

## 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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# The Characterization of Trace Metals and Organics in Spent Foundry Sands Over a One-Year Period

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**ABSTRACT:** Millions of tons of spent sand, used to create metalcasting molds, are generated by the foundry industry each year in the United States. Not surprisingly, spent foundry sands (SFSs) are an excellent substitute for virgin sands that are currently used in manufactured soils and geotechnical applications. The purpose of this study was to characterize trace metals and EPA-priority polycyclic aromatic hydrocarbons (PAHs) and phenolics in ferrous and non-ferrous SFSs over a one-year period. Overall, the total metal concentrations in the SFSs were similar to those found in native soils, while the PAHs and phenolic concentrations were relatively low. Metal leaching tests were also performed, which revealed that the SFSs have a low metal leaching potential under the specific test conditions. The data from this study suggests that the majority of SFSs are not hazardous in nature, except those that use olivine sands or are from brass foundries, due to the presence of elevated concentrations of Ni or Cu, Pb, and Zn, respectively. This information will be useful to environmental regulators who are considering including SFSs in their beneficial use regulations.

## INTRODUCTION

**E**ACH year foundries in the U.S. discard about 10 million tons of spent sand in private and municipal landfills. The most commonly used molding process is green sand molding, which is used to produce 90% of the casting volume. Green sands are a mixture of sand (usually silica sand, 85–95% by weight) and lesser quantities of bentonite clay, carbonaceous additives, and water. Efforts to divert green sands and other molding sands (e.g. chemically bonded) from landfills, reduce disposal costs, and encourage their beneficial use are currently being encouraged by the U.S. EPA [16]. Although spent foundry sands (SFSs), such as green sands, are being successfully used in a few states as a component in manufactured soils and geotechnical applications [11,15], many states are reluctant to develop beneficial use regulations or relax current regulations due to a lack of detailed information on metals and organics.

The purpose of this study was to quantify trace metals and EPA-priority polycyclic aromatic hydrocarbons (PAHs) and phenolics in ferrous and non-ferrous SFSs

during three separate sampling events over a one-year period. Trace metal and organic data from the initial sampling event can be found in Dungan and Dees [7] and Dungan [5], respectively. In addition to quantifying total metals, a determination of Ag, As, Ba, Be, Cd, Cr, Cu, Ni, Pb, Sb, and Zn in toxicity characteristic leaching procedure (TCLP), synthetic precipitation leaching procedure (SPLP), and water extracts was performed. The results from this study will ultimately be used to assess the potential risks of using SFSs in manufactured soils for agricultural or horticultural applications. The results will also be of interest to state regulators who are developing or reviewing current beneficial use regulations.

## MATERIALS AND METHODS

### Spent Foundry Sands

In June 2005, September 2005, and July 2006 (which will be referred to as the first, second, and third sampling events, respectively), SFSs were collected from ferrous and non-ferrous foundries located in 13 states (Table 1). The June 2005 samples were collected as described by Dungan [5], while the remaining sets were collected by foundry personnel after receiving training

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**Table 1. Description of the Spent Foundry Molding Sands and Core Binder Systems.**

Sand	State	Metal Poured	Molding Sand	Core Binder System and Process
1	PA	Iron	Green sand	PU coldbox, PU no-bake, shell, core oil
2	PA	Aluminum	Green sand <sup>†</sup>	Shell
3	PA	Iron	Green sand	Shell, furan warmbox
4	PA	Aluminum	Green sand	Shell
5	PA	Iron	Green sand	PU no-bake, shell, sodium silicate
6	PA	Steel	PU no-bake <sup>†</sup>	PU no-bake
7	PA	Iron	Green sand	PU no-bake
8	OH	Iron	Green sand	PU coldbox, PU hotbox
9	OH	Iron	Green sand	PU coldbox, PU hotbox
10	OH	Iron	Green sand	PU coldbox, PU hotbox
11	OH	Iron	Green sand	PU coldbox, PU no-bake, shell
12	IN	Iron	Shell	Shell
13	OH	Iron	Green sand	PU coldbox, PU no-bake, shell
14	OH	Aluminum	Green sand	PU no-bake, shell, core oil
15	IN	Iron	Green sand	PU coldbox, shell
16	OH	Iron	Green sand	PU coldbox, PU hotbox
17	OH	Iron	Green sand	PU coldbox, PU hotbox
18	IN	Iron	Green sand	PU coldbox, PU hotbox, shell
19	WI	Iron	Green sand	PU coldbox
20	OH	Aluminum	Green sand	Shell
21	IN	Iron	PU no-bake	PU coldbox, PU no-bake, furan warmbox
22	MI	Iron	Green sand	PU no-bake, shell
23	MI	Iron	Green sand	PU coldbox, shell
24	WI	Iron	Green sand	Shell
25	WI	Iron	Green sand	PU coldbox
26	MI	Iron	Green sand	none
27	OH	Iron	Green sand	PU no-bake, shell
28	TN	Iron	Green sand	none
29	WI	Steel	PU no-bake	PU no-bake
30	WI	Iron	Green sand	PU coldbox, shell
31	TN	Iron	Green sand	Shell, resin/CO <sub>2</sub>
32	TN	Iron	Green sand	PU coldbox
33	AL	No lead brass	PU no-bake	PU no-bake
34	AL	No lead brass	Green sand	PU no-bake
35	VA	Iron	Green sand	PU coldbox
36	GA	Iron	Green sand	PU coldbox, shell
37	SC	Iron	Green sand	PU coldbox, shell
38	IA	Steel	Phenolic ester-cured	PU coldbox, shell, resin/CO <sub>2</sub>
39	IA	Steel	Green sand	PU coldbox, shell, resin/CO <sub>2</sub>
40	NC	Iron	Green sand	PU coldbox, shell
41	IN	Steel	PU no-bake	PU no-bake
42	IN	Iron	Green sand	PU coldbox
43	WI	Steel	Green sand	PU no-bake, shell, core oil, resin/CO <sub>2</sub>

PU, phenolic urethane.

<sup>†</sup>Olivine sand utilized.

on sample collection. In brief, a clean section of PVC pipe (5.1 cm i.d.) was used to collect four samples from each waste sand pile. The samples were transferred into 500-mL I-CHEM glass jars with Teflon-lined polypropylene closures (Chase Scientific Glass Inc., Rockwood, TN), immediately shipped to our laboratory in coolers, and then stored at 4°C until processed.

### Total Metal Analyses

The SFSs were digested according to U.S. EPA method 3050B [14]. Prior to digestion, each sample

was passed through a 0.5-mm sieve and homogenized. A 2.5 g sub-sample (dry wt.) was then refluxed in 10 mL of 8 M HNO<sub>3</sub> for 15 min. Afterwards, 5 mL of concentrated HNO<sub>3</sub> was added and samples were refluxed for 2 h. Two mL of DI water followed by 3 mL of 30% H<sub>2</sub>O<sub>2</sub> were added to the samples, which were heated until effervescence subsided. Additional 1 mL aliquots of 30% H<sub>2</sub>O<sub>2</sub> were added until effervescence was minimal. The samples were then refluxed for 15 min. in 10 mL of concentrated HCl. The digests were filtered through Whatman no. 40 paper layered with Whatman 2V fluted filters (Florham Park, NJ). The filtrate was di-

luted to 100 mL with 0.1 M HCl and analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES). Blanks and standard reference material 2709 (San Joaquin Soil, National Institute of Standards and Technology, Gaithersburg, MD) were run regularly to ensure quality control.

### Leach Tests

The TCLP and SPLP were conducted according to U.S. EPA methods 1311 and 1312 [14], respectively, but with modifications. Two g of spent sand was placed into a 50-mL polyethylene centrifuge tube (Fisher Scientific, Waltham, MA; Cat. No. 06-443-20), to which 40 mL of extraction fluid no. 1 (pH 4.9 for TCLP and pH 4.2 for SPLP) was added. The tubes were tightly capped and then tumbled at 30 rev min<sup>-1</sup> for 18 h on a rotary shaker (Appropriate Technical Resources Inc., Laurel, MD). The extracts were centrifuged for 10 min. at 3,000 × g and then filtered through a 0.7 μm glass fiber filter (Fisher Scientific; Cat. No. 09-804-142H). The pH of the recovered extracts was measured and recorded, after which they were acidified with HNO<sub>3</sub> to a pH < 2. The preserved samples were stored at 4°C until processed.

The water leach test was conducted according to ASTM International method D 3897 [1], except that a 2 g sample of spent sand was mixed with 40 mL of deionized (DI) water as described above. The aqueous extracts were centrifuged for 10 min. at 3,000 × g and then filtered through a 0.45 μm membrane filter. All extracts were analyzed for Ag, As, Ba, Be, Cd, Cr, Cu, Ni, Pb, Sb, and Zn by ICP-AES.

