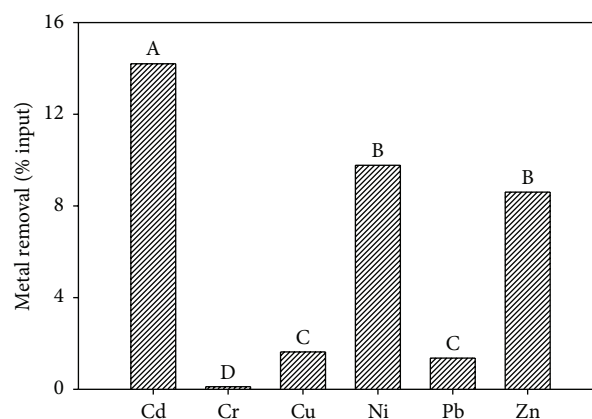


FIGURE 1: Metal removal by corn shoot and root grown on sand media amended with biosolids.

solubility of Cd, Cu, and Zn but increased solubility of Mn and Cr under reducing conditions [36].

The rate of metal uptake, measured as the amount of metal absorbed per unit biomass (data in [5]), increased during the plant growing period ($\mu\text{g g}^{-1} 2 \text{ wk}^{-1}$) (Table 2). The rates of absorption of Cd in shoots of corn grown on biosolids-treated medium and Zn in shoots of corn grown on the sand medium without biosolids remained rather constant for the first 8–12 weeks. For Cd accumulation in shoots and roots in the sand medium without biosolids where the supply was limited, there was insignificant additional Cd uptake after the first 4 weeks of growth, after which additional uptake was not detected (Table 2). When the Cd supply was not limiting (i.e., biosolids treatments), the uptake rate of Cd remained relatively constant over the entire growing period (0–12 weeks for roots and 0–16 weeks for shoots). When Zn supply was not limiting (such as shoots in the sand medium without biosolids and biosolids-treated medium), the uptake rate of Zn by corn shoots also remained constant over the same period. Toward the end the growing season, however, there was a tendency for the accumulation rate of the shoot to rise as the production of biomass slowed down, while at the same time the transpiration and translocation of metals continued.

The uptake rate for Zn was considerably higher than that for Cd (Table 2); the latter rates for shoots and roots from biosolids treatment were 5–7 and 25–79 $\mu\text{g g}^{-1} 2 \text{ wk}^{-1}$, respectively, and the rates from the same treatment for Zn were 127–687 and 31–235 $\mu\text{g g}^{-1} 2 \text{ wk}^{-1}$ for shoots and roots, respectively. In the sand medium without biosolids where Zn was supplied, the Zn accumulation in shoots remained steady until the 12th week. The biosolid and nutrient solution represent different source term for the heavy metals of interest. While metals in nutrient solution are totally soluble, those in the biosolids had to be solubilized before they become phytoavailable. Despite this discrepancy in the source term, Zn uptake from biosolid was substantially higher (127–687 $\mu\text{g g}^{-1} 2 \text{ wk}^{-1}$) than from the solution (19–63 $\mu\text{g g}^{-1} 2 \text{ wk}^{-1}$). In the sand medium without biosolids, Pb was not supplied but was present in the trace amounts in reagents used. Thus, the amount of Pb absorbed appeared to be limited by their supply

TABLE 2: Metal uptake rates (means where $n = 4$) by corn grown on sand media amended, without biosolids (Standard) and with biosolids at different growth stages[†].

Metal	Plant tissue	Treatment	0–2	2–4	Time (weeks)		
					4–8	8–12	12–16
					$\mu\text{g g}^{-1} \text{ 2 wk}^{-1}$		
Cd	Shoot	Standard	0.5 ^a	0.2 ^b	n.d. [‡]	n.d. [‡]	n.d. [‡]
		Biosolids	7.0 ^a	7.0 ^a	5.0 ^a	5.0 ^a	6.0 ^a
	Root	Standard	1.9 ^a	1.8 ^a	n.d. [‡]	n.d. [‡]	n.d. [‡]
		Biosolids	36 ^b	37 ^b	25 ^b	38 ^b	79 ^a
Cr	Shoot	Standard	1.3 ^a	1.0 ^a	0.4 ^b	0.4 ^b	0.4 ^b
		Biosolids	1.9 ^a	1.6 ^b	0.5 ^c	0.5 ^c	n.d. [‡]
	Root	Standard	3.6 ^a	1.7 ^b	0.7 ^c	0.7 ^c	0.7 ^c
		Biosolids	16 ^a	10 ^b	3.0 ^c	3.0 ^c	n.d. [‡]
Cu	Shoot	Standard	13 ^a	10 ^a	3.0 ^b	3.0 ^b	3.0 ^b
		Biosolids	19 ^a	15 ^b	7.0 ^c	5.0 ^c	6.0 ^c
	Root	Standard	23 ^a	20 ^a	10 ^b	8.0 ^b	n.d. [‡]
		Biosolids	71 ^a	54 ^b	22 ^c	16 ^c	12 ^c
Ni	Shoot	Standard	16 ^a	12 ^a	5.0 ^b	4.0 ^b	4.0 ^b
		Biosolids	52 ^a	35 ^b	10 ^c	11 ^c	n.d. [‡]
	Root	Standard	20 ^a	19 ^a	6.0 ^b	5.0 ^b	n.d. [‡]
		Biosolids	321 ^a	215 ^b	81 ^c	59 ^d	16 ^e
Pb	Shoot	Standard	6.0 ^a	5.0 ^a	2.0 ^b	1.0 ^b	2.0 ^b
		Biosolids	15 ^a	12 ^b	5.0 ^c	4.0 ^c	5.0 ^c
	Root	Standard	6.0 ^a	5.0 ^a	1.0 ^b	1.0 ^b	n.d. [‡]
		Biosolids	37 ^a	14 ^b	6.0 ^c	4.0 ^c	5.0 ^c
Zn	Shoot	Standard	30 ^b	30 ^b	21 ^b	19 ^b	63 ^a
		Biosolids	157 ^b	165 ^b	127 ^b	185 ^b	687 ^a
	Root	Standard	58 ^a	60 ^a	57 ^a	73 ^a	n.d. [‡]
		Biosolids	235 ^a	179 ^b	81 ^c	76 ^c	31 ^c

[†] The differences of metal rates among the time periods were tested by one-way ANOVA. Within a row and between shoot and root, values followed by same letters were not significantly different at $P < 0.05$.

[‡] Metal uptake rate was not detected in this period.

in the growing medium, resulting in its uptake continuously decreasing over the entire growing period of 0–8 weeks (Table 2).

The uptake rates for Cr, Cu, Ni, and Pb by corn shoots and roots from biosolids-treated medium decreased with the increasing length of growing period (Table 2). It appeared that the solution concentration of these metals and, therefore, its availability to the corn, were controlled by the rate of dissolution of biosolids-borne metals. Their uptake rates tended to follow a first order reaction model in that the rate of uptake gradually decreased over time as their available pool progressively diminished in the rhizosphere. Once the available pool was exhausted, the rate of Cr and Pb absorption decreased considerably. The persistent low concentrations of Pb and Cr in the aqueous phase of the sand indicate their slow dissolution/desorption kinetics from the biosolid.

Among the metals, Cd and Zn generally accumulated in plant tissue due to their high contents in biosolids, their mobility, and ease of uptake by the plants. On the other hand, Cu, Cr, Ni, and Pb exhibited decreased uptake due to their unavailable nature from the biosolids. Because of similarity in the biogeochemical behavior of Zn and Cd in biosolids-treated

soils, they exhibited a similar pattern of uptake in plants [29]. Metal contents of crops grown on biosolids-treated soils are generally a function of the annual biosolids loading rate. However, long-term changes in certain soil properties can also occur to affect the biogeochemical behavior of the metals. For example, an increase in soil pH can reduce metal phytoavailability and accumulation in plant tissue in spite of a progressive rise in the total metal contents in soil. The cumulative metal input into the soil is also a major factor determining metal uptake by plants [5, 37, 38]. Perceived as typical for biosolids-borne metals, metal concentration in plant tissue may approach a leveling pattern (i.e., a plateau) with progressive metal input, indicating some buffering influence of the biosolids organic matter on phytoavailability. In this respect, Chang et al. [38] established a nonlinear regression model for Swiss chard, radish, and tubers grown in a long-term experiment where composted municipal sewage sludge was applied, at increasing rate, into the soil.

3.1.2. Metal Uptake by Wheat Cultivars Grown on Biosolid-Treated Medium. The metal concentration in the plant tissue of three wheat varieties (e.g. cv. Chinese Spring, cv. Yecora

Rojo, and *Triticum aestivum*) varied with the treatment, metal element, plant part, and length of plant growth. In general, the metal concentrations in tissues harvested from the biosolids treatment were higher or equal than those from the sand medium without biosolids (Table 3). As expected, metal concentrations in the roots of the wheat cultivars at 4th, 8th, and 12th week were considerably higher than those in the corresponding shoots except for Cd and Cr, which were similar in both tissues when grown on the sand medium without biosolids. In all cases, metal concentrations in tissues of the cultivars were highest at the 4th week, decreasing progressively afterward.

Intertreatment differences among the metal contents were greater than the intercultural differences (Table 3). For example, total uptake of metals in the shoots from the biosolids treatment varied by factor of 2-3 (Figure 2). Based on the differences between the mass of metals present in the growth medium and that absorbed by wheat tissue, the percentage of metals that was absorbed could be calculated. It became apparent that the extent of phytoavailability of the metals derived from the biosolid follows the order: Cd > Ni = Zn = Cu > Pb > Cr (Figure 2). The least bioavailability of Pb and Cr to plants follows the general trend reported in the literature because of their strong complexation with organic matter compounds [29] and more specifically the effective role of organic matter, in this case in the form of biosolid, to serve as electron donor for the reduction of Cr(VI) to its immobile and largely unavailable form, Cr(III) [35]. A similar trend for corn (Figure 1) grown on biosolids-treated medium was observed. Because of the lower biomass, the amounts of metals removed by wheat plants were considerably lower than that for corn (Table 2). In general, cv. Chinese Spring removed greater amounts of metals than the other two cultivars (Figure 2). The total content in shoots followed the following order:

Cd: cv. Chinese Spring = *Triticum aestivum* > cv. Yecora Rojo

Cr: cv. Chinese Spring = *Triticum aestivum* > cv. Yecora Rojo

Cu: cv. Chinese Spring > *Triticum aestivum* = cv. Yecora Rojo

Ni: cv. Chinese Spring > *Triticum aestivum* = cv. Yecora Rojo

Pb: cv. Chinese Spring > *Triticum aestivum* > cv. Yecora Rojo

Zn: cv. Chinese Spring > *Triticum aestivum* > cv. Yecora Rojo.

The higher uptake by cv. Chinese Spring can be attributed to its longer vegetative growth period. For example, cv. Yecora Rojo and *Triticum aestivum* reached maturity at the 10-12 week, while cv. Chinese Spring did not reach maturity till the end of the 12th week.

Generally, the uptake rates for the wheat cultivars varied with the growth period (Table 4). Except for Pb and Cr, uptake was higher at the earlier part of the growth period (0-4 weeks), decreasing over time. Again, this indicates the lower

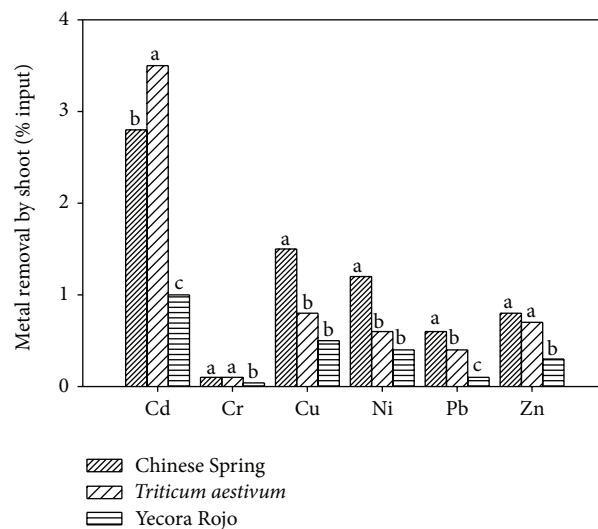


FIGURE 2: Metal removal by shoots of three wheat cultivars grown on sand media amended with biosolids for 12 weeks (the differences of metal removal among the wheat cultivars were tested by one-way ANOVA test and values followed by same lower letter were not significant different at $P < 0.05$).

solubility and subsequent availability of Pb and Cr from the biosolid to the plant.

3.1.3. Metal Uptake by Six Plant Species Grown on Biosolid-Treated Medium. Six plants (*Zea mays*, *Triticum turgidum*, *Brassica napas*, *Sorghum sudanense*, *Cicer arietinum*, and *Beta vulgaris*) grown on biosolids-treated medium accumulated greater amounts of metals in both shoots and roots compared to the sand medium without biosolids and phosphate rock treatments (Table 5). The metal concentrations in roots were considerably higher than in the shoots. Generally, metal concentrations in plant tissues for respective treatments were biosolids-treated > phosphate rock-treated = sand medium without biosolids. The monocots (*Zea mays*, *Sorghum sudanense*, and *Triticum turgidum*) were not able to use the P in phosphate rock as effectively as the P from the nutrient solution (Table 6), consequently lowering the biomass yield [5]. On the other hand, dicots (*Cicer arietinum*, *Brassica napas*, and *Beta vulgaris*) used the P in phosphate rock more effectively. These discrepancies resulted in the P availability following the trend: phosphate rock-treated > biosolids-treated > sand medium without biosolids for the dicots and biosolids-treated > phosphate rock-treated = sand medium without biosolids for the monocots (Table 6). Unlike the metals, the P concentrations in the shoots were considerably higher than those in the roots.

The organic acids in root exudates are considered important for the solubilization of sparingly soluble P in phosphate rock [5]. The factors most likely to limit phosphate rock dissolution are insufficient pH buffering and/or P sorption capacity and increase in Ca^{2+} activity in the soil solution around phosphate rock particles. Phosphate rocks have been reported to be more effective in supplying P to dicots (i.e., white clover) than to monocots (i.e., wheat and barley) [5, 39].

TABLE 3: Metal concentrations (means where $n = 4$) of three wheat cultivars grown on sand media amended, without biosolids (Standard) and with biosolids[†].

Plant tissue	Treatment	Chinese Spring	0–4 <i>Triticum aestivum</i>	Duration (weeks)		Chinese Spring <i>Triticum aestivum</i>	Yecora Rojo
				Yecora Rojo	4–12 <i>Triticum aestivum</i>		
				mg kg ^{−1}			
Cd							
Shoot	Standard	2.53 ^a	2.55 ^a	2.56 ^a	0.56 ^b	0.75 ^b	1.01 ^a
	Biosolids	24.6 ^a	29.8 ^a	24.4 ^a	6.06 ^b	8.75 ^a	8.47 ^a
Root	Standard	2.63 ^a	2.64 ^a	2.84 ^a	0.75 ^a	0.78 ^a	0.72 ^a
	Biosolids	41.8 ^a	39.3 ^a	26.1 ^b	18.0 ^a	12.9 ^c	15.8 ^b
Cr							
Shoot	Standard	1.75 ^a	1.73 ^a	1.75 ^a	1.54 ^a	1.15 ^b	1.52 ^a
	Biosolids	2.77 ^a	2.70 ^a	2.69 ^a	1.51 ^a	1.56 ^a	1.52 ^a
Root	Standard	1.77 ^a	1.76 ^a	1.81 ^a	1.45 ^a	1.44 ^a	1.44 ^a
	Biosolids	34.5 ^b	42.7 ^a	33.2 ^b	12.2 ^a	9.11 ^b	4.99 ^c
Cu							
Shoot	Standard	16.0 ^a	15.5 ^a	16.0 ^a	4.44 ^b	4.46 ^b	5.07 ^a
	Biosolids	27.7 ^a	27.4 ^a	20.0 ^b	9.50 ^a	7.73 ^b	6.41 ^c
Root	Standard	17.4 ^a	17.3 ^a	17.7 ^a	12.0 ^a	12.5 ^a	10.3 ^b
	Biosolids	79.9 ^a	77.1 ^a	77.5 ^a	64.8 ^a	59.9 ^b	60.9 ^b
Ni							
Shoot	Standard	21.1 ^a	21.4 ^a	21.2 ^a	9.82 ^a	9.72 ^a	9.20 ^a
	Biosolids	64.9 ^a	54.6 ^b	54.9 ^b	40.5 ^a	34.5 ^b	34.3 ^b
Root	Standard	52.5 ^a	52.6 ^a	53.7 ^a	34.4 ^a	34.6 ^a	35.1 ^a
	Biosolids	135 ^a	158 ^a	154 ^a	112 ^a	120 ^a	118 ^a
Pb							
Shoot	Standard	2.62 ^a	2.41 ^a	2.63 ^a	1.49 ^b	1.41 ^b	1.93 ^a
	Biosolids	12.6 ^a	10.2 ^b	10.8 ^b	7.49 ^a	7.13 ^a	6.57 ^b
Root	Standard	2.69 ^a	2.72 ^a	2.87 ^a	1.67 ^b	2.03 ^a	2.23 ^a
	Biosolids	14.2 ^a	16.2 ^a	16.6 ^a	9.24 ^a	10.9 ^a	10.0 ^a
Zn							
Shoot	Standard	45.7 ^a	43.4 ^a	42.9 ^a	31.5 ^a	28.7 ^a	31.3 ^a
	Biosolids	319 ^a	338 ^a	271 ^b	124 ^a	144 ^a	125 ^a
Root	Standard	68.5 ^a	60.3 ^b	51.0 ^c	28.5 ^a	28.5 ^a	32.7 ^a
	Biosolids	610 ^a	682 ^a	633 ^a	304 ^a	342 ^a	286 ^a

[†]The differences of metal concentrations among the growth period were tested by one-way ANOVA and Student-Newman-Keuls test. Within a row and between shoot and root of each growth periods, values followed by a different letter were significantly different at $P < 0.05$.

TABLE 4: Metal uptake rates (means where $n = 4$) by shoots of three wheat cultivars grown on sand media amended with biosolids[†].

Time (week)	Variety of wheat	Metal accumulation					
		Cd	Cr	Cu	Ni	Pb	Zn
					$\mu\text{g g}^{-1} \text{ 4 wk}^{-1}$		
4	Chinese Spring	12 ^{Ac}	2 ^{Ae}	14 ^{Ac}	32 ^{Ab}	6 ^{Ad}	160 ^{Aa}
	<i>Triticum aestivum</i>	15 ^{Ac}	2 ^{Ae}	14 ^{Ac}	27 ^{Ab}	5 ^{Ad}	169 ^{Aa}
	Yecora Rojo	12 ^{Ac}	2 ^{Ae}	10 ^{Bc}	27 ^{Ab}	6 ^{Ad}	136 ^{Ba}
8	Chinese Spring	4 ^{Bc}	1 ^{Ad}	4 ^{Ac}	23 ^{Ab}	5 ^{Ac}	96 ^{Ba}
	<i>Triticum aestivum</i>	6 ^{Ac}	1 ^{Ad}	3 ^{Ac}	21 ^{Ab}	4 ^{Ac}	116 ^{Aa}
	Yecora Rojo	7 ^{Ac}	1 ^{Af}	2 ^{Be}	21 ^{Ab}	4 ^{Ad}	104 ^{Aa}

[†]The differences of metal uptake rate among the wheat cultivars were tested by one-way ANOVA. In each column of each growth time for cultivars, values followed by same upper case letter were not significantly different at $P < 0.05$. The differences of the metal uptake rates among the metals in same cultivars were tested by one-way ANOVA. In each row, time, and cultivar, values followed by different lowercase letter were significantly different at $P < 0.05$.

TABLE 5: Metal concentrations (means where $n = 3$) of six plant species grown on sand media amended, without biosolids (Standard), with biosolids, and with phosphate rock[†].

