Aim and Scope

The objective of the *Journal of Residuals Science & Technology* is to provide a forum for technical research on the management and disposal of residuals from pollution control activities. The Journal publishes papers that examine the characteristics, effects, and management principles of various residuals from such sources as wastewater treatment, water treatment, air pollution control, hazardous waste treatment, solid waste, industrial waste treatment, and other pollution control activities. Papers on health and the environmental effects of residuals production, management, and disposal and are also welcome.

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Integration of Solid Residues from the Steel and Pulp and Paper Industries for Forest Soil Amendment

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ABSTRACT: Beneficial utilisation of process industry residues provides possibilities to reduce energy consumption, to avoid environmental impacts caused by increasing landfilling and promotes sustainable management of natural resources. As traditional utilisation of steel industry residues lies within the realm of civil construction, complementary applications could be found from the integration with pulp and paper industry residues to promote sustainable forest management through forest soil amendment. In our study we show that three different soil amendment matrices, providing slow release and materials handling advantages, were successfully produced according to conventional cement testing practices. The concepts we develop for forest soil amendment incorporate the use of fly ash in tandem with granulated blast furnace or steel slag as binder materials, the utilisation of paper mill sludge as reactive aggregate and the use of green liquor dregs and lime waste from chemical pulping as alkaline components. The neutralising (35.8–38.6%) and reactivity (33.3–38.0%) values (expressed as Ca-equivalents d.w.) with supporting high pH-values (12.9–13.0) indicate liming and buffering capacities of the test matrix materials are comparable to commercial ground limestone products. Additionally, concentrations of Ca, K and Mg and concentrations of Cu, Mn and Zn were found to be higher than organic and mineral soils normally found in the Ostrobothnia region of Northern Finland. Only under severe leaching test conditions (HNO_3 and HCl microwave digestion) did the total concentration of Cr in the soil amendment matrix exceed respective Finnish statutory limit value set for the use of fertilisers in forestry. However, as illustrated by the leaching procedure, less than a fifth of the total Cr is likely to become mobile in conditions normally found in nature.

INTRODUCTION

WASTE utilisation is an attractive alternative to disposal since the costs and potential environmental degradation caused by final disposal methods can be reduced or even eliminated and natural resources conserved [1]. In Finland traditional process industries are known for their reliance on high volume raw materials and the generation of large solid residue streams. The relative stability of process conditions and the homogeneous quality of individual residue streams [2] promotes ready utilisation of residues and offers possibilities to reduce energy consumption and to avoid environmental impacts caused by landfilling.

The steel industry in particular generates a considerable amount of metallurgical slag residues during the production of iron and steel. Generally, an average of 200 kg and 50 kg of slags are required per tonne of crude iron and steel products respectively. According to Shi [3], these primary slags are currently utilised as cement replacement or asphalt concrete aggregate in most countries around the world. However, in addition to the hydraulic binding properties and mechanical stability of ground granulated blast furnace slag (GGBFS) and steel slag, the suitable characteristics of slag material enables complementary utilisation in soil amendment [4].

In the case of the pulp and paper industry, high volume acquisition of wood raw material removes vital base cations (Ca, Mg, K) from forest soils, thus decreasing soil buffering capacity and promoting soil acidification. Even though Ca and Na are important process elements [5], considerable amounts of these elements generally end up in process residuals which are removed from the overall system and are currently destined for landfill. Due to increasing costs of landfill disposal and difficulty in acquiring new sites [6, 7], and

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prevailing pressure for increased soil cation removal through whole tree harvesting practices, the investigation of possible recycling of pulp and paper residues back to forest ecosystems should be of primary concern.

Although the use of individual pulp, paper and steel industry residues for soil amendment purposes has received previous attention in the literature [4, 8, 9], this field of research lacks an integrated approach taking into account not only the alkaline nature of pulp and papermaking residuals, but also the respective cementitious and alkaline characteristics of steelmaking residues. The possibility to develop a solid, slow release matrix to prevent the potential pH shock effect possible caused by rapidly dissolving soil ameliorants [9] and the inclusion of alkaline activators with plant nutrient qualities could achieve closure of inorganic cycles between pulp and paper production and forest ecosystems and provide additional applications for metallurgical slags thereby promoting more sustainable management of natural resources.

Green Liquor Dregs and Lime Waste

These wastes are residues emerging from the chemical recovery process of a kraft pulp mill, as illustrated in Figure 1. During chemical recovery, used pulping liquor is concentrated to strong black liquor and incinerated in the recovery boiler for energy recovery from the residual organics. As the products of the recovery boiler operation (an inorganic smelt of mainly sulphides, carbonates, sulphates and chlorides of sodium and potassium) are dissolved in water, the insoluble material (i.e. green liquor dregs) is removed. According to Martins et al. [5], green liquor dregs mainly consist of $CaCO_3$ and $CaSO_4{\cdot}2H_2O$. According to Nurmesniemi et al. [10], green liquor dregs are attested to contain significant amounts of Na and S, most likely originating from the use of Na_2S, NaOH and Na_2SO_4 as cooking and make-up chemicals and were found to be alkaline in nature (pH = 10.7) having a liming effect value of 39.6% expressed as Ca-equivalents (d.w.).

As the main objective of the recovery process is to convert inactive Na_2CO_3 to NaOH through the causticizing reaction, $Ca(OH)_2$ needs to be produced in large quantities from limestone via calcination in the lime kiln. The lime kiln, see Figure 1, operates as a bottleneck in the process chain and hence, due to disturbances in process operation or other abnormal situations, contents of the lime kiln are often purged prior to operation start-up and at shut-down. Lime waste arising from this operation of the lime kiln has a very low

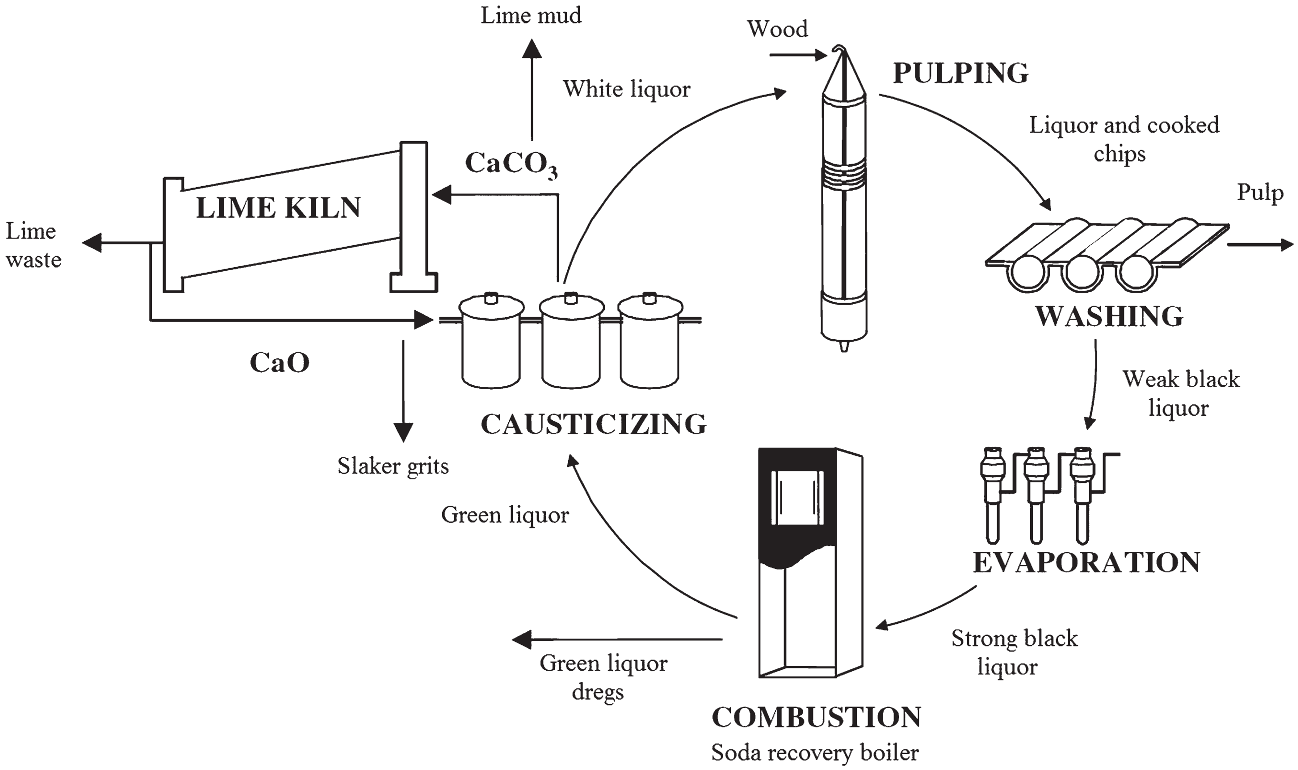

Figure 1. *Green liquor dregs and lime waste from the recovery process of a pulp mill [10, modified].*

moisture content and contains a mixture of partially and fully calcined minerals. According to Pöykiö et al. [6], lime waste was strongly alkaline in nature (pH = 12.8) and had a significant liming effect of 47.9% expressed as Ca-equivalents (d.w.).

Fly Ash

Incineration of forest industry organic residues is most typically managed in auxiliary fluidised-bed boilers allowing the use of additional fuel sources. Fly ash from the incineration is produced during the operation of combustion gas purification equipment, e.g. electrostatic precipitators. Generally, fly ash is perceived to have pozzolanic properties and according to Dahl et al. [11] fly ash from a medium-size fluidised-bed boiler incinerating forest residues and peat mainly consisted of Fe_2O_3, MgO, Al_2O_3 and $Ca_2Fe_2O_5$ and was found to be clearly alkaline in nature (pH = 12.5) with a liming effect value of 28.5% expressed as Ca-equivalents (d.w.).

In tandem with fly ash, the incineration process in fluidised-bed boilers generates a coarser bottom ash fraction. Although the heavy metal content of bottom ash from a medium-size fluidised-bed boiler incinerating forest residues and peat was considerably lower than in respective fly ash [11], the larger particle size and chemical composition of bottom ash (mainly SiO_2) does not support utilisation as binder material. Additionally, as attested by Dahl et al. [11], easily available nutrient concentrations (Ca, Mg, K, P, Cu, Zn) essential for normal plant growth and development, were all enriched in the fly ash fraction.

Paper Mill Sludge

In papermaking, residual paper fibres and additives are purged from the process in the form of paper mill sludge (or fibre clay) generated at the chemical waste water treatment plant that treats the effluent from the paper machines. The main organic components of paper mill sludge or fibre clay are generally cellulose fibres, lignin and possible organic binders. The main inorganic components include $Al_2Si_2O_5(OH)_4$ (kaolinite) and $CaCO_3$ used as paper additives, and metals mainly originating from the wood raw material [12]. Paper mill sludge studied by Kuokkanen et al. [12] had a considerable organic content (LOI value 35.5% d.w.), was slightly alkaline in nature (pH = 8.3) and had a liming effect value of 24.7% expressed as Ca-equivalents (d.w).

Granulated Blast Furnace and Steel Slags

Granulated blast furnace slag (GBFS) and steel slags are by-products of the main processes of steel production, i.e. iron and steel smelting, and their properties vary according to the optimisation achieved in the manufacture of the main products. Iron smelting reduces various oxides of iron ore (e.g. Fe_2O_3 and Fe_3O_4) to elemental iron and the main objective of steel smelting in BOF converters is to reduce the carbon content of iron to acceptable levels with the help of an oxygen blow. Steel industry slags mainly consist of CaO, SiO_2, Al_2O_3 and MgO in addition to a considerable FeO content [3, 13]. Furthermore, the ground form of granulated blast furnace slag (GGBFS) has enhanced hydraulic binding properties and is widely being used in cement making and agricultural liming. According to Shi [3], steel slag has weaker hydraulic binding properties but is also used as a liming agent [4].

Synergistic Utilisation of Residues

As opposed to the separate utilisation of individual residues in e.g. soil amendment, the pozzolanic or cementitious characteristics of fly ash, GBFS and steelmaking slag provide an opportunity to develop a solid slow release matrix, possibly formable to the shape of e.g. pellets, to prevent the pH shock effect potentially caused by rapidly dissolving soil ameliorants [9] and ease the inconvenience of mechanical handling, transport and distribution. Additionally, the possible pelletisation of alkaline activators with plant nutrient qualities and low cost cementitious binders could generate a high volume product stream to reduce reliance on conventional landfilling of wastes and achieve closure of inorganic cycles between pulp and paper production and forest ecosystems, offer additional application for metallurgical slags and promote sustainable resource management. In the future more effort should be made for the utilisation of steel industry slags other than GBFS, as GBFS is currently utilised as a non-waste by-product by the cement industry.

EXPERIMENTAL

Pulp, Paper and Steel Industry Residues from the Ostrobothnia Region in Northern Finland

Stora Enso pulp and paper mill complex in Oulu, Northern Finland, is an integrated chemical pulp and paper mill. In 2005, the Oulu mill produced 297,000 tonnes of sulphate pulp and 769,000 tonnes of fine paper. Subsequently, 1,456 tonnes of green liquor dregs, 644 tonnes of lime waste, 15,055 tonnes of fly ash and 15,959 tonnes of paper mill sludge were generated (measured in 100% dry solids).

Green liquor dregs samples were collected at the dreg percolator used to separate the insoluble solids from green liquor. Lime waste sampling was carried out at the lime kiln outlet used for purging the contents of the kiln in abnormal situations and fly ash samples were collected from the normal fly ash storage area prior to the landfill. Paper mill sludge sampling was performed at a recovery process used at the Oulu mill for recycling paper pigments as fillers in fine paper production. The samples were stored in 10 dm^3 polyethylene containers in room temperature and humidity, except for the paper mill sludge which was stored in a refrigerator (+4°) to prevent degradation of organic fibre content. Sampling was performed during a three-day period in August 2009 in normal plant operating conditions.

Ruukki mill in Raahe is an integrated iron and steel works located approximately 80 km south of Oulu. In 2005, the Raahe mill produced 2,747,000 tonnes of steel and 2,529,000 tonnes of crude iron. Subsequently, 550,000 tonnes of GBFS and 130,000 tonnes of steel slag were generated. GBFS and steel slag samples were collected at the slag pit of Ruukki mill at a particle size of less than 4 mm. Sampling was performed during a one-day period in June 2009 and represented slag generated during normal plant operating conditions. Slag samples were stored in steel containers in room temperature and humidity until specimen manufacture.

Specimen Manufacture and Mechanical Testing

Three different soil amendment matrices were produced using mixing and casting procedures from conventional cement testing. Dried (55°C, 72 h) and ground (ball mill milling times app. 30 min, batch size < 0.5 kg, ball size 1.5 kg) green liquor dregs were mixed with lime waste, paper mill sludge, fly ash and ground GBFS or steel slag (mean particle size 9.0 and 5.8 μm respectively) according to Table 1 for 2 minutes before admixing water to enable fly ash and slag hydration (water/binder ratio 1.125). Water addition was followed by a mixing period of 6 minutes before respective quantities of the slurry were cast in cubic moulds of 1 dm^3. Subsequent to casting, the moulds were subjected to vibration and cured in room temperature and humidity to produce a solidified matrix.[1]

Fly ash and lime waste samples were not subjected to any pretreatment prior to mixing as the apparent fineness of both materials was clearly suitable for a mixing process used in conventional cement testing procedures. The only ingredient with an apparent moisture content was paper mill sludge, which however did not seem to affect the uniform dispersion of individual elements in the matrices produced. According to Kuokkanen et al. [12], normal paper mill sludge from Oulu is produced with a dry matter content of 24.7% and a loss on ignition value of 35.5% (d.w.).

At the age of 28 days, three 1 dm^3 specimens of each formulation were tested for mechanical strength with an unconfined compression strength test with a Zwick RK 250/50 loading machine using a preload of 50 Newtons and a loading rate of 3 mm/min. Compression strength (MPa) of cubic 1 dm^3 moulds was used to establish the solidification of chosen formulations and to evaluate the feasibility of produced matrices in mechanical handling, transport and distribution procedures [9]. After mechanical testing, the specimens were ground with a jaw crusher to a particle size (< 2 mm) suitable for laboratory analysis.

Physicochemical Properties

The determination of pH and electrical conductivity

Table 1. Composition of Soil Amendment Matrices.

Component	Matrix I	Matrix II	Matrix III
Binder[a]	GGBFS 0.15, fly ash 0.15	GSS 0.15, fly ash 0.15	GGBFS 0.075, fly ash 0.075
Reactive aggregate[a]	paper mill sludge 0.30	paper mill sludge 0.30	paper mill sludge 0.45
Reactive alkalia	GLD 0.10, lime waste 0.30	GLD 0.10, lime waste 0.30	GLD 0.10, lime waste 0.30

[a] Individual component quantities expressed in mass fractions prior to water addition.
GGBFS = ground granulated blast furnace slag.
GSS = ground steel slag.
GLD = green liquor dregs.

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[1] Cubic 1 dm^3 moulds are commonly used in mechanical testing (e.g. SFS-EN 12390-1 and SFS-EN 12390-3) and were applied to evaluate the solidification and mechanical stability between different formulations.

were performed at solid to liquid (S/L) ratios of 1:2.5. (v/v). The determinations of loss on ignition (LOI) and total organic carbon (TOC) values and the dry matter content of produced matrices were carried out according to SFS-EN 12879, SFS-EN 13137 and ISO 11465 respectively. Additionally, neutralising (NV) and reactivity (r_{ac}) values were analysed according to SFS-EN 12945 and SFS-EN 13971 respectively.

Total Heavy Metal and Plant Nutrient Concentrations

Easily available plant nutrient (Ca, Mg, K, P, Cu, Zn and Mn) with Na and S concentrations were determined according to the procedure of MTT Agrifood Research Finland [14], where 1 volume part of dry sample is shaken with 10 parts of extraction solution for 1 h. Ca, Mg, Na, K, P and S were extracted with 0.5 M acidic ammonium acetate (pH = 4.65). In the case of Cu and Zn, the acidic ammonium acetate solution contained 0.02 M ethylenediaminetetra-acetic acid disodium salt (Na_2EDTA). After extract and solid residue separation through filtration Ca, Mg, Na, K and S concentrations were determined by ICP-OES and Cu and Zn concentrations by FAAS. The concentration of P was determined spectrophotometrically. Total heavy metal concentrations were analysed according to USEPA 3051, where the dried sample is digested in a microwave oven with a mixture of HNO_3 and HCl.

Leaching Characteristics

Leaching (i.e. extraction) characteristics of certain heavy metals (As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Se, V, and Zn) were investigated to provide information on the mobility and availability of these elements. An integrated leaching procedure, consisting of a two-stage batch test according to SFS-EN 12457-3 and a three-stage sequential BCR test, was utilised. The BCR procedure is described in detail by Bruder-Hubscher et al. [15].

According to Filgueiras et al. [16] and Nurmesniemi et al. [17], metals extracted in respective fractions of the procedure describe natural metal availability as follows:

1. The water-soluble fraction. Represents metals that are relatively labile and thus potentially bioavailable. Provides vital information on the risk of environmental pollution and waste disposition.
2. The exchangeable fraction. Represents weakly adsorbed metals retained on the solid surface by relatively weak electrostatic interaction, metals that can be released by ion-exchange processes and metals that can be co precipitated with carbonates. Most readily available from the environmental point-of-view.
3. The easily reduced fraction. Simulates anoxic conditions likely to occur in a natural medium and metals that are thermodynamically unstable and potentially bioavailable. Usually consists of oxides of Mn and Fe, the well-known sinks for heavy metals in a surface environment.
4. The oxidisable fraction. Represents metals that are organically bound or occur as oxidisable minerals,

Table 2. Physiochemical Properties and Easily Available Nutrient Concentrations of Specimen Amendment Matrices with Reference to Organic and Mineral Soils Normally Found in the Ostrobothnia Region of Northern Finland [17].

