Aim and Scope

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

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REVIEW

Hospital Wastewater Containing Pharmaceutically Active Compounds and Drug-Resistant Organisms: A Source of Environmental Toxicity and Increased Antibiotic Resistance

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INTRODUCTION

THE discharge into and accumulation of pharmaceutically active compounds (PhACs) in bodies of water that receive treated wastewater have recently received significant attention in both the scientific and general-interest media as contaminants because of their potentially directly harmful effects to aquatic life and their possible contribution to the proliferation of drug-resistant microorganisms. PhACs enter water supplies via direct introduction of unused prescription and over-the-counter medications into the wastewater stream, metabolites of these medications that are excreted following administration of the drugs, and pharmaceuticals used in agricultural applications whose metabolites enter groundwater supplies either via runoff (Kummerer 2001), or via direct deposition into the water compartment, as occurs in aquaculture operations such as fish farming (Kummerer 2004). Further, large quantities of disinfectants commonly used in households and commercial settings enter municipal wastewater streams daily, causing further potential toxicity to aquatic organisms (Emmanuel et al. 2005a). Such unregulated compounds have been designated as emerging pollutants of concern, and previously had gone undetected in wastewater or were not considered to be a risk (Polar 2007). As most PhACs are excreted either only slightly changed chemically or not at all (Heberer 2002a), and elimination of toxicity via treatment or biodegradation often does not occur (Kummerer 2001), the continual introduction of these substances into the water supply has prompted concern about their potential hazards.

Of the various wastewater sources whose discharges are received by municipal sewage-treatment plants, hospitals may represent a particularly rich source of PhACs that ultimately flow into drinking water supplies. This paper presents an overview of PhACs found to occur in hospital wastewater, with emphasis on antibiotics and disinfectants; discuss the various mechanisms governing these substances' behavior in the environment; and present specific findings regarding wastewater samples obtained from hospitals in various regions. Also, the paper discusses recent findings regarding the related issue of drug-resistant microorganisms contained in hospital wastewater and how these, along with the PhACs discussed previously, may contribute to the emerging public-health problem of multi-drug-resistant organisms. Finally, the paper briefly discusses new possible treatment methods for hospital wastewater that have been proposed or are being tested, aimed at curbing environmental toxicity and the growing public-health problem of antimicrobial resistance.

OVERVIEW OF ANTIBIOTICS IN WASTEWATER AND THEIR BEHAVIOR IN THE ENVIRONMENT

The recent environmental-science and microbiology literature contain numerous studies of PhACs and other contaminants in municipal wastewater in general and hospital wastewater in particular, indicating a growing recognition in the scientific community of the magnitude of the issue and its potential public-health and ecological impact. As background, contamination of groundwater supplies by released pharmaceuticals and personal care products was first reported in Europe (LaPara 2007). Studies have been conducted in Britain (Richardson & Bowron 1985), Germany (Termes 1998; Hersch et al. 1999), and other countries

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(Halling-Sorensen et al. 1998; Kumpel et al. 2001), with surveys of contamination of U.S. surface waters taking place more recently. The largest U.S. survey to date has been the nationwide study performed by the US Geological Survey (Kolpin et al. 2002), which found over 95 different organic wastewater compounds in streams and rivers in the United States, including many commonly used pharmaceutical products. These substances' presence in groundwater supplies was in part attributable to incomplete removal in the wastewater treatment process (LaPara 2007), as processes in place are primarily targeted toward reduction of nitrates, phosphates, and dissolved organic carbon, not toward organic microcontaminants such as pharmaceutical residues (*Science Daily* 2006), including antibiotics and their metabolites and disinfectant compounds.

Antibiotics are among the most commonly prescribed medications in use today, and are routinely administered to hospitalized patients for prophylaxis and treatment for acute bacterial infections. The armamentarium of modern antibiotics consists of numerous bacteriostatic and bactericidal agents belonging to various classes differentiated by their chemical structure and mechanism of action against various bacteria, discussion of which is beyond the scope of this paper. Among the 18 most commonly used antibiotics, six are of the β-lactam class (amoxicillin, cephalexin, penicillin, cefprozil, cefuroxime, and loracarbef), three are macrolides (azithromycin, clarithromycin, and erythromycin), two are fluoroquinolones (ciprofloxacin and levofloxacin), two are aminoglycosides (neomycin and tobramycin), one is a sulfonamide (sulfamethoxazole), and one is a tetracycline (tetracycline), plus three others (Huang et al. 2001). The β-lactam agents account for the majority of antibiotics used in human therapy, followed by the macrolide, sulfonamide, and fluoroquinolone agents; tetracyclines, aminoglycosides, and other antibiotics account for a comparatively smaller proportion of the total amount of antibiotics used in human therapy (Huang et al. 2001).

The total amount of antibiotics consumed yearly is vast, with approximately 10,000 tons consumed annually in Europe as of 1997 (Kummerer 2001); similar data for U.S. consumption is unavailable (Institute of Food Technologists, 2006), although Levy (1998) notes that over 50 million pounds of antibiotics are produced annually in the United States. Based on this figure, one could conclude that total U.S. antibiotic consumption could be even significantly higher than the European total, especially given that the restrictions against use of some antibiotics in place in Europe do not exist in the United States: Vancomycin, for example, is widely used as a first-line antibiotic in the United States, whereas its use in Europe is highly restricted (Kummerer 2001). Therefore, the composition of the antibiotic load in U.S wastewater may be somewhat different. Of the European total, approximately half is used in veterinary applications such as prophylaxis and growth promotion, with the remainder used in human patients (Kummerer 2001). Giger et al. (2005) have reported that in Switzerland alone in 1997, human consumption of antibiotics totaled 13.2 tons of penicillin and ampicillin antibiotics, 5.5 tons of sulfonamides, 4.3 tons each of cephalosporins and macrolides, 3.9 tons of fluoroquinolones, and 1.0 tons of tetracyclines.

Approximately one-quarter of the total antibiotics used in human applications are administered in hospitals (Kummerer 2001); therefore, hospital wastewater represents a significant contributor to the total load of these substances in municipal wastewater. Antibiotics have been detected at high concentrations in hospital effluents (Hartmann et al. 1998; Adler et al. 2001; Giger 2005). Hartmann and co-investigators (1998) measured 2–83 μg/L of ciprofloxacin in the effluent of a large Swiss hospital. Based on their study of wastewaters produced by hospitals and received by municipal wastewater treatment plants in Switzerland, Giger et al. (2005) conclude that hospital wastewaters contribute from 5%–40% of the total antibiotic loads in municipal wastewaters. Concentrations of antibiotics in the effluent of one hospital sampled in 2004 were found to be approximately 10–20 times higher in some cases than their concentrations in the influent received by the treatment plant that received wastewater from that hospital (Giger 2005). While the measured concentration of trimethoprim in the influent received by the treatment plant was 0.03–0.16 μg/L, for example, the concentration measured in hospital effluent that the plant received was 0.63–1.45 μg/L. As might be expected, comparative concentrations of sulfamethoxazole (which is frequently used in combination with trimethoprim under the brand name Bactrim) in hospital effluent and treatment plant influent were similar to those observed for trimethoprim. More recently, Brown et al. (2006) sampled effluent from five hospitals in New Mexico, and found varyingly high concentrations of six antibiotics: sulfamethoxazole, trimethoprim, ofloxacin, ciprofloxacin, lincomycin, and penicillin G. All six of these antibiotics detected in the study were present in at least one hospital sample, and, confirming the prediction of Huang et al. (2001), the fluoroquinolone and sulfonamide classes were well represented, with ofloxacin and trimethoprim the most commonly occurring compounds (Brown et al. 2006). The relatively high occurrences and concentrations observed support the belief that hospitals are major contributors to the antibiotic loads of municipal wastewaters (Brown et al. 2006).

Antibiotic accumulation in wastewater and thus eventual deposition in drinking-water sources and aquatic environments that support ecosystems has become a concern because of the lack of metabolism and environmental degradation that take place following administration of these drugs and their entry into the wastewater stream. Like other drugs, antibiotics are often only partially metabolized by patients, resulting in unaltered antibiotic and in some cases active lipophilic metabolites being deposited in the wastewater stream. Sedlak and Pinkston (2001) report that the widely used β-lactam antibiotics amoxicillin and cephalexin are excreted mostly (> 50%) in their original form following administration, while the sulfonamide sulfamethoxazole and the fluoroquinolone ciprofloxacin are excreted as a mixture of conjugates and their original form. Excreted antibiotics unaltered by metabolic processes are mostly conjugated to polar molecules (Heberer 2002a). These conjugates can easily be cleaved cleaved during sewage treatment, releasing the original PhAC molecules into the aquatic environment. Giger et al. (2005) report that ciprofloxacin and another fluoroquinolone, norfloxacin, are excreted largely unmetabolized: 45%–65% of the administered dose of ciprofloxacin is excreted through the urine and 15%–25% is excreted through feces, while 20%–40% of the administered dose of norfloxacin is excreted through urine, and 28% through feces. Tetracyclines, by contrast, are only minimally discharged into wastewater because of their high metabolic rate, and their tendency to form relatively stable complexes with calcium ions (Kummerer 2001).

In addition to antibiotics and their metabolites that reach the wastewater stream via excretion, improper disposal of unused drugs into the sewage system rather than in landfills has become a more widely recognized problem, with the U.S Environmental Protection Agency, local and state agencies, trade groups, and academic institutions currently supporting research and public-information efforts aimed at increased understanding of how antibiotics enter the wastewater stream and discouraging the public from improperly disposing of unused medications (No Drugs Down the Drain; http://www.nodrugsdownthedrain.org). Reliable estimates of the amount of antibiotics and other PhACs that enter the wastewater stream and other aquatic environments in this manner are not currently available, but the amount presumably is significant.

Once in the wastewater stream, modern antibiotics persist to varying degrees, depending on their class. In contrast to the naturally occurring antibiotic substances in soil that originate from bacterial or fungal sources, most antibiotics in use today are synthetic or semi-synthetic in nature, and therefore much more stable and non-biodegradable (Kummerer 2004). From a therapeutic standpoint, such stability is a desirable quality, because it allows the drugs to retain their chemical structure long enough to accomplish their intended task (Emmanuel et al. 2001), but environmental persistence can be an unintended undesirable effect. Further, metabolites of drugs may be more lipophilic and more persistent in the environment than the original drugs from which they were derived, and therefore more likely to enter food chains and concentrate via bioaccumulation as they move upward into larger predators (Emmanuel et al. 2001), exerting a toxic effect on the ecosystem.

The three primary processes that antibiotics in both natural and engineered aquatic environments are subjected to include sorption of particles; abiotic transformation; and biotic transformation (Huang et al. 2001; Sedlak & Pinkston 2001). Previous studies have indicated strong adsorption of drugs of the tetracycline class (tetracycline, chlortetracycline, and oxytetracycline) to clay materials and to soil and sediments throughout a wide range of environmental conditions (Huang et al. 2001). Certain macrolide and fluoroquinolone antibiotics also undergo sorption to soil clay materials, although not as strongly as do the tetracyclines (Huang et al. 2001). Sulfonamides exhibit only weak adsorption to soil, and while information regarding sorption properties of aminoglycoside and β-lactam antibiotics is scarce, sorption of the former may be promoted by the positive charging of the aminoglycosides' amino groups via protonation under acidic conditions (Huang et al. 2001). Because the β-lactams are highly polar molecules, their adsorptive ability is expected to be comparatively weak (Huang et al. 2001).

Transformation of antibiotics in the aquatic environment occurs via abiotic as well as biotic means. Hydrolysis is a key degradation pathway for β-lactam, macrolide, and sulfonamide antibiotics, although the process is slow to the point of negligibility for macrolides and sulfonamides under neutral-pH conditions (Huang et al. 2001). Photodegradation of fluoroquinolones and tetracyclines is an important means of transformation of these drug classes (Huang et al. 2001). Regarding biotic transformation, previous studies have shown that aminoglycosides, β-lactams, and some macrolides are more likely to biodegrade to a greater extent than are quinolones, sulfonamides, and tetracyclines, although these processes can be quite slow to occur, and other processes such as sorption and abiotic transformation may have accounted for the observed degradation (Huang et al. 2001). Sedlak and Pinkston (2001) point out that compounds that are metabolized by microorganisms at relatively high concentrations may not be transformed to an appreciable extent when the compounds are present at the low concentrations at which they are typically encountered in wastewater. Kummerer et al. (2000) and several other investigators (Al-Ahmad et al. 1999; Ingerslev & Halling-Sorensen 2000; Hubener et al. 1992; Marengo et al. 1997; Weerasinghe & Towner 1997) have demonstrated the generally low biodegradability of commonly used antibiotics.

Regarding persistence of specific antibiotic classes, in general, antibiotics of the sulfonamide class appear to be the least susceptible to transformation in the aquatic environment (Huang et al. 2001). Quinolone antibiotics also degrade slowly, particularly when exposure to sunlight is limited (Huang et al. 2001), as is typically the case with sewage water (Kummerer et al. 2000). It has been reported that quinolones may have half-lives up to several hundred days in aquatic environments (Holten-Lutzhoft 2000). Neither of the important fluoroquinolones ciprofloxacin nor ofloxacin was found to biodegrade to any significant extent in an experiment performed in 2000 (Kummerer 2000). Also, β-lactams have been reported to have half-lives of up to 200 days (Christensen 1998), while tetracyclines, like quinolones, have half-lives of up to several hundred days in aquatic environments (Holten-Lutzhoft 2000).

Antibiotics and their metabolites in wastewater undergo some degree of degradation during normal sewage-treatment processes, but because these systems often have not been specifically designed to remove the complex molecules that make up modern antibiotics, the systems are not 100 percent efficient. Two attenuation mechanisms are potentially important for the removal of pharmaceuticals in conventional wastewater plants: sorption to particles, followed by settling and removal, and biotransformation (Sedlak & Pinkston 2001). Stripping with air (the Henry constant) is not an important process in the degradation of most pharmaceuticals in the environment (Giger et al. 2005). Some antibiotics exhibit high removal rates when they are exposed to conventional activated sludge treatment, which hydrolyzes penicillins and causes tetracyclines to precipitate with cations (Heberer 2002b). Further, amoxicillin is efficiently removed by biological treatment (Morse & Jackson 2004). The sludge retention time (SRT) of wastewater-treatment plants is an important factor in the degree of antibiotic degradation that occurs, with a longer SRT being correlated with reduced antibiotic loads in wastewater (Giger et al. 2005). (It bears noting, however, that the portion of antibiotic compounds removed via sludge treatment may still enter the water compartment, because if the sludge is then processed and spread on fields as fertilizer, the sorbed pharmaceuticals may be released and enter aquatic ecosystems via runoff; agricultural use of treated wastewater may have the same result [Cordy et al. 2004; Pedersen et al. 2005; LaPara 2007]).

Tertiary wastewater treatment performed via ozonation or a micro-filtration/reverse osmosis (RO) combination can reduce antibiotic loads in effluent to undetectable or nearly undetectable levels (Drewes 2003, Giger et al. 2005), although RO may not be practically be possible or advisable, due to the required pre-treatment of wastewater treatment plan effluent prior to using the technique and the generation of concentrated sidestreams of waste (Pauwels & Verstraete 2006). Slow sand filtration, which is a commonly used wastewater-treatment method in rural regions where source water may be subjected to antimicrobial contaminant loads from waste discharges and diffuse pollution, has been shown to effectively remove tetracyclines, quinolones, and macrolides from wastewater samples, with a > 3-log removal of 1 μg/L influent concentrations within the top 40 cm of the sand column (Rooklidge et al. 2005).

Despite the overall effective removal of antibiotics from wastewater by standard processes, multiple investigators in Europe and the United States have documented the occurrence of detectable levels of many classes of antibiotics in effluents from wastewater-treatment plants and bodies of water receiving those effluents (Heberer 2002). Recent data from Australia (Watkinson et al. 2007) obtained from a study of conventional (activated sludge) and advanced (microfiltration/reverse osmosis) wastewater treatment plants, for example, shows that both varieties of plant effectively reduced antibiotic concentrations, with an average removal rate of 92%. Antibiotics were still detected in both effluents from the low- to mid- ng/L^{-1} range, with antibiotics of the especially persistent synthetic fluoroquinolone class (enrofloxacin and norfloxacin) remaining detectable in microfiltration/reverse osmosis product water, although at low levels (Watkinson et al. 2007). A recent comparison of four different types of full-scale municipal wastewater-treatment plants that employed various means of secondary and tertiary wastewater treatment found a high degree of variation in their antibiotic-removal capability, with detected concentrations of antibiotic contaminants in final effluents ranging from a low of 0.061 μg/L (tetracycline) to a high of 2.4 μg/L (trimethoprim) (Batt et al. 2007). Tertiary treatment often did not result in significant further reduction of antibiotic beyond that achieved by secondary treatment. No treatment plant achieved undetectable levels of the tested antibiotics in the final effluent.

As a result of incomplete efficiency in removal of antibiotics from wastewater, along with the contribution of agricultural use and runoff, numerous studies conducted in the United States and in Europe have found detectable levels of numerous classes of antibiotics in both surface-water and groundwater samples (Heberer 2002a; Brown et al. 2006). Macrolide antibiotics, sulfonamides, fluoroquinolones, chloramphenicol, tylosin, and trimethoprim have all been found up to the low μg/L level in surface-water samples (Heberer 2002a), and occurrence of sulfamethoxazole (up to 41 ng/L) and dehydoerythromycin (up to 49 ng/L) has been reported in groundwater samples taken in Germany (Sacher et al. 2001). Sulfamethoxazole and sulfamethazine have also been detected at low concentrations in a limited number of groundwater samples taken in the United States and Germany (Hartig et al. 1999; Hirsch et al. 1999; Lindsey et al. 2001 [all in Heberer 2002a Toxicol Letters]. More recently in the United States, Brown et al. (2006) have reported finding concentrations of 300 ng/L of sulfamethoxazole in two samples of water taken from the Rio Grande River, which receives treated wastewater from a large treatment plant in Albuquerque, New Mexico. This finding is consistent with those obtained by the U.S. Geologic Survey via surveillance of U.S. streams in 1999 and 2000 (Kolpin et al. 2002). Regarding other antibiotic classes, erythromycin, trimethoprim, ciprofloxacin, ofloxacin, sulfadiazine, and tetracycline have been detected in addition to sulfamethoxazole in effluent from the South District Wastewater Treatment Plant located in the Miami-Dade area of Florida (Lietz & Meyer 2006).

The end result of environmental persistence of antibiotic substances in wastewater and incomplete removal in the wastewater-treatment process is possible environmental toxicity. Several toxic effects on aquatic organisms have been ascribed to environmentally persistent antibiotics used in human medicine. These include mutagenicity and carcinogenicity in the case of the nitroimidazoles (Simon & Stille 1993), the class of drugs to which the commonly used agent metronidazole belongs. Metronidazole has also been reported to be toxic to aquatic algae and daphnids (Lanzky & Halling-Sorensen 1997). Gentoxicity has also been associated with the fluoroquinolones (Stille & Simon 1993; Mersch-Sundermann et al. 1994). Brain et al. (2008) report that multiple aquatic plant species have common receptors for a number of frequently prescribed antibiotics, affecting functions such as chloroplast replication (fluoroquinolones), transcription and translation (tetracyclines, macrolides, lincosamides, aminoglycosides, and pleuromutilins), and metabolic pathways such as folate biosynthesis (sulfonamides). Toxicological investigations into the potency of these compounds have indicated susceptibility across multiple plant species, although sensitivities vary widely between blue-green algae, green algae, and higher plants (Brain et al. 2008).

Further, sulfamethoxazole was recently found by investigators in Korea to be associated with a hazard quotient of 6.3 in an assessment of that antibiotic's aquatic toxicity using the marine bacterium *Vibrio fischeri,* the freshwater invertebrate *Daphnia magna,* and the fish species *Oryzias latipes.* Also, Yamashita et al. (2006) found that the fluoroquinolone antibiotic levofloxacin and the macrolide antibiotic clarithromycin were highly toxic to algal and crustacean test species, with clarithromycin showing a higher degree of toxicity, and therefore potentially disruptive to the aquatic environment. Therefore, high loads of accumulated antibiotics and their active metabolites in bodies of water that support ecosystems have become a justifiable matter of concern.

DISINFECTANTS IN WASTEWATER AND ENVIRONMENTAL TOXICITY

In addition to pharmaceuticals, another type of chemical compound that is heavily used in hospitals and has consequently raised concern about potential environmental toxicity is disinfectants, such as glutaraldehyde and quaternary ammonium compounds (QACs). Glutaraldehyde solutions are cool sterilants frequently used in hospitals to disinfect and clean heat-sensitive equipment such as dialysis and surgical instruments, suction bottles, bronchoscopes, endoscopes, and instruments used in rhinootolaryngologic procedures; it is also used as a fixative in histology and pathology laboratories, and as a hardening agent in the development of radiographs (HSDB 1996; NIOSH 2001). Glutaraldehyde is active against a wide range of micro-organisms, effectively killing aerobic and anaerobic bacteria, moulds and yeast, and algae (FEI 2001). In humans, glutaraldehyde exposure has been associated with proctitis, colitis, and rectitis in patients who underwent medical procedures with instruments that had been disinfected with glutaraldehyde (Burtin et al. 1993; Asselah et al. 1996; Ledinghen 1996); other associated irritations have also been reported (Emmanuel et al. 2005a).

Low-biodegradability quaternary ammonium compounds (QACs) such as benzalkonium chloride (BzCl) represent another extensively used class of surface-disinfecting agent in modern hospitals, along with alcohols and aldehydes (Kummerer 2001). Disinfectants have long been recognized as toxic to aquatic organisms by numerous teams of investigators (Emmanuel et al. 2005a). Concentrations of BzCl up to 6 mg/L have been measured in hospital effluents, while the expected QAC concentration in municipal sewage is in the range of 0.05–0.1 mg/L (Kummerer et al. 1997). Therefore, hospitals may represent a major source of this variety of pollutant in the wastewater stream. Kummerer et al. (1997) estimated that 10–20 tons per year of BzCl was used in German hospitals alone; in one large Austrian hospital, about 900 kg per year had been used before measures were instituted to curb use of this environmentally persistent compound (Kummerer et al. 1997). In general, disinfectant compounds represent a major carrier for halogenated organic compounds in hospital effluents, along with x-ray contrast media, solvents, cleaners, and drugs containing chlorine (Emmanuel et al. 2005b).

Because of the extensiveness of their use in modern hospitals, disinfectants and the detergent surfactants with which they are paired almost inevitably reach the hospital wastewater network (Kummerer 2001), and thus treatment plants and the bodies of water that receive the effluents, together. Surfactants have been shown to be toxic to the three first organization levels of aquatic food chains (algae → crustacean → fish) (Schawartz & Vaeth 1987; Talmage 1994). Hospital wastewater can contain hundreds of toxic and hazardous pollutants (EPA 1989) whose by-products from chemical and physiochemical processes may be more toxic than the initial substances involved (Emmanuel et al. 2005a); the effect of a mixture of chemicals may be simply additive, more than additive (synergistic), or less than additive (antagonistic). In their laboratory-based assessment of the combined effects of glutaraldehyde and various surfactant mixtures on aquatic organisms, Emmanuel et al. (2005a) found an additive joint action of glutaraldehyde and a cationic surfactant on *Vibrio fischeri* bacteria, and a synergistic action on *V. fischeri* of glutaraldehyde and a nonionic surfactant. An antagonistic joint action was observed when glutaraldehyde was paired with an anionic surfactant. This study also confirmed the results of previous investigations showing that surfactants exert toxic effects on ecosystems independently, with cationic and anionic surfactants being more toxic than nonionic surfactants. The synergistic relationship noted above, however, indicates that the acute toxicity of mixtures is greater than the sum of the simple acute toxicities of the mixtures' individual components (Emmanuel et al. 2005a).

DRUG-RESISTANT ORGANISMS IN HOSPITAL WASTEWATER AND THE PROBLEM OF ANTIMICROBIAL RESISTANCE

Besides the negative impact on aquatic ecosystems caused by emissions of antibiotic- and disinfectant-containing wastewaters from hospitals, these effluents pose another danger: the threat of propagation of drug-resistant organisms and drug-resistance genes in the environment, due to the selective pressure imposed by the antibiotic and disinfectant substances contained therein, as well as the direct introduction of drug-resistant microbes excreted by patients taking antibiotics into the wastewater (Kummerer 2004). The presence of detectable levels of antibiotics and disinfectants in hospital wastewater is well-established in the literature, as noted above.

