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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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CONTENTS

Land Application Controversies and Solutions

Independently Submitted Articles

Effects of Sludge Amendments on Heavy Metals Accumulation and Crop Yields

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ABSTRACT: The application of sludge as fertilizer to improve soil properties is generally considered to be one of the best practices around the world. It is benefit from the sequestration of organic carbon and nutrients in the soil, but again brings negative effects as heavy metal pollution when using those wastes. The aim of the study was to evaluate the effects of sludge application on heavy metals accumulation and crop yields in winter wheat-corn rotation system in north China plain. A 3-year field study was carried out to investigate heavy metals of Mn, Cu, Zn, Pb and Cd concentration and crop yields among different sewage sludge treatments, as dewatered raw sludge, sludge compost and sludge compound fertilizer since 2002. The research indicated that three sludge amendments could raise the contents of soil total organic matter and total nitrogen; Compared to CK and chemical fertilizer treatment, sludge amendment had higher concentration of Mn, Cu in the soil and higher Zn in wheat grain. Compared to the chemical fertilizer treatment, the use of sludge had no significant effects on the yield of both wheat and corn.

INTRODUCTION

It was estimated that China generated around 1.0 × $10^8 t$. Wet sludge every year and among those different treatments, composting was accounted for about 45% of the total sludge in the country (Wei *et al.*, 2005; Xu, 2003).

The application of sludge as fertilizer to cropland is one of the best practice as it provides a whole array of nutrients to the soil (Chodak *et al.*, 2001; Tejada *et al.*, 2001), and benefits from decreasing soil acidification (Bengtson and Cornette, 1973), increasing beneficial soil organisms (Zhou *et al.*, 1994; Zou *et al.*, 2005), and improving soil physical and biological properties (Barzegar *et al.*, 2002; Veeresh *et al.*, 2003).

However, the heavy metals risks from the land use of sludge were often discussed and it could inhibit the seed germination, crop development and yield when accumulated in the soil over a long period of time (Wei *et al.*, 2005).

Long-term field study on sludge use are needed because many of its effects, e.g. organic matter enrichment and the possible build-up of toxic elements in soil, evolve slowly and are difficult to predict (Bergkvist *et al.*, 2003; Gaskin *et al.*, 2003; Paolo *et al.*, 2005). Moreover, different treatments of sludge can dramatically affect soil characteristics and performance (Dentel *et al.*, 2001; Renoux *et al.*, 2001). This study was conducted to understand effects of different sludge treatments on: (1) soil nutrients; (2) heavy metals accumulation in soil; (3) uptake of heavy metals by crops and crop yields.

MATERIALS AND METHODS

Field Location

The study was conducted at Quzhou Agricultural Experimental Station (36º52´N, 115º01´E), located in the north of Quzhou county of Hebei province in China. The area has a warm, sub-humid monsoon climate. Annual mean rainfall is about 604 mm with a primary raining season in July and August and accounts for 60% of the rainfall in the whole year. Annual mean temperature is 13.1°C and ranges from a maximum of 26.8°C in July to a minimum of –2.9°C in January. The high annual evaporation of 1841 mm makes spring drought seriously. The annual frost-free period is 201 d. The soil in the study was salinized cinnamon soil.

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Experimental Design

The field study was carried out from October 2002 (before sowing wheat) to September 2005 (after harvesting maize). The cropland has been conventionally cultivated with a double cropping system of winter wheat and summer maize for certain years.

The field trial was conducted from 2002 to 2005 and each plot was 40.6 m^2. A randomized design with three replications was employed by using following five treatments: (1) control with no fertilization; (2) conventional inorganic fertilizer (ammonium carbonate 1.125 $t \cdot ha^{-1}$, superphosphate 1.125 $t \cdot ha^{-1}$, potassium sulphate 0.15 $t \cdot ha^{-1}$, top-dressing urea 0.375 $t \cdot ha^{-1}$); (3) digested sludge (56% water content) 22.5 $t \cdot ha^{-1}$, top-dressing urea 0.3 $t \cdot ha^{-1}$; (4) sludge compost (45% water content) 15 $t \cdot ha^{-1}$, top-dressing urea 0.3 $t \cdot ha^{-1}$; (5) sludge compound fertilizer (1.5 $t \cdot ha^{-1}$, top-dressing urea 0.3 $t \cdot ha^{-1}$). The main characteristics of the soil and sludge are shown in Table 1. Heavy metal contents were much lower than China Standard for sludge agricultural use (GB4284-84) in all original sludge samples.

Sludge and Fertilizers Preparation

The digested sludge was derived from a wastewater treatment plant in Taiyuan city. The composted sludge was made on the site before growing and the raw materials were the mud + corn cob + fly ash (fly ash occupies 20% of whole compost material in dry weight). The proportion of three raw materials was adjusted to have a start formula with C/N ratio 20 and water content 60%. The materials were mechanically turned and the temperature was controlled below 65°C. The composting time was about 49 days until the C/N ratio and the temperature became constant, and other physical characteristics such as the compost color and the smell met the standard as described in the references (Gonzalez *et al.*, 1990, 1992). Compound fertilizer was made from the Taiyuan Yangjiabu composting demonstration factory. The total N, P and K's concentration in the compound fertilizer is 11% (N: P: K = 6:2:3), and the organic matter content is 33.9%.

Analytical Methods

Top soil samples (0–20 cm) were collected before and after each crop harvesting. Samples from the five locations in each subplot were mixed thoroughly to obtain a composite sample, and then was kept in a labeled plastic bag and stored in refrigerator before chemical analysis in the laboratory. Crop samples were taken every year and air dried and stored continually. All plant and soil samples were collected from the central part of each plot to avoid edge effects.

Total organic matter (TOM) was measured by dichromate oxidation (Nelson and Sommers, 1982); Total organic nitrogen (TON) was determined by the semi-micro Kjeldahl method (Bremner and Mulvaney, 1982); Total phosphorous (TOP) was digested by $HClO_4$-H_2SO_4 and used the molybdenum-antimony anti-colorimetric method (Bao, 2000; Lu, 2000). Available P was measured following the Olsen method, available K by 1 N NH_4OAc using a flame photometer (Bao, 2000; Lu, 2000). Soil and sludge pH were measured on air-dried samples by using a combination glass electrode in 0.01M $CaCl_2$ solutions (1:2.5 soil-to-water ratio and 1:6 sludge-to-water ration respectively). Soil water content was determined gravimetrically by drying soils for 24 h at 105°C.

Crop grains were dried at 70°C and then ground in a stainless steel mill to pass 1 mm sieve. Dried crop samples were digested by $HClO_4$-HNO_3 ($HClO_4$:HNO_3:4:9), analyzed for heavy metal contents with graphite and flame atomic absorption spectrophotometer (GFAAS). Soil and sludge samples analysis were evaporated to near dryness on a hot plate with 15 ml HNO_3, then contents were digested with 15 ml HNO_3 and 20 ml $HClO_4$ (70%). The residue was taken in 15 ml of 6N HCl and made to the volume (50 ml) and contents were filtered. The filtrate was analyzed with graphite and flame atomic absorption spectrophotometer (GFAAS) (Thermo Element MKII-M6) according to China Heavy Metals Measurement Standard (GB/T 17141-1997 and GB/T 17138-1997). The plant available metal concentrations

Table 1. The Basic Chemical Characteristics of Tested Soil and Sewage Sludge (sample in 2002).

Items	TON ($g\ kg^{-1}$)	TOP ($g\ kg^{-1}$)	TOM ($g\ kg^{-1}$)	pH	Cu ($mg\ kg^{-1}$)	Mn ($mg\ kg^{-1}$)	Zn ($mg\ kg^{-1}$)	Pb ($mg\ kg^{-1}$)	Cd ($mg\ kg^{-1}$)
Soil	0.90	0.77	11.92	8.02	17.482	518.36	55.33	32.54	0.24
Sludge	37.40	7.60	391.30	8.41	174.31	311.12	979.88	69.51	0.95

Note: People's Republic of agricultural pollutants in sludge control standards (GB4284-84), maximal allowable dose in alkaline soil were: Cu 500 $mg\ kg^{-1}$, Zn 1000 $mg\ kg^{-1}$, Pb 1000 $mg\ kg^{-1}$, Cd 20 $mg\ kg^{-1}$ dry sludge.

Table 2. Effects of Different Treatments on Soil Chemical Properties.

Time	Treatments	TON ($g\ kg^{-1}$)	TOP ($g\ kg^{-1}$)	SOM ($g\ kg^{-1}$)	C/N	pH
2003	CK	0.78a	0.72a	10.90a	7.95a	7.94a
	Chemical fertilizer	0.90a	0.75a	12.40a	7.98a	7.94a
	Digested sludge	0.93a	0.73a	12.60a	7.73a	8.04a
	Composted sludge	0.86a	0.72a	12.70a	8.35a	7.94a
	Sludge compound fertilizer	0.82a	0.78a	11.80a	8.21a	8.00a
2004	CK	0.79a	0.74a	11.50a	8.28b	7.80a
	Chemical fertilizer	1.10bc	0.80a	12.00a	6.29a	7.80a
	Digested sludge	1.00bc	0.77a	14.70b	8.06b	7.81a
	Composted sludge	1.20c	0.73a	15.60b	7.68ab	7.88a
	Sludge compound fertilizer	0.91b	0.73a	12.10a	7.55ab	7.84a

The different lowercase letters denoted reached 0.05 (LSD) level of significance difference.

were determined after extraction with 0.005M DTPA (Lindsay and Norvell, 1978).

Statistical Analysis

Mean values were calculated for each of the variables, and ANOVA was used to assess the effects of different fertilizer treatments on the measured soil proprieties. When ANOVA indicated a significant F-value, multiple comparisons of annual mean values were performed by the least significant difference method. In all analyses, a probability of error smaller 5% (P * 0.05) was considered statistically significant. The SPSS analytical software package (13.0) was used for all the statistical analyses.

RESULTS AND ANALYSIS

Soil Nutrients

There were no significant differences in soil major properties between three sludge treatments, CK, and chemical fertilizers treatment in 2003 (one year after amendment) (Table 2).

After two years field trials (in 2004), soil total phosphorus content and soil pH were still no significant differences between different treatments. But other parameters, as TON, SOM and C/N showed significant differences between different treatments.

Compared with CK, the three sludge treatments significantly increased soil organic carbon and soil total nitrogen as same as chemical fertilizer treatment.

As a result, C/N in the soil was lower in three sludge treatments than CK, and higher than the chemical fertilizer treatment.

Soil Heavy Metals

After two years of wheat-corn rotation cropping, the cumulative results of soil heavy metals showed that, the chemical fertilizer had a minor accumulation of Zn and Cd in soil than CK. And digested sludge treatment had significantly higher Cd content than other treatments, and there were no significant differences of heavy metals content between other treatments and CK. The soil heavy metals contents of three sludge treatments were higher than chemical fertilizer treatment (Table 3).

In 2005, there was no significant difference of soil Pb and Cd content among all treatments. But the significant differences of soil Mn, Zn and Cu content were found between different treatments.

The soil Mn and Cu content of three sludge treatments were significantly higher than CK and chemical fertilizer treatment. Meanwhile soil Zn content of sludge compound fertilizer treatment was significantly higher than other treatments.

Among three sludge treatments, digested sludge treatment showed higher accumulation of soil Mn and Cu, and sludge compound fertilizer treatment showed higher accumulation of soil Zn.

The increased content of soil Zn and Cu after amendments of sledges tell us that we need to track the accumulation of Zn and Cu in the soil and precaution the heavy metal pollution in the future.

Grain Heavy Metals

Wheat Grain Heavy Metals

In 2003, there were no significant differences of heavy metal content in wheat grain between different treatments (Table 4).

Table 3. Effects of Different Sludge Treatments on Soil Heavy Metals Concentration.

Time	Treatments	Mn ($mg\ kg^{-1}$)	Zn ($mg\ kg^{-1}$)	Cu ($mg\ kg^{-1}$)	Pb ($mg\ kg^{-1}$)	Cd ($mg\ kg^{-1}$)
2004	CK	520.47a	54.72a	19.21a	32.14a	0.09a
	Chemical fertilizer	527.91a	59.14a	20.70a	32.67a	0.16ab
	Digested sludge	553.99a	66.67a	20.71a	34.93a	0.34b
	Composted sludge	542.25a	60.88a	21.04a	35.18a	0.26ab
	Sludge compound fertilizer	564.66a	70.37a	21.09a	34.15a	0.16ab
2005	CK	52461a	67.85a	19.81a	34.19a	0.19a
	Chemical fertilizer	535.75a	71.43ab	20.63a	34.38	0.19a
	Digested sludge	587.39b	84.84ab	23.77b	38.13a	0.33a
	Composted sludge	562.85b	81.30ab	23.95b	35.90a	0.24a
	Sludge compound fertilizer	578.34b	93.67b	22.56b	36.59a	0.24a

The different lowercase letters denoted reached 0.05 (LSD) level of significance difference.

But in 2005, the Zn content of wheat grain of three sludge treatments were significantly higher than CK and chemical fertilizer treatment. And digested sludge had higher Pb content in wheat grain than other treatments.

Heavy metals content of wheat grain in all treatments were lower than the national food sanitary standards.

Corn Grain Heavy Metals

There were no significant differences of heavy metals content in corn grain among different treatments both in 2003 and 2005 (Table 4).

The heavy metals content of all treatments in corn grain were lower than the national food sanitary standards.

Different crops grains showed different heavy metal accumulation, the Mn and Cu content in wheat grain was higher than that in corn grain. There were no differences of Zn content between wheat and corn grain.

Crop Yields

The responses of crop yields to different treatments showed that both wheat and corn yield were signifi-

Table 4. Effects of Different Sludge Treatments on Heavy Metals in Crops Grain.

Crop	Time	Treatments	Mn ($mg\ kg^{-1}$)	Zn ($mg\ kg^{-1}$)	Cu ($mg\ kg^{-1}$)	Pb ($mg\ kg^{-1}$)
Wheat	2003	CK	29.88a	26.35a	4.84a	0.13a
		Chemical fertilizer	30.89a	34.85a	4.98a	0.13a
		Digested sludge	31.73a	42.24a	5.52a	0.15a
		Composted sludge	32.50a	42.08a	5.24a	0.14a
		Sludge compound fertilizer	31.03a	34.90a	5.34a	0.13a
	2005	CK	31.99a	29.18a	5.62a	0.13a
		Chemical fertilizer	32.00a	39.74b	5.90a	0.14a
		Digested sludge	38.28a	48.21c	6.31a	0.18b
		Composted sludge	31.55a	47.07c	5.58a	0.14a
		Sludge compound fertilizer	34.56a	46.46c	6.03a	0.15a
Corn	2003	CK	4.98a	30.31a	2.05a	–
		Chemical fertilizer	5.08a	34.07a	2.00a	–
		Digested sludge	5.13a	32.25a	2.20a	–
		Composted sludge	4.97a	32.86a	2.17a	–
		Sludge compound fertilizer	4.85a	31.65a	1.92a	–
	2005	CK	5.13a	29.26a	2.17a	–
		Chemical fertilizer	5.34a	34.76a	2.07a	–
		Digested sludge	6.09a	37.84a	2.65a	–
		Composted sludge	5.72a	36.26a	2.20a	–
		Sludge compound fertilizer	6.24a	33.51a	2.06a	–
National food sanitary standards			–	≤ 50	≤ 10	≤ 0.5

–means no data. The food sanitary standards established by Chinese legislation are shown. The different lowercase letters denoted reached 0.05 (LSD) level of significance difference.

Table 5. Effects of Different Sludge Treatments on Crop Yields Among 2003–2005.

Time	**Wheat Yield (kg hm^{-2})**			**Corn Yield (kg hm^{-2})**			**Total Yield (kg hm^{-2})**		
Treatments	**2003**	**2004**	**2005**	**2003**	**2004**	**2005**	**2003**	**2004**	**2005**
CK	3843a	2218a	3182a	7838a	4406a	4068a	11681a	6625a	7250a
Chemical fertilizer	8946c	8126c	7181b	9011a	9830b	9585b	17957b	17956b	16766b
Digested sludge	7034b	5890b	6866b	9137a	10663b	9495b	16170b	16554b	16361b
Composted sludge	8243bc	6953bc	7572b	9458a	9653b	8700b	17700b	16607b	16272b
Sludge compound fertilizer	8208bc	7027bc	8061b	9080a	10250b	10022b	17288b	17278b	18083b

The different lowercase letters denoted reached 0.05 (LSD) level of significance difference.

cantly higher in all four treatments than CK. Three sludge treatments were close to the chemical fertilizer treatment in terms of the crop yield.

CONCLUTIONS

The experimental results in this paper showed: (1) the sludge amendaments could increase soil nitrogen and soil organic matter content, and improve soil physical properties. A rational use of sludge can effectively improve the crop yields; (2) compared with chemical fertilizer, soil Mn, Zn and Cu content were significant increased in three sludge treatments after 3 years application (in 2005). The short-term land use of three sludge fertilizers was relatively safe but need precaution the potential soil pollution in the later years; (3) the heavy metal content of crop grains was all below the national food sanitary standards, but further study on Zn accumulation need to be done to avoid the pollution risk for a long-term sludge amendment.

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Improve Sludge Dewatering Performance by Hydrothermal Treatment

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ABSTRACT: In China, over 14.3 million tons dewatered sewage sludge, with 80% water content, generated from wastewater treatment plants in 2007. Traditional technologies used by municipal solid waste treatment facilities, such as landfill, composting, incineration, are unsuitable for sludge disposal. High water content is the bottleneck of sludge treatment and disposal. Hydrothermal treatment could disrupt sludge cell and release bound water finally improve sludge dewaterability. In this paper, bench scale experiments of sludge hydrothermal treatment were carried out. Results show that under a temperature from 140°C to 180°C and reaction time from 15min to 90min, water content of treated sludge could reduce from 80% to about 50%. Based on laboratory parameters, a full scale project of hydrothermal process was carried out to treat 30 tons dewater sludge per day. The sludge was heated by high temperature steam generated form a boiler under 180°C. The treated sludge was dewatered by a centrifuge. Water content of 54.66% was obtained in the full scale project.

1. INTRODUCTION

1.1. Production and Disposal of Sewage Sludge in China

WASTE water treatment plant produced large amounts of sludge that were composed primarily of organic microbes and inorganic minerals. In 2007, 3102 million tons of municipal wastewater was generated in China, and 49.1% of those waste waters were treated by bioprocess reported by state EPA. Approximately, 14.3 million tons of dewatered sewage sludge, with water content of 80%, generated from waste water treatment plants (WWTPs). In recent years, the treatment and disposal of sludge is attracting increasing attention. A survey, taken by the author, showed that the WWTPs with a capacity over 0.2 million tons per day treated 22.73 million tons of sewage per day in 2006, which represented about 50.9% of the total sewage treated in the whole country. These plants produced 6.14 million tons of dewatered sewage sludge cake per year. Of those sludges, 83% was not disposed properly. Merely 10% of the sludge was disposed by direct drying, which was the major method for sludge disposal used in developed countries. Another 6% was disposed of by landfill and 1% by composting. The remaining sludge, dumped without any treatment, presents a considerable environmental risk.

1.2. Production and Disposal of Sewage Sludge in China

In some developed countries, special sanitary landfills were required for sludge to be disposed of by landfilling. The construction cost of those sanitary landfill sites was higher than that for municipal solid waste. In China, parts of sludge were transferred into landfill sites together with municipal solid waste. While, the high water content of sludge caused problems with the compaction of waste at the landfill site, and it also affected the stabilization of the waste body. According to the latest national standard issued in 2007, sludge cake with water content below 60% could be accepted by landfills. In fact, this standard has become a great barrier for sludge disposal. Because of the standard limitation, none of the landfills located in the urban area were available to accept the sludge.

Composting as a traditional solid waste treatment technology usually was used to treat sludge. Fertilizer

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products from composting process critically determined the operation of composting facilities. In the large cities, composting as a disposal method was not effective enough. It was difficult to retail all of the compost produced as fertilizer. Heavy metals and pathogens were the barrier for composting product utilization. While, economically developed cities also bring industrial waste water into WWTPs leading a high heavy metals content of sludge. On the other hand, a large amount of leavening agent has to be added into sludge to improve oxygen utilization in compost body. Chen *et al.* developed a fast sludge composting technology that has been used in several projects. Based on this technology, some sludge compost projects have been under operation.

Incineration was another traditional method for municipal solid waste treatment. This process could greatly reduce sludge quantity. Only a small amount of residue produced that could be disposed by landfilling. While, sludge cake can not be directly burned because of it's high water content and low heat value. Generally, thermal drying has been used as an effective way to reduce water from sludge cake before incineration. In thermal drying reactor, water in the sludge cake was vaporized by contact with a heating interface or a high temperature gas. The sludge cake could reach to 10% water content. Xu and Han reported that, in 2004 the first sludge thermal drying plant with a capacity of 200 tons of dewatered sludge cake per day was constructed at Shidongkou WWTP in Shanghai. Another thermal drying facility is under construction in Gaobeidian WWTP, which can treat 800 tons of dewatered sewage sludge per day. Thermal drying was a popular technology, as it was effective for the reduction of redundant water in sludge. However, it has the disadvantage of consuming a very large amount of energy. In the same time, cost of thermal drying plant construction and operation was very high. The application of thermal drying has therefore been restricted due to its high energy consume.

1.3. Principal of Hydrothermal Treatment

High water content was the most important barrier for sludge treatment and disposal. So, the challenging problem was to reduce water content of sewage sludge. Essentially, the sludge dewaterability was determined by the water distribution. In the early 1970s, Vesilind classified the following kinds of water in sludge: free water, interstitial water, surface or vicinal water, and hydration water. Carberry gave a quantitative water distribution for concentrated sludge, indicating that 70% of the total water was interstitial water, 22% was surface and capillary water, and 8% was cellular water. The special cellular and colloid structure brought difficulties in removing interstitial water, surface water, vicinal water and hydration water.

In order to reduce water of mechanical dewatered sludge cake, many technologies developed as sludge conditioning method. The aim of sludge conditioning was to disrupt sludge cell structure and release bound water. Brooks stated that among those technologies hydrothermal has been recognized for many years as a useful means of sludge conditioning. The purpose of hydrothermal treatment was to change sludge physical character so that it could give up its water more readily. Both the settleability and filterability of sludge may be improved and it will also be sterilized. During this process, sludge was heated up to a typical temperature about 170°C for 30–60 minutes at the corresponding vapor pressure. The sludge treated by thermal hydrolysis was partially solubilized and the biological cells were disintegrated. This created a sludge that was more suitable for dewatering and digestion. As cell water become free water by thermal hydrolysis, the viscosity of the sludge also decreased. Hydrothermal technology, by significantly increasing the dewaterability of the sludge, therefore provides a promising way for using a higher sludge concentration in the digester feed, for providing a higher buffer capacity, and for ensuring a stable digestion process. Paul stated that thermal hydrolysis applied in association with a biological system could reduce excess sludge production to about 50%. Skiadas also use a mile temperature (70°C) to improve sludge anaerobic digestion performance.

2. EXPERIMENTS OF SLUDGE HYDROTHERMAL TREATMENT

2.1. Materials and Methods

The sludges used in experiments were collected from Beixiaohe WWTP in Beijing. This plant treats 40 × 104 waste water per day by bioprocess. The sludge cake dewatered by belt press was 80% moisture content. The organic content of the sludge cake was 72%. The sampled sludge cake was first diluted to 90% moisture content for necessary fluidity in following hydrothermal reactor. Before hydrothermal treatment the sludge cake was smashed to get uniform particles with a mixer. Be-

Table 1. Characteristics of Sludge.

TS (mg/L)	VS (mg/L)	SS (mg/L)	VSS (mg/L)	SCOD (mg/L)	TCOD (mg/L)	pH
99.5	64.4	86.9	62.6	19.4	115.5	5.88

fore used in hydrothermal treatment, prepared sludge was stored in a refrigerator at 4°C to avoid microbe degradation. The characteristics of sludge are shown in table 1.

Sludge hydrothermal treatment was carried out in 1L stainless steel reactors. The reactors were heated by oil oven with electricity power. After the oil oven reach to preset temperature, the reactors with sludge were put into the hot oil oven. Temperature of the sludge in the reactors was monitored by a thermocouple. After sludge reach to preset temperature the hydrothermal reaction start. Sludge dewater ability of hydrothermal treatment at different temperature and heating time was evaluated used a belt press. The hydrothermal treated sludge was dewatered at 0.6 Mpa for 20 min through belt press. Water content of dewatered hydrothermal treated sludge was tested using drying method at 105°C for 24 hours.

2.2. Dewaterability of Hydrothermal Treated Sludge

The hydrothermal reaction temperature and reaction time are the most important parameters that determined the effect of treated dewaterability and biodegradation. In this paper, temperature from 145°C to 180°C and reaction time from 15 min to 90 min were investigated. Figure 1 shows the moisture content of hydrothermal treated sludge at different temperature. Untreated sludge means the raw sludge collected from local sewage works. Those sludges water content is about 80%. After hydrothermal treatment the moisture content dropped to about 50%. With the increasing of temperature, the filter pressed sludge cake was drier. Figure 2 shows the moisture content of hydrothermal treated sludge. Compared with temperature, moisture content of sludge was not so sensitive to reaction time. For 15 min reaction, moisture content of treated sludge was 47.85%, and this value reduced to 41.1% for 90 min.

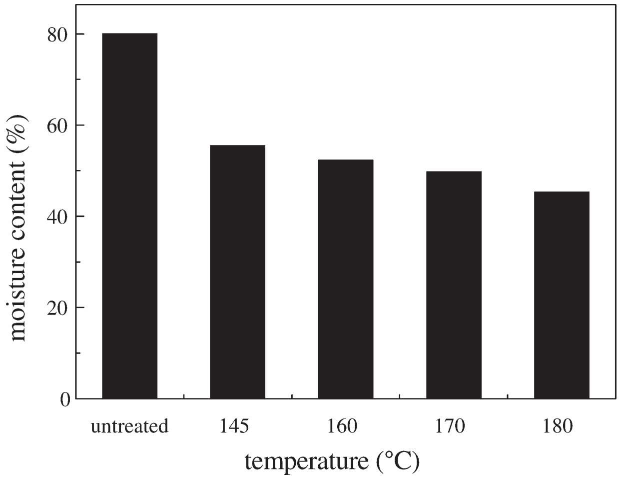

***Figure 1.** Water content at different temperature (30 min).*

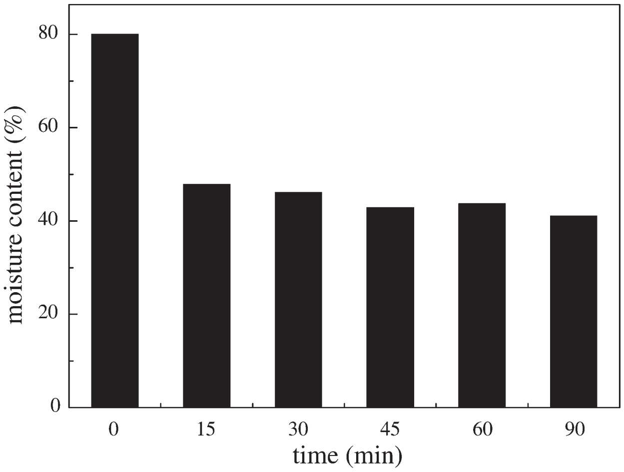

***Figure 2.** Water content at different holding time (170°C).*

3. FULL SCALE PROJECT OF HYDROTHERMAL TREATMENT

The hydrothermal process was also studied in a sludge treatment field in China. The first pilot plant was built in 2002 at the Qinghe WWTP in Beijing and used a low-pressure oxidation process. In 2008, an innovative full sacle project, based on a thermal hydrolysis process, was developed by author's group in Dongguan city, with a capacity of 30 tons of dewatered sewage sludge per day. The sewage works treated mixed waste water containing industry waste water and municipal sewage. This process allowed an increased sludge feed concentration, which resulted in an energy savings in the sludge heating process. Kepp reported that thermal hydrolysis process was effective to stabilize sludge under three year operation of a full scale project.

Figure 3 give the full scale project process of hydrothermal treatment. The sludge was first pumped into homogeneous tank. In the tank, sludge was stirred to get uniform particle size. Then, sludge from homogeneous tank was pumped into pulper reactor. In this reactor

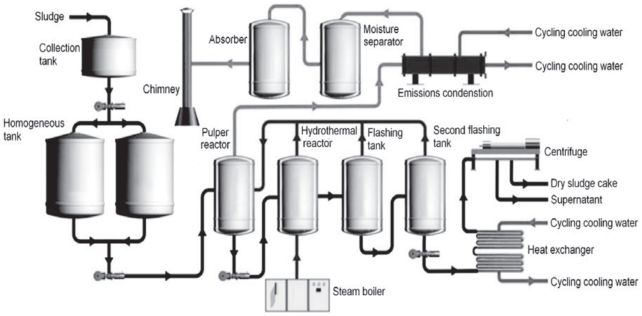

Figure 3. *Full scale project process of hydrothermal treatment.*

sludge was heated to nearly 90°C for 40–60 min with vapor from the back flashing tank. Those preheated sludge was transferred into hydrothermal tank with screw pump. In hydrothermal tank sludge was heated to 170–180°C and retained for 40–60min at this temperature. The pressure of hydrothermal tank was the saturated steam pressure of liquid sludge. The heating steam was generated from an electricity boiler. After hydrothermal reaction sludge was moved into flashing tank with a pressure drop. The vapor produced from the flashing tank was transported to the pulper reactor through pipes. Finally, hydrothermal treated sludge goes to centrifuge. Dry sludge cake was used for following treatment and disposal.

