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Modeling the pH-mediated Extraction of Ionizable Organic Contaminants to Improve the Quality of Municipal Sewage Sludge Destined for Land Application

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Abstract

A model was developed to assess the impact of adding acids and bases to processed municipal sewage sludge (MSS) to mobilize contaminants, facilitating their removal from sludge by flushing prior to land application. Among 312 organic contaminants documented to occur in U.S. MSS, 71 or 23% were identified as ionizable organic contaminants (IOCs), contributing a disproportionately large fraction of 82% of the total mass of sludge-borne contaminants. Detected IOCs included 57 pharmaceuticals and personal care products, 12 perfluorinated compounds, one surfactant and one pesticide. Annually, about 2,000 t of IOCs were estimated to be released to U.S. soils via land-application of MSS. A partitioning model developed to assess the impact of pH on hydrophobic sorption revealed that between 36 and 85% of the mass of individual classes of IOCs potentially could be desorbed from MSS via pH adjustment and flushing. Thus, modeling results suggest that a sequential pH treatment [acidic (~pH 2) followed by basic (~pH 12) treatment] has the potential to reduce the burden of harmful IOCs in MSS applied on U.S. land by up to 40 ± 16 t annually. This approach may serve as a cost-effective treatment process that can be implemented easily in existing sludge treatment infrastructure in the U.S. and worldwide, serving to significantly improve the quality of MSS destined for land application.

Graphical Abstract

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Keywords

Sewage sludge; Biosolids; Ionizable Compounds; Sludge Treatment; Partitioning Model

1. INTRODUCTION

Continuing growth of the U.S. population is creating an increased demand for wastewater treatment capacity. Consequently, the amount of municipal sewage sludge (MSS) produced will increase in the foreseeable future. In 2004, the U.S. EPA estimated that approximately 6.5 million metric tonnes (t) of MSS are produced each year in the U.S. (NEBRA, 2007). About 55% of MSS is estimated to be applied on land for beneficial purposes, totaling approximately 3.6 million t of MSS each year. Treated MSS fit for land application (also termed *biosolids*) is rich in organic carbon content and nutrients that can improve soil properties, crop productivity and fertility (Smith, 1995; Wang et al., 2008). A Life Cycle Assessment (LCA) performed on different treatment and disposal scenario of MSS showed that the combination of anaerobic digestion and agricultural land application was the most viable option creating lower costs and consuming less energy compared to other treatment and disposal options (Suh and Rousseaux, 2002). Landfilling of MSS is becoming difficult due to limited land availability, increased compliance costs, and concerns regarding leachate and greenhouse gas emissions from methane production (Wang et al., 2008). Incineration of MSS, on the other hand, involves high operational costs and concerns over toxic flue gas emissions (Lundin et al., 2004). Recent efforts in using MSS as a resource for energy production and nutrient recovery have increased the beneficial value of MSS (Rulkens, 2007; Venkatesan et al., 2015; Wang et al., 2008). Beneficial use of MSS already is applied to over half of the total U.S. sewage sludge mass and this trend is expected to increase in future.

However, a notable downside to the beneficial use of MSS is the presence of persistent (P), bioaccumulative (B), and toxic (T) chemicals, toxic metals and pathogens, all known to pose significant environmental and human health concerns (Chaney et al., 1996; Dowd et al., 2000; Gerba et al., 2002; National Research Council, 2002). The number of hazardous chemicals detected in MSS is considerable and constantly increasing (U.S. EPA, 2009; Venkatesan et al., 2014a, 2014b). Many of these contaminants are known endocrine disruptors, carcinogens and potent toxicants to aquatic organisms and humans. In addition, a new emerging concern is the presence in MSS of significant quantities of important antibiotics (e.g., ciprofloxacin) that are known to promote antibiotic resistance in human pathogens even when present at nontherapeutic concentrations (Martins da Costa et al., 2006; Pruden, 2013; Reinthaler et al., 2003). Prior screening for 239 contaminants in nationally representative samples of MSS collected from more than 160 U.S. WWTPs, showed the presence of 130 contaminants of emerging concern (CECs) in U.S. biosolids with detection frequency varying between 20 and 100% in the samples analyzed (Venkatesan et al., 2014a,b). Chemicals detected were calculated to contribute about 0.04–0.15% of the total dry mass of MSS produced in the U.S. annually, a mass equivalent to 0.4–1.5 g/kg of dry MSS or about 4,700 t (range: 2,600–7,900 t) of chemicals annually. Many of these contaminants are known to leach out from land-applied MSS to contaminate water