### Extraction of Organics

A Dionex (Sunnyvale, CA) accelerated solvent extractor (ASE 200) was used to extract the PAHs and phenolics for analysis by gas chromatography-mass spectrometry (GC-MS). Twenty g of SFS as received was placed into the center of a 33-mL stainless steel extraction cell, which was then packed at each end with clean Ottawa sand (20–30 mesh, U.S. Silica Corp., Ottawa, IL) to fill the void. If the SFS was moist to the touch, anhydrous Na<sub>2</sub>SO<sub>4</sub> was mixed with the sand prior to addition to the cells. The conditions of the ASE were as follows: solvent, dichloromethane/acetone (1:1); static extraction for 5 min at a pressure of 14 MPa (2000 psi) and an oven temperature of 100°C; flush volume, 60% of the cell volume; N<sub>2</sub> purge, 1 MPa (150 psi)

for 60 s. All extracts were collected in 40 mL I-CHEM vials. Immediately after the extraction, the extracts were evaporated to near dryness under N<sub>2</sub>, then reconstituted with 2 mL of dichloromethane for GC-MS analysis.

### Gas Chromatography—Mass Spectrometry

The GC was a Varian CP-3800 equipped with a Saturn 2200 ion trap MS (Varian Inc., Walnut Creek, CA). The GC capillary column was a VF-5ms (Varian Inc., 30 m × 0.25 mm × 0.25 μm) and helium was used as the carrier gas. For PAH analyses, the oven temperature program was 45°C for 2 min, then ramping at 10°C min<sup>-1</sup> to 325°C, then held at 325°C for 5 min. The temperature program for the phenolics analyses was 40°C for 4 min, then ramping at 12°C min<sup>-1</sup> to 260°C, then held for 1.67 min, followed by ramping at 10°C min<sup>-1</sup> to 280°C, then held at 280°C for 8 min. The injector temperature was 250°C for all analyses. The GC-MS transfer line temperature was 300°C and the ion trap temperature was 210°C. Mass spectra were obtained by electron impact at 70 eV from 50 to 300 m/z (1.7 scans s<sup>-1</sup>).

## RESULTS AND DISCUSSION

A total of 43 spent sands were collected from ferrous (iron and steel) and non-ferrous (aluminum and brass) foundries in 13 states mostly east of the Mississippi river (Table 1). Of the 43 sands, only 7 sands were from foundries that used chemically bonded molding sands; all others were green sands and 89% of the green sands were from ferrous foundries. Metal data from the initial sampling event, conducted in June 2005, is reported in Dungan and Dees [7]. Overall, the total metal concentrations in the SFSs (i.e. Ag, Al, As, B, Ba, Be, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Sb, V, and Zn) were within ranges found in native soils as determined by Smith et al. [13] and other similar reports (Table 2). Of the 19 metals quantified, only Ag, B, Cd, and Sb were not detected in any of the SFSs above the method detection limits (MDLs; i.e. 17.6, 19.2, 5.9, and 4.5 mg kg<sup>-1</sup>, respectively). In a few spent sands, however, the metal concentrations were substantially higher than in most of the sands. For example, sand 34, a green sand from a non-leaded brass foundry, contained relatively high concentrations of Cu at 3318 mg kg<sup>-1</sup> and Zn at 1,640 mg kg<sup>-1</sup>. As per the Smith et al. [13] dataset, the average

**Table 2. Total Metal Concentrations in Soils and Other Surficial Materials.**

Element	Concentration, mg kg <sup>-1</sup>														
	Spent Foundry Sands <sup>1</sup>			U.S. and Canadian Surface Soils <sup>2</sup>			U.S. Soils and Other Surficial Materials <sup>3</sup>			U.S. Surface Soils <sup>4</sup>			U.S. Agricultural Soils <sup>5</sup>		
	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
Ag	<17.6			<1.0											
Al	<311	10048	1853	6900	87300	47597	700	>100000	72000						
As	0.04	4.8	1.0	<1.0	18.0	5.7	<0.1	97	7.2						
B	<19.2						<20	300	33						
Ba	<8.7	151	23.3	58.0	1800	529	10	5000	580						
Be	<1.2	3.1	08	0.2	4.0	1.3	<1	15	0.92						
Cd	<5.9			<0.1	5.2	0.29				<0.004	1.3	0.2	<0.01	2.0	0.18
Co	<0.84	95.3	3.7	0.9	143	8.9	<3	70	9.1	0.1	347	13.4			
Cr	<1.0	149	11.6	3.0	5320	71.3	1	2000	54	<0.007	3361	88.7			
Cu	<23.1	3318	97.1	<0.5	81.9	14.3	<1	700	25	0.3	201	24.7	<0.6	495	18
Fe	<352	44320	6115	3800	87700	20766	100	>10000	26000						
Hg				<0.02	0.71	0.04	<0.01	4.6	0.09	<0.001	2.0	0.04			
Mg	<720	51574	9119	400	173400	7409	50	>100000	9000						
Mn	<45.0	671	189	56.0	3120	610	<2	700	550	<0.01	3560	589			
Mo	<4.4	9.6	2.4	0.11	21.0	1.0	<3	15	0.97						
Ni	<1.2	2328	857	1.6	2314	35.1	<5	700	19	<0.027	3591	59.5	0.7	269	16.5
Pb	<7.7	25.7	5.0	5.3	319	23.3	<10	700	19	<0.034	164	12.7	<1.0	135	10.6
Sb	<4.5			0.14	2.3	0.64	<1	8.8	0.66						
Se				<0.2	2.3	0.38	<0.1	4.3	0.39						
Sn				0.3	8.6	1.4									
Sr				13.0	1382	184									
Ti				<0.1	1.8	0.46									
V	<7.4	9.1	3.8	7.0	380	59.6	<7	500	80						
W				0.1	3.5	0.71									
Zn	<33.4	1640	60.1	8.0	377	58.0	<5	2900	60	<0.16	216	62.6	<3.0	264	42.9

<sup>1</sup>Dungan and Dees, 2008.<sup>2</sup>Smith et al., 2005; A horizon data.<sup>3</sup>Shacklette and Boerngen, 1984.<sup>4</sup>Burt et al., 2003.<sup>5</sup>Holmgreen et al., 1993.

Cu and Zn concentrations in U.S. and Canadian soils are 14 and 58 mg kg<sup>-1</sup>, while maximum reported concentrations were 82 and 377 mg kg<sup>-1</sup>, respectively (Table 2). The majority of the SFSs (i.e. 77%) contained respective Cu and Zn at concentrations of < 23.1 and < 33.4 mg kg<sup>-1</sup>. Sand 2 (iron green sand) and sand 6 (steel phenolic urethane no-bake sand) contained the highest concentrations of Ni at 2,328 and 1,022 mg kg<sup>-1</sup>, respectively. This can be attributed to the fact that these foundries use olivine sand instead of silica sand. The maximum determined concentrations for Ni in soils was 2,314 mg kg<sup>-1</sup> (Table 2). The average As concentration of the 43 sands was 1.0 mg kg<sup>-1</sup>, and 91% of the sand samples contained < 7.7 mg Pb kg<sup>-1</sup>. Arsenic and Pb were the greatest in sand 22 (iron green sand) at 4.8 and 26 mg kg<sup>-1</sup>, respectively. These As and Pb concentrations, however, are close to average concentrations found in soils (Table 2). A comparison of the trace metal concentrations in SFSs to those in native soils is quite useful, since there is interest in using SFSs in

soil-related applications (e.g. manufactured soils). It also brings perspective to the metal concentrations found in the SFSs; demonstrating that trace metals in SFSs will present little risk to humans, wildlife, and the environment when used in manufactured soils. Due to physical limitations, most manufactured soils will contain no more than 30% SFS by weight.

For the second sampling event in September 2005, spent sands were received from all foundries except foundries 2, 15, 32, 38, and 39. Similarly, we did not receive sand samples from foundries 2, 5, 15, 32, 35, and 41 for the third sampling event in July 2006. Unlike the first sampling event, failure to receive samples during the subsequent sampling events occurred because the foundries themselves were responsible for collection. Regardless, participation in our study was quite high and the results for these sampling events can be found in Tables 3 through 10. A survey of the results in Tables 3 and 4 indicates that there was little overall change in the total metal composition of the SFSs over the one-year

Table 3. Total Metal Concentrations in the Spent Foundry Sands from the Second Sampling Event (September 2005).