Resistant bacteria may be selected or favored by antibiotic compounds in hospital effluent, even if concentrations of individual antibiotics are below MIC_{50} values, because groups of antibiotics present in the effluent may act via the same mechanism and thus reach the MIC_{50} (Kummerer 2004). For example, Schwartz et al. (2003) found bacteria carrying vanA genes in hospital effluent; this is significant because *vanA* genes mediate resistance to the powerful glycopeptide antibiotic vancomycin, and such resistance in *Enterococcus* species constitutes a major infection-control issue in healthcare facilities. Harwood et al. (2001) have reported that *Enterococcus* species isolated from wastewater from a hospital in Tampa, Florida, were found to be resistant to ≥ 20 $\mu g/m^{-1}$ and possessed the *vanA* gene; these species could be isolated even without the use of vancomycin during initial screening, indicating high-level resistance. Also, Blanch et al. (2003) have sampled hospital and municipal wastewater from three European countries to characterize their Enterococcus populations, and found an especially high prevalence of vancomycin-resistant *Enterococcus* in Swedish hospital wastewater: 100% of such samples obtained showed evidence of colonization by *E. faecium* organisms resistant to 20 ml/L^{-1}; further, such highly resistant *E. faecium* strains were detected in 85% of hospital-wastewater samples obtained in Spain, and in 70% of samples obtained in the United Kingdom. Also, the *mecA* gene, which encodes resistance to methicillin and is thus at the center of the growing public-health problem of methicillin-resistant S*taphylococcus aureus* (MRSA) infections in healthcare facilities and the outside community, was found only in bacteria in hospital wastewater, but not in bacteria in municipal wastewater (Heuer et al. 2002).

Other drug-resistant pathogens that constitute infection-control challenges within healthcare facilities that have been isolated from hospital wastewater include the gram-negative rods *Pseudomonas aeruginosa* (Tumeo et al. 2007), *Escherichia coli* (Reinthaler et al. 2003), and *Acinetobacter* species (Guardabassi et al. 1998). The above-noted study of *P. aeruginosa*—which in hospitals is responsible for myriad infections including sepsis, pneumonia, meningitis, and infections of surgical sites, the urinary tract, burn wounds, and the eye (Mayhall 1999)—suggests that the risk of spread of antibiotic resistance in hospital wastewater is limited, based on the lack of a common confirmed genetic pattern among isolates obtained from humans and wastewater. The investigators caution, however, that the number of strains they typed via pulsed field gel electrophoresis for their study was limited and results should therefore be interpreted with caution (Tumeo et al. 2007). The researchers state that spread of multi-drug-resistant bacteria through hospital wastewater is a valid cause for concern, especially for hydrophilic species such as *P. aeruginosa* for which the hospital-wastewater environment may be ideal (Tumeo et al. 2007). This concern is echoed by Kummerer (2004), who notes that it is plausible that multi-drug-resistant bacteria are selected mainly in hospitals and passed into wastewater.

Another multi-drug resistant organism of particular concern today is the gram-positive bacterium *Staphylococcus aureus*, which previously had primarily been almost exclusively a healthcare-associated infection but lately has come to be considered a community-acquired, potentially life-threatening infection, in particular, the methicillin-resistant strain now commonly known as MRSA. Ohlsen et al. (2003) report that resistance to the gentamicin in *S. aureus* was transferred as efficiently in hospital sewage agar plates as on rich media, although the number of donor and recipient cells was decrease approximately 1000-fold in the sewage. Transfer of resistance genes was detectable in plain sewage at a frequency of $< 5.0 \times 10^{-8}$ to 2.0×10^{-6}.

The presence of disinfectants in hospital wastewater is viewed as a potential promoter of resistance in bacteria present in the wastewater, due to the selective pressure imposed by these compounds. Tumeo (2007) notes that commonly used healthcare disinfectants such as triclosan and quaternary ammonium compounds act as substrates for the efflux-pump systems of *P. aeruginosa,* which are now recognized as playing a critical role in non-enzymatic mechanisms of acquired drug resistance. As these products are present in high concentrations in hospital effluents, selective pressure for more highly resistant *P. aeruginosa* strains may therefore be exerted.

CONCLUSION

A recent paper by Pauwels and Verstraete (2006) summarizes the state of the science in hospital wastewater treatment systems. A promising new technology that has been proposed as an alternative to conventional activated sludge treatment of hospital wastewater is the membrane bioreactor (MBR), a technology that employs flat porous sheets for microfiltration (~0.1–0.4 μm, depending on growth of microorganisms and fouling proteins that reduce porosity). Complete retention of biosolids by the membrane enables high mixed liquor suspended solids concentrations, yielding long sludge retention time and low sludge loading rates (Pauwels & Verstraete 2006). This is a promising technology in terms of its potential to reduce antibiotic contaminant loads in hospital wastewater, as Radjenovic et al. (2007) found higher removal rates for several tested antibiotics with MBR than with conventional activated sludge treatment. MBR is still far from being widely used, however. Pauwels and Verstraete (2006) emphasize add that several post-treatment technologies such as activated carbon, ozonation, and ultraviolet photolysis remove hospital-related pollutants effectively.

An approach to hospital wastewater treatment that bears further study is on-site treatment of hospital wastewater, either followed by discharge of effluent into the environment or subsequent treatment by a municipal wastewater treatment plant (Pauwels & Verstraete 2006). The potential advantage of on-site treatment followed by environmental discharge is that a 90% decrease in contaminant load may be achieved, while the potential disadvantage is that very strict monitoring and process control by both the process plant operators and municipal authorities are necessary (Pauwels & Verstraete 2006). The potential advantage of the double-treatment approach is maximal safety conferred by two rounds of effluent treatment; the disadvantages are cost and complexity (Pauwels & Verstraete 2006). The potential environmental benefit of these approaches to hospital wastewater treatment necessitates a thorough evaluation (Pauwels & Verstraete 2006).

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Assessing Risk Posed by Land Application of Ash from the Combustion of Wood and Tires

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ABSTRACT: The total and leachable metal concentrations in ash from the combustion of waste wood and vehicle tires (WT ash) were characterized. These data were then used to examine a variety of issues associated with determining whether the WT ash could be beneficially used outside of a landfill (e.g., land application as fill material, soil amendment). Metal release was assessed using standardized batch tests, lysimeter leaching tests, and additional leaching experiments targeting specific factors that impact metal leaching. The toxicity characteristic leaching procedure (TCLP) and the synthetic precipitation leaching procedure (SPLP) extracted similar metal concentrations. Although arsenic was detected at high concentrations in the WT ash totals analysis, it did not leach at concentrations that may pose a risk to human health and the environment. Another metal of potential concern with regard to groundwater contamination is lead. Lead leached from WT ash at 120, 55, 52, and 52 μg/L using the WET, TCLP, SPLP, and DI water extraction, respectively. Lead was also encountered in the lysimeter leachate above its groundwater cleanup target level (GWCTL). In terms of risk assessment, from a direct human exposure pathway, arsenic was found to be the most limiting element. Comparison with the leaching SCTLs indicated that arsenic, chromium, and zinc would pose a potential risk to groundwater. The SPLP results did not find these metals to pose a risk, but has lead concentrations above GWCTL suggesting that using leaching SCTLs that are developed for soil is not appropriate for application to combustion ash. When compared to steady-state concentrations measured in the lysimeters, SPLP, TCLP and DI water lead concentrations matched very well suggesting that these concentrations reflected the pore water concentration for this ash.

1. INTRODUCTION

NON-HAZARDOUS industrial solid wastes are frequently proposed for beneficial use rather than disposal in landfills. Ash resulting from the combustion of fuel (e.g., wood, coal) and solid wastes (e.g., waste wood, municipal solid waste, biosolids) is one such example. Assuming the ash is not a regulated hazardous waste, beneficial use applications where an industry incorporates the ash into a product (e.g., cement, masonry) are largely unregulated. When the ash is directly land applied (e.g., fill material, soil amendment), use may be limited depending on the chemical characteristics of the ash and the relevant regulatory requirements. In the US, the land application of wastes such as biosolids and cement kiln dust is regulated at the federal level, but the land application of other wastes such as ash is regulated, if at all, by state or local government agencies.

This paper reports the results of research conducted to characterize ash from a facility combusting wood waste and tires for energy recovery. Analyses that would typically be required for a beneficial use demonstration in Florida were conducted; this risk assessment process is similar to those used by regulatory agencies in other locations. The results (totals and leachable concentrations of inorganic constituents) were compared to Florida's risk-based target levels. This study was designed to make several contributions valuable to those interested in the characterization and management of residuals such as ash. Data regarding this particular type of ash are not widely available. And perhaps of greater contribution, several complicating issues commonly encountered when applying the typical method-

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ology for beneficial use risk assessments were evaluated. These results thus have relevance to the general topic of land application of waste residuals.

2. BACKGROUND

2.1. Wood and Tire Ash

The co-combustion of vehicle scrap tires and waste wood produces energy and provides a management option for these solid wastes. A byproduct of this combustion process is wood and tire (WT) ash. While landfilling is the most common solid waste disposal option for combustion ash (Campbell et al., 1990), economic factors and the desire for resource conservation have spurred interest in the beneficial use of ash (Lerner and Utzinger, 1986; Naylor and Schmidt, 1986; Vance, 1996; Schreurs et al., 2000). Wood ash from the combustion of clean wood has long been used as a liming agent (soda ash) and a source of plant nutrients (Campbell et al., 1990). Wood ash has also been beneficially used as a partial replacement of cement in concrete mixes, road-base, and fill material (Campbell et al., 1990; Schreurs et al., 2000), although the most commonly employed beneficial use option for wood ash is as an agricultural amendment (Risse and Gaskin, 2002). A study examining the effect of wood ash on a northern European pine forest soil concluded that the buffering capacity of wood ash was similar to conventional lime (Bramryd and Fransman, 1995). Other studies concluded that the availability of potassium in wood ash was similar to that of fertilizers (Naylor and Schmidt, 1986; Erich, 1991; Ohno, 1992).

Ash from the combustion of some wood wastes, such as wood recovered from the recycling of construction and demolition (C&D) debris, may contain impurities which increase metal concentrations in the resulting ash. High concentrations of arsenic, chromium (from treated wood), and lead (from wood painted with lead-based paint) have been observed in ash from the combustion of C&D debris waste wood (Beebe and England, 1998; Tolaymat et al., 2000; Jacobi et al., 2007). Similarly, the addition of tires to the wood fuel could also change the composition of the ash.

The chemical and physical characteristics of wood ash vary depending on the species of wood combusted and the incineration conditions (Campbell et al., 1990; Misra et al., 1993). Metal concentrations (mg/kg) in ash from the combustion of clean wood have been previously characterized (Lerner and Utzinger, 1986; Naylor and Schmidt, 1986; Erich, 1991; Etiegni et al., 1991; Ohno, 1992; Bramryd and Fransman, 1995; Vance,

Table 1. Average metals concentration[§] in wood, tires, and wood/tire ash.

Metal	Wood Ash (from literature)	Tire Ash (from literature)		WT Ash Mean ± SD[e] (from present study)	SCTL			Form
		Fly	Bottom		Residential	Industrial	Leaching	
Al	14.5 ± 7[a,b]	7,600[d]	20,600[d]	3.94 ± 0.7 (g/kg)	80,000	NA	NA	$AlPO_4$
As	23.2 ± 20[c]	200[d]	10[d]	37.2 ± 6	2.1	12	29	ND
Ba	–	–	–	39.3 ± 7	120	130,000	1,600	ND
Ca	171 ± 80[a,b]	–	–	223 ± 50 (g/kg)				CaO, $CaCO_3$
Cd	5.0 ± 5[c]	500[d]	10[d]	2.71 ± 0.5	82	1,700	8	ND
Co	8.7 ± 5[c]	–	–	129 ± 30	4,700	110,000		ND
Cr	39.0 ± 30[c]	300[d]	5,230[d]	46.3 ± 5	210	420	38	ND
Cu	75.3 ± 45[c]	–	–	162 ± 30	110	76,000		ND
Fe	9.31 ± 5[a,b]	63,300[d]	96.2%[d]	34.7 ± 5 (g/kg)	23,000	480,000		Fe_3PO_7
K	25.8 ± 7[a,b]	–	–	6.67 ± 0.8 (g/kg)				K_2SO_4,$KClO_3$
Mg	12.2 ± 5[a,b]	–	–	5.42 ± 1 (g/kg)				Al_3Mg_2
Mn	4370 ± 2700[c]	–	4,160[d]	307 ± 80	1,600	22,000		ND
Na	1.8 ± 1.3[a,b]	–	–	1.80 ± 0.02 (g/kg)				ND
Ni	23.5 ± 20[c]	–	–	16.7 ± 4	110	28,000	130	ND
Pb	65.6 ± 40[c]	2,200[d]	10[d]	63.1 ± 10	400	920		ND
V	–	–	–	5.49 ± 2	15	7,400	980	ND
Zn	443 ± 400[c]	51.48%[d]	1,060[d]	18.2 ± 3 (g/kg)	23,000	560,000	6,000	ZnP_4O_{11}, $ZnSO_4$

[§] Units mg/kg dry mass unless otherwise indicated
[a] Muse and Mitchell, 1995
[b] Campbell et al., 1990
[c] Someshwar, 1996
[d] Levie et al., 1995
[e] average ± standard deviation from 8 WT ash samples in triplicates)
ND = not detected

1996); typical concentrations of metals in wood ash are summarized in Table 1. A smaller but still significant number of studies have evaluated the leachable metal concentrations from wood ash (Erich, 1991; Xiao et al., 1999). Most leaching research on wood ash, however, has been conducted to determine available plant nutrients for agricultural purposes, not to evaluate potential environmental impacts of heavy metal leaching to groundwater (Erich, 1991). Xiao et al. (1999) demonstrated the potential for heavy metals such as lead to leach from wood ash when exposed to de-ionized water. Campbell et al. (1990) concluded that since wood ash is not a toxicity characteristic hazardous waste as defined by the resource conservation and recovery act (RCRA) and since nutrients are readily available, it could be used as an agricultural additive; as will be described later in this paper, criteria for land application of waste materials typically go beyond hazardous waste characterization alone.

There has been very limited characterization of scrap tire ash since it is uncommon for scrap tires to be used as the sole fuel source in a combustion process. The Rubber Manufacturers Association (RMA) estimated that approximately 155 million (52%) of the 298 million scrap tires generated in 2005 were incinerated (RMA, 2006) for tire-derived fuel (TDF). Tires are made from vulcanized rubber reinforced with a metallic (primarily steel) mesh. Most of the ash remaining after scrap tire combustion is comprised of the metallic mesh (Rodriguez et al., 2001). Levie et al. (1995) reported that scrap tire bottom ash contained 96% by weight iron and that scrap tire fly ash was 51% zinc; both fly ash and bottom ash also contained trace levels of other elements such as arsenic, chromium, cadmium, and lead (see Table 1). The study did not assess the leaching of metals from waste tire ash.

2.2. Evaluating Risk from Land Application of Residuals

Several risk pathways are typically explored to evaluate the risk posed by the land application of a residual such as ash. Examination of the direct human exposure pathways (ingestion, dermal contact, and inhalation) and impact to groundwater is common; assessing risk to ecosystems is less common. Direct human exposure is typically addressed by measuring the total concentration of various chemicals of concern (mg/kg) and comparing the results to risk-based target concentrations. In Florida, USA, for example, the risk-based target concentrations used are the Florida Department of Environmental Protection's (FDEP) soil cleanup target levels (SCTLs; units = mg/kg) (FAC 62-777, FDEP, 2005). The direct exposure SCTLs are based on assumed exposure scenarios, toxicological information, and acceptable risk.

The potential risk of groundwater contamination as a result of leaching is evaluated by one of several methods. One method is to compare the total concentration (mg/kg) to an SCTL derived specifically for leaching (units = mg/kg). The leaching SCTL is determined from an assumed value for "leachability" of the metal from a solid matrix (partition coefficient or K_d, typically derived for a soil). It represents the theoretical amount of metal that would have to be present (mg/kg) to result in a pore water concentration equal to the groundwater standard or target level (mg/L). A dilution factor is often incorporated into the leaching SCTL to account for potential dilution and attenuation that might occur between the contaminated media (soil, ash) and the point of interest in the groundwater. A second method for evaluating potential risk to groundwater from a land-applied ash is to produce a leachate from the ash and to compare the pollutant concentration in the leachate (mg/L) to a risk-based groundwater target concentration. The FDEP has developed a set of groundwater cleanup target levels (GWCTL; unit = mg/L); these are based on federal drinking water standards or additional toxicity and exposure assumptions. The most common procedure to produce the ash leachate is to conduct a batch leaching test, and the US EPA's synthetic precipitation leaching procedure (SPLP) is commonly used (the SPLP simulates leaching as a result of acid rainfall). Professionals in the waste management community might be more familiar with other batch leaching tests such as the Toxicity Characteristic Leaching Procedure (TCLP) and California's Waste Extraction Test (WET), both of which are designed to simulate leaching within a municipal solid waste (MSW) landfill. In some cases, procedures such as the TCLP and WET are used for initial risk assessment screening if no other data are available. Researchers have developed a myriad of other leaching methodologies that may provide helpful information for a detailed risk assessment.

3. MATERIALS AND METHODS

3.1. Sample Collection

The ash for this study was generated at a waste-to-energy (WTE) facility in Florida that combusts waste wood amended with shredded scrap vehicle tires. The facility accepts wood from land clearing and construction and demolition (C&D) activities, as well as some industrial wood sources and yard trash. Shredded and whole (without rims) scrap tires are also accepted by the facility. Larger pieces of waste wood and tires are shredded to less than 3 and 6 cm, respectively, before combustion. Shredded tires comprise up to 10% of the fuel stream. The facility generates 150 to 300 tons of WT ash daily; the ash is co-disposed of with MSW at a neighboring lined sanitary landfill. The WT ash sampled for this study consisted of a mixture of bottom and fly ash as well as air-pollution control (APC) residues. The samples were collected from eight ash truckloads during one sampling event. Each truck emptied its load near the working face of the landfill and a front-end loader mixed the WT ash before sample collection. Eight samples (one from each truckload) were collected in 40-L (10-gal) PVC containers and transported to the laboratory. Each of the eight samples was mixed again to promote homogeneity and then equal amounts of the eight samples were used to generate a composite sample. The bulk of the analysis described in this paper was conducted on each of the eight truckload samples; where indicated, some analysis procedures were only conducted on the composite sample.

3.2. Ash Characterization

Solid samples were digested for total metal analysis as prescribed in US EPA Method 3050B (EPA, 2003). Between 1 and 2 g, corrected for moisture content, of WT ash samples were weighed into a flask. The digestion procedure used a hot-plate open-vessel method and required the use of nitric acid, hydrogen peroxide, and hydrochloric acid (for inductively coupled plasma (ICP) analysis as per US EPA Method 6010B (EPA, 2003)). This type of analysis indicates the maximum extractable metals but not the leachable metal content.

Morphological analyses were conducted on the composite WT ash sample. A 20-gram WT ash sample was used for scanning electron microscope (SEM) analysis. SEM analyzes the morphology of the ash samples using a SEM Jeol JSM 35CF (Sollentuna, Sweden) with a typical penetration depth of 10 Å. Another (20 g) WT ash sample was manually size reduced and then analyzed using X-ray diffraction (XRD) using a Philips APD 3720 (New York, US). XRD is a bulk analytical technique with a penetration of 1 nm. This technique is used to identify crystalline phases in the ash sample.

3.3. Analysis of Leachable Elements and Compounds

The leachable elements were analyzed using both batch leaching tests and column leaching tests. Batch leaching tests provide a more rapid means to assess the leachability of elements from a waste sample; these tests are relatively simple to perform and can be completed within a few days. Column tests provide a more realistic measure of leachate concentrations from a layer of waste, but are more complicated and take longer.

3.3.1. Batch Leaching Tests

The regulatory batch leaching tests performed (in triplicate) included the TCLP, SPLP, a de-ionized (DI) water extraction test, the multiple extraction procedure (MEP), and California's waste extraction test (WET). While the TCLP is the batch test required by the RCRA for hazardous waste characterization, the State of California also uses the WET for that purpose. Both the TCLP and the WET examine metal leachability from solid wastes in MSW landfill environments and thus use organic acids. The MEP examines long-term metal leachability by using an organic acid extraction solution followed by a slightly acidic rainwater extraction solution. All of the procedures employ a liquid-to-solid ratio of 20:1 with the exception of WET which requires a 10:1 ratio. The TCLP, SPLP, WET and the test using DI water were performed on each of the eight samples, while the MEP was performed on the composite sample. The leaching procedures were performed in accordance with US EPA SW 846 methods and the California Code of Regulation method for WET (EPA, 2003; CCR, 1998). The impact of pH of chemical leachate was evaluated on the composite sample. For a target pH, 150 mL of deionized water to 10 g of ash, the slurry was mixed, and the pH was monitored continuously with a pH probe. Either diluted nitric acid or sodium hydroxide was added to reach and maintain the desired pH. Tests were conducted for pH from 1 to 13 pH units. Once the pH stabilized at the predetermined set point, enough reagent water was added to achieve a liquid-to-solid ratio of 20:1 and the slurry was rotated for 18 hours. Filtration and preservation followed the same method as the TCLP. Liquid samples were digested according to US EPA SW-846 method 3010 for inductively coupled plasma analysis or 3020 for graphite furnace analysis (EPA, 2003). Liquid samples that were analyzed for arsenic were digested using US EPA SW-846 method 7060A (EPA, 2003). Specific methodology details, including quality control procedures, are provided in Tolaymat (2003).

3.3.2. Column Leaching Tests

Leaching column experiments (lysimeter tests) were carried out in stainless steel leaching lysimeters. See Brantley and Townsend (1999) for a complete description of these devices. Thirty cm (one foot) of ash was placed in three 1.2-meter-tall, 15-cm-diameter lysimeters. The ash was placed in eight 4-cm (one and a half inch) lifts, with each lift representing one of the eight samples. Simulated rain water was applied to the top of the lysimeter and leachate was regularly collected from a reservoir at the bottom of each column. Approximately 70 L of SPLP solution was added to each lysimeter, a volume equivalent to 384 cm of rainfall or approximately 3 years of average Florida rainfall. Leachate samples were digested and analyzed in the same fashion as described for the batch leachate samples. The detailed procedure is presented in Tolaymat (2003).

3.3.3. Risk Assessment Approach

The resulting data were evaluated following standard risk assessment approaches for land application of waste materials. Risk-based thresholds for Florida were used, but the approach is typical for other locations. First, the total concentrations of inorganic chemicals of concern measured in the WT ash sample were compared to Florida SCTLs for direct exposure. The risk from pollutant leaching was then evaluated in several different manners, and the results of each methodology were compared. Total concentrations were compared to SCTLs derived for leaching. Leachate concentrations (SPLP, TCLP, WET, lysimeters) were compared to GWCTLs. The limitations of each approach with respect to beneficial use assessments were assessed.

For a small sample size (fewer than 50 samples), the US EPA suggests using a conservative estimate of the arithmetic mean concentration for each contaminant (EPA 2000), thus the 95-percent upper confidence limit (UCL_{95}) of the mean was determined for each parameter. A chemical concentration was treated as problematic if the UCL_{95} of the mean was greater than the respective SCTL or GWCTL. In cases where some measurements were below the detection limit of the instrument, a value of 50% of the detection limit was assigned for any needed statistical calculations.

4. RESULTS

4.1. Total Metal Concentrations in Ash Samples

The average concentrations (from the eight samples; each sample was measured in triplicate) of 17 inorganic elements in the WT ash were determined (see Table 1). All 17 elements were measured in concentrations above their respective detection limits. Because of the high concentrations of some elements relative to others, the morphological analyses (SEM, XRD) were unable to evaluate elements at trace concentrations. The results (Table 1) indicated crystalline forms consistent with those reported in the literature to be present in wood ash (Misra et al., 1993; Steenari and Lindquist, 1999).

The concentrations of elements in the WT ash were compared with values compiled from the literature from wood ash and tire ash (fly ash and bottom ash) individually as presented in Table 1. The wood ash concentrations from the literature as presented in Table 1 represent an average concentration (± standard deviation) from a variety of sources and thus represent a wide range of wood species and combustion conditions. The concentrations of iron, zinc, copper, cobalt, and sodium in the WT ash were higher ($\alpha = 0.05$) than those in wood ash alone. The WT ash iron concentration, however, was much lower than that in tire fly ash (63.3g/kg). Although the zinc concentration relative to iron was low in WT ash, the co-combustion of tires with wood had a larger impact on the zinc concentration in WT ash than that of wood ash. The zinc concentration in WT ash (18,200 mg/kg) was much higher than in wood ash (443 mg/kg). The concentrations of arsenic, chromium, lead, and calcium in the WT ash were similar ($\alpha = 0.05$) to that in wood ash alone. These results were unexpected since this facility combusted some wood from C&D activities. Research suggests that tires as well as C&D wood waste contain elevated levels (relative to wood) of arsenic, chromium, and lead. Levie et al. (1995) concluded that tire ash also contains some of the more toxic metals such as arsenic (200 mg/kg in fly ash and 10 mg/kg in bottom ash) and lead (2,200 mg/kg in fly ash and 10 mg/kg) in bottom ash. Studies have found that the ash from the combustion of C&D debris recovered wood often contains arsenic, chromium, and copper as a result of the presence of pressure-treated wood (Tolaymat et al., 2000; Solo-Gabriele et al., 2002). The arsenic concentration of WT ash (37.2 mg/kg) was lower than expected from combusting C&D debris wood, suggesting that the fraction of C&D debris wood burned at this facility at the time of sampling was small relative to other wood sources. The concentrations of nickel, cadmium, potassium, magnesium, manganese, and aluminum were lower ($\alpha = 0.05$) in the WT ash than in the wood ash.