Plant	Treatment	Cd		Cr		Cu		Ni		Pb		Zn	
		Shoot	Root	Shoot	Root	Shoot	Root	Shoot	Root	Shoot	Root	Shoot	Root
		mg kg ⁻¹											
Chickpea	Standard	1.7 ^b	1.0 ^c	1.5 ^b	1.6 ^c	4.9 ^b	9.0 ^b	22 ^b	51 ^b	3.1 ^b	6.2 ^b	15 ^c	38 ^b
	Biosolids	14 ^a	34 ^a	3.7 ^a	17 ^a	16 ^a	51 ^a	50 ^a	172 ^a	9.1 ^a	13 ^a	201 ^a	636 ^a
	Phosphate rock	1.6 ^b	1.7 ^b	0.8 ^c	2.1 ^b	4.8 ^b	6.8 ^c	3.9 ^c	26 ^c	2.3 ^c	1.5 ^c	25 ^b	36 ^b
Rape	Standard	1.9 ^c	1.1 ^c	1.4 ^c	1.2 ^c	6.5 ^b	11 ^c	8.5 ^b	38 ^b	1.1 ^c	2.6 ^b	30 ^b	34 ^b
	Biosolids	16 ^a	23 ^a	4.2 ^a	77 ^a	16 ^a	93 ^a	25 ^a	104 ^a	13 ^a	31 ^a	253 ^a	344 ^a
	Phosphate rock	2.5 ^b	2.2 ^b	1.9 ^b	3.6 ^b	3.4 ^c	8.4 ^b	3.9 ^c	36 ^b	3.6 ^b	1.0 ^c	19 ^c	23 ^c
Swiss chard	Standard	1.4 ^c	1.1 ^c	0.9 ^b	1.7 ^c	9.8 ^b	17 ^b	12 ^b	38 ^b	2.4 ^c	5.0 ^b	21 ^b	32 ^b
	Biosolids	29 ^a	56 ^a	4.6 ^a	34 ^a	23 ^a	241 ^a	27 ^a	399 ^a	6.0 ^a	13 ^a	335 ^a	676 ^a
	Phosphate rock	2.2 ^b	3.6 ^b	1.5 ^b	3.9 ^b	7.8 ^c	13 ^c	4.9 ^c	35 ^b	3.7 ^b	2.8 ^c	22 ^b	33 ^b
Corn	Standard	1.2 ^c	1.6 ^c	1.1 ^b	1.3 ^b	4.9 ^b	18 ^b	12 ^c	24 ^c	1.9 ^b	7.8 ^b	25 ^b	32 ^b
	Biosolids	22 ^a	33 ^a	1.3 ^a	45 ^a	12 ^a	58 ^a	41 ^a	242 ^a	11 ^a	21 ^a	226 ^a	479 ^a
	Phosphate rock	1.4 ^b	2.5 ^b	0.7 ^c	1.0 ^c	4.5 ^b	8.6 ^a	20 ^b	40 ^b	2.1 ^b	0.2 ^c	22 ^c	18 ^c
Sudan grass	Standard	1.7 ^c	1.1 ^c	1.6 ^a	1.3 ^c	8.1 ^b	11 ^b	21 ^b	21 ^c	1.4 ^c	5.1 ^b	27 ^c	29 ^b
	Biosolids	20 ^a	29 ^a	1.7 ^a	26 ^a	12 ^a	88 ^a	65 ^a	184 ^a	7.0 ^a	11 ^a	316 ^a	598 ^a
	Phosphate rock	4.9 ^b	3.8 ^b	1.6 ^a	1.8 ^b	9.2 ^b	11 ^b	22 ^b	45 ^b	2.8 ^b	2.2 ^c	51 ^b	29 ^b
Durum wheat	Standard	1.8 ^c	2.0 ^c	2.0 ^b	1.2 ^c	14 ^b	16 ^b	23 ^b	61 ^b	2.3 ^b	2.6 ^b	37 ^b	42 ^b
	Biosolids	26 ^a	31 ^a	3.2 ^a	42 ^a	18 ^a	91 ^a	73 ^a	168 ^a	12 ^a	20 ^a	249 ^a	614 ^a
	Phosphate rock	2.7 ^b	3.1 ^b	1.3 ^c	1.5 ^b	11 ^c	17 ^b	23 ^b	39 ^c	3.0 ^b	3.2 ^b	36 ^c	39 ^b

[†] The differences of the metal concentrations among the treatments for each plant were tested by one-way ANOVA. In each column of each plant and among the treatments, values followed by same lowercase letter were not significantly different at $P < 0.05$.

Dicots can acidify their rhizosphere more effectively when they fix nitrogen. Nitrogen enters the root as an uncharged molecule, and an excess of cations over anions can be absorbed by the root to balance the negative charge on newly formed proteins and organic acids, which are products of carbon and nitrogen assimilation. The excess cation uptake is balanced by a net H⁺ efflux into the rhizosphere [40, 41]. Some organic acids (i.e., citric and malic) are well known for their capacity to desorb phosphate rock from sesquioxide surfaces by anion exchange [42]. Combinations of both desorption and chelation are responsible for phosphate rock mobilization. The capacity of organic acids in root exudates also depends on their concentration per unit volume of soil. Thus, it can be anticipated that with increasing density of root hairs or of lateral roots, the likelihood of organic acids mobilizing phosphate rock becomes higher [5, 43]. In the previous paper [5], we reported that the composition of root-borne dicarboxylic organic acids (i.e., succinic, tartaric, and oxalic) varied between dicots and monocots and the total amount and production rate of organic acids from dicots were higher than those from monocots.

Data suggest the occurrence of interspecific variation in metal uptake (Table 5). For Cd, which is generally readily absorbed by plants, the average concentrations among the six species varied between 1.11–1.85, 13.9–29.4, and 1.38–4.87 mg kg⁻¹ for the sand medium without biosolids, biosolids-treated, and phosphate rock-treated medium, respectively (Table 5). The slightly higher Cd concentration in the shoots from phosphate rock treatment (versus nutrient solution) may be reflecting the presence of trace amounts of Cd in

the phosphate rock. Plant absorption of Cu, Ni, Pb, and Zn followed a similar trend. As in corn, Cr was not accumulated in the shoots, and the differences in tissue concentrations between the treatments were considerably smaller. For example, Cr concentrations in shoots were 0.86–1.96, 1.31–4.61, and 0.79–1.91 mg kg⁻¹ for the sand medium without biosolids, biosolids-, and phosphate rock-treated medium, respectively. In the roots, as expected, Cr concentrations were 1.16–1.73, 16.8–77.1, and 1.02–3.86 mg kg⁻¹ for the sand medium without biosolids, biosolids treatments, and phosphate rock treatments, respectively. The trendy greater accumulation of metals in the roots is consistent with the general observation in the literature [29].

4. Conclusions

In this study, metal concentration in plant roots generally exceeded those in the shoots, irrespective of treatment. Exception was Cd in the shoots for the dicots. The amounts of metal transferred from the biosolids-treated medium to the plant varied with the metal element and followed the order: Cd > Ni = Zn > Cu = Pb > Cr. For corn grown on biosolids-treated medium, the amounts of metals removed by the plant were 14.2, 9.8, 8.6, 1.6, 1.4, and 0.1% of the biosolids-borne metals in the rhizosphere, respectively, for the metals above. Interspecies and intercultivar differences in the metal uptake were trivial compared to intertreatment variations. Uptake rates for Cd and Zn by corn shoots remained constant for the first 8–10 weeks and tended to increase toward the end of the growth period. Among the metals examined, Pb and

TABLE 6: P concentration of six plant species grown on sand media amended, without biosolids (Standard), with biosolids, and with phosphate rock[†].

Plant	Treatment	Shoot mg kg ⁻¹	Root mg kg ⁻¹
Chickpea	Standard	1,260 ^c	922.0 ^c
	Biosolids	2,044 ^b	1,137 ^b
	Phosphate rock	2,580 ^a	1,513 ^a
Rape	Standard	1,743 ^c	1,564 ^c
	Biosolids	2,189 ^b	2,203 ^b
	Phosphate rock	3,354 ^a	2,707 ^a
Swiss chard	Standard	1,753 ^c	1,372 ^c
	Biosolids	2,141 ^a	3,261 ^a
	Phosphate rock	2,029 ^a	2,631 ^b
Corn	Standard	1,198 ^a	707.0 ^b
	Biosolids	1,192 ^a	763.0 ^a
	Phosphate rock	638.0 ^b	556.0 ^c
Sudan grass	Standard	1,088 ^b	676.0 ^b
	Biosolids	1,138 ^a	814.0 ^a
	Phosphate rock	756.0 ^c	553.0 ^c
Durum wheat	Standard	1,744 ^b	956.0 ^b
	Biosolids	2,537 ^a	1,716 ^a
	Phosphate rock	783.0 ^c	638.0 ^c

[†]The differences of the P concentrations among the treatments for each plant were tested by one-way ANOVA. In each column of each plant and among treatments, values followed by same lowercase letter were not significantly different at $P < 0.05$.

Cr apparently were only sparingly soluble from their biosolid source as indicated by their waning uptake as the growth period progressed.

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Research Article

Nursery Growing Media: Agronomic and Environmental Quality Assessment of Sewage Sludge-Based Compost

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There is a stringent need to reduce the environmental impact of peat in the plant nursery production chain. In this experiment, the use of different rates of sewage sludge compost in the preparation of growing media for potted *Bougainvillea* was evaluated to assess its efficiency for the replacement of peat and to quantify the environmental impact of such alternative substrates by the life cycle assessment (LCA) method. Five substrates containing increasing proportion of composted sewage sludge to peat (0%, 25%, 40%, 55%, and 70% v/v) were used, and their physicochemical properties were measured. *Bougainvillea* plant growth, biomass production, and macro- and micronutrient absorption were also determined. The main results were that compost addition improved the plant nutrient and increased the substrate pH, electrical conductivity (EC), and dry bulk density values. Globally, the results showed that compost could be used at up to 55% by volume with no negative effects on plant growth. The LCA showed that use of compost reduced the environmental loads of the growth media, except the Global Warming Potential value (GWP100). Environmental implications of the use of compost in the plant nursery chain are discussed.

1. Introduction

Ornamental plant nursery production is one of the most specialized examples of intensive agriculture, with the large use of nonrenewable resources to maximize plant growth and reduce production time in an effort to capitalize on-sale profits. Because of this, the “green industry” is often considered a nonpoint (or diffused) polluting industry, due to the low efficiency in the management practices. The most common growing media used in Mediterranean ornamental nursery is peat, alone or mixed with inorganic coarse materials [1], because of its good chemical and physical properties. The development of substrates alternative to peat is necessary for three main reasons: (i) peat resources are limited and costly; (ii) the social pressure to reuse the waste resulting from human or industrial activities is growing rapidly, (iii) the economic need for reusing locally produced waste is

more and more urgent [2, 3]. In Italian ornamental nurseries the cost of the substrate affects by up to 12–15% the overall production cost of the potted plants [4]. It is appropriate to consider replacing peat with other organic resources with favorable economically and environmentally features [5].

Composted organic wastes, properly mixed, can make excellent substrates for vegetable transplants [6, 7], especially sewage sludge due to its widespread production. Composting transforms sewage sludge into a drier, more uniform, and biologically stable product potentially suitable for plant rooting and rich in plant nutrients [8]. However, the proportion of compost in the final substrate is also very important, in order to minimize potential hazards due to the presence of heavy metals and pathogens. Combinations of peat with sewage sludge compost and other materials can minimize the negative properties of single materials (high salinity, heterogeneity, and contaminants) [9]. Reduced use of nonrenewable

resources and use of new materials for production of growing media would allow a reduction in the environmental impact of industrial processes. Positive results can be quantified by the life cycle assessments (LCA) analysis method of environmental impact of the composting processes and to the growth media production [10, 11]. The European Commission considers the LCA method as an instrument with a scientific bases able to provide the overall environmental costs of any productive process throughout its whole life cycle.

Previous studies on compost use in agriculture have focused on specific agronomic aspects such as plant nutrition, water holding capacity, and species specificity. Differently, the choice of a growing media composition is constrained technical considerations (e.g., growing medium characteristics, crop requirements, safety, reliability, availability of constituents, and price). In substituting a peat substrate for a peat-biosolid compost mix, it is essential for the grower to consider crop quality. However few studies have addressed the global quality (agronomical and environmental) of horticultural growing media [12]. A previous study reported that to reduce the environmental impacts of a peat growing medium it is necessary to replace peat for alternative materials (e.g., perlite, wood fiber, and green compost) [13]. Currently, there is a lack of environmental quality data relating to sewage sludge compost application and rates in ornamental nursery as growing medium [14].

In this research, the use of different rates of sewage sludge compost in the preparation of growing media for potted *Bougainvillea* was evaluated in order to assess its efficacy as a peat replacement and to quantify the environmental impact of the substrate, by the LCA method, to optimize the ornamental nursery production chain. The simultaneous evaluation of the agronomic quality and environmental impact of the different rates in volume of biosolid compost in the production chain of the growing media consists in the innovative aspect of this research: actually data for the Mediterranean shrubs production does not exist.

In this research, the use of different rates of sewage sludge compost for the preparation of growing media for potted *Bougainvillea* was evaluated in order to assess its suitability to replace peat in the ornamental nursery production chain and to quantify the environmental impact of the substrate by the LCA method.

2. Materials and Methods

2.1. Characteristics of the Compost. The compost used as a component of growing media for this experiment (SSC) was obtained by mixing of urban sewage sludge (30% by volume) from Manduria municipality (TA, Southern Italy) and pruning rejects: urban "green" and olive grower (70% by volume), both locally available, in a composting plant. The mixture (about 3 m³) was composted in a pilot plant, using the Rutgers static pile composting system, with forced aeration and controlled temperature. The mixture reached temperature values greater than 60°C and the thermophilic phase lasted 60 days. After 95 days, the biooxidative phase of

TABLE 1: Physical and physicochemical characteristics of sewage sludge.

Parameter	Value in dry sewage sludge (SS)	Limit value in dry SS (according to Italian Legislation Lgs D. 99/1992)
Colour	7.5Y 2/1	
Moisture content (%)	11.8	—
Total OM (%) ^a	42.3	—
Oxidizable OC (%) ^a	21.9	≥20.0
pH (H ₂ O)	7.64	—
EC (dS m ⁻¹)	4.10	—
C : N ratio	6.12	—
CaCO ₃	19.8	
CHA/CFA	n.d.	—
Total Kjeldahl Nitrogen TKN (%) ^a	3.21	≥1.50
P ₂ O ₅ (%) ^a	1.91	≥0.40
K ₂ O (%) ^a	0.21	—
CEC (cmol ⁽⁺⁾ kg ⁻¹)	n.d.	—
Pb (%) ^a	49.0	750
Cd (%) ^a	5.21	20.0
Ni (%) ^a	24.0	300
Zn (%) ^a	1057	2500
Cu (%) ^a	216	1000
Hg (%) ^a	5.10	10.0
Cr ⁺⁶ (%) ^a	1.20	—

^aValues on a dry matter basis; data are mean values, *n* = 3.

composting was over and then the pile was allowed to mature for an additional month.

The main physical, physicochemical, and chemical parameters were analyzed in sewage sludge (Table 1) and SSC (Table 2) and raw materials added subsequently to prepare the growing media (Table 3).

Concerning the dry sewage sludge (Table 1), the pH value was slightly alkaline and the EC value was medium-high, whereas the CaCO₃ content was largely due to the wastewater treatments of the sewage sludge with CaO and FeCl₃. The P content was in the common range of values for an organic fertilizer, whereas the K content was relatively small, possibly due to its solubility and transport in sewage sludge wastewater. According to Italian Law (Legislative Decree 99/1992), the heavy metal contents measured in the dry sewage sludge sample were under the limits.

The obtained compost showed a good degree of maturity (Table 2), according to different criteria suggested in the literature [15], such as the ratio of total organic carbon to total nitrogen (TOC/TN).

The compost showed an absence of phytotoxicity, according to the germination index (GI) > 50% (data not shown).

The main physicochemical parameters of the used materials are reported in Table 3. The commercial *Sphagnum* peat (P) from Germany was used in combination with pumice and

TABLE 2: Physical and physicochemical characteristics of sewage sludge compost.

Parameters	Value in sewage sludge compost (SSC)	Limit values in SSC (according to Italian Legislation Lgs D. 75/2010)
Colour	10YR 3/2	
Moisture content (%)	44.4	≤50.0
Total OM (%) ^a	58.6	—
Oxidizable OC (%) ^a	29.0	≥20.0
C : N ratio	10.2	≤25.0
CHA/CFA	1.96	—
Total Kjeldahl Nitrogen TKN (%) ^a	2.83	—
P ₂ O ₅ (%) ^a	0.91	—
K ₂ O (%) ^a	0.71	—
CEC (cmol ⁽⁺⁾ kg ⁻¹)	77.0	—
Pb (%) ^a	6.40	140
Cd (%) ^a	0.10	1.50
Ni (%) ^a	3.20	100
Zn (%) ^a	394	500
Cu (%) ^a	14.1	230
Hg (%) ^a	0.10	1.50
Cr ⁺⁶ (%) ^a	0.10	0.50

^aValues on a dry matter basis; data are mean values, $n = 3$.

pozzolana (volcanic materials) and almond shell that improve aeration and water holding capacity of the growth substrates.

2.2. Experimental Procedure and Greenhouse Experiment. A greenhouse pot experiment was carried out to evaluate the main physical and chemical properties of five growing media obtained by mixing sewage sludge-based compost and peat in different ratios and to evaluate the potential use of these substrates as growing media for commercial *Bougainvillea* production.

The five compared substrates were obtained by mixing increasing rates of sewage sludge compost (25%, 40%, 55%, and 70% v/v) with a fixed rate of inert the other materials (30% v/v) to fulfillment to 100% of the substrate volume, including the *Sphagnum* peat. A peat based and compost-free substrate (SSC0), typically used in the Apulia nurseries, was also prepared as control by mixing peat (70%) pumice (15%), almond shells (10%), and pozzolana (5%).

Heavy metal content was also determine (Table 6).

The experiment was conducted in a commercial nursery located in Monopoli SE Italy, 40° 57' 00"N, 17° 18' 00"E 23 m a.s.l.), in a greenhouse at keeping the temperature between 15 ± 2°C at night and 28 ± 2°C during the day temperature 60% relative humidity. On December 4 2012 rooted cuttings of *Bougainvillea glabra* "Sanderiana" were potted singly in brown plastic containers (5 L volume). Each pot was filled with one of the test substrates. The young plants (one month

old) had the following size: 12 cm height, 7 cm diameter, and 18 g fresh weight.

The growing density, on bench, was 8 plants m⁻² for a total of 135 plants (27 plants per growing medium). The irrigation system was a microdrip. The plants were irrigated with only water during the first week, and then they were daily fed with a water soluble fertilizer N : P : K (5 : 1 : 7.5) plus microelements in dose of 0.5 g/L water. From the beginning of trial to 90 (days after transplant) DAT the nutrient solution was diluted according to the compost percentage of the substrate (Table 7). The plants grown in SSC45 and SSC70 have shown N deficiency symptoms (91 DAT); then the solutions were unified in all treatments, with the dose 0.5 g/L water (N : P : K = 5 : 1 : 7.5).

From the beginning of the trial up to 90 DAT the nutrient solution quantity per pot was of 250 mL/d; then, up to the May 6 (trial end), they received 4 interventions per day with a volume of 250 mL/pot per intervention.

2.3. Measurements and Analytical Methods. The greenhouse experiment ended at 150 DAT when, on average, the plants reached the commercial size. The plant growth was determined after 90, 120, and 150 DAT. On each sampling date nine plants per treatment (three per replicate pot) were randomly harvested and used for the following biometric measurements: number of leaves, leaf area (cm²) (LI-COR 3100 area meter), and fresh and dry weight. The growing media were dried in an air-forced oven at 60°C to constant weight and milled to below 0.25 mm by a Tecator Cyclotec, 1093 PBI. The parts of the plants above ground were separated from the roots and gently washed many times with tap water and then finally with deionized water. A mixed sample of all the replications of each treatment was collected. Next, the samples were dried at 60°C to constant weight and crushed to 0.25 mm. The total Kjeldahl nitrogen (TKN) was measured using 1 g samples of both growing media and plant tissues using the Kjeldahl method after 96% H₂SO₄ hot digestion. Total phosphorus was determined (P) by the colorimetric molybdovanadate phosphoric acid method. The remaining nutrients and the heavy metal content were determined in digested samples by inductively coupled plasma atomic emission spectrometry (ICP-AES). One gram of dried samples was mineralized using 20 mL of 65% HNO₃ solution. After digestion, samples were transferred into 50 mL volumetric flasks and then filtered through a Whatman 42 filter. The analyses were carried out in triplicate.