Table 2 gives the characteristics of sludge cake before and after hydrothermal treatment. It can be seen that moisture content of sludge reduced from 90.3% to 54.66%. The dewaterability of sludge improved greatly. Considering the latest national standard for sludge landfill together with municipal solid waste, sludge only with moisture content less than 60% was allowed. So, at the most adverse conditions, hydrothermal technology provide a way for sludge final disposal. During hydrothermal reaction, organic matters liquefied and hydrolysis into low molecular weight materials. Volatile matter of sludge reduced from 42.56% to 38.45% after hydrothermal treatment. The dissolved volatile matter move into aqueous that increased the COD concentration of supernatant of dewatered hydrothermal treated sludge. The path way of organic hydrolysis was given by brooks. Under the brooks' principle, carbohydrate of sludge molecular was broken down to smaller molecular weight polysaccharides and possibly even to simple sugars. Free amino acids and amino acids are the main components of protein in sludge. Those amino acids form a series of saturated and unsaturated acid, ammonia and some carbon dioxide by heating. Lipids of sludge may hydrolysis into glycerol and then into final products such as palmitic acid, stearic acid and oleic acid. Acid reduced the pH value of treated sludge.

Table 2. Characteristics of Sludge Cake Before and After Hydrothermal Treatment.

Freezing Speed	Untreated Sludge	Treated Sludge	Unit
Moisture content	90.3	54.66	%
Volatile matter	42.56	38.45	%
pH	5.57	4.88	%
Ash	42.56	50.62	%
Fixed carbon	2.75	0.32	%
Total phosphor (P_2O_5)	3.117	3.97	%
Chlorine	0.103	0.04	%
Total nitrogen	3.00	3.32	%
Organics	22.5	23.20	%
Heat value (dry sludge)	11616	9998	kj/kg
O	25.17	19.87	%
S	0.505	0.37	%
Cu	311	318	mg/kg
Zn	305	416	mg/kg
Ni	35.3	95.4	mg/kg
Total K	0.580	0.80	mg/kg
Total Cd	0.13	1.66	mg/kg
Total Cr	107	307	mg/kg
Total As	8.8	6.4	mg/kg
Total Hg	1.59	0.08	mg/kg

4. CONCLUSIONS

Treatment and disposal is important for environmental protection and municipal solid waste management. High water content brings difficulties for sludge treatment process. Traditional technologies can not treat sludge with 80% water content. National standard for sludge treatment and disposal methods limit the use of traditional techniques. Cell structure makes it difficult to remove more water from sludge cake by mechanical dewatering unit. Hydrothermal treatment is effective to reduce water content of sludge cake. The results of hydrothermal full scale project operation provide that this technology could produce dry cake that could be disposed more readily.

ACKNOWLEDGEMENTS

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Improving Guidelines for the Plant Available Nitrogen Value of Biosolids from Wastewater Treatment

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ABSTRACT: It is important to accurately quantify the amount of plant available nitrogen (PAN) in land applied biosolids to achieve maximum crop production, yet reduce the risk of pollution through nitrate leaching and gaseous losses following excess applications or incorrect management. For this reason, biosolids application rates are frequently determined by the PAN content based on the mineralisable portion of the organic nitrogen (N). The findings of this field experiment, conducted in an acidic sand under a Mediterranean-type climate in Western Australia, demonstrate that the PAN of biosolids relative to an inorganic source of N is dependent on the treatment method of the biosolids, with greater PAN from lime amended biosolids (65.1%) and alum-dosed biosolids (63.4%) in comparison to dewatered biosolids cake (39.4%). The amount of organic N that becomes available in the first season may be 2–3 times greater than the current estimate of 20% used to calculate application rates in Western Australia. It is suggested that current biosolids guidelines in Australia require further investigation to maximise crop yield and economic benefits of biosolids application and prevent pollution from leaching of excess mineral N.

1. INTRODUCTION

SEWAGE sludge is typically stabilised and dewatered to reduce odour and pathogen content and produce 'biosolids', which are less bulky and more acceptable for land application. To enable sustainable, environmentally sound and economically beneficial land application it is important to apply biosolids at a safe rate to maximise benefits to crop growth, whilst preventing over-applications and reducing the risk of leaching or runoff of nutrients and pollution of waterways. Furthermore, it is important to manage applications of biosolids correctly to reduce gaseous losses of nitrogen (N) by ammonia (NH_3) volatilisation or nitrous oxide (N_2O), which is 296 times more powerful than CO_2 as a greenhouse gas (IPPC, 2001).

The majority of N in biosolids is present as organic forms and must be mineralised before it is available for crop uptake. The proportion of biosolids organic N that is mineralised and the rate at which it becomes available is dependent on several factors including environmental conditions such as soil temperature (Smith *et al.*, 1998a;b;c; Honeycutt *et al.*, 1999), soil moisture (Sierra *et al.*, 2001; Rahman and Rashid, 2002; Wennman and Kätterer, 2006) and pH (Tester *et al.*, 1977) and soil type (Tester *et al.*, 1977; Smith *et al.*, 1998a; Hernandez *et al.*, 2002; Breedon *et al.*, 2003). The method of stabilisation used to produce the biosolids will also affect the availability of N and other nutrients (Smith *et al.*, 1998a; Morris *et al.*, 2003; Pu *et al.*, 2008). For example, anaerobic digestion tends to produce a more stable product than aerobic digestion, with a smaller fraction of mineralisable organic N, as a result of more complete biological degradation during treatment (Hérnandez *et al.*, 2002; Morris *et al.*, 2003; Pu *et al.*, 2008). Heat drying or lime treatment produce a biosolids product with a lower total N content due to loss of ammonia by volatilisation during the treatment process (Cogger *et al.*, 1999; Smith *et al.*, 2002; Morris *et al.*, 2003; Cogger *et al.*, 2004; Corrêa *et al.*, 2004; O'Connor *et al.*, 2004). Biosolids application rates are frequently determined by the N content, specifically, the plant available N (PAN) content should match crop requirements in the

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year of application and in subsequent years residual N from biosolids application should be taken into account. For example, in the UK, in 'Nitrogen Vulnerable Zones' (NVZs), which have been designated in areas at risk of pollution from nitrate leaching, there is a farm-based limit for total N applications of 170 kg ha^{-1}, and plant available N applications in organic wastes must not exceed crop requirements. In Australia, the rate of agricultural application of biosolids is generally determined by the 'Nitrogen Limited Biosolids Application Rate' or NLBAR, where the amount of plant available N (PAN) applied in the biosolids must match the crop N requirement in the year of application. In Western Australia this is calculated assuming 50% volatilisation of the ammonium N (NH_4-N) content and 20% mineralisation of the organic N content in the first growing season after application (DEP, WRC and DOH, 2002), and is loosely based on assumptions from research on biosolids mineralisation carried out in temperate regions. The aim of this field experiment was to accurately quantify the amount of plant available biosolids N in acidic sand under Mediterranean-type climatic conditions, relative to urea. From these results an estimate of the proportion of organic N that is mineralised during the first growing season, typical of Western Australian conditions, can be calculated.

2. METHODS

2.1. Study Site

The field experimental site was established at Goomalling, Western Australia (31.19159°S, 116.57083°E) on acidic dark yellowish-brown sand (10YR 4/4 as per Munsell). The region has a Mediterranean-type climate with cool, wet winters and hot, dry summers, and average rainfall of 302 mm over the growing season (April–October). Total rainfall over the 2008 growing season (April-October 2008) was 281 mm. Some properties of the < 2 mm fraction in the surface soil (0–10 cm) are as follows: 97.0% sand, 1.0% silt, 2.0% clay; pH 6.0 (0.01M CaCl2;1:5); 6 mS m^{-1} EC (1:5); 0.79% organic carbon (W/B); 0.066% total N; 97 mg kg^{-1} total P; 16 mg kg^{-1} bicarbonate extractable P; –0.2 mL g^{-1} P Retention Index; 18 mg kg^{-1} bicarbonate extractable K; 3.79 cmol(+) kg^{-1} total exchangeable cations (Ca, Mg, Na, K). All analyses were performed by the Chemistry Centre of Western Australia, East Perth, which is accredited by the National Association of Testing Authorities (NATA).

2.2. Biosolids

The biosolids investigated were lime amended biosolids (LAB) from Subiaco Wastewater Treatment Plant (WWTP), dewatered anaerobically digested biosolids cake (DBC) from Beenyup WWTP and alum biosolids (AB) from Kemerton WWTP, which uses alum as a P removal mechanism in the treatment process; these are representative of the biosolids types produced in Western Australia (Pritchard *et al.*, 2009). The dry solids (DS) and total, mineral and organic N concentrations of each biosolids type are shown in Table 1.

Dewatered biosolids cake (DBC) and AB had the greatest total N contents of 5.2% and 5.0% respectively compared to the lower value of 3.7% total N in LAB, due to dilution of the total N content by addition of lime during the treatment process. Dewatered biosolids cake (DBC) had the greatest mineral N component, equivalent to 10.4% total N, compared to only 5.0% and 1.2% in AB and LAB, respectively. This is because DBC had undergone anaerobic degradation of the organic matter during the treatment process, and subsequent conversion of organic N to NH_4-N. Alum biosolids (AB) are digested aerobically, a less complete degradation process and LAB is raw undigested sewage sludge with lime added to reduce the pathogen content. The DBC used in this experiment had been stockpiled for 2 weeks prior to setting up the experiment, whereas the AB and LAB were applied fresh. The DS content of the DBC increased from 25% to 32% during this time. However, this may be typical of the product used in land application, which is generally stockpiled for up to 30 days before land application.

Table 1. Dry solids (DS) Content and Total, Mineral and Organic N Concentration in DBC (mesophilic anaerobically digested dewatered biosolids cake), AB (alum biosolids) and LAB (lime amended biosolids) Applied in the Field Experiment at Goomalling, Western Australia.

Biosolids Type	DBC	AB	LAB
DS (%)	32.0	14.0	34.0
Total N (%)[a]	5.20	5.00	3.70
NH_4-N (mg kg^{-1})[a]	5400	2500	350
NO_3-N (mg kg^{-1})[a]	6	11	70
NO_2-N (mg kg^{-1})[a]	< 5	< 5	37
Mineral N (mg kg^{-1})[a]	5406	2511	457
Mineral N (% total N)	10.4	5.02	1.24
Organic N (% total N)	89.6	95.0	98.8
PAN[b] (% total N)	23.1	21.5	20.5

[a] Dry solids (DS) basis

[b] Estimated available N calculated according to NLBAR formula ([NH_4 – N × 0.5] + [NO_3-N] + [NO_2-N] + [organic N × 0.2])

2.3. Experimental Design

The field experiment used a systematic design (Cleaver *et al.*, 1970; Smith and Hadley, 1988; Smith *et al.*, 2002; Morris *et al.*, 2003) arranged as three replicate blocks each with 4, 1.2 m × 12 m main plots. The main plots were divided into 6 subplots, each 2.4 m^2. Urea was used as a readily available source of N as a reference comparison. The biosolids were applied at rates of 0, 2.5, 5, 7.5, 10 and 15 t DS ha^{-1} and urea was applied at rates of 0, 50, 100, 150, 200 and 250 kg N ha^{-1}, in a systematic gradient of application. The direction of the gradient was randomised between each main plot. Basal dressings of all other nutrients (Super Copper Zinc Moly at 120 kg ha^{-1}; Muriate of Potash at 120 kg ha^{-1}) were applied at seeding so that the response to N alone could be quantified. A crop of ryegrass (*Lolium hybrid* cv. Safeguard) was sown on 7/6/08 as an indicator crop as it is effective at recovering N. The biosolids and urea were applied to the soil surface by hand, and immediately incorporated by raking, and further incorporated at seeding using a 12-row disc combine. To compensate for atypically low rainfall over the course of the experiment, the crop was irrigated on an approximately weekly basis (a total of 88 mm was applied). The ryegrass was cut by hand to a height of 2 cm from the centre 1.5 m^2 of each subplot at 95 and 123 days after sowing (DAS). Fresh weights were measured and plant tissue was dried to a constant mass at 70°C in a forced-air oven to determine dry matter yield. The dried material was ground to < 2 mm and total N was analysed by the Chemistry Centre, Western Australia using a Leco N analyser. Yield response of ryegrass to applied N is considered to be linear between applications of 0–300 kg N ha^{-1} (Whitehead, 1995), it was therefore appropriate to consider the linear response to N applied in the biosolids and urea. Linear regression analyses of fresh yield relative to rate of total N application in each biosolids or urea treatment were performed. Linear regression coefficients for the biosolids treatments were expressed as a proportion of the regression coefficient for urea to obtain relative PAN values, and then was repeated for dry yield and N offtake measurements.

At 178 DAS, following the final harvest, soil samples were taken at depths of 0–10 cm, 10–20 cm and 20–30 cm from selected subplots. The rates sampled were 0, 2.5, 7.5 and 15 t DS ha^{-1}, in the biosolids treatments and 0, 50, 150 and 250 kg N ha^{-1} in the urea treatments. Samples from nil control subplots (0 t N ha^{-1}/0 kg N ha^{-1}) were pooled for each block. Soil samples were frozen immediately at −19°C on return to the laboratory, prior to analysis for NH_4-N and NO_3-N.

3. RESULTS AND DISCUSSION

3.1. Crop Response to Biosolids and Urea

There was a highly significant relationship ($P < 0.001$) between rate of N application and crop response, as measured by fresh yield, dry yield and N offtake. The linear regression coefficients and R^2 values for harvests 1 and 2 are summarised in Table 2. The cumulative response to urea or biosolids application is shown in Figures 1–3.

3.2. Plant Available Nitrogen of Biosolids Relative to Urea

Plant Available Nitrogen (PAN) values were calculated for each biosolids type relative to urea as an inorganic source of N, and are shown in Table 3.

Plant Available Nitrogen content of all biosolids sources were lower than urea at each harvest. In the majority of cases PAN calculated from the different measures of crop response (fresh yield, dry yield and N offtake) were similar. However, in the first harvest, PAN values for AB and LAB estimated using N offtakes were greater than PAN estimated from yield values. This is because in these treatments there was a higher N concentration relative to the plant dry matter. This may indicate that the ryegrass on the AB and LAB treatments was at a different stage of maturity than the

Table 2. Summary Table of Linear Regression Coefficients (slope) and R^2 Values for Urea, Mesophilic Anaerobically Digested Biosolids (DBC), Alum-biosolids (AB) and Lime Amended Biosolids (LAB) at Each Harvest.

			Urea	DBC	AB	LAB
Harvest 1	Fresh yield	slope	10.1	5.16	7.07	6.98
		R^2	0.91	0.94	0.79	0.89
	DM yield	slope	2.56	1.2	1.53	1.49
		R^2	0.9	0.94	0.79	0.89
	N offtake	slope	0.41	0.02	0.04	0.03
		R^2	0.67	0.94	0.9	0.9
Harvest 2	Fresh yield	slope	5.97	1.62	2.64	3.65
		R^2	0.67	0.7	0.75	0.82
	DM yield	slope	2.2	0.6	0.97	1.3
		R^2	0.75	0.71	0.71	0.82
	N offtake	slope	0.066	0.015	0.037	0.038
		R^2	0.78	0.78	0.911	0.87

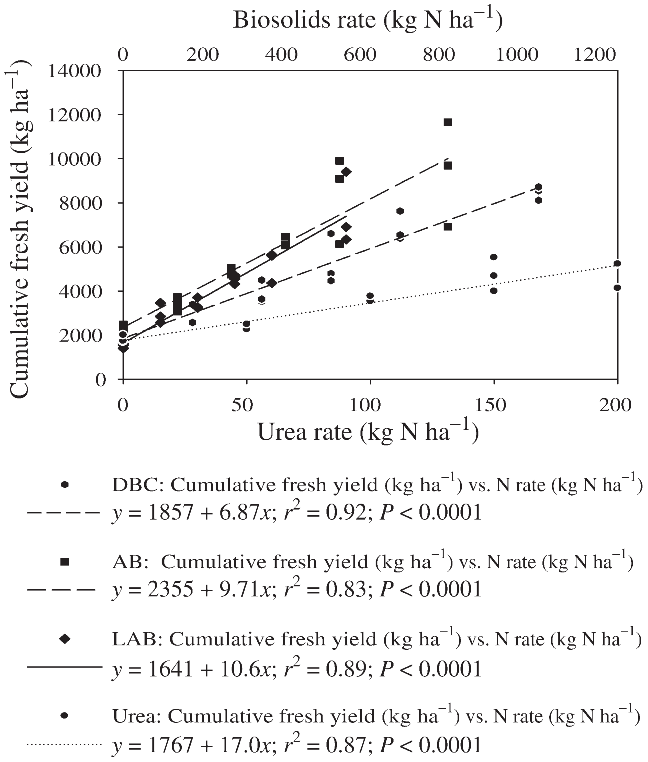

***Figure 1.** Cumulative fresh yield (kg ha^{-1}) of ryegrass in relation to rate of total N application in biosolids (top axis) or urea (bottom axis).*

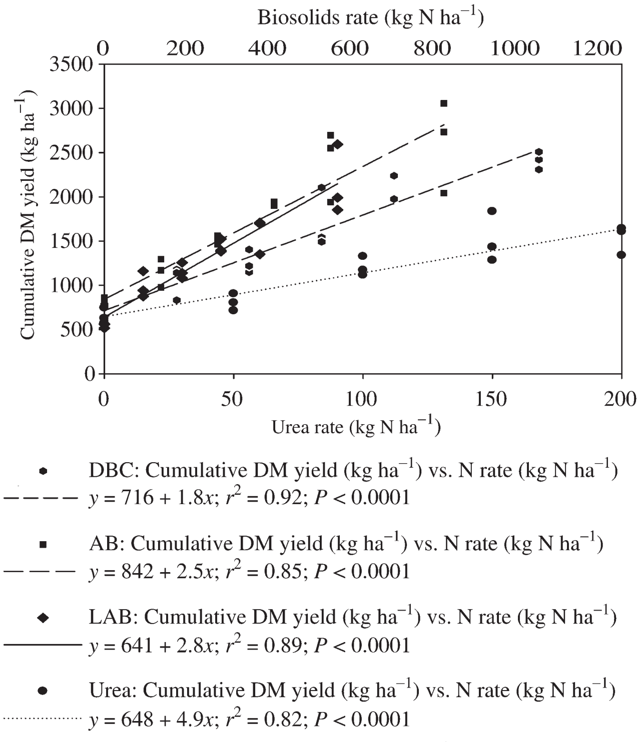

***Figure 2.** Cumulative dry matter yield (kg ha^{-1}) of ryegrass in relation to rate of total N application in biosolids (top axis) or urea (bottom axis).*

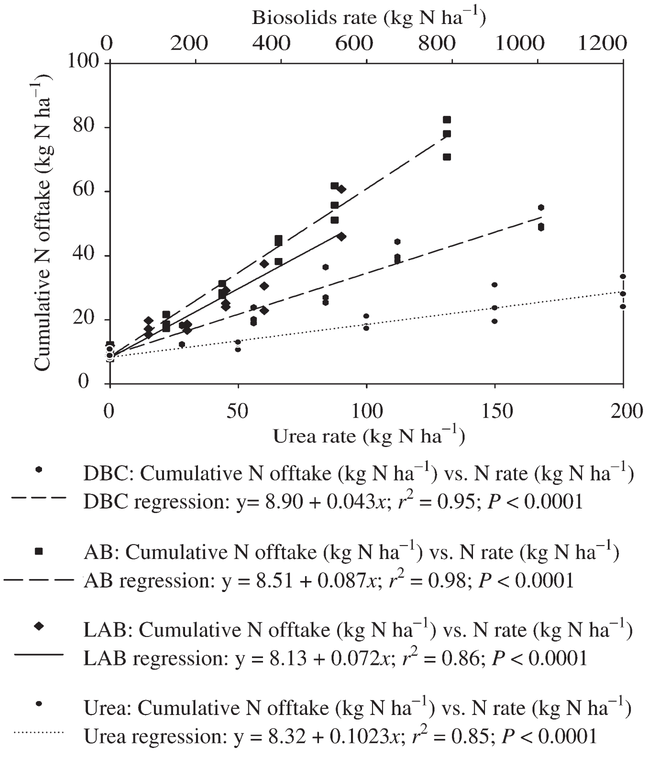

***Figure 3.** Cumulative N offtake (kg N ha^{-1}) of ryegrass in relation to rate of total N application in biosolids (top axis) or urea (bottom axis).*

ryegrass on DBC treatments. This may be due to in timing of availability of N from AB and LAB, which may not be as rapidly released in these materials, resulting in less rapid increases in yield. The PAN content of DBC was lower in the second harvest than the first harvest, indicating that the available N was rapidly mineralised at the start of the season for this biosolids type. Alternatively, it may be an effect of stockpiling DBC for 2 weeks, during which time a proportion of the mineralisable N would have been released, and N would also have been lost due to NH_3 volatilisation.

Table 3. Plant Available Nitrogen Values of Biosolids for Each Measure of Crop Response (fresh yield, dry yield, N offtake) Relative to Urea Based on Comparison of Linear Regression Coefficients.

		DBC	AB	LAB
Harvest 1	Fresh	0.51	0.70	0.69
	Dry	0.47	0.60	0.58
	N offtake	0.55	0.94	0.77
Harvest 2	Fresh	0.27	0.44	0.61
	Dry	0.27	0.44	0.59
	N offtake	0.22	0.57	0.58
Cumulative	Fresh	0.40	0.57	0.63
	Dry	0.36	0.51	0.56
	N offtake	0.42	0.82	0.76

The PAN contents for LAB and AB were similar in the first and second harvests indicating that N continued to be mineralised over the season. Mean relative PAN values for DBC, AB and LAB, calculated from the cumulative crop response over the season compared to urea, were 39.4%, 63.4% and 65.1% respectively (Table 4).

3.3. The Proportion of Biosolids Organic N Mineralised

The proportion of organic N mineralised in biosolids-amended soil in this experiment was estimated by subtracting the initial amount of biosolids available N from the PAN values of the biosolids relative to urea. The majority of N in the biosolids, 90–99% (Table 4), was in organic forms so these values were approximately equal to the proportion of organic N mineralised from each biosolids type, estimated from the PAN values as 38.1%, 64.1% and 65.1% for DBC, AB and LAB, respectively.

The initial amount of biosolids N available was estimated assuming that 50% of the NH_4-N was available, and 50% was lost by NH_3 volatilisation following spreading to the soil surface. This assumption requires validation under Western Australian conditions and is an area that requires further research.

The mineralisation of organic N in biosolids calculated from this experiment was appreciably higher than the estimate of 20% that is currently used in NLBAR calculations, with values for DBC, AB and LAB up to 18%, 44% and 45% greater, respectively. This is consistent with findings in Queensland, where there is a sub-tropical climate, on a clay loam, which demonstrated N mineralisation of between 43–59% from anaerobic and aerobic biosolids (Pu *et al.*, 2008). An estimated 34% of organic N was mineralised from DBC in silty clay in a field trial with turf in New South Wales (Eldridge *et al.*, 2008) similar to the value of 38% obtained for DBC in this experiment. Lime amended biosolids (LAB) had not undergone a biological digestion process, as it was raw sewage sludge treated with lime to raise the pH and to destroy pathogens, whereas AB had undergone aerobic digestion. The differences in treatment process may explain the greater PAN of these two materials in comparison to DBC, which had been digested anaerobically and therefore had a more stable organic N fraction, and was mineralised to a lesser extent when added to the soil. The DBC would also have undergone further stabilisation during the two week period in which it was stockpiled as there would have been further mineralisation of the organic N fraction during this time. However, a greater fraction of mineralisable organic N in aerobically digested biosolids as compared to anaerobically digested biosolids has been reported elsewhere (Hérnandez *et al.*, 2002; Morris *et al.*, 2003; Pu *et al.*, 2008). These results and ours indicate that it is not appropriate to use the same estimate of the available fraction of organic N for biosolids undergoing different treatment processes.

Table 4. Estimated Mineralised N (% organic N) Calculated from Mean Cumulative PAN Values Relative to Urea.

	DBC	AB	LAB
PAN (% total N)[a]	39.4	63.4	65.1
Organic N (% total N)	89.6	95	98.8
Initial available N (% total N)[b]	5.2	2.52	0.76
Mineralised N (% organic N)[c]	38.1	64.1	65.1

[a] Calculated from cumulative response of ryegrass to biosolids application relative to cumulative response to urea (mean of fresh yield, dry yield and N offtake).

[b] $(NH_4 - N \times 0.5) + (NO_3\text{-}N) + (NO_2\text{-}N)$

[c] $[(PAN - \text{initial available N})/\text{organic N}] \times 100$

This field experiment in Western Australia was conducted following the same systematic design as Smith *et al.* (2002) and Morris *et al.* (2003), who conducted a three year program of field trials to calculate the PAN of biosolids relative to inorganic fertiliser N in the UK in a cooler, temperate climate. The authors reported relative PAN values of approximately 30% for DBC and 37% for LAB in all three years of investigation. The comparatively greater mineralisation of biosolids N found in Western Australia was presumably due to the warmer soil temperature.

It is suggested that current guidelines require modification, to account for higher proportions of PAN obtained than was previously assumed. However, it is also necessary to consider the rate at which mineral N becomes available, which is dependent on environmental factors such as soil temperature and moisture (Smith *et al.*, 1998a;b;c; Honeycutt *et al.*, 2001; Sierra *et al.*, 2001; Rahman and Rashid, 2002; Wennman and Kätterer, 2006). The experiment was irrigated to compensate for low rainfall at the start of the growing season, however, under normal growing conditions a dry start to the season may result in PAN limiting crop growth in biosolids-amended soil. A possible approach would be to apply biosolids at a lower rate of PAN than required and top up with mineral fertiliser N. This is the best practice recommended for use of organic manures in the UK (MAFF, 2000), and would ensure that there is sufficient N at the start of the growing season, particularly given low residual N values in Western Australian sands. The gradual release of biosolids organic N over the season may then be an advantage as it would reduce risk of leaching of excess NO_3-N during a rainfall event.

3.4. Soil Mineral N

Following the final harvest, soil samples were collected from 0–10 cm, 10–20 cm and 20–30 cm for mineral N analysis (Table 5). In the 10–20 and 20–30 cm profiles, very little mineral N was measured, < 1 mg kg^{-1} NH_4-N and < 3 mg kg^{-1} NO_3-N. This indicated there may have been little mobility of mineral N below the incorporation depth of the biosolids. The results were, therefore, expressed as the total NH_4-N or NO_3-N in the 0–30 cm profile. Soil mineral N concentrations increased with increasing rate of application of urea or biosolids. The results demonstrated that at 7.5 t DS ha^{-1}, which is the approximate rate at which biosolids are currently applied, between 14–37 mg kg^{-1} mineral N may remain in the soil at the end of the season in this soil type. This is therefore at risk of leaching during a rainfall event.

The recommended loading rates for biosolids in Western Australia may need to be reviewed to allow for higher concentrations of PAN than previously assumed, and investigate the risk of nitrate leaching due to over-application. This would reduce the potential for pollution of waterways and improve the use of biosolids as a replacement for inorganic fertiliser N.

Table 5. Soil Mineral N Concentrations in Nil Control and Biosolids-amended Soil at 178 DAS (0–30 cm) (dry soil basis).

	Rate	PAN applied (kg ha^{-1})[a]	NH_4-N (mg kg^{-1}) (± S.E.)	NO_3-N (mg kg^{-1}) (± S.E.)
Nil Control	0		0 1 (± 0.2)	4 (± 0.7)
Urea (kg N ha^{-1})	50		2 (± 0.3)	3 (± 0.2)
	150		2 (± 0.7)	5 (± 1.3)
	250		4 (± 1.5)	7 (± 1.2)
DBC (t DS ha^{-1})	2.5	66 (39)	2 (± 0.2)	5 (± 0.2)
	7.5	199 (116)	9 (± 1.6)	11 (± 0.3)
	15	397 (223)	18 (± 3.5)	16 (± 1.2)
AB (t DS ha^{-1})	2.5	83 (28)	1 (± 0.2)	2 (± 0.4)
	7.5	250 (85)	26 (± 11.4)	11 (± 0.7)
	15	499 (169)	9 (± 0.6)	14 (± 1.6)
LAB (t DS ha^{-1})	2.5	59 (18)	1 (± 0.2)	5 (± 0.4)
	7.5	176 (55)	4 (± 0.4)	10 (± 1.0)
	15	352 (111)	3 (± 0.5)	14 (± 1.1)

[a] Rate of Plant available N (PAN) applied in biosolids assuming mineralisation of organic N of 38.1%, 64.1% and 65.1% for DBC, AB and LAB respectively. Figures in parenthesis are rates of PAN applied assuming 20% mineralisation of organic N. Both PAN values were calculated assuming volatilisation of 50% of the NH_4-N applied in the biosolids.