4.2. Leachable Metal Concentrations

TCLP and WET Leaching Results: Metal concentrations in the TCLP and the WET leachates were an order of magnitude below the hazardous waste limits presented in RCRA and the California Code of Regulations (CCR, 1998). For example, the average TCLP and WET concentrations of lead in the composite WT ash samples were 0.055 and 0.12 mg/L, respectively, compared to the RCRA and CCR hazardous waste regulatory limit of 5.0 mg/L. Previous research suggested that citric acid (WET) complexes heavy metals at a higher level than acetic acid (TCLP) (Hopper et al., 1998; Bassi et al., 2000, Jang and Townsend, 2003; Dubey and Townsend, 2004; Townsend et al., 2004). This was found true for several elements in the WT ash; when compared with the TCLP, the WET extracted higher ($\alpha = 0.05$) concentrations of chromium, copper, iron, potassium, magnesium, and zinc. In the WET leachates, nickel, manganese, arsenic, and aluminum were encountered at measurable concentrations while in the TCLP leachates these elements were below detection limit. The WET and the TCLP extracted similar ($\alpha = 0.05$) concentrations of barium, calcium, and lead.

SPLP and DI Leaching Results: When metal concentrations extracted by the SPLP are compared to those of the TCLP, copper was detected in the TCLP but not in the SPLP, while aluminum, arsenic, cobalt, manganese and nickel were not detected in either test (Table 2). Potassium concentrations in the TCLP leachate were higher ($\alpha = 0.05$) than the SPLP leachate, but relatively close. Only sodium was dramatically greater in the TCLP compared to the SPLP, but this was because sodium is used in the TCLP solution. The TCLP and SPLP extracted statistically similar ($\alpha = 0.05$) concentrations of zinc, barium, chromium, iron, magnesium, and lead.

Comparisons of TCLP and SPLP for other wastes have found that TCLP typically extracts more metals than SPLP because of the buffered pH of the TCLP and the ability of acetic acid to complex heavy metals (Carey and Nagelski, 1996; Hopper et al., 1998; Jang and Townsend, 2003; Townsend et al., 2004, 2005; Dubey and Townsend, 2004). In the present study, the observation that TCLP and SPLP extracted similar amounts of most elements illustrates the importance of specific waste chemistry when assessing potential differences among leaching tests. The high pH of the ash negated differences normally encountered between TCLP and SPLP. When the ash samples were leached with DI water, extracted concentrations were statistically similar ($\alpha = 0.05$) to the SPLP.

Long-term Leaching Assessment: The MEP is used to assess long-term leaching from solid wastes. The initial (first day) leaching conditions under MEP are similar to

Table 2. Metal concentrations in batch leaching tests on wood and tire (WT) ash (8 samples in triplicates).

Metal	Units	Detection Limit	RCRA TC Limit	GWCTL	TCLP Mean ± SD	WET Mean ± SD	SPLP Mean ± SD	DI Mean ± SD
Al	(mg/L)	0.007	–	0.2	< 0.007	1.32 ± 0.1	< 0.007	< 0.007
Ca		0.1	–	–	1,490 ± 50	2,970 ± 170	1,070 ± 53	628 ± 30
K		0.1	–	–	167 ± 7	392 ± 9	153.3 ± 5.7	165 ± 8
Na		0.1	–	160	821 ± 30	–	32.5 ± 3.9	27.4 ± 1
Zn		0.02	–	5.0	1.92 ± 10	69.3 ± 3	1.72 ± 0.19	1.27 ± 0.3
As	(µg/L)	5.0	5,000	10	< 5	102 ± 1	< 5	< 5
Ba		40	100,000	2,000	207 ± 10	149 ± 60	218 ± 80	95 ± 10
Co		11	–	420	< 11	650 ± 30	< 11	< 11
Cr		1.0	5,000	100	9.0 ± 3	73 ± 10	7.0 ± 0.4	19 ± 10
Cu		14	–	1,000	34 ± 7	1,450 ± 600	< 14	< 14
Fe		40	–	300	93 ± 8	7,280 ± 400	116 ± 50	112 ± 60
Mg		100	–	–	376 ± 30	3,110 ± 200	424 ± 40	242 ± 60
Mn		14	–	50	< 11	193 ± 20	< 11	< 11
Ni		15	–	100	< 15	55 ± 10	< 15	< 15
Pb		5.0	5,000	15	55.2 ± 10	118 ± 60	52.3 ± 9	51.5 ± 5

the TCLP (concentrations were found to be statistically similar). However, subsequent days MEP results may not be directly compared to the previously examined batch tests since the MEP involves subsequent leaching of the WT ash. Of the 17 metals analyzed, arsenic, cobalt, cadmium, copper, manganese, and nickel were below their respective detection limits. Because the concentrations of aluminum and iron were close to their detection limits (7 and 20 μg/L respectively) as well as the high variability of the results, these two metals were not examined further. Sodium concentrations were not reported because sodium acetate was used as an extraction solution on day-1. Calcium, chromium, barium, potassium, and zinc concentrations in solution showed an initial decrease with consecutive extractions (Figure 1). As the test proceeded and fresh extraction fluid was added to the same WT ash, the pH decreased. After the initial decrease, some metals showed a slight increase in concentrations after Day 4. Factors that impact changes in element concentrations with successive leaching included changing pH conditions (see next section), element mass loss, and possibly changes to the surface layer of ash particles (Poon and Chen, 1999).

Impact of pH on metal leachability: pH is known as a major controlling factor in the mobility of most metals (Fytianos et al., 1998; Kanungo and Mohapatra, 2000; Li et al., 2001; Van der Sloot et al., 2001; Van der Sloot, 2002; Townsend et al., 2004; Dubey and Townsend, 2004). To examine the effect of extraction solution pH on metal leachability from WT ash, batch leaching tests were carried out at different leaching solution pH values ranging from 1 to 13. All 17 metals analyzed were detected at pH values less than 4. But as pH values increased above 4, chromium, cadmium, iron, and vanadium concentrations fell below their respective detection limits. Figures 2 and 3 plot leached element concentrations (mg/L) against extraction pH. The solubility of some metals increased under extreme pH values while for others the change in pH had no effect (Chuan et al., 1996; van der Sloot et al., 1997).

The concentrations of sodium, potassium, and calcium (calcium not presented) were not affected by the change in pH. Campbell (1990) suggested that solubility rather than pH controls potassium, calcium, and sodium availability from wood ash. Lead solubility (Figure 2) was highest under extreme pH values ($pH < 2$ and $pH > 12$) and lowest around pH 9. The increase in metal solubility under alkaline conditions is attributed to the formation of soluble metal hydroxides under extreme alkaline conditions (Fytianos et al., 1998). This behavior was also observed with aluminum, barium, copper, cobalt, nickel, manganese, and zinc. Steenari et al. (1999) concluded that under acidic conditions ($pH < 4$) dissolution from wood ash increased significantly; therefore the solubility of metals also increases. This phenomenon was also observed in WT ash. At pH values less than 4, metal leachability was high relative to that at other pH values ($pH > 4$). However, in this pH range (pH less than 4) the change in pH did not greatly affect the solubility of these metals. Magnesium was extracted at constant concentrations until approximately a pH of 6, where it dropped dramatically, as presented in Figure 3. Although arsenic (Figure 3) was relatively more leachable under acidic conditions, it demonstrated a large decrease in concentration between pH 1 and 5. The rate of arsenic decrease leveled off at pH values above 6. At pH values above 10, arsenic was not detected as the concentration fell below the instrument's detection limit of 0.07 mg/kg.

Metals in lysimeter leachate: Of the 13 metals examined in this experiment (Tolaymat, 2003), only five (lead, zinc, iron, aluminum and barium) were detected on a consistent basis in the lysimeter leachate. Two dominant leaching trends were observed. Barium and iron (iron presented in Figure 4) leached most in the initial phase of the experiment (often described for column experiments as the wash-off phase) followed by lower concentrations over time (a more diffusion controlled phase). Lead and zinc behaved differently (lead is presented in Figure 5). The concentration of these two metals started lower and increased to approach a relatively steady concentration. Lead started at a concentration of less than 10 μg/L and reached an average concentration of approximately 50 μg/L.

5. RISK ASSESSMENT

Beyond a simple characterization of this particular type of combustion ash, a goal of the research was to evaluate several issues associated with the application of typical beneficial use risk assessment procedures. This evaluation is presented as follows.

5.1. Risk Based on the Total Metal Concentration

The SCTL are risk-based contaminant thresholds used by the Florida Department of Environmental Protection (FDEP) to assess the human-health risk posed by direct exposure to soils at contaminated sites (FAC, 2005), and are frequently used as part of the process for

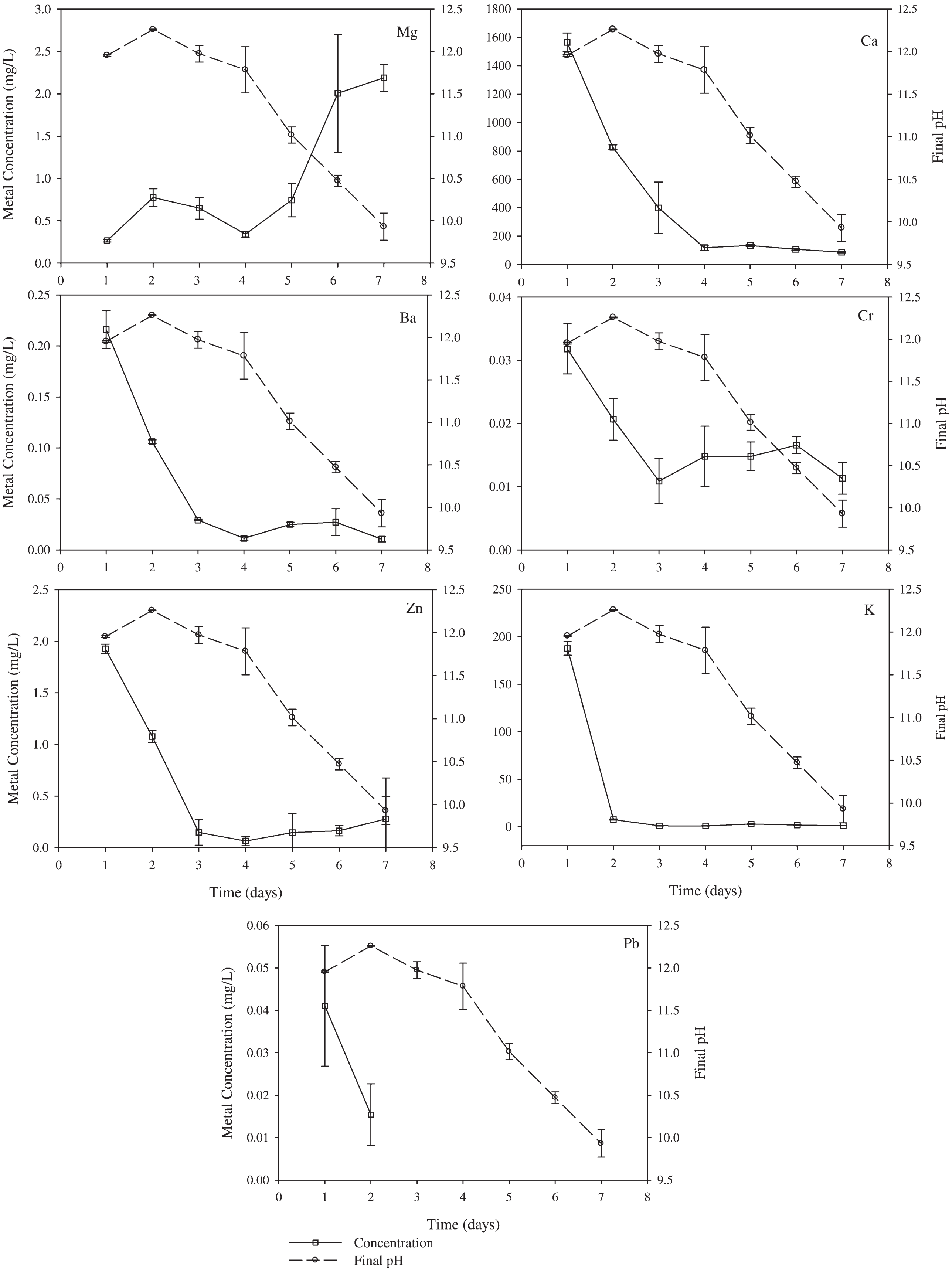

Figure 1. *Wood/Tire ash metal leachability in USEPA's MEP leaching test.*

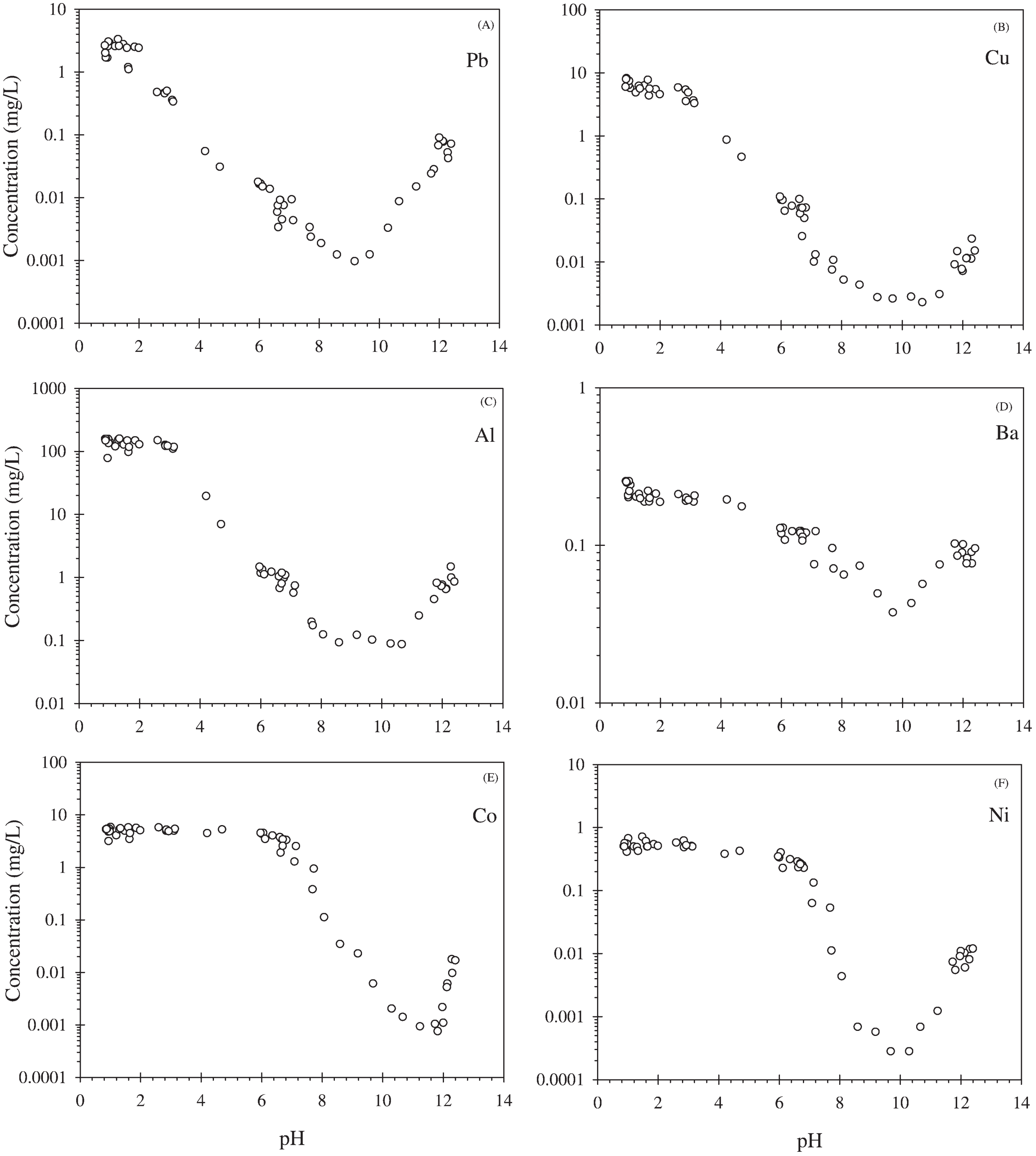

Figure 2. Wood/Tire ash metal leachability as a function of change of pH of the extraction fluid (Pb, Cu, Al, Ba, Co, Ni).

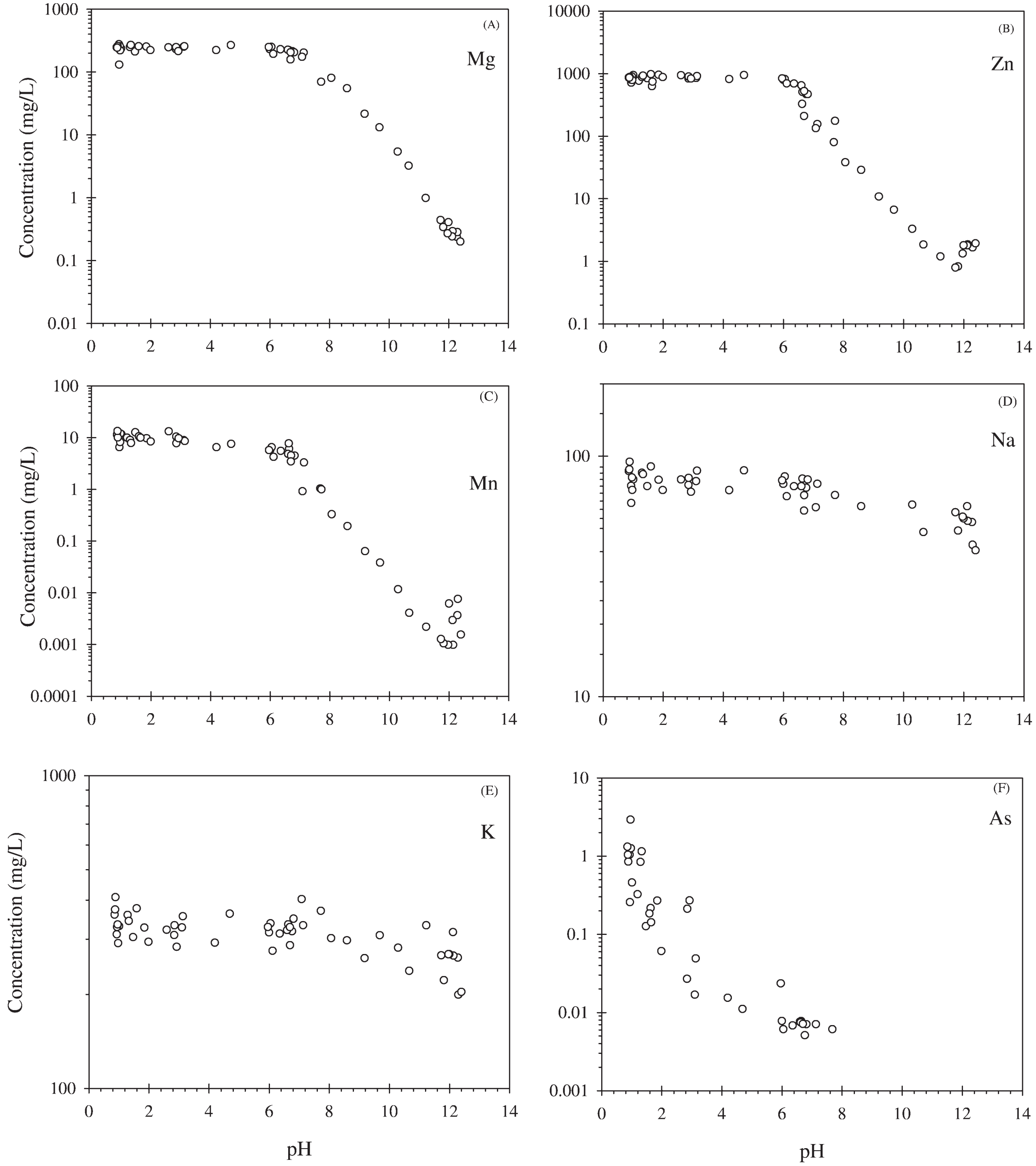

Figure 3. *Wood/Tire ash metal leachability as a function of change of pH of the extraction fluid (Mg, Zn, Mn, Na, K, As).*

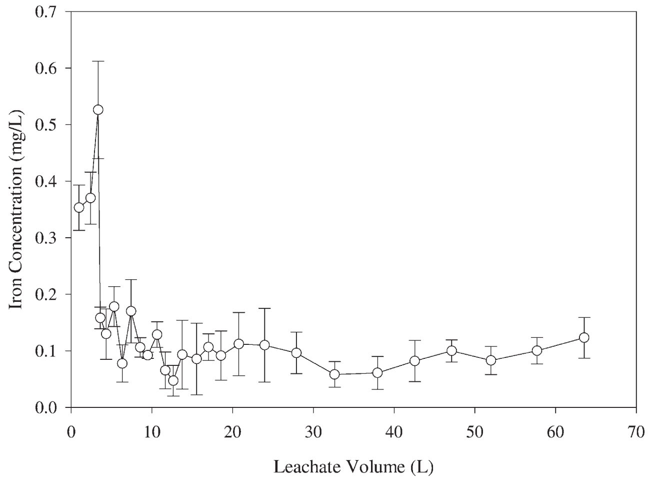

Figure 4. *Iron concentration in lysimeter leachate.*

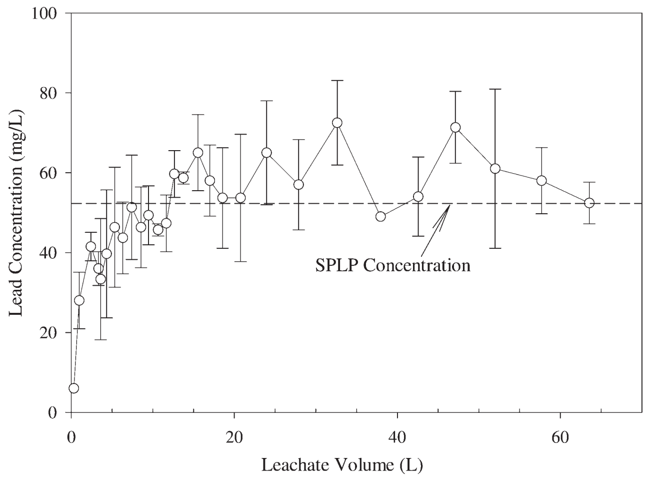

Figure 5. *Lead concentrations in lysimeter leachate and SPLP leachate.*

determining whether waste-derived materials can be land applied (FDEP, 1998, 2001). Other US states and many countries have developed similar thresholds for human-health risk assessments and beneficial use determinations (WDNR, 1998; DEFRA and EA, 2002; MHSPE, 2000). As the first step of the risk assessment, the UCL_{95} calculated for the elements detected in eight WT ash samples were compared to the Florida SCTL as presented in Table 3. Of all the trace elements analyzed, only arsenic was found to exceed its respective SCTL values (both categories of residential and industrial) while copper exceeded its corresponding FL residential SCTL limit. Following typical risk assessment procedures, this suggests that the WT ash cannot be land applied in a setting where direct human exposure might occur.

Several issues merit additional discussion with respect to potential limitations for land application of the WT ash because of the total element concentrations (arsenic in particular). First, it is acknowledged that Florida's residential SCTL is low compared to some other locations (AEHS, 1998). The state has a relatively low natural soil arsenic concentration (Chen et al., 1999). The arsenic SCTL was based on a 10^{-6} cancer risk through a combined direct exposure pathway (ingestion, inhalation and dermal contact). Given conservative assumptions of arsenic's nature as a carcinogen and potential bioavailability (assumed 33% bioavailable), the resulting SCTL is low, but other programs using similar methodologies (e.g., the US EPA's soil screening guidance used as part of the superfund program; US EPA, 1996) have similar values. More to the point when assessing land application of residuals is that ash from the combustion of clean wood (see Table 3) is greater than the arsenic SCTLs. This effectively means that in Florida, or locations with similar pro-

Table 3. Comparison of total metals UCL_{95} and the FDEP Soil Cleanup Target Levels (SCTL).