The main chemical and physicochemical properties of the five growing media were determined according to the following standardized UNI EN methods: 12579 (for sampling), 13037 (for the pH value), 13038 (for electrical conductivity, EC), 13041 (for dry bulk density and shrinkage), 13654-1 (for nitrogen), and 13652 (for quantification of H₂O-soluble nutrients and heavy metals) [16, 17].

The germination index (GI) was calculated using seeds of *Lepidium sativum* L. [18].

2.4. Statistical Analysis. The greenhouse experiment was carried out following a randomized block designed with three

TABLE 3: Physical and physicochemical characteristics of the raw materials used: compost (SSC), almond shell (A), pumice (Pu), pozzolana (S), and sphagnum peat (P).

Raw materials	pH	EC (dS m ⁻¹)	Dry bulk density (g cm ⁻³)	Easily available water (%V)	Shrinkage (%V)
SSC	7.90	5.54	0.45	9.93	13.17
A	5.71	0.26	0.38	1.19	00.00
Pu	6.72	0.08	0.81	2.88	00.00
S	6.43	0.10	1.62	10.43	00.00
P	5.62	0.33	0.13	6.53	15.33

Data are mean values, $n = 3$.

TABLE 4: Physical and physicochemical characteristics of the growing media used (at transplant).

Growing medium	pH	EC (dS m ⁻¹)	Bulk dry density (g cm ⁻³)	Easily available water (%V)	Shrinkage (%V)
Acceptable range (¹)	5.2–6.5	<0.5	≤0.4	20–30	<30
SSC0	5.80 ^c	0.45 ^e	0.28 ^c	13.71 ^a	15.87 ^a
SSC25	6.36 ^b	1.52 ^d	0.35 ^b	12.01 ^a	14.97 ^a
SSC40	6.50 ^b	2.15 ^c	0.39 ^b	6.01 ^b	14.10 ^b
SSC55	6.85 ^a	2.85 ^b	0.45 ^{ba}	5.86 ^b	13.40 ^c
SSC70	6.90 ^a	3.80 ^a	0.55 ^a	5.06 ^b	13.01 ^c
Significance	*	**	*	**	*

(¹): ideal substrate. Data are mean values, $n = 3$.

In each column different letters indicate significant differences for $P \leq 0.05$ (test S.N.K.).

* indicates difference at $P \leq 0.05$; ** indicates difference at $P \leq 0.01$.

TABLE 5: Chemical characteristics of the growing media used (at transplant).

Growing medium	mg kg ⁻¹						
	N	P	K	Total Ca	Mg	Fe	Mn
SSC0	330 ^d	1561 ^d	1027 ^c	5927 ^c	660 ^e	239 ^c	69 ^b
SSC25	550 ^c	2962 ^c	2058 ^b	17346 ^b	1682 ^d	933 ^b	114 ^a
SSC40	790 ^b	3050 ^c	2765 ^a	18652 ^b	2783 ^c	1056 ^{ab}	128 ^a
SSC55	890 ^b	3858 ^b	2692 ^a	20857 ^{ab}	3732 ^b	1188 ^a	136 ^a
SSC70	1010 ^a	4413 ^a	2805 ^a	22328 ^a	4040 ^a	1320 ^a	151 ^a
Significance	**	**	**	**	**	**	**

Data are mean values, $n = 3$. ** indicates difference at $P \leq 0.01$.

In each column different letters indicate significant differences for $P \leq 0.05$ (test S.N.K.).

TABLE 6: Average values of the heavy metals content of the growing media used (at transplant).

Growing medium	mg kg ⁻¹					
	Pb	Cd	Ni	Zn	Cu	Cr ⁺⁶
Italian Law value	140	1.50	100	500	230	<0.5
SSC0	12.04 ^c	0.06 ^b	1.58 ^c	12 ^c	13 ^b	<0.5
SSC25	33.23 ^b	0.19 ^a	1.78 ^c	82 ^b	13 ^b	<0.5
SSC40	34.00 ^b	0.22 ^a	2.56 ^b	102 ^{ab}	15 ^{ab}	<0.5
SSC55	35.66 ^b	0.28 ^a	3.33 ^{ab}	122 ^a	19 ^a	<0.5
SSC70	47.49 ^a	0.31 ^a	4.13 ^a	143 ^a	18 ^a	<0.5
Significance	**	*	**	**	**	n.s.

Data are mean values, $n = 3$.

In each column different letters indicate significant differences for $P \leq 0.05$ (test S.N.K.).

* indicates difference at $P \leq 0.05$; ** indicates difference at $P \leq 0.01$; n.s. indicates nonsignificant difference.

TABLE 7: Dilution ratio of nutrient solution supplied to the growing media from 1 to 90DAT.

Growing medium	Dilution ratio (% V : V)	
	Nutrient solution	Water
SSC0	100	0
SSC25	64.29	35.71
SSC40	42.84	57.16
SSC55	21.43	78.57
SSC70	0	100

TABLE 8: Raw materials used for the production of the tested growing media and their transport distance from the production areas to the firm.

Materials	Transport distance (km)
Urban sewage sludge	130
Green wastes	40
Peat	2500
Pumice	600
Almond shell	150
Pozzolana	100
Sewage sludge compost	0

replications. To compare the differences between specific treatments, the S.N.K. test was used. All statistical tests were conducted using the CoStat software package (2002).

2.5. Environmental Analysis. A comparison of the growing media production used in the experimental test was carried out (from June to November 2012) by means of a life cycle assessment (LCA) analysis, to gain more knowledge about the environmental impact and the resource use along the substrate production chain. The LCA is a method to analyse and assess the potential environmental impact caused by the used materials (ISO 14040-44) [19]. The product system comprising the composting plant and technique, the compostable organic sewage sludge, the produced compost, peat, pumice, almond shell, and pozzolana, and the five formulated growing media were included in the LCA. In accordance to the ISO 14040 standards, the inventory of the inputs (matter and energy) and the environmental outputs (water, air, and soil emissions) was accomplished using data obtained by direct interviews with the entrepreneurs, business inspections, and previously published data [20]. The transport distance of each raw material from the production area to the composting farm was also included as an input value (Table 8).

The data were elaborated using GABI 04 software with the CML2010 interpretation method [21] to determine the impacts indexes, expression of the environmental load of the growing media productive process. In the LCA evaluation of the composting process and all the assumptions about the boundaries of the production system, the adopted functional unit, and the objectives of the study were evaluated in accordance with [12, 22]. For the growing media comparison, the process functional unit has been set at 1 kg. The limits of the productive system include the wastes transport to the

firm and the growing media components production and packaging.

3. Results and Discussion

3.1. Physical and Chemical Characteristics of the Growing Media. Main physicochemical properties of the different raw materials and growing media used are shown in Tables 3 and 4 and the values established for an optimal substrate [23]. At start of the experiment the percentage in the mixtures of compost from urban sludge significantly affected values of the physical and physicochemical properties in relation to those observed in the control treatment (SSC0) (Table 4). Compost addition produced increased the values of pH and electrical conductivity (EC). The pH values of SSC0, SSC25, and SSC40 were within or close to the acceptable range (5.2–6.5) and significantly increased with the highest proportion of CSS (55% and 70%) in the substrate.

The electrical conductivity (EC) values of the growth media were strongly affected by the addition of CSS; the values exceeded the limit for an optimal growth substrate in the mixtures having more than 25% compost: the SSC0 being the only substrate that fulfilled optimal reference level (Table 4).

The physical parameters at transplanting were influenced by the percentage of compost in the growing media. The increases in bulk density were within acceptable values only in SSC0, SSC25, and SSC40 treatments. Compost addition to the mixtures decreased the values of shrinkage and easily available water, and only the substrate with SSC25 showed similar values to those found in the control treatment as regards the shrinkage. Main macro- and micronutrient contents were also significantly affected by compost rate in the media (Table 5). The TKN quantity was more than triple in peat free substrate (SSC70) compared to the control. The heavy metal content was also increased by the higher proportions of compost additions, but all the measured values were under the Italian legal thresholds for its safe use in agriculture (Table 6).

3.2. Plant Growth and Tissue Composition. Significant increases were observed in the growth of *Bougainvillea* plants with increasing compost rates in the mixtures (Figures 1(a)–1(d)).

On average, at 120 and 150 DAT, leaves number increased in SSC40, SSC55, and SSC70 growing media (Figure 1(a)). The leaf area only differed between treatments only at 150DAT with the lowest value found in plants grown on SSC0 and SSC25 substrates (Figure 1(b)). The weight also increased at 120 DAT in compost enriched substrates (Figure 1(c)), with the highest values recorded for SSC55 and SSC70 (peat free) substrates. The increasing rates of compost at 120 DAT also increased the dry weight values, compared to the control, with no difference between the rates (Figure 1(d)); at 150 DAT the dry weight showed the highest values in SSC55 and SSC70.

The increase in plant biomass production with the use of compost as a growing media component could be attributed

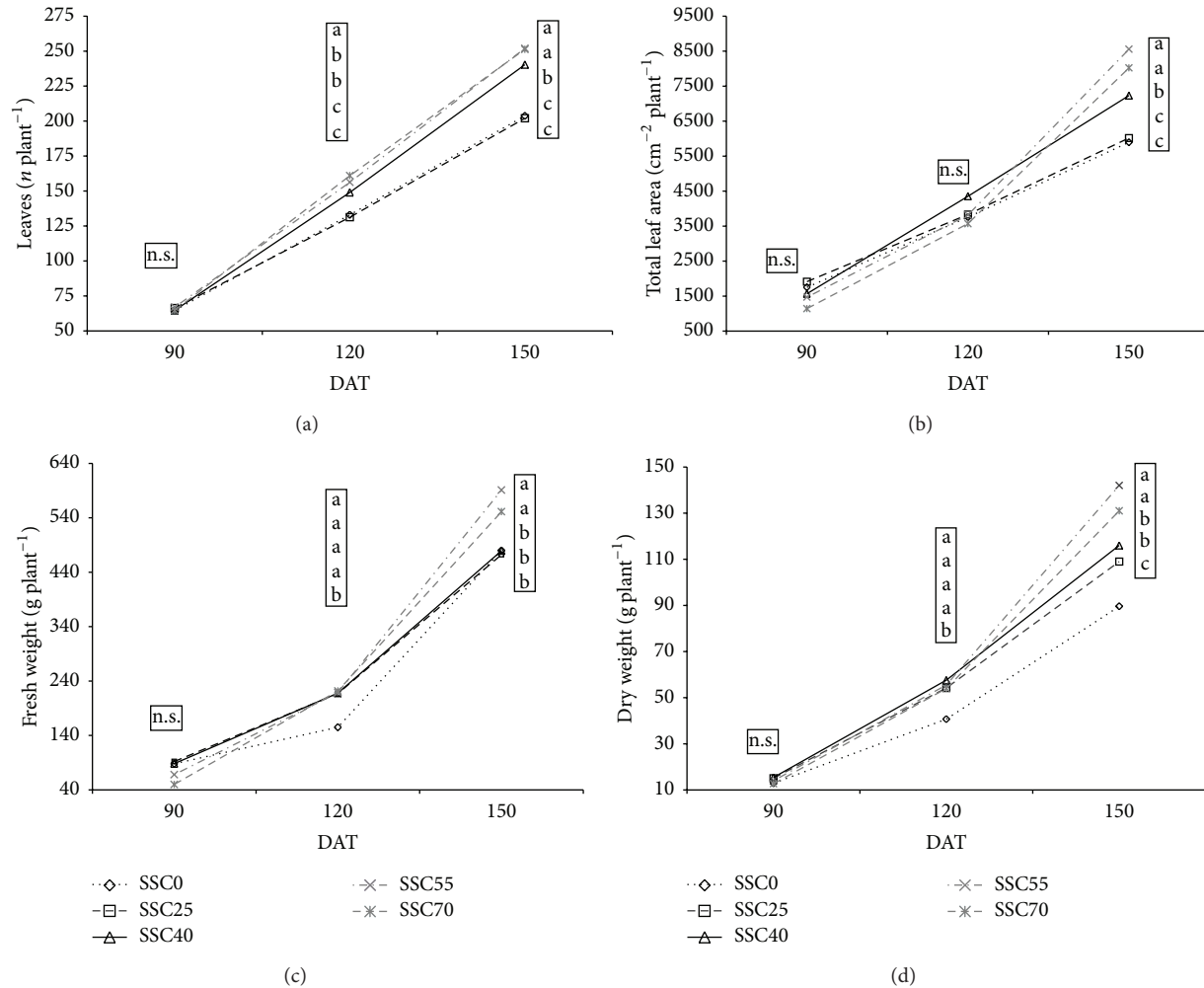


FIGURE 1: Leaves number (a), leaf area (b), fresh (c), and dry (d) weight in *Bougainvillea* potted plants at 90, 120, and 150 DAT as influenced by growing media. Each point is the mean of three replications. Within the same DAT values with the same letter are nonsignificantly different $P \leq 0.05$.

to the high input of nutrients provided by composts, and in our experiment increases in P, Ca, Mg, Fe, Mn, Cu, and Zn (Tables 5 and 6) likely played a key role. Improvement of plant biomass production by CSS was higher on a dry basis than on a fresh basis, confirming the increased plant uptake of nutrients. In general, compost addition significantly influenced the nutritional status of the *Bougainvillea* aerial part (Tables 9 and 10). Macronutrient contents were significantly enhanced with the increasing rate of compost in the substrate. This result is probably due to a higher macronutrient availability in compost based growing media (Table 5).

A decrease of Mn concentration in plant tissue was observed with increasing compost presence in growing media (Table 10).

Tognetti et al. (2007) reported that the pH increases when mature composts are applied, [24]. The increase in EC values with rising proportions of composts in amended soils was reported by De Lucia et al. [25] where composted sewage sludge was incorporated into urban soils for three landscaping plants (*Phillyrea angustifolia*, *Myrtus communis*,

and *Pistacia lentiscus*). The results showed that the chemical properties of the amended soils were also directly affected by the SSC rate, but the effect of the compost on organic matter, nitrogen, and potassium contents decreased over time. Perez-Murcia et al. (2006), in experiments using substrates obtained by mixing sewage sludge compost with peat to grow horticultural plants (broccoli), found that the EC values of the growth media were strongly affected by the addition of CSS; the values exceeded the limit for an ideal substrate in the mixtures having more than 30% compost [9]. Bulk density increased with the adding of compost, as reported in previous studies that used compost as substrate component [26].

Hidalgo and Harkess [27] evaluated vermicompost as a substrate amendment mixed at different ratios with peat moss for chrysanthemum production and reported that the bulk density, the percentage of pore space, and water holding capacity increased as the vermicompost content increased. Presence of coarse particles in the compost increased the substrate aeration and water retention in compost enriched plant growth substrates [27, 28]. Macro- and micronutrients

TABLE 9: Concentrations of macronutrients in tissues of Bougainvillea plants as influenced by growing media (150DAT, on dry matter basis).

Growing medium	mg kg ⁻¹					
	N	P	K	Ca	Mg	Na
SSC0	25.1 ^c	6.53 ^d	38.3 ^c	19.7 ^c	9.63 ^c	4.01 ^b
SSC25	27.3 ^c	7.02 ^c	40.4 ^c	19.1 ^c	12.4 ^b	4.55 ^b
SSC40	30.2 ^b	7.51 ^b	45.2 ^b	20.9 ^b	14.3 ^b	5.30 ^a
SSC55	31.5 ^b	7.74 ^b	48.3 ^b	21.1 ^b	15.7 ^b	5.70 ^a
SSC70	35.4 ^a	8.40 ^a	56.2 ^a	23.4 ^a	18.5 ^a	5.92 ^a
Significance	*	*	**	*	*	*

Data are mean values, $n = 3$.

In each column different letters indicate significant differences for $P \leq 0.05$ (test S.N.K.).

* indicates difference at $P \leq 0.05$; ** indicates difference at $P \leq 0.01$.

TABLE 10: Concentrations of micronutrients in tissues of Bougainvillea plants as influenced by growing media (150DAT, on dry matter basis).

Growing medium	mg kg ⁻¹				
	Fe	B	Mn	Cu	Zn
SSC0	138 ^c	32.1	121.0 ^a	27.9 ^b	75.4 ^c
SSC25	141 ^c	30.3	90.6 ^b	30.5 ^b	124.7 ^b
SSC40	146 ^b	33.3	88.3 ^b	32.2 ^b	133.1 ^b
SSC55	156a ^b	30.95	82.2 ^c	36.9 ^a	151.7 ^a
SSC70	169 ^a	31.4	85.4 ^{bc}	40.2 ^a	160.8 ^a
Significance	*	n.s.	**	*	**

Data are mean values, $n = 3$.

In each column different letters indicate significant differences for $P \leq 0.05$ (test S.N.K.).

* indicates difference at $P \leq 0.05$; ** indicates difference at $P \leq 0.01$; n.s. indicates nonsignificant difference.

increased in compost-based mixtures compared to the control, confirming that sewage sludge compost can be a source of macro- and micronutrients [29]. The increase in macronutrient levels with compost incorporation was also observed by in an experiment of potted *Pelargonium* production [30]. Research has shown that the use of sewage sludge generally increases the heavy metal contents in compost: comparable results were reported by Wuest et al. (1995) in experiments involving aged mushroom compost [31].

Concerning the plant growth, positive correlations between the leaf area and the shoot dry weight have been reported by Tremblay and Senecal [32]. The increase in plant biomass production with the use of compost as a growing media component has been previously reported [9, 33]. The macronutrient availability improved with compost addition to the media: our results are in agree with Stellacci et al. in the growth of containered *Quercus ilex* [34]. Similar to our findings, Ostos et al. found that the P uptake was notably enhanced in *Pistacia lentiscus* cultivation [29]. Pinamonti et al. [35] found significant increases in the N, P, and K contents in cucumber, tomato, and strawberry plants grown in peat-sewage sludge compost media. Falahi-Adrakani et al. (1987) reported that cabbage and broccoli accumulated greater amounts of N and K from the composted sewage sludge amended medium [36]. The Mn decreases have been reported by other authors [5] and it is probably a consequence of the reduced Mn availability induced by the high pH values of these growing media (Table 5).

3.3. Life Cycle Analysis (LCA) Analysis. The results of the environmental analysis are reported in Figure 2.

The environmental burden of SSC25 was considered as a reference value equal to 100% of environmental burden. The growing media environmental loads decreases by reducing the peat content for all the compared indexes apart from GWP₁₀₀ (Global Warming Potential), even if the compost content increases atmospheric emissions due to the composting process emissions and waste transport (Figure 2).

These results were influenced by the long distance of the peat production areas (North Europe) from the composting and packaging plant. The GWP₁₀₀ index showed an opposite trend, indicating a potential growing media environmental burden increase as the added compost dose increases. This could be attributed to the increase of atmosphere emissions associated to the composting process. Our results were in line with previously published data on the environmental impact of growing media [13]. The LCA also showed that the SSC70 medium produced the best environmental performance for all the indices, except for GWP. This environmental benefit could be attributed to the absence of peat in such substrate.

In addition, a higher use of compost produces C sink phenomena [37–39] because the composting process retains part of the original sewage sludge C in the mature compost, rather than its release by oxidation or fermentation when the same wastes are landfilled.