Nitrogen requirements in the second and subsequent growing seasons following biosolids application need to be calculated to take into account the residual value of the biosolids, as there may be further mineralisation of organic N (Antolín *et al.*, 2005; Pritchard and Collins, 2006). During the Australian National Biosolids Resarch Project (NBRP), Pritchard and Collins (2006) found the residual fertiliser value of DBC applied at approximately 7 t DS ha^{-1} to a wheat and canola crop, continued into the third growing season following application. Grain yield of canola applied at the NLBAR (7 t DS ha^{-1}) remained statistically similar to grain yield on a freshly applied inorganic fertiliser control until year 2, and at another field site wheat on the 7 t DS ha^{-1} DBC treatment was no different to the freshly applied inorganic fertiliser control in years 2 and 3 following application.

As a consequence of the findings of this experiment, it is necessary to examine existing data on nutrient release and uptake in wheat and canola obtained during three years of research trials in Western Australia as part of the NBRP, to re-evaluate suitable nutrient loading rates from biosolids.

4. CONCLUSIONS

Mineralisation of organic N from biosolids in the first growing season at this site in Western Australia was 2–3 times greater than the currently assumed value of 20% and was greater for biosolids which had not been treated to stabilise their organic matter content. Therefore, current guidelines for biosolids (DEP *et al.*, 2002) may require modification to prevent the inadvertent over application of N. This will maximise the economic benefit and reduce the loss of nitrate by leaching and the risk of pollution. It is tentatively suggested that a value of 40% mineralisation of organic N is used for DBC, and 65% for AB and LAB; however, this may require validation for different crop and soil types. The rate of N mineralisation should be taken into account to ensure there is sufficient N for crop growth at the start of the growing season in biosolids-amended soil. Further research is also required to investigate gaseous losses of N from biosolids-treated soil through ammonia volatilisation and denitrification.

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Investigation and Analysis on the Treatment and Disposal of Sewage Sludge in China

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ABSTRACT: The paper simply introduces the survey on sewage sludge disposal and treatment in China, the policy in relation to sewage sludge in China and the investigation on development of sewage sludge treatment and disposal technology in China.

1. SURVEY ON SEWAGE SLUDGE TREATMENT AND DISPOSAL IN CHINA

RECENTLY, municipal wastewater treatment plants in China have sharply been increased. According to incomplete investigation, by the end of 2008, the number of established municipal wastewater treatment plants were up to 1320, its wastewater treatment capacity was amounted to $9725 \times 10^4 m^3/d$. And there is around 890 municipal wastewater treatment plants still under constructing, of which the treatment capacity amounts to $3639 \times 10^4 m^3/d$. Meanwhile, a series of serious water environmental pollution event in China promoted the construction of more municipal wastewater treatment plants, as well as more strict standards for discharge (upgrading class I-B to class I-A). Because of the more strict standard, the amount of wastewater treatment, sewage sludge yield also sharply increased. If we estimated according to the ratio 1.5 ton dry sludge yield from every 10,000 m^3 treated wastewater, the amount of sewage sludge 532×10^4 tDS/a (2662×10^4 tWS/a, 80% water content) were conduced in China every year. By the year of 2010, this number will climbed to 570×10^4 tDS/a (2850×10^4 tWS/a. Consequently, sewage sludge would be a new pollution source to cities and villages.

Over years, because of the problems such as: overlook of the importance of treatment and disposal of sewage sludge, shortage of treatment investment, lag in technology, absence of policy in China, frequently environmental pollution crisis were caused.

Investigation of the treatment and disposal of sewage sludge showed that majority of the municipal wastewater treatment plants only treated with the sewage sludge simply, disorderly piled it and landfilled it mixing with other municipal solid waste. The two main disposal styles applied to disposed sewage sludge were the dewatering, and landfilling sludge, or agriculture land application; landfilling style took up 31%, agriculture land application took up 44.8%, and others 10.5% (contain incineration). The main landfilling style was mixing sewage sludge with the municipal solid waste and the amount of sewage sludge landfilled was 10% of the total waste amount. There were less than a quarter of the total municipal wastewater treatment plants had stablilization treatment facilities of sewage sludge , the plants which had well-operated treatment process and supporting facilities was not up to 1/10 of total plants, only few facilities can operated without failure. Even though in Yangzi delta district, the most developed region in China, the sewage sludge in all municipal wastewater treatment plants was only dealt with dewatering, dewatered sludge in 60% plants can't reach water content of 80% for the standard requirement.

2. THE POLICY IN RELATION TO SEWAGE SLUDGE IN CHINA

The success experience of developed countries shows that development and application of environmental technology cannot only be driven by market, but also required relative law, economic policies, advanced technology, and indispensable administrative means together to work effectively. Therefore, Ministry of Environmental Protection of the People's Republic of

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China learns success experience from USA and EU and starts to set up the Environmental Technology Management System of China in Aug, 2007. The system is based on systemic and scientific research and assessment on the environmental pollution prevention and control technologies. The core element based on the Best Available Technology Guidelines and the Engineering Design Specification, and through established and issued a series of guidance of Environmental Technology, which will provide technical support for each environment management objective setting and environment management control system application.

In order to boost development of the sewage sludge treatment and disposal, the Ministry of Environmental Protection was about to declare a series documents of sewage sludge, i.e "Best Available Techniques Directive for Treatment and Disposal of Sewage Sludge from Municipal Wastewater Treatment Plant", and "Engineering Design Specification for Treatment and Disposal of Sewage Sludge", and "The Technology Policy of Pollution Prevention and Control for Treatment and Disposal of Sewage Sludge". These documents direct and regular sewage sludge treatment and disposal from Technology Guideline and Engineering Design Specification and Technology Policy. These documents keep to the principle that is Source Control, and the Whole Process Control, and Energy Conservation and Emission reducing, and Recycling Economic, Adjust Measures to Local Conditions, and "Three Concurrent". Simultaneity, they determine the objective of sewage sludge treatment and disposal is "Reducing, stabilizing, harmless, the final safe and environment friendly disposal and comprehensive utilization. These documents together with a series of standards published by Ministry of Housing and Urban-Rural Development form preliminary complete sewage sludge treatment and disposal technology management system in China.

2.1. Best Available Technology Directive

The purpose of implementing the Best Available Pollution Prevention and Control Technology Directives (hereinafter referred to as Directives) is to select effective and executable technologies and pollution prevention approaches to treat and dispose sewage sludge; control and reduce the environment pollution during sewage sludge treatment and disposal, together with available environment management, eliminate pollution and protect environment. The core requirement of the Directive is that require the operator of sewage sludge treatment and disposal facilities should try to select sewage sludge treatment methods and disposal technologies that are consistent with the environment and condition, to ensure the ultimate safe and environmental friendly disposal of sewage sludge.

On the foundation of systematic investigation and scientific assessment, the directive brings up best four available technologies which include anaerobic digestion, high-temperature aerobic composting, land application (include landscaping and soil improvement, excluding agriculture application), and drying-incineration, and further put forward the best pollution prevention and environment management practice of the process from sewage sludge yield to the ultimate safe and environmental friendly disposal and comprehensive utilization.

Contrasting to EU and USA, Chinese BAT's characteristics are:

1. Definition difference. In the definition of EU and USA, best technology is combined with practice, but in the Chinese definition, best available technology is combined with best available management practice.
2. The scope of technology options difference. the scope of technology options for all the world's technology for the European Union and the United States, even if the technology is still in the course of the experiment, but for China, the technology of choice to those who have limited access to the application of domestic environmental technology or management practices, at least the requirements of this technology demonstration project has been to verify. The main purpose of doing so is to prevent, in the current China-related sludge treatment and disposal technology is still in a backward state, if not restricted to a variety of technologies to allow access to the domestic market, thereby enabling China to become a variety of technology abroad Proving Ground .
3. Focused on differences. China's guidelines for best available techniques, in the emphasis on technology, more emphasis on environmental management and related management practices.

2.2. Engineering Design Specification

The purpose of implementing engineering design specification is to guide and standardize the sludge planning, design, environmental impact assessment, construction, inspection, operation, supervision and monitoring of behavior through the sludge generated from the storage, handling, transport, safety and environmental protection to the final disposal of the whole process of the technical requirements, so that control pollution and prevent the environment.

Chinese specification has the following characteristics:

1. The implementation of the principle of non-discriminatory and non-selective. Of all mature technologies may be used to carry out the detailed requirements. However, sludge treatment and disposal in order to comply with the guiding principles and objectives of treatment and disposal, to encourage technological progress, the intention of the specification through the application of process technology and environmental management requirements, design and operating parameters, pollution control and monitoring requirements of the different provisions to encourage or restrict the application of certain technologies, For example, agricultural land use from separated, and through the sludge and its derivatives for agricultural use at the time of the quality standards more stringent requirements, such as the stability of indicators (such as organic matter degradation rate to be (%, etc.), physical indicators (to meet the secondary standards of the odor, etc.), indicators for heavy metal content, soil environmental quality standards, biological indicators, application requirements, environmental pollution control measures and management requirements in order to achieve restrictions on sludge and its derivatives for the purpose of agricultural use.
2. Requirements of sludge production, treatment, disposal and transport units are required to establish a good measurement, monitoring, recording, archiving and reporting system, to establish single-track transit system in conjunction between urban sewage treatment plants, transport units and the receiving unit in order to strengthen the supervision of sludge treatment and disposal.
3. Concerned about the technical requirements, but more concerned with the environmental management elements related to technical requirements.

2.3. The Technical Policy

China's "The Technology Policy of Pollution Prevention and Control for Treatment and Disposal of Sewage Sludge" (for trial implementation) is published by Ministry of Environmental Protection and Ministry of Housing and Urban-Rural Development together, considering the needs of both the functions of the department, from the sludge generated, stored, handling, transportation and final disposal of the whole process of management and technical aspects of the selection requirements..

The policy bring forward clearly that the sewage sludge treatment and disposal is an importance component of municipal wastewater treatment system(MWTS), and the local government is to deal with responsibility for planning and construction of sewage sludge treatment and disposal facilities, and the planning of the sewage sludge treatment and disposal must be incorporated into the national and local MWTS construction planning, Sludge treatment and disposal facilities and sewage treatment facilities should be at the same time planning, while building and at the same time put into operation. The sewage sludge treatment technology options must be consistent with the requirement of sewage sludge disposal, not require the project will be not able to be accepted. The policy recommend that every city shall determine the distribution and scale of the sewage sludge treatment and disposal facilities in accordance with its own region characteristics and local conditions, such as sewage sludge yield, to encourage the relative concentration of settings.

The policy require sludge treatment and disposal must be qualified by the operating units, through establishing single-track transit system in conjunction between urban sewage treatment plants, transport units and the receiving unit and a complete manifest of the detection, recording, archiving and reporting system, and commission qualified third parties with relevant agencies to regularly monitor emissions during the treatment and disposal of sludge and to assess changes in environmental quality caused by the treatment and disposal of sludge, so that the relevant national and local departments can be in charge of strengthening supervision and management of sludge treatment and disposal facilities planning , construction and operation.

The policy made the first attempt to bring forward that the country shall set up complete investment and financing system of sewage sludge treatment and disposal. The policy clearly recommend that the government at all levels must gather sewage sludge treatment and disposal cost into wastewater treatment fee, increase captial investment, improve the level of sewage treatment fees, support the provisions of financial subsidies tax incentives and government procurement policies to guarantee adequate funding of sludge treatment and disposal. The policy require state and local governments to establish and improve the diversification of investment and operation mechanism, promote the development of sludge treatment and disposal market and technological innovation.

The policy is firstly attempted to unify a technical route of the sewage sludge treatment and disposal, and to encourage to give priority to the adoption of sludge treatment and disposal technologies which can be reached by energy recovery and material recycling, for instance, the policy require that large and medium-sized sewage treatment plants give priority to the adoption of anaerobic digestion process, and shall be carried out on the comprehensive utilization of biogas generated, small and medium-sized sewage treatment plants give priority to the adoption of high-temperature aerobic composting process, and encourage Sludge and its derivatives which are in consistent with national environmental regulator and standard to be applied to land use, which is composed of greening and soil improvement , or to be used as cover in MSW landfill. The policy clearly put forward that the nation will restrict agriculture use of sludge and gradually prohibit the sludge without inorganic treatment to be carried out of the landfill disposal in MSW landfill, and encourage in some areas to actively promote the use of sludge and its derivatives as raw materials, manufacturing in line with national regulations and standards related to use of building materials, and in developed large and medium-size city the sludge incineration process can be used, but the priority should be make full use of exiting industrial furnace (such as MSW incinerator, coal-fired power plant boilers, cement kiln, etc), followed by the burning of dry and try to avoid the use of high-quality primary energy as heat drying.

3. INVESTIGATION ON DEVELOPMENT OF SEWAGE SLUDGE TREATMENT AND DISPOSAL TECHNOLOGY IN CHINA

In recent years, with emphasis on government spending at all levels of sludge treatment and disposal, the market expanding, funding for research and development increasing continuously in the sludge treatment and disposal equipment, the technology research and equipment development has progressed by leaps and bounds.

Overall, the majority of current research and technological development is also mainly concentrated in the sludge treatment process specific, such as sludge reduction technology of, sludge dewatering technology, sludge stabilization and sludge incineration technology, etc.

3.1. Process Reduction Technology

Keep to Source reducing principal, since 1990's, in order to minimize excess activated sludge produced in the biological treatment process of wastewater, in the world the researcher investigated and developed many physical, chemical and biological technologies, such as uncoupling metabolism, increasing maintenance energy requirement, cryptic growth, microfauna prey, high dissolved oxygen process, membrane bioreactor (MBR), etc. In China, there were some process reduction technologies which were in the stage of demonstration project. In this paper, only do introduce some of the more prominent examples.

3.1.1. The Water Earthworm Biological Digestion Technology

The technology, which is developed by Institute of hydrobiology, Chinese Academy of Sciences, make full use of ecological theory that the consumer (water earthworms) is introduced to a biological chain of the second ring, which is constituted by the producers (excess sludge) and decomposers (microbes), to create a three-ring chain, then creating a simple and efficient artificial ecosystems circulatory system. Collaborative Earthworms and microorganisms water go through the material and energy conversion means to digest the sludge, so as to achieve the purpose of sludge reduction. A certain amount of water earthworms are placed in the aeration tank of modified SBR, AO, oxidation ditch respectively in order to investigate the reduction effects of sewage sludge. The water earthworm has the following features:

- Be fond of serving sewage sludge as the food;
- Can ingest bacteria, organic chipping granule and benthic algae in the sludge;
- Like to stick to surfaces of the filling and grow by cling together closely;
- hermaphroditic and allogamous aquatic annelids
- lives for up to 80 to 120 days

The results from testing in the aeration tank of modified SBR, which sewage treatment capacity was 20,000m^3/d, showed that the annual sludge production was less than 200 tons (WS85%) in two years running, water quality in winter was very poor and produced sludge was more, water quality in summer was better and almost no excess sludge was discharged. In addition, the analysis showed that discharged sludge were mostly composed of inorganic impurities, which heavy metals and phosphate content was very high.

3.1.2. Immerge Membrane Biology Reactor

The technology?which is developed by Beijing University of Technology and is called as immerge membrane biology reactor, relies on reducing microorganisms yield and enhancing endogenous respiration of micro-organisms to promote their own micro-organisms break down. In constant membrane flux and in the running conditions, which are long SRT (up to 500d) and low BOD load (≤ 0.5 kg/m^3), the sludge yield coefficient is only 0.118 kg MLSS/kgCOD, which is obviously lower than that of conventional activated sludge.

3.1.3. The Ultrasonic Pretreatment Technology

In China, some companies and research institutions are studying the use of low frequency ultrasonic (20 kHz~100 kHz) equipment for pre-treatment of sewage sludge, and then the pretreated sludge to anaerobic digestion test. The test result shows that the technology can improve the anaerobic digestion efficiency of sewage sludge, and shorten digest period from one month to 12 days, and raise biomass productive rate, and increase CH_4 content of biomass by 1%~2%, and prevent sludge bulking, and make anaerobic digestion a more stable, and greatly reduce volume and quality of sewage sludge, and heighten mineralization, and kill effectively most of pathogens, and improve the performance of sludge dewatering, and decrease flocculating agent consumption. When the process is used in sludge return system in the municipal wastewater treatment system, it can improve content of degradable organic substance, microbial activity and enzymatic activity.

3.2. New Dewatering Technology and Equipment

Currently, in China, the sludge dewatering technology in common use is the belt press filter technology, which took up about 73.4%, but its treatment effect is not good. For instance, the water content of dewatered sludge is still more than 80% and special energy consumption and flocculant consumption are clearly rather high and malodor pollution problem stand out.

Now in China, there are some MWWT plants, using a new type of sludge dewatering equipment imported from abroad, to obtain a good effect. For example, a sewage treatment plant in Xian, in Shaanxi province, China, using screw press dewaterer made in Japan, reduce the water content of dewatered sludge from 97% to 75%~77%. As well as one municipal wastewater treatment plant in Suzhou, in Jiangsu province, China, using full-automatic diaphragm plate frame press dewaterer made in Anderiz, reduce the water content of dewatered sludge to be 70% or so.

Greenland company in China developed a new plate frame press dewaterer, which was made up of high-pressure dewatering system, transfer system and auto control system. In addition, the system also contain a storage system and a conditioning system.

The dewatered sludge, which is from dyeing/printing wastewater treatment factory and the water content is still up to 87%, is entered into a series of machine dewatering installations, The installation is made up of multi independent units by parallel connection, and every unit has two systems, which contain a low-pressure unit (the lowest pressure is 40 kg) and a high-pressure unit (the highest pressure is 240 kg). Every unit for each cycle is less than 8 minutes. In normal operation, the filter cloths life is extended to 1 to 2 months and without washing, and the water content of sludge is reduced from 87% to 50%~60%.The electricity consumption is 25 kWh per one ton (80% WS), operation cost is 80 yuan RMB per one ton (80% WS), investment cost was 80,000 to 100,000 yuan RMB per one ton (80% WS).

3.3. New Stabilization Technology

The traditional sludge stabilization technology contain anaerobic digestion, high-temperature aerobic composting and lime alkali stabilization. In China, the existing municipal wastewater treatment plants have very limited sludge stabilization facility. Because the environmental laws and regulations require that sewage sludge must be stabilized recently in China, it compels MWWT plant has to actively seek for solutions, and promotes the development of new technology.

3.3.1. Alkali Stabilization Technology

In Shanghai, Jiading MWWT plant, has a established pilot plant for a lime alkali stabilization, the studies are in progress. The sludge treatment capacity is 70 tons per day (the water content of the dewatered sludge cake is 80%~82%). The system is mainly made up of the lime storage tank, sludge pump, twin screw conveyor, chemical adding and mixing unit, the reactor, ammonia gas collecting tower, treated sludge storage tank and relevant auto control system, etc.

The dewatered sludge is sent into material mix system via screw conveyor, and well mixed with lime powder (10% of the wet sludge weight) and amino-sulfonic acid (6% of the wet sludge weight). The pH is raised to more 12, and then the mixture is pumped into the reactor by high-pressure piston pump and the retention time is extended to 30 minutes or so, the temperature of the reactor is kept to be more than 70°C and the highest temperature is up to 73°C, the reacted sludge is sent into storage tank, emission gas is absorbed by ammonia gas collecting tower.

The treated sludge is piled up in air storage for some days, its appearance has gradually shown white grey and very hard.

For the whole system, the operation cost is about 60 yuan RMB (WS83%) (no depreciation), installation capacity is added up to 37 kWh, the special investment cost is about 80,000~100,000 yuan RMB(WS83%).

The technology has the following feature:

- The retention time in the reactor is short, only about 30 minutes;
- High organic compounds degradation rate, more than 60%;
- Low lime adding, only 10% of wet sludge weight;
- The treated sludge stabilization, no mouldy, undissolved in water, odorless, low water content, up to the Class A standard of EPA CFR 40 Part 503;
- Simply waste gas treatment, good sanitation conditioning in plant area.

3.3.2. High Temperature Aerobic Composting Technology

The technology is developed by Tongji University, in Shanghai. The whole system is mainly made up of pretreatment system, material mixing system, first step composting system, secondary step composting system, ventilation system, deodorization system, auto control and monitoring system etc.

Dewatering sludge is crashed to be 2 cm in particle by special crushing equipment, it is mixed with wood crumbs and secondary step sludge (dewatered sludge to secondary step sludge ratio is 1:1~2), in order to justify C/N ratio to 15~20:1 and to reduce water content of sludge. The retention time the mixture in the first step composting is about extended to 7 days, and the height of the mixture piled up is about 2 meters. The composting process apply the fan to distribute air uniformly through the distribution system in the bottom of the compost, the oxygen concentration is kept between 12% and 15% and the temperature is maintained over 55°C, The retention time in the secondary composting is about extended to 10 to 20 days, the temperature is maintained in 50°C or so.

In order to remove a major part of toxic and refractory organic compounds, one liter enzyme is added into per one ton wet sludge. The appearance of the treated sludge has shown dark brown, its oxygen uptake rate is about 0.1 kgO_2/ min, seed germination is more than 90%.

For the whole system, the special operation cost is about up to 140~150 yuan RMB per one ton wet sludge (WS80%), the special investment cost is about 180,000 yuan RMB per one cubic metre wet sludge (WS80%), the special power consumption is about 1.1 kWh/m^3 wet sludge (WS80%).

3.4. Incineration

In China, although there are some examples of sludge incineration, such as a sludge drying incineration project in Shanghai Shidongkou Municipal wastewater treatment plant and a sludge drying project in Beijing Qinghe municipal wastewater treatment plant, the development of complete technology and heavy-duty equipment for incineration of sewage sludge is run behindhand for years in China when compared to the foreign advanced techniques.

The sludge drying incineration project in Shanghai Shidongkou Municipal wastewater treatment plant was established in 2006 ,the adoption of the treatment technique was the imported fluidized bed dryer and the domestic fluidized bed incinerator, the design treatment capacity was up to 64 tons dry sludge per one day, but the real treatment demand was only one half of the design treatment capacity, the total investment cost of the whole project was up to 80 million Yuan RMB (in 2006) and the operation cost is up to 300Yuan RMB or so (in 2008).

The sludge drying project in Beijing Qinghe municipal wastewater treatment plant was established in 2008, now it is in debugging, the adoption of the treatment technique was the imported fluidized bed dryer, the design treatment capacity was up to 102 tons dry sludge per one day, the hot source is the nature gas and the consumption is 30,000 m^3 every day, the total investment cost is 0.13 billion Yuan RMB (in 2008).

Now, in China, there are some examples applied sewage sludge co-incineration, which is such as the sewage sludge mixed with the municipal solid waste is combusted in the MSW incinerator in Shaoxing, Zhejiang province, the sewage sludge added into coal firing is injected into coal fired boiler in the large thermal power station to co-incinerate in Changzhou city, Jiangsu province, the sewage sludge used as cement production material is combusted in cement kiln in Guangzhou, Guangdong province, etc.

Furthermore, in sewage sludge drying-incineration, Beijing Institute of Science and Technology of Environmental Protection united Zhejiang Huanxing Machinery Co., Ltd developed a new sewage sludge drying incineration integrated technology and equipment that was mainly comprised of the spraying drying and rotary hearth incinerator, and directly use high temperature flue gas to dry wet sewage sludge that the moisture is still up to 80%, after drying the moisture of dried sludge is controlled within the range of 5% to 30%, the thermal efficiency of the whole system is more than 85% and the coal consumption rate is 45 kg per one ton wet sludge (WS80%).

4. CONCLUSSION

Over, with the European Union and the United States in regard to sewage sludge treatment and disposal of more advanced countries, China, whether in the sewage sludge treatment and disposal technology and equipment, or technology-oriented aspects of policy are still in the more behind. To make China's sewage sludge treatment and disposal business to a new level, it is clear that we still have a long way to go. But at the same time, we should see China in recent years to both in the sewage sludge treatment and disposal technologies policy, economic policy, environmental standards and engineering design specification, or in sewage sludge treatment disposal technology research and development of new equipment, at present, has made great progress. For example, in sludge reduction process, physicochemical and biological stability, and physical and chemical pre-treatment and heat treatment technology, there are a lot of new research results, developed many new techniques and new equipment. In the future, China is still the need to intensify efforts in this regard, especially in the sludge final disposal technology research and development equipment.

Controls of Fugitive Emissions of Residual Ethylene Oxide in Commercial Medical-supply Sterilization

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ABSTRACT: Residual ethylene oxide (EO) off-gassed from sterilized products is the main source of worker exposures in medical-supply sterilization. Three engineering designs that potentially reduce exposures were proposed, and their effectiveness was determined via exposure monitoring. Installation of additional venting ducts on the sterilizer significantly improves venting function and reduces worker short-term (~15 min.) exposure during un-loading sterilized goods. Similarly, application of a canopy-type exhaust hood, with baffles to minimize air shortcut, near the sterilizer door to vent the newly sterilized goods also reduces short-term exposure. Lastly, establishment of enclosed and venting systems for product aeration was effective in controlling fugitive run-away of EO during aeration/storage, and reducing air concentrations in the relevant areas. The improvements were significant and met the permissible exposure limits.

INTRODUCTION

ALTHOUGH a known human carcinogen with various health effects, ethylene oxide (EO) is used extensively in hospitals to sterilize re-usable medical devices such as endotracheal tubes, and in the medical-supply industry to sterilize disposable products such as plastic syringes that are heat or radiation sensitive [1–12].

Workers at factories manufacturing medical supplies, and particularly sterilization system operators and stock workers, are exposed to high levels of EO [13]. Sterilization operators, who are considered to have the highest exposure, had mean short-term (~15 min) exposure of 20–30 ppm when opening the sterilizer door during un-loading, while their mean time-weighted average work-shift (8 hr) exposure level was nearly 10 ppm. Furthermore, area monitoring revealed high EO concentrations throughout the facilities. Specifically, mean EO concentrations in the aeration area, near the sterilizer and in the warehouse were approximately 10, 6 and 9 ppm, respectively. Each value markedly exceeds the current Taiwan work-shift permissible exposure limit (PEL-TWA) of 1 ppm or short-term exposure limit (PEL-STEL) of 2 ppm [14]. Consequently effective methods must be found to reduce worker exposure.

Previous studies have demonstrated that plastics absorb EO during sterilization and release it during subsequent aeration [15–21] and considerable time is required for sterilized products to fully release the EO residual [22]. Residual EO off-gassed both in the sterilizer and during subsequent aeration/storage were the two main exposure sources for workers [13]. Control measures should thus focus on minimizing residual EO emissions. Increasing the number of post-sterilization purge cycles offers a simple means of reducing residual EO levels and eliminating extremely high short-term exposure while unloading sterilized goods. However, cycle-purging is not adequately implemented since it is relatively time consuming. Moreover, respiratory protection such as airline respirator is rarely adopted. Consequently, other control measures, particularly engineering modifications, should be considered.

This study, which was part of an on-site consulting program aiming to minimize EO-related health risks, attempted to provide practical engineering designs and parameters for reducing air EO concentrations and worker exposures in sterilization operations. The effectiveness of these control measures was evaluated

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through comparing worker EO exposure concentrations before and after control implementation.

METHODS

Overview of the Sterilization Process

The sterilization process is described in detail elsewhere [13]. Briefly, products are typically manufactured on-site, packaged individually in special paper-backed polyethylene bags, then packed in cardboard cartons. After logging the products were loaded into the sterilizer. Sterilization takes 3–8 hr, including chamber pre-conditioning, filling with EO, sterilization and in-chamber purge cycles (to reduce residual EO). Three types of EO gases—100% EO (single-use cartridge), 90% EO with 10% CO_2 in a cylinder, and 20% EO with 80% CO_2 in a cylinder—were used depending on sterilizer type. Sterilization frequency varied, from one load every few days in small factories with one sterilizer to ~10 loads daily in factories with multiple sterilizers.

Following sterilization, some operators unloaded the sterilized products shortly after the completion of the process, whereas others left the loads in the sterilizers overnight for convenience and unloaded the next morning. Before unloading, some operators fully opened the sterilizer door and ventilated the chamber with large floor fans for ~10 min. The sterilized loads were then transferred, by cart or by hand, to temporary storage areas (usually next to the sterilizers), where they were aerated and the biological indicators (BI) removed for additional quality assurance testing. When the results of BI met the quality criteria, the sterilized products were sent to warehouses or shipped.

Principles of Control

Residual EO emitted during un-loading and subsequent storage was the main exposure source for workers [13]. Therefore three designs that potentially reduce exposures in these operations were proposed.

1. *Improvement of sterilizer venting function*—to reduce EO off-gassing inside sterilizer before unloading. This could be achieved by adding a set of venting duct/pump to the sterilizer that is independent of the normal sterilizer operations. Sterilizers in most factories generally have small-sized vacuum ducts (for after-sterilization purging cycles) and cannot promptly remove EO off-gassed within the sterilizer chamber, potentially leading to high worker exposure during unloading.
2. *Improvement of local ventilation near the sterilizer door*—to promptly reduce EO off-gassed from product cartons and thus minimize worker exposure during un-loading. Such improvement represents an alternative means of reducing worker short-term exposure for factories that are unable to modify their sterilizers.
3. *Enclosure and venting of the aeration area*—to provide sufficient ventilation and limit fugitive EO emissions during aeration. It is known that sterilized products continue to emit EO for days, even after purge cycles, causing contamination in the air. Such contamination is particularly severe in storage areas with stagnant ventilation, a common phenomenon in this industry.