Element	Concentration, mg kg <sup>-1</sup>																							
	1 <sup>†</sup>	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22		
Ag	<17.6 <sup>‡</sup>	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	
Al	3496	1740	1304	1482	353	<311	655	512	0.83	2.0	2.1	0.64	1.9	2.1	1143	3173	1044	3574	6940	311	0.66	5.1	3267	
As	2.4	2.0	0.42	1.8	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2
B	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2
Ba	38.2	23.7	<8.7	9.6	39.7	<8.7	<8.7	<8.7	<8.7	<8.7	13.1	<8.7	15.1	<8.7	28.8	19.2	10.1	27.1	19.0	<8.7	<8.7	20.4	<19.2	
Be	1.3	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2
Cd	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9
Co	1.1	<0.84	<0.84	<0.84	9.10	<0.84	<0.84	<0.84	<0.84	1.07	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	2.90	<0.84	<0.84	<0.84	1.26	
Cr	21.4	5.1	4.0	5.6	25.2	7.9	9.0	1.3	51.6	2.0	2.5	2.1	2.5	3.7	2.9	2.7	196	7.5	3.5	32.5	32.5	32.5	32.5	
Cu	115	<23.1	<23.1	<23.1	<23.1	<23.1	<23.1	<23.1	<23.1	85.1	<23.1	<23.1	<23.1	<23.1	<23.1	<23.1	<23.1	<23.1	114	<23.1	<23.1	<23.1	53.5	
Fe	22989	5635	2516	5754	4558	727	4938	1071	21860	2073	904	4070	3357	2520	3942	2391	60020	3132	5386	20340	20340	20340	20340	20340
Mg	1295	1946	<720	<720	26994	<720	<720	<720	<720	<720	<720	<720	<720	1678	<720	971	1310	1267	<720	954	<720	<720	954	
Mn	199	139	<45.0	121	184	<45.0	81.6	<45.0	149	<45.0	<45.0	<45.0	<45.0	<45.0	45.1	94.6	<45.0	920	135	<45.0	<45.0	458	458	
Mo	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	9.2	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	19.8	<4.4	<4.4	<4.4	6.1	
Ni	17.0	3.7	3.5	6.4	139	3.1	4.5	<1.2	18.0	2.0	<1.2	3.2	2.5	2.2	3.3	2.0	36.7	6.9	2.0	15.4	15.4	15.4	15.4	
Pb	18.4	<7.7	<7.7	<7.7	<7.7	<7.7	<7.7	<7.7	<7.7	<7.7	<7.7	<7.7	<7.7	<7.7	<7.7	<7.7	<7.7	<7.7	11.0	<7.7	<7.7	<7.7	14.0	
Sb	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	
V	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	19.3	<7.4	<7.4	<7.4	<7.4	<7.4	
Zn	88.2	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	87.8	

Ag	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	
Al	2705	2150	2103	1865	2431	2500	<311	2120	1213	<311	513	2072	2529	1811	1823	<311	1162	1856	1856	1856	1856	1856	1856	1856
As	2.7	2.4	1.2	2.0	2.2	2.1	0.39	1.7	1.5	0.82	0.78	2.6	3.0	1.0	0.67	0.13	1.1	1.4	1.4	1.4	1.4	1.4	1.4	1.4
B	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2
Ba	29.3	12.0	18.7	19.6	15.1	31.2	68.4	30.0	14.5	<8.7	<8.7	25.9	20.9	13.1	15.8	24.4	10.0	72.5	72.5	72.5	72.5	72.5	72.5	72.5
Be	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2
Cd	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9
Co	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84
Cr	2.6	4.0	2.6	2.1	13.0	5.5	7.0	2.0	11.0	2.5	3.5	1.5	2.4	2.3	1.7	<1.0	1.7	5.7	5.7	5.7	5.7	5.7	5.7	5.7
Cu	<23.1	<23.1	<23.1	<23.1	<23.1	<23.1	<23.1	<23.1	<23.1	14360	14220	<23.1	<23.1	<23.1	<23.1	<23.1	<23.1	<23.1	<23.1	<23.1	<23.1	<23.1	<23.1	<23.1
Fe	3343	4031	2265	2793	10358	3810	1087	2704	3564	789	1704	4196	3962	3048	1760	4926	2743	2647	2647	2647	2647	2647	2647	2647
Mg	1031	<720	<720	<720	979	813	<720	859	<720	<720	<720	807	<720	<720	<720	<720	<720	<720	<720	<720	<720	<720	<720	<720
Mn	<45.0	62.2	<45.0	<45.0	89.9	57.0	<45.0	<45.0	<45.0	<45.0	<45.0	<45.0	<45.0	50.6	67.1	<45.0	<45.0	<45.0	<45.0	<45.0	<45.0	<45.0	<45.0	<45.0
Mo	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4
Ni	2.8	3.7	1.9	2.4	20.6	3.0	15.7	1.9	14.0	34.5	21.1	2.1	2.6	2.1	<1.2	5.9	<1.2	7.4	7.4	7.4	7.4	7.4	7.4	7.4
Pb	<7.7	<7.7	<7.7	<7.7	<7.7	<7.7	<7.7	<7.7	<7.7	20.6	28.9	<7.7	<7.7	<7.7	<7.7	<7.7	<7.7	<7.7	<7.7	<7.7	<7.7	<7.7	<7.7	<7.7
Sb	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5
V	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4
Zn	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	986	1732	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4

<, Less than the method detection limit.  
<sup>†</sup> Foundry identification number; refer to Table 1.  
<sup>‡</sup> Average of four replicates.

Table 4. Total Metal Concentrations in the Spent Foundry Sands from the Third Sampling Event (July 2006).

Element	Concentration, mg kg <sup>-1</sup>																						
	1 <sup>†</sup>	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	
Ag	<17.6 <sup>‡</sup>	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6	<17.6
Al	3431	1780	1072	<311	816	370	650	2197	1416	1870	2086	981	3068	1044	2092	4680	<311	6189	4.9	<19.2	<19.2	<19.2	<19.2
As	2.0	1.0	0.47	0.24	0.07	0.68	0.31	1.2	1.1	0.34	1.0	1.3	0.68	1.4	1.8	0.72	0.85	0.47	4.9	<19.2	<19.2	<19.2	<19.2
B	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2	<19.2
Ba	45.5	24.1	<8.7	<8.7	<8.7	<8.7	<8.7	<8.7	<8.7	<8.7	<8.7	<8.7	<8.7	<8.7	<8.7	<8.7	<8.7	<8.7	<8.7	<8.7	<8.7	<8.7	<8.7
Be	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2
Cd	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9
Co	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84
Cr	5.0	<1.0	2.2	2.9	5.3	6.8	1.3	30.5	2.1	1.6	<1.0	2.2	4.0	4.0	2.2	12.7	7.6	2.9	32.1	<23.1	47.0	<23.1	63.2
Cu	31.3	<23.1	<23.1	<23.1	<23.1	<23.1	<23.1	<23.1	<23.1	<23.1	<23.1	<23.1	<23.1	<23.1	<23.1	<23.1	<23.1	<23.1	<23.1	<23.1	<23.1	<23.1	<23.1
Fe	5265	15.75	1542	4287	566	4549	931	15596	2530	710	1841	2970	2770	3751	2263	7727	2473	3760	25310	<720	<720	<720	<720
Mg	<720	2218	<720	<720	<720	<720	<720	<720	<720	<720	<720	<720	<720	<720	<720	<720	<720	<720	<720	<720	<720	<720	<720
Mn	80.7	46.5	<45.0	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4
Mo	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4
Ni	3.2	<1.2	1.9	<7.7	<7.7	<7.7	<7.7	<7.7	<7.7	<7.7	<7.7	<7.7	<7.7	<7.7	<7.7	<7.7	<7.7	<7.7	<7.7	<7.7	<7.7	<7.7	<7.7
Pb	10.6	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5
Sb	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5
V	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4	<7.4
Zn	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4	<33.4

<, Less than the method detection limit.

<sup>†</sup> Foundry identification number, refer to Table 1.

<sup>‡</sup> Average of four replicates.

sampling period. Some of the largest fluctuations that did occur, occurred with Fe, but this was expected since most of the sands are from ferrous castings. In sand 27, for example, the Fe concentration decreased from 29,950 mg kg<sup>-1</sup> to 4,748 mg kg<sup>-1</sup> by the third sampling event. In sand 19, the Fe concentration increased to 60,020 mg kg<sup>-1</sup> by the second sampling, but then was lower at 7,727 mg kg<sup>-1</sup> by the third sampling. The average concentration of Fe in U.S. soils is 20,766 mg kg<sup>-1</sup>, with a maximum concentration of 87,700 mg kg<sup>-1</sup> (Table 2). Iron is an essential nutrient for plants and animals, and phytotoxicity of Fe is not an agronomic problem [9]. While animals can tolerate higher concentrations of Fe than normally occur in feeds, chronic Fe toxicity is expressed as Fe-induced Cu deficiency only when Cu is low in the diet [3].