Considering the environmental burdens avoided by the accumulation of organic waste in landfills and the reduction

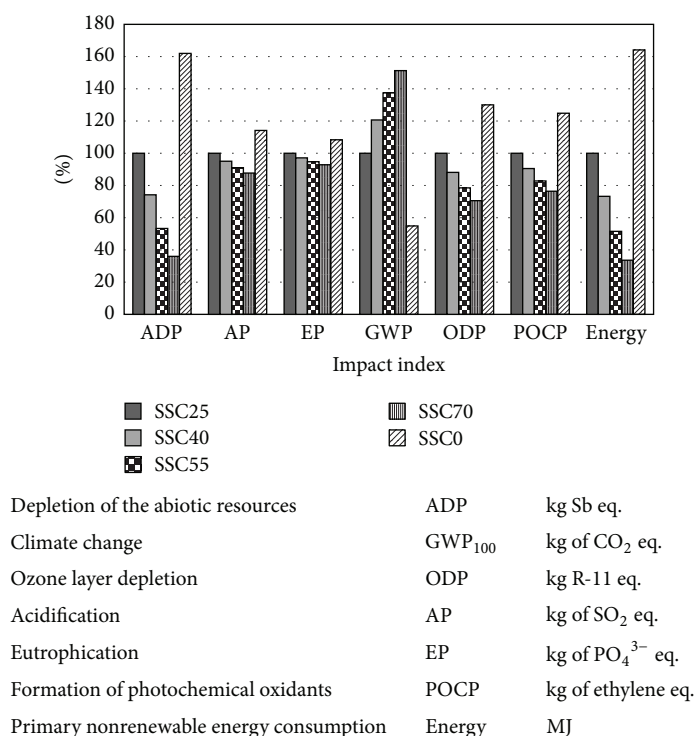


FIGURE 2: LCA of growing media compared: analysis results.

of fertilizers, some authors [22, 40, 41] have obtained an environmental credit for the production of compost. In this case, the use of compost can reduce the overall environmental load of the substrates or field crops. Finally, by maximizing the peat replacement by compost produced near the growing media production farms, the impact due to its transport is further reduced [42].

4. Conclusion

The presented results showed that replacement of peat by sewage sludge compost can increase as compared to the typical plant nursery substrates, mainly by increasing macro- and micronutrients supply to plants. In our experiment, replacement of peat up to 55% yielded in *Bougainvillea* plants of comparable quality as to the typical peat based substrate. The LCA showed that the addition of compost greatly reduced the environmental impact of the plant nursery chain.

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Research Article

Establishment of Native Grasses with Biosolids on Abandoned Croplands in Chihuahua, Mexico

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The objective of the work was to evaluate establishment and forage production of native grasses with application of biosolids, a byproduct of waste-water treatment, at an abandoned field, in Ejido Nuevo Delicias, Chihuahua, Mexico. Four biosolids rates from 0 (control) to 30 dry Mg ha⁻¹ and two methods of application, surface applied (BioSur) and soil incorporated (BioInc), were evaluated. Seedbed preparation included plowing and harrowing before rainfall. Field plots of 5 × 5 m were manually sown with a mix of blue grama (*Bouteloua gracilis*) (50%) and green sprangletop (*Leptochloa dubia*) (50%) in early August 2005. Experimental design was a randomized block with a split plot arrangement. Grass density, height, and forage production were estimated for three years. Data were analyzed with mixed linear models and repeated measures. Green sprangletop density increased under all biosolids rates regardless of method of application, while blue grama density slightly decreased. Biosolids were more beneficial for green sprangletop height than for blue grama height. Blue grama forage production slightly increased, while green sprangletop forage production increased the most at 10 Mg ha⁻¹ biosolids rate under BioSur method. It was concluded that BioSur application at 10 and 20 Mg ha⁻¹ rates had positive effects on the establishment and forage production of native grasses, especially green sprangletop.

1. Introduction

Native grasslands in Mexico comprehend about 9.9 million ha within central and north regions of the country [1]. Approximately 6.5 million ha shows different degradation types, including soil, wind, and water erosion and chemical and physical degradation [2]. Chihuahua grasslands, at northern Mexico, comprise about 4.5 million ha, supplying forage to livestock, habitat for wildlife, as well as ecosystem services [3, 4], and recreational activities. A study performed in 2002 [5] found that most of Chihuahua grasslands were affected by overgrazing, that caused grassland degradation. Also, recent studies showed that most of Chihuahua grasslands were in moderate-extreme to extreme rangeland health [6] and severely invaded by native shrubs and exotic grasses [7].

There are several techniques to rehabilitate degraded rangelands, including grazing management, brush management, prescribed fire, and range seeding. Each technique is recommended according to the severity of the grassland degradation and climate conditions. Range seeding is an alternative for rehabilitation of severely degraded rangelands and abandoned croplands. Some authors [8, 9] recommended native grasses such as sideoats grama (*Bouteloua curtipendula* (Michx.) Torr.), green sprangletop (*Leptochloa dubia* (Kunth) Nees), and Arizona cottontop (*Digitaria californica* (Benth.) Henr.) for restoration of degraded grasslands in Mexico. Blue grama (*Bouteloua gracilis* (Willd. ex Kunth.) Lag. ex Griffiths) is a native grass that needs high soil humidity and moderate temperatures for germination, emergence, and establishment [10, 11]. Therefore, techniques that increase soil water may

have a beneficial effect on blue grama seedling establishment. Other successful strategies such as the use of biofertilizers on blue grama and sideoats grama [12, 13] and straw amendments under greenhouse conditions [14] have also been used to increase grass establishment. Green sprangletop is a grass species showing adequate germination rates and good establishment under dry conditions in desert grasslands and is recommended for rangeland revegetation [15, 16]. Use of grass mixes for rangeland seeding is recommended to increase the success of seeding rangelands [17]. Blue grama and green sprangletop are two of the most important grasses in the semiarid region of Chihuahua and are decreasing because of overgrazing and drought [18, 19].

Application of biosolids, produced from wastewater treatment plants, may be a sustainable approach for promoting grass establishment as shown by several studies and biosolids disposal practice. In fact, surface application of biosolids can increase soil water infiltration [20, 21] and supply nutrients for plant growth [22, 23] in grasslands of arid and semiarid regions. However, research on the effects of biosolids on grass emergence under controlled conditions has shown variable results. A study conducted in Texas (USA) found no effects of surface-applied biosolids on blue grama or green sprangletop emergence under greenhouse conditions [24], whereas biosolids have increased seedling biomass of blue grama with surface-applied and soil-incorporated biosolids [25]. In a greenhouse study, beneficial effects of biosolids applied both at the surface or incorporated into soils on sideoats grama seedling growth were reported [26].

However, little research has been done on the use of biosolids for seeding native grasses under field conditions in arid or semiarid conditions. The only one field study found an increase in grass emergence with biosolids applied at the surface with moderate irrigation in desert grassland [24]. No research has been done either on the effects of biosolids on native grasses emergence and growth in abandoned croplands. Therefore, this study was designed to evaluate the effect of biosolids on grass density and forage production on an abandoned cropland in Chihuahua, Mexico.

2. Materials and Methods

The study was conducted in an abandoned field for 3 years at the Ejido Nuevo Delicias, Chihuahua, 75 km north of Chihuahua, Mexico. The study site is located within the Central Valleys region of Chihuahua, with a dry temperate climate, mean annual precipitation of 350 mm, mean annual temperature of 16°C, and an altitude of 1,640 m [27]. Soils have alluvial-colluvial origin with a sandy-loam texture. Original vegetation before crop cultivation was a shortgrass prairie with *Bouteloua-Aristida* grasses [28].

Thirty-two field plots of 5 × 5 m, with 10 m distance from each other, were established in June 2005 and marked with metal bars. Seedbed preparation included disk plowing and harrowing in June before rainy season (July to September). At the beginning of the rainy season, another disk harrowing was done to eliminate weeds and prepare seedbed. Seeding was broadcasted manually with a mix of blue grama var. Hachita and green sprangletop on August 3, 2005, according

TABLE 1: Soil chemical properties before biosolids application and biosolids composition from the North Wastewater Treatment Plant at Chihuahua city, Mexico.

Constituent ^a	Soil	Biosolids	Element	Soil	Biosolids
pH	6.5	6.7	Ca (mg kg ⁻¹)	850	3,412
OM (%)	0.55	12	Mg (mg kg ⁻¹)	125	1,037
TCC (%)	Free	Free	Na (mg kg ⁻¹)	237	1,312
EC (dS m ⁻¹)	1.4	3	Cu (mg kg ⁻¹)	1	9
N-NO ₃ ⁻ (mg kg ⁻¹)	60	66	Fe (mg kg ⁻¹)	4	30
P (mg kg ⁻¹)	8	7	Mn (mg kg ⁻¹)	14	15
K (mg kg ⁻¹)	362	962	Zn (mg kg ⁻¹)	3	111

^aOM: organic matter; TCC: total calcium carbonate; EC: electrical conductivity; N-NO₃⁻ and the rest of the elements are extractable and expressed on a dry weight basis.

to recommended seeding rates [17]. Blue grama was 64.3% pure live seed and 66% germination rate, and seeding rate at 50% was 1.5 kg ha⁻¹, with 8 gr plot⁻¹; Green sprangletop was 95% pure live seed, and 60% germination rate, and seeding rate at 50% was 1 kg ha⁻¹, with 4 gr plot⁻¹. After seeding, seeds were raked down to approximately 1 cm soil depth.

Anaerobic-stabilized biosolids from the North Wastewater Treatment Plant at Chihuahua city, receiving domestic sewage and treated with aerobic process, were applied to field plots, according to water content of biosolids (determined gravimetrically), plot size, and biosolids rate. Six biosolids samples of about 1 kg each were taken from the biosolids pile (approximately three tons) and a composite sample with about 200 gr of each 1 kg sample was taken and used for the following chemical analysis (Table 1): pH value (in CaCl₂), organic matter (OM) content by the K₂Cr₂O₇ wet oxidation method (Walkley and Black) [29], electrical conductivity (EC) by the saturated paste method, extractable nitrate-nitrogen (NO₃-N) [30], and plant available P (Bray-1 fraction) [31]. Concentrations of plant available K, Ca, Mg, and Na were determined by extractions with ammonium acetate, whereas the plant available Cu, Mn, Fe, and Zn were determined by extractions with DTPA [32]. The elemental analysis was carried out by Atomic Absorption Spectroscopy.

Biosolids were applied at 0 (control), 10, 20, or 30 ton DM ha⁻¹ rates using two application methods, either surface-applied (BioSur) or soil incorporated (BioInc), at the same date of seeding. For the BioSur method, seeding was done first and then biosolids were surface-applied and distributed within the plot through raking, while for the BioInc treatments, biosolids were surface-applied, distributed within the plot through raking, and incorporated into the soil through harrowing at approximately 20 cm soil depth before seeding. Study area was protected from grazing through fencing with barbed wire and poultry netting. Precipitation was measured during the growing seasons (Figure 1) and was low (84 mm) in the seeding year (2005) and during 2007 (180 mm) and above normal during 2006 (450 mm) and 2008 (285 mm).

Soil sampling at 0–15 cm soil depth was done with soil auger before biosolids application. Biosolids were removed from the soil surface (in biosolids-applied plots), and approximately 250 gr soil samples were taken in each plot, placed

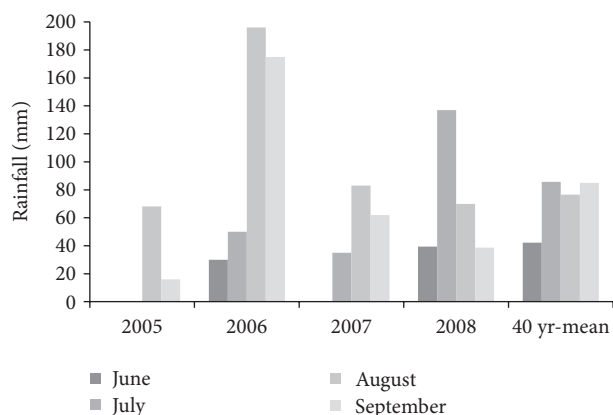


FIGURE 1: Monthly precipitation (June to September) at the study site from 2005 to 2008. Ejido Nuevo Delicias, Chihuahua.

in plastic bags in a portable cooler, and dried at ambient conditions for 48 hr. Then, soil samples were stored in a refrigerator for a week until chemical analysis. Results of the analysis are shown in Table 1. Soil sampling was repeated in early September, approximately one month after the biosolids application, for the measurement of electrical conductivity, organic matter content, and $\text{NO}_3\text{-N}$, P, and K availability with the same above mentioned methods.

Grass density was estimated by counting plants from both grasses within two 0.25 m^2 random quadrats plot^{-1} at the end of each growing season (September) from 2006 to 2008. Grass height in four random plants $\text{species}^{-1} \text{ plot}^{-1}$ and aboveground grass forage production by clipping in a 1 m^2 random quadrat plot^{-1} were estimated annually at the end of each growing season (end of September) during 2006 to 2008. Forage samples were oven-dried at 60°C for 48 hr, and forage production at kg ha^{-1} was estimated on a dry weight basis.

Experimental design was a randomized block with a split plot arrangement [33] with method of application as the main plot and biosolids rate as the subplot, with four replications. Linear models were used for statistical analysis on soil properties with Proc GLM [34]. Linear mixed models and year as repeated measures were used for grass height and density and forage production statistical analysis with Proc Mixed [35]. Several covariance structures were used to fit the best model including unstructured variance, compound symmetry, heterogeneous compound symmetry, and autoregressive. The best model for all variables was that with heterogeneous compound symmetry as a covariance structure, showing the smaller Akaike Information Criterion (AIC). A $P = 0.05$ probability was used to indicate significant effects. Mean separation was done using LSD test when significant effects were observed. Trend analyses were performed on some variables [34], and significant effects were declared at $P = 0.05$.

3. Results and Discussion

Soil organic matter and concentration of available P and K were not affected by biosolids rate or application method

TABLE 2: Chemical soil properties at 0–15 cm depth (mean \pm SE) one month after biosolids application at an abandoned field in Chihuahua, Mexico.

Biosolids rate (Mg ha^{-1})	EC ^a (dS m^{-1})	$\text{NO}_3\text{-N}$ (mg kg^{-1})
0	0.76 ± 0.2^b	6.8 ± 1.3^b
10	0.97 ± 0.1^b	11.0 ± 1.6^{ab}
20	1.01 ± 0.1^b	15.3 ± 3.3^a
30	1.65 ± 0.2^a	14.7 ± 2.8^a

^aEC: electrical conductivity. Biosolids rate mean values within each soil property followed by different letters are significantly different ($P < 0.05$; $n = 8$).

TABLE 3: Grass density (plants m^{-2} ; mean \pm SE) under different biosolids rates and two methods of biosolids application at a seeded abandoned field in Chihuahua, Mexico.

Biosolids rate (Mg ha^{-1})	BioInc ^a	BioSur
0	5.6 ± 0.7^{bcA}	6.0 ± 0.7^{abA}
10	8.0 ± 0.7^{aA}	7.6 ± 0.7^{aA}
20	4.9 ± 0.7^{cB}	7.3 ± 0.7^{aA}
30	7.2 ± 0.7^{abA}	4.5 ± 0.7^{bB}

^aBioInc: soil-incorporated method; BioSur: surface-applied method. Biosolids rate mean values followed by different lowercase letters within each method of application are significantly different ($P < 0.05$; $n = 24$). Method of application mean values followed by different uppercase letters within each biosolids rate are significantly different ($P < 0.05$; $n = 24$).

with an overall mean of $0.59 \pm 0.02\%$, $51.3 \pm 5.4 \text{ mg kg}^{-1}$, and $278 \pm 8 \text{ mg kg}^{-1}$, respectively, whereas the soil electrical conductivity (EC) was significantly increased ($P = 0.0023$) by the highest biosolids amendment rates (Table 2). The soil nitrate-nitrogen was significantly increased ($P = 0.0239$) by the 20 and 30 Mg ha^{-1} biosolids amendment rates (Table 2).

Beneficial effects of biosolids application related to the increase in soil water infiltration and soil $\text{NO}_3\text{-N}$ have been observed on arid grasslands [20–22]. Increase in water availability and plant available nitrogen were also observed with biosolids application on semiarid grasslands in central Mexico [23] and at greenhouse research with surface-applied and soil-incorporated biosolids [25, 26].

Grass density was influenced ($P = 0.0089$) by a rate \times method interaction, where grass density increased at 10 Mg ha^{-1} rate regardless of method of application (Table 3). At 20 Mg ha^{-1} biosolids rate, grass density was higher with BioSur method, whereas at 30 Mg ha^{-1} rate the grass density was higher at the BioInc method. A significant rate \times species interaction ($P = 0.0001$) was also found for grass density (Figure 2). In the control plots, green sprangletop density was low and was increased by all biosolids rates, whereas blue grama density was high in the control plots and decreased with biosolids application.

Effects of surface-applied biosolids on blue grama and green sprangletop emergence were evaluated under field conditions in west Texas rangelands [24], observing an increase in plant density with surface-applied biosolids and moderate irrigation in both grasses. Decreasing the blue grama density could be partially attributed to two factors: the possible

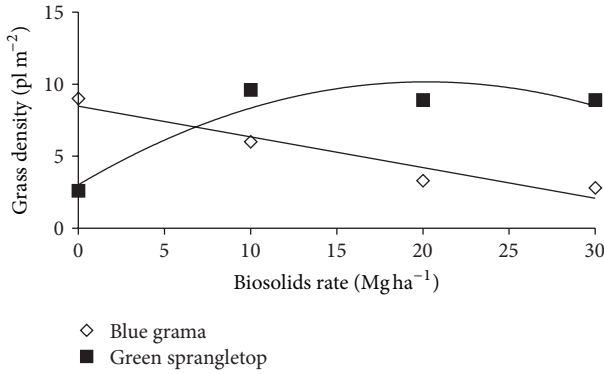


FIGURE 2: Grass density of blue grama (*Bouteloua gracilis*) and green sprangletop (*Leptochloa dubia*) under different biosolids rates during four years at a seeded abandoned field in Chihuahua, Mexico. $Y_{\text{Green-sprangletop}} = 3.02 + 0.707x - 0.017x^2$, $P = 0.001$, $r^2 = 0.89$, $n = 24$; $Y_{\text{Blue-grama}} = 8.47 - 0.213x$, $P = 0.0001$, $r^2 = 0.92$, $n = 24$.

physical obstruction effect of biosolids that interfered with blue grama emergence and/or a plant competition between blue grama, which is a slow growth species [36], and green sprangletop, which is a rapid growth grass [37]. Greenhouse studies have also shown a decrease in blue grama [25] and sideoats grama [26] emergence under both biosolids surface applied and soil incorporated.

The observed significant ($P = 0.0001$) rate \times species interaction showed that grass height increased with increasing biosolids rate for both grass species (Table 4). However, grass height was higher for green sprangletop than that of blue grama grass. A significant ($P = 0.0138$) three-way interaction (rate \times method \times sampling time) was also found for grass height (Figure 3). In the control plots, the grass height was low and increased with biosolids rate for both methods of application. However, BioSur showed a stronger effect on plant height compared to BioInc, especially at the intermediate biosolids rates, except in 2007 where BioSur and BioInc resulted in similar plant heights. Increases in grass height with surface application of biosolids have also been reported in tobosagrass (*Pleuraphis mutica* Buckl.), alkali sacaton (*Sporobolus airoides* (Torr.) Torr.), and blue grama [38–40] under arid and semiarid conditions, attributed to the improvement of plant growing conditions with biosolids application.

A significant ($P = 0.0031$) three way interaction (rate \times method \times species) was found for forage production (Figure 4). Blue grama forage production slightly increased at the 10 Mg ha^{-1} rate regardless of the application method, whereas it was similar between control and 20 and 30 Mg ha^{-1} rates. Differently, green sprangletop forage production was much higher than blue grama at all biosolids rates regardless of application method. Also, BioSur applications benefited green sprangletop forage production more than BioInc applications. Species \times date interaction was also significant ($P = 0.0001$) in forage production (Table 5). Blue grama forage production was lower than that of green sprangletop and also varied among sampling times. However, correlation between

TABLE 4: Grass species height (mean \pm SE) of blue grama (*Bouteloua gracilis*) and green sprangletop (*Leptochloa dubia*) under different biosolids rates at a seeded abandoned field in Chihuahua, Mexico.

Biosolids rate (Mg ha^{-1})	Blue grama (cm)	Green sprangletop (cm)
0	$27.2 \pm 4.8^{\text{cA}}$	$19.6 \pm 4.8^{\text{bA}}$
10	$71.6 \pm 4.8^{\text{aA}}$	$84.4 \pm 4.8^{\text{aA}}$
20	$52.2 \pm 4.8^{\text{bB}}$	$81.1 \pm 4.8^{\text{aA}}$
30	$39.1 \pm 4.8^{\text{bcB}}$	$83.3 \pm 4.8^{\text{aA}}$

Biosolids rate mean values followed by different lowercase letters within each grass species are significantly different ($P < 0.05$; $n = 24$). Grass species mean values followed by different uppercase letters within each biosolids rate are significantly different ($P < 0.05$; $n = 24$).