Parameter/element	Unit	Matrix I	Matrix II	Matrix III	Soil (organic; mineral)
pH	$mS{\cdot}cm^{-1}$	12.9	13.0	13.0	
Electrical conductivity (E_c)	% (d.w.)	8.8	9.8	11.1	
LOI (loss on ignition, 550°C)	$g{\cdot}kg^{-1}$ (d.w.)	6.3	5.1	5.2	
TOC (total organic carbon)	%	18	20	27	
Dry matter content (105°C)	% (Ca, d.w.)	97.1	97.0	97.1	
Neutralising value (NV)	% (Ca, d.w.)	36.6	35.8	38.6	
Reactivity value (r_{ac})	$mg{\cdot}kg^{-1}$ (d.w.)	34.1	33.3	38.0	
Ca	$mg{\cdot}kg^{-1}$ (d.w.)	180,000	201,000	184,000	3,340; 960
Mg	$mg{\cdot}kg^{-1}$ (d.w.)	10,200	5,000	12,500	520; 135
Na	$mg{\cdot}kg^{-1}$ (d.w.)	4,900	4,100	6,700	35; 14
K	$mg{\cdot}kg^{-1}$ (d.w.)	950	750	870	130; 770
P	$mg{\cdot}kg^{-1}$ (d.w.)	8	2	3	180; 120
S	$mg{\cdot}kg^{-1}$ (d.w.)	3,000	2,700	2,800	130; 23
Cu	$mg{\cdot}kg^{-1}$ (d.w.)	20	22	25	8.5; 3.3
Zn	$mg{\cdot}kg^{-1}$ (d.w.)	110	96	140	11; 3.8
Mn	$mg{\cdot}kg^{-1}$ (d.w.)	1390	96	1360	94; 28

e.g. sulphides. Not considered to be very mobile or bioavailable.

RESULTS AND DISCUSSION

Physicochemical Properties and Plant Nutrient Concentrations

As illustrated in Table 2, the matrices had high neutralising (35.8–38.6%) and reactivity (33.3–38.0%) values (expressed as Ca-equivalents d.w.) with supporting alkaline pH-values (12.9–13.0) indicating liming and buffering capacities comparable to commercial ground limestone products [7]. LOI (5.1–6.3% d.w.) and TOC (18–27 $mg \cdot kg^{-1}$ d.w.) values suggest that matrices comprised mostly of inorganic components and that the share of organic elements increased with increasing paper mill sludge additions most likely due to residual cellulose fibres. According to Brown et al. [17], organic content could enhance Ca movement through the soil profile by fulvic acid formation but could also increase heavy metal availability through the decomposition and release of complexed heavy metals under oxidising conditions [18]. Easily available concentrations of Ca, Mg, Na and S and micronutrient concentrations of Cu, Zn and Mn in all matrices were higher than in organic and mineral soils normally found in the Ostrobothnia Region of Northern Finland [18].

The elevated Na and S concentrations in amendment matrices are reasonable due to the inclusion of green liquor dregs and lime waste from the chemical recovery cycle of the pulping process and the use of Na_2S, NaOH and Na_2SO_4 as pulping chemicals. Na also derives in moderate amounts from the wood raw material and from make-up and bleaching chemicals used in pulping [18]. Although the adverse effects of easily available Na through salinity and sodicity processes in soils are moderated by easily available Ca and Mg [19], elevated Na concentrations could require consideration in future research efforts. Sodium adsorption ratio (SAR) could ensure the feasibility of the concept with described formulations.

In the case of micronutrient Zn (Tables 2 and 3), phytotoxicity is well established and was extensively researched during the 1970's and 1980's regarding anthropogenic soil contamination and soil conditioning through sewage sludge application. Currently, as stated by the European Commission [20], Zn accumulation in regional soils and surface waters is not expected. On the basis of risk assessment, the European Commission concluded that existing legislation concerning e.g. sludge management provides an adequate framework to address and prevent future risks related to Zn accumulation. According to the Council Directive on sewage sludge application [21], the EU limit value for the total concentration of Zn in soil is 150–300 $mg \cdot kg^{-1}$ (d.w.). Additionally, based on the average annual appli-

Table 3. Total Heavy Metal Concentrations (USEPA 3051; $mg \cdot kg^{-1}$ d.w.) and Heavy Metal Recovery of Specimen Amendment Matrices During the Leaching Procedure with Current Finnish Statutory Limit Values Set for Fertilisers Used in Forestry [20].

	Matrix I		Matrix II		Matrix III		
Element	**Leaching Recovery (%)[a]**	**Total**	**Leaching Recovery (%)[a]**	**Total**	**Leaching Recovery (%)[a]**	**Total**	**Fertiliser Limit Value (forestry)**
As	57.5	6	40.8	6	50.8	6	30
Ba	70.8	400	66.0	340	69.1	310	
B	—	20	—	21	—	18	
Cd	74.1	208	77.7	3.3	82.5	3.0	15
Co	46.3	3	46.3	3	69.5	2	
Cr	24.0	75	19.4	370	32.0	50	300
Cu	15.9	50	81.7	51	13.4	50	700
Mo	88.9	<1	107.0[b]	<1	75.0	<1	
Ni	47.5	16	46.9	16	53.8	15	150
Pb	16.3	20	10.5	20	19.6	14	150
Sb	50.0	<4	50.0	<4	50.0	<4	
Se	66.9	<4	66.9	<4	66.9	<4	
V	65.5	140	51.7	2,740	60.3	81	
Zn	72.5	300	68.7	320	65.9	330	4,500
Hg[c]	—	<0.04	—	<0.04	—	<0.04	1.0

[a] Leaching recovery calculated as (the sum of individual leaching fractions from the two-stage batch test and the BCR procedure)/(total element concentration)·100%.

[b] Mo recovery >100% as concentrations from individual leaching fractions were below limit of detection.

[c] B and Hg leaching were not analysed.

cation rate for Zn metal (kg·ha^{-1}) in agriculture, application of approximately 90–100 t·ha^{-1} per year could be applied for produced specimen matrices. Hence, Zn concentrations of produced matrices do not seem to restrict use in forestry. However, in the proximity of water catchment areas, further research regarding potential surface water and groundwater contamination would be required.

Total Heavy Metal Concentrations and Leaching Characteristics

According to Table 3, the total concentrations of As, Cd, Cu, Ni, Pb, Zn and Hg in the specimen matrices were lower than respective Finnish statutory limit values set for fertilisers used in forestry [22]. Only the total concentration of Cr (370 mg·kg^{-1}) in the steel slag matrix (Matrix II in Table 3) exceeded respective limit value (300 mg·kg^{-1}). However, as illustrated by the leaching results, less than a fifth of the total Cr concentration was likely to become mobile in conditions normally found in nature.

The recovered Cr in the steel slag matrix accounted for 19.4% of the total concentration as presented in Table 3 and was only extractable in the oxidisable fraction of the leaching procedure. Cr concentrations in previous fractions, i.e. the water-soluble, exchangeable and easily reduced fractions, remained below 1 mg·kg^{-1} (not shown in Table 3). According to Filgueiras et al. [16], the oxidisable fraction is not considered to be very mobile or bioavailable, however could be released through the decomposition of e.g. organic matter. The remaining Cr (80.6%), calculated as the difference between the total metal concentration and the sum of extracted concentrations, is often referred to as the residual fraction or the 'inert phase' and, as stated by Zufiaurre et al. [23], corresponds to the fraction of metals which cannot be easily mobilised.

The elevated Cr content of Matrix II is most likely due to the replacement of GBFS with steel slag as opposed to Matrices I and III (see Tables 1 and 3). According to Rex [4], the higher concentration of Cr in steel slags mostly depends on the qualities of the iron ore and recycled steel scrap. In addition, the Cr present in steel slag occurs only in trivalent form Cr(III), which is non-toxic and essential for e.g. human health [4]. However, as stated by Vitale et al. [24], formation of highly toxic Cr(VI) could be increased in alkaline conditions or through redox reactions with e.g. Mn [25].

In Finnish fertiliser regulation, the differences in distict forms of Cr were acknowledged in the Statute on fertilizer products by the Ministry of Agriculture and Forestry [22] in 2009 [26]. Consequently, the limit value for the total concentration of Cr regarding the utilization of steel slag (as such) for fertilisation was transformed to a limit value for soluble hexavalent Cr(VI), which was set to 2 mg·kg^{-1} (d.w.). Soluble hexavalent Cr(VI) was not determined in this study and requires attention in future research efforts.

Mechanical Performance

At the age of 28 days, 1 dm^3 cubical specimen matrices I, II and III attested to respective average compression strengths of 2.0, 1.4 and 3.4 MPa in an unconfined compression strength test. Interestingly, superior mechanical strength was attained with a lower relative quantity of binder constituents in the respective matrix as shown in Table 1. Whether this increase in mechanical strength is due to the additional moisture or chemical activation capacity provided by an increased share of paper mill sludge for binder hydration reactions is not clear.

However, the results clearly show that the mechanical strength obtained during 28 days by using fly ash in tandem with ground GBFS or steel slag with respective curing conditions (room temperature and moisture) is sufficient for the manufacture of e.g. pellets thus providing potential soil amendment product physical handling advantages. In the case of the moulding procedure used in the presented study, no additional hydraulic pressing as presented by Mahmoukhani et al. [9] would be needed, as the possible pellets could be manufactured by a cold moulding process. Further application to forest ecosystems in e.g. Northern Finland has been established [27].

CONCLUSIONS

Due to the attested neutralising (35.8–38.6%) and reactivity (33.3–38.0%) values (expressed as Ca-equivalents d.w.) and supporting high pH-values (12.9–13.0), the specimen matrices produced indicate liming effects comparable to commercial ground limestone products [7]. Additionally, the concentrations of Ca, K, and Mg and the concentrations of Cu, Mn and Zn of the specimen matrices were found to be higher than in organic and mineral soils normally found in the Ostrobothnia region of Northern Finland. As only the total concentration of Cr (370 mg·kg^{-1}) observed in the steel slag matrix (of which less than a fifth is likely to become mobile in conditions found in nature) exceeded respective Finnish statutory limit value set for the use of fertilisers in forestry, produced matrices are potential novel concepts for forest soil amendment. The use of steel industry slags other than GBFS or steel slag in tandem with pozzolanics such as fly ash requires further research.

Additionally, although the utility of low cost pellet systems allowing the easy mechanical handling and application of soil ameliorants to land is clear, the function of a possible pellet as a slow release dosing method for reducing possible pH shock effects and allowing mineral release through physical decay over time requires further research. Possible pellet dimensions, nutrient release characteristics and performance in the field would need to be investigated to determine how application rates affect plant/tree growth. Furthermore, the way in which available process industry residues vary over time due to variations in mill operations and how potential application rates to land and the associated metal loadings to, e.g. surface waters, compare to allowable legal limits with potential Cr and Na considerations through soluble Cr(VI) analysis and SAR determination require further study.

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A Comparative Study of Acid Red 119 Dye Adsorption onto Dried Sewage Sludge and Sewage Sludge Ash: Isotherm, Kinetic and Desorption Study

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ABSTRACT: This study presents a comparison between dried sewage sludge (DSS) and sewage sludge ash (SSA) for Acid Red 119 dye removal. Results revealed that optimal pH, contact time and adsorbent dosage for DSS and SSA were (3, 11), (120, 30 min) and (5, 4 g/L), respectively. Isotherm and kinetic studies revealed that both adsorbents follow Freundlich isotherm and second-order kinetic models. The maximum adsorption capacities of DSS and SSA were found 90.91 and 142.88 mg/g, respectively. For SSA, a significant decrease in the decolourization efficiency from 98.87% to 79.31% was observed when a simulated wastewater containing the dye, acetic acid and Glauber's salt dissolved in tap water was used whereas for DSS, the efficiency was not changed significantly. Additionally, desorption/reuse studies of the dye-loaded adsorbents were found unsuccessful.

INTRODUCTION

INCREASING environmental pollution caused by toxic dyes is a matter of great concern. Even small traces of the non-biodegradable and highly toxic dyes can be harmful to the mankind. Effluents from dye production and dying mills are highly objectionable if discharged into open water without any proper treatment [1]. Most treatment technologies presently employed for dye removal are based on physicochemical processes such as adsorption [2], coagulation/flocculation [3, 4] and oxidation [5]. Among these processes, physical adsorption technology is attractive for the dye treatment from the wastewater, due to its easy availability, simplicity of design, high efficiency, ease of operation, and ability to treat dyes in more concentrated form [6]. Although the removal of dyes through adsorption is effective, its use is sometimes restricted due to the high cost of activated carbon and the difficulties associated with regeneration. Therefore, many researchers focused on cheaper substitutes, which are relatively inexpensive, and are at the same time endowed with reasonable adsorptive capacity.

During the last decade there has been a worldwide movement towards a common strategy for all kinds of wastes. Reusing waste materials and taking advantage of their energy content have become priorities, instead of simple disposal, with the addition of the need to achieve in the future more sustainable strategies [7]. A waste material such as waste activated sludge generated in wastewater treatment plants provides an excellent opportunity for removal of textile dyestuffs by adsorption [8]. It will be considerably cheaper and is a great headache for sludge management to its safe and environmentally-friendly disposal [9].

This study focuses on comparing Acid Red 119 (AR119) dye adsorption onto dried sewage sludge (DSS) and sewage sludge ash (SSA) as low cost adsorbents from aqueous solutions. The main objectives are to (1) study the effect of different operating variables (contact time, pH, adsorbent dosage and initial dye concentration) on the dye removal efficiency, (2) determine the isotherms, kinetics and (3) evaluate the influence of some additives of dying process on adsorption performance. Furthermore, desorption and reuse

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potential of the used adsorbents are also investigated in the present study.

MATERIALS AND METHODS

Preparation of Dye-containing Solutions and Simulated Wastewater

Dye-containing solutions were prepared by dissolving AR119 (trade name: Polar red brown V), that is widely used in the dyeing process of textile industries in Iran. The molecular formula of this dye is $C_{31}H_{25}N_5Na_2O_6S_2$. In addition, the chemical structure of AR119 dye is presented in Figure 1. Test solutions were prepared by diluting 1 g/L of stock dye solution with distilled water according to the working concentrations (50, 100 and 200 mg/L). The solution pH was adjusted by sulphuric acid or sodium hydroxide. pH measurement was carried out using a 340i/SET pH meter (WTW-Germany) and preliminary calibration is systematically carried out using suitable buffer solutions.

In addition, for simulating a more practical condition, an investigation was carried out using synthetic wastewater including tap water (instead of distilled water) and/or acetic acid (1 g/L) and Glauber's salt (3.33 g/L).

Preparation and Characterization of Adsorbents

In this study, DSS and SSA were used as adsorbents for the removal of AR119 dye. The sewage sludge sample was collected from drying beds of municipal wastewater treatment plant of Shahrak-e-Gharb in Tehran/Iran. Activated sludge process is used in this wastewater treatment plant. Sludge from primary and secondary sedimentation tanks are treated and transfer to drying beds. When preparing DSS, the sludge sample was dried at 105°C to a constant weight in the laboratory. The production procedure for SSA was to combust DSS in an incinerator at 700°C for 3 hours. The finer part of DSS and SSA passing through the No.100 mesh was collected and tested in our experiments. The chemical composition of sludge was carried out by X-ray fluorescence (XRF, X"Uniqe II-Philips). The result of XRF analysis is presented in Table 1. As indicated in this Table, the major elements of sludge sample include CaO (16.2%), SiO_2 (8.3%), P_2O_5 (4.06%) and SO_3 (2.77%).

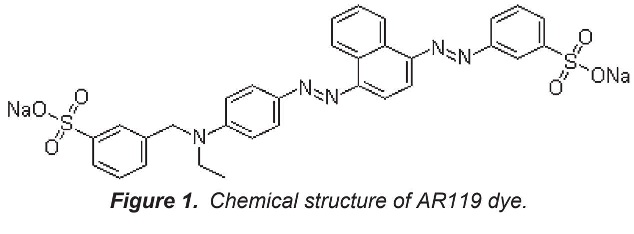


Figure 1. Chemical structure of AR119 dye.

Table 1. Chemical Composition of the Sewage Sludge Used in this Study.

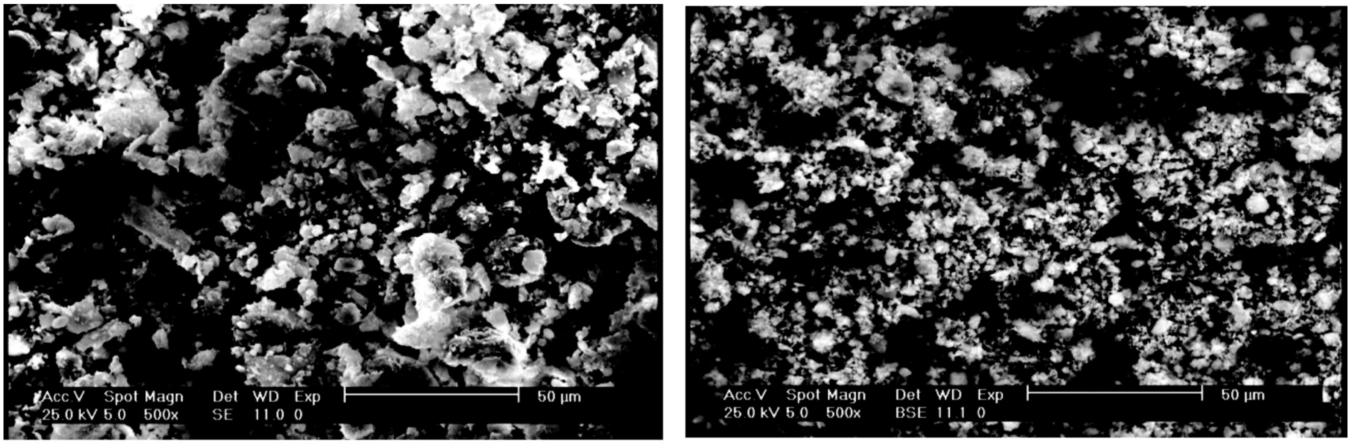
Elements	Amount (%wt)
MgO	2.06
Al_2O_3	2.63
SiO_2	8.30
P_2O_5	4.06
SO_3	2.77
CaO	16.2
Fe_2O_3	1.94
K_2O	0.99
Cl	0.109
Na_2O	0.054
SrO	0.056
ZnO	0.23
MnO	0.051
TiO_2	0.27
CuO	0.026
Cr_2O_3	0.022
V_2O_5	0.0067
Rb_2O	0.0022
ZrO_2	0.0104
Ga_2O_3	0.002
NiO	0.0038
BaO	0.011

Note: Lost on Ignition (L.O.I) = 60.19%.

In addition, a scanning electron microscope (SEM) (XL-C/Philips) using 25 kV accelerating voltage was also used to characterize the adsorbents for morphological information. The SEM examination showed that the solid porosity of SSA and accordingly the number of accessible sorption sites for dye uptake was much higher if compared with the DSS sample (see Figure 2).

Experimental Procedure

Batch experiments for the removal of AR119 dye were carried out in a six-beaker jar-test apparatus at an agitation speed of 150 rpm to study the effect of operating variables including contact time (5–240 min), pH (3–11), adsorbent dosage (1–6 g/L) and initial dye concentration (50,100 and 200 mg/L). When the adsorption procedure was completed, the 50 ml of supernatant withdrawn from a height of 2–3 cm below the surface was centrifuged at 5000 rpm for 5 min. The clear supernatants were analyzed for AR119 dye concentrations using a UV-vis HACH spectrophotometer DR/4000 at 526 nm wavelength (λ_{max}).



(a)

(b)

Figure 2. *SEM images of (a) DSS and (b) SSA.*

The adsorption experiments were conducted at room temperature (25 ± 1°C). To increase the accuracy of the data, each experiment was replicated at least 2 times, and the mean values were used in our analyses.

Adsorption Isotherms

In this study, the widely used adsorption models for single-solute systems, i.e. Langmuir and Freundlich isotherms, were employed to describe the AR119 dye adsorption equilibrium. Adsorption isotherm studies were carried out with different adsorbent doses ranging from 1 to 5 g/L in pH of 3 for DSS and 1 to 6 g/L in pH of 11 for SSA, while the initial dye concentration was kept constant at 100 mg/L. The applicability of the isotherm models to the adsorption study was compared by judging the correlation coefficients (R^2) values. The isotherms were summarized in Table 2.

Adsorption kinetics

In order to identify the potential rate-controlling steps involved in the process of adsorption, three kinetic models (the pseudo first- order, pseudo-second-order and intraparticle diffusion kinetic models) were used to fit the experimental data from the adsorption of AR119 dye onto the adsorbents at various pH ranging from 3 to 11 for DSS and 5 to 11 for SSA. The validity of the order of adsorption process was based on the two criteria, first based on the regression coefficient and secondly based on the calculated qe values. The tested Kinetics models in this study are explained briefly in Table 3.