In the non-leaded brass foundry sand (i.e., sand 34), the Pb concentration was 19 mg kg<sup>-1</sup> during the first sampling event [7], but surprisingly it increased to 29 and 212 mg kg<sup>-1</sup> by the second and third sampling events, respectively (Tables 3 and 4). In this sand the Cu concentration increased to 14,220 mg kg<sup>-1</sup> by the second sampling event, while Zn increased to 2,829 mg kg<sup>-1</sup> by the third sampling event. Sand 33, a chemically bonded sand from the same brass foundry, contained substantially less Cu, Pb, and Zn during the first and last sampling events; however, Cu was at a similar concentration during the second sampling event (Table 3). Since the concentrations of Cu, Pb, and/or Zn in brass foundry sands are generally at the high end of the range found in soils, they should not be considered for unconsolidated beneficial uses (e.g., manufactured soils). In two ferrous waste sands (i.e., 22 and 38), Pb was found to increase by the third sampling event; respective concentrations were as high as 63 and 47 mg kg<sup>-1</sup>. Nickel which was at 1,022 mg kg<sup>-1</sup> in sand 6 during the first sampling [7], dropped to 139 and 111 mg kg<sup>-1</sup> by the second and third sampling events, respectively (Tables 3 and 4). No other dramatic fluctuations in the Pb and Ni concentrations were noted during the year-long study.

The SFSs were also subjected to the TCLP, SPLP, and the ASTM water leaching procedure. The metals quantified in the extracts were Ag, As, Ba, Be, Cd, Cr, Cu, Ni, Pb, Sb, and Zn. Leaching data from the first set of samples can be found in Dungan and Dees [7]. In brief, none of the 43 waste moldings sands failed the TCLP for elevated concentrations of Ag, As, Ba, Cd, Cr, and Pb. While Hg and Se are also required under SW-846 method 1311, they were not tested in our study.

Fahnline and Regan [8] conducted the TCLP on 52 foundry sands and Hg and Se were  $\leq 0.10$  and  $\leq 0.83$  mg L<sup>-1</sup>, respectively. These concentrations are below the respective regulatory concentrations of 0.2 and 1.0 mg L<sup>-1</sup> [4]. The TCLP results from the second and third sampling events are shown in Tables 5 and 6, respectively. These results were markedly similar to the first sampling event and, as a result, they also would not exceed the TCLP regulatory concentrations for Ag, As, Ba, Cd, Cr, and Pb. Even sand 34 with a total Pb concentration of 212 mg kg<sup>-1</sup> (third sampling event only), contained 1.1 mg Pb L<sup>-1</sup> in the TCLP extracts, which is below the regulatory concentration of 5.0 mg L<sup>-1</sup>. In addition, the SPLP and ASTM leach test results from the second and third sampling events were very similar to the first sampling event, with most concentrations being less than the MDL (data not shown). The TCLP, SPLP, and ASTM results indicate that the SFSs have a low metal leaching potential; however, the results should be used cautiously as they are not representative of leaching under field conditions.

The concentration of EPA-priority PAHs in the waste moldings sands are shown in Tables 7 and 8. As with the metals, the organic results from the second and third sampling events were very similar to the results obtained in June 2005 [5]. During the first sampling event, the 2-ring and 3-ring PAHs (i.e. acenaphthene, acenaphthylene, anthracene, fluorene, naphthalene, and phenanthrene) were generally detected at concentrations above the MDLs. Of these PAHs, anthracene, fluorene, naphthalene, and phenanthrene were the most abundant, as they were detected in > 79% of the SFSs. In the first set of samples, the average concentrations of these PAHs were 0.40, 0.34, 3.9, and 0.64 mg kg<sup>-1</sup>, with high concentrations of 0.95, 2.6, 48, and 2.2 mg kg<sup>-1</sup>, respectively. In sand 6, the naphthalene concentration declined from 48 mg kg<sup>-1</sup> to 8.3 and 0.16 mg kg<sup>-1</sup> by the second and third sampling events, respectively. Likewise, in sand 33 the naphthalene concentration decreased from 28 mg kg<sup>-1</sup> to about 10 mg kg<sup>-1</sup> during the last two sampling events. The average naphthalene concentrations, during the second and third sampling events, were 1.6 and 2.2 mg kg<sup>-1</sup>, respectively. In sand 6 naphthalene increased about 10 times from the first sampling to 42 mg kg<sup>-1</sup> by the third sampling event. Aside from these major fluctuations with naphthalene, no other dramatic increases or decreases of anthracene, fluorene, naphthalene, and phenanthrene occurred over the course of this study. In the case of the 4-ring, 5-ring, and 6-ring PAHs, most were not detected a concentra-

**Table 5. Metal concentrations in the TCLP Extracts from the Spent Foundry Sands from the Second Sampling Event (September 2005).**

Element	Concentration, mg L <sup>-1</sup>																							
	1 <sup>†</sup>	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22		
Ag	<0.04 <sup>‡</sup>	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04		
As	<0.001	0.001	0.001	0.018	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.019	0.003	<0.001	0.002	0.001	0.013	0.001	<0.001	<0.001	0.001	0.001	0.001	<0.001	
Ba	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	
Be	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
Cd	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
Cr	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	
Cu	0.14	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	0.14	<0.10	<0.10	<0.10	<0.10	0.11	
Ni	0.15	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	0.25	<0.14	<0.14	<0.14	<0.14	0.17	
Pb	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	
Sb	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	
Zn	9.6	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	0.58	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	1.3	
<b>Element</b>	<b>23</b>	<b>24</b>	<b>25</b>	<b>26</b>	<b>27</b>	<b>28</b>	<b>29</b>	<b>30</b>	<b>31</b>	<b>32</b>	<b>33</b>	<b>34</b>	<b>35</b>	<b>36</b>	<b>37</b>	<b>38</b>	<b>39</b>	<b>40</b>	<b>41</b>	<b>42</b>	<b>43</b>	<b>44</b>	<b>45</b>	
Ag	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	
As	0.007	0.002	0.003	0.008	<0.001	0.003	0.005	0.004	0.001	<0.001	<0.001	<0.001	0.003	0.013	0.005	0.003	<0.001	0.001	<0.001	0.001	0.001	0.006	<0.001	<0.001
Ba	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	
Be	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
Cd	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
Cr	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	
Cu	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	43.9	0.65	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	
Ni	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	0.30	0.14	0.26	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	
Pb	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.24	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	
Sb	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	
Zn	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	6.5	40.3	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	

<, Less than the method detection limit.  
<sup>†</sup> Foundry identification number; refer to Table 1.  
<sup>‡</sup> Average of four replicates.

Table 6. Metal Concentrations in the TCLP Extracts from the Spent Foundry Sands from the Third Sampling Event (July 2006).

Element	Concentration, mg L <sup>-1</sup>																							
	1 <sup>†</sup>	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22		
Ag	<0.04 <sup>‡</sup>	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	
As	0.004	0.003	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.001	<0.001	0.004	0.001	0.004	0.006	<0.001	0.007	0.001	<0.001	<0.001	0.001	<0.001	<0.001	<0.001	<0.001
Ba	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86
Be	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cd	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cr	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46
Cu	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Ni	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14
Pb	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Sb	<0.02	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07
Zn	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	0.68	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	4.5
Element	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	
Ag	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	
As	0.005	0.003	0.003	0.012	<0.001	<0.001	0.002	0.001	<0.001	<0.001	<0.001	0.001	0.001	0.017	0.001	0.007	0.004	0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Ba	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86
Be	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cd	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cr	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46
Cu	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Ni	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14
Pb	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Sb	<0.02	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07
Zn	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	0.68	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41

<, Less than the method detection limit.

<sup>†</sup> Foundry identification number, refer to Table 1.

<sup>‡</sup> Average of four replicates.

Table 7. Concentration of polycyclic Aromatic Hydrocarbons in the Spent Foundry Sands from the Second Sampling Event (September 2005).