resources. Studies have shown contamination of groundwater, surface water, and uptake of CECs by agricultural crops from soils amended with MSS (Clarke and Smith, 2011; Lapworth et al., 2012; Sepulvado et al., 2011; Wu et al., 2010; Xia et al., 2010). Nonylphenol and their ethoxylates (NP & NPEOs), perfluorinated compounds (PFCs) and pharmaceuticals and personal care products (PPCPs) have been shown to leach from MSS at significant concentrations (Edwards et al., 2009; La Guardia et al., 2001; Lindstrom et al., 2011; Sepulvado et al., 2011). PFC concentrations in well water and surface water resulting from contaminant leaching from nearby fields amended with MSS were shown to be in excess of U.S. EPA's health advisory level for drinking water (Lindstrom et al., 2011). This brings up the important question of what fraction of the estimated contaminant load of 4,700 t can readily leach from land-applied MSS to contaminate surrounding water resources?

One of the factors that influence water solubility and mobility (leachability) of organic contaminants from MSS is the pH of the environment. This is especially the case for ionizable contaminants (like PFCs and several PPCPs including antibiotics) that are prone to leach out of MSS under acidic or basic pH conditions, depending on the compounds' physical-chemical properties (e.g., ionization constants or pK_A). The hydrophobic sorption behavior of neutral compounds on the other hand is constant, irrespective of pH. Hence, adjusting the pH of MSS has the potential to mobilize these ionizable organic contaminants (IOCs) that can then be extracted by flushing and removed prior to land application. Adjustment of sludge pH to a value of greater than 12 via lime addition is a common process for sludge stabilization and has been employed in WWTPs for more than four decades (U. S. EPA, 1979). However, this treatment is currently focused only on a reduction of the pathogen content of MSS. The secondary, major benefit of mobilizing IOCs during lime stabilization has not yet been evaluated and utilized to date and, as practiced today, the lack of sludge flushing after lime treatment prevents successful removal of pollutants prior to disposal. Moreover, certain IOCs require a shift to low or acidic pH to become mobilized, a process that is not commonly used for MSS stabilization. Current safety assessments of land-applied MSS are incomplete, as this information is not currently available. The objectives of the present study were to: (i) perform a meta-analysis of contaminants detected in nationally representative samples of MSS to identify the fraction of IOCs sequestered in U.S. sludge; (ii) model the sorption behavior of sludge-borne IOCs as a function of pH; (iii) estimate nationwide inventories of IOC removal from MSS by pH adjustment, and (iv) forecast future opportunities of pollution prevention from MSS using population growth predictions up to the year 2060.

2. MATERIAL AND METHODS

2.1. Meta-analysis of contaminants in U.S. MSS

In order to obtain an unbiased estimate of the fraction of IOCs detected in U.S. MSS, contaminant data were collected and compiled from the U.S. EPA's national sewage sludge surveys and from the analysis of the U.S. national sewage sludge repository (NSSR) samples at Arizona State University (U.S. EPA 2007, 2009; Venkatesan et al., 2014a). These representative samples were collected from more than 160 WWTPs across the contiguous United States. The facilities were statistically selected by U.S. EPA to represent the more

than 16,000 WWTPs that are operational in the U.S. to provide unbiased estimates of contaminant levels in U.S. MSS. To date, a total of 429 legacy and emerging organic contaminants have been screened for in these nationally representative samples. Chemicals included in the screening were chlorinated dioxins and furans (Cl-D/F), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), pharmaceuticals and personal care products (PPCPs), brominated flame retardants (BFRs), perfluorinated compounds (PFCs), hormones, alkylphenols and their ethoxylates, brominated dioxins and furans (Br-D/F) and nitrosamines. Physical-chemical properties for all detected contaminants were obtained from SciFinder scholar (American Chemical Society).