Assessment of Worker Exposure and Effectiveness of Controls

The sampling and analysis protocol was detailed previously [13]. In short, two types of air sample, including personal and area, were taken to assess worker exposure to EO, and to assess the effectiveness of the control measures. Personal samples were collected, usually over 15-min periods, near the breathing zones of sterilizer operators, who potentially had high EO exposure while unloading sterilized products. Area samples were collected at locations potentially contaminated with EO, at heights of ~150 cm.

Airborne EO was collected with an HBr-coated charcoal tube connected to a portable sampling pump. Sampling rates varied, from 50 to 200ml/min, based on a pre-determined sampling time of ~15min to 6hr, to optimize analytical sensitivity. Samples were desorbed with 10% dichloromethane in methanol, and analyzed with GC/MS by a certified laboratory. The lowest quantifiable levels used by the current method ranged from approximately 0.05 ppm (for a typical 6 hr sampling time and 50ml/min sampling rate) to 0.56 ppm (for a typical 15 min sampling time and 200ml/min sampling rate). Concentrations of EO were investigated before and after the implementation of each specific control measure.

RESULTS AND DISCUSSION

Plastics absorb EO during sterilization and release it during subsequent handling, potentially leading to worker exposure. EO remaining in the sterilization chamber was the main source of high-level, short-term worker EO exposure. However, EO emitted from sterilized products during aeration/storage should not be overlooked as certain workers stay in these areas for long periods [13]. Accordingly, this study proposed and evaluated three engineering designs controlling off-gassed EO:

Improvement of Venting Function of the Sterilizer

Figure 1 presents a design that improves the post-sterilization venting function of the sterilizer. The model sterilizer had a volume of ~20m^3 and was used primarily to sterilize hemodialysis-tube. Four openings, each with a diameter of ~5cm, were installed on one side of the sterilizer and connected to a venting duct and blower. The system had a venting rate of 14.4 m^3/min, corresponding to a theoretical air change rate of 42.2 hr^{-1}. Airflow pattern evaluation, assessed via smoke visualization, indicated that venting system performance was satisfactory since all released smoke was sucked into the sterilizer chamber.

Following sterilization, including 20 purge cycles, the sterilizer door was opened slightly and the venting pump was operated for 30min before un-loading the sterilized goods. Worker short-term (15 min) exposure levels during un-loading were 6.3 ppm (n = 2) when the venting system was off, whereas the concentration reduced to 2.0 ppm (n = 2) when the venting system was in use. These figures corresponded to a 68% improvement in exposure concentration, and met the PEL-STEL of 2 ppm.

Sterilizer workers experienced high EO exposure during unloading as a result of residual EO off-gassed and retained in the sterilizer chamber [13]. Cycle purges after sterilization reduced residual EO in hospital and medical-supply sterilization. When sufficient purging is infeasible, as in some factories, it is useful to draw the off-gassed EO out of the sterilizer chamber via an additional ventilation system. Venting a sterilization chamber not only removes residual EO from the chamber but also eliminates heat associated with sterilization, thereby further reducing the emission potential of sterilized goods.

Improvement of Local Ventilation Near the Sterilizer Door

Figure 2 illustrates an engineering design that improves ventilation around the sterilizer door. In the model presented, a canopy-type hood was installed adjacent to and above the sterilizer door. Meanwhile, baffles (retractable, sliding plastic film) were positioned on both sides and in the front to minimize air shortcut. The dimensions of the hood opening were 2.53 m (W) × 1.77 m (L), sufficient to cover the size of the pallet used to hold goods during sterilization. A perforated plate (with uniformly distributed round slots representing ~19% of its total area) was applied inside the hood for air current stabilization. The venting rate was 159 m^3/min. Subjective airflow pattern evaluation indicated that the hood performed satisfactorily and no smoke escaped.

After sterilization, including five purge cycles, a pallet load of sterilized goods (comprising hemodialysis- and infusion-tube, syringe etc.) was automatically re-

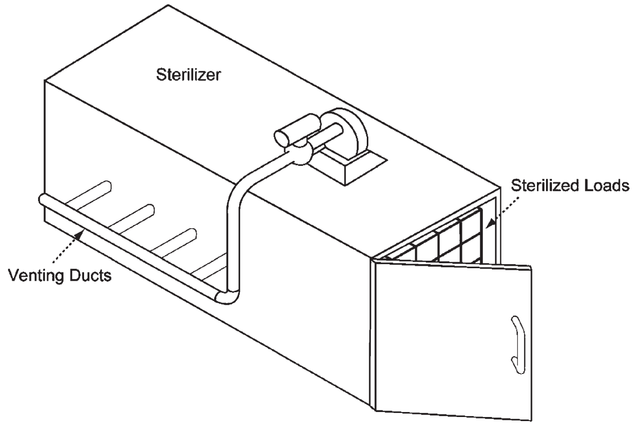

Figure 1. Schematic representation of an engineering design that improves the post-sterilization venting function of the sterilizer.

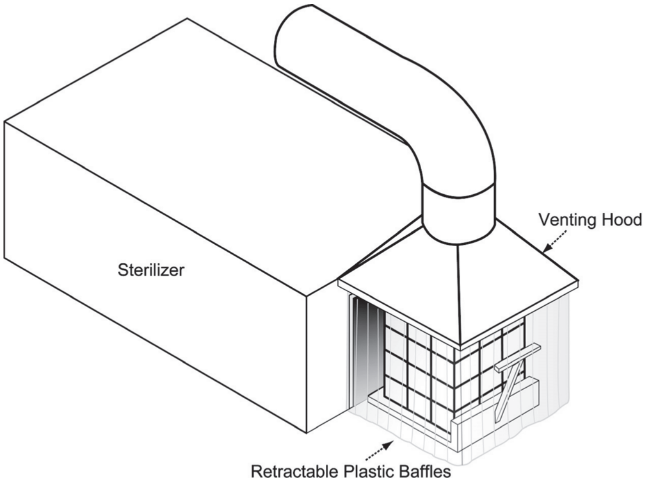

Figure 2. Schematic representation of an engineering design that improves ventilation around the sterilizer door.

moved from the sterilizer and placed underneath the hood, where the goods remained for 15 min for venting before being moved elsewhere for further aeration/storage. Subsequent pallet loads were treated similarly until all three were ventilated. Worker short-term exposure levels during un-loading were 10.2 ppm (n = 2) before control, but reduced to 2.0 ppm (n = 2) after the hood was utilized. This reduction represented an 80.4% improvement in worker exposure level and met the PEL-STEL of 2 ppm.

Although EO is heavier than air, it generally follows natural warm air currents and flows upward from a sterilizer after normal sterilization. Thus an exhaust hood immediately above the sterilizer door efficiently reduces peak EO levels. Numerous investigations have recommended using local exhaust ventilation near hospital sterilizer doors to reduce worker exposure to EO during sterilizer door opening [23–27]. For example, Samuel proposed a side-draft hood with a baffle above the door of a table-top sterilizer and demonstrated that this design effectively reduced worker exposure to well below the permissible level [24]. Although some medical-supply manufacturers utilized exhaust hoods immediately above/around the sterilizer door, such arrangement did not effectively limit worker exposure [13]. This insufficiency was likely because the sterilizers used in medical-supply factories were generally much larger than those used in hospitals, meaning an exhaust hood outside the sterilizer was insufficient to draw the EO out of the sterilizer chamber.

Enclosure and Venting of the Aeration Area

Figure 3 shows a typical enclosure design for the aeration area that improves dilution ventilation and limits fugitive emission. Enclosure is necessary since EO is a known carcinogen.

In one model factory, a room [4.3 m (W) × 6.1 m (L) × 2.6 m (H)], next to the sterilizer, was dedicated to this application. Sliding plastic doors were installed at the entrance to minimize EO runaway, while two window-mounted axial fans were installed on the opposite side of the room for venting. This layout generated an overall flow rate of ~3000 m^3/hr, equaling a theoretical air change rate of 44 hr^{-1}. After sterilization (including six purge cycles), sterilized products (comprising a mixture of infusion, respiratory and urinary supplies) were transferred to the room for 24–48 hr aeration before being moved to a warehouse for further storage. Air measurement from the area samples indicated that EO concentrations before and after the utilization of the control were 5.67 and 0.58 ppm, respectively. This improvement represented an 89.8% reduction, and the concentration met the PEL-TWA of 1ppm for an 8-hr work shift.

In the second factory, a room [4.1m (W) × 4.2 m (L) × 4.4 cm (H)], next to the sterilizer, was used for this application (enclosure and venting). Plastic film (multi-piece type) was placed at the entrance of the room to minimize EO runaway. A tube-type axial fan, venting at 60 m^3/min, was installed at the inner bottom corner since the room was windowless and EO at room temperature is heavier than air. The fan was operated at a frequency of 5min per 15mins, creating a theoretical air change rate of 16 hr^{-1}. Following sterilization (comprising nine purge cycles), sterilized products (mainly urological and anesthetic supplies etc.) were transferred into the room for aeration for 48 hr before further handling. Area sample results indicated that EO concentrations after design implementation were 0.68 ppm (n = 2), meeting the PEL-TWA. Since the establishment was new there were no pre-control data. Notably, the factory sterilized and aerated loads using plastic baskets (with products individually packaged) while in other factories products were typically sterilized/aerated in partially sealed cardboard boxes.

Sterilized products continue to emit EO for days, contaminating the aerating zone. Previous investigations have demonstrated that environmental factors such as temperature, relative humidity, air change rate and the amount of plastic in a product carton significantly impacted and interactively affected EO emission kinetics [22]. Air change rate is a simple and achievable

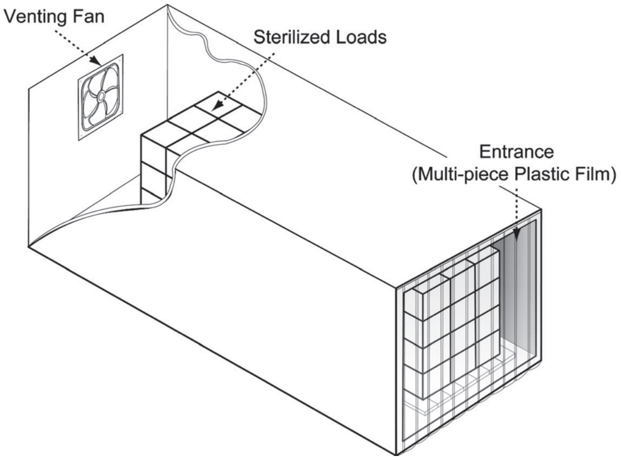

Figure 3. *Schematic representation of an engineering design that incorporates enclosure and venting function for the aeration area.*

means of controlling air EO concentrations. However, enclosure design should be incorporated into the system to minimize fugitive emissions and ensure that desired ventilation is achieved. Additionally, since the plastic content (types and amounts) in a product carton significantly influences EO emission characteristics, different aeration schedules should be utilized. Accordingly, multiple aeration systems may be necessary for manufacturers that handle large loads or sterilized products with various plastic compositions.

Significance of Findings

Sterilization characteristics (e.g. EO concentration and dwell time) and product characteristics (e.g. composition of sterilized materials, load density, and packaging type) [15–21, 28–30] are the main determinant of residual EO. Thus the design parameters presented in this study, despite having been proven effective, should be considered factory-specific. Time, venting rate and system integrity are just three of the determinants of the actual performance of these control measures. Although plastics are known to absorb EO during sterilization and release it during the subsequent aeration, other medical materials should also be applicable to current findings. Notably, this study focused on controlling of worker exposures resulting from EO residue, other EO-related operations such as maintenance and production that also had exposure potential were not addressed [31].

In hospitals, the use of combined sterilizer-aerator eliminated the need to transfer sterilized loads for aeration, thus significantly reducing worker exposure to EO [25]. However, such practice is rarely implemented in this industry because the sterilizers generally lack an additional venting function for removing residual EO, and sterilization generally faces time constraints.

Although multiple aeration systems are recommended to accommodate large quantities of sterilized products for sufficient aerating time, these facilities may not be achievable owing to space limitations typically encountered in this industry. Furthermore, tight manufacturing schedules prevent sterilized goods from being retained for the time required form sufficient aeration. Given these unfavorable conditions, aerating sterilized stocks in an independent aeration area/system for at least 1–2 days offers a practical alternative since the mean EO emission rate from sterilized products on the first day following sterilization was twice that after the second day [22].

CONCLUSIONS

EO emitted from sterilized goods has been identified as the major source of worker exposure in hospital and medical-supply sterilization. Although increasing post-sterilization purge cycles offers a simple means of reducing residual EO levels and eliminating extreme worker exposure while unloading, it is time-consuming and may not completely eliminate EO residue. Consequently, promptly removing the off-gassed EO from the sterilization chamber through enhancing the sterilizer venting function may be desirable. Alternatively, placing newly-sterilized stocks within a well-designed local exhaust system for some time also partially withdraws emitted EO and reduces worker short-term exposure during unloading. Moreover, uncontrolled aeration/storage of sterilized stocks results in high EO concentrations in the relevant areas and associated worker exposure. Such conditions can be resolved by enclosure and venting. However, sterilized products should stay in the aeration system for sufficient periods of time as they continue emitting EO for many days.

This work has explored feasible engineering controls for reducing worker EO exposure in medical-supply sterilization, both during unloading and aeration. The designs and parameters presented herein effectively reduced the worker short-term exposure during unloading below the PEL-STEL, and reduced mean air EO concentrations in the aeration/storage areas below the PEL-TWA.

Finally, as residual EO in sterilized products is influenced by numerous factors such as product types, the parameters used in engineering control for each factory should be adjusted accordingly for optimal performance.

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Effect of Sewage Sludge on Mercury Accumulation in Soil and Corn

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ABSTRACT: The objective of this study was to determine the effect of heavy sewage sludge application on concentration of mercury (Hg) in a calcareous soil (fine loamy, mixed thermic Typic Haplarigid) and corn (Zea mays). Sludge was applied at 25, 50 and 100 Mg ha^{-1} for five consecutive years. Sludge application significantly increased total Hg concentration in soil and in corn roots, stems and grains. At the end of the fifth year the average Hg concentrations in roots, stems, and grains were 91, 9, and 8 μg kg^{-1}, respectively. Although, Hg uptake by corn did not exceed the US-EPA control levels of food and feed quality, using heavy sludge application may eventually lead to the build-up of metal concentrations which do no longer allow the production of safe food, despite the high potential of this calcareous soil to immobilize the metals.

1. INTRODUCTION

SEWAGE sludge is rich in plant nutrients such as nitrogen (N) and phosphorous (P) [3,22,29], so land application as a fertilizer has been proposed as a cost—effective means of disposal [5,21,31]. However, the presence of toxic elements such as Hg and their subsequent transfer into soil and food chains, limit high utilization of sewage sludge on agricultural lands [15,17,19]. In this regard two parameters "amount of cumulative sludge" and "expired time" after sludge application have important effects on concentration, plant availability and mobility of heavy metals in soils amended with sewage sludge [15,18].

Research clearly shows that under some conditions (which are not fully understood), toxic metals including Hg can be transferred from sludge-treated soils into crops, and metals from the soil may be absorbed onto roots of plants. A more important source of danger for human health is the dirt and contamination that may enter the food chain directly, rather than through plant uptake [25]. Another important pathway for entry into the food chain is through grazing animals on plants treated with sewage sludge, which ingest the pollutants either through the grazed plants, or by eating sewage sludge along with the plants [10].

Mercury is considered an important pollutant because of its toxicity, plant availability and potential for bioaccumulation. The natural background concentration of mercury in soil is normally less available for crop uptake and hence less hazardous than mercury introduced through sewage sludge applications [24]. Terrestrial plants could accumulate mercury through assimilation from soil into roots and direct absorption from the air through leaves, by means of stomata, and emit mercury vapor from leaves [9]. Depending on plant species and metals ions, the uptake could be through roots, stomata or other points of entry [34]. Assimilation through plants plays a major role in the entry of mercury into terrestrial food chain [2,7]. Plants function as conduits for the interfacial transport of mercury from the geosphere to the atmosphere, and this role is undervalued in models of the behavior of mercury in terrestrial ecosystems and in the atmosphere on a global scale [16]. Studies on Hg specially the fate of Hg in the sludge amended soil and the plant in such soils are very limited.

In the arid region of Central Iran, farmers extensively use sewage sludge as fertilizer. However, a comprehensive survey of mercury pollution of soil and plant has not yet been carried out. We conducted a five-year field

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experiment to investigate the long term fate of mercury in soil amended with Hg enriched sewage sludge. Therefore, the objective of this study was to determine the cumulative and residual effects of repetitive sewage sludge applications on the concentrations of mercury in soil and its uptake by corn crops.

2. MATERIALS AND METHODS

2.1. Experimental Design

The experiment was conducted at Isfahan University of Technology research station site, at the latitude of 32°32′ N and longitude of 51°23′ E (coordinate system: LATLON WGS84). The site has an arid climate and is 1630 m above sea level. The average annual rainfall and temperature at the site are 140 mm and 14.5°C, respectively. The soil is a fine-loamy, mixed, thermic, Typic Haplargid. Selected soil chemical and physical properties are shown in Table 1.

Corn (*Zea mays*) as spring crop and wheat (*Triticum aestivum*) as winter crop were planted at the site. In this paper only the result for corn will be presented. The sludge used in this experiment was secondary, aerobically digested municipal sewage sludge from city of Isfahan (Table 2). The sludge Hg concentration ranged from 4 to 10 mg kg^{-1} with mean concentration of 7 mg Hg kg^{-1}.

A spilt plot experiment arranged in a randomized complete block design with three replications was used in this study in which the amount of sludge and years of sludge application were considered as the main and sub factors, respectively. We started the experiment in June 2000. In first year (2000), different levels (0, 25, 50 and 100 Mg ha^{-1}) of air dried sewage sludge were applied to plots of 15 × 3 m and mixed into the topsoil (20 cm depth). In order to study not only cumulative, but also residual effects, applications were discontinued in subsequent years on part of the area to which sludge had been applied in the preceding year. Thus, in 2001, each plot was divided into two subplots (12 × 3 m and 3 × 3 m), and sludge was again applied to the larger subplot, using the same dosage as in the first year. In the third year (2002), the same sludge dosages were applied on three fifths of the original plots or in the larger subplots (9 × 3 m), in the fourth year (2003) applications of sludge were repeated in the larger the subplots (6 × 3 m) or on two fifths of the original plots and in the fifth year (2004) same sludge dosages were repeated on one fifths of the original plots or in the 3 × 3 m subplots.

Table 1. Selected Physical and Chemical Characteristics of the Soil of the Experimental Plots.

Parameter	Unit	Amount
Texture	–	Clay loam
Sand	$g\ kg^{-1}$	140
Silt	$g\ kg^{-1}$	500
Clay	$g\ kg^{-1}$	360
pH	–	8.3
Organic carbon	$g\ kg^{-1}$	4.6
Cation Exchange Capacity	$cmol_c\ kg^{-1}$	14
Electrical Conductivity	dSm^{-1}	1.07
Total lead	$mg\ kg^{-1}$	19.3
Total cadmium	$mg\ kg^{-1}$	0.33
Total arsenic	$mg\ kg^{-1}$	10.6
Total mercury	$mg\ kg^{-1}$	1.64
Total zinc	$mg\ kg^{-1}$	82.2
Total copper	$mg\ kg^{-1}$	33.1

Table 2. Selected Chemical Properties of the Applied Sewage Sudge.

Parameter	Unit	Amount
pH	–	6.4
Electrical Conductivity	dSm^{-1}	9.4
Organic Matter	$g\ kg^{-1}$	310
Nitrogen	$g\ kg^{-1}$	19
Phosphorous	$g\ kg^{-1}$	14.3
Potassium	$g\ kg^{-1}$	6.4
Iron	$g\ kg^{-1}$	18.7
Manganese	$g\ kg^{-1}$	0.33
Arsenic	$mg\ kg^{-1}$	110.7
Lead	$mg\ kg^{-1}$	180
Cadmium	$mg\ kg^{-1}$	5
Copper	$mg\ kg^{-1}$	385
Mercury	$mg\ kg^{-1}$	7
Zinc	$mg\ kg^{-1}$	1885

The total sludge application were, 0, 25, 50 and 100 Mg ha^{-1} for one year application, 0, 50, 100 and 200, Mg ha^{-1} for two years application, 0, 75, 150 and 300 Mg ha^{-1} for three years application, 0, 100, 200 and 400 Mg ha^{-1} for four years of applications and 0, 125, 250, and 500 Mg ha^{-1} for five years of sludge applications. We had 16 treatments in this experiment which their differences related to time and sludge application rate (Table 3). The plants were irrigated as needed using the well water at the site. Weeds control in the plots was done mechanically. According to the amount of Hg in the sludge and the sludge application rate we can compute the cumulative Hg loading rates in soil (kg ha^{-1}) (Table 4).

2.2. Sampling and Analysis

In fall of 2005, at the end of corn growing season, five

Table 3. Scheme of Treatments and Sludge Application in Different Years of Study.

Treatment* (Mg ha^{-1})	2000 First Year	2001 Second Year	2002 Third Year	2003 Fourth Year	2004 Fifth Year
25	25	0	0	0	0
25×2	25	25	0	0	0
25×3	25	25	25	0	0
25×4	25	25	25	25	0
25×5	25	25	25	25	25
50	50	0	0	0	0
50×2	50	50	0	0	0
50×3	50	50	50	0	0
50×4	50	50	50	50	0
50×5	50	50	50	50	50
100	100	0	0	0	0
100×2	100	100	0	0	0
100×3	100	100	100	0	0
100×4	100	100	100	100	0
100×5	100	100	100	100	100
Control	0	0	0	0	0

*25, 50, 100: sludge was applied one year.
25×2, 50×2, 100×2: sludge was applied two consecutive years.
25×3, 50×3, 100×3: sludge was applied three consecutive years.
25×4, 50×4, 100×4: sludge was applied four consecutive years.
25×5, 50×5, 100×5: sludge was applied five consecutive years.
0 means that no sludge was added to the plot.

soil samples were taken from each plot separately and then mixed by putting the samples in a plastic bag shaking it to make a composite sample. The soil samples were collected at 0–20 and 20–40 cm soil depth. Soil samples were air-dried, sieved (2 mm), homogenized in a porcelain mortar and analyzed for total mercury using Mercury Analyzer.

The mercury was measured by the LECO AMA 254 Advanced Mercury Analyzer (USA) according to ASTM, standard No. D-6722. The LECO AMA 254 is a unique Atomic Absorption Spectrometer (AAS) that is specifically designed to determine total mercury content in various solids and certain liquids without sample pre-treatment or sample pre-concentration [11,12]. This instrument allows for analysis of total mercury and is matrix independent. Samples were analyzed in sample boats with drying, decomposition (550°C), and waiting times of 100, 320, and 45 s, respectively Ultra pure oxygen was used as the carrier gas, with an inlet pressure of 250 kPa and a flow rate of 150–200 mL/min. The AMA 254 has a detection limit of 0.01 ng of Hg and a linear range of 0.05–40 ng. All samples analyzed were within the calibration range. In order to assess the analytical capability of the proposed methodology, accuracy of total Hg analysis was checked by running three samples of Standard Reference Materials (SRM). SRM is an agricultural soil that was oven-dried, sieved, radiation sterilized; and blended to achieve a high degree of homogeneity. Quality assurance/quality control (QA/QC) was performed with National Institute of Standards and Technology (NIST), nine analyses of NIST 1633b, nine analyses of NIST 2709 and four NIST 2711 that were included in all the runs to check the calibration of the instrument throughout all sequential extraction steps. In addition, some mercury standards of NIST were analyzed every 10–15 runs (Table 5).

At the outset, sampling of plants roots, stems and grains was done separately.

In the field, plant samples were collected (stems and grains), washed several times, labeled and stored in plastic bags. Several replicates of each specimen were collected. In the laboratory, roots and aboveground corn samples were carefully washed using distilled water. The plant samples that were dried at 65°C for 48 h ground by a mortar and pestle.

2.3. Statistical Analysis

The data were analyzed based on the model of randomized complete block design. A Fisher's LSD (Least Significant Difference) test (P ≤ 0.05) was used to determine the statistical differences among the treatment means [30]. The statistical analyses were performed us-

Table 4. The Amounts (kg ha^{-1}) of Hg Added to Soil of Different Treatments.

Sludge Application Rates	Number of Sludge Applications 1	2	3	4	5
25	0.17	0.35	0.52	0.70	0.87
50	0.35	0.70	1.05	1.40	1.75
100	0.70	1.4	2.10	2.80	3.50
Control	0	0	0	0	0

*The amounts were calculated by multiplying the Hg concentration (mg kg^{-1}) in sewage sludge by amount of air dried sludge (Mg ha^{-1}) added in different treatments.

Table 5. Results of Quality Assurance Procedure for Mercury (mg/kg).

SRM[a]	No.	Certified Value	Obtained Mean	SD[b]	*R*[c]
NIST-1633b	9	0.141	0.134	0.042	94.8
NIST-2709	9	1.400	1.470	0.131	105
NIST-27119	4	6.250	6.438	0.197	103

[a] Standard Reference Material.
[b] Standard Deviation.
[c] Recovery (%).

Table 6. Average Corn Stem and Grain Dry Weight and Average Hg Uptake by Corn Stem and Grains (Average ± standard deviation in kg ha^{-1}) in Different Years of Sewage Sludge Application.

Number of Sludge Application Years	Dry Matter Weight of Stem (kg ha^{-1})	Dry Matter Weight of Grain (kg ha^{-1})	Hg Uptake by Corn Stems (kg ha^{-1})	Hg Uptake by Corn Grains (kg ha^{-1})
1	18535bc ± 5523.2	9310b ± 3207.0	169025b ± 77257.7	81281b ± 34389.3
2	20507bc ± 7284.7	14326a ± 4254.0	133952b ± 54127.3	99793ab ± 58828.9
3	22465b ± 6161.5	16515a ± 6557.8	188848b ± 67880.0	117134ab ± 63250.0
4	17872c ± 3636.3	8230b ± 3102.9	174723b ± 118373.9	75399b ± 34231.2
5	27014a ± 7979.6	13776a ± 5648.0	261210a ± 104960.8	144498a ± 85786.2
Control	12806d ± 1795.9	5226.7b ± 1523.3	78222c ± 20663.3	37591c ± 12834.5

Values with same letters are not significantly different from each other according to Fisher's LSD at $P \leq 0.05$.

ing SAS program, version 6.10 for personal computers [27].

3. RESULTS AND DISCUSSION

3.1. Effect of Cumulative Sludge Application on Dry Matter Weight of Corn

Corn dry matter significantly increased in proportion to sludge addition. Corn dry matter in plots that had received a single sludge application 5 years ago was still higher than control. This result shows that positive effects of sewage sludge on crop yield can remain at least for five years without application of any fertilizer even at 25 Mg ha^{-1} sludge application rate (Tables 6 and 7). This is important since majority of soils in central Iran are low in organic matter content and have poor physical and chemical properties. Addition of macro- and micronutrients plus the improvement of soil physical properties due to sludge application are assumed to be the main reasons for sludge effect on increasing of corn dry matter [1]. In the fourth year corn yields decreased significantly this was mainly because of the drought that occurred at the site in that year (Table 6).

3.2. Effect of Cumulative Sludge Application on Soil Hg Concentration

Total Hg concentration in soil ranged from 20 μg kg^{-1} in control plots to 1200 μg kg^{-1} in plots with 500 Mg ha^{-1} sludge application. Annual application of sludge significantly ($P \leq 0.01$) increased Hg total concentration in soil at both depths. The concentration of Hg in single sludge application was significantly higher than control, even after 5 years (Table 8). The Hg concentration at 0–20 cm depth was significantly higher than the concentrations at 20–40 cm depth (Table 8). In general, Hg is very insoluble which limits its movement in soil [6,20,32]. Nevertheless, as the cultivation and plowing of the plots has caused the sewage sludge to completely be mixed with the soil and transferred to the deeper in the soil profile. Regression analysis indicates that from 90 to 100% of the Hg applied to soils in sewage sludge since 2000 still remain in the top 40 cm of soil [(Figure 1(a)]. Similar results were reported by Granato *et al.* (1995); at a site where sewage sludge was applied for twenty years, 80 to 100% of the sludge borne mercury was accumulated in the top 15-cm soil depth.

In this study the correlation observed between the mercury concentration of the soil and the cumulative Hg loading rate in the soil was significant ($R^2 = 0.95$). The greatest concentration of Hg in the soil (2.15 kg ha^{-1}) belongs to the plot which had received five consecutive years of sludge applications at 100 Mg ha^{-1}. Also the least concentration of Hg (0.18 kg ha^{-1}) was measured in the plot where the least sludge application (the one year sludge applications of 25 Mg ha^{-1}). In our study the applications of 100 Mg ha^{-1} for five consecu-

Table 7. Average Corn Stem and Grain Dry Weight and Average Hg Uptake by Corn Stem and Grains (Average ± standard deviation in kg ha^{-1}) in Different Sludge Application Rates.