Desorption and Regeneration Tests

In order to evaluate the mechanism involved in AR119 dye adsorption, desorption experiments were conducted. For this purpose, 0.2 g of the dye-loaded adsorbent was shaken with 50 ml of different desorbing agents (distilled water and different concentrations of HCl and NaOH solutions) for 3 h and then centrifuged at 5000 rpm for 2 min. The centrifuged liquid was analyzed for the dye concentration.

The most promising desorbing agent was selected and used to prepare the dye-loaded adsorbent for adsorption process in further experiments. For the subsequent adsorption test cycle, the desorbed adsorbent

Table 2. Isotherm Equations.

Isotherm Name	Linearized Equation		Equation parameters
Langmuir Isotherm	$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m b C_e}$	(1)	C_e (mg/L) = the equilibrium concentration q_e (mg/g) = the amount adsorbed per amount of adsorbent at the equilibrium q_m (mg/g) = the maximum adsorption capacity b (L/mg) = adsorption equilibrium constant related to the free energy of adsorption
Freundlich Isotherm	$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$	(2)	K_F (L/mg) = an indicator of the adsorption capacity n = adsorption intensity

Table 3. Kinetics Equations.

Kinetic Model	Kinetic Equation		Equation Parameters
Pseudo First-order	$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t$	(3)	q_e (mg/g) = adsorption capacity at equilibrium q_t (mg/g) = adsorption capacity at time t k_1 (min^{-1}) = the rate constant of adsorption
Pseudo Second-order	$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}$	(4)	k_2 (g/(mg.min)) = the rate constant of pseudo second-order adsorption
Intraparticle Diffusion	$q_1 = k_p t^{1/2} + C$	(5)	k_p (mg/g.min$^{(1/2)}$) = the intraparticle diffusion rate constant C = the intercept

was rinsed with distilled water to neutral pH, dried in oven at 40°C for 24 h and then reused under the optimum conditions.

RESULTS AND DISCUSSION

Effect of Different Operating Variables on the Performance of Adsorbents

Effect of pH and Contact Time

pH and contact time are the effective factors in batch adsorption process. In this stage, the effect of contact time on the adsorption performance of DSS and SSA was investigated under various pH ranging between 3 to 11, while the dosages of DSS and SSA were both kept constant at 2 g/L. Initial dye concentration and agitation speed was respectively 100 mg/L and 150 rpm for all solutions during the experiment. Figure 3 shows the time profiles of dye removal for the two experimental adsorbents at various pH.

As shown in Figure 3, all quantities of dye sorption by DSS and SSA increase quickly during the first 5 min of reaction, indicating that the dye particles are rapidly occupying the empty sorption sites on adsorbents. Nevertheless, the dye sorption on both adsorbents becomes slow as the number of the sites is decreasing and a steady state was reached within 120 min and 30 min for the adsorption of AR119 dye onto DSS and SSA, respectively.

Results also indicate that the effectiveness of adsorbents in removing dye was more sensitive to the pH variations. It is well known that acid dyes release negative charges when dissolved in water. The adsorption of these charged dye groups onto an adsorbed surface is influenced by the surface charge on the adsorbent. At lower pH values, more protons will be available to protonate the adsorbent surface, thereby increasing the electrostatic attractions between negatively charged dye anions and positively charged adsorption sites and causing an increase in the dye adsorption [10].

As it can be seen from Figure 3, DSS showed a very good dye removal at lower pH (pH of 3) which proved the mentioned theory. However, in the case of SSA, the dye removal efficiency increased with increasing the pH of dye-containing solutions. Hence, for SSA, it can be found that electrostatic attraction was not the only and predominant mechanism by which removal of the dye particles occurred. In other words, there are also other adsorption mechanism/mechanisms which enhance the dye removal efficiency in different conditions. As a myriad of functional groups is often present on the biomass surface, various sorption mechanism including ion exchange, chelation, microprecipitation

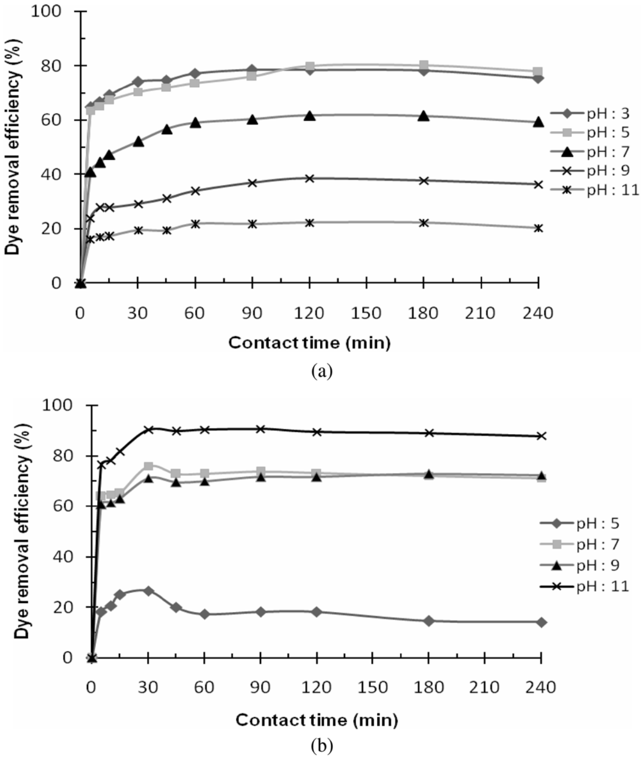


Figure 3. *Variation of dye removal efficiency with contact time for different pH at adsorbent dosage of 2 g/L and initial dye concentration of 100 mg/L; (a) DSS, (b) SSA.*

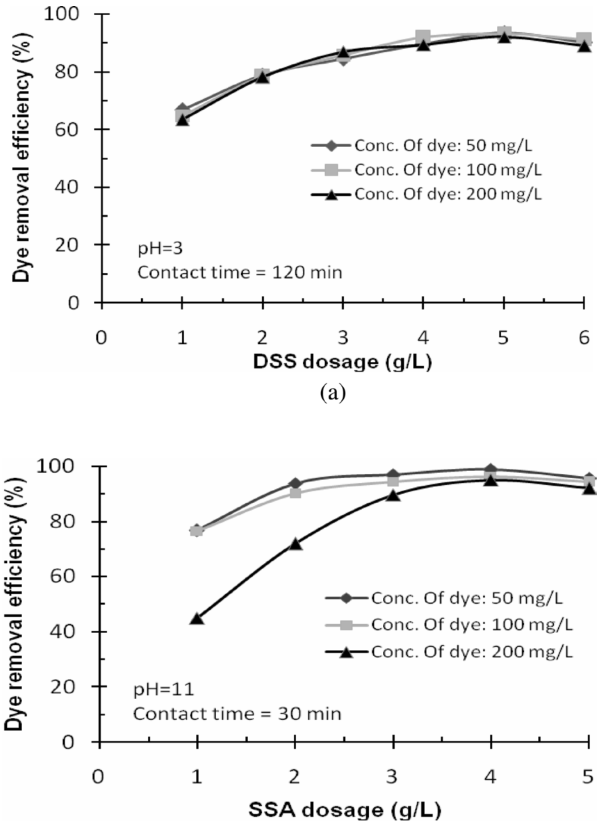
and complexation may be involved in the adsorption process [11].

Further experiments were carried out by fixing a contact time of 120 min at pH of 3 and adsorption period of 30 min at pH of 11 for AR119 dye sorption on DSS and SSA, respectively.

Effect of Adsorbent Dosage and Initial Dye Concentration

The variation of dye removals with adsorbent dosage for different initial dye concentration (50, 100 and 200 mg/L) at the end of 120 min for DSS and 30 min for SSA are compared in Figures 4(a) and 4(b), respectively. Experiments were conducted at pH of 3 for DSS and 11 for SSA which was selected in the previous stage.

As shown in Figure 4, dye removals by adsorption increased with increasing adsorbent dosage for all the initial dye concentrations tested and reached a maximum level at 5 g/L for DSS and 4 g/L for SSA. Beyond these values, regarded as being optimal, dye removals did not change significantly or dropped slowly. The decrease in amount of dye adsorbed with increasing adsorbent mass is due to adsorption sites remaining unsaturated during the adsorption process [12].



(a)

(b)

Figure 4. *Variation of dye removal efficiency with adsorbent dosage for different initial dye concentration; (a) DSS, (b) SSA.*

The lower amount of SSA for high removal efficiency (4 g/L vs. 5 g/L) could be explained by the comparative morphology of the used DSS and SSA samples (Figure 2). It indicates that SSA sample with higher surface area is more likely to adsorb AR119 dye molecules. On the other hand, in the case of DSS, with the increase of initial dye concentration (from 50 mg/L to 200 mg/L), the rate of dye removal was not significantly changed, whereas for SSA, the percentage of dye removal decreased with increasing the initial dye concentration at a fixed SSA dosage. In other words, the residual concentration of dye molecules will be higher for higher initial dye concentrations. This could be ascribed to the accompanying increase in dye aggregation and/or depletion of accessible hydrolysis products of the adsorbent.

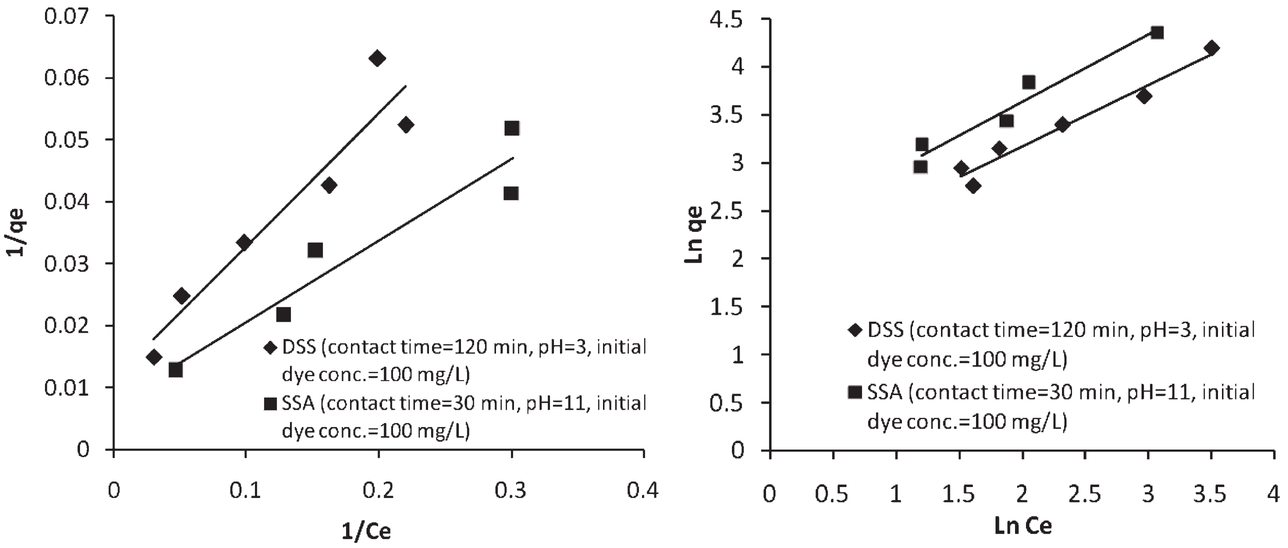
Based on the results, the optimal conditions to obtain the maximum dye removal efficiency using DSS were pH 3, contact time of 120 min, adsorbent dosage of 5 g/L and initial dye concentration of 50 mg/L while the optimal pH, contact time, adsorbent dosage and initial dye concentration for SSA were 11, 30 min, 4 g/L and 50 mg/L, respectively. Under these optimal values of process parameters, the maximum dye removal of 93.46% and 98.87% was observed for DSS and SSA, respectively.

Adsorption Isotherms

Analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design of adsorption systems [13]. The Langmuir adsorption isotherm plots ($1/q_e$ versus $1/C_e$) and the Freundlich isotherm plots ($\mathrm{Ln}q_e$ versus $\mathrm{Ln}C_e$) for the adsorption of AR119 are shown in Figure 5. The values of Langmuir constants (q_{max} and b) and Freundlich constants (K_F and $1/n$) obtained from intercept and slope of the plots are presented in Table 4 along with the regression correlation coefficients.

Regarding the isotherms fittings for data corresponding to the DSS and SSA, as shown in Table 4, quite high regression correlation coefficients ($R^2 > 0.9$) were found for both isotherms models. However, the Freundlich model showed somewhat better fit (R^2 of 0.957 for DSS and R^2 of 0.948 for SSA) for both adsorbents.

With respect to the Langmuir model, qmax defines



(a) (b)

Figure 5. *(a) Langmuir and (b) Frendlich plots of the AR119 dye adsorption on DSS and SSA.*

the maximum capacity of the adsorbents. According to the obtained results, the maximum adsorption capacity of SSA for AR119 dye was rather high (142.88 mg/g), while the maximum capacity of DSS was 90.91 mg/g. As b values reflect equilibrium constant for the adsorption process, it shows the affinity of the adsorbent for dye. Thus higher b value of SSA (0.0514) in comparison with DSS (0.0514) indicates that the SSA has more affinity for AR119 dye.

As compared to the literature studies on the low-cost adsorbents for acid dye adsorption, this study revealed high adsorption capacity of both DSS and SSA samples for AR119 dye. Maximum adsorption capacity of 142.88 mg/g for SSA and 90.91 mg/g for DSS was clearly higher than those reported in the literature [14–16].

Adsorption Kinetics

Adsorption is a multi-step process involving transport of the adsorbate molecules from the aqueous phase to the surface of the solid particles then followed by diffusion of the solute molecules into the pore interiors [17]. The overall adsorption process may be controlled either by one or more steps. The calculated kinetics constants for both adsorbents at different pH are given in Table 5, along with the qe,exp (experimental adsorption capacity value) and corresponding correlation coefficients.

Table 4. The Coefficients Isotherm Parameters for AR119 Dye Adsorption onto DSS and SSA.

Adsorbent Type	Isotherms	Constants		R^2
DSS	Langmuir	q_{max} = 90.91	b = 0.0514	0.905
	Freundlich	K = 6.6127	n = 1.5576	0.957
SSA	Langmuir	q_{max} = 142.88	b = 0.0534	0.914
	Freundlich	K = 9.3371	n = 1.4245	0.948

The results of Table 5 show that for both adsorbents, the R^2 values for the pseudo-second order kinetic model was higher than 0.99 and the calculated equilibrium adsorption capacity values (qe,cal) were very close to the experimental qe values (qe,exp). Furthermore, the values of k_2 had obvious decreasing trend with an increase in pH. These imply that the adsorption of the dye on both adsorbents followed the second-order kinetics rather than the first-order kinetic models. Similar result has been reported by other researchers for the adsorption of different textile dyestuffs onto modified sludge [18] and acid pre-treated powdered waste sludge [19].

Effect of Some Additives of Dying Process on the Performance of Adsorbents

Apart from dyes, the wastewaters from textile-manufacturing or dye-producing industries also contain various types of suspended and dissolved compounds including acids, alkalis, salts, surfactants or metal ions [20]. In practice, Acid Red 119 is dyed from a dye bath with addition of 1–3% acetic acid (80%) and 10% Glauber's salt (sodium sulphate). Therefore, for simulating a more realistic condition, an investigation was carried out on the effect of tap water (instead of

Table 5. Adsorption rate constants for adsorption of AR119 dye using DSS and SSA at different pH.

			Pseudo-first-order			**Pseudo-second-order**		
Adsorbent	**pH**	**q_e,exp**	**k_1**	**q_e,cal**	**R^2**	**k_2**	**q_e,cal**	**R^2**
DSS	3	39.3	0.0437	9.660	0.982	0.0122	40.00	0.999
	5	38.55	0.0368	10.79	0.929	0.0097	40.00	0.999
	7	30.84	0.0414	15.00	0.951	0.0064	32.258	0.999
	9	19.23	0.0184	7.311	0.924	0.0069	20.00	0.993
	11	11.14	0.0345	4.074	0.931	0.0203	11.494	0.998
SSA	5	13.3	0.1842	13.65	0.984	0.0192	14.92	0.995
	7	37.93	0.2026	37.15	0.869	0.0117	40.00	0.992
	9	35.6	0.1358	17.66	0.899	0.0135	38.46	0.995
	11	45.1	0.1612	26.67	0.921	0.0116	47.62	0.997

distilled water) and addition of acetic acid (1 g/L) and Glauber's salt (3.33 g/L) on the AR119 dye adsorption at optimal experimental condition obtained at the previous sections. The results are presented in Figure 6.

According to the observed results (see Figure 6), for both adsorbents, the utilization of tap water instead of distilled water for preparing the dye containing solutions had negligible effect on the removal efficiency (ΔR = the difference between removal efficiencies of AR119 dye prepared in distilled water and tap water ≤ 2.5%) whereas, the addition of acetic acid and Glauber's salt influenced the process performance. The worst effect on the process performance was observed in the case of SSA for the simulated dye wastewater (prepared with AR119 dye, tap water, 1 g/L of acetic acid and 3.33 g/L Glauber's salt) with dye removal efficiency of 79.31%. The decrease in dye removal efficiency can be explained by decreasing the electrostatic interactions between dye molecules and adsorbent surface as the positive and negative ions in salts can neutralize the surface charge of the adsorbent and charged dye molecules [21]. In addition, the presence of salts can compete with adsorbate for the active sites, which leads to the decrease of adsorption capacities [22]. Santos research group similarly reported that the maximum dye removal efficiency using waste metal hydroxide sludge as adsorbent for the dye solution prepared with distilled water was much higher than the simulated dye effluent containing the selected dye, salts and dyeing auxiliary chemicals [23].

Desorption and Reuse of the Adsorbents

To understand the nature (or the process) by which the dye remains adhered to the surface of the adsorbent and also to make the adsorption process more economical, it is necessary to study desorption and reuse of the dye-loaded adsorbents. Desorption tests were carried out by utilizing distilled water and different concentrations of HCl, NaOH aqueous solutions for 3 h. The obtained results of desorption study for the first cycle are presented in Figure 7. It should be noted that the adsorption experiments were conducted at optimal conditions obtained in the previous sections.

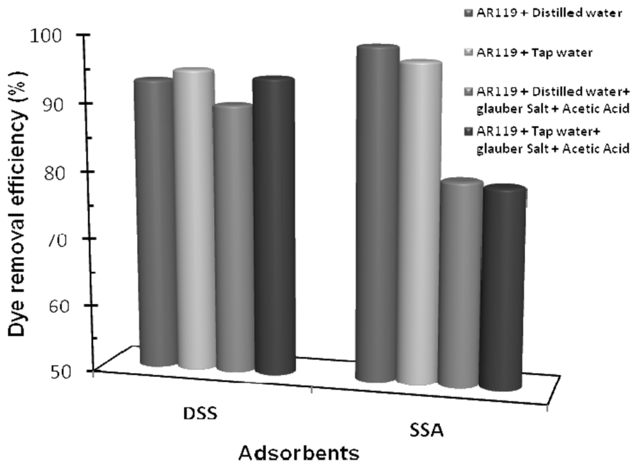


Figure 6. *The effect of some additives of dying process on the AR119 dye adsorption.*

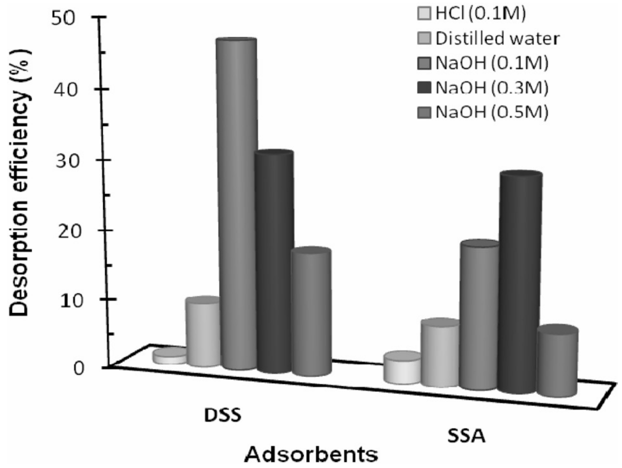


Figure 7. *Effect of desorptive agents on AR119 dye desorption for the first cycle.*

Table 6. Adsorption and Desorption Behaviors of AR119 Dye Ions on DSS and SSA.