Metal	Units	Mean Concentration	UCL_{95}	SCTL Residential (Direct Exposure)	SCTL (Leaching)
Alc	g/kg	3.94 ± 0.7	4.41	80	Site specific
Fe		34.7 ± 5.0	38.0	53	Site specific
Zn		18.2 ± 3.0	20.2	26	0.019
As	mg/kg	37.2 ± 6.0	41.2	2.1	29
Ba		39.3 ± 7.0	44.0	120	1,600
Cd		2.71 ± 0.5	3.04	82	7.5
Cr		46.3 ± 5.0	49.6	210	38
Co		129 ± 30	149	1,700	Site specific
Cu		162 ± 30	182	150	Site specific
Pb		63.1 ± 10	70	400	Site specific
Mn		307 ± 80	361	3,500	Site specific
Ni		16.7 ± 4.0	19.4	340	130
V		5.49 ± 2.0	6.83	67	980

grams, ash of nearly any nature (including coal ash and municipal waste combustion ash) cannot be beneficially reused in a manner where direct human exposure is a risk pathway.

The above analysis suggests that alternative approaches—either alternative risk assessments or alternative reuse scenarios—must be considered. In Florida, several beneficial ash reuse applications are under development, but all involve the ash being encapsulated or otherwise contained in a manner where direct exposure is not an expected exposure route. In these applications, the leaching pathway still requires evaluation to protect water resources. Another consideration that merits consideration is how the ash is used when land applied. When the SCTLs (which were developed for soils) are utilized to assess risk from a land applied waste, the waste materials are assumed to be present in a manner where they replace the soil. In the case of an amendment such as WT ash, the waste is mixed with soil and the concentration of chemicals that an individual is exposed to is not only a function of the WT ash composition, but also of the background soil concentration and the rate of application. The quality of the materials that the WT ash replaces in a recycling operation merits evaluation. For example, when the US EPA evaluated the land application of cement kiln dust (CKD) as an agricultural soil amendment, concentrations of arsenic in this residual were found limiting based on a risk assessment. The US EPA cited, however, that the concentration of arsenic in agricultural lime ranged up to 13 mg/kg, and thus set the limit at this concentration (FR, 1999).

5.2. Risk Based on the Leaching

As the first step of assessing the risk based on leaching, the total metal concentration measured from the WT ash sample was compared to the SCTL for leaching (see Table 3). Of the 13 metals detected, only seven are assigned a Florida SCTL for leaching. The UCL_{95} calculated for arsenic, chromium, and zinc exceeded their respective SCTL for leaching. It should be noted that the chromium Florida SCTL for leaching is based on hexavalent chromium; no chromium speciation was performed as part of this study. The Florida leaching SCTLs are based on the assumption that the fraction of a pollutant will leach from the waste product and that its concentration in the leachate may be estimated from previously measured or modeled partition coefficients (usually measured on typical soil). Using this approach it was found that the WT ash would pose a risk to groundwater because of its content of arsenic, chromium, and zinc exceeded the SCTL for leaching. Since the waste characteristics will be much different from the soil, leaching tests are normally considered needed to evaluate waste-specific contaminant release.

When the SPLP leachate concentrations were compared to the GWCTLs, arsenic, cadmium, cobalt, copper, and vanadium were consistently below their detection limits of 5, 55, 1, 5, and 10 μg/L, respectively. Lead was the only element with primary drinking water standard for which the UCL_{95} on the mean of its SPLP concentration exceeded the GWCTL standard. The UCL_{95} of the leached lead concentration (59 μg/L) was approximately four times greater than its GWCTL (15 μg/L). On comparing the results from this method of risk assessment with the previous approach of using the partition coefficient, results were very different. In partition coefficient approach, the result suggested that WT ash would pose a risk to groundwater because of its content of arsenic, chromium, and zinc where as from the SPLP data it was found that lead is a concern in terms of risk assessment.

While the SPLP provides an advantage by using the waste of interest to predict contaminant leachability, uncertainty exists as to what the leachate concentrations measured represent. Since the SPLP is conducted at a 20:1 liquid-to-solid ratio (L/S), the resulting leachate concentrations may, in some cases, represent the pore water concentration expected to occur if the waste is applied as fill material in the environment. In other cases, the SPLP leachate concentration represents a diluted concentration (relative to the pore water), as might be expected after mixing with underlying groundwater. Depending on the requirements of the regulatory agency (e.g., whether compliance must be met in the pore water or down gradient in the aquifer),

Table 4. Comparison of SPLP metals UCL_{95} and the risk based Groundwater Cleanup Target Level (GWCTL).

Metal	DL[a] (μg/L)	FDEP (GWCTL) (μg/L)	Mean SPLP Concentration (μg/L)	UCL_{95} (μg/L)
Ba	20	2,000[c]	218 ± 80	272
Cr	1	100[c]	7.0 ± 0.4	7.3
Fe	20	300[b]	116 ± 50	150
Pb	5	15[c]	52.3 ± 9.0	59
Zn	50	5,000[b]	1,720 ± 190	1,847

[a] DL = Detection Limit
[b] Secondary Drinking Water Standard
[c] Primary Drinking Standard

the SPLP could either underestimate or overestimate the actual risk of groundwater contamination. Regulations and policies regarding how to interpret SPLP results differ among federal and state regulatory agencies. Townsend et al. (2006) found that depending on different waste type and pollutant of concern, at times SPLP results are reflective of pore water concentrations, (and thus merit application of dilution factor) and in other cases SPLP results represent diluted pore water concentrations (and thus may not merit application of a dilution factor in the risk assessment).

As presented earlier, results from the TCLP were for the most part not different from the SPLP or the DI water batch leaching procedures. Thus, while the TCLP is normally not considered a good test for assessing beneficial use of waste materials in the environment (the TCLP solution was designed to represent the leaching conditions inside a biologically active municipal waste landfill), in this case, it was an equally good predictor as SPLP and DI water. This is a result of the alkaline nature of the ash negated the impact of the TCLP solution's buffered pH and acetate ability to complex many metals. The alkaline nature of the ash also negated any different between the results using SPLP (which uses a small amount of acid to achieve an initial pH of 4.2) and those using DI water. For all three of these tests, only lead concentrations were measured above the GWCTL. The WET, however, which uses citric acid, was different than the other leaching tests. If WET were used for the beneficial use assessment, the results would have indicated that aluminum, arsenic, cobalt, copper, iron, lead and zinc all posed a risk to groundwater.

The SPLP, TCLP and DI tests all indicate (much differently than the partition coefficient based approach) that lead is the element of greatest risk to groundwater. However, it is not directly evident from this data whether the lead concentrations represent the levels that would be expected in the groundwater under the land-applied waste (no dilution factor warranted) or whether they represent the pore water concentration that occurs when the leachate leaves the land-applied waste (application of dilution factor may not be justified). The lysimeter results, on the other hand, do provide a means of assessing the true leachate concentration that would be expected in the field. Five of the elements analyzed (aluminum, barium, iron, lead, and zinc) were consistently detected in the lysimeter leachate. The lysimeter results also indicated that lead would be primary element of concern when assessing risk to groundwater. The lead concentrations reached in the lysimeters were similar to those measured in the SPLP, TCLP and DI tests, indicating that the batch tests were representative of pore-water concentrations for lead. This suggests that it would be appropriate to apply a dilution factor to account for mixing in the groundwater. If a dilution factor were allowed, it would likely indicate that the expected lead concentration in the groundwater would be less than the GWCTL. The MEP and the pH impact results indicate that over time the lead concentration would be expected to decrease (as a result of a decrease in pH), the volume of water that must pass through the ash would be so large that it would not impact the results of the beneficial use risk assessment.

6. CONCLUSIONS

This study provides a characterization of ash from a facility which combusts scrap wood and automobile tires along with a risk assessment for beneficial reuse of this waste residual. Many of the issues encountered in the risk assessment evaluation are common to assessing land application of other residuals that are not covered under specific regulations.

Upon examining direct human exposure as a risk pathway, arsenic was found to be the most limiting element. The evaluation identifies that arsenic will likely be limited regardless of the type of ash, and thus alternative risk assessment procedures and/or reuse scenarios warrant evaluation and discussion. With examination of the risk pathway of leaching-to-groundwater, the use of partition coefficient based target levels derived for soils did not match the elements of concern determined using waste-specific leaching tests. This approach is not advised for land applied wastes; leaching tests should be used. The SPLP, the typical test of choice for assessing leaching risk when wastes are land applied, found lead to be the element of greatest concern. TCLP and DI water found similar results, which illustrate how the waste type in this case dominated leaching conditions much more than the leaching solution themselves (with the exception of the WET). The lysimeters also found that lead as the primary concern, but through this type of procedure it is clear that an application of a dilution factor might be appropriate when assessing the true potential risk to a groundwater receptor point.

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Spent Foundry Sand and Compost in Blended Topsoil: Availability of Nutrients and Trace Elements

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ABSTRACT: Uncertainties concerning the fate in soil of potential contaminants in spent foundry sand (SFS), thus limiting their use in manufactured topsoils. A column experiment investigated plant growth, leaching and uptake of nutrients, trace elements, and organics from blends of SFSs and composts. Ryegrass growth was excellent with no toxicities. Very small effects on uptake and leaching of trace elements and organics were associated more strongly with compost than SFS. Large differences in macronutrient leaching were attributed to the type of compost. SFSs with low trace element content can be safely utilized for manufactured soil production however composts used could leach large quantities of nutrients.Keywords: spent foundry sand, compost, manufactured soil.

INTRODUCTION

EVERY year, the metal casting industry generates between nine and thirteen million tons of spent foundry sand (SFS), most or all of which is disposed of in landfills. Due to increased regulatory constraints and rising disposal costs, this practice is being reevaluated by individuals in the industry and regulatory agencies. According to the USEPA industrial waste division, only two percent of this material is classified as hazardous waste [1]. The physical characteristics of these sands could allow them to be beneficially reused in manufactured topsoil blends in combination with composted organic material and low value subsoil materials. Uncertainties regarding the bioavailability, solubility, and persistence of organic and inorganic contaminants potentially present in SFS have made regulators hesitant to either dewaste certain types of SFS or to develop less restrictive permitting that would allow its reuse without extensive testing and monitoring.

Most spent foundry sands are termed “green” sands and consists primarily of silica sand coated with a thin layer of burnt carbon, residual bentonite clay binders, and dust [2]. Spent green sands from most foundries will also include some sands from core molds constructed using organic-based binder systems. A binder is any material, added to virgin sand, which by means of cohesion and/or adhesion, bonds sand grains together so that they may be used for metal casting [2]. The core mold binders are the primary source of potential organic contaminants in sands whereas metals being cast are the source of potential trace element contaminants. Promising potential uses of SFS are as substitutes for virgin sand in construction activities or in manufactured soils. Any revision of regulations allowing for soil based beneficial reuse of SFS, will require characterization of potential contaminants that may be present in foundry sand as well as their behavior in a soil environment. A study conducted to determine the extent of groundwater contamination from landfills containing exclusively ferrous foundry wastes indicated the presence of a wide variety of organic compounds; however, all sample results were below the regulatory toxicity limits [2]. Extracts of pure SFS typically contained concentrations of metallic compounds below regulatory toxicity characteristic levels [2]. Furthermore, quantities of total metal content in spent and virgin foundry sand and in sandy soils were of the same order of magnitude, with total metal content of foundry sands sometimes lower than levels in sandy soils [2]. However, none of these studies investigated the behavior of SFS in a soil environment.

Sand based blended topsoils require inclusion of a large amount of organic material, usually in the form of compost. Due to the high nutrient content of composted

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organic materials, the potential exists for nutrient leaching. Nitrate losses from land application of spent mushroom substrate (SMS) compost may pose a threat to groundwater quality. Soil leachate samples collected underneath 90-cm and 150-cm deep piles of SMS at a soil depth of 90 cm contained NO_3-N concentrations as high as 50-times greater than the drinking water standard [3]. In a greenhouse column study, it was determined that soil leachate total P concentrations in biosolids amended sandy soils were not significantly different than control soils [4]. These results suggest that the potential for P leaching from manufactured soils containing biosolids is quite small.

This greenhouse column experiment was conducted to evaluate the suitability of SFS for use in manufactured soils by measurement of plant growth; and to assess potential environmental risks associated with these manufactured soils by measurement of plant uptake and leaching of nutrients, trace metals, metalloids, and organics in blended soils containing SFS, compost, and subsoil.

MATERIALS AND METHODS

Spent Foundry Sands

Spent green sands representative of three different binder systems widely used in the metal casting industry were used in this experiment. The three binder systems are: phenolic urethane no-bake (PUNB, iron foundry), furfuryl alcohol no-bake (FNB, iron foundry), and Shell (aluminum foundry). Spent sands were collected from two iron foundries (PUNB and FNB), and one aluminum foundry (Shell) in Pennsylvania and brought to Penn State University for analysis and use in the greenhouse column experiment. Prior to use in the experiment, all SFSs were passed through a 2 mm sieve to screen out foreign materials present in the sands. Any pieces of metal caught on the sieve were removed. Any SFS aggregates and core butts caught on the sieve were reduced to particles < 2 mm diameter by grinding with a mortar and pestle. Macroelement and trace element content of the SFSs was determined by strong acid digestion (EPA method 3051 and analysis by ICP, As by graphite furnace AA for As and Se), and by EPA 7471 for Hg (Tables 1 and 2). Particle size analysis of the SFSs was determined by the hydrometer method (Gee and Bauder).

Composts

Three compost materials were selected for blending with SFS: yard trimmings compost, spent mushroom substrate (SMS), and biosolids compost. These materials were analyzed for solids content (drying at 105ºC), total N (Kjeldahl), NH_4-N (ion selective electrode), organic N (subtraction of NH_4-N from total N), total P and total K (EPA 3051 digestion, ICP analysis), As, Cd, Cr, Cu, Pb, Mo, Ni, Se, and Zn (EPA 3051 digestion, graphite furnace AA for As and Se, ICP analysis for all other elements) and Hg (EPA 7471) (Tables 1–3). Although the spent mushroom substrate is not a completely composted material, in this paper the term "compost" will be used to refer to all three of these organic materials. These composts are widely available and may be sold or given away to the general public without any regulatory limitations on their distribution or use.

Topsoil and subsoil were obtained from a Hagerstown silt loam (fine, mixed, semiactive, mesic Typic Hapludalfs) located on the Penn State University research farm located at Rock Spring, PA. Topsoil material was collected from the Ap horizon (0–20 cm) and subsoil material was collected from the Bt horizon (30–50 cm). The soil materials were analyzed for particle size distribution by the hydrometer method (Gee and Bauder).

Table 1. Macroelement concentrations in spent foundry sands and compost materials used in the greenhouse experiment.

Material	Al	Ca	Fe	K	Mg	Mn	Na	P	S
	mg kg^{-1}								
FNB	425	200	1001	55.7	909	47.6	65.1	10.7	375
Shell	1925	1020	1402	363	569	16.8	138	17.7	203
PUNB	1278	708	47480	63.7	252	286	296	< 6.0	299
SMS	314	73799	4410	27463	13089	326	2648	6129	10156
Biosolids	8602	18636	71423	1910	3784	2777	444	21705	8536
Yard	6573	38248	11693	8867	7745	1022	536	3480	2666

Table 2. Trace element concentrations in spent foundry sands and compost materials used in the greenhouse experiment.

	As	Ba	Cd	Cr	Cu	Hg	Mo	Ni	Pb	Se	Zn
Material	**mg kg^{-1}**										
FNB	< 0.30	27.2	< 0.40	5.25	3.90	< 0.007	0.85	9.15	1.07	< 0.51	7.54
Shell	< 0.30	5.63	< 0.40	3.51	4.44	< 0.007	< 0.50	1.96	0.86	< 0.51	11.9
PUNB	7.50	7.95	< 0.40	51.8	137	< 0.007	6.97	26.3	2.42	< 0.53	5.32
SMS	24.8	78.4	< 0.40	20.5	78.3	0.032	3.27	8.19	4.89	0.84	153
Biosolids	5.74	451	4.36	66.0	460	1.255	16.6	22.5	148	4.04	1158
Yard	6.88	145	0.61	25.1	55.7	0.188	2.10	13.2	73.5	1.04	200

Column Establishment

Soil blends were made by combining each type of SFS with each type of compost and with subsoil at a dry weight ratio of 6.5:1.5:2.0 (SFS:compost:subsoil). All soil blends were characterized as sandy loams (Table 4). The greenhouse experiment then consisted of these nine blends and also the natural topsoil as a control. Columns for the plant growth and leaching experiment were constructed using 15-cm diameter PVC pipe cut to 30 cm lengths. The PVC pipe was glued to a flat PVC base plate with a nipple tube fitting mounted in the center. A Teflon® tube directed flow to amber glass bottles for leachate collection. The inner surfaces of the columns were lined with Teflon® sheeting to minimize potential interference from PVC constituents. A 5 cm layer of acid washed virgin sand was placed in the bottom of each column. Columns were then filled with a 21.5 cm depth of manufactured soil blend or with natural topsoil. Material was added in 3 "lifts" and columns were tamped following the addition of each lift to achieve the same extent of packing with each material. Inorganic fertilizer was added to each treatment: 68 mg N, 10 mg P, and 20 mg K per column as urea, triple super phosphate and potassium chloride respectively. The fertilizer was mixed into the upper 5 cm of each column and was further incorporated by watering. Because one objective of this experiment was to determine the amounts of N, P, and K fertility supplied by the compost materials, inorganic fertilizer addition was kept to the minimum amount needed for plant growth in the natural topsoil.

Table 3. Chemical characterization of compost materials used in manufactured soil blends.

Analyte	Yard Compost	Spent Mushroom Substrate	Biosolids Compost
pH	7.9	8.1	7.1
Soluble Salts (mmho/cm)	2.33	16.45	6.87
Organic Matter (%)	47.4	53.7	52.4
Total Nitrogen (%)	1.8	2.1	3.3
Organic Nitrogen (%)	1.8	2.1	2.8
Ammonium Nitrogen (mg/kg)	4.5	5.3	5024.5
Carbon (%)	287	29.9	29.0
Carbon/Nitrogen Ratio	15.7	14.2	8.7

After filling each column, the moisture content was adjusted to 80% of field capacity by adding de-ionized water. One day after the columns were filled, they were planted with 40 seeds of annual ryegrass (*Lolium multiflorum* Lam.). De-ionized water was added as needed to maintain sufficient moisture for ryegrass growth but not enough to cause any leaching.

Leachate Collection and Analysis

Columns were intentionally leached two weeks after planting and once each month thereafter for a total of 6 leaching events. One day prior to leaching the columns were weighed and sufficient water was added to each column to adjust soil moisture content to 80% of field

Table 4. Particle size distribution of SFSs, soils, and blends.

	Sand	Silt	Clay	Textural Class
Material	**mg kg^{-1}**			
Spent foundry sands				
FNB	975	12	13	Sand
Shell	907	57	35	Sand
PUNB	976	11	12	Sand
Hagerstown soil				
Topsoil	332	543	225	Silt loam
Subsoil	151	379	470	Clay
Blended soils (SFS+subsoil)				
FNB	781	98	121	Sandy loam
Shell	729	133	137	Sandy loam
PUNB	782	98	120	Sandy loam

capacity. Leaching was done by adding 50 ml of de-ionized water to the surface of each column every 30 minutes until approximately 500 ml of leachate had been collected. Leachate samples were analyzed immediately for pH and electrical conductance and for Al, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S and Zn by inductively coupled plasma (ICP) emission spectroscopy, and corimetrically for NO_3-N, NH_4-N, and Ortho-P using an autoanalyzer and the following QuikChem methods: 10-107-04-1-A (NO_3-N), 10-107-06-1-B (NH_4-N), and 10-115-01-1-T (Ortho-P) [6; 7; 8]. Total N and total C were analyzed by combustion using a Carlo Erba analyzer. Leachate samples from the first two leaching events were analyzed for As and Se by high resolution ICP-MS, and for Hg using EPA Method 7470 (cold vapor atomic absorption). The quantity of nutrients and trace elements leached from each column was calculated by multiplying the volume of leachate collected by the concentration of each constituent analyzed. Leachates from the first three leaching events were analyzed for the following polyaromatic hydrocarbon and phenolic organic compounds following extraction with SPME fibers with a 85µm polyacrylate coating and the method described by Doong [9]: PAHs; Acenaphthene, Acenaphthylene, Anthracene, Benzo(a)anthracene, Benzo(b)-fluoranthene, Benzo(k)fluoranthene, Benzo(a)pyrene, Chrysene, Fluoranthene, Fluorene, Naphthalene, Phenanthrene, Pyrene; Phenols: 4-Chloro-3-methylphenol, 2-Chlorophenol, 2,4-Dichlorophenol, 2,4-Dimethylphenol, 2,4-Dinitrophenol, 2-Methyl-4,6-dinitrophenol, 2-Nitrophenol, 4-Nitrophenol, Pentachlorophenol, Phenol, 2,4,6-Trichlorophenol.

Ryegrass Collection and Analysis

Ryegrass vegetative growth was clipped at a height of 4 cm whenever the grass began to flower (43 days after planting and every 2–3 weeks thereafter) for a total of 7 harvests. Clippings were dried for 48 hours at 65°C, weighed, and ground to pass a 1 mm screen. Yield data were obtained using the mass of oven dry matter collected from each column. A 5 g oven-dry composite tissue sample was prepared for analysis by determining the fractional contribution of each clipping to the total yield and adding the corresponding proportion from each clipping. When total cumulative yield was less than 5 g pot^{-1}, all of each clipping was used for the composite sample. Tissue N was determined by combustion using a Carlo Erba analyzer. Composite samples were analyzed for the following nutrients and trace elements by ICP following microwave digestion with nitric acid: P, K, Ca, Mg, S, Mn, Fe, Al, B, Cd, Cu, Mo, Na, Ni, Pb, and Zn.

Statistical Analysis

SAS 9.1 statistical software was used to perform analysis of variance (ANOVA) and means comparisons using Fisher's Least Significant Difference (LSD) Treatment effects were considered significant when $Pr > F \leq 0.05$.

RESULTS AND DISCUSSION

Ryegrass Growth and Analysis

Ryegrass grew very well in all SFS-based soil blends and greatly exceeded growth in the control topsoil (Table 5). As previously mentioned, minimal fertilizer was added to all treatments in order to assess the fertility contribution of the composts. Since topsoil yields would likely have been much greater with larger fertilizer additions, these data do not provide a valid comparison of yield potential for SFS based soil blends and natural topsoil. No differences were detected among SFS type, however, yields were influenced by compost type. Means comparison showed larger yields in blends using either SMS or biosolids compost than in blends containing yard compost. Differences in ryegrass yield among composts were most likely due to nitrogen availability. SMS and biosolids compost contained more total nitrogen, organic nitrogen, and ammonium nitrogen than the yard compost (Table 3).

As was observed with growth response, compost had a much greater effect on ryegrass tissue nutrient content than SFS (Table 4). For nearly one-half of all elements analyzed, compost type affected tissue concentrations while SFS did not. The type of sand used in the blend influenced tissue content of one-third of all elements analyzed; however, SFS type was never the only factor in determining tissue concentration of a particular element. That is, whenever tissue composition was affected by SFS it was also affected by compost which generally exhibited a larger effect than SFS. Nitrogen levels were largest in ryegrass grown on blends containing biosolids compost and were within the tissue sufficiency range (33.4–51 g N kg^{-1}) for all biosolids blends except the blend with PUNB [10]. Differences in

Table 5. Cumulative yields and tissue nutrient and trace element concentrations of ryegrass grown in SFS and compost based manufactured soil.