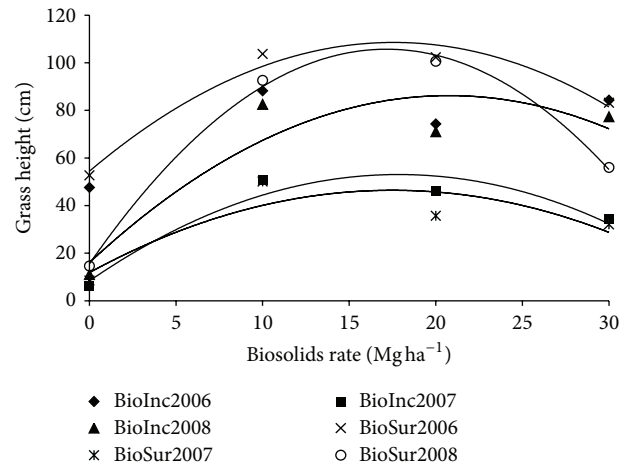


FIGURE 3: Grass height under different biosolids rates, methods of application (BioInc: soil-incorporated method; BioSur: surface-applied method), and dates (year 2006, 2007, or 2008) at a seeded abandoned field in Chihuahua, Mexico. $Y_{\text{BioInc2006}} = \text{no linear}$ ($P = 0.1320$) or quadratic effect ($P = 0.2348$), $n = 8$; $Y_{\text{BioInc2007}} = 8.33 + 5.00x - 0.14x^2$, $P = 0.0001$, $r^2 = 0.92$, $n = 8$; $Y_{\text{BioInc2008}} = 16.04 + 6.76x - 0.163x^2$, $P = 0.0139$, $r^2 = 0.84$, $n = 8$; $Y_{\text{BioSur2006}} = 54.43 + 6.15x - 0.17x^2$, $P = 0.96$, $r^2 = 0.96$, $n = 8$; $Y_{\text{BioSur2007}} = 11.84 + 3.95x - 0.11x^2$, $P = 0.0003$, $r^2 = 0.75$, $n = 8$; $Y_{\text{BioSur2008}} = 15.47 + 10.51x - 0.30x^2$, $P = 0.0001$, $r^2 = 0.93$, $n = 8$.

forage production and precipitation was very low ($r = 0.05$), which is possibly attributed to the different morphology and slow growth rate of blue grama [36]. Green sprangletop forage production was high during 2006, a wet year, and decreased the following two years that were drier than 2006, showing a low correlation to precipitation ($r = 0.31$).

Forage production was highly benefited by biosolids application in some rate-method combinations, which is attributed to the improvement of plant growing conditions as mentioned earlier. However, these benefits were species specific. Green sprangletop is characterized as a rapid seed spread rate, high seedling vigor, and a higher moisture user [37]; therefore, this grass may have taken advantage of the improved soil conditions under biosolids application. Conversely, blue grama is a slow seed spread rate, low seedling vigor, and a low moisture user grass [36] which could have negatively

TABLE 5: Forage dry matter production (mean \pm SE) of blue grama (*Bouteloua gracilis*) and green sprangletop (*Leptochloa dubia*) under different dates at a seeded abandoned field in Chihuahua, Mexico.

Date	Blue grama (kg ha ⁻¹)	Green sprangletop (kg ha ⁻¹)
Growing season 2006	240 \pm 48 ^{abB}	2,297 \pm 360 ^{aA}
Growing season 2007	166 \pm 37 ^{bB}	1,117 \pm 159 ^{bA}
Growing season 2008	394 \pm 89 ^{ab}	1,211 \pm 250 ^{bA}

Date mean values followed by different lowercase letters within each grass species are significantly different ($P < 0.05$; $n = 32$). Grass species mean values followed by different uppercase letters within each date are significantly different ($P < 0.05$; $n = 32$).

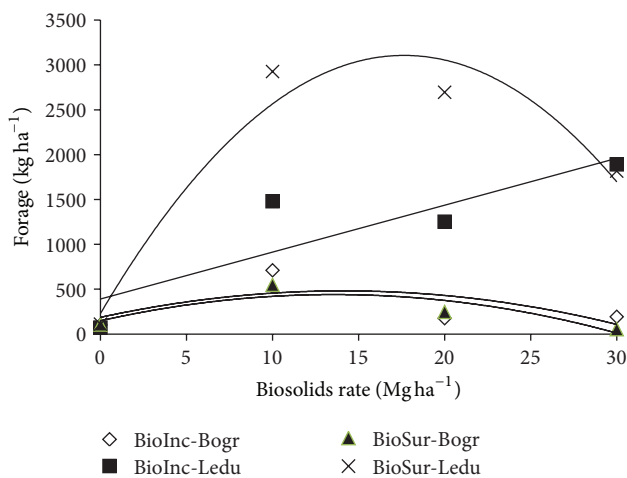


FIGURE 4: Forage production under different biosolids rates, methods of application, and grass species at a seeded abandoned field in Chihuahua, Mexico. BioInc: soil-incorporated biosolids; BioSur: surface-applied biosolids; Bogr: *Bouteloua gracilis*; Ledu: *Leptochloa dubia*; $Y_{\text{BioInc-Ledu}} = 389.4 + 52.29x$, $P = 0.0003$, $r^2 = 0.74$, $n = 12$; $Y_{\text{BioSur-Ledu}} = 229.95 + 325.99x - 9.23x^2$, $P = 0.0001$, $r^2 = 0.94$, $n = 12$; $Y_{\text{BioInc-Bogr}} = 185.65 + 41.86x - 1.48x^2$, $P = 0.0039$, $r^2 = 0.39$, $n = 12$; $Y_{\text{BioSur-Bogr}} = 147.77 + 43.12x - 1.59x^2$, $P = 0.0017$, $r^2 = 0.75$, $n = 12$.

affected blue grama growth when sown along with green sprangletop. Indications of plant competition such as reduced survival, height, and forage, production have been observed in blue grama when sown in western wheatgrass (*Agropyron smithii* Rydb.) sod [41]. Also, forage production of blue grama decreased when seeded in mixtures with western wheatgrass or green needlegrass (*Stipa viridula* Trin.) [42].

In general, BioSur method showed better results than those of BioInc method on both grass height and forage production, especially at the 10 and 20 Mg ha⁻¹ rates. Research supports that surface-applied biosolids increase water infiltration in grassland sites [21]. Also, studies on biosolids application to grasslands have shown that soil volumetric water increases with BioSur compared to BioInc method at 10 and 20 Mg ha⁻¹ rates [25]. Surface applications could

have reduced soil water evaporation underneath biosolids aggregates, while BioInc applications apparently did not affect surface soil water since biosolids are mixed into the soil. Also, method of amendment application matters, since soil-incorporated wood chip amendments decreased grass growth compared to surface-applied amendment [43].

Although only small benefits were observed on blue grama height and forage production, biosolids application exerted an impressive beneficial effect on green sprangletop. This opens the possibility of using biosolids or other organic amendments to increase establishment and forage production of native grasses in degraded grasslands or abandoned fields in arid and semiarid regions. Biosolids generation will increase in the future along with human population and wastewater treatment, and their beneficial use on land application must be preferred as an option for biosolids disposal over incineration or land filling.

4. Conclusions

This field study provided evidence that biosolids application was beneficial for blue grama and green sprangletop establishment and forage production, especially at 10 Mg ha⁻¹ rate. Surface-applied biosolids showed more beneficial effects on grass growth than soil-incorporated biosolids and may represent a strategy for the sustainable management of biosolids produced by wastewater treatment plants. However, these preliminary data need further confirmation by more field experiments involving more plant and soil types and longer sampling periods.

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Research Article

Temperature Effects on Phosphorus Release from a Biosolids-Amended Soil

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This study was designed to evaluate the effects of temperature on the potential leachable P pool and distribution of chemical P forms in a biosolids-amended soil. A P-deficient Spodosol was incubated with seven biosolids and inorganic P fertilizer at 20 and 32°C for 90 days. Amendments were applied to provide a total P concentration of 112 mg kg⁻¹ soil, which correspond to a field application of ~224 kg P ha⁻¹. Cumulative P mass leached during the 90 d study for any P source was <2% of the applied P, but greater cumulative P mass was released from the biological P removal and composted biosolids than from the heat-dried materials. Increasing temperature (20 to 32°C) generally decreased cumulative P mass leached, suggesting greater soil affinity to retain P at 32°C than at 20°C. In a static incubation experiment (no leaching), soil water-extractable P concentrations were reduced over time, but no temperature effect was observed. Similarly, P distribution among the various fractions was not affected by temperature. The relatively great ability of the soil to sorb P masked differences in biosolids properties and the potential impacts of temperature on P lability. Additional work using low P-sorbing soils is warranted.

1. Introduction

Biosolids can provide essential nutrients to plant and improve soil chemical, physical, and biological properties [1]. However, repeated biosolids applications based on plant N requirements supply P in excess of crop requirements, resulting in soil P accumulation. Environmental concerns associated with the buildup of soil P and potential losses of P movement to water bodies via surface runoff, vertical leaching, and erosion exist. Although P is typically immobile in most soils, coarse-textured soils are prone to P transport [2]. Florida Spodosols are particularly susceptible to P leaching due to the lack of reactive minerals, low Fe and Al oxides, and organic matter concentrations in surface horizons [3]. Moreover, poorly drained Spodosols associated with relatively shallow water tables intercepted by drainage ditches increase the potential risks of P edge-field losses.

Phosphorus lability in biosolids-treated soils depends on the forms of P initially present in the biosolids and

the characteristics of the soil receiving the residual. The wastewater treatment processes strongly influence the chemistry and P pools in biosolids [4]. For instance, biological P removal (BPR) processes can increase P extractability and runoff losses [5, 6]. Conversely, biosolids treated with Al and Fe or heat-dried materials generally exhibit low extractable P concentrations [7–9]. According to [10], P lability from biosolids produced via BPR processes was similar to commercial P fertilizer, while in heat-dried materials containing high levels of Al and Fe less than 10% of total P was labile. However, differences in biosolids-P lability in response to biosolids treatment method appear to be less pronounced in P-enriched soils or soils that have high affinity to retain P [11].

Although biosolids have typically a wide range of physical and chemical properties, the vast majority of the P in biosolids is present as inorganic P [12, 13]. Research has shown that P lability in biosolids-treated soils is affected by the organic source as well as the soil P sorption characteristics and initial soil P levels [10, 11]. In addition, P forms

TABLE 1: Selected soil chemical properties.

Soil	Sand %	Organic matter g kg ⁻¹	pH	Total P	Mehlich-1 P	Oxalate -extractable		PSI _{ox} ¹
						P mg kg ⁻¹	Fe Al	
Millhopper	95	19	5.6	1339	5.7	585	2222 956	0.25

¹Phosphorus saturation index (PSI) = $[P \div (Al + Fe)]$ with P, Fe, and Al concentrations expressed as mmol kg⁻¹.

and availability in biosolids-treated soils can be affected by environmental conditions, such as temperature and moisture content. Temperature can also increase the rate of reaction between soil and added P, resulting in a rapid decrease in soluble P [14]. Phosphorus availability increased in manure-treated soils when temperature increased from 10 to 20°C [15] and in a forest soil receiving P fertilizer [16]. Flooded sediments released much more P when incubated at 35°C than at 7°C [16], and temperature increased P release in flooded soils [17]. Fe-strip P concentrations decreased when biosolids-amended soils were incubated at 37°C than at 25°C, suggesting greater microbial immobilization of soluble P at a higher temperature [18]. Chemical mechanisms involved in P dynamics can also be affected by temperature. P extracted by NaHCO₃ was very sensitive to changes in temperature, increasing by ~3% per °C increase [17, 19]. Contrarily, [20] reported no differences in Olsen-extractable (available) P concentrations in calcareous soils incubated at temperatures varying from 5 to 25°C, possibly due the presence of Ca-based minerals that favored P sorption. It has been suggested that in some cases NaHCO₃ might not be a good indicator of soil P changes due to the increasing temperature [21]. Reference [22] found no significant effect of temperature on the amount of P released from swine slurry-treated soils; however, for soils receiving beef cattle manure, temperature increases increased P sorption in heavier-textured soils and decreased P retention in sandy soils. Phosphate adsorption increased with temperature (25 to 55°C) in five tropical soils, and P desorption was markedly reduced. Biosolids incubated at room temperature for 15 months exhibited greater concentrations of water-soluble P as compared to biosolids samples stored at -2°C [13]. The objective of this study was to investigate the effects of temperature on the potential leachable P pool and distribution of chemical P forms in biosolids-amended soils.

2. Material and Methods

2.1. Soil and Biosolids Samples. Composite samples of a sand soil (Millhopper soil series (loamy, siliceous, and hyperthermic Grossarenic Paleudults)) were collected from the 0 to 15 cm depth in Santa Fe Beef Research Unit, FL, USA (29°55'N, 82°30'W). Soil samples were air-dried and sieved to pass through a 2 mm screen sieve. Selected chemical characteristics are shown in Table 1. Seven different types of biosolids were collected at different locations and stored at 4°C until the experiment began. Chemical compositions of the various biosolids (Table 2) were similar to biosolids

produced nationwide [23]. Total P concentrations ranged from ~2% to 4%.

2.2. Incubation Experiment. An incubation study was designed to determine the potential P leachable pool from soils amended with biosolids and fertilizer. Appropriate amounts of biosolids and P fertilizer (triple super phosphate) were applied to provide a total P concentration of 112 mg kg⁻¹ soil, which correspond to a field application of ~224 kg P ha⁻¹ or 10 Mg ha⁻¹ of a typical biosolids containing between 2% and 2.2% of P. For each treatment, 100 g (eq. dry wt.) of soil were thoroughly mixed with biosolids in plastic bags. Samples were wetted to 80% of the field capacity. Biosolids-treated samples and control soils were incubated aerobically in filter chambers in the dark at 20 and 32°C for 90 days. Chambers containing treated samples were capped to reduce evaporation but aerated weekly by removing lids from containers for 2 hours to reestablish ambient conditions. Soil moisture contents were checked regularly by weighing the chambers, and water was added to maintain the samples at 80% of field capacity. Chambers were leached periodically, as described below, to determine potential P losses. Each treatment was replicated three times.

In a separate experiment, soils were treated with biosolids (at a P rate of 112 mg kg⁻¹) and incubated in the dark at 20 and 32°C as described previously but were not subjected to leaching (static incubation). At 0, 15, 30, 45, and 90 days of incubation, subsamples were taken for P analysis. Changes in P forms over time were evaluated using a modification of the sequential extraction procedure developed by [24]. Water-extractable P concentrations were also determined in the treated samples to assess the effects of time and temperature on P extractability.

2.3. Leaching Protocol. Samples were leached with 60 mL of DDI water (~2 pore volume) at 15, 30, 60, and 90 days. Immediately after the discharge, a subsample was filtered through a 0.45 µm membrane filter. Filtered leachates were analyzed for total P using the potassium persulfate/sulfuric acid digestion (EPA method 365.1) [25], soluble reactive P (SRP) [26], pH, electrical conductivity (EC), and dissolved organic C (DOC) concentrations.

2.4. Statistical Analysis. Statistical analyses were performed using Proc Mixed [27]. Biosolids type and temperature were considered fixed effects, with replicates and their interactions being considered as random effects. Mean separation of treatment differences was by LSD. Treatments and their interactions were considered significant when *F*-test *P* values

TABLE 2: Selected properties of biosolids materials.

Biosolids	Treatment process	Class	pH	Solids %	C	Total N	P	P g kg ⁻¹	Oxalate-extractable Al	Fe	PSI
ATAD ¹	Aerobically digested, biological P removal	A	6.3	3	350	55	40	23	3.2	8.3	2.8
Disney compost ¹	Composted, biological P removal	A	5.7	70	420	28	15	11	7.0	20	0.6
OC South Cake ¹	Anaerobically digested, biological P removal	B	8.1	15	410	66	23	23	5.0	4.4	2.8
OC East Cake ¹	Aerobically digested, biological P removal	NA	5.9	16	430	70	20	17	1.3	3.4	5.0
JE A Cake	Anaerobically digested, thickened	A	7.9	22	360	51	19	18	6.0	5.0	1.9
Tampa pellets	Anaerobically digested, thermally dried	A	5.6	96	410	56	21	19	6.0	5.1	2.0
WPB	Composted	A	5.8	67	420	25	19	19	3.0	3.0	3.7

¹ Denotes biological P removal biosolids.

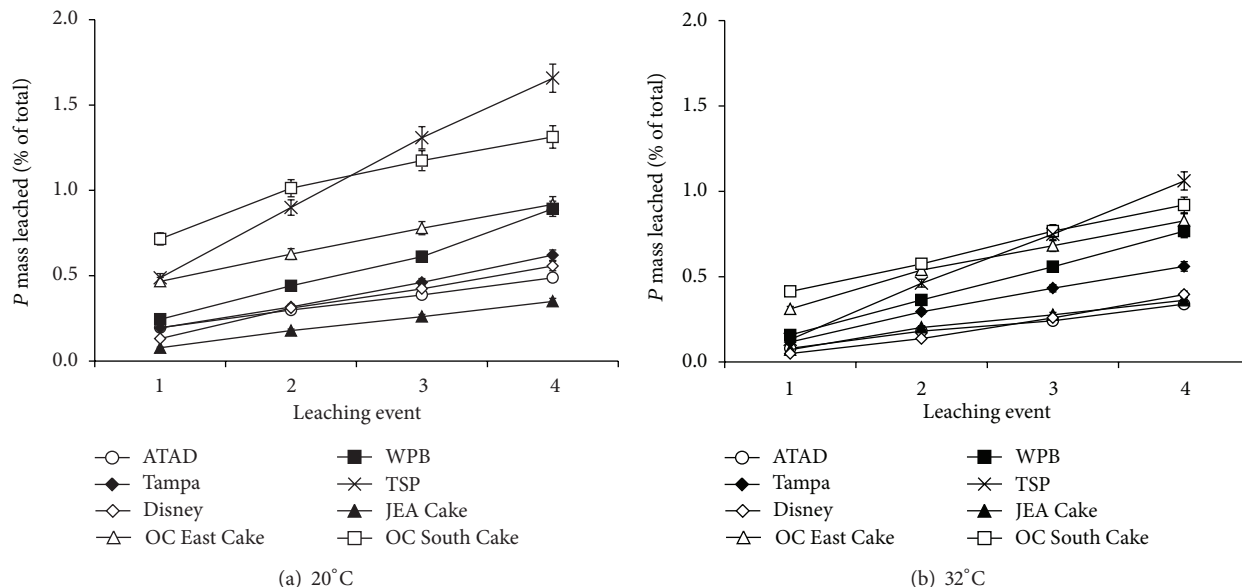


FIGURE 1: Cumulative P mass leached over the 90 d incubation. Leaching events 1, 2, 3, and 4 correspond to 15, 30, 60, and 90 d of incubation. Initial P mass applied 112 mg P kg⁻¹ soil P (224 kg P ha⁻¹). Error bars represent one standard error. Data represent the average of three replicates. Error bars represent one standard error. Open symbols represent biological nutrient removal biosolids.