Compound	Concentration, mg kg <sup>-1</sup>																							
	1 <sup>†</sup>	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22		
Acenaphthene	<0.04 <sup>‡</sup>	<0.04	<0.04	0.06	<0.04	0.09	0.05	<0.04	<0.04	<0.04	0.11	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	0.09	<0.04	<0.04	
Acenaphthylene	0.17	<0.03	<0.03	0.06	0.28	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	0.03	<0.03	<0.03	<0.03	<0.03	0.08	<0.03	<0.03	<0.03	<0.03	0.04	
Anthracene	0.24	0.18	0.33	0.62	0.38	0.27	0.52	0.69	<0.03	0.99	<0.03	0.43	0.84	0.49	0.44	<0.03	0.36	0.83	0.23	0.62	<0.10	<0.10	<0.10	0.10
Benzo[a]anthracene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	0.20	0.13	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	
Benzo[b]fluoranthene	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	
Benzo[k]fluoranthene	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	
Benzo[ghi]perylene	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	
Benzo[a]pyrene	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	
Chrysene	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	0.11	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	
Dibenz[a,h]anthracene	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	
Fluoranthene	<0.06	<0.06	<0.06	0.10	0.06	<0.06	1.03	0.11	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	
Fluorene	0.25	<0.04	<0.04	0.50	0.38	0.25	0.11	0.47	<0.04	0.55	<0.04	0.44	0.53	0.36	0.11	0.36	0.25	0.56	<0.04	0.45	<0.04	<0.04	0.45	
Indeno[1,2,3-cd]pyrene	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	
Naphthalene	1.60	0.26	0.34	0.84	0.84	0.33	0.43	0.16	0.38	0.39	1.49	<0.03	1.87	0.59	0.55	0.34	0.27	0.51	0.66	<0.03	0.81	<0.03	0.81	
Phenanthrene	1.36	0.18	0.37	0.62	0.43	0.29	1.29	0.94	0.94	1.40	<0.03	0.91	1.01	0.77	0.39	1.10	0.40	0.97	0.20	0.64	<0.03	0.64	0.64	
Pyrene	0.06	<0.03	<0.03	0.24	<0.03	0.06	0.86	0.20	<0.03	0.18	<0.03	0.12	0.47	<0.03	<0.03	<0.03	0.16	0.07	0.47	<0.03	0.23	<0.03	0.23	
<b>Compound</b>	<b>23</b>	<b>24</b>	<b>25</b>	<b>26</b>	<b>27</b>	<b>28</b>	<b>29</b>	<b>30</b>	<b>31</b>	<b>32</b>	<b>33</b>	<b>34</b>	<b>35</b>	<b>36</b>	<b>37</b>	<b>38</b>	<b>39</b>	<b>40</b>	<b>41</b>	<b>42</b>	<b>43</b>	<b>44</b>	<b>45</b>	
Acenaphthene	0.17	<0.04	<0.04	<0.04	<0.04	<0.04	0.06	<0.04	<0.04	<0.04	<0.04	<0.04	0.12	<0.04	<0.04	<0.04	0.18	<0.04	0.04	<0.04	<0.04	<0.04	<0.04	
Acenaphthylene	0.10	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	0.32	0.25	0.11	<0.03	0.12	<0.03	0.09	<0.03	<0.03	<0.03	0.20	<0.03	0.20	
Anthracene	0.54	0.97	0.33	0.33	0.28	0.14	0.35	<0.03	0.06	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	0.48	0.53	0.53	0.05	<0.10	<0.10	<0.10	
Benzo[a]anthracene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	
Benzo[b]fluoranthene	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	
Benzo[k]fluoranthene	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	
Benzo[ghi]perylene	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	
Benzo[a]pyrene	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	
Chrysene	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	
Dibenz[a,h]anthracene	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	
Fluoranthene	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	
Fluorene	0.41	1.19	0.19	0.49	0.10	0.08	0.16	0.71	0.11	0.54	0.84	0.26	<0.04	0.88	0.23	0.41	0.38	0.24	0.16	<0.06	<0.06	<0.06	<0.06	
Indeno[1,2,3-cd]pyrene	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	
Naphthalene	0.09	1.37	0.43	0.89	0.19	0.95	<0.03	0.74	0.36	9.76	0.74	0.29	1.12	2.20	1.10	14.6	0.68	0.10	<0.14	<0.14	<0.14	<0.14	<0.14	
Phenanthrene	0.57	1.91	0.45	1.28	0.54	0.14	0.29	1.07	0.26	0.66	0.90	0.57	0.88	1.68	0.77	0.65	0.55	0.23	<0.14	<0.14	<0.14	<0.14	<0.14	
Pyrene	0.22	0.80	0.09	0.33	<0.03	0.07	<0.03	0.49	<0.03	0.23	0.27	<0.03	0.10	0.16	0.04	0.13	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	

&lt;: Less than the method detection limit.

†Foundry identification number; refer to Table 1.

‡Average of four replicates.

Table 8. Concentration of polycyclic Aromatic Hydrocarbons in the Spent Foundry Sands from the Third Sampling Event (July 2006).

Compound	Concentration, mg kg <sup>-1</sup>																							
	1 <sup>†</sup>	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22		
Acenaphthene	<0.04 <sup>‡</sup>	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	0.11	<0.04	0.10	0.11	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	
Acenaphthylene	0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	0.14	<0.03	0.07	<0.03	<0.03	<0.03	<0.03	0.25	<0.03	<0.03	<0.03	<0.03	<0.03	
Anthracene	0.09	0.10	0.10	0.10	0.10	0.11	<0.03	0.25	0.13	0.07	0.69	<0.03	0.25	0.18	0.16	0.16	0.10	0.60	0.13	0.37	<0.03	0.17	<0.10	
Benzo[a]anthracene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Benzo[b]fluoranthene	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12
Benzo[k]fluoranthene	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13
Benzo[ghi]perylene	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14
Benzo[a]pyrene	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20
Chrysene	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08
Dibenz[a,h]anthracene	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16
Fluoranthene	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06
Fluorene	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14
Indeno[1,2,3-cd]pyrene	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14
Naphthalene	0.65	0.67	0.67	0.67	0.67	0.67	0.67	0.67	0.67	0.67	0.67	0.67	0.67	0.67	0.67	0.67	0.67	0.67	0.67	0.67	0.67	0.67	0.67	0.67
Phenanthrene	0.30	0.39	0.39	0.39	0.39	0.39	0.39	0.39	0.39	0.39	0.39	0.39	0.39	0.39	0.39	0.39	0.39	0.39	0.39	0.39	0.39	0.39	0.39	0.39
Pyrene	0.07	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09

Compound	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	
Acenaphthene	<0.04	0.40	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	0.06	<0.04	0.05	<0.04	<0.04	<0.04	0.25	0.04	<0.04	<0.04	<0.04
Acenaphthylene	0.07	0.16	<0.03	0.05	0.04	<0.03	<0.03	<0.03	0.05	0.05	0.08	0.10	<0.03	0.07	<0.03	<0.03	<0.03	0.33	<0.03	<0.03	<0.03	<0.03
Anthracene	0.19	0.56	0.04	0.23	0.15	<0.03	0.17	<0.03	0.05	0.05	0.20	0.35	<0.03	0.27	0.10	0.07	0.60	0.60	0.46	0.10	<0.10	<0.10
Benzo[a]anthracene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Benzo[b]fluoranthene	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12
Benzo[k]fluoranthene	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13
Benzo[ghi]perylene	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14
Benzo[a]pyrene	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20
Chrysene	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08
Dibenz[a,h]anthracene	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16
Fluoranthene	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06
Fluorene	0.12	1.05	0.06	0.42	0.14	0.05	0.07	0.07	0.04	0.04	0.46	0.83	0.22	0.41	<0.04	<0.04	0.41	0.41	0.18	<0.04	<0.04	<0.04
Indeno[1,2,3-cd]pyrene	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14
Naphthalene	0.30	1.88	0.08	0.89	1.00	0.53	0.08	0.12	0.17	0.17	9.60	1.96	5.77	0.67	0.03	0.05	0.54	0.41	0.03	0.41	0.03	0.41
Phenanthrene	0.31	1.14	0.37	0.44	0.44	0.74	0.18	0.25	0.10	0.10	0.46	1.58	0.48	0.81	0.11	0.21	0.73	0.43	0.11	0.43	0.11	0.43
Pyrene	0.08	0.73	0.09	0.13	0.13	0.04	0.06	0.08	0.03	0.03	0.05	0.24	0.09	0.12	0.05	<0.03	0.06	0.05	0.05	0.05	0.05	0.05

<, Less than the method detection limit.

<sup>†</sup> Foundry identification number; refer to Table 1.

<sup>‡</sup> Average of four replicates.

Table 9. Concentration of phenolics in the Spent Foundry Sands from the Second Sampling Event (September 2005).