2.2. Sorption model

A mathematical model based on the chemical sorption equation was used to estimate the fraction of IOCs that can be potentially desorbed from MSS at different pH levels (see supplementary section S1). In order to account for feasibility of the process, only IOCs featuring a pK_a value in the range of 3 to 10 were considered for this model. The fraction of IOCs sorbed onto MSS (f_s) was modeled for any given value of pH-adjusted distribution coefficient (D) using the following modified sorption equation (derived from (Fjeld et al., 2007)):

$$f_s = \frac{D\rho s_f}{1 + D\rho s_f} \quad (1)$$

Where ρ is the density of MSS, s_f is the solids fraction of sludge (the product of ρ and s_f being the sludge solids concentration) and assuming that the contaminants partition onto the total (organic and inorganic) solids fraction. A typical value of $\rho = 1.55 \text{ g/cm}^3$ was used for digested MSS (O'Kelly, 2005). A typical average value of 10% of solids ($s_f = 0.1$) in treated MSS for disposal was used for the model. In case of chemicals with multiple pK_a values, only values within 3 and 10 were considered for modeling purposes. Average pH of MSS can vary between 6 and 8 depending on the type of sludge processing technique (e.g. lime treated sludge can have pH >9). A typical pH of 7.5 was used as the reference pH of MSS to estimate the relative amount of sorption/desorption of contaminants as a function of sludge pH change.

3. RESULTS AND DISCUSSION

3.1. Ionizable organic contaminants in U.S. MSS

Among 429 organic chemicals screened for in U.S. MSS samples, 312 or 73% of the chemicals were detected. The sum of average concentration of 312 chemicals was 727 (sum of minimum: 412; sum of maximum: 1235) mg/kg dry weight (dw) of sludge. A nationwide extrapolation of these levels (considering 6.5 million t of MSS generated in the U.S. per year) yielded approximately 4,750 (range: 3300 to 8000) t of chemicals sequestered in sludge each year. The lack of transformation of these contaminants during optimized biological wastewater treatment and sludge treatment processes (e.g., activated sludge treatment followed by anaerobic digestion), indicates a strong persistence and resistance to biotransformation of these compounds upon release into the environment (Venkatesan and

Halden, 2014a). Out of the 312 contaminants, only 71 (23%) chemicals were identified as ionizable (Figure 1A). Interestingly, these chemicals made up 82% of the total mass of chemicals sequestered in U.S. MSS [594 (range: 440 to 945) mg/kg dw] (Figure 1B). Detected ionizable compounds included 57 PPCPs, 12 PFCs, one surfactant and one pesticide (see Supplemental Table S1), and the annual load of IOC in U.S. MSS are estimated to exceed 3,800 t annually. A breakdown of important class of chemicals falling into this category show that antibiotics alone represent 20% of total IOCs by number (Figure 1C). Of this quantity, 55% is land-applied which means more than 2,000 t of ionizable compounds per year is applied on U.S. soils. Considering a typical average MSS land application rate of 16.8 t/ha (7.5 ± 2.5 dry U.S. tons per acre), this value translates to about 10 (range: 7.4 to 16) kg of IOCs applied per hectare of agricultural land.

3.2. Modeling sorption of IOCs as a function of pH

Out of the 71 detected IOCs, 52 chemicals had at least one of their pK_a value within the range of 3 to 10 and their sorption behavior was modeled using equation 1 (Figure 2). The relative fraction sorbed is defined here as the amount of chemical sorbed on to the sludge at a given pH relative to the initial amount sorbed to the sludge at ambient pH value (in this case pH of 7.5). As shown in Figure 2, the sorption of acids decreases and of bases increases with increasing pH. The sorption behavior is complex for chemicals with multiple pK_a values, and in general peaks in the neutral pH range (7), and drops with increasing acidic or basic pH conditions. The model revealed that between 36 and 85% of the mass of individual classes of IOCs potentially could be desorbed due to ionization forced by adjustment of the typical pH value of 7.5 in MSS. However, this model accounts only for hydrophobic sorption of contaminants and does not include other mechanisms like electrostatic attraction that explains sorption behavior of many ionized compounds (e.g., PFCs and antibiotics). An overall desorption of 30% of IOCs by mass at acidic pH (<3) and 31% of IOCs at alkaline pH (>12) could be achieved by pH adjustment. Depending on the initial sludge pH, a combination of acidic and basic pH treatment could result in desorption of >40% of IOC mass detected in sludge (Figure 3). This estimate is conservative, as it considers only IOCs with pK_a values between 3 and 10 and known contaminants; whereas IOCs featuring a very low pK_a value and those that electrostatically sorb onto solids also potentially can desorb following pH adjustment, as demonstrated for pharmaceuticals and PFCs (Chen et al., 2011; Wang and Shih, 2011). The model results also highlight the importance of land-applied sludge pH on the mobility of IOCs. The current practice of lime stabilization increases the sludge pH to a value of >12, but is not followed up with contaminant flushing. This practice may increase the mobility of certain IOCs to readily leach out from MSS after land application.