Sludge Application Rates (Mg ha^{-1})	Dry Matter Weight of Stem (kg ha^{-1})	Dry Matter Weight of Grain (kg ha^{-1})	Uptake of Hg by Corn Grains (kg ha^{-1})	Uptake of Hg by Corn Stems (kg ha^{-1})
25	10708a ± 256286.3	18620b ± 4042.5	84635a ± 51511.2	162438a ± 82042.9
50	12348a ± 5243.5	23038a ± 5047.9	112006a ± 74278.9	183694a ± 101245.9
100	14238a ± 7801.6	22179a ± 5355.1	114221a ± 59071.3	210523a ± 101248.4

Different letters in a column indicate significant difference between treatments ($P \leq 0.05$).

Table 8. Average Soil Hg Concentrations (Average ± standard deviation in μg kg^{-1}) in Different Soil Depths.

Treatment (Mgha^{-1})	Soil Hg concentrations (μg kg^{-1}) 0–20 cm	20–40 cm	0–40 cm
25	87.5de ± 66.3	58.8de ± 18.8	73.1d ± 42.2
25×2	79.2de ± 26.4	66.4de ± 22.6	72.8d ± 25.5
25×3	81.5de ± 40.3	77.4de ± 37.3	89.8d ± 31.6
25×4	110.3de ± 42.3	106.4de ± 40.6	94.8d ± 34.4
25×5	121.4de ± 38.8	153.6d ± 43.0	137.5cd ± 34.6
50	156.0de ± 108.1	100.0de ± 42.3	128.0cd ± 74.7
50×2	178.8d ± 90.7	139.7de ± 91.0	159.2cd ± 53.7
50×3	284.0cd ± 65.3	207.9cd ± 50.4	245.9cd ± 26.5
50×4	258.2cd ± 46.3	242.3cd ± 50.8	250.2cd ± 30.0
50×5	367.9c ± 91.7	309.3c ± 66.4	338.9c ± 78.7
100	177.9de ± 35.5	218.8cd ± 73.8	198.3cd ± 17.4
100×2	284.5cd ± 175.0	388.9cd ± 220.5	275.2cd ± 130.7
100×3	723.1b ± 226.3	463.0b ± 281.8	593.1b ± 245.7
100×4	823.7b ± 383.6	841.6a ± 234.08	32.7a ± 308.6
100×5	1204.8a ± 58.7	717.9a ± 357.4	961.4a ± 182.9
Control	22.8e ± 6.4	22.4e ± 4.6	22.6e ± 5.3
LSD*	128.2	128.2	238.7

*Least Significant Difference.

Different letters in a column indicate significant difference between treatments (P ≤ 0.05).

tive years led to higher concentrations of Hg (1.2 mg kg^{-1}) than the maximum acceptable concentration (MAC) of this metal in agricultural soil for Germany [28] and BSI PAS 100 (1 mg kg^{-1}) [35].

3.3. Effect of Cumulative Sludge Application on Plant Tissue Hg Concentration

3.3.1. Corn Root Hg Concentration

In general, the average concentration of Hg in roots was higher than other plant tissues (stems and grains) (Table 9). Mercury is taken up by plants mostly accumulates in the roots; this suggests that the roots serve as a barrier to Hg uptake [8].

There was no significant difference between the concentration of mercury in the root of the control plot and different treatments of sewage sludge (Table 9).

The behavior of Hg in the soil is highly influenced by its chemical form which is a function of the initial concentration of Hg in the soluble part of the soil and also several other soil parameters. Among those parameters of the soil we can mention levels of organic matter and clay in the soil, cation-exchange capacity (CEC) and pH of the soil. Increase in CEC, clay and organic matter content of soil decrease plant availability of Hg the soil [14]. The high clay content and high pH of this calcareous soil probably are the main reasons for low Hg con-

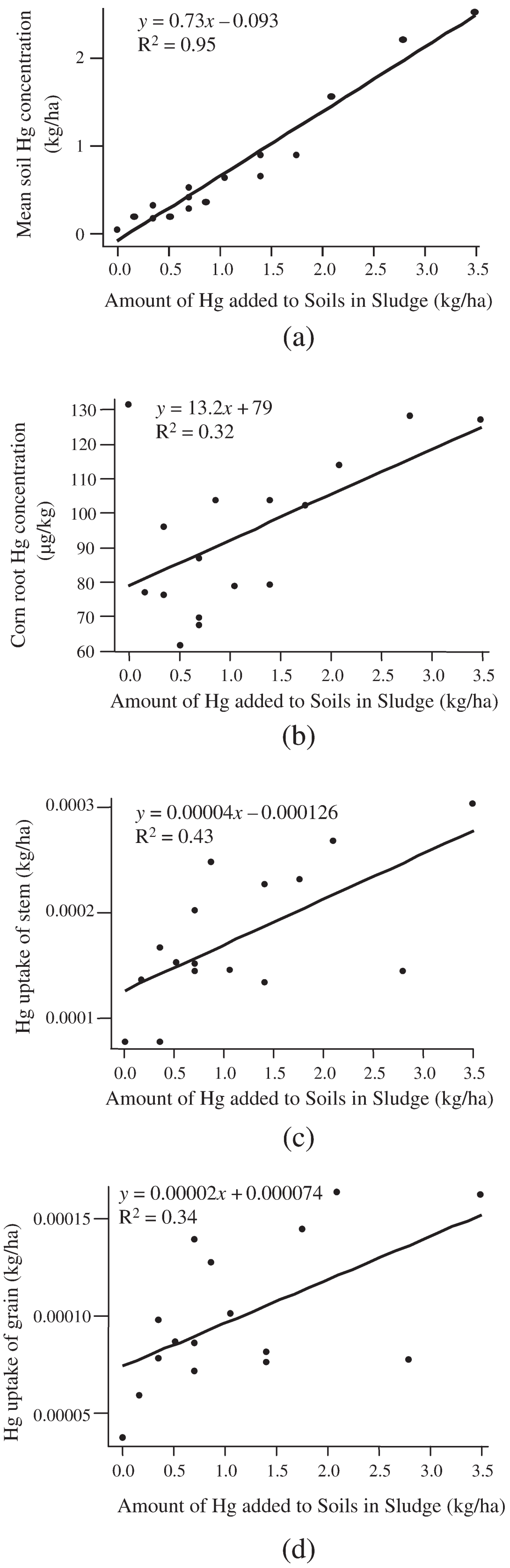

Figure 1. *Effect of sewage sludge application (a) on soil Hg concentrations (depth 0–40 cm) (b) on Corn root Hg concentration (c) on corn stem Hg uptake and (d) on corn grain Hg uptake.*

Table 9. Average Hg Concentration in Corn Roots in Different Sludge Application Years (Average ± standard deviation in μg kg^{-1}).

Number of Sludge Application Years	Corn root Hg Concentration (μg kg^{-1})	Corn stem Hg Concentration (μg kg^{-1})	Corn grain Hg Concentration (μg kg^{-1})
1	80.3b ± 19.9	8.5ab ± 2.0	8.6ab ± 1.9
2	81.1b ± 20.2	6.4b ± 1.3	7.6b ± 2.6
3	84.9ab ± 41.7	8.3ab ± 1.4	7.3b ± 1.4
4	100.6a ± 30.1	8.9a ± 4.4	8.3ab ± 1.5
5	111.1a ± 47.3	9.0a ± 2.2	9.2a ± 4.0
Control	100.3a ± 28.2	6.0b ± 1.4	7.1b ± 2.3

Different letters in a column indicate significant difference between treatments ($P \leq 0.05$).

centration in the corn roots. In addition, as amount of sludge application increased so did organic matter content of the soil which may have resulted in insignificant difference among the treatments. As the number of sludge application years increased the Hg concentration in the corn roots increased significantly (Table 9). This indicates that because of the organic matter decomposition of the sludge heavy metals are released slowly in the soil are adsorbed or precipitate and therefore are not easily available for plant uptake [4].

In the treatments of 1 and 2 years where the sludge was applied 4 or 5 years ago, there was enough time for chemical reactions leading to Hg adsorption and/or precipitation in this calcareous soil. This shows the importance of time as a factor in reducing Hg uptake by the root which probably shows of the "aging effect", that is the availability of heavy metals entered the soil through sewage sludge reduces by time and this can be the reason of their great absorption by the soil and organic matter of the sludge [26].

The correlations between the concentration of Hg in the root and the Hg of the sludge and also the soil were significant ($P \leq 0.05$) [Figure 1(b)]. This shows that the increase in the cumulative loading rate of Hg of the sludge in the soil increases Hg concentration of the soil thus Hg content of corn roots.

3.3.2. *Corn Stem and Grain Hg Concentrations*

Despite expectation the Hg concentration of the stem and grain (μg Hg/kg tissue) did not show any significant correlation with the cumulative loading rates of Hg in the soil and the concentration of Hg in the soil and root. In addition, there was no relationship between the Hg concentration of the grain and that of the stem.

But in case of aerial parts of the plant (stem and grain) "dilution growth" should be considered which is due to the greater biomass production of the plants. Therefore, in these cases that the crop yields of the comparative treatments differ, using the "concentration" of the element is not proper and it is suggested to use the amount of Hg "uptake" by the stem and the grain in each hectare (μg ha^{-1}). Therefore, it is more logical to analyze and study the results of Hg uptake in the stem and grain of the plant. Sludge application rate and years of sludge applications significantly increased Hg uptake in stem and grain (Tables 6 and 7).

The amount of Hg uptake in the stem ($P \leq 0.01$) and grain ($P \leq 0.05$) with the cumulative loading rate of Hg in the soil [Figures 1(c) and 1(d)] and the Hg concentration of the topsoil (0–20 cm) showed significant correlations. The correlation of the amount of Hg uptake in the grain with the amount of uptake Hg in the stem ($P \leq 0.01$) was also significant. But there was no significant correlation between Hg uptake of stem and grain and the Hg concentration in the root and in the second depth of the soil (20–40 cm). This indicates that the amount of Hg transfer from the root to the stem and grain is probably very little. Probably the Hg in the sludge and the soil may enter the plant from other paths (such as sublimated). Similar results were reported by Granato 1995; Eisler 2000; Kabata-Pendias and Pendias 2000; Patra and Sharma 2000.

The US-EPA risk assessment for entry into the human diet of three of the most toxic metals, mercury, cadmium and lead, utilized uptake coefficients (UCs) to calculate the amount of each metal that could enter food crops from the soil. Each UC was calculated as the increment of metal concentration in the edible part of the crop per unit increase of metal loading to the soil.

The US-EPA computed the UC they utilized for various plant tissues by relating plant tissue concentration to soil loading rate. The UC Hg for sweet corn of 0.001 (mg Hg/kg plant tissue)/(kg Hg/ha soil), is a conservative default value assigned to tissues having UC determined to be < 0.001. The UC Hg computed for grains and animal forage by US-EPA, 0.043 (mg Hg/kg plant tissue)/(kg Hg/ha soil), are conspicuously high [13, 33].

We utilized corn stem and corn grain Hg concentration data to compute site specific UC values for the site and compared this site specific values with the UC utilized for grain, animal forage and sweet corn in the Part 503 risk assessment models. For this purpose it is needed to analyze the regression for the relation between Hg concentration of stem and grain with Hg loading rate of sludge in the soil [relations (1) and (2)].

$$\text{Corn stem Hg concentration} = 0.53\ (\text{Hg Loading Rate}) + 7.4 \quad R^2 = 0.14 \tag{1}$$

$$\text{Corn grain Hg concentration} = 0.31\ (\text{Hg Loading Rate}) + 7.7 \quad R^2 = 0.06 \tag{2}$$

The slope of the regression line can be converted to UC by multiplying by 0.001 (to convert the plant tissue concentration units from μg kg^{-1} to mg kg^{-1}).

Thus UC for Hg into corn stem and corn grain at site is 0.0005 and 0.0003 (mg Hg/kg tissue)/ (kg Hg/ha soil), respectively.

These results indicate that the UC utilized for grain and animal forage by the US-EPA over estimates the uptake of Hg into these crops in our study. The US-EPA's UC for grain and animal forage predicts that for each kg of Hg loaded onto a hectare of soil, the concentration of Hg in the grains and animal forages grown on that soil should increase by 0.043 mg kg^{-1} or by 43 μg kg^{-1}. However, even if crop tissue contained no Hg on fields prior to sludge applications, the US-EPA's UC predicts that at Hg loading rates of 5 kg ha^{-1}, the grains and animal forages grown on this sludge amended soils should contain 215 μg Hg kg^{-1}. This tissue Hg concentration is nearly eleven times higher than the highest tissue Hg concentrations ever observed at our site.

4. CONCLUSIONS

Application of sewage sludge increased the mean concentration of Hg in soil by about 14 folds as compared to the plots with no sludge application. Concentration of Hg in root, stem and grain of corn also increased with sludge application and thereafter decreased again as time passed since the last sludge application. In general, the mean concentration of Hg in different corn tissue grown in sludge treated plots was about 200% more than the control. In general, the mean concentration of Hg in stem and grain grown in sludge treated plots were 2 and 3 folds as compared to the control plot, respectively.

Sewage sludge applications also increased crop yield significantly. The effect of sludge on corn yield was still visible even five years after a single sludge application.

Because of limited information on Hg uptake of plants in sewage sludge treated soils and the plant in such soils, the results of this study can be useful in definition and amendment of standards by the U.S EPA.

Although the increased uptake of Hg by corn, was comparatively small and did not exceed control levels of food and feed quality, using sludge with high heavy-metal concentrations as fertilizer may eventually lead to the build-up of metal concentrations which do no longer allow the production of safe food, despite the high potential of the investigated soil to immobilize the metals. Thus, we recommend regulation of the quality of the applied sewage sludge with respect to heavy metals.

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Effect and Distribution of a Metabolic Uncoupler, 2,6-dichlorophenol in Activated Sludge Batch Culture

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ABSTRACT: The effects of 2,6-DCP on excess sludge reduction and COD removal efficiency, and the distribution of 2,6-DCP between wastewater and activated sludge were investigated in laboratory batch experiments. The results confirmed that 2,6-DCP was an effective chemical in limiting the sludge growth which was able to reduce sludge growth rate by around 43.27% at 2,6-DCP dosage of 20 mgL^{-1} with the COD removal efficiency decreased by 6.25%. An average of 81% of 2,6-DCP in the influent was still persistent in the effluent independent of the influent concentration, whereas between 6.51% and 30.53% was adsorbed to the activated sludge.

INTRODUCTION

THE activated sludge process is the most widely used biological treatment system for both municipal and industrial wastewater plants in the world. However, the increase in excess sludge production, together with the more stringent regulations, generates a real challenge in the field of environmental engineering technology. There is considerable impetus to develop strategies and technologies for reducing excess sludge production in biological wastewater treatment processes [1–4]. An ideal way to solve the above problem is to reduce sludge production in the wastewater treatment rather than the post-treatment of the sludge produced [5]. Therefore, intensive attention has been received during the past years on the technologies for minimization of excess sludge production applied in the wastewater purification processes based on the following mechanisms: lysis-cryptic growth, maintenance metabolism, predation on bacteria and uncoupling metabolism [5–8].

Addition of protonphores to uncouple the energy generating mechanisms of oxidative phosphorylation will stimulate the specific substrate uptake rate while reducing the rate of biomass production [5]. In view of the engineering feasibility of utilizing the above strategies to reduce the excess sludge production, only the introduction of chemical uncoupler seems to be feasible, provided that only the addition of low-price chemical uncoupler dosing without process changing, while the other means are either technically impossible or too expensive to implement though significant sludge reduction can be observed [2,9–19]. For example, sludge ozonation is considered one of the most effective techniques in the strategy of lysis-cryptic growth for sludge reduction, when the ozone dose was kept as high as 20 mgg^{-1} MLSS in aeration tank per day, no excess sludge was produced [10]. However, high costs involved in ozonation must be considered [5]. Recently, worms grazing on sludge is attractive for sludge production minimization because it is energy saving and brings no secondary pollution, however, the practical application of worms for sludge reduction is still uncontrollable in biological wastewater treatment processes because of unstable worm growth, high variation of worm density, nitrate and phosphate concentration increase in the effluent [3,20–22].

Therefore, chemical uncoupler has been given increased attention to be used for sludge reduction. Nowadays, many researchers have focused on sludge reduction induced by chemical uncouplers, such as chlorinated and nitrated phenols and TCS [1,23–30]. Strand *et al.* screened the most effective uncoupler 2,4,5-trichlorophenol (TCP) from 12 chemicals and found that the sludge yield was decreased by 50% after

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TCP addition, which suggested that addition of chemical uncouplers to biological wastewater treatment systems could significantly reduce sludge production [25]. Low *et al.* investigated the effectiveness of pNP on reducing biomass production in a bench-scale activated sludge process [1]. The results revealed that the biomass reduction was 49% but the total substrate removal efficiency was also decreased by 25%. Chen *et al.* evaluated the feasibility of using TCS as the energy uncoupler to reduce activated sludge production [23]. The sludge production can be reduced by around 40% when the TCS concentration was 0.8 mgL^{-1}. With such TCS concentration, substrate removal capability was not affected significantly. Yang *et al.* compared four metabolic uncouplers (pCP, mCP, mNP and oNP) in reducing sludge production from an activated sludge process [24]. Results of batch experiments showed that mCP was the most effective for sludge reduction which was able to reduce sludge growth rate by 86.8% at a mCP concentration of 20 mgL^{-1}, while the COD removal efficiency was lowered by 13.5%. Table 1 summarizes the effects of different chemical uncouplers on sludge production and performance of activated sludge systems.

Although a number of investigators have studied chemical uncouplers, previous works only focused on the evaluation of their effects on excess sludge reduction and system performances in terms of substrate removal efficiency and sludge characteristics [1], and information on the fate of chemical uncoupler in the sewage treatment system is lacking. If these compounds are not completely mineralized within a treatment system then it is possible for some fraction of the chemicals involved to be released into the environment as part of the final effluent discharge, which may pose serious ecological problem as environmental secondary pollutants. Therefore, before using chemicals as metabolic uncouplers to reduce excess sludge production in practical operation, the distribution of a metabolic uncoupler in the activated sludge system, the bio-safety of the remaining uncoupler in the effluent should be studied first.

In the present study, batch test systems were utilized to examine the distribution and effect of a metabolic uncoupler, 2,6-dichlorophenol in activated sludge culture. Specific objectives were to determine the distribution of 2,6-DCP between the dissolved phase of wastewater and the sorbed phase of sludge, to investigate to what extent volatilization and biodegradation contribute to removal of 2,6-DCP in sewage treatment process. Moreover, the effects of 2,6-DCP on the sludge growth rate and COD removal efficiency were studied.

MATERIALS AND METHODS

Cultivation of Activated Sludge

As initial seed for the fed-batch reactor, the activated sludge used was taken from a local municipal wastewater treatment plant in Harbin, China. After screening through a 2 mm sieve, activated sludge was cultivated in a 80 L SBR reactor housed in a room at 25 ± 1°C as fed-batch reactor. SBR was operated sequentially in 8 h cycle with 10 min for the fill phase, 6 h for the aeration phase, 1.5 h for the settling phase and 10 min for the drawing phase. Excess sludge withdrawing did not start until the mixed liquor suspended solids

Table 1. Effects of Chemical Uncouplers on Excess sludge Production and System Performance.

Chemical Uncouplers (mgL^{-1})		Sludge Reduction (%)	Substrate Removal (%)	References
3,3’,4’,5-tetrachlorosalicylanilide	1.0	40	nearly unaffected	[8,23]
	0.8	60	ammonia-N decreased by 77	[31]
2,4-dinitrophenol	5	21	not affected	[29,32]
	35	0.3[a]	COD decreased by 3.7	[33]
p-nitrophenol	100	49	COD decreased by 25	[1]
	100	62–77		[34]
m-nitrophenol	20	65.5	COD decreased by 13.2	[24]
m-chlorophenol	20	86.8	COD decreased by 13.5	[24]
2,4-dichlorophenol	20	0.59a	nearly unaffected	[28]
o-nitrophenol	20	86.1	COD decreased by 26	[24]
2,4,6-trichlorophenol	2.0	47	nearly unaffected	[35]
p-chlorophenol	20	58	COD decreased by 8.9	[24]
2,4,5-trichlorophenol	2.0–2.5	50		[25]

[a] The average sludge yield, mg SS/mg COD.

(MLSS) level exceeded 2500 mgL^{-1}. The dissolved oxygen (DO) level was kept above 5 mgL^{-1}. Tap water was used to prepare feed solutions throughout SBR operation. Synthetic wastewater, composed of glucose and starch (final concentration equal to 400 mg CODL^{-1}), ammonium chloride and carbamide (final concentration 40 mg NL^{-1}), phosphate (final concentration 8 mg PL^{-1}), and other minerals were fed to SBR reactor daily. The same synthetic substrate was used in the following batch experiments. The cultivation continued for one month without the addition of 2,6-DCP. The composition of synthetic wastewater is shown in Table 2.

Response of Activated Sludge Culture Cultivated Without 2,6-DCP to Addition of 2,6-DCP at Various Levels

In order to identify the effects of 2,6-DCP at different concentrations on the sludge production and COD removal performance, batch tests were conducted in 7 L reactors at various influent concentrations of 2,6-DCP ranging from 0.5 mgL^{-1} to 30 mgL^{-1}. For all the batch tests, initial biomass and influent substrate concentrations were fixed at 1200 mg MLSSL^{-1} and 400 mg CODL^{-1}, respectively. Batch tests were carried out for 3 h at 25 ± 1°C and pH 7.0 ± 0.3, and the reactors were aerated with air pumps to maintain a dissolved oxygen concentration of at least 5 mgL^{-1}. Meanwhile, control tests without the addition of 2,6-DCP were also conducted in parallel. In this paper, S-COD was represented by COD.

Distribution of 2,6-DCP in the Effluent and Activated Sludge

Distribution experiments of 2,6-DCP were conducted in 7 L reactors at various influent concentrations of 2,6-DCP ranging from 0.5 mgL^{-1} to 30 mgL^{-1}. Other operation conditions were the same as the details in the 2.2. Batch tests were carried out for 9 hrs (9 hrs for the aeration phase) and sample solutions were taken from reactors at fixed intervals of time (3 h, 6 h and 9 h) to study the distribution of 2,6-DCP in the effluent and activated sludge with reaction time.

Table 2. Composition of the Synthetic Wastewater.

Constituents	Concentration (mgL^{-1})	Constituents	Concentration (mgL^{-1})
Glucose	200	$MgSO_4$	40
Starch	200	$MnSO_4 \cdot H_2O$	1.25
$CO(NH_2)_2$	32.1	$FeSO_4 \cdot 7H_2O$	1.25
NH_4Cl	95.5	$CoCl_2$	0.3
KH_2PO_4	17.6	$ZnSO_4 \cdot 7H_2O$	1.25
K_2HPO	29.4	$CaCl_2$	5
$NaHCO_3$	300	$CuSO_4$	0.25

Influences of Volatilization and Biodegradation on the 2,6-DCP Mass Loss

Volatilization and biodegradation were studied in the batch tests by monitoring the effluent concentrations of 2,6-DCP under operating conditions similar to those of 2.2 and 2.3. To investigate the influence of volatilization on the 2,6-DCP mass loss, the reactors were filled with water instead of sludge at different influent concentrations ranging from 1 mgL^{-1} to 40 mgL^{-1}. For the biodegradation influence tests, 0.1% (wv^{-1}) sodium azide (NaN_3) inactivated sludge was used to compare with the control without NaN_3 dosing under three concentrations (10–30 mgL^{-1}). Samples were taken at certain intervals.

Chemicals and Analytical Methods

Stock solutions of the tested compound were prepared in ultra-pure water by weighting appropriate amounts of 2,6-DCP (99%, AccuStandard, USA), and stored at 4°C. Working solutions were prepared by diluting proper volumes of stock solutions in influent wastewater.

Before analysis, samples were centrifuged at 5000 g for 10 min to separate the aqueous phase from the sludge, the supernatant fluid filtered immediately through 0.45 μm membranes. Analytical parameters, including dissolved COD (S-COD), MLSS, mixed liquor volatile suspended solids (MLVSS) were measured according to the Standard Methods [36]. The activated sludge yield (Y) was determined from the increase in MLSS divided by the decrease in COD during the batch tests, while the ratio of ($Y_0 - Y$) to the respective corresponding value without the addition of metabolic uncoupler (Y_0) was defined as the sludge reduction rate (R).

The concentration of 2,6-DCP in the effluent was analyzed using an HPLC (Shimadzu, LC-10AT) equipped with an ultraviolet detector. The measurements were performed at 203 nm. The column was an Waters symmetry C-18 4.6 mm × 150 mm (USA). A mixture of acetonitrile (70%) and water (30%) was used as solvent at a flow rate of 1 mL min^{-1} at room temperature. The sample injection volume was 20 μL.

A mixture of acetone-hexane (80 mL, 1:1 vv^{-1}) was used to extract 2,6-DCP from sludge solids because acetone is an extremely polar solvent assisting the penetration into the matrix. The weighed sample and anhydrous sodium sulfate (1 g, dehydrated, extra pure) were piaced into the thimble. The sample was extracted by Soxhlet for 20 h (124 cycles). The extracts were further dried with anhydrous sodium sulfate and concentrated to 10 mL for the GC analysis under nitrogen flow.

The 2,6-DCP concentration of activated sludge were determined with Gas Chromatography (GC) operated on a Agilent 7890 chromatograph. The optimal condition was set for 150°C, injector temperature; 270°C, FID temperature; 30 kPa, inlet pressure; 35, split ratio and the temperature program followed as 150°C (5 min), then to 280°C at 55°C min^{-1}.

RESULTS AND DISCUSSION

Effects of 2,6-DCP Concentration on Sludge Reduction and COD Removal

Figure 1 shows the effects of 2,6-DCP concentration on the activated sludge yield (Y) and sludge reduction rate (R) during the 3 h batch tests conducted at various 2,6-DCP influent concentrations, ranging from 0 mgL^{-1} to 30 mgL^{-1}. It is apparent that the sludge yield significantly decreased with an increase in 2,6-DCP concentration. This phenomenon became more significant when the 2,6-DCP concentration was beyond 5 mgL^{-1}. For instance, the sludge reduction rate increased from 16.32% ($Y = 0.56$) to 43.27% ($Y = 0.38$) with an increase of 2,6-DCP concentration from 5 mgL^{-1} to 20 mgL^{-1}. This conclusion was found to be similar to that of other researchers [23,24]. Chen and Yang also found that increased metabolic uncoupler concentration resulted in a decreased activated sludge yield. When p-chlorophenol concentration was increased to 20 mgL^{-1}, a sludge reduction of 58% was observed compared with the control test [24]. In this study, the analysis results confirmed that 2,6-DCP could reduce the excess sludge production significantly.

The COD removal efficiency under various 2,6-DCP concentrations after the 3 h batch tests is shown in Figure 2, which exhibits a decreasing trend with an increase of 2,6-DCP concentration in a range of 0–30 mgL^{-1}. Compared with the control, 2,6-DCP at a low level, e.g., 5 mgL^{-1} or lower, COD degradation was influenced slightly. However, a further increase in 2,6-DCP dosage to a higher level, e.g., 30 mgL^{-1}, COD removal efficiency was severely inhibited. For example, at a 2,6-DCP concentration of 30 mgL^{-1}, it was decreased by 15.25% as compared to the control test (96.18%) without addition of 2,6-DCP, which demonstrated that addition of 2,6-DCP to the activated sludge culture had adverse impact on system performance especially when dosed at a high level. The decline in the COD removal efficiency may be the result of combined effects of species shift, reduced biomass production and potential inhibition induced by chemical uncoupler [1,24].

In order to analyze the cause of the sludge reduction, the specific biomass growth rates (μ, h^{-1}) and specific

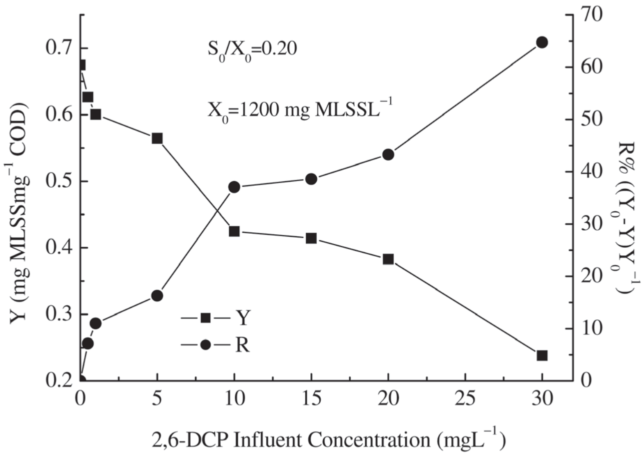

Figure 1. Effects of 2,6-DCP concentration on the sludge yield (Y) and sludge reduction rate (R).