	Yield	**N**	**P**	**K**	**Al**	**B**	**Cd**	**Cu**	**Fe**	**Mn**	**Mo**	**Na**	**Ni**	**Zn**
Treatment	**g m^{-2}**	**mg kg^{-1}**												
Control (Topsoil)	112f*	24.1cd	5.3a	32.6d	53.5bc	25.5d	1.05a	35.3a	113b	99.7c	0.76d	141b	2.40a	103abc
PUNB + yard	784e	21.7d	3.5d	32.9d	79.7a	28.5d	0.40b	29.3a	126b	41.2c	4.16bc	371b	2.35a	57.4d
PUNB + SMS	1338abc	32.5abc	4.3bc	45.4a	65.5abc	17.6d	0.15b	26.6a	120b	48.9c	2.60c	858b	0.69b	48.2d
PUNB + biosolids	1052bcde	32.0c	2.5e	22.0e	77.1a	22.6d	0.17b	33.5a	289a	637b	4.25bc	3088a	2.25a	84.3abcd
FNB + yard	934cde	20.4d	4.3bc	32.8d	73.4ab	41.2d	0.27b	25.1a	113b	48.8c	5.83ab	224b	0.60b	61.2cd
FNB + SMS	1395ab	27.2cd	4.4b	40.5b	62.2abc	16.5d	0.12b	27.0a	106b	39.2c	3.59c	603b	0.33b	58.3d
FNB + biosolids	1587a	40.5ab	3.9cd	21.8e	48.3c	28.5d	0.11b	37.4a	110b	1055a	3.30c	3546a	0.41b	106ab
Shell + yard	852de	23.6cd	4.5b	34.6cd	66.4abc	231b	0.23b	25.3a	102b	42.5c	6.66a	163b	0.46b	60.8cd
Shell + SMS	1333abc	25.2cd	4.4b	38.2bc	68.9abc	107c	0.15b	27.4a	100b	39.5c	3.82c	399b	0.43b	60.4cd
Shell + biosolids	1230abcd	42.3a	4.2bc	33.4d	61.6abc	283a	0.08b	32.3a	140b	544b	4.02c	1313b	0.42b	128a
Mean of SFS (average of 3 composts)														
PUNB	1058a	28.7a	3.4b	33.4ab	74.1a	22.9b	0.238a	29.8a	178a	242b	3.67b	1439a	1.77a	63.3a
FNB	1305a	29.4a	4.2a	31.7b	61.3a	28.7b	0.167a	29.8a	110a	381a	4.24ab	1458a	0.45b	75.1a
Shell	1139a	30.4a	4.4a	35.4a	65.6a	207a	0.154a	28.4a	114a	209b	4.83a	625a	0.44b	83.0a
Mean of Compost (average of 3 SFSs)														
Yard	857b	21.9c	4.09b	33.4b	73.2a	100a	0.301a	26.6ab	114a	44.1b	5.55a	253b	1.14a	59.8b
SMS	1355a	28.3b	4.36a	41.4a	65.5a	46.9b	0.139b	27.0b	108a	42.5b	3.34b	620b	048b	55.6b
Biosolids	129a	38.2a	3.55c	25.7c	62.3a	111a	0.119b	34.4a	108a	745a	3.86b	2649a	1.03a	106a
							ANOVA							
Source of Variation														
SFS	NS†	NS	**	**	NS	**	NS	NS	NS	**	NS	NS	**	NS
Compost	**	**	**	**	NS	**	**	NS	NS	**	**	**	**	**
SFS x Compost	NS	NS	**	**	NS	**	NS	NS	NS	**	NS	NS	**	NS

*Fisher's LSD: Within columns and sections, means with the same letter are not significantly different.

**Significant at the 0.05 level.

†Not significant at the 0.05 level.

tissue N content are likely due to the large amounts of nitrogen found in biosolids compost relative to the yard and SMS composts (Table 1). Tissue P levels were lower in samples from the blended soils compared to the topsoil, but were still within the sufficiency range (3.5–5.5 g P kg^{-1}) in all blends except the one containing PUNB and biosolids compost, which was below the range [10]. The difference in P content may simply reflect the concentrating effect of much lower biomass production on the natural topsoil. Sufficient amounts of K (20–34.2 g K kg^{-1}), Ca (2.5–5.1 g Ca kg^{-1}), and Mg (1.6–3.2 g Mg kg^{-1}) were present in ryegrass samples from all blended soils and S levels were within the sufficiency range (2.7–5.6 g S kg^{-1}) in all blends except the one made with Shell and SMS compost [10]. In this blended soil, the tissue S level was 2.6 mg kg^{-1} and was slightly below the sufficiency range.

We observed no evidence of trace element deficiencies or toxicities in ryegrass grown on the SFS and compost blends. As with macronutrients and yields, tissue trace element concentrations were affected mainly by compost type and less so by SFS, with the exception of Shell for certain elements. Almost all tissue B concentrations were above the normal sufficiency range (5–17 mg B kg^{-1}), and very large increases in B were observed in tissue grown on all blends containing Shell (Table 4) [10]. We did not measure B in the SFSs or composts and so cannot conclusively state the source of B. However, plant tissue data suggest Shell was the B source and that SMS compost was able to suppress B uptake. Tissue Mo levels from all blends were above the sufficiency range (0.5–1.0 mg Mo kg^{-1}), but well below the toxicity level of 90 mg kg^{-1} [10; 11]. Tissue micronutrient concentrations were within the specified sufficiency ranges for both Fe (97–934 mg Fe kg^{-1}) and Cu (6–38 mg Cu kg^{-1}) and were not affected by treatment [10]. Blends containing biosolids compost produced ryegrass with tissue levels of Mn and Zn above the sufficiency range (30–73 mg Mn kg^{-1}; 14–64 mg Zn kg^{-1}), but well below the toxicity levels of 600 mg kg^{-1} and 400 mg kg^{-1}, respectively [10; 11]. Tissue Al concentrations were in the normal range for all treatments and were not affected by treatment.

Tissue analysis of the nonessential elements, Na and Al, determined that Al concentrations were within the normal range (52–922 mg Al kg^{-1}) and Na levels were above the normal range (229–1107 mg Na kg^{-1}) in blends containing biosolids compost [10]. Tissue concentrations of Cd and Ni in blended soils were either lower than or not different from the control concentrations. All samples analyzed were below the detection limit of 0.25 mg kg^{-1} for Pb.

Overall the yield and plant tissue composition results indicate that blended topsoils made with SFS and composts could provide a growth media with good yield potential and the composts appear to supply adequate macronutrients for ryegrass growth. Plants grown in the constricted root environment of a greenhouse pot or column often exhibit increased uptake of micronutrients and other trace elements. In this experiment measured increases in plant tissue trace element concentrations were relatively small and in most cases could be attributed to the compost rather than to the SFS component of the blended topsoil.

Inorganic Leachate Chemistry

In this experiment we utilized a leaching frequency and intensity that exceeded that expected due to natural rainfall to simulate worst case scenario conditions and to amplify both SFS and compost effects on leachate quality. On average, the amount of water added to columns for each leaching event was equivalent to a 65 mm rainfall on columns that had been brought to 80% of field moisture capacity the day before. It is unlikely that such excessive, regular leaching would occur in a natural setting. Consequently the leachate quality and quantity results from this greenhouse are not representative of what might occur in natural systems but are useful predictors of potential effects of the various blended soil components.

Macronutrients

Similar to what we observed with plant tissues, the leachate macronutrient concentrations and total amount of macronutrients leached (N, P, K, Ca, Mg, and S) were more strongly influenced by compost than by SFS. These results correspond to, and likely can be attributed to, the generally much larger concentrations of these elements in the composts than in the SFSs (Table 1). Biosolids compost with any of the SFSs greatly increased leaching of N (total N, NO_3^-, and NH_4^+), while smaller increases were observed with SMS, and yard compost did not increase N leaching relative to the natural topsoil (Table 5). These results correspond to the total N and NH_4-N contents and the C:N ratio of the composts and expected N mineralization rates (Table 1). Further evidence of substantial N mineralization and nitrification in biosolids compost was seen in the NO_3-N leaching pattern which increased to very large concentrations in the second and third leaching event for all biosolids compost mixes (Figure 1). The corresponding pH suppression in leachates from biosolids containing blends also indicates much more nitrification was occurring in biosolids compost than in blends made with the other composts or in the topsoil (Figure 1). After the spike in leachate NO_3-N concentrations during the 2nd leaching event in the biosolids-containing blends, all treatments followed the same general trend of decreasing NO_3-N concentrations. Leachate nitrate concentrations above the USEPA Maximum Contaminant Level of 10 mg NO_3-N L^{-1} were seen in all blends, including the control; however, by the 6th leaching event NO_3-N levels from all treatments were below EPA standards [12].

The use of SMS compost resulted in increased leaching of total P, ortho-P (data not shown), and K as compared to other blends and the control (Table 5). Although the biosolids compost contained a larger concentration of P (Table 2), blends containing biosolids compost lost smaller quantities of both P and ortho-P than the other blends. Similar results were observed in a greenhouse column study of biosolids amended sandy soils where P loss from columns amended with biosolids compost was negligible and the

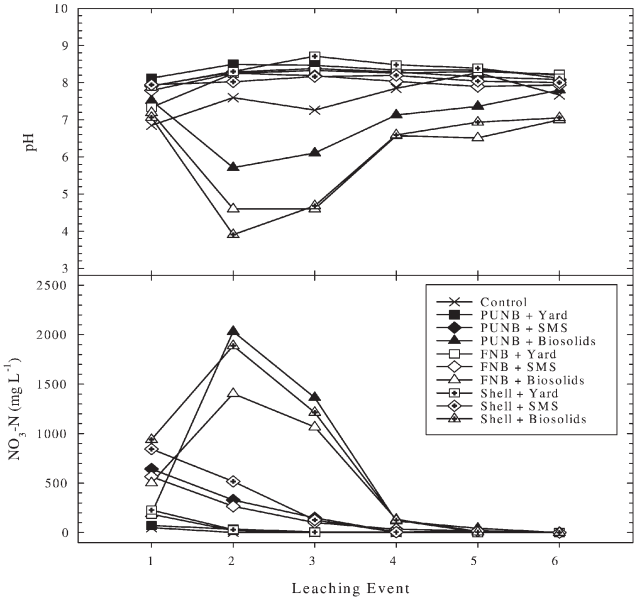

Figure 1. *Effect of SFS and compost blended soils on column leachate pH and NO_3-N concentrations.*

Table 6. Effect of SFS and compost on the cumulative nutrient loss from 6 leaching events.

	Total N	**NO_3-N**	**NH_4-N**	**P**	**K**	**Ca**	**Mg**	**S**
Treatment	**g column^{-1}**				**mg column^{-1}**			
Topsoil (Control)		0.33d†	11.3d	0.27e	24.7d	34.8g	14.6d	099d
PUNB + yard		0.58d	45.2d	0.53e	1699c	370g	104cd	97.0d
PUNB + SMS		1.20c	425c	16.95c	6452b	1254e	603b	554ab
PUNB + biosolids		2.87ab	2080a	0.81de	125d	2768b	928a	635ab
FNB + yard		0.62d	53.9d	5.95d	2132c	778f	211c	100d
FNB + SMS		1.22c	380c	39.43a	5976b	1343e	736b	240cd
FNB + biosolids		2.46b	1735b	1.28de	79.7d	2231c	944a	507b
Shell + yard		0.54d	77.3d	3.55de	1851c	791f	171c	25.4d
Shell + SMS		1.32c	587c	27.43b	8468a	1804d	940a	460bc
Shell + biosolids		3.08a	2057a	1.11de	141d	3233a	1027a	813a
Mean of SFS (average of 3 composts)								
PUNB		1.55a	850ab	6.10c	6.10c	1464b	545b	428a
FNB		1.44a	722b	15.6a	15.6a	1451b	630ab	283a
Shell		1.65a	907a	10.7b	10.7b	1943a	713a	433a
Mean of Compost (average of 3 SFSs)								
Yard		0.58c	58.8c	3.34b	3.34b	646c	162c	74.3c
SMS		1.25b	464b	27.9a	27.9a	1467b	760b	418b
Biosolids		2.81a	1957a	1.06b	1.06b	2744a	966a	652a
Source of Variation								
SFS		NS	NS	**	**	**	**	NS
Compost		**	**	**	**	**	**	**
SFS*Compost		NS	NS	**	**	**	NS	NS

†$LSD_{0.05}$: Within columns means with the same letter are not significantly different.
‡Results from leaching events 4–6 only, S not analyzed in leaching events 1–3.
§NS, not significant.
**$Pr > F \leq 0.05$.

amount of P leached was not different than control columns [4]. Differences in phosphorous leaching may also be due to differences in phosphorous-fixation capacity of the blends. Soluble iron, aluminum, and manganese can fix phosphorous in unavailable, insoluble forms [11]. Since SMS compost contains smaller quantities of Fe, Al, and Mn than biosolids and yard composts contain, blends containing SMS compost may be less able to fix P and greater amounts of P may be lost in leachates from blends utilizing SMS (Table 2). The large amount of K lost from SMS blends appears to result from the much larger amount of K present in this compost compared to the other two and to the SFSs. The amounts of Ca, Mg, and S lost in leachates varied depending on compost type (Table 5). The greatest losses were from blends containing biosolids compost, followed by blends containing SMS compost, and the smallest losses were from blends containing yard compost.

Trace Elements

Although we were able to measure SFS and compost effects on the leaching of trace elements, in most cases the concentrations and quantities leached were very small. All samples were below detection limits for mercury (< 0.0004 mg L^{-1}) and lead (< 0.025 mg L^{-1}). Leachate concentrations of Ba, Cd, Cr, and Cu (data not shown) were below the maximum contaminant levels (MCL) of 2 mg B L^{-1}, 0.005 mg Cd L^{-1}, 0.1 mg Cr L^{-1}, and 1.3 mg Cu L^{-1} set forth by EPA in the National Primary Drinking Water Standards [12]. Concentrations of Al and Fe in leachates were lower than leachate concentrations from the control treatment but were above the EPA National Secondary Drinking Water Standards of 2 mg Al L^{-1} and 0.3 mg Fe L^{-1} [12]. Secondary drinking water standards are non-enforceable guidelines regulating contaminants that may cause cosmetic or aesthetic effects in drinking water. While it is not expected that leachates from natural or synthetic topsoil should meet primary or secondary drinking water standards, these standards provide a benchmark level for comparison.

Leachate concentrations of most measured trace metals were affected by both SFS and compost type. The use of biosolids compost resulted in increased Mn and

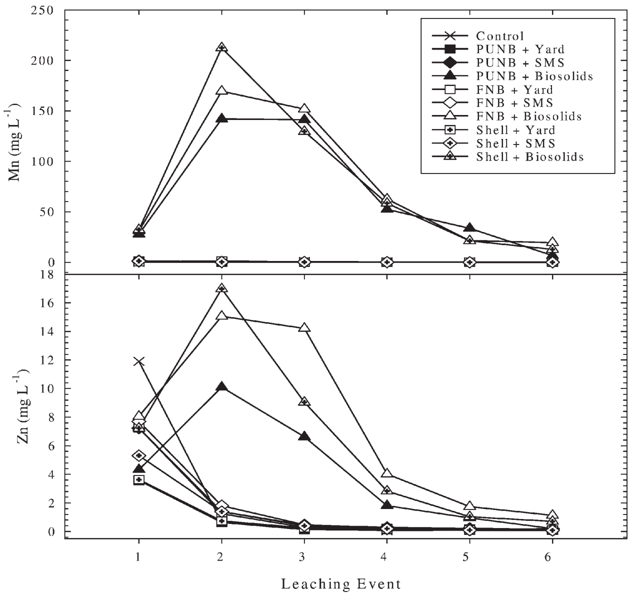

Figure 2. *Effect of SFS and compost on leachate Mn and Zn concentrations of samples collected in the greenhouse study.*

Zn leaching as compared to the other blends and the control and were above the EPA National Secondary Drinking Water Standards of 0.05 mg Mn L^{-1} and 5 mg Zn L^{-1}. These results in part reflect the much larger amounts of Mn and Zn in biosolids compost than in the other composts (Table 2). In addition, Mn and Zn solubility increase as pH decreases [13], and the greatest amount of Mn and Zn mobilization occurred during the period of leachate pH depression (Figures 1 and 2). Soil blends made with SMS compost leached greater amounts of Mo and Na than other soil blends and the control (Table 6). Mobilization of Na from blends containing SMS compost is not surprising since the SMS compost contained the greatest amount of Na (Table 2) and Na is relatively soluble in comparison to polyvalent trace metals. The larger amount of Mo loss from SMS was somewhat surprising given that biosolids compost had much greater Mo content (Table 3). Molybdenum solubility decreases as pH decreases and thus the lower pH in the biosolids compost blends may have limited Mo mobilization.

Although statistical analysis indicated SFS*compost interactions for several trace metals, this was most clear-cut when PUNB-SFS was used in combination with biosolids compost. In this particular blend, the quantity of Ni lost was nearly double the amounts lost by other blends (Table 6). Among sands, PUNB SFS contained more Ni, and biosolids compost contained more Ni than other composts (Table 3). When used together, the potential for increased Ni losses is clearly evident. As with Mn and Zn, the solubility of Ni is increased when pH is decreased and leachate pH will affect Ni concentrations [13]. It should be noted however, that despite these interactive effects, leachate Ni concentrations never exceeded 0.25 mg L^{-1}. And although ryegrass tissue Ni was greater from blends with PUNB than with other SFSs, it did not exceed tissue Ni from the natural topsoil.

Leachate As concentrations were greater than the USEPA MCL level of 10 ppb in most of the blends (Table 7). Only blends made with yard compost were at or below the MCL in both leaching events. The greatest amount of As was lost from blends containing SMS compost (Table 7). Due to the greater concentrations of arsenic found in SMS compost than in the other compost materials (Table 3), it is not surprising that leachate concentrations were greater. The feedstocks used to produce the SMS included broiler litter. It is possible this material was the source of the As since roxarsone is often included in broiler feed as a disease control agent and is associated with increased As in the litter [13]. In neutral to alkaline soils, As may be mobile in the soluble Na arsenate (AsO_4^{3-}) form [14]. Thus the high Na content in SMS compost may also have enhanced As mobility. SFS type did not affect the amount of As lost from the blends, as no differences were detected in the quantity leached.

Selenium levels in all leachates were below the National Primary Drinking Water MCL of 50 ppb (Table 7).

Organics

All leachates analyzed were below detection limits for PAHs (0.22 μg ml^{-1}) and phenols (0.44 μg ml^{-1}) with the exception of two leachate samples collected from one replicate of the blend containing PUNB and SMS compost. The second leachate of this blend contained 0.41 ppb fluoranthene and 0.22 ppb pyrene, and the third leaching contained 0.33 ppb fluoranthene. Due to the non-detectable levels of organic constituents in leachates collected from all but one blend, and the extremely small concentrations present where detected, the potential for these organics leaching from blends containing SFS and compost appears to be minimal.

CONCLUSIONS

Results from this greenhouse experiment demonstrate that manufactured soil blends containing spent

Table 7. Effect of SFS and compost on the cumulative trace element loss from 6 leaching events.

	Al	**Ba**	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Mo**	**Na**	**Ni**	**Zn**
Treatment						**mg column^{-1}**					
Topsoil (Control)	127a†	0.50a	0.016bc	0.09a	0.08e	75.4a	1.16c	0.02e	5.84e	0.08cd	3.02d
PUNB + yard	2.25b	0.15c	0.016bc	0.02e	0.18de	2.17b	0.33c	0.05e	367c	0.08cd	1.42d
PUNB + SMS	0.82b	0.18c	0.015c	0.04cd	0.55b	2.26b	0.26c	0.39c	974b	0.13b	2.97d
PUNB + biosolids	0.09b	0.23bc	0.015c	0.02e	0.17de	6.16b	231b	0.02e	275cd	0.35a	12.3c
FNB + yard	19.0b	0.47a	0.015c	0.04de	0.30c	12.7b	0.49c	0.17d	298cd	0.06cde	2.86d
FNB + SMS	0.58b	0.22bc	0.015c	0.06bc	0.69a	1.64b	0.60c	0.55b	830b	0.06cde	3.22d
FNB + biosolids	0.50b	0.19c	0.019b	0.02e	0.38c	3.98b	267a	0.02e	120de	0.09c	24.2a
Shell + yard	2.19b	0.43a	0.015c	0.02e	0.20d	1.68b	0.87c	0.21d	457c	0.04e	1.57d
Shell + SMS	2.86b	0.28b	0.016bc	0.08ab	0.64ab	2.53b	0.53c	0.70a	1374a	0.06de	2.38d
Shell + biosolids	2.91b	0.23bc	0.025a	0.02e	0.35c	1.73b	264ab	0.03e	332c	0.08cd	19.2b
Mean of SFS (average of 3 composts)											
PUNB	1.05b	0.18b	0.015b	0.03b	0.30b	3.53ab	77.2a	0.16c	539b	0.18a	5.55c
FNB	6.70a	0.29a	0.016b	0.016b	0.46a	6.12a	89.3a	0.25b	416c	0.07b	10.1a
Shell	2.65ab	0.31a	0.019a	0.04a	0.40a	1.98b	88.5a	0.31a	721a	0.06b	7.72b
Mean of Compost (average of 3 SFSs)											
Yard	7.82a	0.35a	0.015b	0.03b	0.23c	5.53a	0.56b	0.14b	374b	0.06c	1.95b
SMS	1.42b	0.22b	0.015b	0.06a	0.63a	2.14b	0.46b	0.55a	1059a	0.08b	2.85b
Biosolids	1.17b	0.21b	0.020a	0.02b	0.30b	3.96ab	254a	0.03c	242c	0.17a	18.5a
Source of Variation											
SFS	**†	**	**	**	**	**	NS	**	**	**	**
Compost	**	**	**	**	**	NS	**	**	**	**	**
SFS*Compost	**	**	**	**	NS	**	NS	**	NS	**	**

†LSD0.05: Within columns and sections, means with the same letter are not significantly different.
‡NS, effect not significant.
**Pr > F ≤ 0.05.

Table 8. Leachate arsenic and selenium concentrations from leaching events 1 and 2.

	Se			**Se**		
	Leach 1	**Leach 2**	**Quantity Leached**	**Leach 1**	**Leach 2**	**Quantity Leached**
Treatment	**μg L^{-1}**	**μg L^{-1}**	**μg column^{-1}**	**μg L^{-1}**	**μg L^{-1}**	**μg column^{-1}**
Control (Topsoil)	1.31	1.12	0.89c	<0.3	< 0.3	< 0.15d
PUNB + yard	2.79	2.09	1.76c	<0.3	< 0.3	< 0.15d
PUNB + SMS	91.7	62.3	48.6b	9.94	< 0.3	1.49bcd
PUNB + biosolids	27.0	16.17	13.4c	0.48	< 0.3	0.27d
FNB + yard	5.45	8.54	5.72c	<0.3	< 0.3	0.42d
FNB + SMS	199	144	122a	9.70	1.62	2.70abc
FNB + biosolids	28.3	15.3	14.5c	4.86	0.65	3.23ab
Shell + yard	5.46	10.1	6.82c	<0.3	<0.3	0.85cd
Shell + SMS	155	172	136a	15.2	2.11	4.07a
Shell + biosolids	31.6	15.3	14.0c	4.26	<0.3	1.21cd
Mean of SFS (average of 3 composts)						
PUNB	40.5	26.9	21.3a	3.47	< 0.3	0.58a
FNB	77.6	56.0	47.3a	4.85	0.76	2.12a
Shell	64.2	65.9	52.4a	6.49	0.70	2.04a
Mean of Compost (average of 3 SFSs)						
Yard	4.56	6.91	4.77b	< 0.3	< 0.3	0.42a
SMS	149	126	102a	11.6	1.25	2.75a
Biosolids	29.0	15.6	14.0b	3.20	0.22	1.57a

*Fisher's LSD: Within columns and sections, means with the same letter are not significantly different.

foundry sand and compost provide a good medium for annual ryegrass growth. Our results showed that the compost rather than the SFS component of the blends had the dominant effect on ryegrass growth, nutrient and trace element uptake, and nutrient and trace element leaching. Ryegrass tissue analysis indicated that most tissue trace metal concentrations were lower or the same as the control and most tissue nutrient concentrations fell within the sufficiency range for annual ryegrass. Compost selection is important due to its effects on tissue trace metal and nutrient concentration.

We also conclude that the use of SFSs with low total concentrations of trace elements (such as those generated from ferrous and aluminum foundries) in blended synthetic topsoils will not increase risk of trace element or organic contaminant transport to surrounding soils or waters. The compost component of such blends, however, could impact transport of nutrients (particularly N and P) as well as some trace elements. These potential detrimental effects could likely be avoided by selecting fully mature composts with low inorganic N levels and high C:N ratios (14:1). To fully test the efficacy and potential environmental impacts of blended topsoils containing SFS and compost in the natural environment, we plan to conduct multi-year and multi-location experiments in the field. However this short-term greenhouse study indicates the use of SFS in manufactured soils is a viable beneficial reuse strategy that could potentially be employed to reduce the volume of SFS sent to landfills.

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Mathematical Model to Predict Pathogen Die-off in Biosolids

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ABSTRACT: Solar drying has been utilized as a method for dewatering and pathogen reduction in biosolids for land application. The objectives of this laboratory study were to quantify the effects of moisture and temperature on the inactivation rate of fecal coliforms in biosolids and develop a mathematical model to predict their level in biosolids in solar drying beds at any time during the drying process. A two way ANOVA confirmed that temperature and moisture have significant main and interactive effects on the inactivation rate of *Escherichia coli* in biosolids. Chick's Law was used as the basis of the prediction model and the inactivation constant was further defined as a function of moisture and temperature of the biosolids. Observed and predicted inactivation rates from the microcosm study correlated well ($R^2 = 0.81$). The model was validated by comparing observed results for fecal coliform density levels in solar drying experiments to predicted values calculated from the model. There was a good agreement between observed and predicted values with the correlation coefficient ($R^2 = 0.84$) and RMSE = 0.07.

INTRODUCTION AND BACKGROUND

SOLAR drying of biosolids refers to methods of dewatering by exposure to the sun, but does not necessarily imply pathogen reduction by solar radiation, especially if biosolids are not turned regularly. Experimental field studies have demonstrated that solar-drying of biosolids in semi-arid and arid regions during warm and dry seasons can successfully convert Class B biosolids to Class A [1, 2, and 3]. However, it is not fully understood if pathogen inactivation during a solar-drying process is due to the elevated temperature of the biosolids, the decreased moisture level, or a combination of these two factors. Review of studies found in the literature indicated that there are numerous variables affecting the inactivity of pathogens and pathogen indicators in soil and in sewage sludge mixed with soil. The primary factors can be narrowed to moisture, temperature, rate of desiccation, and competing microorganisms [4, 5, 6, 7, and 8].