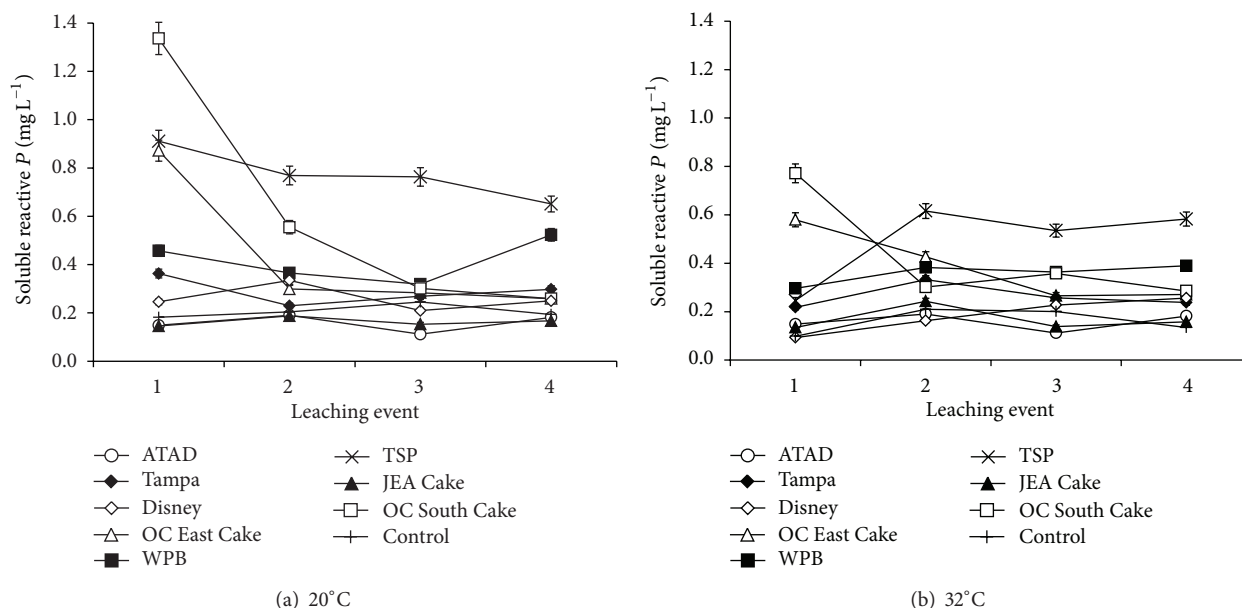


FIGURE 2: Leachate soluble reactive P (SRP) concentrations. Leaching events 1, 2, 3, and 4 correspond to 15, 30, 60, and 90 d of incubation. P rate 112 mg P kg⁻¹ (224 kg P ha⁻¹). Error bars represent one standard error. Data represent the average of three replicates. Open symbols represent biological nutrient removal biosolids.

were <0.05. Interactions not discussed in the results and discussion section were not significant ($P > 0.05$).

3. Results and Discussion

3.1. Phosphorus Leaching. After 90 d of incubation and a total of 8 PV of drainage, cumulative P mass leached was

greater for TSP-treated soils than biosolids-treated soils at both temperatures (Figure 1). Biosolids-treated soils leached ~20% to 87% less P than TSP-treated samples, suggesting that P availability in the biosolids was much smaller than in TSP. Greater cumulative P mass was released from two of the Cake materials (OC South and OC East) and from composted biosolids (WPB) as compared to the JEA Cake, Tampa, and Disney biosolids. This indicates that there was a significant

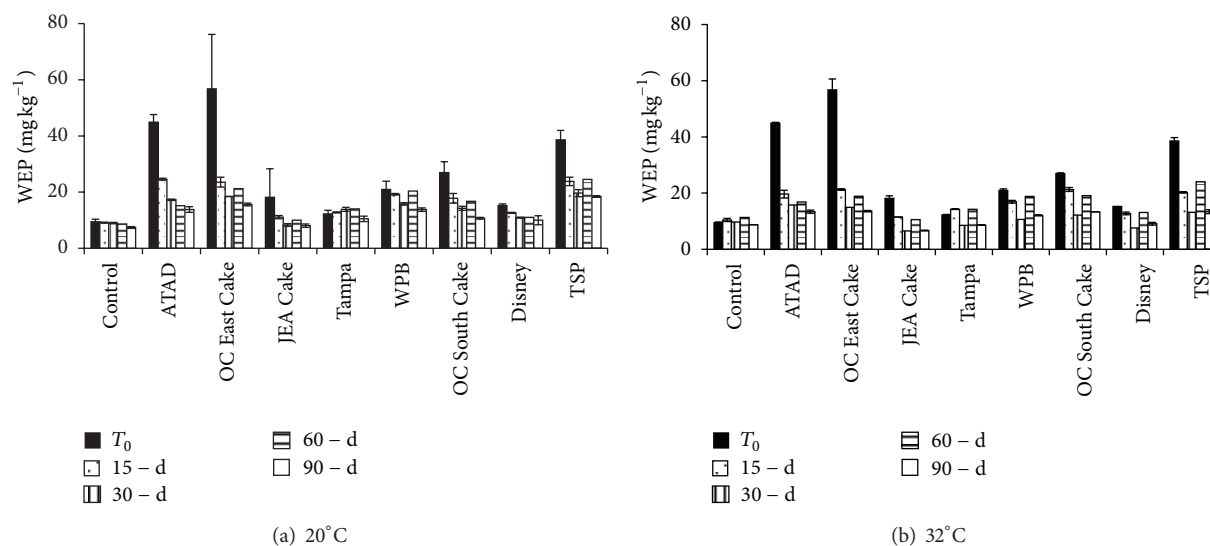


FIGURE 3: Changes in WEP concentrations as affected by incubation period and temperature.

TABLE 3: Leachate dissolved organic C concentrations.

Biosolids	Dissolved organic C (mg L ⁻¹)							
	1st leaching		2nd leaching		3rd leaching		4th leaching	
	20°C	32°C	20°C	32°C	20°C	32°C	20°C	32°C
Control	11	5	12	12	12	14	12	15
ATAD	39a ¹	10b	13	11	10	10	12	14
OC East Cake	32a	14b	15b	18a	11b	16a	12	13
JEA Cake	26a	11b	14	16	10b	14a	10b	14a
Tampa	38a	16b	16	18	12b	15a	12b	18a
WPB	35a	14b	22	20	21	17	26	23
OC South Cake	19a	10b	18	20	16	14	12	15
Disney	30a	7b	24a	12b	13	18	15	22
TSP	14a	3b	15	14	14	16	14	17

¹Statistical analysis is valid within each leaching event. Means followed by different letters within biosolids source and leaching event are significantly different using the LSD procedure ($P \leq 0.05$).

effect of biosolids sources on the amount of P leached. Greater cumulative P release from OC South compared to OC East material is due to the digestion process. While OC East is aerobically digested, the OC South is anaerobically digested which may result in nearly complete release of biologically fixed P [28]. Results observed in this current study are consistent with previous studies [9]. These authors concluded that P release from biosolids depends on the treatment by which the material is being produced.

Compared to the initial P load ($112 \mu\text{g P g}^{-1}$ soil or $\sim 224 \text{ kg P ha}^{-1}$), cumulative P mass leached represented $<2\%$ of the applied P. At 20°C, between 0.3% to 1.3% of total applied P was leached throughout the 90 d incubation (for JEA and OC South Cake biosolids, resp.). This suggested the great affinity of the Millhopper soil to retain added P (mainly because of the considerable concentrations of oxalate-extractable Fe and Al) and the negligible potential for P leaching in this soil even when highly soluble P sources such as TSP are applied. Perhaps greater P rates or repeated

application of biosolids would increase the risks associated with P leaching if the sorption sites became significantly occupied.

The majority (80% to 100%) of the P leached at both temperatures was SRP, with no differences in P form among the biosolids sources. Large SRP concentrations were observed in the first leaching event (15 d) for the OC South and East Cake treatments especially at 20°C (Figure 2(a)). This suggests the presence of readily available forms of P in these materials, preferentially released in the first leaching event. TSP followed the same pattern at the lower temperature; however, at 32°C, SRP concentrations increased after the second leaching event (Figure 2(b)). The other biosolids did not show a clear trend, and, despite some fluctuations, SRP concentrations were, in general, almost constant during the various leachings.

In general, cumulative P mass leached was significantly smaller when biosolids were incubated at greater temperature (32°C). For instance, cumulative P mass released by OC South

TABLE 4: Soil P distributions among the various fractions at the beginning (T_0) and after 90 days of incubation (90 d).

Biosolids	Soil P fractions ¹									
	H ₂ O		KCl		NaOHP _i		NaOHP _o		Residual	
	T_0	90 d ²	T_0	90 d	T_0	90 d	T_0	90 d	T_0	90 d
	Average P concentration (mg kg ⁻¹)									
Control	9.5 (0.9) ³	8.1 (0.7)	2.7 (0.2)	3.7 (0.3)	760 (68)	726 (61)	67 (6.0)	95 (8.0)	68 (6.0)	43 (3.6)
ATAD	45 (3.8)	14 (1.1)	3.9 (0.3)	10 (0.9)	683 (57)	799 (67)	66 (5.5)	72 (6.0)	71 (6.0)	46 (3.8)
OC East Cake	57 (4.3)	15 (1.1)	8.9 (0.7)	10 (0.8)	779 (59)	773 (59)	78 (6.0)	71 (5.3)	79 (6.0)	48 (3.7)
JEA Cake	18 (1.6)	7.4 (0.7)	3.3 (0.3)	6.3 (0.5)	764 (67)	763 (67)	51 (4.5)	73 (6.4)	90 (7.9)	48 (4.2)
Tampa	12 (1.0)	9.6 (0.8)	4.5 (0.4)	7.3 (0.6)	783 (65)	775 (65)	74 (6.2)	45.4 (3.8)	89 (7.5)	53 (4.4)
WPB	21 (1.8)	13 (1.1)	5.5 (0.5)	6.5 (0.5)	775 (65)	794 (66)	70 (5.9)	78 (6.5)	79 (6.6)	56 (4.7)
OC South Cake	27 (2.2)	12 (1.0)	6.9 (0.6)	9.3 (0.8)	761 (62)	762 (62)	77 (6.3)	56 (4.5)	83 (6.8)	48 (3.9)
Disney	15 (1.2)	9.5 (0.8)	3.3 (0.3)	5.4 (0.4)	786 (63)	853 (69)	35 (2.8)	63 (5.1)	86 (6.9)	55 (4.4)
TSP	39 (3.3)	16 (1.4)	6.2 (0.5)	6.8 (0.6)	739 (62)	823 (74)	54 (4.5)	67 (6.0)	74 (6.2)	49 (4.4)

¹ H₂O and KCl represent water-soluble and exchangeable P fractions, respectively; NaOHP_i and NaOHP_o represent the Al- and Fe-bound inorganic and organic P; HCl is Ca-bound P; Residual is mineral-associated inorganic P.

² Values represent average P concentration of samples incubated at 20°C and 32°C.

³ Data in parenthesis are % of total P.

Cake decreased by 57% when treated soils were incubated at 32°C compared with release at 20°C. Exceptions were JEA Cake and Tampa biosolids, which exhibited no significant effect of temperature on P release. TSP-treated soils exhibited similar patterns and leached much less P when incubated at the greater temperature. It was not clear if the temperature effects on P leachability were due to the greater soil affinity to retain P at 32°C compared to 20°C or if biosolids-borne P availability was also affected by increased temperature. A number of studies document the impacts of temperature on soil P sorption reactions [29–32]. In general, high temperatures increase the rate of P transfer to strongly bond forms and thus decrease P concentration in solution. Therefore, the reductions in P leaching concentrations at 32°C observed in this current study can be attributed to the greater soil affinity to retain P in stable forms at a higher temperature.

3.2. Changes in P Extractability and Distribution over Time.

Results from the static incubation (samples not subjected to leaching) revealed that, at both temperatures, WEP concentrations were significantly reduced over time (Figure 3). The decrease in P extractability was similar when samples were incubated at 20°C (Figure 3(a)) or 32°C (Figure 3(b)), suggesting that there was no significant effect of temperature on WEP concentrations. The reactions between biosolids-borne P with the soils matrix were favored with time, and thus, P extractability was considerably reduced. Similar results were also reported by [28, 32] who observed that P becomes less bioavailable with time due to P diffusion into soil sorption sites.

Overall P distribution among the various fractions was the same after 90 d of incubation (static incubation) (Table 4). NaOH-P (Al- and Fe-bound P) was the dominant fraction controlling P retention in the biosolids-treated soils, in agreement with other numerous studies [33–35]. The NaOH fraction is widely assumed to represent P associated with poor crystalline Al and Fe oxides and is the most important fraction controlling the P reactions in noncalcareous biosolids-treated soils.

3.3. Biosolids Dissolved Organic C Release. Large differences in DOC concentrations at 20°C and 32°C were observed in samples from the first leaching event (Table 3). The more easily degradable C fraction was likely leached in the first leaching event, the less available compounds remained in the treated soils. In the first leaching event, DOC release was, on average, ~3-fold greater at 20°C than at 32°C. Because complex processes control DOC release from biosolids-amended soils, it is difficult to distinguish whether greater mineralization of C compounds to CO₂ occurred at 32°C resulting in less DOC released or a larger proportion of complex, water-insoluble C was converted into labile, water-soluble C forms at 20°C. Numerous studies suggested that soil microbial activity is promoted at the greater temperature; thus, it is possible that microbes at 32°C were more efficient in complete utilization C from the various biosolids as an energy source. Reference [36] also observed greater biosolids mineralization rates when the material was applied in the

summer (higher temperature and rainfall) as compared to spring application. Leachate pH and EC data further support the hypothesis that greater biosolids mineralization rates occurred at 32°C than those at 20°C (data not shown). In subsequent leaching events, however, there was no clear evidence of temperature effect on DOC release. Some biosolids increased DOC release at 32°C (OC East Cake, JEA Cake, and Tampa), while others (ATAD, OC South Cake, Disney) did not show a clear pattern.

Dissolved C released clearly did not follow the same pattern as P leaching. This occurred because the mechanisms by which these elements are retained and mineralized in biosolids-treated soils are not related. Although the majority of the P present in the biosolids is inorganic P, our hypothesis was that P release increases as mineralization of biosolids occurs. However, our results suggested that the interaction between biosolids degradation and P availability is much more complex. For instance, OC East and South biosolids Cakes showed a decline in the amounts of P leached as a function of leaching event for both temperatures (Figure 2), but DOC concentrations in the leachates followed a different pattern (Table 3). Perhaps, the great affinity of the Millhopper soil for P played a major role by masking any relationship between DOC release and P leaching.

4. Conclusions

Negligible amounts (<2%) of the total P applied as either biosolids or TSP were leached from the Millhopper soil during the 90 d study (total of 8 pore volumes of drainage). The appreciable amounts of oxalate-extractable Al and Fe oxides in the soil apparently retained most of the applied P and prevented leaching. The relatively great ability of the soil to sorb P masked differences in P solubility among the various sources and the potential impacts of temperature on biosolids-P availability. Additional work using other soils is warranted because this study focused on a Spodosol with relatively high P-sorbing capacity. Studies on other sandy soils in Florida reveal much greater P mobility [35].

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Research Article

Residual Effects of Biosolids Application on Forage Production of Semiarid Grassland in Jalisco, Mexico

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Single application of biosolids increases forage production on semiarid grasslands. Residual effects of biosolids on forage production have been scarcely measured in semiarid grasslands. The objective was to evaluate the residual effects of biosolids application on forage production of blue grama (*Bouteloua gracilis* (Willd. ex Kunth) Lag. ex Griffiths) and other grasses at a semiarid grassland in Jalisco, Mexico. The study was performed at shortgrass prairie in northeast Jalisco. Field plots were selected to include blue grama plants before rainy season in 2002. Aerobic biosolids were applied at 0 (control), 15, 30, 45, 60, 75, or 90 dry Mg ha⁻¹ under a completely random design with five replications. Forage production was estimated by clipping at the end of the growing season during five years. Data analysis was performed with linear mixed model and repeated measures. Forage production was influenced by a rate × year × species interaction ($P = 0.0001$). Blue grama forage production increased with increasing biosolids rates during all years, with the magnitude of this response varying among years. Forage production of other grass species slightly decreased with biosolids application. Single biosolids application had a residual effect on forage production throughout five years in semiarid grasslands.

1. Introduction

Approximately half of the world native grasslands show moderate to strong degradation [1], while approximately 95% of the grasslands are overgrazed and show degradation in Mexico [2]. Studies in Mexico indicate that most of the shortgrass prairie in Jalisco [3], Zacatecas, and Chihuahua [4] show moderate-extreme to extreme rangeland health. Oak-bunchgrass and Halophyte grasslands also show deterioration, including high invasion of native shrubs and exotic grasses in Chihuahua [5].

Practices to recover degraded grasslands may include use of fertilizers, prescribed fire, shrub management, and soil and water conservation techniques. Fertilizer application to native grasslands has increased forage production [6, 7] although high fertilizer costs make this a low profitability

technique. An alternative might be application of organic byproducts such as biosolids that are generated at wastewater treatment plants and can be used as fertilizer and soil amendments [8, 9].

Several studies have shown that surface-applied biosolids promote grass production at arid and semiarid grasslands [10–12]. Biosolids rates from 18 to 45 Mg ha⁻¹ have been recommended for arid rangelands with good agronomic results in terms of grass forage production and soil fertility [13]. Also, residual effects have been observed on soil fertility [14–16] and on forage production of arid grasslands [10, 11]. However, limited information is available on the residual effects of biosolids application in semiarid grasslands. Then, the objective of this study was to evaluate the residual effects of biosolids application on forage production of blue grama and other grasses at a semiarid grassland in Jalisco, Mexico.

2. Materials and Methods

The study was conducted at the Vaquerias Experimental Station, INIFAP, located at km 8 of Ojuelos-Lagos de Moreno highway, Ojuelos, Jalisco, Mexico, at 21.77927°N, 101.61133°W at 2,150 m altitude. Climate is semitropical [17] with a mean annual temperature at 17°C and mean annual precipitation at 425 mm. Topography is flat to less than 3% slope. Soil is Haplic Calcisol [18], alluvial origin, sandy loam texture, and a cement phase (“tepetate”) with a 50–100 cm soil depth. Dominant vegetation is composed of *Bouteloua-Lycurus* with huizache (*Acacia schaffneri* (S. Watson) F.J. Herm.) and prickly pear (*Opuntia* spp.) invasion [19].

Thirty-five field plots 1 × 1 m were selected at a native shortgrass prairie at regular range condition including blue grama (*Bouteloua gracilis* (Willd. ex Kunth) Lag. ex Griffiths) plants with an initial mean forage production of 843 ± 101 kg ha⁻¹ estimated by clipping before biosolids application. Square plots with a plywood frame were used to retain biosolids. Domestic, aerobic biosolids from the wastewater treatment plant at Aguascalientes city, Mexico, were applied one time only at 0 (control), 15, 30, 45, 60, 75, or 90 Mg ha⁻¹ on a dry weight basis, with five replications in June 2002. Previous to biosolids application, four random 1 kg samples were taken to determine moisture content and the following chemical analysis (Table 1): pH (CaCl₂/electrometric pH meter); electrical conductivity (saturated paste/Solu-bridge); organic matter through Walkley and Black combustion method [20]; total nitrogen (Kjeldahl) [21]; phosphorus (Bray-1) [22]; potassium, calcium, and magnesium, extracted by ammonium acetate; aluminum, zinc, iron, copper, manganese, boron, lead, arsenic, chromium, and cadmium extracted by DTPA [23] and analyzed by Atomic Absorption Spectroscopy; sulfur was extracted with calcium chloride and determined by turbidimetric method and chloride by volumetric methods. Chemical analysis of biosolids (Table 1) showed that pH and electrical conductivity were lower, and organic matter, nitrogen, and phosphorus were slightly higher than values in other studies [10, 11]. Because of their N and P contents, biosolids have the potential to improve soil fertility and promote plant growth at different agricultural scenarios. Biosolids composition complies with the Official Regulation of SEMARNAT in Mexico and was rated “Excellent” in terms of metal content [24].

Chemical analyses of initial soil samples before biosolids application were done similar to biosolids and are shown as follows (mean ± SE): pH = 6.3 ± 0.03; electrical conductivity = 0.028 ± 0.001 dS m⁻¹; organic matter = 1.28 ± 0.03%; extractable nitrogen = 3 ± 0.3 mg kg⁻¹; extractable P = 2 ± 0.2 mg kg⁻¹; and extractable potassium = 352 ± 10 mg kg⁻¹.

Biosolids rates were randomly assigned to field plots [25]. Biosolids were surface-applied and uniformly distributed around the plots by hand at the beginning of the rainy season in June 2002. Plots were excluded to grazing during the study and kept under natural rainfall conditions. Precipitation was measured at a meteorological station close to the study site (Table 2). Forage production was estimated by clipping blue grama forage separated from other grasses including hairy

TABLE 1: Chemical composition of aerobic biosolids from the wastewater treatment plant at Aguascalientes city ($n = 4$).