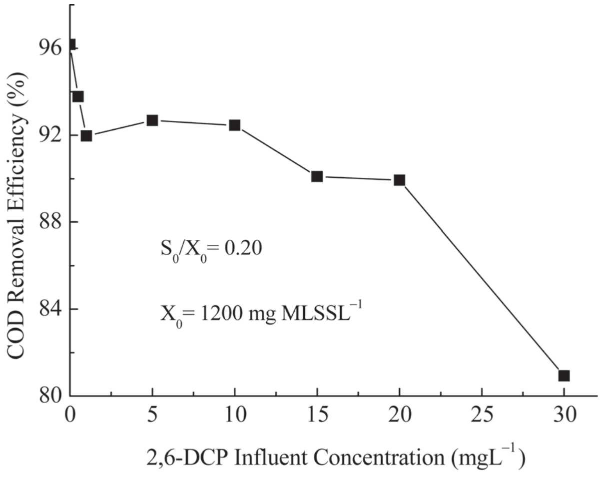

Figure 2. Effect of 2,6-DCP influent concentration on the COD removal efficiency.

substrate removal rates (q, h^{-1}) were determined from the change in MLSS or COD over the batch tests divided by both the testing duration (3 h) and the mean MLSS concentration in the tests. The ratio of the μ or q at various 2,6-DCP concentrations to the respective corresponding value without the addition of 2,6-DCP is defined as a relative specific sludge growth rate (μ/μ_0) and a relative specific substrate removal rate (q/q_0) [8,23].

The effects of 2,6-DCP dosage on these two parameters are shown in Figure 3. Both the relative rates decreased with the increasing 2,6-DCP concentration. However, the response of μ/μ_0 to 2,6-DCP dosage exhibited a different pattern as that of q/q_0. The 2,6-DCP concentration had a more inhibitory effect on μ/μ_0 than on q/q_0. This reveals that the reduction in Y is predominately due to the significant decrease in sludge growth, which is induced by 2,6-DCP. Another finding from this figure was the slopes of μ/μ_0 and q/q_0 were well associated when the 2,6-DCP concentration was below 5 mgL^{-1}, indicating the coupling of catabolism with anabolism; When the concentration was beyond this level, a large discrepancy or uncoupling between these two parameters occurred. Thus, a 2,6-DCP concentration higher than 5 mgL^{-1} stimulated the energy spilling that resulted in a significant reduction in sludge growth in this study. Similar phenomenons were also observed when 2,4-DNP and 2,4-DCP were dosed into the activated sludge processes, and 10 mgL^{-1} and 5 mgL^{-1} were found to be the threshold of triggering a sludge reduction, respectively [28,32]. It was clear that the threshold obtained varied with different metabolic uncouplers under different operation conditions in the activated sludge systems.

Based on the above experimental results, it is understood that the effective concentration of 2,6-DCP for sludge reduction should be kept above 5 mgL^{-1}. However, a much higher dosage may not only hinder the substrate remove rate (Figure 2) but also increase operational cost. Thus, 20 mgL^{-1} was selected as the optimal concentration for sludge reduction compared with 10 mgL^{-1} and 15 mgL^{-1}, if a compromise of sludge reduction and COD removal efficiency was taken into account.

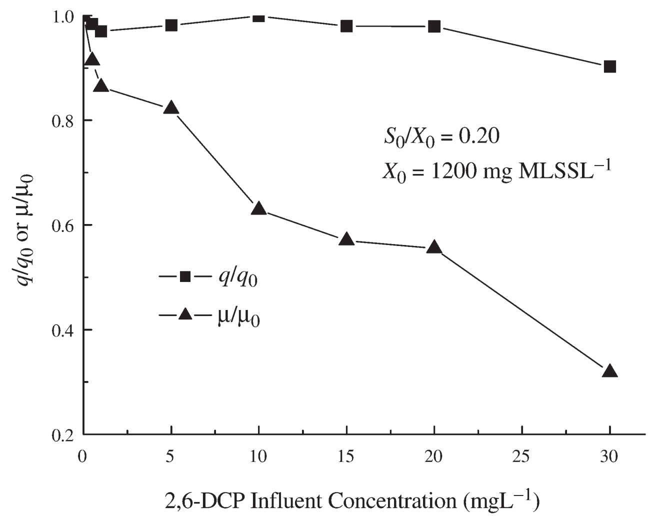

Figure 3. Relative specific COD removal rates (q/q0) and sludge growth rates (μ/μ_0) at various 2,6-DCP concentrations.

Distribution of 2,6-DCP in the Effluent and Activated Sludge

To determine the distribution of 2,6-DCP in the activated sludge system, six concentrations of 2,6-DCP were dosed to activated sludge, and the effluents were monitored with time. The relative distribution of 2,6-DCP between the dissolved phase of wastewater and the adsorbed phase of sludge samples obtained in this study is presented in Table 3. As shown, hourly effluent samples obtained over the course of 9 hrs showed no significant variability in 2,6-DCP concentrations at six influent concentrations (0.4 mg, 0.8 mg, 4 mg, 8 mg, 16 mg and 24 mg) of 2,6-DCP demonstrating that up to 80% of the entering mass, with a range of

Table 3. Concentrations of 2,6-DCP Determined in Influent, Effluent and Activated Sludge.

Influent (mg)	Activated Sludge (mgg^{-1} dry weight)	Sorption to Sludge (%)	Effluent (mgL^{-1}) 3h	6h	9h	Percentage Effluent Recovered (%)
0.4	0.09 ± 0.01	26.84 ± 0.06	0.30 ± 0.02	0.29 ± 0.01	0.28 ± 0.02	73.01 ± 0.01
0.8	0.18 ± 0.01	30.53 ± 0.92	0.57 ± 0.01	0.52 ± 0.06	0.56 ± 0.04	69.26 ± 0.02
4	0.46 ± 0.03	14.19 ± 0.05	3.41 ± 0.05	3.38 ± 0.09	3.42 ± 0.02	85.12 ± 0.02
8	0.66 ± 0.01	10.97 ± 0.03	6.94 ± 0.12	6.96 ± 0.08	6.98 ± 0.01	87.03 ± 0.02
16	1.06 ± 0.01	7.98 ± 0.08	13.91 ± 0.10	13.75 ± 0.08	14.09 ± 0.02	87.02 ± 0.17
24	1.29 ± 0.02	6.51 ± 0.12	20.96 ± 0.21	21.97 ± 0.16	21.49 ± 0.20	89.49 ± 0.51

69.26%–89.49% and an average of 81.82%, was still persistent in the liquid phase independent of the influent concentration. When reported on a dry weight basis, the mean concentration of 2,6-DCP in activated sludge was about 0.62 $\mathrm{mgg^{-1}}$. Minimum and maximum values spanned the range of 0.09 ± 0.01 $\mathrm{mgg^{-1}}$–1.29 ± 0.02 $\mathrm{mgg^{-1}}$ demonstrating that between 6.51% and 30.53% and an average of 16.17% of the initial mass of 2,6-DCP was sorbed to the activated sludge.

On the basis of data collected in the experiments of 3.3 and 3.4, neither 2,6-DCP volatilization nor biodegradation was observed throughout the 48-h batch tests, and the effluent was the major process governing the distribution behavior of 2,6-DCP in this study. Data in Table 3 suggests that 2,6-DCP existence in the effluent could not be ignored because it is present in relatively high concentration. Before using chemicals as a metabolic uncoupler to reduce sludge generation in practical operation, the fate of the metabolic uncoupler in the sludge system during a long-term period should be studied and the bio-safety of the remaining uncoupler in the effluent should also be investigated for further study.

Abiotic Removal of 2,6-DCP in the Batch Culture

Considering that the combined effects of sorption, advection, volatilization and biotransformation may, in any particular system, determine the overall removal of the selected compound from the wastewater, the following experiments were performed to estimate the removal of 2,6-DCP in the reactor by abiotic processes, such as volatilization, photodegradation and physical adsorption to the reactor. The reactors were filled with water instead of activated sludge, according to Quan *et al.* who studied biodegradation removal of 2,4-DCP in an air-lift honeycomb-like ceramic reactor [37], to maximize the mass loss of 2,6-DCP induced by the abiotic removal during the batch tests, whereas operated the same as the above batch experiments. The abiotic loss of 2,6-DCP from wastewater containing various initial concentrations of 2,6-DCP in the reactors was investigated (Figure 4). Samples were taken after 48 hrs to analyze the concentrations of 2,6-DCP in the effluents. The removal percentage of 2,6-DCP by volatilization and photodegradation was calculated through Equation (1):

$$R(\%) = 100 \times \frac{(M_i - M_e)}{M_i} \tag{1}$$

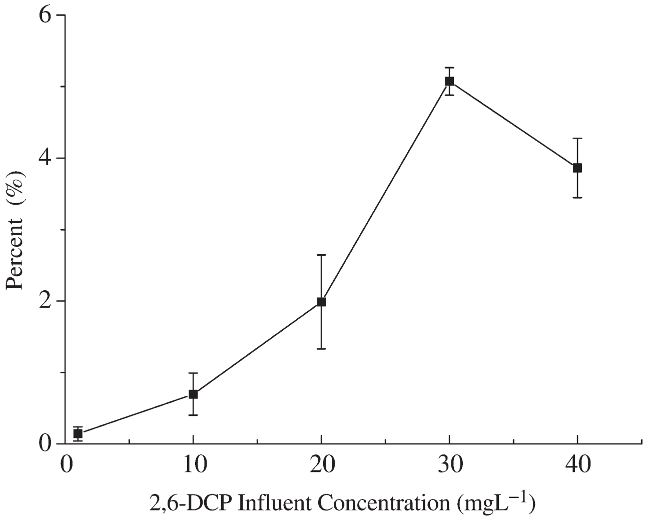

***Figure 4.** Abiotic loss of 2,6-DCP at various influent concentrations in the reactors.*

where $R\%$ is the removal percentage of 2,6-DCP by abiotic loss including volatilization and photodegradation; M_i is the influent 2,6-DCP mass, M_e is the 2,6-DCP mass in the effluent after 48-h operation.

As shown in Figure 4, when the initial concentrations of 2,6-DCP varied between 1 $\mathrm{mgL^{-1}}$ and 40 $\mathrm{mgL^{-1}}$, the abiotic loss was within around 5%, which indicated that abiotic loss of 2,6-DCP accounted for a small part of removal efficiency compared with the mass persistent in the dissolved phase. This finding is consistent with work by Quan *et al.*, who observed the abiotic loss of 2,4-DCP was within 5% when the initial concentrations of 2,4-DCP were between 10 $\mathrm{mgL^{-1}}$ and 60 $\mathrm{mgL^{-1}}$ in an air-lift honeycomb-like ceramic reactor [37].

Biodegradation Removal of 2,6-DCP in the Batch Culture

The effect of biodegradation on the removal of 2,6-DCP in the activated sludge system was estimated by using the inhibitor of activated sludge microbial activity, sodium azide (NaN_3). The results are presented in Figure 5. Figure 5 showed no significant differences of 2,6-DCP concentrations in the effluents between activated and inactivated sludge cultures under all the three concentrations investigated. Furthermore, a significant part of 2,6-DCP was persistent in the effluent during the first 10 h of the experiment, which was consistent with the results of the distribution of 2,6-DCP in the effluent and activated sludge (Section 3.2), and its mass in the dissolved phase remained almost constant up to the end of the experiment (48 hrs).

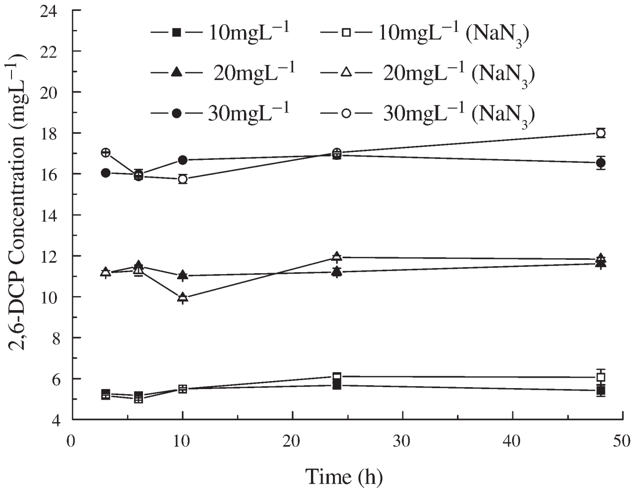

Figure 5. *Influence of biodegradation on 2,6-DCP removal in the batch cultures.*

This observations lead to the conclusion that the influence of biodegradation and transformation on the 2,6-DCP removal is negligible or insignificant at three influent concentrations (10 mgL^{-1}, 20 mgL^{-1} and 30 mgL^{-1}) of 2,6-DCP within the contact time of 48 hrs for activated and inactivated sludge batch cultures. In order to obtain a chlorophenol degrading culture, 5 months or longer time was adopted for biomass selection [37,38], which also demonstrated that the cultivation of 2,6-DCP degrading culture in short time is difficult.

According to the results of this study, persistent in the liquid phase was the major mechanism affecting its behavior during the short-term activated sludge batch culture. As shown in Figure 6, 16 ± 10% of the initial mass of 2,6-DCP on average was sequestrated in the sludge with an average of 81 ± 8% of the total mass dissolved in the out-flowing water. No more than 3 ± 2% of the mass was lost as a result of the sum of potential removal mechanisms including abiotic loss and biodegradation.

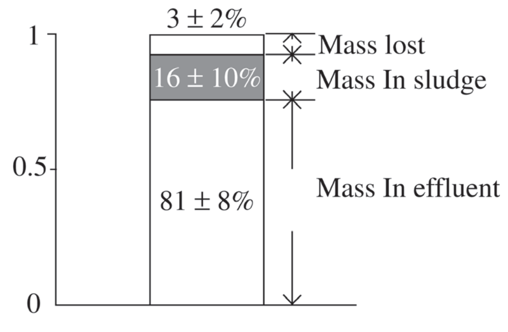

Figure 6. *Distribution of 2,6-DCP in activated sludge batch culture.*

CONCLUSIONS

The effect and distribution of a metabolic uncoupler, 2,6-dichlorophenol in activated sludge batch culture were examined in this study. 2,6-DCP has been confirmed to be effective in limiting excess sludge production. The 5 mgL^{-1} concentration of 2,6-DCP was found to be the threshold of triggering the energy uncoupling and 20 mgL^{-1} was the optimal dosage. The 3 h batch tests have demonstrated that sludge growth can be reduced by around 43.27% at a 2,6-DCP concentration of 20 mgL^{-1} while the COD removal efficiency was lowered by 6.25% as compared to the control test. Up to 81±8% of the entering mass still remained in the effluent independent of the influent concentration and hourly effluent samples obtained over the course of 9 hrs showed no significant variability in 2,6-DCP concentrations under six influent concentrations. Between 6.51% and 30.53% of 2,6-DCP and 16% on average was sorbed to the activated sludge. It was also found that the impact of abiotic loss and biodegradation on the removal of 2,6-DCP can be negligible during the batch tests. Thus, the current concern over the metabolic uncoupler entering the aquatic environment would indicate the need for further careful investigation and reporting.

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Long-term Effects of Land Application of Class B Biosolids on Soil Chemical Properties

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ABSTRACT: Currently about 60% of all biosolids are land applied in the United States. The long-term influence of land application has been questioned due to public concern over potential hazards. The objective of this study is to evaluate the influence of land application of Class B biosolids on the soil chemical properties by analysis of depth (0–150 cm) soil samples collected 9 months after the 20th annual land application. The study showed that land application of Class B biosolids had no significant long-term effect on soil pH and $CaCO_3$. However, land application significantly increased soil macro-nutrients (C, N and P). Soil nitrate values in plots that received biosolids or inorganic fertilizer amendments were high indicating the potential for groundwater contamination. In addition, total and available soil P concentrations increased to values above that necessary for plant growth but P values attenuated to background levels at a soil depth of 150 cm. Total metal concentrations attenuated rapidly with increasing soil depth, and were generally similar to values found in control soils at a depth of 150 cm. Application of biosolids for nonfood agricultural crop production at this arid southwest site seems to be sustainable with respect to soil chemical entities.

INTRODUCTION

IN 1986, a study was initiated at the University of Arizona Marana Agricultural Center, 21 miles north of Tucson to determine the effects of long-term annual applications of biosolids on an irrigated agricultural field annually planted with cotton. In the United States, the term biosolids implies treatment to produce Class A or Class B biosolids that meet the land-application standards in the Part 503 Environmental Protection Agency regulations [1]. Biosolids are a complex mixture of organic and inorganic compounds of biological and mineral origin resulting from treatment of sewage at wastewater treatment plants and approximately 5.6 millions of dry tons are produced every year [2]. Class B biosolids are normally produced as a "cake" (≅ 20% solids) or as liquid biosolids (≅ 5–8% solids). In this present study, the applied biosolids consisted of anaerobically liquid digested Class B biosolids (≅ 5–8% solids) that resulted from wastewater treatment of sewage from the City of Tucson.

Generally, sustainability of any process implies that the process can be maintained indefinitely but also addresses the needs of the present practice without compromising the ability of future generations to meet their needs. In this context, this study focuses on the effect of 20 years of repeated annual land applications of biosolids on soil quality with respect to chemicals. Biosolids can contain organic compounds and depending on its origin, biosolids may also contain variable amounts of trace metals [3]. These have resulted in public health concerns with regard to risks of exposure to hazardous chemical components found in soils following biosolid amendment of soils [4]. However, congressional and U.S.EPA actions resulted in many industries being banned from discharging metals or organics into wastewater without strict pretreatment of unwanted organic compounds (e.g. PCBs, DDT, heptachlor, etc) because of the health problems that could result [5]. Other chemicals of concern that have recently become the target of EPA investigation are "emerging chemicals of concern" including: endocrine disrupting compounds (EDCs), polybrominated diphenyl ethers (PBDEs), pharmaceuticals, personal care products (PPCPs), and endotoxins [4,5,6]. However, several

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studies reported that EDC levels following land application were very low because a wide range of them were rapidly degraded or mineralized in soil. This indicates that current practices of land application are likely to be sustainable with respect to EDCs [7,8,9]. Currently about 60% of all biosolids are land applied in the United States with most of the land receiving Class B biosolids [2].

Current debates and concerns of public health risks from trace metals as a result of land application of biosolids focus on two hypotheses known as the sludge protection hypothesis and sludge time-bomb hypothesis. Advocates of the biosolids protection hypothesis predict that trace metals are bound within biosolids components in forms that are not readily available as long as trace metals of concern persist in soils [10]. On the contrary, the biosolids time-bomb hypothesis predicts the release of trace metals as more biosolids-derived organic matter becomes degraded [3,11,12]. However, several studies have shown that the potential public health hazard from trace metals is very low for two major reasons. First, trace metals bioavailability tends to decrease over time. Secondly, metal concentrations found within biosolids have decreased over the past 20 years due to improved point-source control or enhanced pretreatment technologies. Thus, the potential for metal contamination of soil or surface waters from land application of biosolids has decreased [13,14,15].

Other researchers have shown that long-term land application of biosolids can have significant positive effects on the microbial and chemical properties of the soil [16,17,18,19]. However, monitoring soil quality by measuring soil chemical properties is also useful in managing and maintaining the sustainability of soils that receive biosolids as a land application [20]. Thus, having an agricultural field with a 20 year history of land application of biosolids provided a unique opportunity for evaluation of the long-term effects of biosolids on various chemical nutrients and metal levels in soils.

In the prior study conducted on the same fields, the effect of land application of biosolids on the soil microflora at the Marana study site was evaluated [17]. That study showed that 4 years of land application of biosolids to an agricultural desert soil in the southwest U.S.A did not adversely affect soil chemical properties. The goal of this study was to evaluate the influence of 20 annual land applications of Class B biosolids on the soil chemical properties. Specifically, interest centered on several questions: (1) Are there benefits to the soil or crop following long-term land application? (2) Are there potential hazards to human or ecosystem health? Finally, the study provides information on the sustainability of long-term land application of Class B biosolids in the arid southwest.

MATERIALS AND METHODS

Municipal Class B biosolids have been used as a soil amendment for 20 years at the University of Arizona Marana Agricultural Center (1986–2005). The design of the experiment was a randomized block design, with four replicates of four treatments. Plots were 5 m wide and 101 m long. The four treatments were: (1) control (no amendment); (2) inorganic fertilizer control (160 kg ha^{-1} of N and 20 kg ha^{-1} of P); (3) biosolids at an agronomic rate (1×) based on the nitrogen requirements for the growth of cotton (*Gossypium hirsutum* L.) (160 kg N ha^{-1}) (8.0 t ha^{-1} yr^{-1}), and (4) biosolids at a high rate (24.0 t ha^{-1} yr^{-1}). Total N in the biosolids applied to the field was available over the course of the study and ranged from 3–5%. Comparable values for total organic carbon were 15–28%. The land applied biosolids contained 8% solids and were applied by injection or spray irrigation throughout the 20 year study. Regardless of the method of application, the depth of biosolids incorporation was similar (30 cm) since spray applied biosolids were subsequently disked into the soil. Biosolids were applied in the spring of each year around March/April. All plots were subsequently utilized for the growth of cotton and furrow irrigated as necessary for optimum plant growth under the environmental conditions of the Sonoran Desert. Water supplied as irrigation was approximately 100 cm per growing season, since the consumptive water use requirements for cotton are 92 cm per season (Personal communication, J.C. Silvertooth). The soil at this site is classified as a Pima clay loam. This fine textured soil is classified as a Typic Torrifluvent (38% sand, 36% silt and 26% clay). Soil pH was 7.7 with a cation exchange capacity of 249 mmol (+) kg^{-1} dry soil. The site is located within the arid Sonoran Desert environment where summer temperatures are routinely above 35ºC and rainfall is minimal (30 cm annually).

Four cores were collected from each treatment (one soil core sample from each replicated plot) using a soil auger cores 7.5 cm in diameter to a depth of 150 cm depths in 30cm intervals. Soil samples were taken from each of the treatment plots across a transect line down the length of the plot to determine the soil chemical properties as a function of depth. The samples were taken in December 2005, nine months after the 20th land application in March 2005. Soils were air dried, sieved through a 2 mm sieve, and sent for analysis to the University of Arizona, Water Quality Center Lab (WQCL).

Analysed soil chemicals clustered into two main groups: soil macro elements (N, P, and C) and heavy metals. Specifically, soil samples were analyzed for: soil pH; electrical conductivity (EC); $CaCO_3$; NO_3; total organic carbon (TOC); total nitrogen (TN); total phosphorus (TP); available phosphorus (Olsen bicarbonate extraction); total metals; and diethylene triamine penta-acetic acid (DTPA) metal concentrations. The pH and EC were measured in 1:1 soil: deionized water ratio (Accument pH 50, Fisher Scientific, Pittsburg, PA) [21] and $CaCO_3$ concentration was determined using H_2SO_4 digestion and back titration [22]. NO_3 was measured from a 1:1 soil: water extracts using ion chromatography (Dionex ICS-100 Ion Chromatography, Sunnyvale, CA) [23]. Soil samples were also pretreated with phosphoric acid for TOC and TN analysis using CNS analyzer (Carlo Erba NA-1500, Milan, Italy) [24], while available P was extracted using the ascorbic acid colorimetric extraction method (Olsen P) extraction) [21]. The EPA-3050B [25] microwave digestion (CEM, MDS-2100, Matthews, NC) procedure was employed to determine total P, total metal, DTPA metal concentrations and extracts were measured using optical emission spectrometry and inductively coupled plasma-mass spectrometry (ICP-MS Elan 6100/ICP-OES, Perkelmer Instruments, Shelton, CT).

Analysis of variance (one-way ANOVA) was performed using the statistical software package (SYSTAT Software, Inc, San Jose, CA). Results of all tests were considered significant at the 95% confidence level.

RESULTS AND DISCUSSION

Influence of Land Application of Biosolids on Macro Elements

Land application of biosolids did not significantly affect $CaCO_3$ or salinity (measured by electrical conductivity, EC) values as compared to the control (no amendment) plots. Soil pH values in the surface control plots were 7.7 compared to 7.9 in the high rate (3×) biosolid plot, but differences were likewise not significant. Soil $CaCO_3$ values in surface control plots were 5.0% compared to 4.6% in the biosolid amended plots. EC values in all plots were between 0.6–0.9 mmhos/cm. Other researchers have also reported that the long-term application of biosolids did not significantly affect soil pH [26,27]. However, previous studies at this same Marana site reported that there were significantly elevated EC levels in the high biosolid treated soils immediately after biosolids application [17]. In this present study, all plots were utilized for the growth of cotton and furrow irrigated as necessary for optimum plant growth, prior to soil sampling. Water supplied as irrigation was approximately 100 cm per growing season, since the consumptive water use requirements for cotton are 92 cm per season. Therefore the lack of salinity 9 months after the final biosolids application was likely due to the leaching of soluble salts through the soil profile since irrigation rates were almost twice the evapotranspiration requirements for cotton. A recent study, [27] showed that increased levels of EC in soils were due to high application rates of biosolids as compared to untreated controls. It is important to note that there are differences between these studies with respect to different cropping systems, biosolids type, climate and soil type, as well as irrigation rates utilized in the arid southwest.

Long-term land application significantly increased soil macro-nutrients including soil nitrate, total nitrogen (TN), total organic carbon (TOC) (Table 1, Figure 1), and both available and total phosphorous (P) concentrations (Table 1, Figure 2). Soil nitrate concentrations in both biosolid amended soils and soils that received inorganic fertilizers for 20 years were significantly higher than control (no amendment) plots when averaged over all soil depths (0–150 cm), and total nitrogen increased significantly in the high biosolid-amended soils. Plots which received the high biosolids rate had a significantly higher concentration of soil nitrate in the surface soil layers (0–30 cm) than the low biosolid treament. The lack of significant differences in soil nitrate between the low and high rates of biosolid application when averaged over 0–150 cm could be due to leaching losses over time to depths greater than 150 cm (Table 1). In addition, soils have varied retentive properties that are affected by biosolid addition through improved soil structure. As discussed later, the high biosolid plots had significantly increased total organic carbon concentrations which may have af-

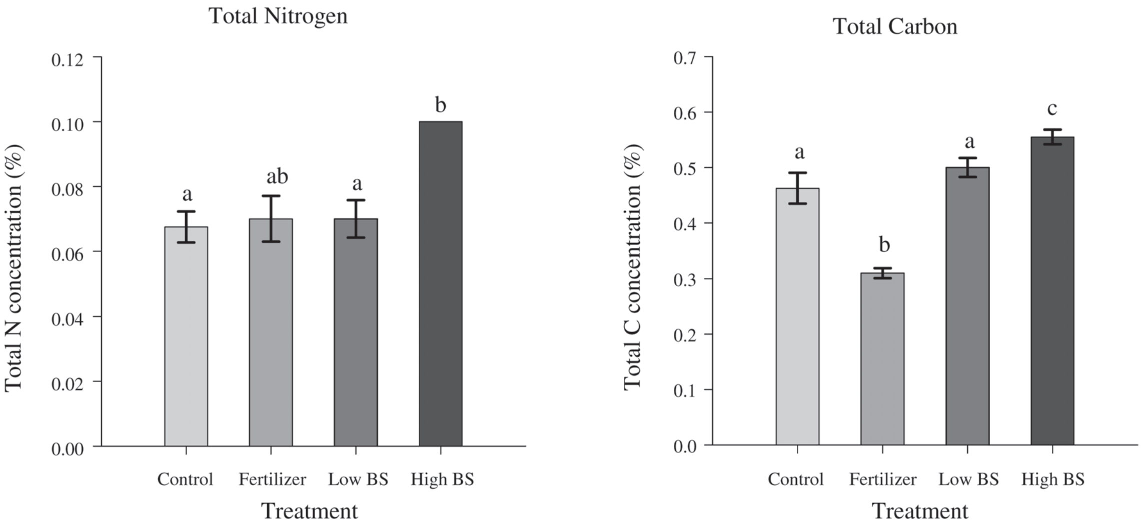

Figure 1. *Total soil nitrogen (%) and total soil carbon (%). Values are the average of all soil samples from 0–150 cm and values with different letters are significant at the 95% confidence level.*

Table 1. N, P and TOC Chemical Analyses. Mean Values (and ± standard deviation) Averaged Over 0–150 cm Soil Depths that are Significantly Different at the 95% Confidence Levels are Indicated by Different Leters.