	Cycle 1		Cycle 2		Cycle 3	
Adsorbent	Dye Removal Efficiency (%)	Recovery (%)	Dye Removal Efficiency (%)	Recovery (%)	Dye Removal Efficiency (%)	Recovery (%)
DSS	93.46	46.8	70.3	38.6	41.8	32.9
SSA	98.87	29.7	9.6	26.5	5.2	26.3

As shown in Figure 7, NaOH solutions proved to be more effective desorptive agents among which 0.1M and 0.3M NaOH solutions were found out to be the most efficient one for DSS and SSA, respectively.

The reversibility of adsorption depends on whether there is a strong binding bond such as ionic or covalent bonding or weak binding forces such as Van der Waals' forces or a dipole–dipole interaction formed between the adsorbent surface and the dye molecules [22]. Since at the first cycle of regeneration, more than half of the dye (53.2% for DSS and 70.3% for SSA) still remained in the solid phase even at the most effective desorptive agents, it can be implied that strong chemical bonds are present between the dye and the adsorbent surface. The strong interactions such as ionic or covalent bonding forces seem to be dominant and control the adsorption process of both adsorbents.

Furthermore, desorption was fulfilled in the most effective desorptive agents and then the regenerated adsorbents were reused under the optimum adsorption conditions. The observation presented in Table 6 suggested that the dye removal efficiency decrease significantly as the number of cycle increases (from 93.46% to 41.8% for DSS and 98.87% to 5.2% for SSA). Therefore, it can be implied that binding sites of the both adsorbents were negatively affected or deteriorated by the regeneration process.

CONCLUSIONS

The main results of this study are summarized as follows:

- The optimum conditions for the maximum dye removal were found at pH 3, contact time of 120 min and adsorbent dosage of 5 g/L for DSS while the optimal pH, contact time and adsorbent dosage for SSA were 11, 30 min and 4 g/L, respectively.
- Isotherm studies revealed that the Freundlich model yields a somewhat better fit than the Langmuir model for both adsorbents.
- Kinetics studies showed that the adsorption of the dye on the both adsorbents followed second-order kinetics rather than first-order kinetic models.
- The process performance of the SSA becomes worse when some additives including acetic acid and Glauber's salt were added to dye containing solutions whereas, no significant change in process performance of the DSS was observed.
- Desorption studies of the dye-loaded adsorbents with the used desorbents were found unsuccessful since more than half of the dye still remained in the solid phase at the first cycle.
- Regenerations carried out with NaOH solutions resulted in a remarkable decrease in dye removal efficiency at the subsequent adsorption cycles (from 93.46% to 41.8% for DSS and 98.87% to 5.2% for SSA).

It can be concluded that both of DSS and SSA can be used as low cost natural abundant sources for the removal of AR119 dye and they can be an alternative to more costly materials such as activated carbon.

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Gaseous Nitrogen Losses Following Soil Amendment with Biosolids under Controlled Conditions

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ABSTRACT: This paper quantifies gaseous N losses due to ammonia volatilisation and denitrification under controlled conditions at 30ºC and 75% to 150% of Field Capacity (FC). Biosolids were mixed with two contrasting soils from subtropical Australia at a rate designed to meet crop N requirements for irrigated cotton or maize (i.e., equivalent to 180 kg N ha^{-1}). In the first experiment, aerobically (AE) and anaerobically (AN) digested biosolids were mixed into a heavy Vertosol soil and then incubated for 105 days. Ammonia volatilization over 72 days accounted for less than 4% of the applied NH_4-N but 24% (AN) to 29% (AE) of the total applied biosolids' N was lost through denitrification in 105 days. In the second experiment AN biosolids with and without added polyacrimide polymer were mixed with either a heavy Vertosol or a lighter Red Ferrosol and then incubated for 98 days. The N loss was higher from the Vertosol with16–29% of total N applied versus the Red Ferrosol with 7–10% of total N applied, while addition of polymer to the biosolids increased N loss from 7 to 10% and from 16 to 29% in the Red Ferrosol and Vertosol, respectively. A major product from the denitrification process was N_2 gas, accounting for >90% of the emitted N gases from both experiments. Our findings demonstrate that denitrification could be a major pathway of gaseous N losses under warm and moist conditions.

INTRODUCTION

The area of agricultural land to which biosolids (i.e., nutrient rich organic matter derived from wastewater treatment processes) is being applied and quantities of biosolids being applied to cropping land have significantly increased in the past two decades. This increase has been due to both an increasing recognition of biosolids' nutrient value and environmental concerns about 'traditional' disposal methods such as the use of a landfill. Land application has been suggested as a way of replenishing soil organic matter stores as well as supplying nutrients such as nitrogen (N), phosphorus (P), sulphur (S), potassium (K) and essential micronutrients.

When biosolids' N is added to soil it will undergo a series of transformations which may add to pools of plant available mineral N in the soil but also may lead to gaseous losses to the atmosphere, including the heavily weighted greenhouse gas N_2O. The supplemented organic N can be mineralised to NH_4-N and NO_3-N, but this newly formed NH_4-N and any initial NH_4-N in the biosolids may be lost via NH_3 volatilisation. Additionally, NO_3-N can be lost through denitrification (i.e., formation of N_2 and N_2O), with key soil factors affecting the extent of denitrification activity being both air-filled porosity and concentrations of NO_3-N and labile carbon (C) in the soil (Pu et al., 2001). Quantitative information about these N transformations and gaseous loss pathways is essential for developing effective N management strategies so that land application of biosolids minimises any unintended adverse effects on the environment (Vieira et al., 2005).

Results from field trials at four different locations covering different soil types and cropping systems in subtropical southeast Queensland indicated a significant amount of applied biosolids' N ranging from 12–40% could not be accounted for one year after biosolids application (Barry et al, 2006). Since three of the four sites did not experience runoff or show any evidence of leaching losses, it was hypothesised that unaccounted for N was lost by either denitrification or NH_3 volatilisation. While there have been reports of gaseous N losses from biosolids due to NH_3 volatilisation (Harmel et al., 1997; 2003; Robinson and Röper,

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2003), little has been done to quantify N lost through denitrification. The difference between applied and recovered N from both the plant and soil has usually been attributed to leaching of NO_3 and volatilisation of NH_3, with any N loss unaccounted for by these two processes attributed to denitrification (Mendoza et al., 2006).

Field trials reported by Barry et al. (2006) provided favourable conditions for denitrification losses in that both biosolids and soils were characterised by low C:N ratios, soil textures were mostly medium-heavy clays and high concentrations of NO_3-N were found in the soils as a result of rapid mineralisation of organic N from biosolids (Bell et al., 2004). In addition, biosolids used in field trials contained a flocculent polymer. This is often added during biosolids processing to help in the dewatering process. The added polymer, however, can affect water holding characteristics of the biosolids. Biosolids with added polymer tended to lose water more slowly than surrounding soil during dry periods and also absorbed water more quickly after a rain. This additional moisture retention combined with high mineral N and C levels would favour denitrification activity in and near biosolids' lumps.

The aim of the two experiments reported here was to directly quantify gaseous N losses through direct measurement of denitrification and ammonia volatilisation. Impact of variables like soil type, prevailing moisture, and biosolids characteristics such as the production process (anaerobic or aerobic), and presence of added polymer on the extent of these gaseous losses was assessed under controlled conditions.

MATERIALS AND METHODS

Soil and Biosolids

Soils from the top 10 cm of the soil profile was used in experiments were a heavy Black Vertosol collected from Cecil Plains (27.40S, 151.74E, elevation: 400m), and a strongly structured Red Ferrosol from Kingaroy (28.33S, 152.30E, elevation: 507 m). Both soils came from sites in subtropical Australia previously used to conduct a series of field trials investigating effects of biosolids application on crop productivity and fate of biosolids-derived major nutrients and trace metals (Barry et al., 2006).

Biosolids (i.e., dewatered cake) were sourced from waste water treatment plants also located in subtropical Australia. In Experiment 1, two biosolids were used: an anaerobically digested product from an urban catchment area and an aerobically digested product from a semi-urban catchment area. In Experiment 2, an anaerobically digested product from an urban catchment area different than the one in Experiment 1 was used.

Experiment 1

The experiment included a control soil with no added biosolids in addition to other treatments in which soil was amended with aerobically or anaerobically digested biosolids. Biosolids were mixed with sieved (<10 mm) moist field soil at rates equivalent to 20 dry Mg anaerobic biosolids ha^{-1} (23g dry biosolids kg^{-1} dry soil) and 14 dry Mg aerobic biosolids ha^{-1} (17 g dry biosolids kg^{-1} dry soil) and are equivalent to the Nitrogen Limited Biosolids Application Rate (NLBAR) for each biosolids' batch determined using methods described by NSWEPA (1997). Biosolids lumps >25mm diameter were removed prior to mixing.

Moist soil (i.e., control) and mixtures of moist soil and added biosolids were packed to a height of 100 mm in PVC cylinders with an inner diameter of 125 mm and height of 150 mm. A PVC cover with an O-ring fixed on the inside was screwed to the top of the cylinder. A hole of 5 mm diameter was drilled in the centre of the top cover with a hole able to be sealed with a silicon septum. Additional sets of cylinders were prepared in the same fashion for each treatment to allow temporal variation in background NO_3-N in the soil to be monitored. However, only two replications were established for this purpose.

Packed soil cores were wetted to 75% of FC and then kept in an incubator at a constant temperature of 30±1°C. On days 14, 28, and 42 after commencement, moisture content was increased to FC by adding the required amount of deionised water and on day 77 moisture content was further increased to 150% of FC. After each wetting, soil was allowed to gradually dry down. Although, from days 1 to 42 and day 77 to 85, covers were left on with septum's removed to reduce rate of moisture loss. For the remainder of the experiment, cylinders were left open except during periods of gas sampling.

Soil cores in additional sets of cylinders were sampled at 14, 21, 28, 42, 56, and 70 days after incubation started by removing two cylinders per treatment at each time. Soil NO_3-N was determined for the moist soil. After 105 days, all remaining soil cores were taken out and re-mixed. Half of the soil from each cylinder was kept moist prior to analysis for mineral N. Remaining soil was oven dried at 40°C and ground to pass a 2 mm sieve before conducting other chemical analyses.

Experiment 2

Experiment 2 used only 3 replications and consisted of unamended Black Vertosol or Red Ferrosol soils (controls) as well as soils amended with an anaerobically digested biosolids with and without added polymer (cationic flocculent type FO 4490 supplied by SNF Australia Pty Ltd).

Procedures and materials in Experiment 2 were similar to those used in Experiment 1 except for the following details. Cylinders were slightly smaller with an inner diameter of 85 mm. Moisture regimes imposed on soil cores inside the cylinders were adjusted to 75% of FC on days 1 and 12, 100% FC on days 21 and 51, and 150% of FC on day 52. Except for days 21 to 52 when the cylinder covers were left on with the septum's removed, cylinders were left open with PVC covers removed to facilitate gas exchange after gas samples were actually being collected. Soil NO_3-N status was again monitored using soil cores in the additional sets of cylinders with sampling undertaken 14, 28, and 42 days after incubation started. The experiment was terminated once gaseous N emissions dropped to insignificant levels.

Ammonia Volatilisation Determination

A PVC container with 5 ml of 4% boric acid was attached to the inside wall of each cylinder containing various soil and soil-biosolid mixtures after which cylinders were sealed and returned to the incubator for periods ranging from 4 to 48 hours. NH_3-N entrapped in boric acid was determined by titration using 0.0025 M H_2SO_4 (Khan et al., 1997). Measurements of ammonia volatilisation were terminated on day 72 when emissions dropped below detection limits. Accumulated amount of volatilised NH_3-N over the experimental period was calculated using the trapezoidal integration method.

N_2O Gas Determination

Denitrification losses were assessed in all soil and soil-biosolids treatments with and without added acetylene gas. During the incubation period, Acetylene was added to inhibit transformation of N_2O into N_2 and to ensure all N losses from denitrification were captured. After sealing cylinders with covers, the 'plus acetylene' treatments had the gas injected into the cylinders at 8% (v/v) of the air phase. All cylinders were then kept in the incubator at 30°C and gas samples were collected after periods of 12 to 48 hours using a 12 ml pre-evacuated glass tube. Concentration of N_2O in gas samples was determined using a Varian CP-3800 GC (Varian, Netherlands). Accumulated N_2O-N lost over the measurement period was calculated in a similar fashion to cumulative NH_3 volatilisation losses using the trapezoidal integration method.

Soil and Biosolids Chemical Analyses

Standard soil analyses were conducted using methodology outlined in Rayment and Higginson (1992). Total soil and biosolids C concentrations were determined by a dry-combustion method using a LECO CNS-2000 analyser (LECO Corporation, MI, USA). Total N concentration of both soils and biosolids was determined by the semi-micro Kjeldahl digestion method (Bremner and Mulvaney 1982). Biosolids and soil mineral N (i.e., NH_4 and NO_3) was extracted using a 1:10 ratio of biosolids/soil:2M KCl solution and then determined by an automated colorimetric method (Method 7C2, Rayment and Higginson, 1992). The N quantity determined by this method included both NO_2-N and NO_3-N.

Statistical Analysis

Differences between treatment means were tested for statistical significance using the least significant difference (LSD) procedure in the Genstat® statistical package (8th Edition). Figures were produced using Microsoft® Excel 2000 with standard error bars presented in the relevant figures.

RESULTS

Characterisation of the Soils and Biosolids

Selected soil properties as displayed in Table 1 and demonstrate that while both soils contained similar proportions of silt + clay (viz. 86% and 79% for the Vertosol and Ferrosol, respectively), gravimetric soil moisture content at FC was much higher for the Vertosol (50%) than the Ferrosol (29%). In addition, the Vertosol contained lower concentrations of both C and TKN and had a higher pH, EC, and C:N ratio than the Ferrosol (see Table 1). Little NO_3-N and NH_4-N were found in either of the soils before incubation.

Table 1. Soil Properties (0–10cm depth) used in the Experiments.

Soil	pH 1:5 H_2O	EC mS cm^{-1}	NH_4-N	NO_3-N	K_{total}	P_{total}	S_{total}	C_{total}	TKN	Sand	Silt	Clay	C:N ratio
			mg kg^{-1}		%								
Red Ferrosol	6.2	0.05	19	19	0.2	0.08	0.03	1.85	0.2	22	19	60	9.3
Black Vertosol	8.1	0.12	5	15	0.43	0.03	0.01	1.29	0.08	14	15	71	16.1

TKN of the biosolids ranged from 5.9% (i.e., anaerobic biosolid B without polymer) to 6.5% (i.e., anaerobic biosolid A with polymer). See Table 2. Concentrations of NO_3-N were low in all biosolids used, but concentrations of NH_4-N were much higher ranging from 4% (i.e., anaerobic biosolid B without polymer) to 19% (i.e., anaerobic biosolid A with added polymer) of total biosolids' N. In Experiment 2, concentrations of both NH_4-N and TKN were lower in polymer free anaerobic biosolids (i.e., 2500 mg kg^{-1} and 5.9%, respectively) than in the same biosolid with added polymer (i.e., 5300 mg kg^{-1} and 6.2%, respectively). This is most likely due to gaseous N losses during the extended period on drying beds required for polymer free biosolids. All biosolids contained significant amounts of C which ranged from 33–37% on a dry weight basis and very low C:N ratios (5–6).

Temporal Changes in NO_3-N Concentrations

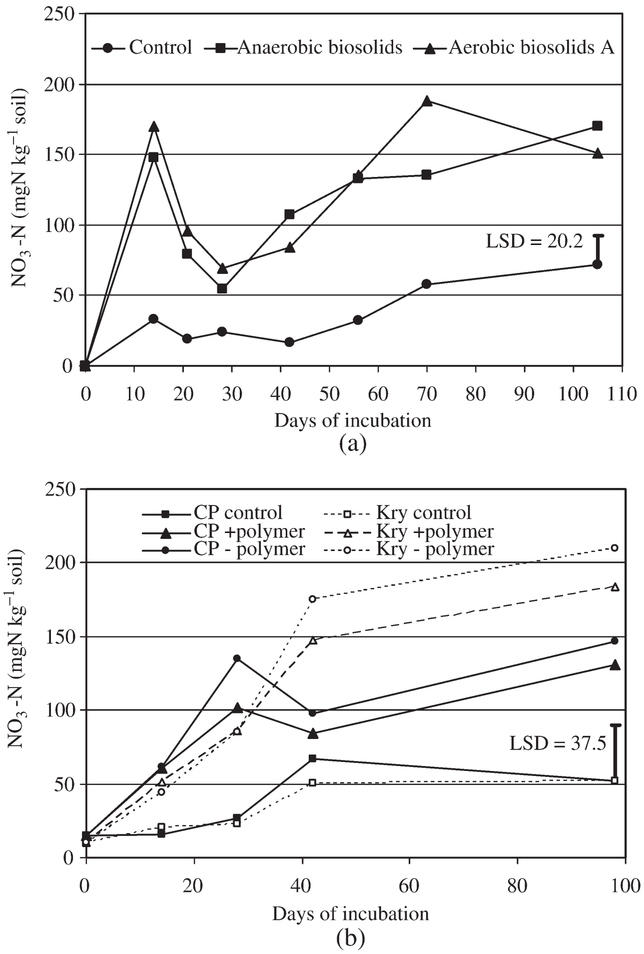
During experiment 1, NO_3-N concentrations in the Vertosol reached an early peak at 14 days after commencement of incubation (i.e., 170 and 150 mg NO_3-N kg^{-1} soil for the aerobic and the anaerobic biosolids-amended soils, respectively) and then rapidly declined to reach a minimum on day 28 (i.e., 70 and 55 mg NO_3-N kg^{-1} soil for the same treatments respectively) See Figure 1(a). After this minimum was reached, NO_3-N concentrations then increased continuously until day 70 for soil amended with aerobic biosolids and until the end of the experiment on day 105 for soil amended with anaerobic biosolids. At the end of the 105 day incubation period, NO_3-N concentrations were 150 and 170 mg NO_3-N kg^{-1} soil for the aerobic and anaerobic biosolids-amended soils, respectively. The same general pattern of fluctuations in NO_3-N was found in the control treatment (i.e., soil without added biosolids). Although, concentrations were much lower differing by > 100 mg kg^{-1} at both the very early and late stages of the incubation period.

There were similar fluctuations in NO_3-N concentrations in the Vertosol soil amended with anaerobic biosolids in Experiment 2 where concentration peaked on day 28 and decreased sharply until day 40. Then, it increased until the end of the incubation period [Figure 1(b)]. The pattern in the Vertosol control treatment differed somewhat with a slow and early increase in NO_3-N concentration that accelerated during the middle of the incubation period but declined slightly from day 40 to day 98. Although not significant, NO_3-N concentration in the Vertosol mixed with polymer-added biosolid (i.e., 85–130 mg NO_3-N kg^{-1}) was consistently lower than in the same soil mixed with polymer-free biosolids (i.e., 98–147 mg NO_3-N kg^{-1}) from day 28 until the end of the study.

In the Red Ferrosol soil this trend for consistently lower NO_3-N concentrations in soil mixed with polymer-added biosolids (i.e., 150–180 mg NO_3-N kg^{-1} soil) compared to that in soil mixed with polymer-free biosolids (i.e., 180–210 mg NO_3-N kg^{-1} soil) was also observed, particularly after day 40. However, trends differed between the two soil types in earlier periods where there was no peak concentration at day 28 for either polymer treatment as found in the Vertosol soil

Table 2. Chemical Properties of Biosolids used in the Experiments.