Compound	Concentration, mg kg <sup>-1</sup>																					
	1 <sup>†</sup>	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
2-sec-Butyl-4,6-dinitrophenol	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21
4-Chloro-3-methylphenol	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18
2-Chlorophenol	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11
2,4-Dichlorophenol	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12
2,6-Dichlorophenol	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06
2,4-Dimethylphenol	<0.08	0.19	0.66	0.19	0.86	0.10	<0.08	0.23	<0.08	0.24	<0.08	3.12	<0.08	2.10	1.48	0.78	0.13	<0.08	0.46	7.45	<0.08	0.09
2,4-Dinitrophenol	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24
2-Methylphenol	0.67	0.26	1.33	1.23	2.94	<0.21	<0.21	0.67	<0.21	5.30	<0.21	2.99	1.25			1.54	0.34	<0.21	1.15	5.52	<0.21	0.56
3- and 4-Methylphenol	0.20	0.21	0.43	0.46	0.73	0.14	0.09	0.34	<0.08	2.27	<0.08	1.34	0.36			0.65	0.30	0.08	0.42	1.71	<0.08	0.20
2-Methyl-4,6-dinitrophenol	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16
2-Nitrophenol	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09
4-Nitrophenol	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44
Pentachlorophenol	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24
Phenol	2.28	0.41	0.85	4.75	50.0	0.74	0.63	1.73	<0.07	8.12	<0.07	4.78	0.47			4.57	0.44	0.37	2.75	4.95	<0.07	1.33
2,3,4,6-Tetrachlorophenol	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09
2,4,6-Trichlorophenol	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12
2,4,5-Trichlorophenol	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14
<b>Compound</b>	<b>23</b>	<b>24</b>	<b>25</b>	<b>26</b>	<b>27</b>	<b>28</b>	<b>29</b>	<b>30</b>	<b>31</b>	<b>32</b>	<b>33</b>	<b>34</b>	<b>35</b>	<b>36</b>	<b>37</b>	<b>38</b>	<b>39</b>	<b>40</b>	<b>41</b>	<b>42</b>	<b>43</b>	<b>44</b>
2-sec-Butyl-4,6-dinitrophenol	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21
4-Chloro-3-methylphenol	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18
2-Chlorophenol	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11
2,4-Dichlorophenol	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12
2,6-Dichlorophenol	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06
2,4-Dimethylphenol	<0.08	0.52	<0.08	0.23	<0.08	<0.08	0.71	<0.08	<0.08	<0.08	0.21	0.13	<0.08	0.33	2.74	3.34	0.27	0.63	<0.06	<0.06	<0.06	<0.06
2,4-Dinitrophenol	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24
2-Methylphenol	<0.21	0.68	0.27	0.46	0.21	<0.21	0.26	<0.21	<0.21	<0.21	0.69	0.27	0.23	0.74	4.42	9.90	0.74	3.36	<0.21	<0.21	<0.21	<0.21
3- and 4-Methylphenol	<0.08	0.65	0.11	0.87	0.17	0.15	0.25	0.13	<0.08	<0.08	0.19	0.12	0.96	0.32	3.21	3.98	0.09	0.78	0.09	<0.16	<0.16	<0.16
2-Methyl-4,6-dinitrophenol	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16
2-Nitrophenol	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09
4-Nitrophenol	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44
Pentachlorophenol	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24
Phenol	0.16	0.93	0.54	0.89	0.53	0.24	0.77	0.10	0.48	13.2	0.73	1.57	1.28	11.0	14.2	20.2	11.2	0.12	<0.09	<0.09	<0.09	<0.09
2,3,4,6-Tetrachlorophenol	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09
2,4,6-Trichlorophenol	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12
2,4,5-Trichlorophenol	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14

&lt;, Less than the method detection limit.

<sup>†</sup> Foundry identification number; refer to Table 1.<sup>‡</sup> Average of four replicates.

Table 10. Concentration of Phenolics in the Spent Foundry Sands from the Third Sampling Event (July 2006).

Compound	Concentration, mg kg <sup>-1</sup>																						
	1 <sup>†</sup>	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	
2-sec-Butyl-4,6-dinitrophenol	<0.21 <sup>‡</sup>	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21
4-Chloro-3-methylphenol	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18
2-Chlorophenol	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11
2,4-Dichlorophenol	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12
2,6-Dichlorophenol	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06
2,4-Dimethylphenol	0.33	1.05	0.59	<0.24	<0.24	0.61	<0.08	0.28	<0.08	4.38	<0.08	4.25	10.85	<0.24	<0.24	0.80	<0.08	0.32	0.62	6.42	<0.08	<0.08	<0.08
2,4-Dinitrophenol	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24
2-Methylphenol	1.00	2.63	0.69	<0.24	<0.24	0.17	<0.21	0.53	<0.21	8.82	<0.21	5.44	8.74	<0.24	<0.24	1.56	<0.21	<0.21	2.27	10.5	<0.21	<0.21	0.22
3- and 4-Methylphenol	0.42	1.56	0.23	<0.16	<0.16	0.33	<0.08	0.20	<0.08	0.11	4.08	<0.08	2.62	2.74	<0.16	0.64	<0.08	0.15	0.76	4.70	<0.08	<0.08	0.27
2-Methyl-4,6-dinitrophenol	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16
2-Nitrophenol	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09
4-Nitrophenol	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44
Pentachlorophenol	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24
Phenol	1.05	4.47	0.38	<0.24	<0.24	28.5	<0.07	0.91	<0.07	0.47	23.4	<0.07	7.68	6.10	<0.24	3.90	<0.07	0.10	4.52	23.7	<0.07	<0.07	1.16
2,3,4,6-Tetrachlorophenol	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09
2,4,6-Trichlorophenol	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12
2,4,5-Trichlorophenol	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14

Compound	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	
	2-sec-Butyl-4,6-dinitrophenol	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21
4-Chloro-3-methylphenol	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18
2-Chlorophenol	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11
2,4-Dichlorophenol	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12
2,6-Dichlorophenol	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06
2,4-Dimethylphenol	0.26	0.78	<0.08	2.11	0.24	<0.08	0.44	0.09	<0.08	<0.24	<0.24	0.56	0.82	1.01	2.18	<0.08	<0.08	1.44	<0.24	<0.24	0.23	0.11	<0.24
2,4-Dinitrophenol	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24
2-Methylphenol	0.73	0.84	0.29	1.70	1.47	<0.21	<0.21	0.21	<0.21	<0.21	1.85	3.81	2.91	3.86	<0.21	<0.21	<0.21	4.00	<0.21	<0.21	1.13	<0.21	<0.21
3- and 4-Methylphenol	0.26	0.83	0.08	3.19	0.49	<0.08	0.13	0.20	<0.08	<0.16	0.41	1.46	1.42	2.88	<0.08	<0.08	2.39	<0.16	<0.16	0.30	<0.08	<0.16	<0.16
2-Methyl-4,6-dinitrophenol	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16
2-Nitrophenol	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09
4-Nitrophenol	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44
Pentachlorophenol	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24
Phenol	1.45	1.45	1.64	3.15	2.44	0.29	1.05	0.65	0.46	20.0	11.5	10.0	7.10	<0.07	<0.07	6.10	2.71	0.10	<0.09	<0.09	<0.09	<0.09	<0.09
2,3,4,6-Tetrachlorophenol	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09
2,4,6-Trichlorophenol	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12
2,4,5-Trichlorophenol	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14

<, Less than the method detection limit.  
<sup>†</sup> Foundry identification number; refer to Table 1.  
<sup>‡</sup> Average of four replicates.

tions above the MDLs during all three sampling events (i.e. benz[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[ghi]perylene, benzo[a]pyrene, chrysene, dibenz[a,h]anthracene, fluoranthene, and indeno[1,2,3-cd]pyrene). The respective MDLs were 0.10, 0.12, 0.13, 0.14, 0.20, 0.08, 0.16, 0.06, and 0.14 mg kg<sup>-1</sup>.

Tables 9 and 10 show the concentrations of 17 U.S. EPA-priority phenolics in the SFSs collected in September 2005 and July 2006, respectively. Phenolics were targeted since many of the core binders are phenol-based resins. Their thermal degradation results in the production of 2-methylphenol, 3-methylphenol, 4-methylphenol, and 2,4-dimethylphenol [6], all of which are on the U.S. EPA's priority list. Along with phenol, these phenolic compounds were quantitatively detected above the MDL in the majority of the SFSs. The sands with higher concentrations of phenol, also generally contained higher concentrations of 2,4-dimethylphenol, 2-methylphenol, and 3- and 4-methylphenol. During the first sampling event, the phenol concentration was the highest in sand 6 at 186 mg kg<sup>-1</sup> [5]. In the second set of samples, the phenol concentration ranged from < 0.07 to as high as 50 mg kg<sup>-1</sup> in sand 6. By the third sampling event, the phenol concentration in sand 6 was 29 mg kg<sup>-1</sup>, which was the highest concentration compared to all other sands. In comparison, the remaining phenolic compounds (i.e. 2-sec-butyl-4,6-dinitrophenol, 4-chloro-3-methylphenol, 2-chlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol, 2,4-dinitrophenol, 2-methyl-4,6-dinitrophenol, 2-nitrophenol, 4-nitrophenol, pentachlorophenol, 2,3,4,6-tetrachlorophenol, 2,4,6-trichlorophenol, and 2,4,5-trichlorophenol) were not found to be above the MDLs in the majority of the SFSs during all three sampling events.