Depth (cm)	**Control**	**Inorganic Fertilizer**	**Low Biosolids**	**High Biosolids**
NO_3 (mg kg^{-1})				
0–30	7.5 ± 3.8	19.4 ± 3.7	16.4 ± 3.7	57.6 ± 29.7
30–60	8.2 ± 3.2	17.2 ± 9.6	26.9 ± 20.9	93.6 ± 141.7
60–90	5.2 ± 2.2	6.0 ± 71.2	41.4 ± 40.7	7.8 ± 76.6
90–120	4.1 ± 2.9	35.8 ± 44.0	70.4 ± 110.3	36.8 ± 40.8
120–150	11.9 ± 17.0	26.5 ± 25.4	62.1 ± 107.8	15.4 ± 8.9
Mean	7.4^{a}	21.0^{b}	43.4^{c}	42.3^{c}
Total Nitrogen (%)				
0–30	0.08 ± 0.01	0.08	0.10 ± 0.01	0.14 ± 0.02
30–60	0.06 ± 0.01	0.05 ± 0.01	0.06 ± 0.01	0.06 ± 0.01
60–90	0.05 ± 0.01	0.09 ± 0.01	0.05 ± 0.02	0.05 ± 0.02
90–120	< 0.01 ± 0.00	< 0.01 ± 0.00	0.04 ± 0.01	< 0.01 ± 0.00
120–150	< 0.01 ± 0.00	< 0.01 ± 0.00	< 0.01 ± 0.00	< 0.01 ± 0.00
Mean	0.06^{a}	0.07^{ab}	0.06^{a}	0.08^{b}
Total Organic Carbon (TOC) (%)				
0–30	0.8 ± 0.08	0.7 ± 0.04	0.9 ± 0.06	1.3 ± 0.09
30–60	0.6 ± 0.05	0.4 ± 0.03	0.6 ± 0.07	0.7 ± 0.05
60–90	0.4 ± 0.12	0.2 ± 0.06	0.4 ± 0.06	0.4 ± 0.07
90–120	0.3 ± 0.05	0.1 ± 0.02	0.3 ± 0.04	0.3 ± 0.04
120–150	0.2 ± 0.01	0.1 ± 0.04	0.3 ± 0.05	0.2 ± 0.06
Mean	0.5^{a}	0.3^{b}	0.5^{a}	0.6^{c}
Total Phosphorous (mg kg^{-1})				
0–30	803 ± 68	864 ± 37	1037 ± 76	1978 ± 35
30–60	670 ± 53	710 ± 19	734 ± 65	943 ± 93
60–90	585 ± 115	605 ± 64	582 ± 58	602 ± 93
90–120	548 ± 84	607 ± 54	643 ± 80	579 ± 55
120–150	523 ± 120	540 ± 43	612 ± 72	603 ± 82
Mean	626^{a}	665^{a}	722^{a}	941^{b}
Available Phosphorous (mg kg^{-1})				
0–30	9.9 ± 3.6	10.4 ± 2.9	46.0 ± 4.9	94.9 ± 3.9
30–60	2.6 ± 0.8	1.2 ± 0.6	10.2 ± 5.3	44.2 ± 15.2
60–90	2.1 ± 1.3	0.5 ± 0.4	1.6 ± 0.8	3.1 ± 1.9
90–120	1.9 ± 0.8	0.7 ± 0.1	2.0 ± 1.3	2.0 ± 2.0
120–150	1.9 ± 0.8	0.4 ± 0.3	1.0 ± 0.9	2.0 ± 1.3
Mean	3.7^{a}	2.6^{a}	12.2^{b}	29.2^{c}

fected nitrate leaching. Nitrate values in both biosolid amended plots and fertilizer plots exceeded 10 ppm NO_3-N at many soil depths down to 150 cm. These data indicate the potential for nitrate pollution of groundwater regardless of whether biosolids or inorganic fertilizer is applied to the soil. However, nitrate can be lost from the soil system at lower depths due to reduced redox conditions. Such denitrification was demonstrated earlier in this study [28], and may mitigate nitrate contamination of groundwater. Other studies have shown that N mineralization was affected by soil type and temperature [19, 29] and further research on these fields may help to determine irrigation strategies and N loading rates in order to minimize potential leaching loss of biosolid-derived N.

Previous studies from Marana experimental field indicated that, after five annual applications of biosolids and inorganic fertilizer, plots showed no significant differences of total N concentrations at any depth [28]. In the current study, the data showed that in surface soil (0–30 cm), the high biosolids plots had significantly higher levels of total N than the other treatments. However, analyses on the data from the low biosolids, inorganic fertilizer, and control plots showed no treatment differences in terms of total N content when averaged over all soil depths (Table 1). Our results are similar to other studies of long-term land applications of biosolids which showed that high application rates of biosolids increased total N concentration [19,27,30].

Total organic carbon significantly increased in biosolid amended (3× rate) soil after 20 years of land application (Figure 1). This is in contrast to analyses of the same plots following 5 land applications. Currently in the surface 0–30 cm layer of the high rate biosolid plots, soil organic carbon levels were 1.3% as compared to control values of 0.8%. This represents a relative increase of 62.5%. Note also that based on acre furrow slice being approximately 1000 tons weight, this represents the sequestration of 50 tons of carbon per acre. These values are slightly higher than previous TOC in desert soils [16]. Data from core soil samples (0–270 cm) collected in 1990 showed no differences in the soil total organic carbon when compared to control versus biosolid amended soils [16]. However, dissolved organic carbon increases were detected in the 1990 biosolid amended soil samples. These data illustrate how difficult it is to increase soil organic matter in soils of the arid southwest U.S.A, due to high mineralization rates [16]. But, it is important to note that even the modest increases in total organic carbon found here are important to soil fertility in soils which are traditionally low in soil organic matter (0.5–1%) [31]. Land application of biosolids has also been shown to increase soil organic carbon in other studies [14, 32].

However, the effect of land applications on TOC was diminished at the lower (90–150 cm) depths of the soil profile. This is consistent with other reports [33], who found the mean organic levels were 0.72% at the surface (0–10 cm), 0.42% at a depth of 20–30 cm, and 0.12% at depths of 120–150 cm. Our data also showed that that control plots had significantly higher levels of TOC than plots which received inorganic fertilizer per-

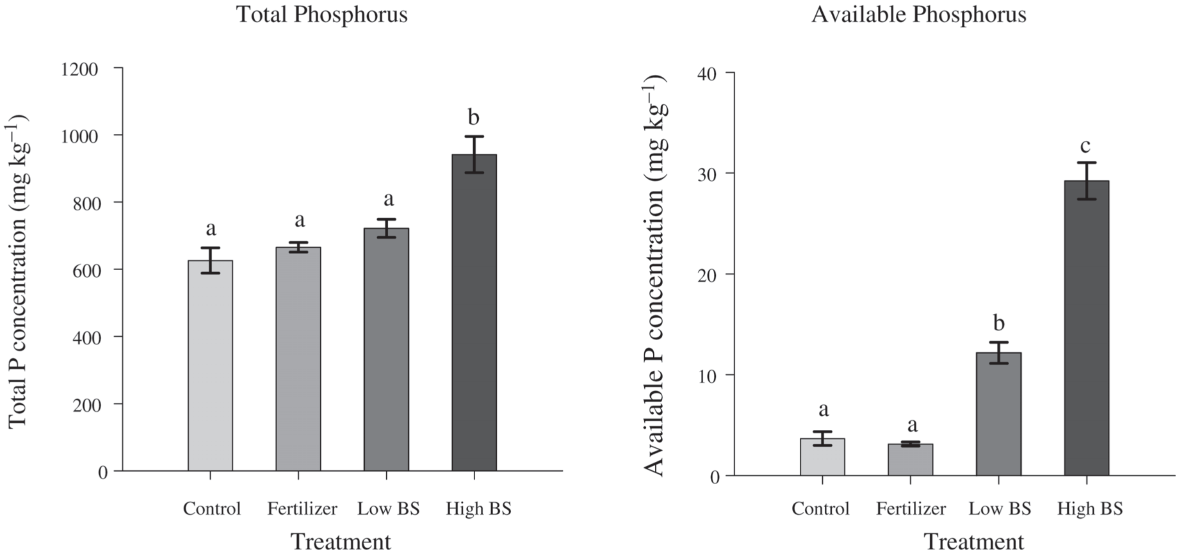

Figure 2. *The influence of biosolids on soil P. Values are the mean of all soil samples from 0–150 cm and values with different letters are significant at the 95 % confidence level.*

haps due to enhanced oxidation of indigenous organic matter when nitrogen alone is added to soil [34].

Land application of biosolids at either rate also significantly increased total and available soil phosphate concentrations, relative to control or inorganic fertilizer plots, particularly in the surface (0–30 cm) soil (Table 2). Available soil phosphate concentrations were in excess of cotton plant requirements. Increases in soil phosphate concentrations of biosolid amended soil were already evident in soil samples collected from the same study after 4 years of land application [17]. In our study, the data agrees with the study [31] documented phosphate increases following land application. In addition, recent reports showed that long-term land application of biosolids resulted in accumulation of P in surface (0–15 cm) soils [18], and that P concentrations were greater than that needed for optimum crop yields [35]. They also stated that P was "at the forefront of biosolids-related issues that may adversely affect the long-term sustainability of land-based recycling programs in the U.S." Such concern is based on the potential for water quality deterioration that can occur in surface waters due to eutrophication following phosphate accumulations in surface water runoff.

Biosolids are good sources of P for crop productions in soils [36], but are typically applied at rates designed to satisfy crop N requirements mainly to avoid nitrate leaching to groundwater. Several studies have reported that there is a mismatch between the biosolids N nutrient content and crop requirements of P, such that P is supplied in excess of the optimum levels needed for crop growth, and because application of biosolids is based on the N requirement of crops [27,36]. While this surplus of soil P from biosolids is not harmful to crops [37], there is a potential for off-site migration that can cause eutrophication in most P limited surface waters [38]. However, it appears that these issues are more important in the eastern U.S.A, since in the arid southwest, surface waters are rare. In arid lands, frequently the only potential P contamination of water resources is groundwater. However, data in Table 1 show that at soil depths of 120–150 cm, P concentrations within biosolid amended plots were similar to control and inorganic fertilizer plots. In areas where surface waters are present, care must be taken to minimize run off of water laden with P sediments. That notwithstanding, phosphorus management will continue to be important for sustainable biosolids recycling in the U.S.

Throughout the study, cotton yields from the low biosolid amended plots were similar to yields from inorganic fertilizer plots (data not shown). In contrast, yields from the high biosolid treatment were reduced, although vegetative growth was enhanced.

Effect of Land Application of Biosolids on Soil Heavy Metals

The biosolids applied in the University of Arizona 20 year land-application study contained relatively low levels of total heavy metals (Table 2). Copper, lead, and zinc had the highest biosolid concentration of all these metals (Table 2). After 20 annual land applications, soil data showed that significantly higher concentrations of available diethylene triamine penta-acetic acid (DTPA) metals including Cu, Zn and Ni were detected within the biosolids treated plots (Table 3, Figure 3). With respect to total metal concentrations, Hg and Se, values were significantly higher in the high biosolids treated

Table 2. Representative Total Heavy Metals Concentrations in US Biosolids.

Metal	Mean[1]	Minimum[1] (mg kg^{-1})	Maximum[1]	Range[2] (current study)
Arsenic	12.4	0.3	316	3–23
Cadmium	65.5	0.7	8,220	7–15
Chromium	258	2.0	3,750	32–95
Copper	665	6.8	3,120	568–957
Lead	195	9.4	1,670	89–221
Mercury	4.1	0.2	47	0.1–6
Molybdenum	13.1	2	67.9	5–83
Nickel	77	2	976	26–51
Selenium	6.2	0.5	70.0	2–32
Zinc	1,693	37.8	68,000	800–1590
Silver	NA	NA	NA	3–60

[1] National biosolids survey (209 randomly selected wastewater plants from all regions of the U.S.). Adapted from [46].
[2] Pima County biosolids used in current study. Adapted from [41].
NA = Data not available.

Table 3. N, P and TOC Chemical Analyses. Mean Values (and ± standard deviation) Averaged Over 0–150 cm Soil Depths that are Significantly Different at the 95% Confidence Levels are Indicated by Different Leters.

Depth (cm)	Control	Inorganic Fertilizer	Low Biosolids	High Biosolids
DTPA Cu (mg kg^{-1})				
0–30	3.49 ± 0.1	3.46 ± 0.2	5.24 ± 0.4	11.19 ± 0.8
30–60	2.95 ± 0.2	2.87 ± 0.2	3.36 ± 0.5	4.95 ± 0.4
60–90	2.24 ± 0.9	2.21 ± 0.5	2.41 ± 0.7	2.08 ± 0.4
90–120	1.51 ± 0.4	1.53 ± 0.1	1.87 ± 0.5	1.57 ± 0.3
120–150	0.94 ± 0.2	0.87 ± 0.3	1.26 ± 0.5	1.37 ± 0.5
Mean	2.23^{ab}	2.19^{a}	2.83^{b}	4.23^{c}
DTPA Cd				
0–30	0.06 ± 0.00	0.01 ± 0.00	0.06 ± 0.04	0.01 ± 0.00
30–60	0.04 ± 0.01	0.07 ± 0.01	0.06 ± 0.01	0.13 ± 0.00
60–90	0.03 ± 0.01	0.05 ± 0.01	0.04 ± 0.01	0.07 ± 0.01
90–120	0.01 ± 0.00	0.03 ± 0.01	0.02 ± 0.01	0.03 ± 0.01
120–150	0.01 ± 0.00	0.02 ± 0.00	0.01 ± 0.00	0.01 ± 0.00
Mean	0.02^{a}	0.04^{a}	0.03^{a}	0.06^{a}
DTPA Zn				
0–30	0.90 ± 0.10	1.02 ± 0.22	2.83 ± 0.23	8.58 ± 0.79
30–60	0.41 ± 0.11	0.47 ± 0.12	0.89 ± 0.42	2.37 ± 0.37
60–90	0.17 ± 0.03	0.26 ± 0.12	0.21 ± 0.02	0.26 ± 0.10
90–120	0.16 ± 0.03	0.16 ± 0.11	0.25 ± 0.15	0.26 ± 0.09
120–150	0.18 ± 0.01	0.21 ± 0.08	0.24 ± 0.05	0.23 ± 0.06
Mean	0.23^{a}	0.28^{a}	0.40^{b}	0.78^{c}
DTPA Pb				
0–30	2.48 ± 0.16	2.36 ± 0.05	2.69 ± 0.17	3.02 ± 0.22
30–60	1.97 ± 0.15	1.98 ± 0.10	2.00 ± 0.23	2.35 ± 0.12
60–90	1.58 ± 0.37	1.72 ± 0.32	1.65 ± 0.29	1.45 ± 0.21
90–120	1.20 ± 0.28	1.42 ± 0.23	1.50 ± 0.34	1.30 ± 0.25
120–150	0.89 ± 0.24	0.80 ± 0.19	1.01 ± 0.25	1.13 ± 0.21
Mean	1.41^{a}	1.48^{a}	1.54^{a}	1.56^{a}
DTPA Ni				
0–30	0.08 ± 0.01	0.09 ± 0.00	0.11 ± 0.02	0.17 ± 0.02
30–60	0.05 ± 0.01	0.05 ± 0.01	0.05 ± 0.00	0.07 ± 0.01
60–90	0.04 ± 0.01	0.04 ± 0.01	0.04 ± 0.01	0.04 ± 0.01
90–120	0.03 ± 0.01	0.03 ± 0.00	0.04 ± 0.01	0.04 ± 0.00
120–150	0.03 ± 0.01	0.02 ± 0.00	0.03 ± 0.01	0.04 ± 0.01
Mean	0.04^{a}	0.04^{a}	0.04^{a}	0.05^{b}
Total Hg				
0–30	0.04 ± 0.005	0.04 ± 0.011	0.06 ± 0.009	0.15 ± 0.009
30–60	0.03 ± 0.011	0.03 ± 0.004	0.04 ± 0.005	0.06 ± 0.005
60–90	0.03 ± 0.006	0.02 ± 0.003	0.02 ± 0.002	0.03 ± 0.003
90–120	0.02 ± 0.007	0.03 ± 0.027	0.02 ± 0.003	0.02 ± 0.004
120–150	0.01 ± 0.004	0.01 ± 0.003	0.02 ± 0.010	0.02 ± 0.004
Mean	0.03^{a}	0.02^{a}	0.03^{a}	0.06^{b}
Total Se				
0–30	0.96 ± 0.06	0.80 ± 0.05	0.89 ± 0.08	1.03 ± 0.05
30–60	0.78 ± 0.11	0.75 ± 0.07	0.77 ± 0.05	0.96 ± 0.03
60–90	0.67 ± 0.17	0.69 ± 0.06	0.74 ± 0.08	0.77 ± 0.11
90–120	0.59 ± 0.04	0.63 ± 0.07	0.70 ± 0.08	0.64 ± 0.10
120–150	0.52 ± 0.13	0.53 ± 0.05	0.64 ± 0.15	0.66 ± 0.09
Mean	0.70^{ab}	0.68^{b}	0.75^{ac}	0.80^{c}
Total Cr				
0–30	13.4 ± 0.8	13.9 ± 0.6	13.5 ± 0.9	14.6 ± 0.4
30–60	13.2 ± 1.5	14.1 ± 0.4	13.5 ± 1.4	13.2 ± 0.7
60–90	11.6 ± 1.8	13.0 ± 1.6	11.9 ± 1.2	11.1 ± 1.2
90–120	10.7 ± 0.4	11.7 ± 0.8	11.8 ± 1.1	10.4 ± 1.2
120–150	9.5 ± 1.8	11.6 ± 1.2	12.2 ± 0.6	10.8 ± 1.0
Mean	11.7^{a}	12.9^{bc}	12.6^{ac}	12.0^{ac}

(continued)

Table 3 (continued). N, P and TOC Chemical Analyses. Mean Values (and ± standard deviation) Averaged Over 0–150 cm Soil Depths that are Significantly Different at the 95% Confidence Levels are Indicated by Different Leters.

Depth (cm)	**Control**	**Inorganic Fertilizer**	**Low Biosolids**	**High Biosolids**
Total B				
0–30	7.0 ± 1.3	8.5 ± 1.8	7.9 ± 1.9	5.4 ± 2.8
30–60	7.3 ± 1.4	7.6 ± 1.1	7.8 ± 2.1	5.2 ± 0.8
60–90	5.3 ± 1.8	6.7 ± 1.8	6.4 ± 1.6	4.4 ± 1.3
90–120	4.2 ± 1.0	5.4 ± 1.4	6.1 ± 1.7	3.9 ± 1.3
120–150	3.7 ± 1.1	4.2 ± 1.5	5.5 ± 1.0	3.8 ± 0.5
Mean	5.5^{ac}	6.5^{ac}	6.7^{ab}	4.5^{c}

plots but Cr, and B concentrations were not significantly affected by land application. Surface (0–30 cm) values were: 0.15 mg kg^{-1}; 1.03 mg kg^{-1}; 14.6 mg kg^{-1}; and 5.4 mg kg^{-1}, respectively. For both total and DTPA metals, values decreased with increasing soil depth over all treatments, and frequently had attenuated to background levels at the 120–150 cm soil depth. In general, total and available metals increased with increased biosolids application rates.

Overall, data showed that low biosolids land application rates (1×) did not significantly increase metal concentrations with the exception of a few metals (DTPA Zn, Cu, and total Se) as compared with the control plots that did not receive biosolids. Of these Zn and Se values

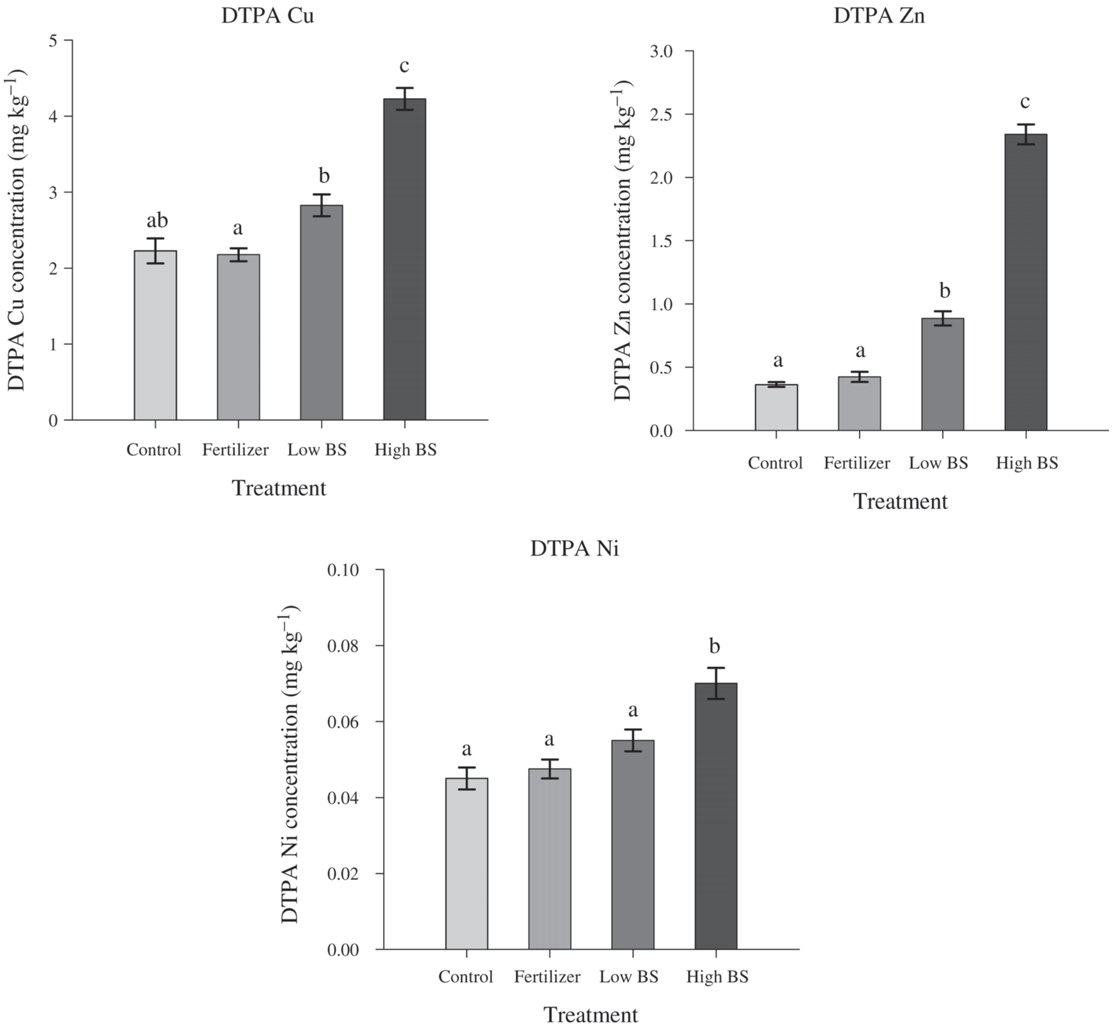

Figure 3. *Available and total heavy metals concentrations averaged over 0–150 cm. Values with different letters are significantly different at the 95% confidence level.*

remained within normal soil background concentrations. Copper had slightly higher levels than normal background ranges but was still lower than the maximum limit for Cu reported for major agricultural areas of the US [39] (Table 4). The biosolid amended soil concentrations of other available and total metals (Cu, Cd, Pb, Ni, As and Mo) were not significantly different between plots that received biosolids and control plots. Application of biosolids did not significantly affect Cd soil concentrations, but values were higher in the high biosolid amended plots as compared to plots that did not receive biosolids (control and inorganic fertilizer) (Table 3). Overall, these modest increases in soil metal concentrations would not prove hazardous to plant growth [13,40].

Other studies have indicated that although metal concentrations can increase in soil due to biosolids application, these increases are frequently below the U.S. EPA cumulative limits [13]. In addition, metal concentrations in biosolids have been decreasing over the past several decades due to improved point-source controls [41]. It has been also reported that annual application of biosolids over a 13 yr period did not affect metal concentrations in soils as compared to the normal level found in agricultural soils of the United States [42]. The current study has shown that the long-term annual applications of biosolids did not increase soil heavy metal concentrations above normal background concentrations or typical soil metal concentrations except for Cu and Pb which had slightly higher levels than normal background ranges (Table 4). Overall, this study shows that metal concentrations of soil resulting from long-term land application of biosolids did not accumulate above levels known to be hazardous. The promulgation of the 40 CFR Part 503 regulations and new understanding of trace element chemistry in biosolid-amended soil has shown that following termination of land application; available metal concentrations essentially remain constant or decrease as long as the soil pH remains constant [43,44,45]. In this present study, long-term land application increased soil pH slightly but differences were not significant. Decreases may be due to sorption to inorganic oxide surfaces or very recalcitrant organics present in soil of non-biosolid origin [43].

SUMMARY

In this study, the effect of long- term land applications of biosolids on soil chemical properties were variable with respect to parameters analysed. Long-term application of biosolids did not significantly affect soil pH, $CaCO_3$ or soil EC. Long-term land application significantly increased soil macro-nutrients including soil nitrate, total nitrogen (N), total organic carbon (C), and both available and total phosphorous (P) concentrations. One possible negative effect of long-term land application was the potential for nitrate pollution of groundwater. However, leaching of nitrates to lower soil depths occurred regardless of whether biosolids or inorganic fertilizer was applied to the soil. Therefore, further research on controlled irrigation rates for cotton may help to determine N loading rates in order to minimize potential leaching loss of biosolid or fertilizer-de-

Table 4. Representative heavy metal concentrations in agricultural soils compared to metal concentration in high biosolid amended soils (current study).

Metal	Geometric Mean[1]	Minimum[1]	Maximum[1] (mg kg^{-1})	Typical Concentration in Soil[2]	Biosolid Amended Soil[3] (current study)	Range[4] (Background Concentration)
As	–	–	–	5.4	6.4	0.10–55
Cd	0.18	< 0.1	2.0	0.1	0.4	0.03–0.94
Cr	–	–	–	89.3	14.6	10–150
Cu	18.0	1.4	495.0	17.9	73.0	1.0–50
Pb	10.6	3.0	135.0	13.4	22.4	2–300
Hg	–	–	–	0.03	0.2	0.20–5
Mo	–	–	–	–	< 0.5	–
Ni	16.5	2.2	269.0	35.7	12.1	5–500
Se	–	–	–	0.2	1.0	–
Zn	42.9	3.2	264.0	44.6	10.4	1.0–900

[1] Summary statistics for concentrations of microelements in 3045 surface soil from major agricultural production areas of the U.S.A. Adapted from [39].

[2] Typical soil concentrations of heavy metals. Adapted from Adapted from [46].

[3] Total metal concentrations in surface soils (0–30 cm) which received repeated high rate (3×). (24 t ha^{-1}) land applications of Class B biosolids (Current Arizona study).

[4] Adapted from [27].

rived N. Total organic carbon significantly increased in biosolid amended (3× rate) soil to values of 1.3% in the surface (0–30 cm) soil which is higher than the normal reported total organic C in desert soils.

Land application (3× rates) of biosolids also significantly increased total and available soil P concentrations, particularly in the surface (0–30 cm) soil. Therefore P could adversely affect the long-term sustainability of land-based recycling programs in the U.S. However, it appears that these issues are more important in the eastern USA, since in the arid southwest, surface waters are rare. That notwithstanding, phosphorus management will continue to be important for sustainable biosolids recycling in the U.S.

Long-term land application of biosolids increased the concentration of some soil heavy metals. However, this study shows that long-term annual applications of biosolids did not increase soil heavy metal concentrations above normal or background soil concentrations except for Cu and Pb, which showed slightly enhanced levels that were still below the maximum limit reported for major agricultural areas of the U.S. Finally, metal concentrations attenuated rapidly with increasing soil depth, and were generally similar to values found in control soils at a depth of 150 cm. Based on all data, this study shows that long term land application resulted in few adverse effects on soil chemical properties. This indicates that land application with respect to chemical entities can be sustainable in the arid southwest if prudent management of soil nitrate and phosphate is practiced.

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Management Practices of Sludge and Biosolid Treatment and Disposal in Jordan

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ABSTRACT: The recent expansion of activated sludge treatment of domestic sewage in Jordan has resulted in approximately 85% of the population now served by this treatment process. A survey was conducted to assess the current management practices, volumes of biosolids being generated and the fate of the generated biosolids. Jordan is currently served by 18 wastewater treatment facilities (16 of which have been detailed in this study) generating about 300,000 m^3 of liquid sludge as well as 15,000 m^3 of dewatered sludge annually. All wastewater treatment plants use solar drying beds or/and thickening of sludge/biosolids before being hauled off for disposal. Most of the generated biosolids are disposed of at nearby landfills or stored on-site. Water Authority of Jordan costs to transport biosolids for disposal is slightly more than one million US dollars per year. Recent studies indicate that the biosolids are equivalent in metal and pathogen loads to that of Class B biosolids in the United States. Recent changes in Jordanian regulations create the opportunity for beneficial use of these biosolids through land application.

INTRODUCTION

DISPOSAL of sewage sludge represents an increasing challenge all over the world (Spinosa *et al.*, 2007). During recent years there has been a worldwide movement toward a strategy of reusing and taking advantage into useful products (bricks, aggregate, use in cement manufacturing, energy product) or recycling through land application to farm or range land (Spinosa, 2004; Spinosa and Vesilind, 2001). The presence of chemical contaminants and pathogenic microorganisms in sewage sludge are a potential health risk as a consequence of the ultimate disposal and utilization practices (i.e. ocean disposal, land application, landfill and incineration). The term biosolids in this study refers to treated sewage sludge to any treatment level.

Recent modernization of municipal wastewater treatment to activated sludge in Jordan has resulted in a significant increase in the amount of sludge being generated. With the opening of the As-Samara expanded wastewater treatment plant in April 2008, which serves Amman (the capital) and several surrounding communities, 85% of the population are being served by activated sludge or trickling filter treatment. In Jordan, biosolids are characterized as Types I, II and III. Table 1 shows chemical, physical and pathogenic concentration requirement for each type (JS: 1145/2006).