The ecology of the medium also plays a role in pathogen survival. Field studies by Yeager and O'Brien [9] indicated that virus adsorption is dependent on soil pH, cation exchange capacity, organic matter content, and clay content. Viruses survived longer in septic liquor than in ground water and surface water, due to the organic content of the septic liquor and water adsorption properties. Solar drying field studies by Zaleski et al. [3] demonstrated that fecal coliform levels decreased as the percent of total solids (%TS) of the biosolids increased; coliform levels also rose sharply after rainfall events suggesting that fecal coliforms are dependent on ambient moisture levels. In a controlled study published by Song et al. [10], the effects of temperature and moisture on virus survivability in soil showed similar results, i.e. inactivation rates of PRD-1 increased as the soil temperature increased and the largest inactivation rate, k_d, occurred at a 5% soil moisture content with a soil temperature of 38.4°C. West et al. [11] showed in laboratory experiments that the respiration and metabolic activity of microorganisms in soil decreased linearly with the decline of volumetric moisture content of the soil. According to Stark and Firestone [12], moisture limits microbial activity in a wide range of environments, including salt water, food, soil and biofilms.

The causes for pathogen inactivation may be due to abiotic or biotic stressors and their synergistic effects. Heat, another critical, abiotic factor, was known to in-

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jure cells by damaging cell membranes when heat is transferred from surrounding water molecules. At high temperatures, heat impacts microorganisms by damaging their cellular membranes and possibly their intracellular proteins, DNA, and ribosomes [13]. As biosolids dry, they become very porous and the air replaces the water within the pores. The specific heat of air is much less than that of water (1.005 kJ/kg·K at 300 K compared to 4.179 kJ/kg·K at 300 K, respectively), thereby more energy is required to raise the temperature of wet biosolids as compared to dry biosolids. As water evaporates from biosolids in the field, the temperature increases 5 to10°C above ambient air temperature, making cooling by evaporation no longer feasible at the surface (S.A. O'Shaughnessy and C. Y. Choi, unpublished data). The temperature of dried biosolids in solar drying beds has been shown to reach temperatures above 60°C [2, 14].

The use of a mathematical model for fecal coliform inactivation is a reasonable approach to predicting pathogen density levels in biosolids at any time during the solar-drying process and may prove to be an economical strategy for testing biosolids for Class A microbial designation. This study was designed to investigate the influence of two key factors on pathogen reduction in biosolids with the objectives to: (1) quantify individual or combined contributions of temperature and moisture on fecal coliform reduction in biosolids; and (2) develop a model to predict the level of fecal coliform in biosolids in solar drying beds by defining the inactivation rate as a function of temperature and moisture content of biosolids.

METHODS AND MATERIALS

Preliminary Microcosm Study

A preliminary laboratory study was conducted to determine if anaerobic-like conditions (capped jars) impacted pathogen inactivation in biosolids. Fecal coliforms were used in these experiments because they serve as pathogen indicators and are frequently assayed (in lieu of *Salmonellae*) for the purpose of designating the bacterial microbial quality of biosolids [15].

To maintain constant moisture levels throughout the factorial experiment, the moistened biosolids were contained in sterile capped Nalgene® jars. The preliminary study was conducted to ascertain if the capped jars would significantly impact fecal coliform inactivation. A comparison was then made between the fecal coliform survival rates in biosolids in open jars versus biosolids in closed jars stored at room temperature. Freshly produced, aerobically-digested biosolids with initial total solids of 14.6% (dry weight) were collected from the Green Valley Wastewater treatment plant (GVWWTP), stored on ice and transported to the laboratory for analysis. The biosolids were packed into the sterile Nalgene® jars; two of the sets were tightly capped, while the second two sets were left uncapped. All jars were placed into an incubator at 25°C with a high relative humidity (approximately 60%). Two replicates from each set were sacrificed on the sampling days of 0, 1, 3, 5, 7, 10, 19 and 20 and fecal levels were analyzed using a three-tube "most probable number" (MPN) method adapted from the U.S. EPA Standard Method 9221[16, 17]. Ten g of the biosolids were added to 90 ml of sterile buffered peptone water (Difco Co., Detroit, MI) and shaken for 10 mins. Serial dilutions of the sample were made and 1 ml was transferred to each of three10 ml tubes of Laurel Tryptose Broth and incubated at 35ºC in a walk-in incubator. After 48 hrs., 0.1 ml from each positive sample was transferred to 10 ml tubes of sterile EC Medium (Difco Co., Detroit, MI) and incubated in a water bath (Precision Scientific, Model No. 253, Winchester, VA), at 44.5°C for 24 to 48 hrs. All tubes were scored for gas production; the presence of gas being indicative of lactose fermentation by coliforms.

Temperature and Moisture Factorial Study

This controlled study was designed as a factorial experiment to investigate the significance of temperature and moisture and their impact on the inactivation rate of fecal coliforms. Three temperature levels (25°C, 32°C and 38°C) and four moisture levels [10%, 35%, 65%, and 80% (g water/g wet sample)] were investigated as presented in Table 1.

The experimental temperature values represented the average hourly temperature readings of the biosolids measured during summer solar drying field experiments at the GVWWTP during 2004 and 2005. The experimental moisture levels approximated the range of water content of the biosolids during these field drying experiments. Solar-dried, aerobically-digested biosolids were collected from the GVWWTP and stored at 4°C. 10 g of biosolids were placed in each sterile jar and appropriately amended with sterile distilled water and inoculated with high levels (10^8 to 10^9) of *Escherichia coli* ATCC 15592 to the desired mois-

Table 1. A summary of the experimental design.

Average Oven Temperature ± std deviation (°C)	% Moisture Levels* (g/g)	Experiment Duration (days)	Initial %TS of Biosolids	Inoculum Titer Level
25 ± 1.7	10-35-65-80	20	95.2	10^9
32 ± 2.4	10-35-65-80	15	96.3	10^8
38 ± 2.1	10-35-65-80	9	95.1	10^8

*Moisture levels of prepared samples for each temperature study.

ture level noted in Table 1. A total of eighty-four samples were prepared at the onset of each temperature run, which included three replicates for each moisture level for each day of sampling. The jars were prepared as described in the preliminary laboratory study. A total of three experimental runs at the temperature levels of 25°C, 32°C, and 38°C were conducted. Thermocouples (TTT- EXT-20, Omega Engineering, Inc., Stamford, CT) were secured to the top, middle and bottom racks of the isotherm oven. Continuous data-logging provided the average and standard deviation of the oven temperature for the duration of each experimental run.

Fecal coliforms were enumerated over time using plating and dilution techniques. Dilutions of the samples were made with sterile K_2PHO_4 to the appropriate levels, spread plated onto m-FC agar (Acumedia, Baltimore, MD) and incubated at 44.5°C for 18–24 hrs. The three-tube MPN method was used in addition to plating and dilution on the 10% moisture level samples to obtain fecal coliform readings below $\log_{10}2$. The MPN method is particularly useful for low concentrations of organisms (< 100/g), especially, for those samples whose particulate matter may interfere with accurate colony counts [17]. Titer levels on Day 0 of the experiments were determined by plating dilutions of the inoculum on m-Endo Agar (Difco Co., Detroit, MI) and were determined to be in the range of $\log_{10}8$ CFU/ml and $\log_{10}9$ CFU/ml as shown in Table 1.

Heterotrophic Plate Counts (HPC)

Dilution and spread plate techniques for heterotrophic bacteria were performed on R2A agar (Difco Co., Detroit, MI) to investigate whether the biotic affect was present in the laboratory studies. Plates were incubated at room temperature (25°C) for 7 to 10 days.

RESULTS

Preliminary Microcosm Study

The inactivation rate of fecal coliform in open versus capped sampling jars proved to be insignificant. The inactivation pattern was assumed to follow the first order die-off model known as Chick's Law, Equation (1) from Maier et al. [18]:

$$k_d = -\log \frac{\left({N_o}/{N_t} \right)}{t} \tag{1}$$

The average inactivation rates were 0.08 day^{-1} ± 0.013 and 0.05 day^{-1} ± 0.025 for the open and capped samples, respectively. The Student's *t*-test (two sided) for the paired samples established that the means were not significantly different at an alpha level of 0.05, $p = 0.32$.

Temperature and Moisture Factorial Study

First-order inactivation rates for fecal coliforms, k_d, were calculated for each replicate in each moisture block at the three different temperature levels are listed in Table 2. The inactivation rates were calcu-

Table 2. Inactivation rate constant, k_d, (3 replicates) for temperature and moisture matrix.

	Moisture			
Temperature	10%	35%	65%	80%
25°C	0.74, 0.88, 0.91	0.25, 0.26, 0.26	0.31, 0.02*, 0.25	0.02, 0.03, 0.05
32°C	0.69, 0.66, 0.51	0.02*, 0.39, 0.29	0.70, 0.57, 0.41	0.30, 0.30, 0.40
38°C	3.30, 2.70, 2.60	1.47, 0.41, 0.50	1.10, 0.50, 1.20	1.10, 0.90, 1.10

*Value is an outlier, i.e. $k_d < 3\sigma$.

lated to the Class A level or to the point at which N_t was initially ≤ 10^3 CFU/g or 10^3 MPN/g [15]; die-off patterns are shown in Figure 1. Further review of the data in Table 2 indicated that within each moisture treatment block, k_d values generally tended to increase as temperature levels increased and within each temperature treatment block, k_d values tended to increase as moisture decreased. Figure 2 clearly illustrates the effects of increased temperature (T) and decreased moisture (Θ) on k_d as well as the synergistic impact of T and Θ.

As each physical stressor became more extreme (minimal moisture and amplified temperature), the inactivation rate, k_d, changed significantly. The greatest rate of inactivation occurred when the temperature was at its highest level and moisture was at the lowest level as evidenced by the peak shown along the positive z-axis in Figure 2.

An analysis of variance of the inactivation rates produced relatively large F statistic values, 33.59, 67.65, and 10.07 for the independent variables of moisture (Θ), temperature (T), and their interaction ($\Theta * T$), respectively, with $p << 0.01$ for all cases.

The inactivation rates (k_d) and corresponding temperature and moisture values from the factorial study were utilized to develop a mathematical model that defined kd in non-linear terms and as a function of T and Θ. Equation (2) was utilized to determine the non-linear relationship:

$$k_d = \left(\frac{k_1}{k_1 + \Theta}\right) \times \left(\frac{T}{k_2 - T}\right) \times k_3 \qquad (2)$$

where Θ = average moisture (g H_2O/g total sample) of the biosolids and T = average daily temperature, and k_1, k_2, and k_3 are coefficients to be determined through modeling.

The basic template of equation (2) stems from the behavior of fecal coliform inactivation rates as a function of temperature and moisture. This pattern is similar to the Michaelis-Menten-type kinetics traditionally used to summarize mineralization data from aqueous incubation, the biodegradation of organic compounds and substrate depletion [19, 20]. Non-linear multiple regression analysis using the Gauss-Newton procedure to determine the coefficients k_1, k_2, and k_3 (SYSTAT®, Version 8.0, Copyright SPSS, Point Richmond, CA) provided empirical values of 0.112, –41.88, and –0.5357, for all $T \leq 38°C$ (correlation coefficient, R^2 = 0.81). This method is most commonly used in software computing algorithms for finding the least squares estimator in a nonlinear model [21].

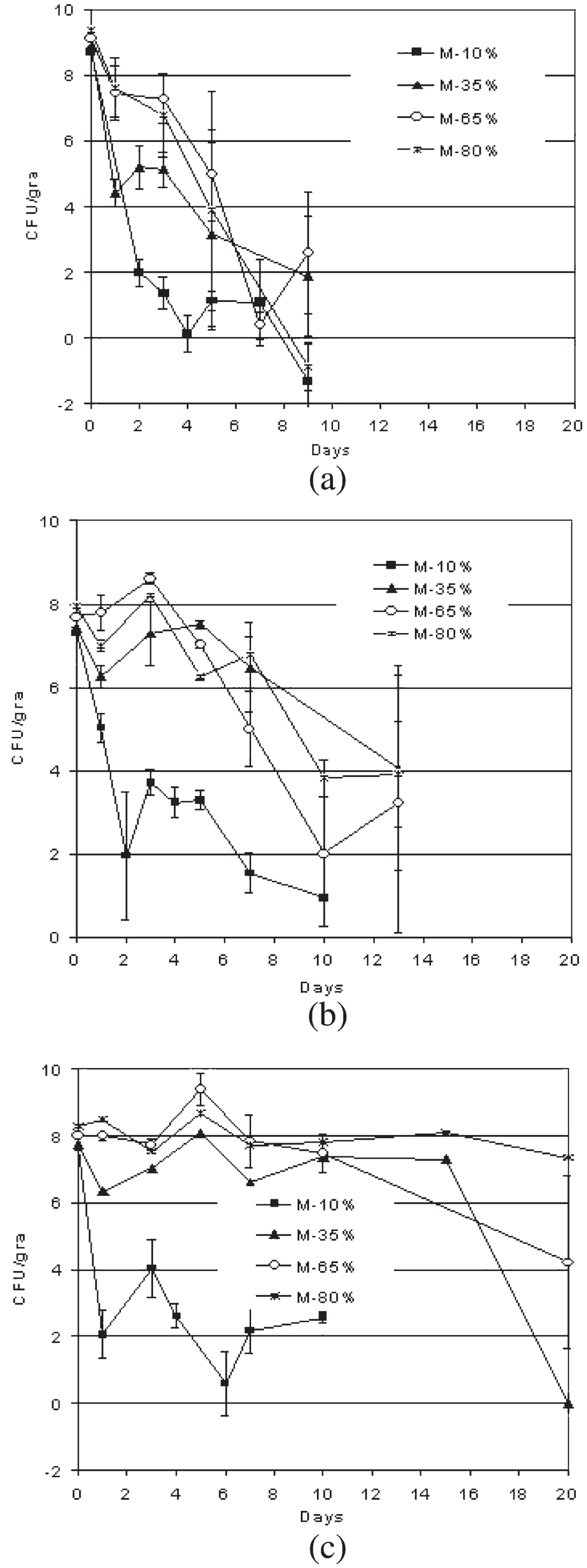


Figure 1. *Fecal coliform levels over time. Data points with standard deviations represent the average of three replicates at the environmental temperature of: (a) Temperature = 38°C; (b) Temperature = 32°C; and (c) Temperature = 25°C. (Values at the 10% moisture levels are MPN/g).*

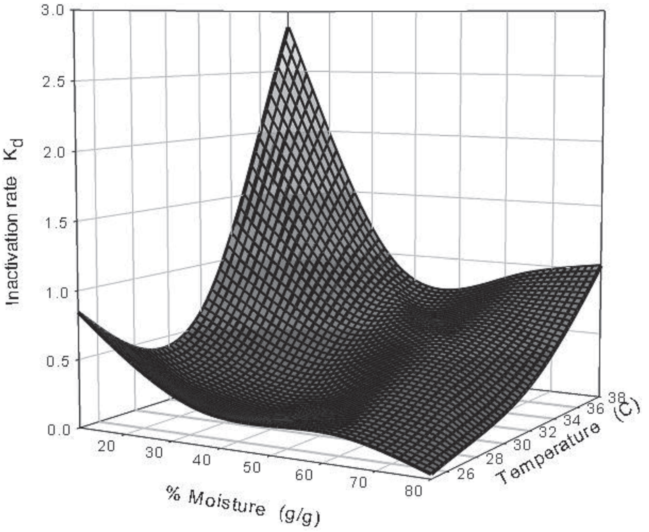


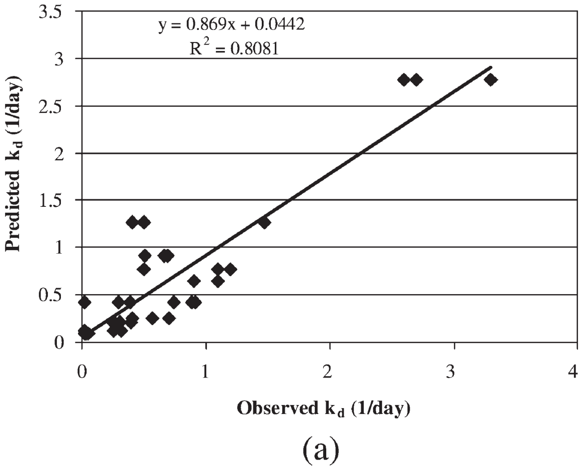
Figure 2. *Surface contour plot of fecal coliform inactivation versus temperature and moisture of biosolids.*

HPC

The results indicated that heterotrophic bacteria were present in the samples throughout the experiment at levels ranging from $\log_{10}12$ CFU/ml at the beginning (Day 0) to $\log_{10}5$ CFU/ml towards the end of the experiment.

Model Validation

The mathematical model, Equation (2), was validated using data from field solar-drying experiments conducted in Quartzsite, Arizona [2] and Wadi Hassan, Jordan [1] in addition to the data measured from the solar drying experiments at the Avra Valley and Green Valley Wastewater Treatment Plants (S. A. O'Shaughnessy and C. Y. Choi, unpublished data) see Table 3. Figure 3 shows a comparison of observed log N_t levels and predicted log N_t levels. Observed values of k_d were calculated based on linear regression of log $[N_t/N_o]$ measured over the time needed to reach Class A during the summer solar drying experiments. The values for the predicted inactivation rate constants, k_d, were calculated using equation (2). Average daily temperature and average moisture content values of the biosolids from the field data were substituted for T and Θ, respectively. A comparison of the observed versus the predicted inactivation rates demonstrated a Root Mean Square Error (RMSE) = 0.07. The error can be attributed to a number of factors, including spatial variability when sampling, inconsistency between different types of biosolids, applied treatments (tilling), regrowth of fecal coliforms, tailing effects, and incongruities between the field and laboratory environment such as hysteresis in following pathogen inactivation from a wet medium to a dry medium (field scenario) versus following inactivation in a medium held constant (experimental scenario).



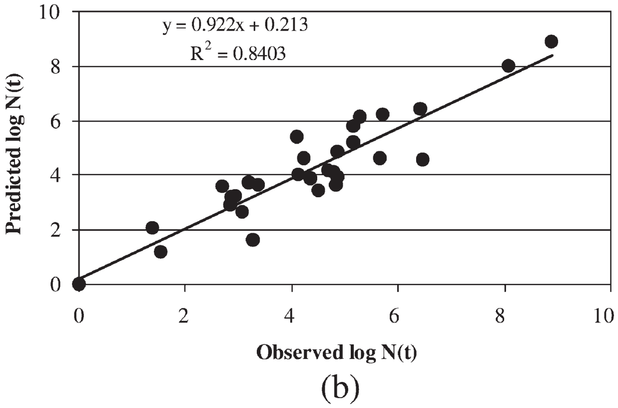


Figure 3. *(a) Observed inactivation rates (k_d) in comparison to measured inactivation rates for the microcosm study; and (b) Comparison of field observed log N_t values of fecal coliforms and predicted log N_t values using equation (2).*

Data sets from various locations yielded good results for estimating fecal coliform density levels despite climatic differences and variations in the stabilization processes of the biosolids. Increased accuracy between observed and predicted inactivation rates were demonstrated in semi-arid locations when no additional treatments were applied, see Table 3.

DISCUSSION

Municipalities in the United States and developing countries are investigating solar drying as a means to re-

Table 3. Comparison of predicted and observed inactivation rates (based on obtaining Class A levels).

Experiment	Biosolids Treatment	k_d observed	k_d predicted	Avg % Moisture (g /g)	Avg Temp (°C)
GVWWTP					
Summer 2005	Aerobic no till	0.14	0.12	83.82	27.22
Summer 2005	Aerobic covered	0.49	0.55	84.54	37.59
Summer 2005	Aerobic tilled	0.18	0.15	83.55	29.47
Summer 2005	Aerobic tilled	0.18	0.17	81.53	30.44
Summer 2004	Aerobic no till	0.14	0.15	51.91	25.75
Summer 2004	Aerobic no till	0.20	0.21	38.07	26.30
Wadi Hassan					
Summer 2004	Aerobic no till	0.17	0.13	67.25	26.64
Spring 2005	Aerobic	0.18	0.19	66.35	29.83
Quartzsite†					
Summer 2004	Anaerobic no till	0.50	0.38	67.55	34.85
Summer 2004	Anaerobic moderately tilled	0.88	0.76	65.65	42.00*
Summer 2004	Anaerobic intensively tilled	1.19	0.92	53.44	55.00*

†Grabau, [14].
*Temperatures limited to 38ºC when placed into Equation (2).

duce pathogens in biosolids for land application. Many of the solar drying sites are remotely located. Therefore, predicting pathogen density levels in biosolids during the drying process can aid generators in establishing economical methods towards qualifying the biosolids and establishing best management protocols for producing Class A materials. The preliminary study demonstrated that capping the sample jars was a suitable method to maintain constant moisture levels in the samples without significantly affecting fecal inactivation rates. Fecal coliforms are facultative and the existence of air space at the head of the jar may have limited the influence of anaerobic-like conditions on their survival.

Pathogen inactivation in biosolids exposed to open solar drying is likely the result of a number of parameters and their complex interaction—abiotic (physical, chemical), and biotic. This study demonstrated that temperature and moisture are two major physical factors impacting inactivation. Maintaining levels of known temperature and moisture over time in aerobically-digested biosolids demonstrated that an increase in the inactivation rate for fecal coliforms occurs at a threshold temperature near 38ºC and also at a minimum threshold moisture level near 10% (g/g).

Physical factors are not the only parameters that significantly affect pathogen inactivation in biosolids. Further studies should be performed on the biotic effects (competition and predation) on pathogen inactivation in biosolids as well as the impact of the desiccation rate of biosolids on pathogen survivability. When future instrumentation designs become available, the use of accurate quantitative analog moisture measurements of the biosolids during the solar drying process will improve the functionality of the mathematical model in predicting Class A microbial quality independent of microbiological laboratory testing.

ACKNLOWEDGEMENTS

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Note: Mention of trade names or commercial products in this publication is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture.

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The Evaluation of Pumice Stone Applicability at Struvite Crystallization by Using Box-Benhken Experimental Design

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ABSTRACT: This paper presents the results on phosphorus recovery from a phosphorus rich synthetic solution using pumice stone as a seed material. The factors affecting the precipitation mechanism as struvite for phosphorus recovery were investigated using a model reactor. The experimental setup is composed of the model reactor, three injection tubes, a pH-probe, a temperature sensor, two stirrers, and feeding tank.

Box-Benhken Experimental Design was used to determine the effects of pH, pumice amount, and temperature as independent variables on PO_4-P, NH_4-N, and Mg removals as dependent variables. It was found that the temperature and pH were the main parameters affecting phosphorus, ammonium and magnesium removals. In addition to this, it was observed that pumice amount has a slight effect on phosphorus removal. The best combination of independent variables to maximize the dependent variables was determined as a pH value of 9.5, the pumice amount of 12.9 g, and the temperature of 29°C. Scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS) was used to detect struvite crystals on pumice stone and to analyze the struvite compounds. SEM-EDS results showed that the struvite crystals were precipitated on pumice stone and major elements of all precipitates in the general composition were found as phosphorus, magnesium, nitrogen, oxygen, silica, and calcium.

1. INTRODUCTION

STRUVITE (MAP—Magnesium Ammonium Phosphate) is composed of magnesium, ammonium and phosphate and has a white orthorhombic crystalline structure [1, 2, 3]. The Mg:P ratio has a central role in the formation of struvite. Nelson et al. [4] studied the effects of Mg:P ratios between 1:1 and 1:6 on phosphorus recovery in liquid phase coming from anaerobic swine lagoons. They found that phosphorus concentrations decreased with increasing Mg:P ratio. Furthermore, Rahaman et al. determined that better removal of phosphorus was achieved at higher Mg:P ratios in the range of 1:1-1:6 [5]. The specific gravity of struvite is about 1.7 [1,6,7]. The struvite formation reaction is shown below:

$$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4(H_2O)_6$$

Struvite is soluble at low pH values and becomes insoluble at high pH values in wastewater. The orthophosphate concentration increases with the increasing of pH whereas the magnesium and ammonium concentrations decrease [1]. The solubility of struvite begins to increase at high pH values (above 9) since the ammonium ion concentration will decrease and the phosphate ion concentration will increase [8]. When the concentration product of Mg^{2+}, NH_4^+ and PO_4^{3-} exceeds the struvite solubility limit, struvite precipitates [6].

In the formation of struvite, precipitation kinetics are divided into two phases, nucleation and growth. Ions combine to form crystal embryos at nucleation phases and then the embryos can act as the foundation for growth into detectable crystals. Growth results from the assimilation of ions into the lattice structure established by the crystal embryo foundation [9]. Grains of seeding material like sand or phosphate rocks assist struvite nucleation of the crystals and recovered phosphorus precipitate on the seeding material [10].