Biosolid Description	pH 1:5 H_2O	EC mS cm^{-1}	Total Solids	C_{total}	TKN	P_{total}	K_{total}	S_{total}	NH_4-N	NO_3-N	C:N ratio
			%						mg kg^{-1} dry matter		
Experiment 1											
Aerobic (polymer added)	6.5	199	12	33.5	6	4.3	1	0.8	5600	10	5.6
Anaerobic A (polymer added)	7.6	681	18.7	33	6.5	3.5	0.3	1.4	12200	20	5.1
Experiment 2											
Anaerobic B (polymer added)	8.1	431	12.2	36.7	6.2	1.5	0.2	1.5	5300	15	6
Anaerobic B (no added polymer)	8.1	431	11.8	36.7	5.9	1.5	0.2	1.5	2500	15	6.2



(a)

(b)

Figure 1. Temporal changes in soil NO_3-N concentration during incubation at 30°C for (a) Black Vertosol soil amended with anaerobic or aerobic biosolids in experiment 1 and (b) Black Vertosol and Red Ferrosol soils amended with anaerobic biosolids in experiment 2. Values are the means of two replications, except for data collected at the end of the incubation period when there are four and three replications for experiments 1 and 2, respectively. Different soil types are designated as CP (heavy black Vertosol) and Kry (Red Ferrosol).

but a consistent increase in NO_3-N concentration over the whole incubation period. At the end of the incubation period, significantly higher NO_3-N concentrations were found in the biosolid-amended Ferrosol soil (i.e., 184–210 mg NO_3-N kg^{-1}) versus the biosolid-amended Vertosol (i.e., 130–147 mg NO_3-N kg^{-1}), irrespective of polymer treatment.

Ammonia Volatilisation

Ammonia volatilisation was low during the 72 day monitoring period in Experiment 1, accounting for <4% of applied NH_4-N (see Figure 2), with most of the NH_3 volatilised during the first few days. Subsequent wetting and drying cycles had little effect on cumulative NH_3 volatilisation. Soil amended with anaerobically digested biosolids lost more N through NH_3 volatilisation in absolute terms than soil amended with biosolids produced under aerobic conditions. Addition of acetylene gas led to a slight but significant increase in NH_3 volatilisation. Volatilisation losses of NH_3 were not measured in Experiment 2 as the results from Experiment 1 displayed N loss by this pathway was small.

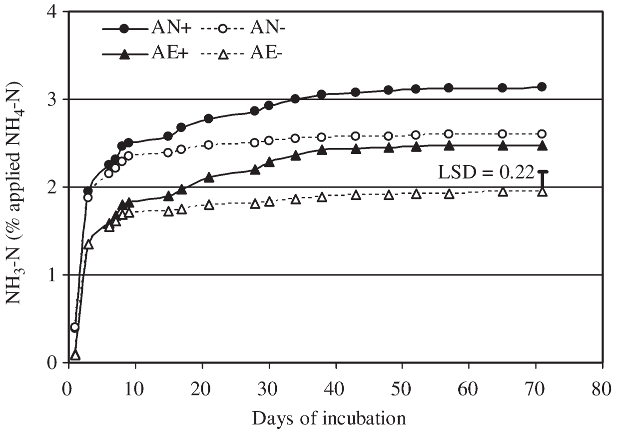


Figure 2. Cumulative N loss via ammonia volatilisation during a 72-day incubation at 30°C, from a Black Vertosol soil amended with anaerobic or aerobic biosolids in the presence or absence of acetylene gas during the measurement period. AN+ and AN- indicate anaerobic biosolids with and without acetylene, while AE+ and AE- indicate similar treatments with aerobic biosolids.

Denitrification

Significant amounts of the applied biosolids' N were lost through denitrification during Experiment 1 (see Figure 3) with percentage N loss higher from soil amended with aerobically digested biosolids (~30%) than from soil amended with anaerobically digested biosolids (24%). This was despite the fact the absolute amount of N lost was higher from soil mixed with anaerobically digested biosolids (0.26g N $cylinder^{-1}$) versus those mixed with aerobically digested biosolids (0.20g N $cylinder^{-1}$) which reflected total amounts of biosolids' N added.

There were big differences in N_2O gas emissions between treatments in which acetylene gas was either added (i.e., 24–29% total added N denitrified) or omitted (i.e., ~2% total added N denitrified) during measurement periods (See Figure 3) in Experiment 1. Based on the difference between N_2O gas emitted from treatments with and without acetylene, it could be concluded that the predominant form of denitrified N was as N_2 (>90%) rather than N_2O (<10%). There was no difference in ratios of N_2O/N_2 generated from the Vertosol soil amended with two types of biosolids.

Cumulative denitrification losses during Experiment

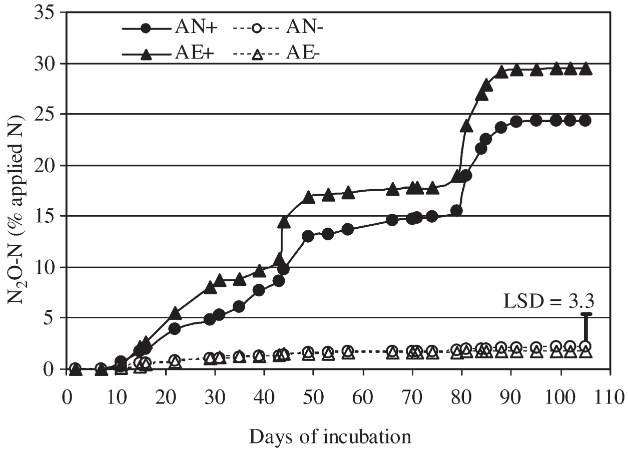
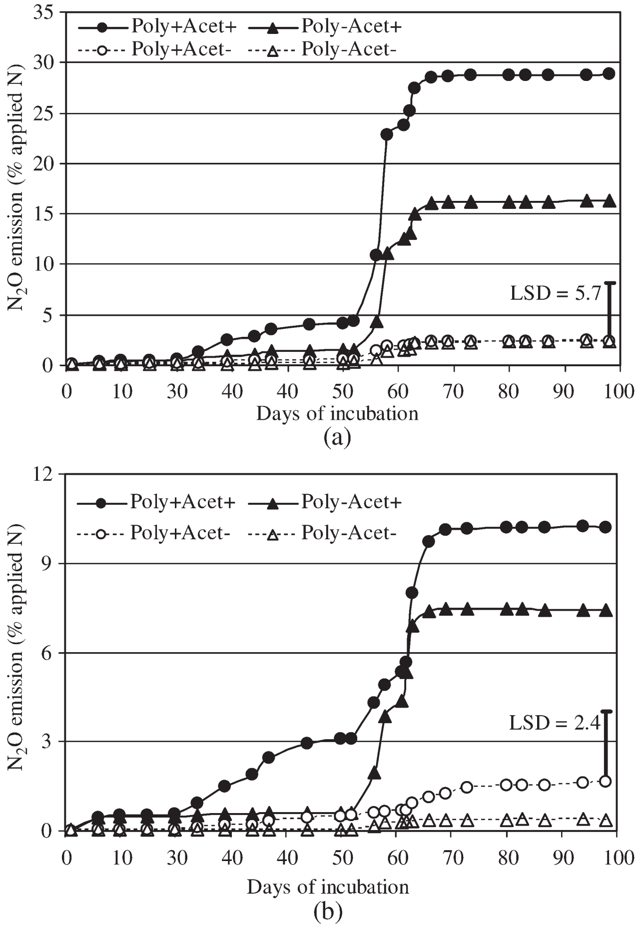


Figure 3. Cumulative N_2O emissions during a 105-day incubation period at 30°C from a Black Vertosol soil amended with anaerobic and aerobic biosolids in the presence or absence of acetylene gas during the measurement period. AN+ and AN- indicate anaerobic biosolids with and without acetylene, while AE+ and AE- indicate similar treatments with aerobic biosolids.



(a)

(b)

Figure 4. *Cumulative N_2O emissions during a 98-day incubation period at 30ºC from (a) Black Vertosol soil amended with anaerobic biosolids with and without added polymer and in the presence or absence of acetylene gas and (b) Red Ferrosol soil amended with anaerobic biosolids with and without added polymer and in the presence or absence of acetylene gas. Poly+ or Poly- indicate presence or absence of polymer in the aerobically digested biosolid. Acet+ or Acet- indicate presence or absence of acetylene during the measurement period.*

1 accrued by way of a series of stepwise increases that corresponded to various wetting events during incubation indicating the key role played by soil water content on denitrification activity (see Figure 3). The first significant denitrification activity started 14 days after the incubation period started when soil water content was raised to 75% of FC. Significant increases in denitrification losses were subsequently observed when soil/biosolids' mixtures were rewetted on day 42 at 100% FC and on day 77 at 150% FC.

Patterns of denitrification activity were similar for both the heavy Vertosol and the lighter Red Ferrosol [see Figure 4(a) and 4(b), respectively] in Experiment 2. Losses were low in the first 3 weeks and then started increasing from day 24 and following the increase of soil moisture content to FC. However, by far the greatest increase in denitrification activity occurred on day 52 and just a few days after moisture content of the cores was increased to 150% FC. Subsequent activity was minimal as soil cores were allowed to dry.

Interestingly, proportional N losses from denitrification recorded in the Vertosol soil amended with polymer-added biosolids in both Experiments 1 and 2 were similar ranging from 24–30% of applied N irrespective of biosolids type. Cumulative N loss was much lower at 16% of applied biosolids' N for the Vertosol soil in which anaerobic biosolids without polymer were added [see Figure 4(a)]. N lost through denitrification was much lower in the lighter Red Ferrosol compared to the Vertosol for both the polymer-added and polymer-free treatments [see Figure 4(b)]. While presence of polymer in biosolids added to the Red Ferrosol had a much smaller impact on denitrification losses than in the Vertosol soil, loss of 10% of applied biosolids' N denitrified in the presence of a polymer compared to 7% biosolids' N denitrified in the absence of polymer was still significant. Consistent with findings from Experiment 1, comparisons of losses with and without added acetylene suggested the dominant denitrification product in both soil types was N_2 gas representing 85 to 95% of total N lost via this process.

N Loss Determined by Mass Balance

34–45% of applied biosolids' N was unaccounted for in experiment 1. See Table 3. Gas measurements suggest most of this loss was probably via denitrification activity as NH_3 volatilisation accounted for <4%

Table 3. Fate of Applied N at 105 Days for Experiment 1 or at 98 days for Experiment 2 After Amending Soils with Biosolids and Incubating them at 30°C. Data represent the Means of 4 Replicates for Experiment 1 or 3 Replicates for Experiment 2, Respectively.

	Applied N		Net Recovered N				Lost N
	N_{total}	$N_{mineral}$	N_{total}	$N_{mineral}$	$N_{organic}$	N_{total}	
	mg N		mg N			% Applied N	% Applied N
Experiment 1							
Anaerobic Acetylene+	1057	200	603	89	514	57.1	42.9
Aerobic Acetylene+	684	64	450	55	395	65.8	34.2
Anaerobic Acetylene–	1057	200	580	59	521	54.9	45.1
Aerobic Acetylene–	684	64	409	41	368	59.8	40.2
Lsd ($P < 0.05$)	ND	ND	111	35	114	12.1	12.1
Experiment 2							
Black Vertolsol							
Polymer+ Acetylene+	485	42	311	58	253	64.0	36.0
Polymer– Acetylene+	473	21	337	39	298	71.3	28.7
Polymer+ Acetylene–	485	42	290	31	260	59.8	40.2
Polymer– Acetylene–	473	21	314	36	278	66.4	33.6
Red Ferrosol							
Polymer+ Acetylene+	485	42	388	187	201	80.0	20.0
Polymer– Acetylene+	473	21	400	102	298	84.6	15.4
Polymer+ Acetylene–	485	42	369	171	198	76.0	24.0
Polymer– Acetylene–	473	21	405	130	275	85.7	14.3
Lsd ($P < 0.05$)	ND	ND	64	24	65	13.4	13.4

of applied NH_4-N or <1% of total applied biosolids' N. In treatments receiving aerobic biosolids applications, N loss measured by mass balance method (i.e., 34% of applied N) was similar to combined gaseous emissions at 29% of applied N. See Figure 3. However, for the treatment receiving anaerobic biosolids' N loss measured by gas emissions at 24% of applied N was much lower than that measured by mass balance at 43% of applied N. See Figure 3.

Mass balances of applied N from Experiment 2 indicated that 29–36% of Black Vertosol and 15–20% of Red Ferrosol of the applied biosolids' N could not be accounted for from cylinders with added acetylene at the end of the incubation period. Although NH_3 volatilisation measurements were not carried out in this experiment, relative unimportance of this loss pathway in Experiment 1 suggests apparent N loss was most likely due to denitrification. Apparent N loss was similar in cylinders with 15–36% of applied N or without 14–40% of applied N added acetylene for both soil types. However, presence of polymer in the biosolids increased denitrification losses from 14–33% of applied N to 20–40% of applied N for both soil types. Apparent N loss from cylinders with added acetylene determined by mass balance method at 15–36% was notably higher than that measured by the gas emissions at 7–29% which was consistent with observations during Experiment 1.

DISCUSSION

While biosolids contain significant amounts of potentially available nutrients like N, these experiments also provide clear evidence that appropriate management strategies will be needed to ensure biosolids' N is retained in soil for crop/pasture use rather than lost to the atmosphere. Apparent N losses due to NH_3 volatilisation represented only a very small proportion of both total applied N and biosolids' N that could not be accounted for at the end of the incubation period (see Figure 2). While quantities of N volatilised were greater in anaerobically digested biosolids, this was not unexpected due to greater rate of total N addition (see Table 3) and that approximately 20% of total N added was already in the form of NH_4-N (see Table 2).

Low NH_3 volatilisation losses observed in Experiment 1 in which biosolids were incorporated into soil were consistent with other incubation studies which displayed much reduced losses after biosolids were incorporated into soil rather than applied by surface. This finding provides a strong incentive to retain the current licensing requirement to incorporate land-applied biosolids within 36 hours of application (NSWEPA, 1997). If these requirements are adhered to then NH_3 volatilisation might not be an important pathway for gaseous N losses from biosolids-amended soils.

In contrast to volatilisation, biosolids' N loss due to denitrification could represent significant proportions of total N applied. Treatment impacts on denitrification losses in these two experiments indicated that denitrification rates were regulated by two key factors. These two key factors were concentration of NO_3-N controlled by mineralisation activity and air-filled porosity. Soil water status can be used as a surrogate for the latter factor. While addition of sucrose was still able to accelerate denitrification activity (see Table 4), availability of a C substrate to sustain microbial activity was unlikely to be a limitation as biosolids contained approximately 35% organic C with low C:N ratios (5–6). See Table 2.

In Experiment 1 (see Figure 3), the very low level of gaseous N emissions during the early stage of incubation could be attributed to low initial NO_3-N concentration as little nitrate was found in either the soil or biosolids before incubation (see Tables 1 and 2). Mineralisation activity seemed to have started quickly once biosolids were applied under the warm and moist conditions of incubation as the NO_3-N concentration quickly rose to > 100 mg kg^{-1} 14 days after commencement for both anaerobic and aerobic biosolids [see Figure 1(a)]. The first big flush of denitrification came with the combined effects of accumulated NO_3-N and elevated soil moisture content at 100% FC on day 14 in biosolids treated soils. It is likely that denitrification activity may have occurred mainly in or near applied biosolids lumps. Here required anaerobic conditions for denitrifying bacteria could be satisfied where the highest concentrations of mineralised NO_3-N were likely to be located and there would have been plentiful supplies of labile C. Decreases in soil NO_3-N concentrations from day 14 to 28 (see Figure 1) were consistent with increased denitrification losses during the same period (see Figure 3). Although concentrations of NO_3-N increased between days 28 and 72, there were rapid increases in denitrification losses with increased soil moisture on day 42 at 100% FC and on day 80 at 150% FC. These flushes of denitrification therefore corresponded to periods of low air-filled porosity but could not be discerned in the net nitrification trend evident over the same time period.

Findings from our incubation experiments support denitrification as an important pathway for N losses when biosolids are applied to land under warm and moist conditions. Rate of mineralisation of biosolids' N and in particular rate of nitrification both are likely to play a key role in regulating potential denitrification losses in biosolids-amended soils.

In both experiments impact of acetylene addition for increasing detection of denitrification losses was illustrated with denitrification almost undetectable unless acetylene gas was added to inhibit conversion of N_2O to N_2. This large impact of acetylene allowed us to conclude N_2 gas was a major product of denitrification activity as the N_2O generated in the absence of acetylene accounted for less than 10% of total emitted N gases (i.e., N_2 and N_2O). Weier et al. (1993) reported that high soil water content (i.e., low air-filled porosity) and high NO_3-N concentrations in soil favoured N_2 generation from the denitrification process while Mathieu et al. (2006) found large stores of labile organic C in soil were also conducive to N_2 generation. Pu et al. (1999) found that N_2 was the dominant product from denitrification activity at 99% after applying enriched NO_3-15N to a similar Black Vertosol soil in Queensland under waterlogged conditions.

Estimations of N loss by the mass balance method (see Table 3) suggested that while addition of acetylene gas had greatly increased detection of denitrification losses, this method was still not able to detect all gaseous N losses (i.e., presumably additional denitrification) that occurred in these studies. Results from Experiment 1 demonstrated total N losses averaged 44% of applied N for treatments receiving anaerobically digested biosolids and 36% of applied N for treatments receiving aerobically digested biosolids. These losses compared to total measured gaseous losses (i.e., volatilisation of NH_3 plus denitrification of N_2O) that are equivalent to 25% (anaerobic) and 31% (aerobic) of applied biosolids' N, respectively. Smaller N loss estimated by the acetylene inhibition method have previously been attributed to incomplete inhibition of conversion from N_2O to N_2 (Watts and Seitzinger, 2000) and entrapment of N_2O in the soil profile (Weier et al., 1993; Mahmood et al., 1999).

Effects of polymer addition during biosolids' dewatering process on the gaseous N emissions were apparent in both the heavy Vertosol and the strongly structured Red Ferrosol with more applied biosolids' N lost from soils treated with the biosolids-polymer combination (see Figure4). This response could be largely attributed to increased moisture holding capacity, moisture retention, and lumpiness of the biosolids-polymer mix. The amount of biosolids' N lost (see Figure 4 and Table 3) combined with net residual mineral N in the soil are a reflection of N mineralised from organic sources in the biosolids. It may also be possible that the net mineralisation rate was higher in soils amended with the biosolids-polymer mix—perhaps by maintaining adequate moisture around biosolids lumps for longer time periods during the dry down process. This would cause more rapid increases in NO_3-N concentrations in the soils amended with the polymer-biosolids mix increasing the risk of denitrification. This issue requires further investigation.

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Effects of Sewage Sludge, Animal Manure, Compost and Cadmium Chloride on Cadmium Accumulation in Corn and Alfalfa

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ABSTRACT: The objective of this study was to investigate cadmium (Cd) availability to alfalfa and corn in a soil amended with organic and inorganic Cd sources. A greenhouse experiment with completely randomized design performed with four treatments and three replicates. Soil was treated with 25 t ha^{-1} sewage sludge, compost and cow manure including three rates of Cd (initial level, 5 and 10 mg kg^{-1}). An inorganic Cd source was also applied at two rates of 5 and 10 mg Cd kg^{-1} in the form of $CdCl_2$ salt. Results displayed that plants grown in soil treated with $CdCl_2$ salt accumulated significantly greater Cd in their tissues compared to those grown in soil treated with organic amendments. Amount of Cd translocated to the shoots of plants in the $CdCl_2$ treatment was greater compared with those in organic residuals treatments. Results from this experiment point to the fact that the Cd source, loading rate and plant species are important factors in evaluation of Cd phytoavailability.

1. INTRODUCTION

CADMIUM (Cd) is of great concern in environment, because of its toxicity to animals and humans. Cadmium is a cumulative toxin and known carcinogen [39]. Although, plants do not require Cd for growth, the bioaccumulation index of Cd in plants exceeds that of most other trace elements [18]. Many plants can accumulate relatively high levels of Cd without phytotoxicity or yield reduction but in more cases it can reach the food chain [14]. The entry of Cd into the food chain is of particular concern as it can cause chronic health problems in humans such as bone disease, lung edema, renal dysfunction, liver damage, anemia, hypertension [30, 17]. In addition, the balance of other elements such as phosphorus (P) and calcium (Ca) in the body is also disturbed by high intake of Cd [16].

It is therefore important to control Cd concentration in plants, especially in the edible parts of crops to ensure food safety. In order to limit the accumulation of Cd in crops, a good understanding of the transfer characteristics of Cd from soils to crops is required.

There are many factors that control accumulation and availability to plants of Cd in agricultural soils such as Cd source, Cd loading rate, soil pH, soil cation change capacity, chloride concentration in soil solution, and soil organic matter content. These are important factors that should be considered in the evaluation of Cd phytoavailability [23].