Parameter	Mean	Element (ppm)	Mean
pH (water 1:5)	6.6	Zinc	972
EC [†] (water 1:5) (dS m ⁻¹)	1.5	Boron	2
Organic matter (%)	35.2	Iron	8564
Nitrogen (%)	4.1	Copper	272
Phosphorus (%)	3.4	Lead	38
Potassium (%)	0.1	Arsenic	11
Calcium (%)	2.7	Chromium	60
Magnesium (%)	0.3	Cadmium	6
Sulfur (%)	1.0	Manganese	153
Aluminum (%)	1.0	Chloride	832

[†]Electrical conductivity.

TABLE 2: Annual, growing season (June to September), and mean precipitation (mm) on a semiarid grassland in Jalisco, Mexico.

Time	2003	2004	2005	2006	Mean
Annual	439	550	264	463	439
Growing season	367	369	186	297	319

grama (*Bouteloua hirsuta* Lag.), poverty three-awn (*Aristida divaricata* Humb. & Bonpl. Ex Willd.), common wolfstail (*Lycurus phleoides* Kunth), or *Bouteloua scorpioides* Lag. at 5 cm stubble height at the end of the growing season each year during four years. Forage production was determined by oven-drying forage samples at 60°C during 48 hr and is expressed on a dry weight basis.

Forage production data was analyzed with linear mixed models and year as repeated measures [26]. The first analysis included forage production of blue grama and other grasses from 2003 to 2004 to estimate changes of blue grama and other grasses production over time. The second analysis included total forage production (sum of blue grama and other grasses) from 2003 to 2006 to determine residual effect of biosolids on forage production. Several covariance structures including unstructured variance, compound symmetry, heterogeneous compound symmetry, and autoregressive were tested to select the best models. The models with unstructured variance were selected due to lower Akaike Information Criterion [26]. Significant effects were declared at a 5% probability level.

3. Results and Discussion

The analysis on forage production of blue grama and other grasses was affected ($P = 0.0001$) by a rate × year × species interaction (Table 3). Blue grama and other grasses forage production varied as a response to biosolids application and year of forage production (Figure 1). Blue grama forage increased from 2,533 ± 354 to 7,224 ± 354 kg ha⁻¹ in 2003 and from 2,375 ± 227 to 5,385 ± 227 kg ha⁻¹ in 2004, with 15 and 90 Mg ha⁻¹ biosolids rates, respectively (Figure 1) showing a high residual effect. In contrast, forage production of other

TABLE 3: Statistical results of blue grama, other grasses, and total forage production data on a semiarid grassland in Jalisco, Mexico.

Effect	F value	Probability > F
(Blue grama and other grasses)		
Biosolids rate	33.4	0.0001
Year	20.1	0.0001
Species	1142.9	0.0001
Biosolids rate × year	3.9	0.0014
Biosolids rate × species	43.3	0.0001
Biosolids rate × year × species	6.3	0.0001
(Total forage production)		
Biosolids rate	61.3	0.0001
Year	116.7	0.0001
Biosolids rate × year	5.1	0.0001

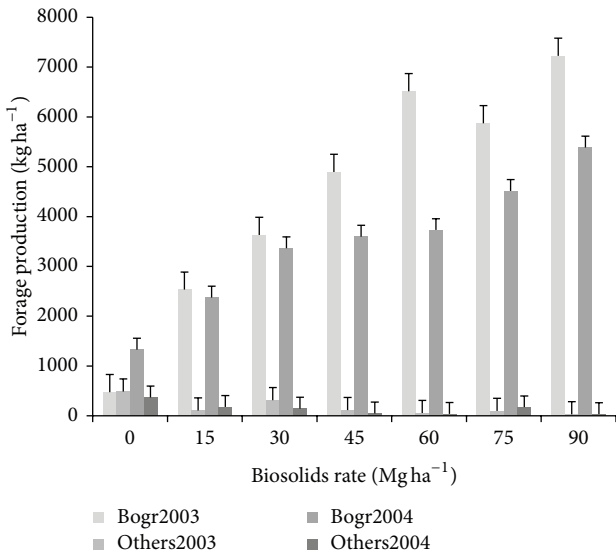
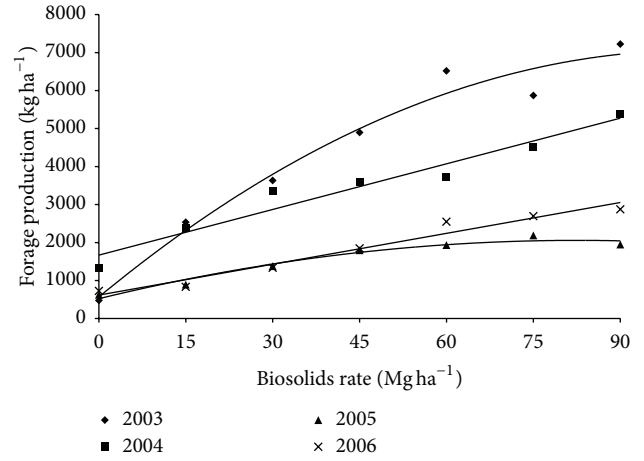


FIGURE 1: Forage production of blue grama and other grasses as affected by biosolids rate and year on a semiarid grassland in Jalisco, Mexico. Bogr2003 = blue grama forage production in 2003; Others2003 = forage production of other grasses in 2003; Bogr2004 = blue grama forage production in 2004; Others2004 = forage production of other grasses in 2004.

grasses was low and decreased from 106 to 30 kg ha⁻¹ in 2003 and from 181 to 36 kg ha⁻¹ in 2004 at the same rates (Figure 1). At control rate, forage production of blue grama (mean ± SE; 475 ± 148 kg ha⁻¹) was similar ($P = 0.9797$) compared to other grasses (488 ± 148 kg ha⁻¹) in 2003 and slightly higher ($P = 0.0035$) in 2004 (Figure 1).

Similar trends on increasing forage production of blue grama with biosolids and slighter effects of biosolids on other grasses such as galleta (*Hilaria jamesii* (Torr.) Benth.) and bottlebrush squirreltail (*Sitanion hystrix* (Nutt.) J.G. Sm.) have also been observed on arid grasslands in New Mexico [27]. However, blue grama forage production was lower in their study varying from 392 kg ha⁻¹ at control rate to a maximum of 1,067 kg ha⁻¹ at a biosolids rate of 90 Mg ha⁻¹, probably attributed to a lower mean annual precipitation of

FIGURE 2: Total forage production as affected by biosolids rate and year on a semiarid grassland in Jalisco, Mexico ($Y_{2003} = 569.05 + 125.88x - 0.6101x^2$, $r^2 = 0.97$, $P = 0.0290$; $Y_{2004} = 1,668.5 + 40.045x$, $r^2 = 0.94$, $P = 0.0001$; $Y_{2005} = 522.97 + 37.19x - 0.22x^2$, $r^2 = 0.96$, $P = 0.0369$; $Y_{2006} = 617.5 + 27.09x$, $r^2 = 0.96$, $P = 0.0001$).

267 mm in their study site. Blue grama forage production was much higher in our study due to more favorable growing conditions such as a higher precipitation in the study site (Table 2). Another study showed variable effects of composted biosolids on plant cover in a shortgrass prairie dominated by western wheatgrass (*Pascopyrum smithii* (Rydb.) Love) and needle and thread grass (*Hesperostipa comata* (Trin & Rupr.) Barkworth) in a semiarid grassland in Colorado with 355 mm annual rainfall [28].

The residual effect of biosolids application on total forage production was affected ($P = 0.0001$) by a rate × year interaction (Table 3). Total forage production increased with biosolids application rates, and the effect was greater in 2003 and 2004 (Figure 2), showing a residual effect even four years after biosolids application. Increases of forage production varied from 5 to a maximum of 15 times at 15 to 90 Mg ha⁻¹ rates, respectively, in 2003. However, the residual effect was lower in 2005 and 2006 attributed to a low precipitation during the growing season in both years (Table 2). Results of a similar study in New Mexico [27] showed increases of forage production up to 74% at the second year and up to 74% at the fourth year with 45 Mg ha⁻¹ rate at an arid blue grama grassland in poor range condition. Research in Texas [10] showed a maximum increase of 92% on forage production of tobosa grass (*Pleuraphis mutica* Buckley) at the fourth year with single application of 36 Mg ha⁻¹ rate and up to 80% with double annual applications of biosolids at 35 Mg ha⁻¹ rate in arid grasslands [11]. The lower forage production in New Mexico and Texas can be attributed to low precipitation in their study sites with 267 and 310 mm of mean annual precipitation and lower than average at three out of four years during the study.

Also, forage production of winter grasses has increased with biosolids application at 40 to 120 Mg ha⁻¹ rates after three years of application at a degraded native grassland in

Spain [29]. A later study [15] showed that forage production only increased at 80 and 120 Mg ha⁻¹ rate after five years of application at the same site.

Our data showed the greatest forage production of grasses at native grasslands obtained under rainfed conditions, and they could be partially attributed to the precipitation observed during the years of study. Besides precipitation, the higher forage production with biosolids application could also be attributed to the plant growth nutrients provided by biosolids as shown by several studies [16, 27] and to the improvement on soil water infiltration and water availability with biosolids application [16, 30].

Soil fertility was evaluated during the first and second years after biosolids application in this study [16], showing beneficial effects on soil nutrients such as nitrogen and phosphorus. These beneficial results on soil fertility are partially responsible for the increases on grass forage production observed in this study. Improvement on soil fertility was more beneficial to blue grama, a dominant species in this grassland that had a better use of soil nutrients; meanwhile, other associated species were displaced as biosolid rates increased.

Residual effects of biosolids on soil fertility have been observed with increases on soil nitrogen and phosphorus after eight years of application of 45 and 90 Mg ha⁻¹ rates on degraded native grassland of blue grama-galleta (*Hilaria jamesii* (Torr.) Benth.) in New Mexico [14]. Other authors also found residual effects on soil nitrogen and available phosphorus after five years with biosolids applications from 40 to 120 Mg ha⁻¹ rates compared to control rate in native grassland in Spain [29]. Residual effects on soil available nitrogen and phosphorus after 12 years have also been observed in a shortgrass prairie with biosolids application from 5 to 30 Mg ha⁻¹ rates in Colorado [31]. However, organic matter from biosolids decreased with time, and soil nitrogen availability has been shown to decrease from 5 to 1% in a seven-year period in desert grasslands in Texas [32].

Although biosolids application has shown favorable effects on forage production and consequently could have an impact on animal production, there are some limitations that make this practice not suitable for all grasslands. First, even though biosolids generation will increase due to increasing world population and to increasing environmental concerns for wastewater treatment, biosolids availability is still low in some remote and rural areas; second, high transportation and application costs [33, 34] make this practice more suitable for those grasslands closer to the wastewater treatment plants; and third, caution is advisable due to content of pathogens and heavy metals on biosolids. Despite this, land application of biosolids is still a recommended option to recycle organic matter and nutrients for plant growth in grasslands [13] and to restore degraded ecosystems [35].

4. Conclusions

Single biosolids application on the surface showed a residual effect on forage production even five years after application. The major effects on forage production were on blue grama at all biosolids rates. Other grasses such as hairy grama

(*Bouteloua hirsuta* Lag.), poverty three-awn (*Aristida divaricata* Humb. & Bonpl. Ex Willd.), common wolfstail (*Lycurus phleoides* Kunth), and *Bouteloua scorpioides* Lag. showed no response to biosolids application. The residual effect on forage production is still very strong at 45 to 90 Mg ha⁻¹ rates and is fading on biosolids rates from 15 to 30 Mg ha⁻¹. A biosolids rate of 45 Mg ha⁻¹ is recommended, based on the residual effect on forage production during the years evaluated.

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Research Article

Monometal and Competitive Adsorption of Cd, Ni, and Zn in Soil Treated with Different Contents of Cow Manure

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This study was conducted to assess the monometal and competitive adsorption of Cd, Ni, and Zn in the soil incubated with different contents of decayed cow manure (T_1 : 0, T_2 : 25, and T_3 : 50 tha^{-1}) for 90-d at 25°C. Sorption isotherms were characterized using the linear Freundlich equation. Most sorption isotherms were well described by the Freundlich equation (maximum $R^2 = 0.988$ and minimum $R^2 = 0.618$) and the monometal and competitive adsorption isotherms of Zn, Cd, and Ni followed the L-curve type (L-2). Results showed that the mono- and multimetal sorption amounts increased with an increase in organic amendment content as the sorption capacities for Cd, Ni, and Zn followed the following sequence: $T_2 \geq T_3 > T_1$. This sequence was consistent with the CEC and particularly pH for the three soils. All soils showed greater sorption capacity for Zn than the other trace elements as the sorption sequence in T_1 was $\text{Zn} > \text{Cd} > \text{Ni}$, while in both T_2 and T_3 was $\text{Zn} > \text{Ni} \geq \text{Cd}$. Therefore, the metal-binding sites in OM were more selective for Zn and Ni than Cd. Competition significantly reduced metals K_d , especially for Cd and Ni.

1. Introduction

Heavy metal pollution of soils has become a dangerous problem in agricultural production around the world in the past few decades, as a result of anthropogenic activities, such as mining or industrial activities and improper use of heavy metal-enriched materials in agriculture, including chemical fertilizer and pesticides, industrial effluents, sewage sludge, and wastewater irrigation [1, 2]. Anthropogenic trace elements are easily accumulated in the surface soil [3], leading to serious environmental concerns [4]. There is concern that increased anthropogenic inputs of trace elements in soils may result in transport of these metals in the soil profile, leading to the increased concentrations of trace elements in the ground or surface waters [5]. The movement of trace elements in soil is greatly affected by their physicochemical forms in the soil solid phase [6] and adsorption [4]. The most important process that affects heavy metal availability and mobility is sorption onto soil solid phases. Sorption of heavy metals by soil depends on factors such as the nature and content of the mineral and organic constituents, the nature

and concentration of the metal, the composition of the soil solution, and pH [7, 8].

Organic matter is one of the major contributors to the ability of soils for retention of heavy metals in an exchangeable form. Moreover, organic matter also improves soil fertility and structure and other soil properties. The effect of organic matter on the reduction of metals in soil solutions is highly complex. It depends on the other soil components and the chemistry of the metals and also the characteristics of the OM, particularly with respect to its degree of humification, content of heavy metals, salts, and its effect on soil pH [9–14]. Application of fresh manure can increase heavy metal mobility in soil due to the production of soluble organic compounds which form complexes with the metals [9, 12], while the humic substances which constitute a major part of the OM of compost, peats, or decayed manure can reduce metal solubility and bioavailability by adsorption and by forming stable complexes with metals [11, 12]. It was reported that heavy metals' adsorption onto soil constituents declines with decreased organic matter content in soils [15, 16]. The ability of OM to bind heavy metal ions can be

attributed to their high content of oxygen-containing functional groups, including carboxyl, phenol, hydroxyl, enol, and carbonyl structures of various types [17]. Clemente et al. [18] showed that cow manure and compost can be useful for the immobilization of heavy metals in calcareous-contaminated soils, particularly manure, an organic material rich in P, which plays an important role in the reduction of their solubility. OM has been of particular interest in studies of heavy metal fixation in soils due to the tendency of transition metals to form stable complex with organic ligands [19].

Heavy metal adsorption and hence their plant availability do not only depend on soil constituents (inorganic and organic), but also on the nature of metals involved, and on their competition for soil sorption sites. Usually when competitive sorption of metals is compared with their monometal behavior, it is found that their adsorption is lower in the competitive systems [20]. More strongly sorbed metals, such as lead and copper, are less affected by competition than mobile metals, such as cadmium and zinc [21, 22]. However, the effect of competition among poorly sorbed metals, such as Cd, Ni, and Zn, especially in organic amended soils, has not been documented. Moreover, it is not clear how the competitive adsorption of poorly sorbed heavy metals affects their behavior and availability over time.

While numerous studies have been conducted to understand monometal and competitive adsorption of trace elements in pure minerals and other soil components, their noncompetitive and competitive adsorptions in the presence of different contents of animal manure are barely known and there is limited information on the effects of the manure on the availability of metals in contaminated soils. Therefore, the objectives of present study were to evaluate the adsorption of Cd, Ni, and Zn applied as single or together affected by adding different contents of cow manure to soil after an incubation period of 90-d from the addition date of cow manure and also their Freundlich isotherms. Changes in the physical and chemical nature of the manure-soil mixture after the incubation period were also quantified.

2. Materials and Methods

2.1. Sample Collection. Soil samples were collected from the surface layer (0–30 cm) of the field in Agricultural Faculty of Shahid Chamran University of Ahvaz, air-dried at room temperature, and sieved through a 2 mm plastic sieve. A subsample of soil was used to determine chemical and physical properties.

Decayed cow manure sample obtained from the Ahvaz ranches was used as the organic amendment, air-dried, and sieved through a 2 mm plastic sieve to increase the active surface area of the amendment particles. Some of the chemical and physical characteristics of the soil and cow manure are reported in Table 1.

2.2. Preparation of Treatments and Heavy Metal Solutions. The sampled soil was used to fill greenhouse pots and three levels of cow manure including 0 (control), 25, and 50 tha^{-1} were amended to soils. Soil-manure mixtures were placed

TABLE 1: Some chemical and physical properties of the soil and manure.

Variable	Soil	Manure
pH	7.16	7.9
EC (ds/m)	1.9	10.8
OM (%)	0.16	0.41
Zn (mg Kg^{-1})	2.47	48.4
Cu (mg Kg^{-1})	0.047	14.5
Fe (mg Kg^{-1})	1.15	293.7
Cd (mg Kg^{-1})	<0.05	<0.05
Ni (mg Kg^{-1})	<0.05	<0.05
CEC (cmolc kg^{-1})	15.3	—
Soil texture	Loam	—
Soil classification	Torrertic Haplustepts	—

in plastic bags, wetted to 65–70% of their water holding capacity, and then incubated for 90 days in a temperature-controlled chamber at 25°C. During this period, soil-manure mixtures were weighed and rewetted so as to maintain the soil moisture content constant, as appropriate. Soil samples were air-dried after 90 days and prepared for next experiments. Three replicates were arranged for each treatment.

Ni, Cd, and Zn were, respectively, used as NiCl_2 , CdCl_2 , and ZnCl_2 in varying concentrations, including 10, 25, 30, 40, 50, and 100 mg L^{-1} . Stock solutions of the metal salts were prepared in distilled water.

2.3. Noncompetitive Adsorption Experiments. 2 gr from each air-dried soil sample was weighed and poured into acid-washed polyethylene tubes and 20 mL of solution of Cd^{+2} , Ni^{+2} , or Zn^{+2} , in the above concentrations, individually added to the tubes. Then, the tubes were shaken at 150 rpm (rate per minute) with a rotator agitator for 24 h, as the equilibrium time, at 25°C. The soil samples dissolved in metal solutions (1:10 w/v) were centrifuged initially at 3000 rpm for 15 min to remove soil. Then, the supernatant was filtered through filter paper (Wathman filters Number 42). Cd, Ni, and Zn concentrations in the supernatant were measured by atomic adsorption spectrophotometer (model: Unicam 939).

2.4. Competitive Sorption Experiments. Competitive adsorption isotherms were performed in the same way, but by adding Cd, Ni, and Zn at a 1:1:1 mole ratio.

Monometal and competitive adsorption experiments had been conducted in constant pH. The control of pH was done by acid or base solutions and both experiments were carried out in a background electrolyte of 0.01 M CaCl_2 and were replicated three times.

2.5. Sorption Equations. The amount of trace elements sorbed by soil was calculated with the following equation:

$$Q = \frac{(C_o - C_e)V}{M}, \quad (1)$$

where Q is the amount of adsorbed species (mg kg^{-1}), C_o is the initial concentration of the species in solution (mg L^{-1}), C_e is the equilibrium concentration of the species in solution (mg L^{-1}), V is the solution volume (mL), and M is the weight of air-dried soil (kg).