Various magnesium sources like $MgCl_2$, MgO, $Mg(OH)_2$ in different phosphorus recovery processes

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have been used. In the case of MgO usage, the main advantages are that this chemical can be readily found as an industrial by-product and therefore it is available at low prices. MgO increases the pH value of the solution which promotes struvite precipitation [11]. The advantage of $MgCl_2$ is that it disassociates faster than $Mg(OH)_2$, resulting in shorter reaction times. $Mg(OH)_2$, however, is generally cheaper, and has the advantage of raising the pH [7]. Beyond these, Lee et al. recommended the usage of bittern as a magnesium source for struvite precipitation [2].

Struvite is a high quality fertilizer due to its composition and low solubility [12]. The main advantage of struvite as a fertilizer is that plants particularly uptake the nutrients without waste by leaching. In addition to this, less frequent application is sufficient, and no fertilizer burn can occur, even at high application rates [7].

As previously mentioned, various materials in struvite precipitation have been used to assist nucleation. The purpose of the current study is to investigate the precipitation of struvite using pumice stone as a seeding material, and to determine the parameters affecting struvite precipitation such as pH, temperature and pumice amount. Pumice stone has been used in various sectors. It is abundant in Turkey and was chosen as seeding material because of its porous structure and easily supplied.

2. MATERIAL AND METHODS

2.1 Model Reactor

Figure 1 depicts a schematic view of model reactor used in this study. It was made from stainless steel and has a volume of 30 liters. The model reactor consists of two parts in order to avoid having fines in the effluent. The outward part of the model reactor is the settling zone while the inward part is the reaction and mixing zone. The experimental setup is composed of the model reactor with three injection tubes (feeding solution, $MgCl_2$ solution, and NaOH solution), a pH-probe, a temperature sensor, two stirrers, and feeding tank.

The outer surface of the model reactor was covered with an oil jacket to control temperature in reactor. The temperature in the reactor was measured with a temperature sensor and kept at the desired value with an accuracy ±2°C. The pH was continuously monitored and maintained by dosing with NaOH at desired pH value. The influent tank which has a volume of 30 liters was continuously mixed during the process so as not to settle the pumice stone and to supply a homogeneous mixture (pumice stone + feeding solution).

Three different solutions namely ammonium-phosphate, a concentrated NaOH, and $MgCl_2{\cdot}6H_2O$ were prepared for different purposes. All chemicals purchased from Merck. An ammonium-phosphate solution prepared with $NH_4H_2PO_4$ was fed to the model reactor. The concentrated NaOH solution was used for pH adjustments while $MgCl_2{\cdot}6H_2O$ was used as a magnesium source due to its shorter reaction times. The model reactor was operated as steady state. Feeding solution and $MgCl_2$ solution were added to the reactor with the flow rate of 8.13 L/h, and 5.22 L/h, respectively. Both the feeding solution and the pumice stone which has a size 150–200 μm were simultaneously fed to the reactor.

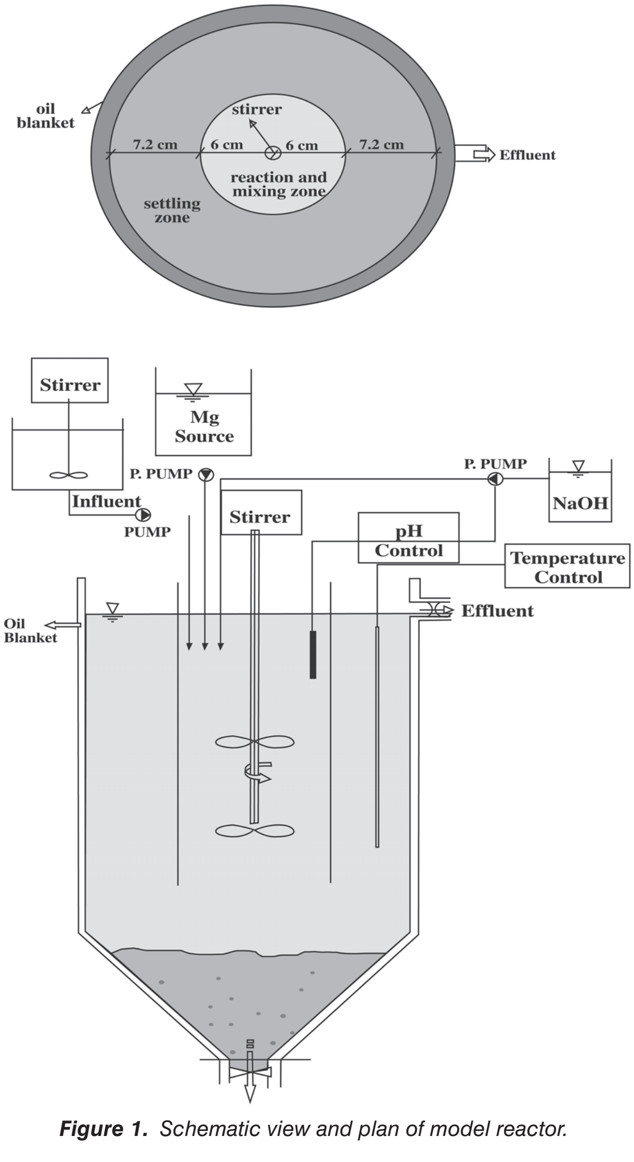

Figure 1. Schematic view and plan of model reactor.

The molar ratio of $Mg:PO_4:NH_4$ was adjusted as 1.5:1:1 which was determined in previous experimental studies. Stratful pointed out that as the reaction time was increased from 1 to 180 min, crystal size was found to increase from 0.1 to 3mm [19]. Therefore, reaction time was chosen as 3 hours.

The phosphate concentration in the solution before and after the struvite process was analyzed using Stannous Chloride Method; 4500-P D given in Standard Methods [13]. The ammonium concentration was also determined with ammonia-selective electrode method; 4500-NH_3 D in Standard Methods [13]. Magnesium concentrations were measured by using ICP-OES (Inductively coupled plasma optical emission spectroscopy—Perkin Elmer Optima 2100 D). Effluent PO_4, NH_4, and Mg concentrations were controlled during the time of the reaction inside the reactor. It was observed that the residues taken from the bottom part of the reactor composed of struvite forms and pumice stone. After drying of the residues at 103°C, microphotographs were taken using SEM-EDS (Scanning Electron Microscope equipped with a energy dispersive spectrometer—Jeol 6060).

2.2. Experimental Design

Box-Benhken Experimental Design [14] based on Response Surface Method was used to determine the effects of pH, pumice amount and temperature on PO_4-P, NH_4-N, Mg removals in the model reactor. Actual values of independent variables; namely, pH (X1), pumice amount (X2), and temperature (X3) used for experimental design and Box-Behnken Experimental Design Matrix are given in Table 1. Ranges of pumice amount were chosen according to previously conducted laboratory studies [15].

Response functions defining variations of dependent variables with the independent variables can be described as (1).

$$Y = B_0 + \sum_{i=1}^{k} B_i X_j + \sum_{i=1}^{k} B_{ii} X^2 + \sum_{i=1}^{k} B_{ij} X_i X_j \qquad (1)$$

Where, Y is the predicted response, B_0 is a constant; B_i and B_{ij} are cross product and quadratic coefficients respectively ($i, j = 1, 2, 3$). Box-Behnken design matrix with 17 experimental runs including five replicates of the center point was determined and the responses of the dependent variables obtained from the experimental studies were applied to the model (Table 1).

Table 1. Actual values of independent variables and Box-Behnken Experimental Design matrix.

	Independent Variables		
Runs	X1 pH (pH)	X2 Pumice Amount (g)	X3 Temperature (°C)
1	9	10.5	22.5
2	11	10.5	10
3	7	10.5	10
4	7	20	22.5
5	11	1	22.5
6	9	10.5	22.5
7	9	10.5	22.5
8	9	10.5	22.5
9	11	10.5	35
10	9	20	10
11	9	1	35
12	7	10.5	35
13	7	1	22.5
14	9	20	35
15	11	20	22.5
16	9	1	10
17	9	10.5	22.5

3. RESULTS

The response function coefficients were determined by using the Stat-Ease Design Expert 7.1.3 (Trial version) software program. The predicted values of dependent variables were in good agreement with the observed values.

The response functions for phosphorus removal (Y_{PO4-P}), ammonium removal (Y_{NH4-P}) and magnesium removal (Y_{Mg}) were determined by using the estimated coefficients (Bo, Bi, Bij) and shown as below:

$$Y_{PO4-P} = -947.52807 + 172.67030X_1 + 9.57794X_2 + 15.00791X_3 - 0.33605X_1X_2 - 0.94590X_1X_3 - 0.00273684X_2X_3 - 7.80456X_1^2 - 0.31929X_2^2 - 0.11221X_3^2$$

(R-Squared Adjusted = 0.9277)

$$Y_{NH4-P} = -459.36523 + 91.58039X_1 + 2.19009X_2 + 5.54113X_3 - 0.33289X_1X_2 - 0.16050X_1X_3 + 0.064547X_2X_3 - 4.9781X_1^2 - 0.021205X_2^2 - 0.092264X_3^2$$

(R-Squared Adjusted = 0.9367)

$$Y_{Mg} = -219.00218 + 40.15376X_1 - 6.47311X_2 + 5.11228X_3 + 0.57974X_1X_2 + 0.54890X_1X_3 + 0.024758X_2X_3 - 2.60219X_1^2 + 0.025526X_2^2 - 0.16127X_3^2$$

(R-Squared Adjusted = 0.9242)

p-value < 0.05 or 0.01 was evaluated as significant. The ANOVA regression analysis of PO_4-P, NH_4-N and Mg removal indicated that the suggested quadratic model was adequate at lowest standard deviation, the highest R-Squared and the lowest press value (Table 2).

The variations of phosphorus, ammonium, and magnesium removals with pH at different reactor temperature values and at 10.5 g constant pumice amount were illustrated in Figure 2. It was observed that temperature, pH and pumice amount have a positive effect on phosphorus removal. The pH, a significant model term was determined and the best phosphorus removal was detected at pH 9 and 10. It was observed that the phosphorus removal increased with increasing temperature in the model reactor and reached to 100% at 22.5°C at pH 9–10 [Figure 2(a)]. The variation of temperature and pH has significantly been affected by ammonium removal similar to the phosphorus removal at a pumice amount of 10.5 g [Figure 2(b)]. It was observed that ammonium removal profiles increased with increasing

Table 2. ANOVA regression analysis for PO_4-P, NH_4-N and Mg removal efficiency.

Source	Sum of squares	df	Mean Square	F value	p-value Prob<F	
PO_4-P						
Means vs Total	61448.65	1	61448.65	1.45	0.27	
Linear vs Mean	4282.28	3	1427.43	0.77	0.5372	
2FI vs Linear	2400.31	3	800.10	42.57	<0.0001	Suggested
Quadratic vs 2FI	9865.05	3	3288.35	1251.43	<0.0001	
Cubic vs Quadratic	540.17	3	180.06			
Residual	0.58	4	0.14			
Total	78537.04	17				
Lack of Fit Tests						
Linear	12805.53	9	1422.84	9889.05	<0.0001	
2FI	10405.22	6	1734.20	12053.12	<0.0001	
Quadratic	540.17	3	180.06	1251.43	<0.0001	Suggested
Cubic	0.0000	0				
Pure Error	0.58	4	0.14			

Model Summary Statistics	**Std. Dev.**	**R-Squared**	**Adjusted R-Squared**	**PRESS**	
Linear	31.39	0.2506	0.0777	20381.34	
2FI	32.26	0.3911	0.0257	26752.99	
Quadratic	8.79	0.9684	0.9277	8643.55	Suggested
Cubic	*0.38*	*1.000*		+	

Source	Sum of squares	df	Mean Square	F value	p-value Prob<F	
NH_4-N						
Means vs Total	13750.74	1	13750.74			
Linear vs Mean	639.42	3	213.14	0.91	0.46	
2FI vs Linear	459.43	3	153.14	0.59	0.63	Suggested
Quadratic vs 2FI	2482.58	3	827.53	56.81	<0.0001	
Cubic vs Quadratic	101.28	3	33.76	196.28	<0.0001	
Residual	0.69	4	0.17			
Total	17434.13	17	1025.54			
Lack of Fit Tests						
Linear	3043.29	9	338.14	1965.95	<0.0001	
2FI	2583.86	6	430.64	2503.74	<0.0001	
Quadratic	101.28	3	33.76	196.28	<0.0001	Suggested
Cubic	0.0000	0				
Pure Error	0.69	4	0.17			

Model Summary Statistics	**Std. Dev.**	**R-Squared**	**Adjusted R-Squared**	**PRESS**	
Linear	15.30	0.1736	–0.0171	5083.86	
2FI	16.08	0.2983	–0.1227	7924.68	
Quadratic	3.82	0.9723	0.9367	1621.52	Suggested
Cubic	*0.41*	*0.998*	*0.993*	+	

(continued)

Table 2. ANOVA regression analysis for PO_4-P, NH_4-N and Mg removal efficiency.

Source	Sum of squares	df	Mean Square	F value	p-value Prob<F	
Mg						
Means vs Total	53212.37	1	53212.37			Suggested
Linear vs Mean	16105.49	3	5368.50	0.0003		
2FI vs Linear	1273.12	3	424.37	0.4048		
Quadratic vs 2FI	3255.48	3	1085.16	0.0052		Suggested
Cubic vs Quadratic	707.82	3	235.94		<0.0001	
Residual	0.19	4	0.048	12071.06	<0.0001	Suggested
Total	74554.48	17	4385.56	13704.37	<0.0001	
Lack of Fit Tests				4895.05	<0.0001	Suggested
Linear	5236.43	9	581.83			
2FI	3963.3	6	660.55			
Quadratic	707.82	3	235.94			
Cubic	0	0				
Pure Error	0.19	4	0.048			
Model Summary Statistics	**Std. Dev.**	**R-Squared**	**Adjusted R-Squared**		**PRESS**	
Linear	20.07	0.7546	0.6980		9777.06	Suggested
2FI	19.91	0.8143	0.7029		15439.44	
Quadratic	10.06	0.9668	0.9242		11325.48	Suggested
Cubic	0.22	1.000	1.000		+	

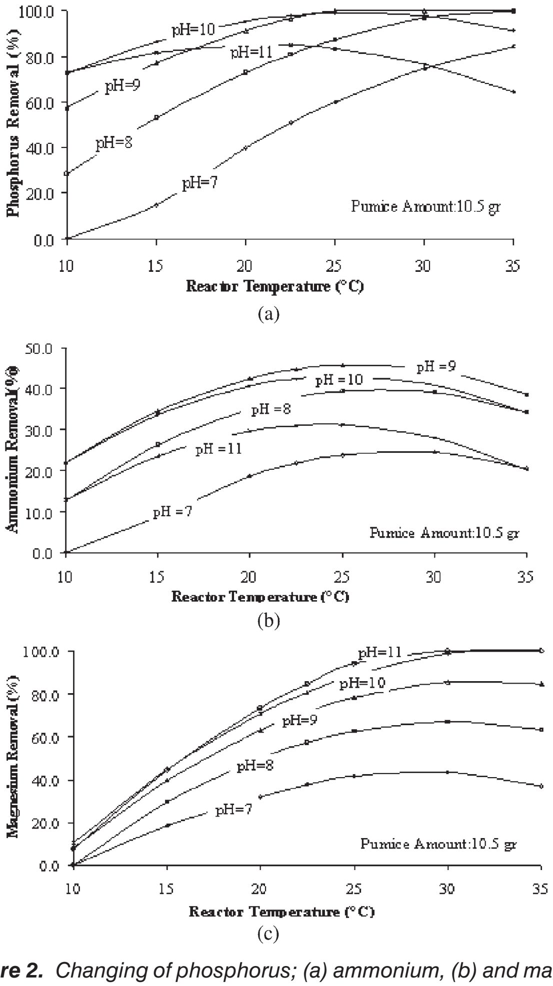

Figure 2. *Changing of phosphorus; (a) ammonium, (b) and magnesium, (c) removal with reactor temperature at different pH values.*

temperature until 25°C at all pH values. While minimum ammonium removal was achieved at pH 7, maximum removal was at pH 9. Temperature and pH are very effective parameters for magnesium removal, although the pumice amount has a negative effect [Figure 2(c)]. Magnesium removal rapidly increased with increasing temperature and reached to 100% at 22.5°C as in phosphorus removal. The best magnesium removal was obtained at pH 11 contrary to phosphorus and ammonium removal. The results showed that the reactor should be kept at pH 8.7 and 22°C in the model reactor, when 10.5 g pumice was added to it in order to accomplish maximum removal efficiency for phosphorus, ammonium, and magnesium.

As can be seen in Figure 3(a), phosphorus removal was effected in the progressive stages of the reaction with increasing temperature at constant pH 9 and reached to 100% at temperatures greater than 25°C. It was observed that 1^{-10} g pumice amount have a positive effect and pumice amount greater than 10 g had a negative effect on phosphorus removal for all temperatures levels. The ammonium removal was affected significantly by increasing temperature at constant pH 9. No effective change has been detected on ammonium removal beyond 25°C [Figure 3(b)]. The increases in the pumice amount at 25°C did not enhance the ammonium removal. Magnesium removal significantly increased with increasing temperature in the model reactor and

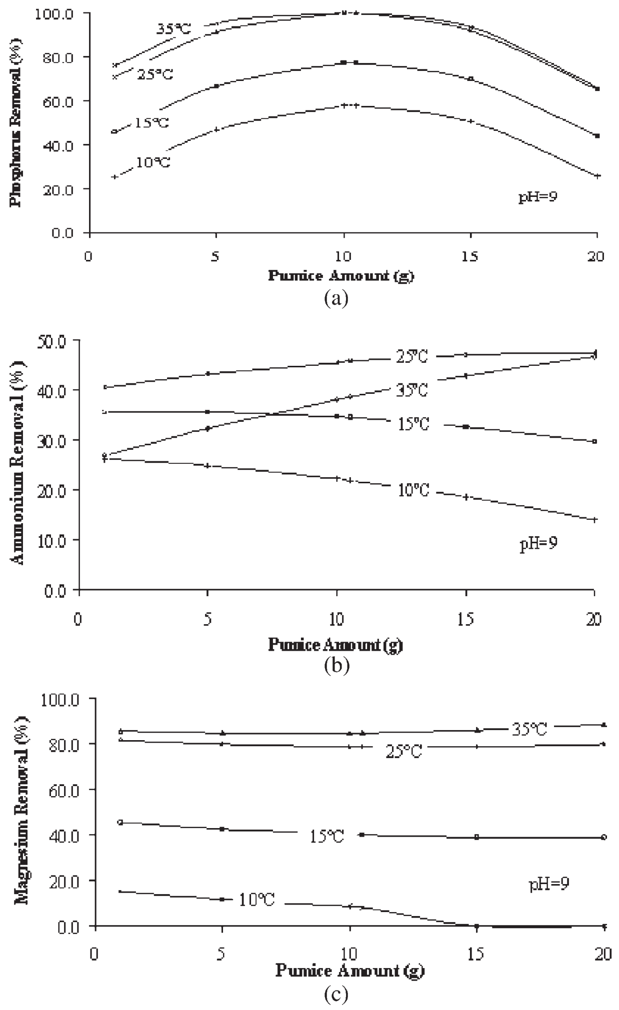

Figure 3. *Variation of phosphorus; (a) ammonium, (b) and magnesium, (c) removal with pumice amount at different reactor temperature.*

decreased slightly with the increasing of pumice stone [Figure 3(c)]. Maximum magnesium removal was accomplished at pH 11. These results show that the model reactor should be kept at 21.5°C and 3.3 g pumice amount should be added at constant pH 9 to achieve maximum removal efficiencies for phosphorus, ammonium, and magnesium.

A Scanning Electron Microscope (SEM) equipped with a energy dispersive spectrometer (EDS) was used to determine structure of the struvite with its chemical constituents. A zone called "p" was first selected in the pumice stone sample and its chemical composition was determined. It was found that the major elements are silica, oxygen, aluminum, and potassium in the sample. The ratio of the components is given in Table 3. The microphotographs of pumice stone taken by SEM are illustrated in Figure 4. The porous surface of pumice was clearly seen from the microphotographs.

Table 3. Components of pumice stone taken at SEM-EDS.

Element's Name	Pumice Stone (%)
O	42.831
Mg	2.747
Al	6.811
Si	34.313
P	2.744
Na	2.615
K	3.048
Ca	1.339
N	2.629
Cl	–
Fe	0.823

Precipitates consist of struvite particles that were taken out of the reactor. The microphotographs of dried precipitates taken by SEM are shown in Figure 5. Microphotographs of dried precipitates show that the precipitates on pumice were in a rectangular shape. The chemical constituents of determined zones called "a" and "b" were analyzed by SEM-EDS. The results are given in Table 4. The major elements of zone a are phosphorus, magnesium, nitrogen and oxygen, while the major elements of zone b are phosphorus, magnesium, nitrogen, oxygen, silica and calcium in the dried precipitates.

4. DISCUSSION

The Box-Benhken Experimental Design was used to determine the effects of pH, pumice amount and temperature on PO_4-P, NH_4-N, and Mg removals in the model reactor. A quadratic model was employed at the

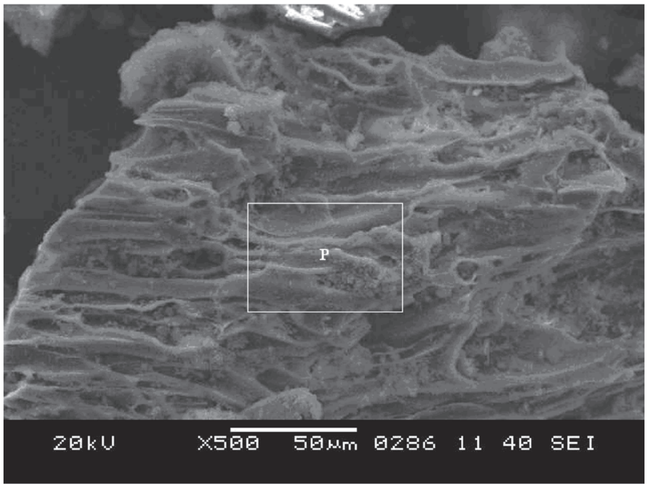

Figure 4. *Scanning electron micrograph of pumice stone (500×).*

Table 4. Components of dried precipitates taken at scanning electron micrograph.

Element's Name	Chemical constituents of a zone	Chemical constituents of b zone
O	46.189	45.148
Mg	21.291	11.675
Al	0.033	0.833
Si	–	4.618
P	27.346	12.309
Na	0.277	0.834
K	0.011	0.358
Ca	0.287	3.418
N	4.362	2.838
Cl	0.064	0.163
Fe	0.140	0.186

lowest standard deviation, highest R-Squared, and lowest press value ANOVA regression analysis as the result of the evaluation of PO_4-P, NH_4-N, and Mg removal.

It was observed that the temperature, pH, and pumice amount have a positive effect on phosphorus removal. Regy et al. [1] pointed out that an optimum pH exists to precipitate struvite which is in the pH range of 7 and 11. The minimum solubility in the wastewater is around pH 9 [1]. In another study, Song et al. stated that the optimum pH value was at the range of 9.5–10.5 and the highest P removal efficiency of 93% was obtained [16]. Similarly, the best phosphorus removal was detected at pH 9 and 10 values in this study. The variations of temperature and pH have been significantly affected by ammonium removal similar to phosphorus removal. The maximum ammonium removal was obtained at pH 9 while minimum removal was at pH 7. Although temperature and pH are very effective, the pumice amount has a negative effect on magnesium removal. The best magnesium removal was achieved at pH 11 contrary to phosphorus and ammonium removal. It can be seen that temperature in the model reactor is the main parameter affecting phosphorus, ammonium and magnesium removals. The phosphorus removal was affected in progressive stages with increasing temperature at constant pH 9 and reached to %100 at temperatures greater than 25°C. It was observed that 1–10 g pumice amount have a positive effect and pumice amount greater than10 g was negatively affected on phosphorus removal for all temperatures levels. The ammonium removal was significantly affected with the increasing temperature at constant pH 9 and no effective change has been detected on ammonium removal beyond 25°C. Ammonium removal was not significantly affected with the increasing pumice amount at 25°C. Magnesium removal significantly increased with the increasing temperature in the model reactor, but decreased slightly with the increasing of pumice stone. It was observed that the best combination of independent variables to maximize the dependent variables is pH value 9.5, pumice amount of 12.9 g, and temperature of 29°C.