Desorption of the modeled individual contaminants from a combination of acidic and basic pH treatment of MSS is shown in Figure S1. The model results show that 12 IOCs feature desorption of >50% with the proposed pH adjustment of MSS: three antibiotics (clarithromycin, enrofloxacin, norfluoxetine), three antihistamines (atorvastatin, amlodipine, diphenhydramine), two analgesics (hydrocodone, oxycodone), one anti-inflammatory (ibuprofen), one antidiabetic (gemfibrozil), one antifungal (thiabendazole) and one diuretic (triamterene). Antihistamines ($n = 3$) were shown to feature maximum desorption of 64%

from MSS with the proposed pH adjustment, followed by anti-inflammatory drugs ($n = 2$) and analgesics ($n = 6$) at 51% and 33%, respectively. Many of these contaminants have been shown to occur in runoffs, tile water and groundwater near MSS-applied agricultural lands (Edwards et al., 2009; Gottschall et al., 2012).

One important limitation of the present model is that it does not account for electrostatic sorption of chemicals. Antibiotics, an important class of contaminants falling into this category, have been detected widely in the environment including in MSS ($n = 14$), even when their sorption coefficients are low (Batt et al., 2006; Kummerer, 2003; McClellan and Halden, 2010). Leaching of antibiotics from soils has been identified as one of the most important pathways for contamination of water bodies (Overcash et al., 2005; ter Laak and Gebbink, 2006; Thiele-Bruhn, 2003). Batch sorption experiments conducted in the laboratory showed that the interaction between antibiotics and soil particles were governed predominantly by solution pH (Hari et al., 2005; ter Laak and Gebbink, 2006). Transport of the antibiotic ciprofloxacin ($pK_{a,1} = 6.2$; $pK_{a,2} = 8.8$) through a column of porous media was studied at two different solution pH of 5.6 and 9.5 (Chen et al., 2011). The column showed no breakthrough of ciprofloxacin when flushed with a solution of pH 5.6 (lower than its $pK_{a,1}$ value of 6.2). However, at a pH of 9.5 (greater than its $pK_{a,2}$ value of 8.8) ciprofloxacin showed high mobility and about 93% of the compound was observed to desorb from the porous media and left the column after flushing with four pore volumes of deionized water (Chen et al., 2011). Interestingly the present sorption model estimated only 7% desorption rate for ciprofloxacin from MSS after acidic (<3) and basic (>12) pH treatment. This huge difference (92%) between the model and experimental data is due to the exclusion of electrostatic attraction of ciprofloxacin in the present model and hence underestimating the desorption capability of the compound. One of the major concerns with regards to environmental presence of antibiotics is the promotion of antibiotic resistance genes in microorganisms (Pruden, 2013; World Health Organization, 2010). Electrostatic attraction has also been observed for PFCs (Johnson et al., 2007; Wang and Shih, 2011). The pH dependence of the sorption characteristics of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA), have been studied in the past. These PFCs having very low pK_a values (<0.52) and high solubility in water have been detected in MSS at parts-per-billion levels. Sorption of PFOS to five different materials (goethite, kaolinite, Ottawa sand, iron oxide-coated sands, and sediment from Lake Michigan) showed notable decreases at increased pH, suggesting electrostatic interactions as a prominent parameter governing PFOS partitioning and mobility (Johnson et al., 2007). A similar observation of reduced sorption of PFOA and PFOS to alumina was made as a function of increased pH and ionic strength (Wang and Shih, 2011). There are several other compounds in sludge that may behave similarly to antibiotics and PFCs, and hence are not captured by the model.

This suggests that the desorption estimates from the model are very likely to be less than the true value, that may result in an overall higher removal of contaminants from MSS via pH treatment. Modeling such complex interactions (π - π interactions, complexation, etc.) of contaminants requires a thorough understanding of the cation exchange capacity, ionic strength, organic carbon content, pH, etc. of the sorption media (Figuerola et al., 2004; Tang et al., 2010; Wang and Shih, 2011), which typically are unavailable to practitioners, as was

the case in the present study for the MSS samples from which the data were extracted. Also, a universal model to capture both hydrophobic and other such interactions of IOCs with MSS is currently unavailable. To the best of our knowledge, the present modeling study reports the first pH-adjusted sorption behavior of several IOCs in MSS, making it a unique contribution to the literature highlighting an opportunity for removal of such contaminants through simple pre-treatment (pH adjustment) of MSS.