Many types of organic residual materials (e.g. sewage sludge, animal manure, and municipal solid waste compost) with a wide range of properties have been applied to agricultural land. Since residuals contain plant nutrients and organic matter (OM), it may be used to supplement or replace commercial fertilizers for crop production [31]. However, residuals also contain heavy metals such as Cd, which can have adverse effects on humans when entering the food chain in elevated amounts [28].

The phytoavailability of Cd can vary with the source of Cd applied. The phytoavailability for inorganic Cd (e.g. Cd salt, Cd in phosphate fertilizer) is generally higher compared with biosolid-derived Cd [10, 35]. Residuals typically contain significant amounts of sorbents (OM; Fe, Mn, Al oxides; and anions) that can adsorb or precipitate trace elements and reduce trace element solubility and phytoavailability [31]. Some suggest trace elements are sequestered in biosolids mainly by chelation with OM [26], whereas others point out the importance of the inorganic surfaces in biosolids on sequestering trace elements [15].

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However, organic amendments also can add soluble organic ligands which may increase the mobility of metals. Lamy et al. (1993) showed that adding sewage sludge raised soil OM and increased Cd in the drainage water. The enhanced mobility of Cd was attributed to the role of soluble organic ligands in decreasing Cd adsorption on soil surfaces [21]. In soils treated with biosolids, trace elements are initially bound by OM and released from their bound or chelated state as OM mineralizes [2].

Reusing organic residuals is a good way of returning organic matter and some nutrients into the soil, particularly in arid and semi-arid regions. However, the possibility of accumulation of heavy metals such as Cd in soil and contamination of human and animal food chains should be determined before using the organic wastes.

The objective of the present study was to investigate Cd availability to alfalfa and corn in a calcareous soil amended with organic (sewage sludge, cow manure, compost) and inorganic ($CdCl_2$) Cd sources.

2. MATERIALS AND METHODS

2.1. Experimental Design

This pot experiment was conducted at Isfahan University of Technology research greenhouses using a Fine loamy, mixed, thermic, Typic Haplargids soil. Selected chemical and physical properties of the soil used are shown in Table 1. The organic amendments used in this experiment were sewage sludge of Isfahan Polyacryl Industry, municipal waste compost from Isfahan city, and animal manure. Cow manure was produced in a local farm and aged for two years before the experiment. The sewage sludge is a secondary digested sludge from Polyacryl Company that is the largest fiber manufacturer in Iran. The sewage sludge contains high concentrations of plant nutrients and organic matter and thus, can be used on farmland as fertilizers. Selected chemical properties of the organic amendments are given in Table 2. The concentrations of heavy metals in the organic amendments were lower than the standards suggested by the US Environmental Protection Agency [38].

Table 1. Soil Chemical Characteristics.

Characteristic	Unit	Amount
pH	—	8.5
Electrical Conductivity (EC)	dS m^{-1}	2.7
Orgainic Matter (OM)	%	1.4
Cation Exchangeable Capacity (CEC)	$cmol^+ kg^{-1}$ soil	14.8
DTPA-Extractable Cd	mg kg^{-1}	0.03
HNO_3-Extractable Cd	mg kg^{-1}	0.80

The soils were amended with 25 t ha^{-1} sewage sludge, compost, and cow manure at three rates of Cd (initial level, 5, and 10 mg kg^{-1}). Initial level of Cd in sewage sludge, compost, and cow manure was 1.5, 3, and 2 mg kg^{-1}, respectively (Table 2). The amount of Cd in cow manure, sludge and compost were increased to 5 or 10 mg kg^{-1} by adding Cd in the form of $CdCl_2$. An untreated soil was also used as control treatment. Three kg of dried soils were transferred to plastic pots (24 cm in diameter by 28 cm depth). Soils were incubated in greenhouse for 15 days. Soil water was kept at the field capacity. Then, seeds of corn (*Zea mays* L.) and alfalfa (*Medicago sativa* L.) were sown with four seedlings kept in each pot. During the plant growth, pots were irrigated with tap water to about 70% of water holding capacity. Plants were harvested after 60 days and shoots and roots were separated, then washed with tap water and rinsed with de-ionized water. The plants were oven-dried at 65°C to a constant weight, and the dry weight was recorded. The dry plants were ground with a stainless steel miller and prepared for further analyses.

Table 2. Applied Organic Residuals' Properties.

Characteristic	Unit	Sewage Sludge	Compost	Manure	U.S. EPA Regulations
pH	—	7.3	7.5	7.7	—
Electrical Conductivity (EC)	dS m^{-1}	19.3	15.8	19.8	—
Orgainic Matter (OM)	%	28.26	48.54	18.8	—
N	%	7.44	1.78	0.94	—
Mn	mg kg^{-1}	1024	900	1150	—
Fe	mg kg^{-1}	9125	5875	12175	—
Zn	mg kg^{-1}	388	381	193	2800
Cu	mg kg^{-1}	74	235	69	1500
Ni	mg kg^{-1}	3.3	22.6	35.9	420
Cd	mg kg^{-1}	1.5	3.0	2.0	39
Cr	mg kg^{-1}	49.4	109.0	40.7	3000
Co	mg kg^{-1}	5.0	3.1	5.8	—

2.2. Analysis

2.2.1. Plant Analysis

Roots and shoots were digested with a mixture of concentrated HCl, 70% HNO_3 and 30% H_2O_2 on a hot plate. One gram of oven-dried plant samples was put into the 200 ml Erlenmeyer, followed by the addition of 10 ml 1:1 (v/v) nitric acid. The Erlenmeyers were heated to 90°C on the hot plate for 15 min. After cooling, 5 ml 70% nitric acid was added and the mixture was heated to 90°C for 30 min. After cooling, 2 ml redistilled water and 6 ml 30% H_2O_2 were added to the mixture and the mixture was heated to 90°C. At the end, 5 ml concentrated HCl and 2 ml redistilled water were added to the mixture. After heating the mixture to 90°C for 15 min, it was filtered through Whatman no. 42 filter paper and diluted with redistilled water into 50 ml. Cadmium concentration in the digested solution was measured using AAS (PerkinElmer 3400, PerkinElmer, Wellesley, MA) [6].

2.2.2. Soil Analysis

After plant harvest, a soil sample was collected from each pot, air dried and sieved (2 mm). Soil samples were analyzed for pH and electrical conductivity (EC) in soil saturation extracts [27]. Organic carbon (OC) was measured by the Walkley-Black method [6]. Soil cation exchange capacity (CEC) was determined by 1 M sodium acetate [32]. Total Cd concentration in soil was extracted using HNO_3. One gram of dry soil samples was put into an Erlenmeyer and 20 ml of 5 N HNO_3 was added. After 12 h, the mixture was heated on a hot plate to 100°C for 10 min. After cooling, 10 ml redistilled water was added to the mixture. Then, the mixture was filtered through Whatman no.42 filter paper and diluted with redistilled water into 25 ml. [37]. The avaiable Cd was extracted using 0.005 M DTPA, 0.1 TEA, and 0.01 M $CaCl_2$, adjusted to pH 7.3 [24]. The soil extracts were analyzed for Cd by AAS with deuterium background correction.

The accuracy of Cd analysis in soil and plant samples was controlled by analyzing certified standards of National Institute of Standards and Technology (NIST) and including blanks in digestion batches. Recovery of Cd was greater than 90% for soil (San Joaquin #2709) and apple leaf standards (#1573A).

2.2.3. Sludge, Compost, and Manure Analysis

Sludge, compost, and manure were air-dried, ground by a steel mill, and analyzed for pH and EC in saturation extracts [28]. Organic carbon and total nitrogen were measured by the Walkley-Black and the Kjeldahl methods, respectively. Total concentrations of Cd, Ni, Cr, Co, Cu, Zn, Fe, and Mn were extracted by using mixture of concentrated HCl, 70% HNO_3 and 30% H_2O_2 on a hot plate and analyzed by AAS [6].

2.3. Translocation Factor (TF)

The TF is defined as the ratio of shoot Cd content to total amount of Cd absorbed by plant and is calculated using the following equation [29]:

TF = Cd content in shoot/Cd content in whole plant

2.4. Bioconcentration Factors (BCF)

The BCF is generally defined as the ratio of metal concentration in plant to the total metal concentration in soil [1] and is calculated using the following equation:

BCF = Cd concentration in shoot/Cd concentration in soil

2.5. Statistical Analysis

This pot experiment was conducted in a completely randomized design with four treatments and three replicates. All data were evaluated by analysis of variance (ANVA) and the means were separation by the least significant difference (LSD) procedures at the 0.05 level of significance [34].

3. RESULTS AND DISCUSSION

3.1. Effect of Organic and Inorganic Cd Sources on Soil Properties

Selected soil chemical properties as affected by organic residuals and $CdCl_2$ application are shown in Table 3. A small decrease in soil pH was observed by sewage sludge application while the effect of compost and cow manure on the soil pH was not significant. This is probably due to higher amounts of organic and inorganic acids in the sludge compared with the compost and manure [7]. Soil EC increased with organic residuals application (Table 3). Increased soil EC in organic amended soils is due to the high level of soluble salts in the organic residuals (Table 2). Increased soil EC may result in some detrimental effects on plant and microorganisms. Adding organic amendments to

Table 3. Influence of Various Cd Sources and Loading Rates on Soil Properties.

Treatment	Cd Concentration (mg kg^{-1})	pH	EC (dS m^{-1})	CEC (cmol^{+} kg^{-1})	OM (%)
Untreated Soil	—	8.0^{abc*} ± 0.30	2.8^{fg} ± 0.55	14.1^{e} ± 0.17	1.5^{d} ± 0.13
Soil treated with CdCl$_2$	5	8.0^{abc} ± 0.05	2.2^{g} ± 0.44	14.1^{e} ± 0.69	1.7^{c} ± 0.07
	10	7.9^{cd} ± 0.02	4.2^{c} ± 0.37	14.8^{cde} ± 0.25	1.4^{d} ± 0.07
Soil treated with sewage sludge	Initial level	7.8^{d} ± 0.10	4.0^{cd} ± 0.51	16.0^{a} ± 0.60	1.9^{ab} ± 0.08
	5	7.9^{cd} ± 0.02	4.2^{c} ± 0.45	15.9^{ab} ± 0.60	1.8^{bc} ± 0.15
	10	7.8^{d} ± 0.04	4.4^{c} ± 0.08	15.4^{abc} ± 0.40	2.0^{a} ± 0.05
Soil treated with compost	Initial level	8.1^{ab} ± 0.17	3.1^{ef} ± 0.45	14.6^{cde} ± 0.51	2.0^{a} ± 0.08
	5	8.0^{abc} ± 0.02	3.5^{de} ± 0.49	15.1^{bcd} ± 0.36	2.0^{a} ± 0.13
	10	8.0^{abc} ± 0.04	3.8^{cd} ± 0.28	15.0^{bcd} ± 0.26	1.9^{ab} ± 0.05
Soil treated with manure	Initial level	8.2^{a} ± 0.05	3.0^{ef} ± 0.35	16.1^{a} ± 0.79	1.9^{ab} ± 0.08
	5	8.0^{abc} ± 0.08	5.0^{b} ± 4.0	15.4^{abc} ± 0.60	1.8^{bc} ± 0.06
	10	7.8^{d} ± 0.02	6.7^{a} ± 0.26	15.6^{ab} ± 1.00	1.7^{c} ± 0.20

*Means in any column followed by the same letter do not differ significantly ($P < 0.05$, LSD test).

the soil caused a significant increase in the cationic exchangeable capacity (CEC) of the soil (Table 3). The sludge, compost, and cow manure contained large amounts of OM and thus, their application to the soil increased soil OM. Increased CEC in soils treated with organic residuals could probably limit the solubility of heavy metals [20].

3.2. Effect of Organic and Inorganic Cd Sources on the Soil DTPA-Extractable Cd

Application of organic and inorganic Cd sources proportional to the application rate of Cd increased the DTPA-extractable Cd (Figure 1). Soils treated with $CdCl_2$ salt had greater concentrations of DTPA-extractable Cd compared to the soils treated with organic residuals. It is widely accepted that the bioavailability and toxicity of metal salts in soil is usually greater than for metals present in sludge-amended soil due to the complexation mechanisms operating within the sludge matrix [5]. The organic residuals generally contain different compounds such as organic materials, and Fe, Mn, and Al oxides which adsorb heavy metals and could reduce the solubility of metals in the polluted soils and thus prevent their uptake by the plants [4].

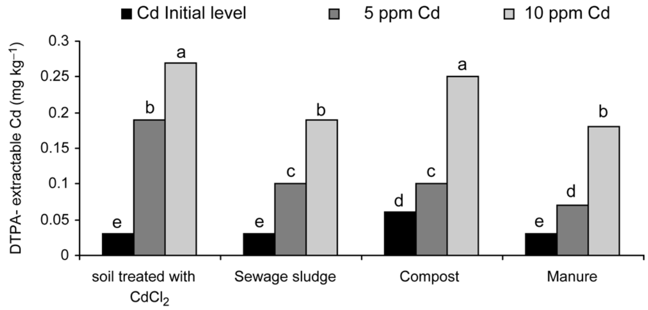

Figure 1. *Influence of various Cd sources and loading rates on soil DTPA-extractable Cd concentration. The same letters on columns are not significantly different from each other ($P < 0.05$, LSD test).*

3.3. Effect of Organic and Inorganic Cd Sources on Crop Yield

Application of organic residues without Cd enrichment significantly increased the shoot and root dry weight of corn and alfalfa while addition of Cd-enriched organic residues to the soil significantly reduced the crop yield (Table 4). In general, increasing the Cd level of the soil from the initial level to the 10 mg Cd kg^{-1} resulted in reduction of dry matter yield of both crops although this reduction was greater in corn in comparison with alfalfa.

The corn plants in the manure-treated soil produced the highest shoot dry matter weight (Table 4). The shoot dry matter yield of corn in the manure treatment at the initial level of Cd was 39% greater than that in the control treatment. In contrast, shoot dry matter yield of alfalfa in the sewage sludge treatment was higher than that in other treatments. Increase in yield with application of organic residuals is due to the beneficial effects of these amendments on soil physical, chemical, and biological properties [25].

In general, the root and shoot biomass production regardless of the crop species, significantly decreased as the level of Cd in soil increased to the 10 mg Cd kg^{-1} level (Table 4). This is probably because of Cd toxicity effects on plant growth [39, 12]. Cadmium causes alteration in various physiological processes such as growth retardation and inhibition of enzymes activities [12]. Photosynthesis is also sensitive to Cd, chlorophyll being one of the targets [36], as well as

Table 4. Influence of Various Cd Sources and Loading Rates on Dry Matter in Corn and Alfalfa.

Treatment	**Cd Concentration (mg kg^{-1})**	**Corn**		**Alfalfa**	
		Shoot	**Root**	**Shoot**	**Root**
Untreated Soil	—	3.20^{def*} ± 0.42	0.68^{cde} ± 0.55	1.31^{bc} ± 0.20	0.61^{cdef} ± 0.08
Soil treated with $CdCl_2$	5	2.96^{ef} ± 0.56	0.60^{de} ± 0.05	1.47^{bc} ± 0.23	0.55^{def} ± 0.05
	10	2.97^{ef} ± 0.24	0.57^{e} ± 0.02	1.31^{bc} ± 0.56	0.53^{ef} ± 0.03
Soil treated with sewage sludge	Initial level	4.02^{abc} ± 0.27	0.86^{ab} ± 0.13	2.11^{a} ± 0.56	0.70^{ab} ± 0.04
	5	3.60^{bcde} ± 0.13	0.64^{cde} ± 0.06	1.40^{bc} ± 0.10	0.60^{cde} ± 0.02
	10	2.66^{f} ± 0.53	0.60^{de} ± 0.05	1.03^{c} ± 0.08	0.50^{f} ± 0.04
Soil treated with compost	Initial level	3.42^{cde} ± 0.19	0.76^{bc} ± 0.09	1.72^{ab} ± 0.24	0.63^{bc} ± 0.06
	5	3.65^{bcd} ± 0.45	0.72^{bcd} ± 0.07	1.21^{bc} ± 0.13	0.61^{cde} ± 0.03
	10	3.10^{def} ± 0.30	0.64^{cde} ± 0.09	1.18^{c} ± 0.39	0.62^{bcd} ± 0.06
Soil treated with manure	Initial level	4.46^{a} ± 0.05	0.90^{a} ± 0.15	1.43^{bc} ± 0.40	0.75^{a} ± 0.07
	5	4.37^{a} ± 0.50	0.71^{cde} ± 0.05	1.35^{bc} ± 0.22	0.65^{bc} ± 0.04
	10	4.18^{ab} ± 0.48	0.65^{cde} ± 0.65	1.20^{bc} ± 0.3	0.64^{bc} ± 0.04

*Means in any column followed by the same letter do not differ significantly ($P < 0.05$, LSD test).

the enzyme involved in CO_2 fixation [12]. Cadmium also alters the water relation in plants [3] and induces metabolic dysfunctions such as production of reactive oxygen species [12], and photosynthesis [36].

3.4. Concentrations of Cd in Plant Tissues

Regardless of crop species, Cd concentrations in shoots and roots of the plants increased with increasing Cd application rate (Table 5). Application of organic residuals enriched to 5 and 10 mg Cd kg^{-1} significantly increased the tissue Cd concentration as compared with the control. Cadmium concentration in plants grown at the sludge and compost treatments were significantly greater than those grown in the manure.

Tissues concentrations of Cd in plants grown in organic residual treatments especially in soils amended with cow manure were significantly less than those grown on soils amended with $CdCl_2$, (Table 5). These results suggest that the potential hazard associated with Cd in soils treated with organic residuals is substantially lower than those treated with inorganic Cd salt. Our results are similar to other studies that showed metals applied by inorganic salt are more phytoavailable than the equivalent quantity of metal applied by sewage sludge, flue dust, or fly ash [13, 8].

Regardless of the crop type, at the same Cd loading rate, Cd concentrations in roots were significantly higher than in shoots (Table 5). Cadmium ions are retained in the roots and only small amounts are transported to the shoots [9]. This different pattern in concentration and distribution of Cd in different plant tissues depends on the plant species [40] and may be related in part to Cd tolerance [20, 33]. Accumulation of high levels of Cd in the non-edible parts may limit the metal accumulation in edible portions of the plant [14]. Results of this study

Table 5. Influence of Various Cd Sources and Loading Rates on Cd Concentration in Corn and Alfalfa Tissues.

Treatment	**Cd Concentration (mg kg^{-1})**	**Corn**		**Alfalfa**	
		Shoot	**Root**	**Shoot**	**Root**
Untreated Soil	—	0.35^{f*} ± 0.04	0.50^{f} ± 0.00	0.16^{g} ± 0.14	0.61^{e} ± 0.19
Soil treated with $CdCl_2$	5	1.40^{cd} ± 0.12	2.20^{b} ± 0.42	0.71^{cde} ± 0.14	2.43^{b} ± 0.37
	10	3.04^{a} ± 0.23	2.95^{a} ± 0.75	2.24^{a} ± 0.33	3.71^{a} ± 0.46
Soil treated with sewage sludge	Initial level	0.42^{f} ± 0.04	1.10^{e} ± 0.05	0.25^{fg} ± 0.01	0.97^{cde} ± 0.06
	5	1.27^{d} ± 0.02	1.72^{bcd} ± 0.34	0.71^{de} ± 0.05	2.23^{b} ± 0.34
	10	2.54^{b} ± 0.25	2.97^{a} ± 0.11	1.41^{b} ± 0.38	2.55^{b} ± 0.18
Soil treated with compost	Initial level	0.40^{f} ± 0.02	1.35^{de} ± 0.34	0.25^{fg} ± 0.15	0.84^{de} ± 0.06
	5	1.15^{d} ± 0.13	1.74^{bcd} ± 0.21	0.66^{e} ± 0.14	1.50^{c} ± 0.32
	10	2.86^{a} ± 0.29	3.23^{a} ± 0.12	1.08^{c} ± 0.38	2.60^{b} ± 0.62
Soil treated with manure	Initial level	0.50^{ef} ± 0.04	0.98^{ef} ± 0.41	0.16^{g} ± 0.10	1.07^{cde} ± 0.36
	5	0.75^{e} ± 0.05	1.40^{cde} ± 0.17	0.58^{ef} ± 0.14	1.20^{cd} ± 0.07
	10	1.58^{c} ± 0.24	1.95^{bc} ± 0.26	1.01^{cd} ± 0.22	3.25^{a} ± 0.52

*Means in any column followed by the same letter do not differ significantly ($P < 0.05$, LSD test).