In conclusion, this one-year study to characterize trace metals, PAHs, and phenolics in SFSs has revealed that the concentrations of these constituents remain relatively consistent. When metal fluctuations did occur, it was usually limited to Fe in the ferrous molding sands or Cu, Pb, and Zn in the brass molding sands. By and large, however, the trace metal concentrations in the SFSs were found to be within ranges normally found in surface soils. While the PAHs and phenolics were detected at relatively low concentrations, with most below our MDLs, a few sands contained higher than usual concentrations of these organic compounds. This was not limited to any particular molding sand type and metal poured, but the sands with the highest PAH and

phenolic concentrations were generally chemically-bonded molding sands. Since the most abundant compounds in the sands are naphthalene, phenanthrene, anthracene, phenol, 2,4-dimethylphenol, 2-methylphenol, and 3- and 4-methylphenol, which are semi-volatile in nature, methods to enhance their dissipation before beneficial use may be required. The soil blending process itself might be sufficient by stimulating volatilization, along with the enhanced chemical and biological degradation from the organic byproducts that are added to manufactured soils.

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# Estimation of Chronic and Acute Air Arsenic Levels from House Dust Composition in Poultry Waste Disposal Areas

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**ABSTRACT:** Attempts to correlate concentrations of contaminants in air with those in household dusts have demonstrated significant trends, but generally have been unsuccessful in establishing any simple mathematical relationship, primarily because it rarely has been possible to collect meaningful air data and dust data at appropriate locations for related time periods. This study demonstrates that mass balance considerations allow settled dust compositions to be related mathematically to air concentrations of settleable nonvolatile particulate matter by use of dust and air measurements in Washington County, Arkansas within comparable time periods. Further, since reasonable information on contaminant source(s) and periodic peak exposure events can be established, acute air exposure levels can then be estimated by use of the mathematical definition of time-weighted average.

## INTRODUCTION

**H**ALTH risk assessments often have considered only long term chronic exposures, when one-time or periodic acute exposure information—if available—could have provided a significantly better basis for assessment. Official U.S. EPA terminology defines *acute exposure* as “one dose or multiple doses of short duration spanning less than or equal to 24 hours” and *chronic exposure* as “multiple exposures occurring over an extended period of time, or a significant fraction of the animal’s or the individual’s lifetime” [1]. As a classic example, mathematical analysis of air in a poison gas atmosphere indicated an 8-hour time-weighted average (chronic exposure) of hydrogen cyanide considered safe, while a 5-minute acute exposure was lethal [2].

The importance of acute exposure has long been recognized in the workplace by such values as Short Term Exposure Level (STEL) or Ceiling Level (CEIL). Acute exposure information is useful in planning in or-

der to avoid measured or estimated exposures expected to exceed safe levels. Additionally, reconstruction of past acute exposure levels can provide valuable insight for medical and forensic causation analysis. In many cases, acute exposures may be much more meaningful than chronic exposure data, as in the hydrogen cyanide example above.

Health impacts of airborne contaminants frequently have been associated with assays of dust samples [e.g., 3, 4], in recognition that they pose both inhalation and—for larger particulates—nondietary-ingestion health risks from swallowing mucus-laden particulates [5]. However, many studies have focused on the health risks posed by existing “dust loading”, i.e., on the mass of contaminants in dust from a measured surface area, without measurement of the mass of dust. Unfortunately, this method cannot distinguish between a small quantity of dust with a very high contaminant concentration and a large quantity of dust with a very low contaminant concentration. Thus, such data are necessarily limited to estimations of health risks and cleanup needs based on current and future exposures to existing dust.

Without an assay of the concentration of contaminants in the dust it is impossible to estimate health risk from prior inhalation and/or nondietary-ingestion of airborne contaminants during the period in which the dust was being deposited, or for ongoing exposures to continuing periodic pollution sources. For persons ex-

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posed to short-term, high levels of contaminated air, dust samples taken months later will fail to assess acute exposures unless the difference between acute and time-weighted average (TWA) exposures can be estimated. Accordingly, any risk assessment other than that limited to current and future risk from existing dust must take into account concentrations of contaminants in the dust, as well as the nature and periodicity of probable contaminant sources.

Several investigators have studied associations between concentrations of contaminants in air and in indoor dust, generally concluding that there are significant correlations but no simple mathematical relationship [e.g., 6, 7, 8]. The U.S. Army and the National Academy of Sciences did suggest a linear mathematical relationship between air concentrations and dust depositions for zinc cadmium sulfide [9], and the U.S. EPA developed a simple linear mathematical relationship between dust lead levels and air lead levels for the purpose of trying to identify new sources of lead contamination [10]. That relationship, between chemical composition of dust and chemical composition of air, can be applied to any settleable nonvolatile substance under the specific circumstances described in this study.

## A MASS BALANCE ANALYSIS

Although the EPA's 1989 equation is strictly exact only under limited conditions (i.e., to dust and air for the same time frame, and for only *settleable, nonvolatile* contaminants), it is useful to have a method for associating at least that portion of airborne particulate matter with dust composition. This involves recognition that there must be a direct linear relationship between composition of *settled* dust and composition of air containing the *settleable* dust, under the specific condition that average air composition corresponds to the time during which dust accumulated. This relationship can be expressed for arsenic, as an example, by:

$$m_{\text{As in dust}} = m_{\text{As non-air}} + m_{\text{As from air}} \quad (1)$$

In which  $m_{\text{As in dust}}$  denotes the amount of arsenic in the total dust sample;  $m_{\text{As non-air}}$  represents a correction factor for a previously accumulated equivalent amount of dust before exposure to the air sample; and  $m_{\text{As from air}}$  represents the amount of *settleable* arsenic in the air sample from which the dust was accumulated.

Each of the mass terms can be represented by expressions involving concentrations, as:

$$m_{\text{As in dust}} = m_{\text{dust sample}} \times C_{\text{As in total dust}} \quad (2)$$

$$m_{\text{As non-air}} = m_{\text{dust sample}} \times C_{\text{As non-air}} \quad (3)$$

$$m_{\text{As from air}} = V_{\text{air sample}} \times C_{\text{As from air}} \quad (4)$$

Of course, this approach only calculates a *minimum* air level, since only nonvolatile species within *settleable* particulates will be accounted for and any smaller (non-settleable) particulates or gases will not be included. The Law of Conservation of Matter requires this to be true for the specific condition that the air sample's composition corresponds to that during which contaminated dust accumulated.

When right-hand terms from Equations (2), (3) and (4) are substituted for their equalities in Equation (1) the following equation results as an alternative expression of mass balance:

$$m_{\text{dust sample}} \times C_{\text{As in total dust}} = m_{\text{dust sample}} \times C_{\text{As non-air}} + V_{\text{air sample}} \times C_{\text{As from air}} \quad (5)$$

Now this relationship can be rearranged to yield:

$$(C_{\text{As in total dust}} - C_{\text{As non-air}}) \times m_{\text{dust sample}} = V_{\text{air sample}} \times C_{\text{As from air}} \quad (6)$$

and

$$(C_{\text{As in total dust}} - C_{\text{As non-air}}) = (V_{\text{air sample}} \div m_{\text{dust sample}}) \times C_{\text{As from air}} \quad (7)$$

Although there is rarely an opportunity for measurement of both the dust sample mass and the corresponding air volume from which the dust settled, it is possible to determine the value of the *ratio* of air-volume-to-dust-sample-mass, which can be represented by  $R$ , such that Equation (7) then becomes the simple linear relationship:

$$C_{\text{As in total dust}} - C_{\text{As non-air}} = RC_{\text{As from air}} \quad (8)$$

If the concentrations can then be measured or reliably estimated, the value of  $R$  can be calculated and subsequently used to estimate air concentrations under similar conditions.

## DUST AND AIR IN WASHINGTON COUNTY, ARKANSAS

Washington County, Arkansas is reported to be in the top ten counties nationwide in terms of broiler chicken production [11]. Until recently, most broiler litters contained significant quantities of *roxarsonic* (3-nitro-4-hydroxyphenylarsonic acid) and/or its degradation products, and the spreading of broiler litter (Figure 1) was a major source of arsenic in the air of areas near litter application [12].