3.3. Other Benefits of pH Treatment

An important additional benefit of pH adjustment is a decrease in the pathogen content of MSS due to acidic or basic stabilization. A combination of acidic followed by basic treatment will produce a high amount of heat from the exothermic reaction or heat of hydration, thus facilitating thermal inactivation of pathogens (Fergen, 1995). In addition to organic compounds, it has been shown that metal mobility also depends on several factors including pH, organic matter content, type of sludge and soil, cation-exchange capacity, etc. Heavy metal mobility in sludge-amended soils at different pH levels has been studied in the past (Nikolaidis and Chheda, 2001; Tackett et al., 1986). It was reported that heavy metals, including Cr, Cu, Pb, Ni, Zn and Cd, featured increased mobility and leaching from MSS as a function of decreased pH. Additionally, batch experiments showed removal of heavy metals when contaminated MSS was treated with 20% (v/v) of sulfuric acid, with removal rates of 74% for Ni, 99% for total Cr, 86% for Cu, 11% for Pb and 72% for Zn (Stylianou et al., 2007) (see supplemental Table S2). Both metals and pathogens are currently regulated in MSS by the U.S. EPA and thus the proposed pH treatment has the potential to further reduce the burden of toxic metals and pathogens in sludge to produce MSS of enhanced quality.

3.4. Estimated removal of IOCs via pH treatment of MSS

The proposed pH treatment system could be augmented in WWTPs after the initial dewatering step of sludge processing (e.g. anaerobic or aerobic digestion process) (Figure S2). The estimated removal of IOCs from the above described pH treatment is provided in Figure 4A. The total concentration of the 52 modeled IOCs in nationally representative MSS samples was 30 mg/kg dw. This concentration translates to 195 t of IOCs in U.S. MSS annually. The model estimates a removal of 40 ± 16 t annually from U.S. MSS; i.e., between 12 and 29% of the selected IOCs could be potentially desorbed and extracted via pH treatment. However, this range is conservative (i.e., lower than the true value) as indicated above due to the exclusion in the model of electrostatic sorption of chemicals and other contaminants with pK_a outside the range of 3 to 10. A prior study that performed Toxicity Leaching Characteristic Procedure (TCLP) showed that an average 2% of NP and NPEOs leached from sewage sludge (La Guardia et al., 2001). Using this value on the national baseline level of NP in U.S. MSS suggests about 69 t/y of NP and NPEOs could leach from land-applied MSS; a fraction of which could be prevented via the proposed pH treatment. In addition, pH treatment could aid in the removal of toxic and regulated metals (Babel and del Mundo Dacera, 2006; Yoshizaki and Tomida, 2000). Using the percentage removal of seven regulated metals (As, Cd, Cu, Pb, Hg, Ni, Zn) reported in the literature, it was estimated that about 1 g per kg of dry sludge or 7000 ± 2300 t annually could be mobilized and removed from U.S. MSS via pH treatment (Table S2).

A comparison of PPCPs data between the 2001 and 2007 national sewage sludge survey revealed that the concentrations of contaminants remained fairly constant over five years (McClellan and Halden, 2010). Hence, assuming similar concentration trends of the selected IOC in MSS in the future and considering a per capita MSS production of 22.5 kg/person/year estimated for the year 2007, the removal of contaminants via pH treatment was extrapolated to the year 2060 based on population projections from the U.S. Census Bureau (Figure 4B). Projections shows up to 30 t of leachable IOCs can potentially be avoided from land-applied MSS via the proposed pH treatment. The estimated removal of IOCs provided above assume a single extraction or flushing event of pH-treated MSS to remove contaminants. The removal can be further enhanced through sequential extraction of MSS; but however cost involved in the excessive use of flushing agents may restrict the number of flushing/extraction events for pH treatment of MSS. A preliminary cost analysis of acid and base requirements for the proposed pH treatment is summarized in the supplemental Table S3 (see supplemental section S3). The most economic extraction agents were determined to be a combination of citric acid for acidification and lime for basic treatment of MSS, for a total cost of $\$83 \pm 36$ per dry t of sludge. The total process costs including an extraction reactor, dewatering of sludge and precipitation (recovery) of metals is estimated at between $\$500$ to 600 per dry t of sludge (current value estimated from Veeken and Hamelers, 1999). It is to be noted that the preliminary cost analysis provided in the supplemental material assumed that the acid/base requirement for removal of IOCs will be similar to that of metal removal from MSS. This estimate serves only as an approximation since organics may behave differently from metals during pH changes.