Table 6. Influence of Various Cd Sources and Loading Rates on Translocation (TF) and Bioconcentration Factor (BCF) of Cd.

Treatment	**Cd Concentration (mg kg^{-1})**	**TF**		**BCF**	
		Corn	**Alfalfa**	**Corn**	**Alfalfa**
Untreated Soil	—	0.75^{bc*} ± 0.04	0.33^{bc} ± 0.20	0.44^{a} ± 0.05	0.20^{ab} ± 0.14
Soil treated with $CdCl_2$	5	0.75^{bc} ± 0.08	0.50^{ab} ± 0.02	0.24^{c} ± 0.02	0.15^{abc} ± 0.02
	10	0.84^{a} ± 0.01	0.60^{e} ± 0.12	0.28^{b} ± 0.02	0.22^{a} ± 0.03
Soil treated with sewage sludge	Initial level	0.63^{d} ± 0.02	0.44^{ab} ± 0.05	0.18^{d} ± 0.01	0.11^{cd} ± 0.05
	5	0.79^{abc} ± 0.04	0.43^{ab} ± 0.06	0.22^{cd} ± 0.003	0.11^{cd} ± 0.00
	10	0.78^{abc} ± 0.04	0.53^{ab} ± 0.06	0.23^{c} ± 0.02	0.13^{bc} ± 0.3
Soil treated with compost	Initial level	0.55^{d} ± 0.09	0.37^{abc} ± 0.23	0.10^{e} ± 0.00	0.06^{d} ± 0.04
	5	0.73^{c} ± 0.30	0.47^{bcd} ± 0.03	0.19^{d} ± 0.01	0.11^{cd} ± 0.01
	10	0.80^{abc} ± 0.00	0.45^{ab} ± 0.13	0.26^{b} ± 0.02	0.10^{cd} ± 0.02
Soil treated with manure	Initial level	0.71^{c} ± 0.06	0.20^{c} ± 0.15	0.17^{d} ± 0.01	0.06^{d} ± 0.03
	5	0.75^{bc} ± 0.02	0.50^{ab} ± 0.08	0.12^{e} ± 0.02	0.10^{cd} ± 0.01
	10	0.81^{ab} ± 0.02	0.37^{abc} ± 0.05	0.17^{d} ± 0.01	0.09^{cd} ± 0.01

*Means in any column followed by the same letter do not differ significantly ($P < 0.05$, LSD test).

showed that concentrations of Cd in roots of alfalfa were much higher than those in edible tissues. The ordinary limit of Cd concentration in several plants species ranges from 0.05 to 0.20 mg kg^{-1}, and the range of its toxicity is from 5 to 30 mg kg^{-1}. Therefore, concentration of Cd in shoot and root of corn and alfalfa was less than the toxicity limit of this metal [19].

In general, tissues Cd concentrations were lower in alfalfa than in corn (Table 5). The phytoavailability of heavy metals can also be regulated biologically, for example by the type of plant. Li et al. (2009) in a pot experiment indicated that legumes generally had lower Cd contents especially in the shoots in comparison with non-legumes [22].

3.5. Translocation (TF) and Bioconcentration Factors (BCF) of Cd

Translocation factor is an index for evaluating the transfer potential of a metal to the plant shoot. The percentage of Cd translocated to the shoots of corn and alfalfa is shown in Table 6. The TF ranged from 0.55 to 0.84 for corn and from 0.20 to 0.60 for alfalfa. The highest percentage of Cd translocated to shoots of both crops was observed in the $CdCl_2$ treatment at the level of 10 mg Cd kg^{-1}. In all treatments, TF values increased with increasing Cd application rate. Results indicate that the presence of organic residuals decreased Cd uptake and its translocation to shoots and in turn decreased the toxicity threat of Cd to humans and livestock. The TF values for corn were much higher than those for alfalfa. Variation among plant genotypes in Cd translocation from root to shoot has been reported by other researchers [22].

Bioconcentration factor (BCF) indicates ability of a plant to absorb a metal from soil. The BCF values for corn and alfalfa in $CdCl_2$ treated soils were higher than those in organic residuals treated soils (Table 6). Most of Cd in the presence of organic materials remained in the soil as probably more in unavailable form. Organic matter amendments can considerably decrease bioavailability of Cd in soil by increasing the soil surface area and the number of specific adsorption sites [35], In general, the BCF values increased with increasing Cd content in soil.

In this experiment BCF values were significantly higher for corn shoots than alfalfa shoots in similar treatments (Table 6). For a given metal, the BCF varies greatly with plant species [11].

4. CONCLUSIONS

The result showed that phytoavailability of Cd in soils treated with organic residuals was significantly less than those amended with $CdCl_2$ salt. This result suggests that the potential hazard associated with Cd in soils amended with organic residuals is substantially lower than those treated with inorganic Cd salt. At the same loading rate of Cd, both corn and alfalfa accumulated greater Cd in tissues in the sludge and compost amended soils than in the cow manure-treated soils. Plants grown in soil treated with $CdCl_2$ salt accumulated much greater Cd in their roots and shoots as compared to those grown in soil treated with organic amendments. Results also indicated that the percentage of Cd translocated to the shoots of plants grown in the $CdCl_2$ salt treatment was greater compared with those grown in organic residuals treatments. At the same treatments, both translocation (TF) and bioconcentration factors (BF) of Cd for corn were much higher than those for alfalfa. The results of this experiment point to the fact that the Cd source, loading rate, and plant species are important factors in evaluation of Cd phytoavailability.

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Effects of Biosolids Application on Temporal Variations in Soil Physical and Unsaturated Hydraulic Properties

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ABSTRACT: The objective of this study was to determine the effects of biosolids on temporal variability of physical and hydraulic properties of a calcareous soil. The biosolids was added to the soil at 0, 25, 50 and 100 Mg ha^{-1}. Soil physical properties including aggregate stability, bulk density, saturated hydraulic conductivity, final infiltration rate and available water capacity were determined at 28, 85, 145, 221, 441 and 530 days after the biosolids application. The soil physical properties significantly changed in different sampling dates showing a significant temporal variation following the biosolids application. The unsaturated hydraulic properties were estimated using van Genuchten (1980) and Mualem (1976) equations. Unsaturated hydraulic properties significantly change following biosolids application and sampling dates. The soil moisture characteristic and unsaturated hydraulic conductivity are key parameters in water flow and solute transport modeling processes. Thus, the temporal variations in soil physical and hydraulic properties should be considered in solute transport modeling and studies following biosolids application.

1. INTRODUCTION

PREDICTION of water flow and contaminant transport through the vadose zone requires knowledge of unsaturated soil hydraulic properties and relationship between unsaturated hydraulic conductivity, soil moisture content and pressure head (Schaap et al., 2001; Li et al., 2007). Costs and difficulty in determination of soil hydraulic properties especially in unsaturated conditions by field and laboratory methods makes alternative indirect method desirable. Various models have been proposed for prediction of unsaturated soil hydraulic properties (Burdine, 1953; van Genuchten, 1980. M.T. van Genuchten, A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. Soil Science Society of America Journal 44 (1980).

Soils are heterogeneous and their properties change continuously in space and time (Heuvelink and Webster, 2001). The soil hydraulic properties are affected by numerous sources of variability mostly associated with spatial, temporal and management related factors (Wilson et al., 2004). The variability of soil properties may be explained by some temporal or spatial deterministic process, but a random component will be present. The variability may be influenced by the size of the samples (Hendrickx et al., 1994; Starr et al., 1995) which is a function of the sampling scale (Western and Bloschl, 1999; Sobieraj et al., 2002)

Effect of organic soil amendments on soil physical properties have been well documented (Navas et al., 1998; Linsay et al., 1998; Aggelides et al., 2000; Veeresh et al., 2002; Ojeda et al., 2008; Delibacak et al., 2009), but reports on the effect of time on soil physical and hydraulic properties in unsaturated calcareous soils are limited.

Felton (1995) reported that bulk density, soil water retention, and hydraulic conductivity in a compost amended soil significantly varied over a three year period. Delibacak et al. (2009) showed that sewage sludge application significantly improved soil physical properties. They also reported that depending on decomposition rate of added organic materials, effect of biosolids

In a greenhouse study, Logan et al. (1996) reported that application of 25% by weight of biosolids significantly affected soil physical properties by decreasing bulk density, and increasing porosity, moisture retention, and saturated hydraulic conductivity. They also reported that many of the observed improvements deteriorated over the first 20-week due to the decompo-

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sition of organic matter in the biosolids. Lindsay and Logan (1998) in a field experiment observed that incorporation of a wide range of biosolids rates had beneficial effects on physical properties of a silty loam soil lasting up to 4 years.

From these and other studies it is clear that biosolids play an important role in improving soil physical properties. Biosolids added to the soils contain a wide range of organic C compounds that vary in the rates of decomposition. The biological breakdown of the organic matter is greatly affected by soil conditions such as soil physical and hydraulic properties, tillage, freezing an thawing in cold season, growth and development of root systems (Ankeny et al., 1990; Meek et al., 1992 Scotte et al., 1994; Willoughby et al., 1996; Logsdon and Jaynes, 1996; McGarry et al., 2000;).

Soils in arid and semiarid regions usually contain less than 0.5% organic matter and thus, have poor physical properties and structural stability. Addition of organic matter to these soils will improve soil physical properties and consequently lead to an increase in soil production (Strudley et al., 2008). However, because of high temperatures and use of extensive irrigation on farm lands the added organic matter rapidly decays. Limited data is available on the effect of time of biosolids application on the changes of soil physical and hydraulic properties in calcareous soils. This information is particularly important for modeling solute transport in biosolids amended-soils.

The objectives of this study were to evaluate (1) the effect of biosolids on selected soil physical properties and unsaturated hydraulic properties (2) the temporal variability in soil physical and unsaturated hydraulic properties after the biosolids application.

MATERIALS AND METHODS

The experiment was established in 1999 to study the cumulative and residual effects of biosolids on soil physical, chemical properties, plant growth yield and heavy metals uptake at the Isfahan University of Technology, Isfahan, central Iran, research station site (32°32' N la., 51° 23' E long.). The site has an arid climate and is 1630 m above sea level. Mean annual rainfall and temperature at the site are 140 mm and 14.5°C, respectively. The soil (fine-loamy, mixed, thermic Typic Haplargid) is formed on the alluvial sediments of the Zayandehroud river initially low in organic matter content (<0.5%), and has been used for agricultural research since 1975. Selected physical and chemical properties of the soil before addition of biosolids are shown in Table 1.

Table 1. Sampling Dates and Times After Biosolids Applications.

Date	Time After the Biosolids Treatment (day)	Events
9-Oct-1999	Start	Treated by Biosolids
10-Oct-1999	1	Tillage & planted to wheat
19-Nov-1999	28	Sampling 1
20-Jun-2000	85	Sampling 2
23-Mar-2000	148	Sampling 3
4-Jun-2000	220	Sampling 4
20-Oct-2000	375	Tillage & planted to wheat
25-Dec-2000	440	Sampling 5
9-Apr-2001	530	Sampling 6

The amendment used in the study was a secondary digested municipal biosolids from the city of Isfahan sewage treatment plant. In October 1999, air dried biosolids was uniformly applied at rates of 0 (control), 25, 50, and 100 Mg ha^{-1} (dry weight) to plots of 3 × 15 m size and mixed into the topsoil (20 cm depth). The plots were tilled and planted to wheat (Triticum aesitivum L.) on October 28, 1999 followed by corn (Zea maize L.) that was planted on October 20, 2000 (Table 1). The plants were irrigated weekly or as needed using the well water at the site, which had an electrical conductivity of 1.2 dS m^{-1}.

To determine the effect of biosolids on soil physical properties we collected surface soil samples (0–20 cm) at 23, 85, 145, 220, 440, and 530 days after biosolids application. Soil properties included bulk density, saturated hydraulic conductivity, water-stable aggregates, final infiltration rate, and water retention at –33 and –1500 kPa.

Soil Physical Analysis

Bulk density was determine on undisturbed soil cores (7.6 cm diameter × 7.6 cm long) taken with an Uhland core sampler. Cores were collected in three positions within each plot and averaged. Bulk density was measured by drying the soil samples to an oven-dry (105°C) basis.

Total porosity was calculated from the bulk density and particle density according to the following equation:

$$\text{total porosity} = \left(\frac{1-\rho_b}{\rho_s} \right) \times 100 \qquad (1)$$

Where ρ_b is the bulk density and ρ_s is the particle density of soil solids (2.65 Mg m^{-3}).

Table 2. Selected Physical and Chemical Soil Properties.

Parameter	Unit	Amount
pH	—	7.9
Electrical conductivity	dS m^{-1}	1.6
Bulk density	kg m^{-3}	1.3
Organic carbon	g kg^{-1}	5
Cation exchange capacity	$Cmol_c$ kg^{-1}	34
Sand	g kg^{-1}	136
Silt	g kg^{-1}	507
Clay	g kg^{-1}	357

Saturated hydraulic conductivity (K_s) was measured on undisturbed soil cores (7.6 cm diameter × 7.6 cm long) using the constant head method of Klute and Dirksen (1986). Tap water was used in this measurement. Triplicate soil cores were collected within each plot and averaged. The soil cores used for K_s measurement were not the same cores we used for bulk density determination.

Water infiltration into the soil was determined using the double ring infiltrometer in three positions and averaged. In this method, double ring cylindrical tubes of diameters 30 cm and 40 cm for the inner and outer rings, respectively and a height of 30 cm were driven 10 cm into the soil. Water was ponded at constant depth inside the two rings (10 cm) and the rate at which water moved into the soil was determined. The infiltration data was fitted into the Kostiakov equation and the infiltration rate (I_r) was calculated.

Water retention measurements were made at –33 and –1500 kPa using a pressure plate on undisturbed samples (Klute, 1986). Measurements were made on 3 samples within each plot and averaged. The results are presented as volumetric water content.

Aggregate stability was determined by wet-sieving using a mechanical agitator as follows: 50 g of air-dry soil were placed in uppermost sieve of a mechanical agitator. The samples and the sieves (5, 2, 1, 0.5, and 0.25 mm) were repeatedly raised and lowered while completely submerged in water for 20 min. Soil aggregates in each sieve was oven-dried (105°C).

Soil Hydraulic Properties

Soil hydraulic properties including soil moisture curve (SMC) and unsaturated hydraulic conductivity (Kh) in different sampling dates were estimated by Rosetta software in each plots and averaged. Rosetta software is used to estimate unsaturated hydraulic properties from soil properties such as soil texture data, bulk density and water retention point at 0.33 and 1500 kPa (Schaap et al., 2001). The Rosetta software estimates water retention parameters based on van Genuchten (1980) model and unsaturated hydraulic conductivity based on Mualem (1960) pore size model. The retention function gives in Equation (2):

$$\theta(h) = \begin{cases} \theta(h) = \theta_r + \dfrac{\theta_s - \theta_r}{[1+(\alpha h)^n]^m} & 0 < h \\ \theta_s & 0 \geq h \end{cases} \tag{2}$$

$$m = 1 - \frac{1}{n}$$

where θ_h is volumetric water content (cm^3 cm^{-3}), h (cm), θ_s and θ_r are residual and saturated water contents, respectively, α is related to inverse of air pressure head (1/cm), and n related to pore size distribution.

Combination of van Genuchten equation with Mualem (1976):

$$K(h) = \begin{cases} K_s Se^{1/2}(1-(1-S_e^{1/m})^m)^2 & 0 < h \\ Ks & 0 \geq h \end{cases} \tag{3}$$

where K_s is saturated hydraulic conductivity, L is an empirical parameter that is normally assumed to be 0.5 in Mualem (1976) and S_e, is effective saturation and computed as:

$$S_e = \frac{\theta_h - \theta_r}{\theta_s - \theta_r} \tag{4}$$

Soil Chemical Analysis

Soil pH (1:2 soil/water) was measured using a digital pH-meter (Model 691, Metrohm AG Herisau Switzerland) and electrical conductivity (ECe) using an EC-meter (Model Ohm-644, Metrohm AG Herisau Switzerland) (Rhoades, 1996). The $CaCO_3$ equivalent was determined by neutralizing with HCl and back titration with NaOH. Organic matter content was determined by the Walkley and Black method.

RESULTS AND DISCUSSIONS

Effect of Biosolids on Soil Chemical Properties

Selected soil chemical properties after biosolids application are shown in Table 3. Biosolids application significantly increased soil OC, CEC and ECe in all the application rates. Soil pH and $CaCO_3$ decreased but the differences were not significant. Our observations

Table 3. Effect of Different Levels of Biosolids Treatment on Some Soil Chemical Properties.

ECe (dS m^{-1})	CEC (Cmol kg^{-1})	pH	OC (%)	$CaCO_3$ (%)	Soil
1.6a	13.2a	8.40a	0.85d	35.9a	Control
1.8b	13.5b	8.25b	0.92c	32.7b	25 Mg ha^{-1}
2.2c	14.6c	8.05c	1.15b	32.3b	50 Mg ha^{-1}
2.1c	15.9d	8.00c	1.27a	31.0c	100 Mg ha^{-1}

following application of biosolids have been widely reported in the literature (Crawford et al., 1995; Navas et al., 1998; Veeresh et al., 2002; Sigh et al., 2007, Julien et al., 2007).

Bulk Density

Bulk density initially significantly decreased with biosolids application [Figure 1(a)]. The mean soil bulk densities in different treatments ranged between 1.3 g cm^{-3} in the control plot to less than 1.12 g cm^{-3} in the application of 100 Mg ha^{-1}. The effect was greatest with 100 Mg ha^{-1} biosolids treatment and bulk densities less than 1.12g cm^{-3} were observed 23 days after biosolids application. The bulk densities increased with time in all the biosolids treatments. However, even 531 days after biosolids application, significantly lower bulk density values were measured in biosolids treated plots compared to control.

Soil total porosity also increased significantly with biosolids application and as time passed the total porosity showed a decreasing effect. Reductions in soil bulk density and concomitant increases in total soil porosity following application of biosolids have been reported in the literature (Cripps, 1992; Marinari et al., 2000; Evrendilek et al., 2004).

Temporal variations were significant for bulk density between sampling dates. Possible reasons for these variations include variation in the effect of tillage (Ankeny et al., 1990; Logsdon and Jaynes, 1996), freezing and thawing (Scotte et al., 1994), various biological activities activity of soil organisms (Beven and German, 1982; Willoughby et al., 1996), and difference in growth and decay of plant during sampling dates (Meek et al., 1992). Temporal variation in treated plots was more intensive in plots with higher biosolids application rates.

Aggregate Stability

Soil aggregate representation by aggregate stability percentage (ASP) was also significantly ($P < 0.05$) affected by biosolids application [Figure 1(b)]. In the first sampling, 23 days after biosolids application, the ASP increased by 53, 67, and 74% in 25, 50 and 100 Mg ha-1 biosolids treatments, respectively. Organic matter makes the aggregates more resistant by increasing their internal cohesion though the binding of mineral by means of organic polymer. The greatest increase in ASP occurred 145 days after biosolids application. The increase of ASP is probably because of the development of fungi mycelium and plant root system in this period (Paglia et al., 1981). The ASP values showed a decreasing trend with time. However, even after 530 days the difference between control and biosolids treatments were still significant ($P < 0.05$). Application of biosolids increased aggregate stability and the greatest effect was observed in the 100 Mg ha^{-1} treatment. Other researchers have reported that the effect of biosolids on aggregate stability decreased with time because of biosolids decomposition (Li et al., 2007; Angela et al., 2005). However, even 530 days after the first biosolids application, all the biosolids treatments had significantly higher stable aggregates compared to the control. Positive significant correlation between soil organic matter and ASP was observed in this study ($r = 0.49$). This correlation is low and shows that aggregate stability is affected by other factors such as fungi mycelium and roots plant system although we did not measure these parameters in this study [Figure 2(a)].

Temporal variations were significant for ASP between sampling dates. Possible reasons for these variations include variation in the effect of tillage and various biological activities, and difference in root system development during sampling dates.