Currently no advanced treatment techniques of sludge to produce Type I biosolids (see Table 1) exist. However, no proper reuse of the biosolids is made available on a wide scale. Although a Jordanian standard (JS: 1145/1996) was issued in 1996 and updated in 2006 to regulate the production and reuse of biosolids for agricultural purposes, there still are no systematic data on the quality and quantities of biosolids generated. Treatment, handling and management practices in general are not well documented.

Objectives

This study was conducted to assess the production of sludge/biosolids from municipal wastewater treatment plants in Jordan and current costs associated with handling and disposing of sludge/biosolids to aid in the assessment of the potential quantities and qualities that would be available for agricultural utilization after

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Table 1. Requirements for Biosolids Types in JS: 1145/2006 (Government of Jordan, 2006).

		Concentration		
Parameter	**Unit**	**Type I**	**Type II**	**Type III**
As	mg/kg DW*	41	75	75
Cd	mg/kg DW	40	40	85
Cr	mg/kg DW	900	900	3,000
Cu	mg/kg DW	1,500	3,00	4,300
Hg	mg/kg DW	17	57	57
Mo	mg/kg DW	75	75	75
Ni	mg/kg DW	300	400	420
Se	mg/kg DW	10	100	100
Pb	mg/kg DW	300	840	840
Zn	mg/kg DW	2,800	4,000	7,500
Total Solids (TS)	%	90%	10%	3%
Fecal Coliforms	MPN/g DW	< 1,000	< 2,000,000	NR**
Salmonella	MPN/4g DW	< 3	NR	NR
Intestinal Pathogenic Nematodes	Eggs/4g DW	< 1	NR	NR
Enteric Viruses	PFU/4g DW	< 1	NR	NR

*DW = Dry Weight.
**NR = No Requirement.

treatment to the level required by the Jordanian standards.

METHODOLOGY

This study was based on consultative approach involving all key stakeholders. For this purpose a biosolids *ad hoc committee* was formed, members of the committee participated and contributed in the study to insure adequacy and reliability of data. The committee provided advice throughout the progress of work as well as in undertaking a survey to the wastewater treatment facilities. The committee was headed by the Environmental Research Center at the Royal Scientific Society of Jordan. Members of the committee represented the following institutions: the Ministry of Water, Irrigation / Water Authority of Jordan (MWI/WAJ—the official body responsible for the provision of water supply and sanitation services), Directorate of Water Quality at WAJ/MWI, National Center for Agricultural Research and Technology Transfer (NCARTT) at the Ministry of Agriculture, Ministry of Environment, Water and Environment Research and Study Center (WERSC) at University of Jordan, Badia Research and Development Center (BRDC), Jordan University of Science and Technology (JUST), the Water and Environmental Office at USAID mission in Amman as an *ex-officio* member and the Sustainable Development of Dry Lands Project as an *ex-officio* member.

The survey team (comprised of selected members of the biosolids *ad hoc committee* with the Environmental Research Center as a lead) visited each of the plants and met the senior operators in order to collect the needed data. The following information was collected for each plant:

- Treatment processes of the generated sludge (design criteria, resident time and others).
- Available data on sludge/biosolids quality (physical, chemical and microbial aspects).
- Testing procedures used to characterize sludge/biosolids.
- Available data on sludge/biosolids generated quantities (liquid, dewatered and others).
- Handling and disposal practices as well as costs entailed.
- Fate of generated sludge/biosolids.
- Previous reuse/application (if any).

RESULTS

Conversion from oxidation ponds to activated sludge or tricking filter types of processes began in the late 1980's in Jordan. When the expanded As-Samara plant became fully operational in April 2008, approximately 85% of the population of Jordan was served by mechanical sewage treatment. This made most of the wastewater in Jordan treated at two newly constructed activated sludge plants in Aqaba (south Jordan) and As-Samara (Jordan center). Figure 1 shows the locations of major wastewater treatment facilities in Jordan with the numbers referring to facilities name indicated in Table 2.

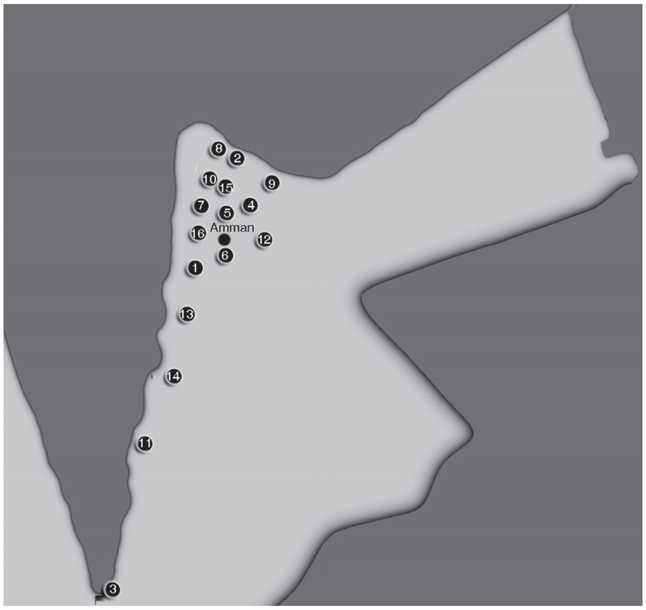

Figure 1. Locations of surveyed treatment facilities in Jordan.

The expanded Aqaba plant began operation in 2005, has a design capacity of 21,000 cubic meters per day and is currently handling 14,000 cubic meters per day. Two thirds of the influent is treated in the new expansion that utilizes activated sludge treatment and the other third is treated using the old stabilization ponds. The liquid sludge generated at the Aqaba plant is dried in 64 drying beds for approximately 14 days during January and December and for approximately 8 days during the rest of the year.

The As-Samra plant is the largest plant in Jordan and serves about 3.0 million people residing in the greater Amman metropolitan area, Zarqa City and Hashimyyah where the treatment plant is located. The designed hydraulic influent flow rate is 267,000 m^3 per day and currently (October 2008) is handling about 140,000 m^3 per day. The sludge is treated by mesophilic anaerobic digestion for 17–20 days utilizing most of the generated biogas for energy production and generating Class B liquid biosolids as per the USEPA Rule 503 requirements (USEPA, 1993) with about 3% total solids. The biosolids are then transferred to lagoons where they are dried to about 90% solids and then stored on site. There is no current firm plan for further treatment, reuse or disposal of the biosolids.

Only the As-Samara plant stabilizes the biosolids by using anaerobic digestion. All the other plants' generated biosolids are thickened to different degrees and either dried in solar drying beds or hauled as liquid sludge for disposal. Drying is usually practiced in the summer months between May and September. The drying technique becomes a challenge during the rainy and cold winter months and therefore it is not practical during the period from October to April. Currently all dried biosolids are either sent to landfills (dumping grounds) or stored on site. According to the survey, this operation currently costs the Water Authority of Jordan a little more than one million US dollars per year.

Table 2 lists major treatment plants in Jordan, their location and type of treatment processes used to treat

Table 2. Major Wastewater Treatment Plants in Jordan treatments Processes and Capacity.

No.**	Name/Location	Start of Operations	Type of Treatment	Capacity (m^3/day)	Actual Load in 2005 (m^3/day)	Size of Population Served
1	Madaba	1988 upgraded in 2002	Stabilization Ponds until 2002. Activated sludge	7,600	5,500	50,000
2	Wadi Hassan	2001	Activated sludge	1,600	1,100	40,000
3	Aqaba	2005	Activated sludge and Stabilization Ponds	21,000	14,000	70,000
4	As-Samra	2008	Activated sludge	267,000	140,000 (2008)	3,000,000
5	Abu-Nuseir	1986	Activated sludge	4,000	2,300	35,000
6	Fuheis	1997	Activated sludge	2,400	1,600	23,000
7	Salt	1982	Activated sludge	7,600	5,200	55,000
8	Central Irbid	1986	Activated sludge	11,023	6,500	70,000
9	Ramtha	2004	Activated sludge	5,400	3,300	40,000
10	Jerash	1985	Activated sludge	3,250	3,600	75,000
11	Wadi Mousa	2000	Activated sludge	3,400	1,200	10,000
12	Kufranjeh	1990	Trickling filter	1,800	2,550	45,000
13	Karak	1988	Trickling filter	1,700	785	60,000
14	Tafilah	1989	Trickling filter	1,600	1,000	12,000
15	Baq'a	1988	Trickling filter	14,090	10,000	250,000
16	Wadi Al-seir	1997	Aerated lagoons	2,700	4,000	NA*

*Not Available.
**Location as referred to as in Figure 1.

Table 3. Influent Wastewater Characteristics of Treatment Plants in Jordan.

Treatment Plant	Total Suspended Solids (mg/L)	BOD_5 (mg/L)
Madaba	2,000	1,400
Wadi Hassan	900	850
Aqaba	450	407
As-Samra	682	663
Abu-Nuseir	509	550
Fuheis	600	600
Salt	880	850
Central Irbid	1,008	1,150
Ramtha	700	950
Jerash	1,150	3,600
Wadi Mousa	972	614
Kufranjeh	891	1,150
Karak	750	700
Tafilah	750	800
Baq'a	907	900
Wadi Al-seir	400	600

the influent. Design capacity, actual loading rates and the size of the population served by the treatment plant are also shown in Table 2.

Table 3 lists the total suspended solids for the influent wastewater and the 5-day Biochemical Oxygen Demand (BOD5) for the different treatment plants surveyed in this study.

Table 4 shows the amounts of biosolids generated at the treatment plants in Jordan and the different methods used for treatment. No dewatering is practiced except drying and thickening if practiced is by sedimentation. The disposal method and the cost of disposal are also shown in Table 4.

At treatment plants where waste stabilization ponds are utilized for wastewater treatment (Wadi Al-Seir and a portion of Aqaba treatment plants) the generally adopted practice is that every 5–8 years of operation, the anaerobic lagoons are desludged for operational purposes (i.e. when the effective depth of the lagoon becomes relatively low). Generated sludge is either piled in an open area or buried within the premises of the treatment plant.

Thickening and natural drying (utilizing drying beds) are the most predominant sludge treatment processes in Jordan. At mechanical treatment plants where sludge is only thickened and not dried utilizing drying beds (Abu-Nuseir and Baq'a treatment plants), relatively large quantities of liquid sludge are generated on daily basis. Cost of transferring sludge at both sites rep-

Table 4. Biosolid Generation, Treatment and Disposal and Cost of Treatment in Jordan.

Plant	Sludge Generated (dry m^3 per year)	Treatment	Disposal Method	Cost of Disposal JD*
Madaba	900 dry	Drying beds	Liquid hauled to Ain Ghazal pretreatment station; dried stored on site	108,500
Wadi Hassan	7,300 liquid; 730 dry	Drying beds	Alakaider dumping site	6,300
Aqaba	1,012 dry	Drying beds	Stored on Site	NA**
As-Samra	100,140 dry	Anaerobic digestion and drying beds	Stored on Site	NA
Abu-Nuseir	29,200 liquid	none	Liquid hauled to Ain Ghazal pretreatment station	16,060
Fuheis	4,380 liquid; 130 dry	Drying beds	Liquid hauled to Ain Ghazal pretreatment station; dried stored on site	8,800
Salt	27,375 liquid; 1,825 dry	Drying beds	Liquid hauled to Ain Ghazal pretreatment station; dried stored on site	62,000
Central Irbid	20,000 liquid; 2,500 dry	Anaerobic digestion and drying beds	Alakaider dumping site	159,000
Ramtha	5,000 liquid; 500 dry	Drying beds	Alakaider dumping site	9,000
Jerash	27,400 liquid; 600 dry	Drying beds	Alakaider dumping site	31,300
Wadi Mousa	Not Available	Drying beds	Stored on site	0
Kufranjeh	11,000 liquid; 700 dry	Drying beds	Alakaider dumping site	24,800
Karak	1,000 liquid; 500 dry	Drying beds	Drying bedsliquid sludge is currently disposed of at Al-Lajoon treatment plant while dewatered bio-solids at Karak landfill	1,070
Tafilah	1,050 liquid; 500 dry	Drying beds	Jarf Al-Daraweesh dumping site	NA
Baq'a	91,250 liquid	none	Hauled to Ain Ghazal pretreatment station	91,000
Wadi Al-seir	4,960 dry	Ponds dried every other year to remove accumulation	Stored on site	NA

*1 JD = $1.42 in 2008.

**NA = Not applicable since biosolids are not hauled.

resents more than (17 %) of the total transfer costs for all designated treatment plants.

About (300,000 m^3) of liquid sludge as well as (15,000 m^3) of dewatered biosolids are generated annually at the treatment plants. The total annual transfer cost of sludge/biosolids to dumping sites is currently exceeding (750,000 Jordian Dinars or $1,062,750). Most of the cost is attributed to hauling liquid sludge. This cost is greatly dependent on existing oil prices in the region.

Almost all generated sludge and biosolids quantities at the surveyed treatment plants are usually disposed of at near-by dumping sites, i.e. there are no wide beneficial usages for sludge and biosolids currently implemented in Jordan; however, there is a high potential for proper reuse as soil amendment.

DISCUSSION

The continued expansion of sewage treatment in Jordan has resulted in generation of significant amounts of sludge and biosolids. Currently all of the biosolids are hauled to landfills or stored on-site. Drying of biosolids to reduce hauling and storage costs is practiced at all of the plants. Currently only two plants practice stabilization by mesophilic anaerobic digestion, which represent two of the largest plants in Jordan (As-Samara and Irbid). Recent changes in Jordanian regulations now allow for land application of treated biosolids (Tamimi *et al.,* 2007a). In terms of metal content and pathogens these biosolids are below those observed in other developing countries (Jiménez et al., 2002) and appear to meet Class B biosolid standards for land application in the United States (USEPA, 1993; Al–Hmoud et al, 2006; Tamimi *et al.,* 2007a, 2007b). However, Class B (Type II under Jordanian regulations) require many limitations on land use and restrictions on crops, grazing, distance to residences, etc., which are difficult to enforce without a well developed infrastructure. To reduce this need treatment of biosolids to a Class A equivalent (Type I under Jordanian regulations) would be desirable. While drying during the summer months appears capable of meeting the pathogen requirements, the cool wet winter months appear to limit this practice to only certain times of the year (Al-Hmoud *et al.*, 1996). Since long term storage is possible, and is currently occurring, this practice may be the best short term option in terms of cost and facility needs until alternative low cost technique(s) can be developed for Jordan for the production of a Class A (Type I) equivalent product. This would require that the storage conditions and time be experimentally validated for existing conditions in Jordan. Jordan has sufficient land used agricultural crop production of folder and range land for where biosolid application would be beneficial.

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Using Acid-washing Leachates of Ground Tire Rubber and its Ash as a Zinc Source for Hydroponics-grown Tomato

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ABSTRACT: Waste ground tire rubber and its ash were washed using different ratios of HNO_3, H_2SO_4, and H_2O and the resultant solutions were analyzed for Zn, Pb, Cd, Fe. The extracted solution with the highest Zn content was then used as a source of Zn for hydroponics-grown tomato. The highest recovery of Zn from rubber and its ash was obtained using 4 M HNO_3. Two levels of Zn supplied by the ash leachate increased the plant Zn concentration compared with the control. The results showed the possibility of using acid-washing leachate of ground tire rubber and its ash as a suitable Zn source in hydroponics solutions.

INTRODUCTION

ACCUMULATION of millions of worn automotive tires poses a considerable environmental problem. On average, approximately one scrap tire per person per year accumulates in industrialized countries [6]. The annual production of scrap tires throughout the world is estimated at 1000 million, representing a significant treatment and disposal problem [4]. As an important part of the solid waste stream in today's society, worn tires have traditionally been discarded in landfills or stored in stockpiles. Over the past several decades, however, innovative alternatives to disposal have been developed, partly as a result of high tipping fees charged by landfill operators [6].

Using ground tire rubber as a substrate for soil-less culture has been considered by several researchers [2]. However, high amounts of Zn may be released from the tire to the root zone and cause Zn phytotoxicity and significant reduction in crop growth and yield. Plants grown in soilless potting media containing ground tire rubber showed elevated Zn concentration in their tissue [2,5]. With increasing rubber content in these media, plant yield decreased [2,5,7,14].

In general, automobile tires consist of rubbers (50%), carbon black (26%), metal codes (10%), additives compounds (6%), and bead wires (5%) [16]. The codes and additives contain iron, copper, zinc, and cobalt [9]. Zinc is added as zinc oxide (ZnO) to the rubber compound for tires as a vulcanizing agent. The average value of ZnO is 1.2% for car tire (0.4 to 9%) and 2.1% (1.2 to 3%) for truck tires [1,10].

Removing excess Zn from the waste tire through acid washing makes this residue more appropriate for using as a substrate in hydroponics system [13] or as a soil amendment in sport fields [11] but disposal of the leachate produced is an environmental concern. The Zn-enriched leachate produced from acid-washing of ground tire rubber and its ash seems to be a cost-effective liquid source of Zn for plants. In this study, different extractants were used to extract excess Zn from the waste tires and their ash. Then, the possibility of using the leachate produced with the highest amount of Zn as a source of Zn for hydroponics-grown tomato was investigated.

MATERIALS AND METHODS

Zinc Extraction from the Used Tire

Ground tire rubber material was obtained from a tire producer company in Isfahan province, Iran. Different ratios (i.e. 1:5, 1:10, 1:25 ground rubber: extractant) of

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ground rubber were mixed with 0.5, 2, and 4 M HNO_3, 1 M H_2SO_4 , and H_2O in 250 ml erlenmeyer flasks and shaken for 24 hours. The extracted solution was filtered and concentrations of Zn, iron (Fe), cadmium (Cd), and lead (Pb) were measured in the filtered solution using atomic absorption spectrophotometry (AAS, Perkin Elmer model 3030). Extractant solution with the highest content of Zn was used for the hydroponics experiment.

Zinc Extraction from the Waste Tire Ash

In the next stage, 20 g ground tire rubber in triplicates was placed in a furnace at 550°C for 4, 6, 8, and 12 hours and the ash was used for further studies. The metal contents of the ash were determined by dissolving 1.0 g ash in 20 ml 4 M HNO_3 and measuring Zn, Fe, Cu, Mn, Pb, and Cd concentrations in the resulting solution by the AAS after filtration and dilution. Metals were extracted from the ground rubber ash using different extractants. One gram ash was dissolved in 20 mL deionized water, 2 M HCl; 0.5, 2, and 4 N HNO_3, 1 M H_2SO_4, and 0.005 M DTPA. Then, the metal concentrations in the resulting solution were measured by the AAS after filtration and dilution. The extractant solution with the highest content of Zn was used in the hydroponics experiment.

Hydroponics Culture Experiment

Nutrient solutions containing two levels of Zn (equal to and twice of full Johnson solution composition) supplied through the leachate of tire and ash were tested. In addition, another full Johnson nutrient solution with $ZnSO_4$ as source of Zn was used as the control treatment. Other macro- and micronutrients were added to the media according to the full Johnson solution composition [8]. The nutrient composition is shown in Table 1. Seedlings of cherry tomato (*Lycopersicon esculentum* var. Cerasiforne) were transplanted into the plastic containers of 2.5 L capacity. There were three replications of each treatment. After 40 days of growth, plants were harvested. At harvest, crop shoots and roots were separated, dried at 75°C, weighed, ground, and digested by 1 N HCl. Zinc, Fe, Cd, and Pb concentrations in the digested solution were measured using the AAS [3].

Table 1. Composition of Nutrient Solution Used for Growth of Tomato at Different Zn Treatments.

Micronutrients (mM)		Micronutrients (µM)		Zn Treatments (µM)
NH_4NO_3	1.5	H_3BO_3	2.0	2, 4
$CaCl_2$	1	$MnSO_4$	5.0	
$MgSO_4$	1.6	$CuSO_4$	2.0	
K_2SO_4	2	$(NH_4)6Mo_7O_{24}$	0.05	
KH_2PO_4	0.1	$FeCl_3$	40	
		$NiS0_4{\cdot}^6H_2O$	1.0	

Statistical Analysis

Each experiment was set up in a randomized complete block design in triplicates. Treatments effects were analyzed by analysis of variance using the *F* test. Means were compared using the least significant differences (LSD) at $P < 0.05$ [15].

RESULTS AND DISCUSSION

Metal Concentration in the Leachates of Waste Tire and its Ash

Zinc was effectively recovered from the tire by all acid washes (Table 2). With increasing ratio of the extractant to the ground rubber, concentration of Zn, Fe, Pb, and Cd in the solution decreased. This decrease in metal concentration in the extraction is attributed to dilution effect. With increase in concentration of HNO_3, much more metal was washed from the ground rubber. The greatest amount of zinc (1231 mg L^{-1}) was removed with the 4 M HNO_3. A significant content of

Table 2. Zinc, Fe, and Pb Concentrations (mg L^{-1}) in the Acid Washing Leachate of Ground Tire Rubber.

Extractant	Zn	Pb	Fe
HNO_3, 4N 1:5	1231a*	1.64	22.45
HNO_3, 4N,1:10	686b	1.17	14.01
HNO_3, 4N,1:25	198f	0.57	7.15
HNO_3, 2N,1:5	415d	0.87	19.80
HNO_3, 2N,1:10	422d	0.87	14.45
HNO_3, 2N,1:25	114gh	0.54	6.22
HNO_3, 0.5N,1:5	464c	0.95	21.79
HNO_3, 0.5N,1:10	217f	0.70	11.27
H_2SO_4, 1M,1:5	92hi	0.52	4.46
HNO_3, 0.5N,1:25	425e	0.82	22.64
H_2SO_4, 1M,1:10	144g	0.70	11.29
H_2SO_4, 1M,1:25	56i	0.40	6.57
H_2O, 1:5	4j	0.01	0.42
H_2O, 1:10	4j	0.02	0.12
H_2O, 1:25	1j		0.05

*Means with common letter in each column are not significantly different at *P* = 0.05.

** Below the detection limit of AAS.

Fe and Pb was washed from the ground rubber as well (Table 2). The highest concentration of Pb and Fe measured in the extraction solution was 22.5 and 1.6 mg L^{-1}, respectively. Cadmium concentration in all leachates was less than the detection limit of the AAS (0.02 mg L^{-1}); commercial grade pure ZnO is used in rubber manufacture, so the low Cd was not unexpected.

Zinc was effectively removed from the ground rubber ash by acids examined as extractants (Table 3). With increasing nitric acid concentration, no significant increase was found in the solution Zn concentration. The highest amount of Zn (about 330000 mg kg^{-1}) in the tire ash was released using HNO_3 solution; although no significant difference was found in the amount of Zn extracted by the HNO_3 and 2 M HCl. Resulting leachates contained Fe as well as Pb contamination (Table 3). The highest concentration of Fe was found in the leachate resulted from washing of waste tire using 1 M HCl. By increasing the concentration of nitric acid, the amount of Fe in the solution increased. The 0.5 N HNO_3 solution extracted a higher level of Pb than other tested extractants.

Iron and Pb concentrations in the DTPA and deionized water solutions were below the detection limit of the AAS (Table 3). Cadmium levels in all extracted solutions were lower than the limit of instrument detection. The 2 N HNO_3 solution that released the highest content of Zn but the lowest Pb concentration among the investigated solutions was used for the hydroponics experiment.

By increasing the combustion period of tire sample, the amount of Zn in the extracted solution increased (Table 3). When the tire wastes were ashed at 550°C for 4 hours, Zn concentration in the resulting extracts was 5450 mg L^{-1}. Increasing the heating time to 12 hours increased Zn concentration to 16400 mg L^{-1}. Concentrations of Fe, Pb, and Cd were below 20 mg L^{-1}.

Table 3. Release of Zn, Fe, and Pb from the Ground Rubber Ash Using Various Extractants.

	Concentration (mg/kg)		
Extractant	**Zn**	**Pb**	**Fe**
HNO_3, 4N	330000a*	4125ab	236ab
HNO_3, 2N	330000a	3875b	204b
HNO_3, 0.5N	330000a	3500b	267a
HCl,1M	325000a	6500a	263a
DTPA 0.0005N	144500b	nd**	nd
H_2O	55000c	nd	nd*

*In each column, means with different letters are significantly different at $P < 0.05$.
** nd: not detected.

Table 4. The Metal Content (%) in the Ash of Ground Rubber as Extracted with 4 N HNO_3 After Different Heating Periods.

Heating Period (hours)	**Zn**	**Fe**	**Pb**	**Cu**	**Mn**
4	11c*	0.13c	0.008c	0.002d	0.002b
6	623b	0.33b	0.019b	0.010b	0.006a
8	825b	0.42a	0.021ab	0.030a	0.008a
12	1233a	0.46a	0.026a	0.014b	0.006a

*In each column means with different letters are significantly different at $P < 0.05$.

Shoot and Root Dry Matter Yield

Differences in plants growth among the treatments became evident within two weeks of transfer of the plants to the nutrient solutions. Tomato seedlings grown in the nutrient solutions supplied with the leachates of waste tire and its ash produced similar shoot dry matter yields, although supplying Zn by the tire leachate at the double Johnson solution level (T2) led to a decrease in shoot and root dry matter yield in comparison to the other treatments (Figure 1). Lower plant growth in the T2 treatment is probably attributed to very low pH (2.3) of the leachate because the leaf Zn concentration is not high enough to suggest Zn phytotoxicity occurred.

Metal Concentrations in Tomato Shoot and Root

The metal concentrations in the tomato shoot and root in different treatments are shown in Table 4. No significant difference was found between the $ZnSO_4$

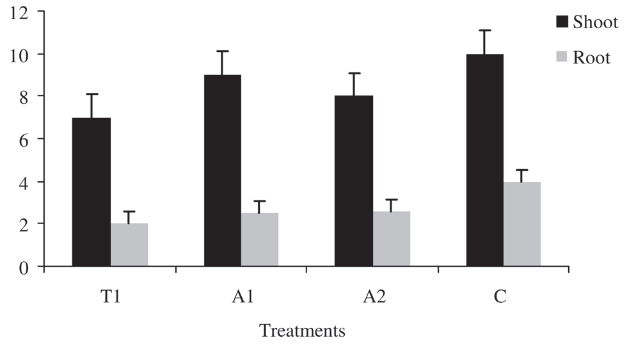

Figure 1. *Shoot and root dry matter yield of tomato grown in different treatments. Error bars represent + SE (n = 3). C is a full Johnson nutrient solution with $ZnSO_4$ as source of Zn; A1 and A2 are full Johnson nutrient solutions containing 2 and 4 µM Zn supplied via leachate of waste tire, and T1 is full Johnson nutrient solution containing 2 µM Zn supplied via leachate of tire ash.*

Table 5. Metal Concentration (mg/kg) in Root and Shoot of Tomato Grown in Different Treatments.

	Zn		Fe		Pb	
Treatment*	Shoot	Root	Shoot	Root	Shoot	Root
Control	80b**	27 b	152a	29a	0.6b	0.7b
A1	82b	31b	165a	23a	0.5b	0.8ab
A2	157a	51a	149a	26a	0.7b	0.9ab
T1	75b	25b	150a	25a	1.3a	1.2a

*Control is a full Johnson nutrient solution with $ZnSO_4$ as source of Zn; A1, A2 are full Johnson nutrient solutions containing 2 and 4 μM Zn supplied via leachate of ground rubber, and T1 is full Johnson nutrient solution containing 2 μM Zn supplied via leachate of tire ash.
**In each column, means with different letters are significantly different at $P < 0.0$.

and T1 treatment in the shoot and root Zn concentration. However, root Zn concentration increased linearly by increasing the amount of Zn in the leachate. In fact, the Zn-enriched leachates of the tire and its ash could supply sufficient content of phytoavailable Zn for plant growth. Although increasing Zn level in the tire leachate reduced the crop yield, that is not attributed to Zn phytotoxicity. No significant difference was found among the treatments in the shoot and root Fe concentration (Table 4). The T2 treatment significantly ($P < 0.05$) increased the tomato root and shoot Pb concentration, but these levels remain lower than soil grown tomatoes, and very little Pb moves to tomato fruits.

Cadmium concentration in the tomato tissues was below the AAS detection limit. Therefore, the risk from cadmium is not be an issue for plants grown in the hydroponics nutrition solution supplied by the ground tire rubber leachate. Using the leachates of the ground rubber ash at both levels produced similar crop yields in comparison with the pots supplied with $ZnSO_4$. In fact, the ground rubber ash could supply sufficient amount of phytoavailable Zn and did not restrict the plant growth. Application of Zn from the tire ash leachate in a concentration equal to the Johnson solution resulted a high crop yield.

CONCLUSION

The leachate produced from acid washing of ground tire rubber and its ash supply sufficient amount of phytoavailable Zn for tomato growth. Also, the risk of Pb and Cd contamination is not an issue in plants supplied with Zn from ground rubber. Based on these results, it would be possible to use acid-washing leachate of the ground tire rubber and its ash as suitable Zn source for tomato in hydroponics system. This can be a good approach to reduce the concern associated with the environmental disposal of waste tires through producing effective and cheap source of Zn for plant nutrition.

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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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