The relation between the concentration of dissolved and adsorbed heavy metal was expressed by the Freundlich isotherm. The linear form of the Freundlich isotherm is given by

$$\log Q = \log K_F + \frac{1}{n} \log C, \quad (2)$$

where Q (or x/m) is the amount of metal adsorbed per gram of sorbent (mg kg^{-1}), C is the equilibrium concentration of the adsorbate (mg L^{-1}), and K_F and n are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively. Freundlich parameters can be obtained by plotting $\log Q$ versus $\log C$, with $1/n$ being the slope and $\log K$ being the intercept of the line. K_F is the Freundlich coefficient, related to the total sorption capacity of the soil and n is a constant that typically has a value of less than 1.

Distribution coefficient, K_d , is an index of a metal's potential mobility and calculated with the following equation:

$$K_d = \frac{\text{Equilibrium metal concentration adsorbed}}{\text{Equilibrium metal concentration in solution}}. \quad (3)$$

The distribution coefficient represents the sorption affinity of the metal cations in solution for the soil solid phase and can be used to characterize the mobility and retention of trace elements in a soil system. Low distribution coefficients indicate that most of the metals present in the system remain in the solution and are available for transport, chemical processes, and plant uptake [23], whereas higher values indicate lower mobility and higher retention of metals in the soil. K_d is positively related to metal sorption capacity of soils. Also, the higher the sorption intensity parameter ($1/n$), the lower the binding affinity (n) of soil with metal. The sorption isotherms were obtained for each soil sample by equilibrating 2 g soil with 20 mL of solutions containing concentrations of 10, 25, 30, 40, 50, and 100 mg L^{-1} of mono- and three metals, separately. Statistical analysis was performed using the Excel programs.

3. Results and Discussion

3.1. Incubation Effects on the Soil Characteristics. As can be seen in Table 1, the cow manure has the near-neutral pH, low salinity and is unpolluted with heavy metals. Therefore, adding the manure to soil led to increase of the soil OM and slight change in the soil pH. Addition of manure amendment affects the properties of soils. The treatments of the soil with different contents of decayed cow manure resulted in increases at pH in the range from 7.56 (25 tha^{-1}) to 7.54 (50 tha^{-1}); when compared to the control soil (7.16), the EC increased to 3.12 and 4.34 dS^{-1} in response to treatments with 25 tha^{-1} and 50 tha^{-1} manure amendment, respectively. Thus, the primary change of soil during incubation and hence

TABLE 2: Some variable properties of soil due to addition of manure in different levels at the end of incubation period.

Variable	T_1	T_2	T_3
pH	7.16	7.56	7.54
EC (ds/m)	1.9	3.12	4.34
CEC (cmolc kg^{-1})	15.3	16.4	16.6
OM (%)	0.16	0.23	0.28

T_1 : control, T_2 : soil treated by 25 tha^{-1} manure, T_3 : soil treated by 50 tha^{-1} manure.

the processes most likely to influence metal sorption were OM and consequently CEC, that the latter factor is affected by the soil OM content. Raising the soil OM content can increase soil CEC, a factor which may affect both soluble and exchangeable metal levels [12, 24] (see Table 2).

3.2. Effect of Contents of Cow Manure and Initial Concentration of Metals on the Sorption Isotherms. Monometal and competitive Zn, Cd, and Ni adsorption isotherms for T_1 , T_2 , and T_3 were obtained based on the Freundlich equation after the 90-d incubation with cow manure. Monometal (Figure 1) and competitive (Figure 2) sorption isotherms by the three soil treatments exhibited differences in shape and in amount retained. Sorption isotherms provide important information about the soil immobilization capacity and the strength with which the sorbate is held onto the soil [25]. On the y-axis S represents the metal concentration sorbed onto solid phases and on the x-axis C represents metal equilibrium concentration in solution.

Experimental data from the adsorption tests for all metals and all treatments in both systems (monometal and competitive) gave a satisfactory fit (Table 3) to the Freundlich model (maximum $R^2 = 0.988$ for Cd-monometal at T_2 and minimum $R^2 = 0.618$ for Cd-competitive at T_1).

Figures 1 and 2 showed that the sorption amount increased with an increase in equilibrium Zn, Cd, and Ni concentrations and approached a plateau value at higher equilibrium concentrations for the soils. Therefore, the monometal and competitive adsorption isotherms of Zn, Cd, and Ni for T_1 (a), T_2 (b), and T_3 (c) were of the L-curve type (L-2), which is characterized by an initial slope that does not increase with the concentration of the added metal in the soil solution. This explains the higher adsorption at lower concentrations, which then decreases as the concentration increases [26]. The isotherm shapes at low concentration range, do not change markedly between T_1 , T_2 , and T_3 , despite the significant increase of organic matter at the end of incubation period, whereas they vary with increasing the heavy metal concentrations in all treatments.

The sorption amount increased with an increase in organic amendment content. Organic matter is considered to play an important role in reducing plant uptake of heavy metals from soils due to its high CEC and complexing ability. Many authors have found that high organic matter content or addition of organic matter by organic amendments decreased

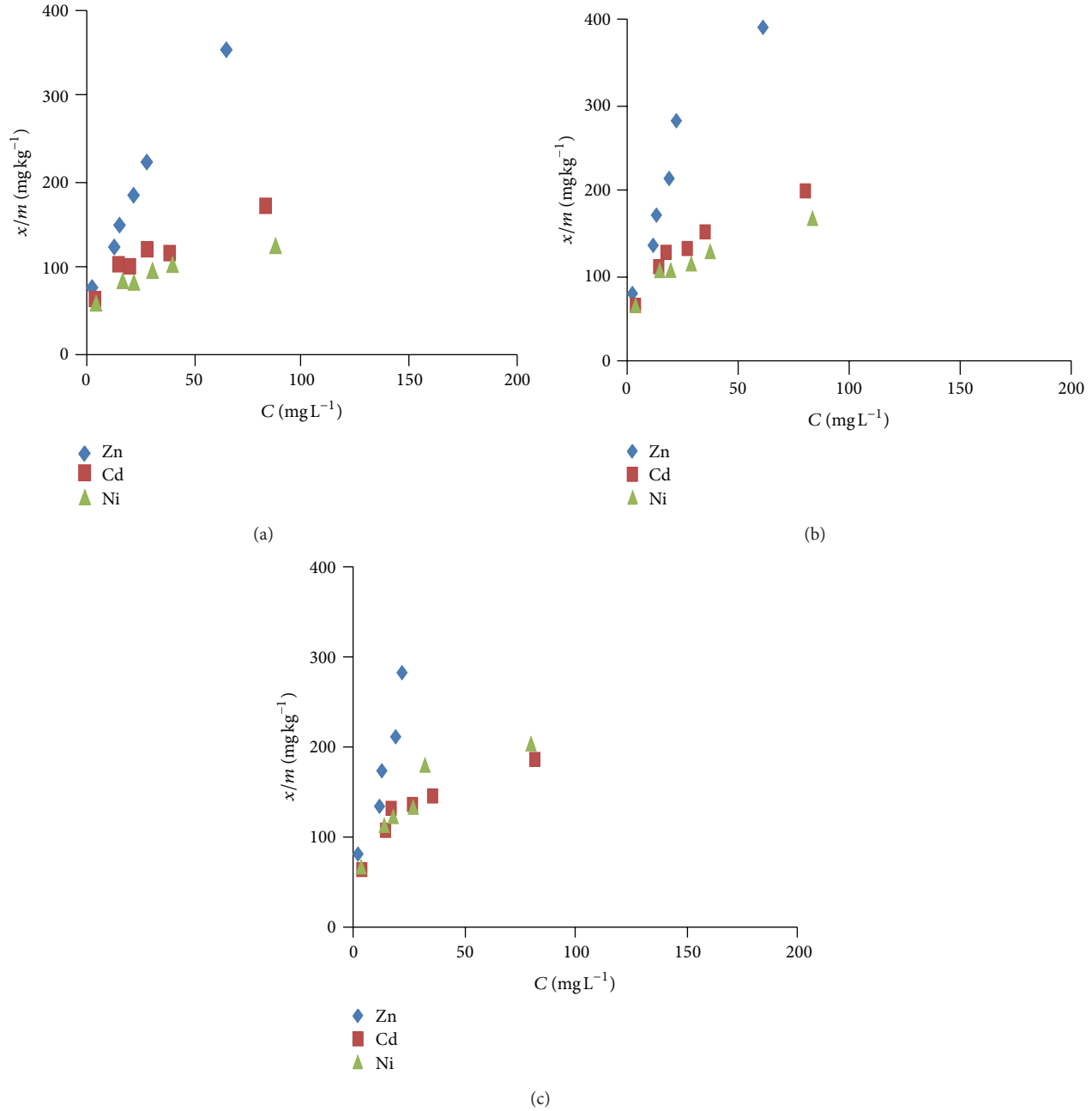


FIGURE 1: Noncompetitive adsorption isotherms of Zn, Cd, and Ni in soil control (a), T_2 (b), and T_3 (c) samples. Data are means of triplicate determinations.

the heavy metals concentration in solution [14, 27–29]. This effect is attributed to the high CEC of organic matter and its ability to form chelate complexes with metals. Haghir [30] concluded that the decreased plant availability of heavy metal concentration with higher levels of organic matter added was predominantly due to the effect of increasing soil CEC.

The adsorption values in the treatments were positively correlated with manure contents, indicating that the organic manure has the capacity of metal adsorption. As seen in Table 3, K_F was increased with increasing amount of the manure in soil; hence the adsorption sequences for three

treatments in both noncompetitive and competitive systems were found: $T_2 \geq T_3 > T_1$. This sequence is consistent with OM and CEC sequences and also is consistent with pH sequence in the treatments. Clemente et al. [18] in their study on the short-term effects of two different OM amendments (fresh cow manure and a mature compost) found that the concentrations of Zn extracted with CaCl_2 were significantly different in every sampling in control, manure-, and compost-treated samples. The main effect of manure treatment on Zn was the significant decrease of NaOH- and EDTA-extractable concentrations of this element

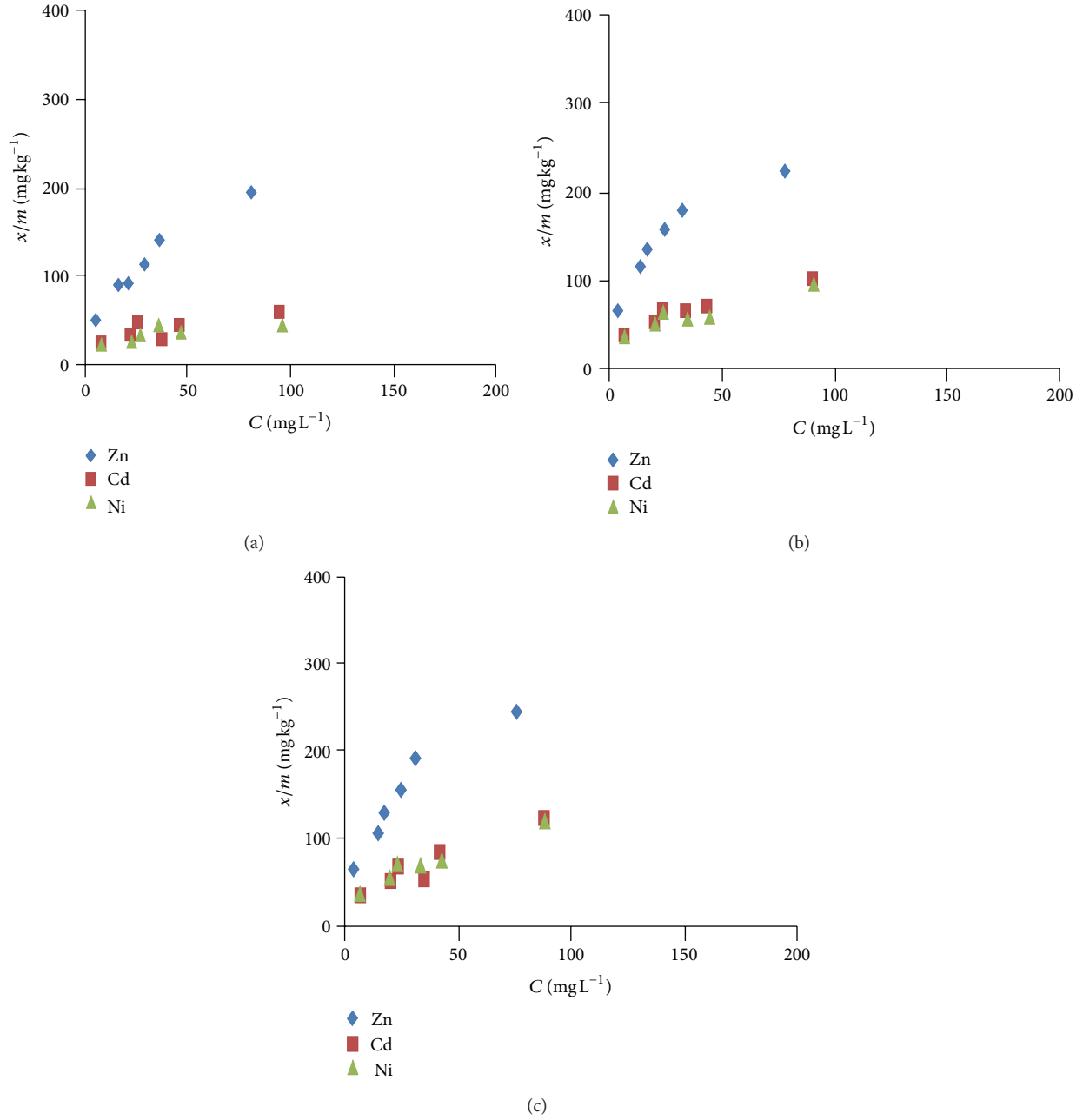


FIGURE 2: Competitive adsorption isotherms of Zn, Cd, and Ni in soil control (a), T_2 (b), and T_3 (c) samples. Data are means of triplicate determinations. Coefficients of variation were less than 10%.

TABLE 3: The Freundlich constants and R^2 values obtained from the Freundlich isotherm in single and multimetal systems.

		T_1			T_2			T_3	
	K_F	N	R^2	K_F	N	R^2	K_F	N	R^2
Zn-monometal	50.815	2.299	0.94	56.234	2.150	0.935	57.147	2.127	0.916
Zn-competitive	24.21	2.101	0.985	43.752	2.538	0.983	38.904	2.304	0.968
Cd-monometal	46.025	3.46	0.959	46.773	2.994	0.988	46.238	3.021	0.962
Cd-competitive	15.031	3.448	0.618	21.183	2.915	0.953	15.667	2.273	0.855
Ni-monometal	43.351	4.184	0.984	48.97	3.650	0.981	46.025	2.841	0.975
Ni-competitive	13.899	3.663	0.74	20.606	3.125	0.861	19.724	2.445	0.951

T_1 : control, T_2 : soil treated by 25 tha^{-1} manure, T_3 : soil treated by 50 tha^{-1} manure.

with respect to control soil after incubation period, showing a decrease in metal availability shortly after amendment addition to soil. Petruzzelli et al. [31] and Agbenin and Olojo [32] report significant decreases in the adsorption of heavy metal on soil after the chemical removal of organic matter.

Sorption values from T_2 to T_3 were decreased slightly, that attributed to increase of pH. Increases in pH decrease surface potential and proton competition and thus favor metal binding [33]. Adding the organic material to soil and the subsequent incubation conditions may influence the pH and therefore modify metal speciation [13]. Walker et al. [34] found that cow manure is capable of preventing soil acidification and decreasing heavy metal bioavailability. Also, they expressed that the increase of soil pH caused by manure addition is the main factor reducing metal availability. Ram and Verloo [35] found that farmyard manure and peat soil enhanced the mobility of Cd at lower pH and decreased it at higher pH.

The steep slope of the Zn and Cd isotherms in contrast to the gentle slope of the Ni isotherm in the control treatment indicated a stronger affinity of the soil for Zn and Cd than Ni. On the basis of K_F values, the following selectivity sequence for T_1 was found: $Zn > Cd > Ni$ (Table 3), which may be attributed to their adsorption affinities and their first hydrolysis equilibrium constant: $(9.0) Zn > (9.9) Ni \geq (10.1) Cd$. Similar result was also reported by Antoniadis et al. [36], who studied monometal and competitive adsorption of Cd, Zn, and Ni by a soil before and after one-year incubation with sewage sludge and observed the decreasing sequence adsorption: $Zn > Cd > Ni$.

Ni sorption increased with an addition of cow manure to soil more than Cd sorption, as in treatments of 25 and 50 tha^{-1} ; sorption sequences followed this sequence: $Zn > Ni \geq Cd$. Zn and Cd were sorbed more favorably than Ni on inorganic surfaces of soil, but organic matter favored retention of Ni over Cd. When OM was added to the soil, $K_{d,Zn}$ (monometal system) increased 9.6% and 12.18% at T_2 and T_3 , and $K_{d,Ni}$ increased 11.5% and 5.9%, respectively, as compared to the control, whereas $K_{d,Cd}$ had no significant change as compared to the control. The higher increasing of $K_{d,Zn}$ and $K_{d,Ni}$ than $K_{d,Cd}$ suggested that the metal binding sites in OM were more selective for Zn and Ni than Cd. Also, these results suggest that Ni has higher affinity for organic activity sites than for inorganic sites, whereas Zn would prefer both inorganic and organic sites. The higher affinity of the control soil for Zn and Cd is probably due to the existence of a greater number of active sites with high specificity for these metals, so when they are present, these sites would not be occupied by other cations [37].

3.3. Effect of Competition on the Sorption Isotherms and the Freundlich Constants. The presence of other metals reduced the amount of each metal sorbed compared to monometal system, so the adsorption capacity (K_d) of each metal in the multimetal condition was lower than that in the monometal condition. This suggests that the metals were competing for the same binding sites as one another, though the total amount of added metals was not so high as to occupy a

large part of the available surface adsorption sites. Significant inhibitory effects of competitive metals on the adsorption of a particular metal have also been reported by Basta and Sloan [27].

Although K_d values indicated a reduction in metal adsorption due to competition sorption, they were evident mostly at the higher end of equilibrium concentrations. Thus, at low metal concentrations, effects of competition were not very strong. This seems to concur with the work of Saha et al. [38], who found no evidence of metal (Cd, Zn, and Pb) competition at low concentrations. They explained that at low added metal concentrations, metals are mainly adsorbed onto specific adsorption sites, while at higher metal inputs, soils lose some of their ability to bind heavy metals as adsorption sites overlap, becoming thus less specific for a particular metal. This, in turn, induces a reduction in metal sorption. Although competition reduced sorption of all three metals, the magnitude of these effects was different for each metal. $K_{d,Zn}$ decreased by nearly 51.3% at T_1 due to competition, by 21.2% at T_2 , and by 31.9% at T_3 . This compares to competition-induced reductions of around 67.3%, 54.7%, and 66.1% for Cd at T_1 , T_2 , and T_3 , respectively, and 67.9%, 57.9%, and 57.1% for Ni at T_1 , T_2 , and T_3 , respectively. Thus, the effect of competition in reducing the sorption of metals followed the following order: $Cd \geq Ni > Zn$. This suggests that upon coaddition of the three metals to the soil, Zn, and to a less extent Ni, became preferentially adsorbed at the expense of Cd. This is likely to have been the result of differences in the nature of the dominant sorbing surfaces for each metal [32].

4. Conclusion

The monometal and competitive adsorption behavior of Cd, Ni, and Zn in soil, affected by different contents of decayed cow manure (0, 25, and 50 tha^{-1}), was investigated in the present study. Evidences showed that soils which received decayed manure exhibited higher CEC and pH in general terms. Therefore, the organic matter had metal immobilization effect after the incubation.

Monometal system K_d values in control soil followed the following order: $Zn > Cd > Ni$. In amended soils, Zn and particularly Ni sorption values increased significantly, while Cd did not after 90-d incubation. The adsorption sequences in T_2 and T_3 were in the order of $Zn > Ni \geq Cd$. The adsorption capacity (K_d) of each metal in the multimetal condition was lower than that in the monometal condition. Low values of K_d for Cd and Ni in competitive system indicate that most Cd and Ni remain in the solution and are available for transport, chemical processes, and plant uptake. The effect of competition in reducing the sorption of metals followed the following order: $Cd \geq Ni > Zn$. Most sorption isotherms for trace elements were adequately described by the Freundlich equation and were of the L-curve type.

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