Saturated Hydraulic Conductivity

Application of biosolids initially increased saturated hydraulic conductivity [Figure 1(c)] for all the treatments. Application of 25, 50, and 100 Mg ha^{-1} of biosolids increased saturated hydraulic conductivity by 63, 46 and 41%, respectively, as compared to the control in the first sampling.

Temporal variations were significant for saturated hydraulic conductivity between sampling dates after biosolids application. As in total porosity, we also observed a temporal decrease in the saturated hydraulic conductivity in the experimental plots [Figure 1(c)]. The reduction of saturated hydraulic conductivity over time is probably due to closing of the pores by decomposing products of organic matter in the biosolids and inactive roots (Paglia et al., 1981; Meek et al., 1992).

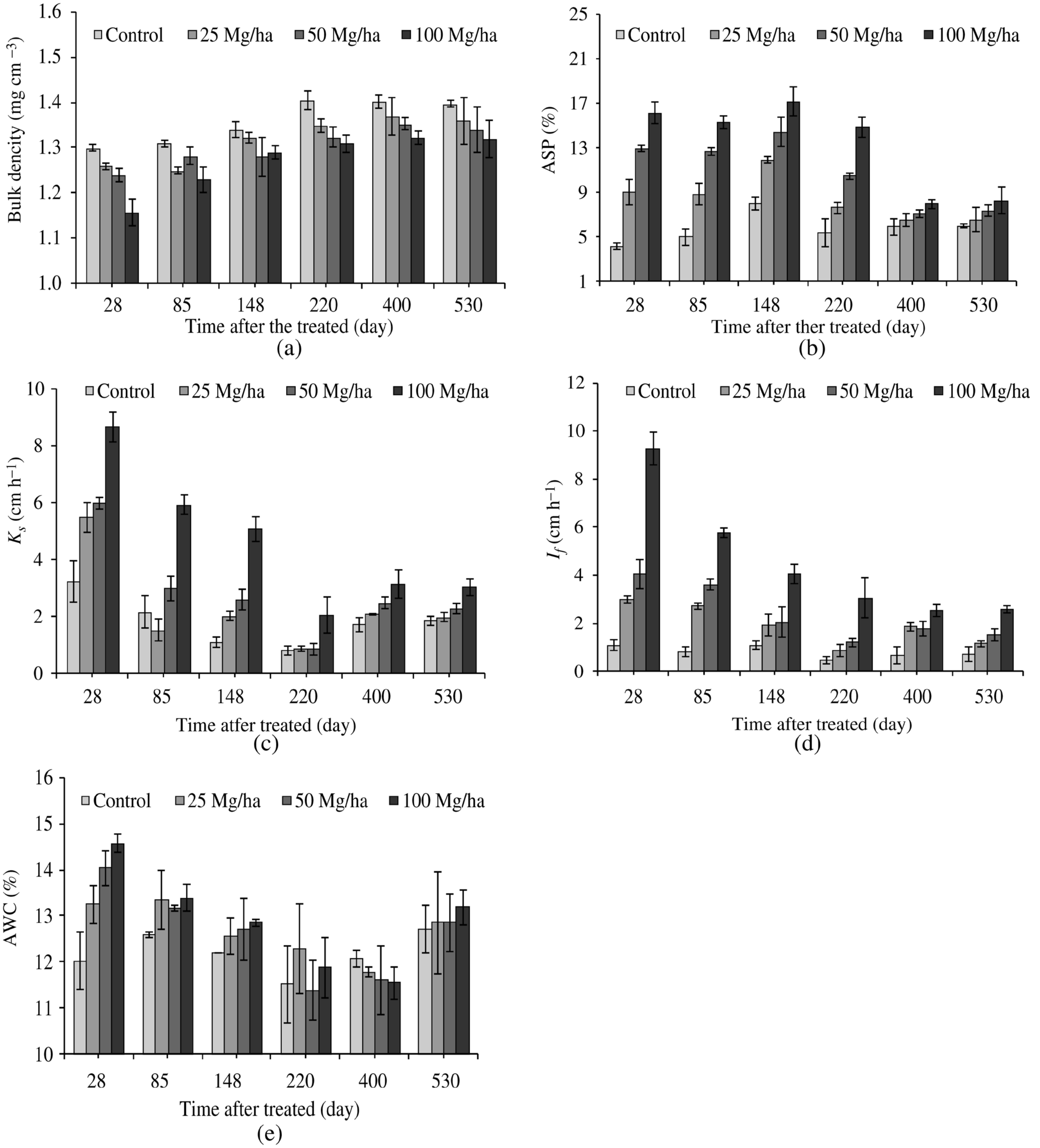

Figure 1. *Effect of biosolids application and time on (a) soil bulk density, (b) soil aggregate stability percentage (ASP), (c) saturated hydraulic conductivity (K_s), (d) final infiltration rate (I_f) and (e) soil available water capacity (AWC).*

The magnitude of decrease was more pronounced in the 25 and 50 Mg ha^{-1} treatments. However, even after 1.5 year from the first biosolids application the saturated hydraulic conductivity in the 100 Mg ha^{-1} treatment was about 39% more than the control treatment indicating some parts of the added organic matter in biosolids application is more resistant to microbial decomposition. We observed a positive significant correlation ($r^2 = 0.83$) between soil organic matter (OM) and saturated hydraulic conductivity [Figure 2(b)]. Similar result have been reported by Paglia et al., 1981; Cripps, 1992; Marinari et al., 2000; Evrendilek et al., 2004.

Final Infiltration

Biosolids application significantly increased final infiltration rate (I_f) [Figure 1(d)]. The If in 25, 50, and 100 Mg ha^{-1} biosolids rates were 88, 73 and 63% greater than the control 23 days after biosolids application, respectively. The increase in I_f is due to the formation of stable and large soil aggregates and lowering of the soil bulk density and increasing soil total porosity.

Similar to the saturated hydraulic conductivity, we observed a temporal variation in the If and decreased with time. The magnitude of decrease in saturated hydraulic conductivity was more pronounced in the 25 and 50 Mg ha^{-1} treatments. However, even 1.5 years after the biosolids application the If values in 25, 50, and 100 Mg ha^{-1} treatments were 37, 52, and 70% greater than the control treatment. Similar to Ks, we observed a positive significant correlation (r^2=0.82) between soil organic matter (OM) and final infiltration rate (*Ir*) the significant relation between OM and If was described by the following linear equation [Figure 2(c)]:

$$I_f = 8.946\ \text{OM} - 4.788$$

Soil Water Retention

Biosolids application significantly increased water retention at –33 and –1500 kPa. Results in Figure 3 show that soil available water content (difference of the volumetric water contents at –33 and –1500 kPa) significantly increased following biosolids application

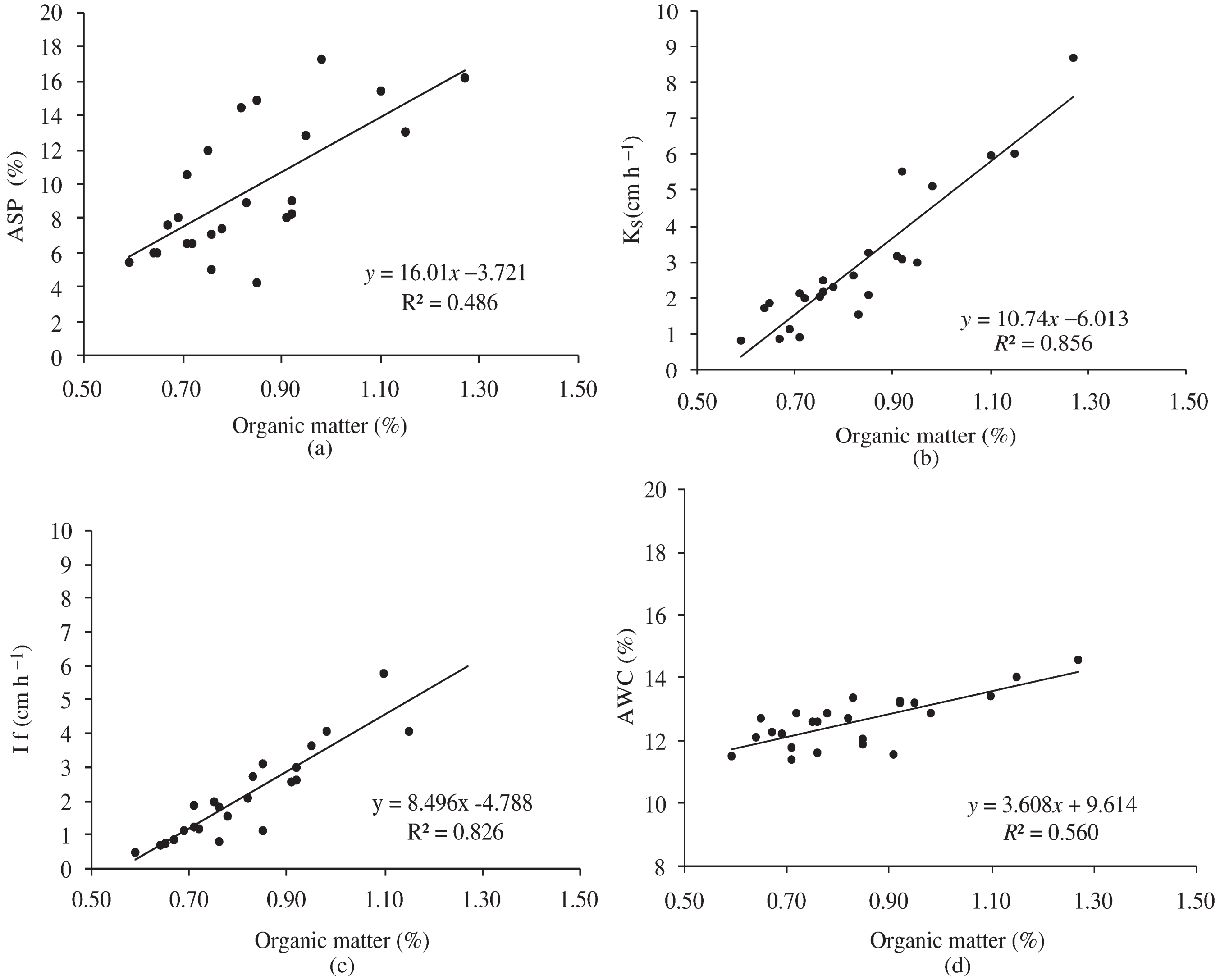

***Figure 2.** Relation between aggregate stability percentage (a), final infiltration rate (b), saturated hydraulic conductivity (c), available water capacity (d) and soil organic matter in a soil with loamy texture amended by biosolids in three levels at duration 530 days after the application of treatments.*

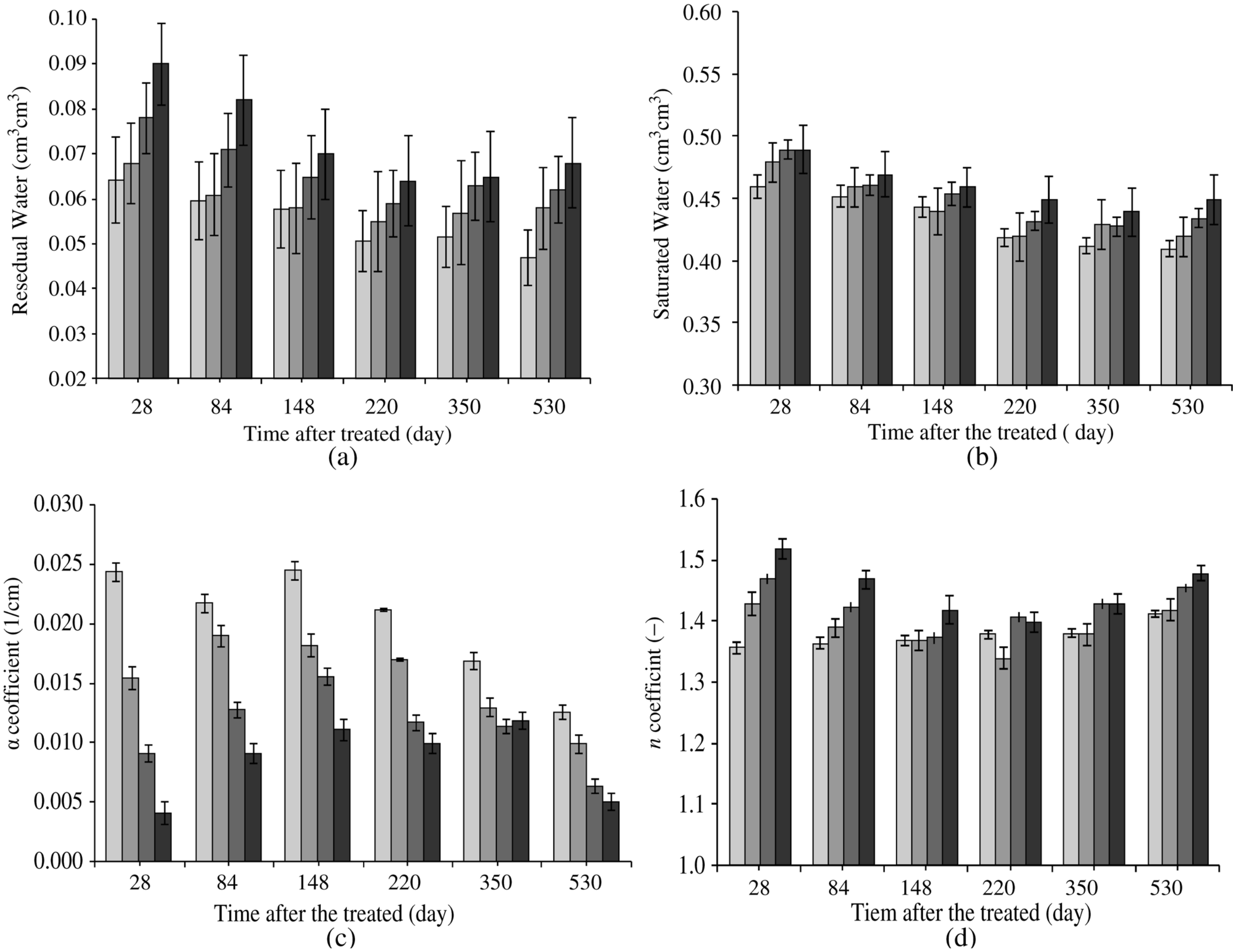

***Figure 3.** Effects of biosolids application and time on soil moisture curve characteristics; (a) residual water content, (b) saturated water content, (c) α coefficient, (d)* n *coefficient.*

[Figure 1(e)]. The increase in water retention was due to the increase in large size aggregates. Also, addition of organic matter increased total porosity and water absorption capacity of the soil (Paglia et al., 1981). Positive significant correlation between soil organic matter and available water content (AWC) was observed in this study ($r = 0.56$) following Equation [Figure 2(d)]:

$$\text{AWC}\ (\%) = 3.68\ \text{OM} + 9.61$$

Temporal variations were significant for soil water retention between sampling dates. Possible reasons for these variations include variation in the effect of tillage and various biological activities, and difference in root system development during sampling dates. Temporal variation in treated plots was more intensive following increase in level application. This contributes to pool of soil organic matter because biological activities in arid region are lower.

Soil Moisture Characteristic Curve

The soil water characteristics were well described with the van Genuchten relationship by indirect method based on soil texture, bulk density and water retention at 0.33 and 1500 kpa pressure that were measured in fields. These characteristics estimated using Rosetta software (van Genuchten, 1980). Residual (θ_r) and saturated (θ_s) water contents significantly increased by biosolids treatment compared with the control in all the sampling dates (Figure 3). The increases in θ_s were more than increases of θ_r following biosolids application.

The α and *n* coefficients are related to inverse of air suction (1/cm) and pore size distribution, respectively. Biosolids application had a significant effect on α and *n* which were estimated by Rosetta (Figure 3). The α and n coefficients were reduced and increased, respectively following rate application of biosolids compared to the control treatment. Our results showed that estimated parameters have a temporal variation in different sampling dates. The temporal variation was more intensive in high levels of biosolids application. The higher estimated value for α coefficient occurs in 145 days after of sludge application in all plots.

Unsaturated Hydraulic Conductivity

Unsaturated soil hydraulic conductivity (K_h) for the different sampling dates were estimated using Mualem (1980) equation only in control and 50 Mg ha^{-1} treatments (Figure 4). The biosolids application significantly increased K_h in the biosolids treated plot. The results of this study show an intensive temporal variability on K_h in different sampling dates. The highest K_h values were estimated in the early sampling. The variations of K_h in different sampling dates were more intensive in saturation and near saturation conditions. This is because, water movement at or near saturation is mainly effected by soil structure which was shown earlier is significantly influenced by organic matter addition to the soil through biosolids applications.

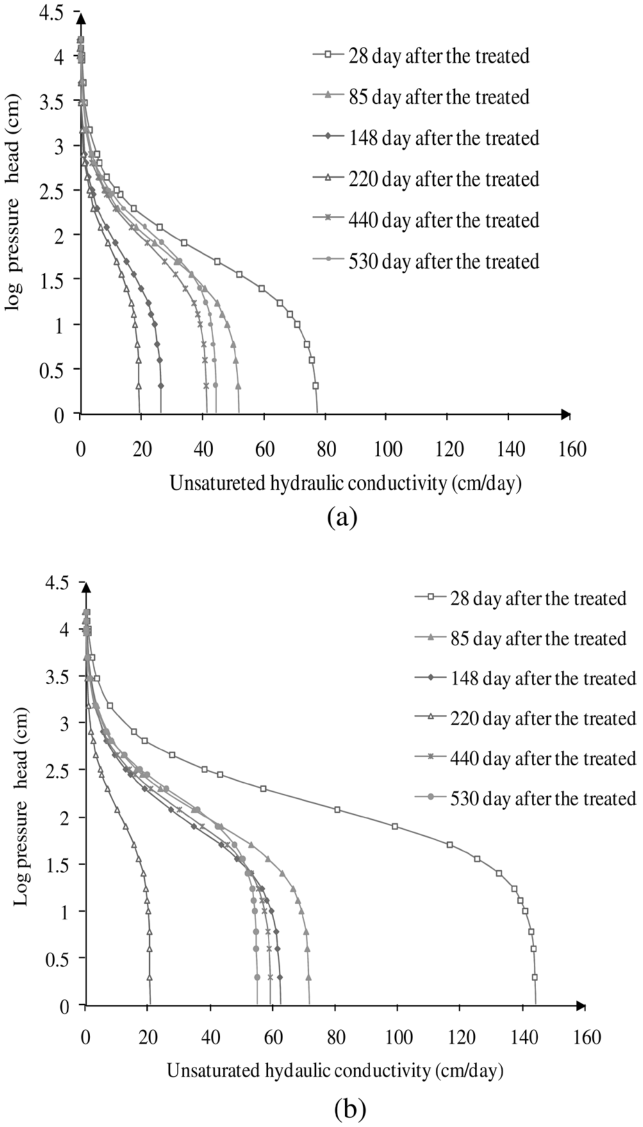

Figure 4. *Effect of biosolids application and time on unsaturated hydarulic conductivity in (a) control and (b) treated plot with 50 Mg ha^{-1} biosolids.*

CONCLUSIONS

Experiments were performed on field plots for more than 1.5 years. We measured soil physical properties 23, 85, 145, 220, 440, and 550 days after incorporation of aerobically digested biosolids. This study served, in part, to document the effects of time on different biosolids rates on soil physical properties after the processes.

The results showed that biosolids application decreased bulk density, and increased saturated hydraulic conductivity, infiltration rate, aggregate stability, and moisture retention. In general, the results were more evident in the 100 Mg ha^{-1} treatment. Over time, soil physical properties approached the control values, but beneficial effects on the soil physical properties were generally significant even after more than 1.5 year after biosolids application. The soil moisture characteristic curve and unsaturated hydraulic conductivity are keys parameters and main inputs in water flow and solute transport modeling process in soil. Our results indicate that the temporal variability of soil physical properties should be considered following application of biosolids in solute transport studies and modeling.

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Table 5. Comparison of state-of-the-art matrix resins with VPSP/BMI copolymers.

Resin System	**Core Temp. (DSC peak)**	**T_E**	**Char Yield, %**
Epoxy (MY720)	235	250	30
Bismaleimide (H795)	282	>400	48
VPSP/Bismaleimide copolymer			
C379: H795 = 1.9	245	>400	50
C379: H795 = 1.4	285	>400	53

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