3.5. Study limitations and future work

The developed model only estimates the fraction of contaminants that will be desorbed via pH adjustment of MSS. However, it does not take into account the extractability of the contaminants from MSS. Many contaminants even when ionized can be adsorbed by sludge due to electrostatic attraction and other biotransformation mechanisms (Gulde et al., 2014). Hence, flushing of MSS after pH adjustment may not remove all ionized compounds from sludge. Further research is needed to test the feasibility of extraction and recovery of constituents via pH treatment. Acidic treatment of MSS is not widely practiced in industries and hence its effect on sludge quality and chemistry is mostly unknown. Thus, the effects of acidification on other inorganic and organic constituents of the MSS matrix should be evaluated in the future. It is also possible for toxic transformation products of IOCs and other byproducts such as silica deposits to form during sludge treatment (Dewil et al., 2006), the effects of which should be further studied. Some limitations of the process in addition to increased operation and maintenance costs of chemical agents are the disposal of the extracting agents. This liquid will be concentrated with the IOCs and metals, and thus needs to be treated (with e.g., activated carbon adsorption) prior to disposal. Another important factor to be considered is the effect of pH treatment on the nutrient content of MSS. It has been shown that acid treatment can remove 80–90% of total phosphate from sludge and thus could open opportunities for phosphate recovery (Veeken and Hamelers, 1999). On the one hand, removal of phosphate may help to favorably reduce the high phosphorus-to-nitrogen ratio typically observed in land-applied MSS. However, excessive removal of P and N could

reduce the value of MSS as a soil amendment. Hence, the effects of pH treatment on both N and P content of MSS should be considered and evaluated through future experiments.

4. CONCLUSIONS

Although pH increase (by lime addition) is a common process for sludge stabilization and to reduce pathogens in land-applied MSS, the proposed treatment for flushing out harmful contaminants is a previously unrecognized and currently unutilized important benefit that provides a new dimension for this conventional treatment process. It is predicted that increased leaching of IOC's will have taken place for lime-stabilized MSS that were applied on land. Using the desorption model developed in the present study, the proposed pH treatment approach has the potential to reduce the burden of harmful IOC's ($n = 52$) in U.S. MSS by 40 ± 16 t annually; i.e., between 12 and 29% of the selected IOC's could be potentially extracted; a pollutant mass that otherwise would contaminate soils and threaten precious U.S. water resources. Considering the cost of pollution prevention of water resources and potential opportunities for valuable metal and nutrient (phosphate) recovery, the pH treatment of MSS may serve to be a cost effective and simple process that could be augmented easily in existing wastewater treatment facilities.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Highlights

- Sorption model predicts the leachability of ionizable organics from sludge
- Ionic organics make up 82% of total contaminant mass in U.S. sludge
- 36–85% of ionic organic pollutants are removable by pH treatment
- Proposed sludge treatment promises cost-effective risk reduction

Figure 1.

Comparison of ionic and neutral contaminants detected in nationally representative U.S. municipal sewage sludge samples by (A) number and (B) by mass. The total (4700 t/y) represents the estimated mean amount of total CEC (both ionic and neutral) mass accumulating in sludge each year. Chart (C) represents the breakdown of the number of ionic contaminants detected in MSS by type.

Figure 2.

Modeling of relative fraction of IOCs associated with the solids content of sewage sludge as a function of pH. Panels show sorption characteristics of individual classes of sewage sludge constituents: acidic (A), basic (B) and zwitterionic (C) compounds (featuring pK_a values between 3 and 10) detected in nationally representative U.S. sewage sludges. Panel (D) shows the overall sorption of 52 IOCs to solids in sewage sludge as a function of pH. 'n' represent the number of contaminants in each class. The dashed vertical line indicates the typical sludge pH value of 7.5. Percentage values shown are the estimated maximum desorption of IOCs from MSS due to ionization as a function of either increasing or decreasing the pH away from the default of 7.5. (*relative to the initial amount sorbed on to the sludge at ambient pH of 7.5).

Figure 3. Estimated percent desorption of ionizable organic compounds (IOCs) ($n = 52$) with a combination of acidic (<3) and basic (>12) pH treatment as a function of initial (ambient) sludge pH. E.g., sludge with initial pH between 6 and 8 is ideal to treat and remove $>40\%$ of IOCs prior to land-application.

Figure 4.

(A) Estimated nationwide removal of ionizable organic contaminants from sewage sludge (initial pH of 7.5) by pH treatment. Error bars represent maxima and minima. (B) Projection of IOCs removed nationwide from land-applied MSS via proposed pH treatment. 'n' represents the number of chemicals removed.