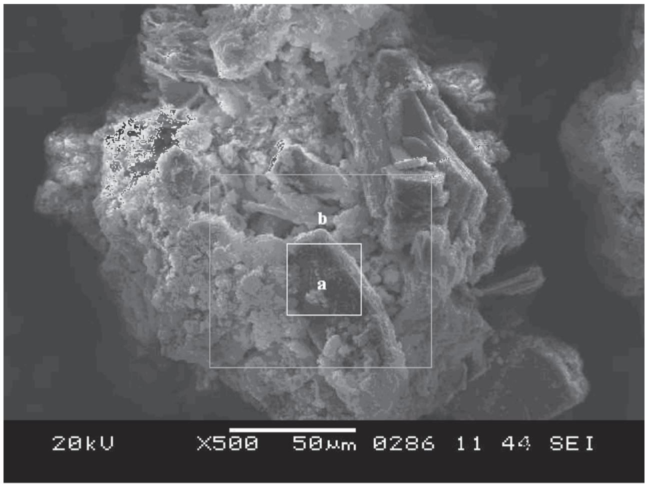

Figure 5. *Scanning electron microphotograph of dried precipitate (500×).*

In recent years, various seeding materials were used in struvite precipitation. For example, the performance of a stainless style mesh system acting as a seed substrate for struvite cystallization in synthetic liquors was investigated by Le Corre et al. [17]. The study conducted by Shimamura et al. presented results for new MAP crystals used as seeding material for struvite particles precipitation on seeding material [18].

In this study, pumice stone was used as seeding material. SEM micrographs of dried precipitates showed that the rectangular shape precipitates occurred on the pumice surface. The major elements were found as phosphorus, magnesium, nitrogen, and oxygen at zone a of these dried precipitates. Beyond them, the major elements of all precipitates (zone b) were phosphorus, magnesium, nitrogen, oxygen, silica, and calcium.

The concluding remarks from this study are given below:

- Predicted values of dependent variables were in good agreement with the observed values at Box-Behnken Experimental Design.
- Temperature and pH in the model reactor are the main parameters affecting phosphorus, ammonium, and magnesium removal.

- Pumice amount was slightly affected the phosphorus, ammonium, and magnesium removal.
- Good phosphorus removal could be achieved using pumice stone as crystal seeding. It was observed that the struvite crystals were precipitated on pumice stone.

5. ACKNOWLEDGEMENTS

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The Financial Feasibility of the Phytoremediation Technology: Assessment of Remediation by Sideritis Galatica, Poplar and Willow

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ABSTRACT: Phytoremediation is a process which uses several plants to remove the pollutants from water and soil to reduce, completely extract, control or immobilize them. The plants used for this reason are referred to as the hyperaccumulators. Metal accumulation can occur in several different families from small annual grass to perennial bushes and trees. For remediation or cleaning of the soils polluted with heavy metals, the ideal plant species are the ones which can produce high amounts of biomass and can accumulate and tolerate the pollutants.

In this research, Cd and Zn metals which occurred because of industrial wastes are observed in the roots of Phragmites Australis, Cyperace carex, Sideritis galatica and Compositae cardueae plants in Kucukcekmece region. Among these, Sideritis galatica was found to be the most beneficial plant for remediation. Furthermore, it was observed that the Kucukcekmece region is also suitable for growth of willow and poplar trees. This study includes a financial feasibility analysis that determines the monetary benefit of phytoremediation as well as the environmental advantages. The financial outputs are compared by the net present value model and internal rate of return approaches.

INTRODUCTION

NATURAL systems have been polluted by the combined action of modern agriculture, increased industrial activity, and rapidly growing global population. Soil pollution has begun to be another environmental problem. Soils are polluted by the actions such as the usage of commercial fertilizers, pesticides, soil regulators and hormones to increase the amount and quality of agricultural production; discharges of soil and liquid wastes, sludge applications, usage of polluted waters in agricultural irrigation, and atmospheric precipitations and radioactive sprays (Chen, et al., 2000). For that reason, the ability of our soils to be used for fertile and non-problematic use is becoming narrow and this problem has been increasing. In addition, free pollutants like asbestos constitute another problem in soil pollution.

Cadmium and zinc are two elements whose chemical properties resemble each other and thus, cadmium can behave similar to zinc regarding the intake and metabolic functions (Mengel and Kirkby, 1987). Cadmium and zinc are hazardous heavy metals for the environment. Excessive amounts of zinc in the soil are toxic for plants and microorganisms. The mobility of zinc increases when the acidity of soil goes down pH 5.5. Cadmium is a powerful toxin for plants, animals and humans by impairing the enzymatic activity (Caliskan, 2007). It is the second most toxic heavy metal after lead. It causes diabetic renal complications, high blood pressure, osteoporosis, renal calculi, leukemia, and carcinogenic activities in some organs like the lungs, kidney, urinary bladder, pancreas, breasts and prostate (Saffron, 2001; Schwartz and Reis, 2000). This heavy metal mostly accumulates on kidneys, lungs, liver, thyroid gland and placenta (Muler, et al., 1998; Starug, et al., 2000). The negative effect caused by cadmium to the immune system is explained by impairing zinc metabolism in the body (Buchet, 1990). In addition to their useful effects, the majority of metals, especially the heavy metals, are toxic to plants and they cause the death of the plant. The extent which the metals behave as toxic is quite variable regarding the plant species and the metal

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in question. The toxic effects of heavy metals (Pb,Zn, Cd, Cu) contamination in the vegetables were investigated (Marshall and Agarwal, 2003).

The first applications of phytoremediation started in the 1990s and artificial marshy areas and oil spillage areas were investigated (USEPA, 2000). The main idea of this application is to use several plants to remove pollutants from water and soil by extracting completely, controlling, or immobilizing them (Salt, et al., 1998; Salt, et al., 1995). The plants used for this purpose are referred to as hyperaccumulators. Metal accumulation can occur in several different families like small annual grass to perennial bushes and trees. For remediation or cleaning of the soils polluted with heavy metals, the ideal plant species are the ones which can produce high amounts of biomass, and can accumulate and tolerate the pollutants (Wu, et al., 2007). However, this combination may not always be possible. It may require choosing plants with hyperaccumulation ability combined with poor biomass (or vice versa), and forsaking something in order to receive another effect. In addition, growing hyperaccumulative plants only in the polluted area may also result in a potentially hazardous biomass production. To receive a pollutant from soil, the plants must find acceptable soil conditions. The most important parameter in this subject is the soil pH value. There are, however, many other factors affecting the heavy metal intake capacity of the plant (Martens and Boyd, 1994; Fergusson, 1990). After gaining mobility, the elements are retarded by the root cells of the plant. They are first bound to the cellular wall, then pass through the membrane with transport systems and intracellular binding regions. It is considered that the intake of element ions is carried out by the channel and/or carrier proteins. The negative charge of inner plasma membrane provides a way for cation intake (USDA, 2000).

Toxic symptoms observed with excessive heavy metal presence is caused by interactions on a cellular and molecular level. In addition, oxidative stress originating from this excess amount of heavy metals is caused by the promotion of free radicals and reactive oxygen species (Clemens, et al., 2002). The heavy metal-tolerant plants can be classified as the plants that can most successfully survive in toxic soils. This is possible with an interaction between the environment and the plant genotype (Hall, 2002).

The suitability of deep-planted hybrid poplars for phytostabilization of a heavy metal-contaminated site was investigated. Zinc, Cd, and Pb were found as high as 3,606, 44, and 33 mg/kg, respectively in leaves and there was little influence of manure amendment or specific hybrid. Average metal concentrations in plant tissues followed the order: leaves > bark > twigs > wood for Zn and Cd, and bark > wood > twigs > leaves for Pb (Kocaer and Baskaya, 2003).

Felix (1997) reported *Salix viminalis* had the highest metal-accumulating ability of the various plants tested: it achieved a transfer coefficient of 3.4 for Cd in a field trial on a contaminated soil. However, the calculated 77 years to decontaminate the soil used in this study to acceptable Cd concentrations were not practicable, highlighting the limitations of yields and/or metal uptake rates to phytoextraction as a remediation tool (Pierzynski, et al., 2002). A characteristic of willow, which makes it a very suitable tree for use in phytoremediation, is that it can be frequently harvested by chopping, yielding as much as 10–15 dry t ha^{-1} $year^{-1}$ (Riddell-Black, 1993).

McGregor et al., (1996) noted that changes in Zn concentrations within tree tissue in different parts of the growing season suggested an optimum harvest time would be during winter, fitting in well with usual chopping practice. However, calculation of the time required to reduce the zinc concentration in the soil to acceptable levels suggest that the timescale is too long (approximately 800 years in this case).

In this investigation, a study area with ca. 6 km Kuçukçekmece (Istanbul) Lake border was chosen, which also embraces the Istanbul University Avcilar campus and Avcilar military region. The purpose of this study is to make a comparative financial analysis of remediation function by poplars, willow and Sideritis galatica. Each element has different economic life and financial benefit.

INVESTIGATED AREA

Kucukcekmece Lake is a lagoon lake situated at the northern side of Marmara Region, 15 km west of the city center and whose length is ca. 7500 m and width is 900 m (at the narrowest place) and 4500 m (at the broadest place). The industrial and residential activities around the lake have grown very rapidly. The south-eastern region of the lake (close to the Marmara Sea) contains a dense residence area. The lake is connected with three rivers to the north and east. It has also a short connection to the Marmara Sea (Figure 1). The total drainage area belonging to the Kucukcekmece Lake is estimated to be 5600 ha and the connecting

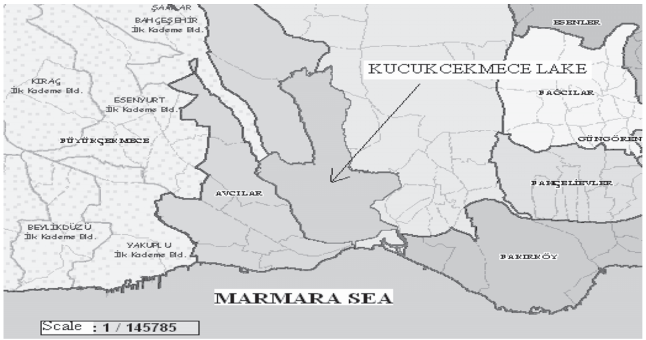

Figure 1. *Map of investigated area.*

rivers have the following areas: Ispartakule river, 15700 ha, Sazlidere, 8400 ha, Meneksedere (Nakkasdere), 4300 ha, all of which add up to an area of 34000 ha. This area has a slope of ca. 5%. The height is zero from the coast, but 100 m in Sazlidere. The vegetation is mainly composed of grass, but there are bare areas as well. The lake is fed from the sea according to the meteorological conditions, and from the land with the involvement of fresh water transported from the stream. Sazlidere is the most important stream feeding the lake.

PHYTOREMEDIATION IN THE KUCUKCEKMECE REGION

Previous studies of Sahmurova, et al., 2007 indicate that Siderites galatica, Compositae cardueae, Phargmites australis and Cyperace carex are found out to have beneficiary effects for remediation. In their studies, Cd and Zn contents were monitored for a 3-month period on samples taken from these plant species and on soil specimens taken from the roots of these plants. In order to determine the phytoremediation performance, the plants, collected in December, March and May, were examined in terms of Cd and Zn concentrations on their roots, stems and leaves. They were also measured on the soil and lake water. The plant and soil samples obtained from the land were sampled and the heavy metal analyses were carried out with ICP (ICP-OES, Perkin Elmer, Optima 2100DV). It was found that Sideritis galatica is the best plant in terms of storing cadmium and zinc on its leaves and in its stem, respectively as exhibited in Tables 1–3.

The current literature concerning the concentration interval of heavy metals in soil reveals that cadmium is present in soil between 0.005–181 ppm (Alloway, 1990; Brummer, et al., 1991; Leita, et al., 1989). Cadmium concentration in plants varies in 0.1–1 ppm range. Tables 1–3 show that cadmium level in the studied plants was between 0.12–0.34 ppm, whereas the range in the soil was 0.21–0.51 ppm. The values for zinc were given by (Bergmann, 1993) and the allowable maximum Zn value is for fresh weight 5 and 15 ppm for fruits and vegetables, respectively. The tolerable and excessive Zn amounts for tomato leaves as dry matter was measured to be 21–120 ppm and 120 ppm, respectively. The allowable zinc concentration for tomato fruit however remains controversial; one group measured 24–28 ppm (Moauro, et al., 1993) whereas another group reported 12–67 ppm (Hobson and Davies, 1971). Tables 1–3 indicate that the heavy metal concentrations in our study lie within the 0.15–1.01 ppm range.

The purpose of this research is to conduct the feasibility analysis of phytoremediation. Beyond Sideritis galatica, the investigated area, Kucukcekmece Lake Border is observed to be suitable for willow and poplar growth. Willow and poplar trees are widely used for remediation. These two tree species grow near by water rapidly. Below, the comparative feasibility analysis is conducted.

FINANCIAL FEASIBILITY OF PHYTOREMEDIATION FUNCTION

This study was designed to determine the most beneficial phytoremediation tool with regard to financial aspects. Poplar, willow and Sideritis galatica are three plants that are highly effective in remediation in the Kucukcekmece region. In this part of the study, the cash flows are computed for each of poplar, willow and Sideritis galatica. The cash flows are then used to estimate the net present value and internal rate of return of each alternative. The sales revenues generated at the end of the economic life of each organism constitutes the cash inflows, while the cash outflows include the establishment of plantation, planting, irrigation, trimming, labor and utilities costs. The financial analysis is profiled for an area of one hectar. The number of poplar, willow and Sideritis galatika is computed and the costs and revenues are estimated. The financial inputs for each alternative are exhibited below.

Remediation by Poplars

The cost for each young poplar is $10.96. The number of poplars planted in an area of one hectar is computed as 300 trees. Each tree has a volume of 0.416 m^3 which makes a total of 124.8 m^3 for each hectar. A poplar tree becomes ready for sale in 12 years. If the tree is not cut on the 12th year, the total volume increases by 39 m^3 per

Table 1. Heavy metal analysis results for soil and plant samples collected in December.

	Phragmites australis		***Cyperace carex***		***Sideritis galatica***		***Compositae cardueae***	
	Cd ppm	**Zn ppm**	**Cd ppm**	**Zn ppm**	**Cd ppm**	**Zn ppm**	**Cd ppm**	**Zn ppm**
Soil	0.14	0.55	0.31	0.21	0.31	0.90	0.40	1.20
Root	0.25	0.34	0.27	0.18	0.28	0.86	0.22	0.90
Body	0.20	0.47	0.11	0.47	0.50	0.94	0.24	0.76
Leaves	0.28	0.88	0.09	0.32	0.27	0.87	0.14	0.62

Table 2. Heavy metal analysis results of plant and soil samples for March.

	Phragmites australis		***Cyperace carex***		***Sideritis galatica***		***Compositae cardueae***	
	Cd ppm	**Zn ppm**	**Cd ppm**	**Zn ppm**	**Cd ppm**	**Zn ppm**	**Cd ppm**	**Zn ppm**
Soil	0.27	1.02	0.42	0.52	0.41	0.70	0.51	1.12
Root	0.16	0.94	0.32	0.42	0.22	0.62	0.34	0.99
Body	0.14	0.82	0.21	0.30	0.17	0.38	0.24	0.82
Leaves	0.12	0.66	0.11	0.18	0.10	0.15	0.13	0.62

Table 3. Heavy metal analysis results for plant and soil samples collected in May.

	Phragmites australis		***Cyperace carex***		***Sideritis galatica***		***Compositae cardueae***	
	Cd ppm	**Zn ppm**	**Cd ppm**	**Zn ppm**	**Cd ppm**	**Zn ppm**	**Cd ppm**	**Zn ppm**
Soil	0.25	1.00	0.31	0.41	0.31	0.46	0.21	0.51
Root	0.19	0.91	0.27	0.31	0.17	0.36	0.19	1.35
Body	0.15	1.01	0.19	0.95	0.21	0.63	0.18	0.30
Leaves	0.12	0.98	0.15	0.52	0.24	0.37	0.10	0.25

Table 4. Costs for Poplar.

Process	**Times cost items appear per year**	**Year process occurs**	**Cost per ha per year (for the first year of process)**	**Expected inflation in costs**
Establishment of plantation	1	1st year	381	–
Labor and utilities for planting	1	1st year	381	–
Labor and utilities for irrigation	1	Each year	212	4%
Labor and utilities for trimming	1	2nd through 25th years	616	4%
Labor and utilities for budding	1	25th year	719	–

Table 5. Costs for Sideritis galatica.

Process	**Times cost items appear per year**	**Year process occurs**	**Cost per ha per year (for the first year of process)**	**Expected inflation in costs**
Establishment of plantation	1	1st year	285	–
Labor and utilities for planting	1	1st, 10th and 20th years	356	–
Labor and utilities for irrigation	3	Each year	712	4%
Labor and utilities for trimming	3	Each year	178	4%

each waiting year for one hectar area. One hectar of poplar (300 trees) are expected to be sold at a price of $125,000. Other costs are exhibited in the Table 4.

The labor and utilities cost for irrigation and trimming are expected to increase by 4% per year. The tax rate is 8%.

Remediation by Willow

The cost for each young willow is $7.32. The number of willows planted in an area of one hectar is estimated as 300 trees. One hectar of willows (300 trees) are expected to be sold at a price of $82,000. The costs for establishment of plantation, labor and utilities for planting, irrigation and trimming are as same as poplar trees (Table 4). The only difference is willows are used as decorative elements. Thus, there is not a need for budding. The labor and utilities cost for irrigation and trimming are expected to increase by 4% per year. The tax rate is 8%.

Remediation by Sideritis galatica

The species *Sideritis* galatika is a member of Labiatae family and is common in mainly Western and Southern Anatolian regions. There are about 40 species of this type growing in Turkey with a high endemism ratio. It blossoms between July and September. The plant is light green or yellowish in color, perannial, and has a simple or branched structure. Sideritis galatica is a convenient plant to be used for remediation process for Kucukcekmece region. 420 Sideritis galatika can be planted for a one hectar of land. The cost for each Siderites galatika is $3.66. It has an economic life of 9 years. Thus, once in every 9 years the plants should be changed. These plants are used in pharmaceutical sector. However, the plants grown for avoiding heavy metals are not allowed from "Ministry of Health" to be used in pharmaceutical productions. Thus, it is not expected to generate any revenue with the siderites. The other costs are exhibited in the Table 5.

The labor and utilities cost for irrigation and trimming are expected to increase by 4% per year. The tax rate is 8%.

The net present value and the internal rate of return of the projects can be employed as good indicators of viability of projects in decision making. The feasibility analysis should provide a positive net present value and a rate of return greater than the respective cost of capital. Net present value is the present value of future net cash flows discounted at the cost of capital of the project. The model is stated below.

$$NPV = \sum_{t=1}^{T} \frac{C_t}{(1+r)^t} - C_0$$

Where C_t is the cash flow at time t, C_0 denotes the initial investment and r is the weighted average cost of capital. The feasibility includes dollar amounts of all cash flows. Thus, "r" is accepted as interest rate for US dollars.

To implement the NPV model, the net cash flows of the project should be estimated. All forecasted expenses are subtracted from all forecasted revenues to obtain the annual net income. The rationale for the NPV method is very straightforward. An NPV of zero signifies that the project's cash flows are exactly sufficient to cover the opportunity cost of the capital invested. If a project has a positive NPV, then it generates more cash than the opportunity cost of capital, leaving excess cash. The other approach to identify the rationality of a project is to compute the internal rate of return. Internal rate of return (IRR) is the discount rate that equates the present value of future cash inflows to the project cost.

Table 6. Financial Outputs of phytoremediation function.

	Net Cash Flows		
Year	**Poplar**	**Willow**	**Sideritis galatika**
0	–4,261	–3,163	–2,890
1	–847	–847	–918
2	–881	–881	–955
3	–916	–916	–993
4	–953	–953	–1,033
5	–991	–991	–1,074
6	–1,031	–1,031	–1,117
7	–1,072	–1,072	–1,162
8	–1,115	–1,115	–1,208
9	–1,159	–1,159	–1,257
10	–1,206	–1,206	–3,703
11	–1,254	–1,254	–1,359
12	–1,200	–1,200	–1,301
13	–1,248	–1,248	–1,353
14	–1,298	–1,298	–1,407
15	–1,350	–1,350	–1,463
16	–1,404	–1,404	–1,522
17	–1,460	–1,460	–1,582
18	–1,518	–1,518	–1,646
19	–1,579	–1,579	–1,711
20	–1,642	–1,642	–4,205
21	–1,708	–1,708	–1,851
22	–1,776	–1,776	–1,925
23	–1,847	–1,847	–2,002
24	–1,921	–1,921	–2,082
25	112,341	73,442	–2,166
NPV ($)	**11,661**	**1,767**	**–22,843**
IRR	**8%**	**6%**	**–**
r	**5%**	**5%**	**5%**

The formula for this is presented below.

$$\text{Initial Investment} = \sum_{t=1}^{N} \frac{C_t}{(1+IRR)^t}$$

Where C_t is the cash flow at time t, IRR is the internal rate of return, N is the number of years in project life.

The IRR on a project is its expected rate of return. If the IRR exceeds the cost of funds used to finance the project, a surplus remains and accumulates for the firm's stockholders. Therefore, projects with an IRR higher than r (as presented above) should be accepted. The net cash flows generated remediation by poplar, willow and Sideritis galatika are illustrated in Table 6. The computation details are exhibited in appendices A-C.

When the financial profiles are compared, beyond the environmental aspects, poplar trees also provide financial benefits. If Siderites galatica is used for phytoremediation, the NPV of this alternative is negative which indicates that this project even does not compensate the costs. The NPV of phytoremediation by willow is $1,767 while the rate of return is 6% that exceeds the cost of capital of 5%. Finally, poplar trees are more financially viable than willow and siderites since the project earns an additional of $11,661 and 8% rate of return.

CONCLUSIONS

The main source of heavy metal for plants is the flora, that is, soil, feed liquor, and air. The most important factor determining the biological intake possibility of a heavy metal is its attachment or adsorption onto the soil elements. The biological intake capacity of heavy metals coming from emission sources via atmospheric means plays an important role. Plants are more sensitive to excessive amounts of Zn and Cd than the animals. Therefore plants can be used as an indicator for alerting against possible dangers for humans and animals. The high concentrations for humans and animals can be tolerated by the plants quite efficiently.

The purpose of this study was to determine if the government authorities responsible for environment protection may have a financial benefit from using phytoremediation. The study covers the remediation of Kucukcekmece Lake border area by willow, poplar and Siderites galatica. Poplars are used for wood industry

Appendix A. Estimation of Cash Flows for Poplar.

	Year					
	1	2	3	. . .	24	25
Revenues from sale of poplars	0	0	0		0	125,000
Costs for poplars ($10.96*300)	3,295	0	0		0	0
Costs for establishment of plantation	381	0	0		0	0
Labor and utilities for planting	381	0	0		0	0
Labor and utilities for irrigation	203	221	220		521	542
Labor and utilities for trimming	0	636	661		1,567	1,629
Labor and utilities for budding	0	0	0		0	719
Gross Income	0	0	0		–2,088	122,110
Tax (8%)	0	0	0		–167	9,769
Net Income	4,261	847	881		–1,921	112,341
Net Cash Flows	–4,261	–847	–881		–1,921	112,341

Appendix B. Estimation of Cash Flows for Willow.

	Year					
	1	2	3	. . .	24	25
Revenues from sale of willow	0	0	0		0	82,000
Costs for willows ($7.32*300)	2,197	0	0		0	0
Costs for establishment of plantation	381	0	0		0	0
Labor and utilities for planting	381	0	0		0	0
Labor and utilities for irrigation	203	221	220		521	542
Labor and utilities for trimming	0	636	661		1,567	1,629
Gross Income	0	0	0		–2,088	79,829
Tax (8%)	0	0	0		–167	9,769
Net Income	3,163	847	881		–1,921	73,442
Net Cash Flows	–3,163	–847	–881		–1,921	73,442

Appendix C. Estimation of Cash Flows for Sideritis galatica.

	Year								
	1	**2**	**. . .**	**10**	**. . .**	**20**	**. . .**	**24**	**25**
Costs for Sideritis galatica ($3.66*420)	1,538	0		1,691		1,861		0	0
Costs for establishment of plantation	356	0		392		431		0	0
Labor and utilities for planting	285	0		313		345		0	0
Labor and utilities for irrigation	712	740		1,054		1,560		1,825	1,898
Labor and utilities for trimming	0	178		253		375		439	456
Gross Income	0	0		0		4,570		–2,263	–2,354
Tax (8%)	0	0		0		366		–181	–188
Net Income	2,890	918		3,703		4,205		–2,082	–2,166
Net Cash Flows	–2,890	–918		–3,703		–4,205		–2,082	–2,166

and willows are used as decorative elements. Both of these trees have monetary benefits as well as remediation function. Sideritis galatica is a cheaper investment for remediation process. Although this plant may be used in pharmaceutical industry, the Ministry of Health of Turkey does not allow the ones used in heavy metal sorption. Thus Siderites galatica does not have financial benefit but can only be used in remediation.

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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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