Fayetteville, Washington County, Arkansas is near the areas of broiler litter application and is the site of a PM 2.5 air monitoring station maintained by the Arkansas Department of Environmental Quality (ARDEQ). The ARDEQ provided their complete set of data for the year 2002 and the filters on which PM 2.5 particulates were collected. For twelve dates selected as representative of typical dry weather, as determined from local weather data, a set of PM 2.5 data were tabulated (Table 1).

Arsenic content of the selected PM 2.5 particulate samples has previously been reported [12], and can be combined with the PM 2.5 particulate concentration data to yield air arsenic levels by the equation:

$$C_{\text{PM 2.5 As in air}} = C_{\text{As in PM 2.5}} \times C_{\text{PM 2.5 in air}} \quad (9)$$

The results of these calculations are given in Table 2, along with estimates of arsenic content of total suspended particulates, which are typically 2–3 times those of just the PM 2.5 particulates in the south-central U.S. ([www.tva.gov/environment/air/ontheair/dustwind.htm](http://www.tva.gov/environment/air/ontheair/dustwind.htm)).

Dusts and soils widely distributed throughout Wash-

**Table 1. Selected Dry Weather Particulate Concentration Data from Washington County, AR (ARDEQ Monitoring Station)**

Filter ID	Run Date	PM 2.5 (ng m <sup>-3</sup> )
2010874	04/05/2002	17,290
2011742	06/19/2002	16,000
2011775	06/22/2002	10,460
2012512	08/21/2002	11,620
2012632	08/30/2002	30,170
2012692	09/05/2002	15,040
2012728	09/08/2002	15,460
2012776	09/11/2002	16,500
2012979	09/26/2002	12,290
2012989	09/20/2002	14,040
2012470	10/02/2002	13,120
2013582	11/22/2002	10,630

**Table 2. Measured Arsenic in Washington County, AR Air (ARDEQ Monitoring Station).**

Filter ID	2002 Date	Arsenic (mg kg <sup>-1</sup> )	PM 2.5 Arsenic (ng m <sup>-3</sup> ) [Equation (9)]	TSP Arsenic (ng m <sup>-3</sup> )	
				Low	High
2010874	04/05	28.0	0.484	0.97	1.45
2011742	06/19	43.9	0.702	1.40	2.11
2011775	06/22	113	1.18	2.36	3.54
2012512	08/21	13.2	0.153	0.31	0.459
2012632	08/30	26.4	0.796	1.59	2.39
2012692	09/05	23.0	0.346	0.69	1.04
2012728	09/08	35.6	0.550	1.10	1.65
2012776	09/11	33.1	0.546	1.09	1.64
2012979	09/26	61.1	0.751	1.50	2.25
2012989	09/29	35.4	0.497	0.99	1.49
2012470	10/02	50.0	0.656	1.31	1.97
2013582	11/22	43.4	0.461	0.92	1.38
<b>Average</b>			<b>0.594</b>	<b>1.19</b>	<b>1.78</b>

ington County were collected and analyzed from September 2002 through September 2005 [12]. In the course of that study, 185 house dust samples were found to have an average arsenic content of 15.3 mg kg<sup>-1</sup> (range: 0.95–152 mg kg<sup>-1</sup>)<sup>†</sup> and 79 “track-in” area top-soil samples were collected with an average arsenic content of 7.3 mg kg<sup>-1</sup> (range: 1.1–36.7 mg kg<sup>-1</sup>). Wind patterns for Washington County were generally similar during the years 2002–2005 (Figure 2). Accordingly, it is reasonable to assume that the average concentration of total suspended (i.e., *settleable*) arsenic during the 2002–2005 time frame was, conservatively, about 2.5 times that of the PM 2.5 arsenic, namely 0.88 ng m<sup>-3</sup>.

Since most household uses of arsenicals have been banned for many years, and since the arsenic from tobacco smoke is recognized as an insignificant contribution to household dusts [14], it is reasonable to assume that the arsenic in house dusts that was not deposited from outdoor air can be attributed mainly to track-in soil. Thus, for Washington County,  $C_{\text{As non-air}}$  is about 7.3 mg kg<sup>-1</sup>. The average value of  $C_{\text{As in total dust}}$  is 15.3 mg kg<sup>-1</sup>. The value of the air-volume-to-dust-sample-mass ratio can then be calculated from Equation (8) as:

$$(15.3 \text{ mg kg}^{-1} - 7.3 \text{ mg kg}^{-1}) = R \times 0.88 \text{ ng m}^{-3} \quad (11)$$

$$R = 8.0 \text{ mg kg}^{-1} \div 0.88 \text{ ng m}^{-3} = 9.1 \text{ mg m}^3 \text{ ng}^{-1} \text{ kg}^{-1} \quad (12)$$

<sup>†</sup> These data do not include dust samples too small for reliable analysis, nor do they include substitutions for such data. Substitution of zero for “nondetect” is indefensible and alternative substitutions are unreliable for low-mass samples, for which sample-specific minimum detection limits can be anomalously high [13].



**Figure 1.** Homes and Schools Impacted by Broiler Litter Dusts. Photographs in Prairie Grove, Arkansas courtesy of Tommy Johnson.

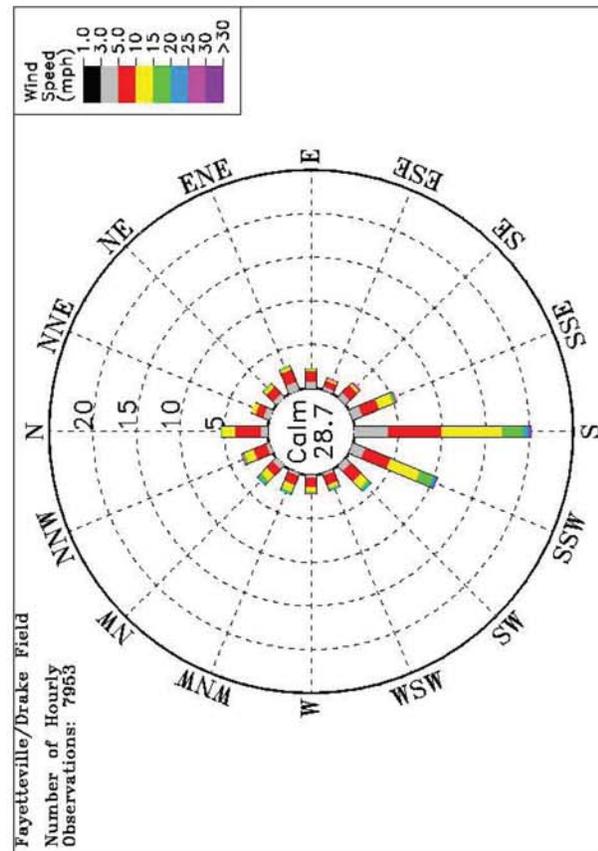
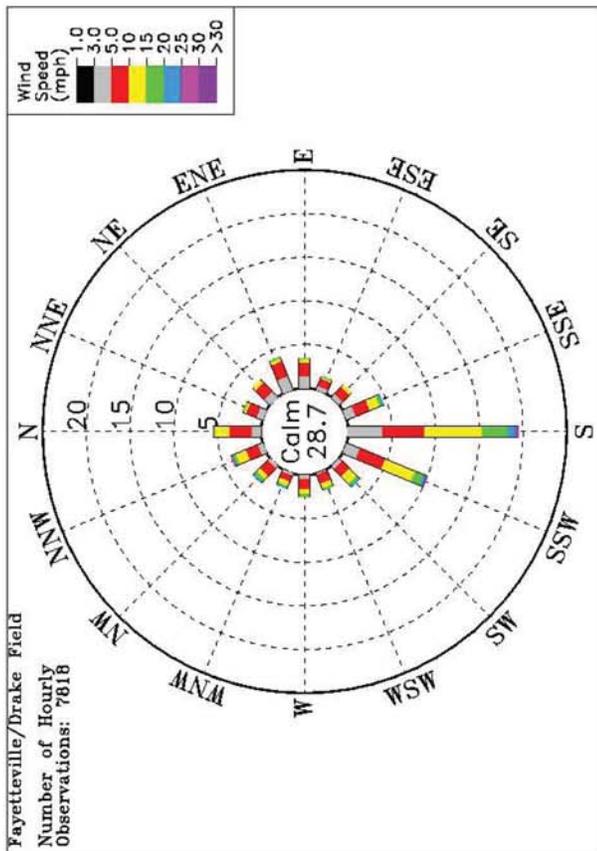
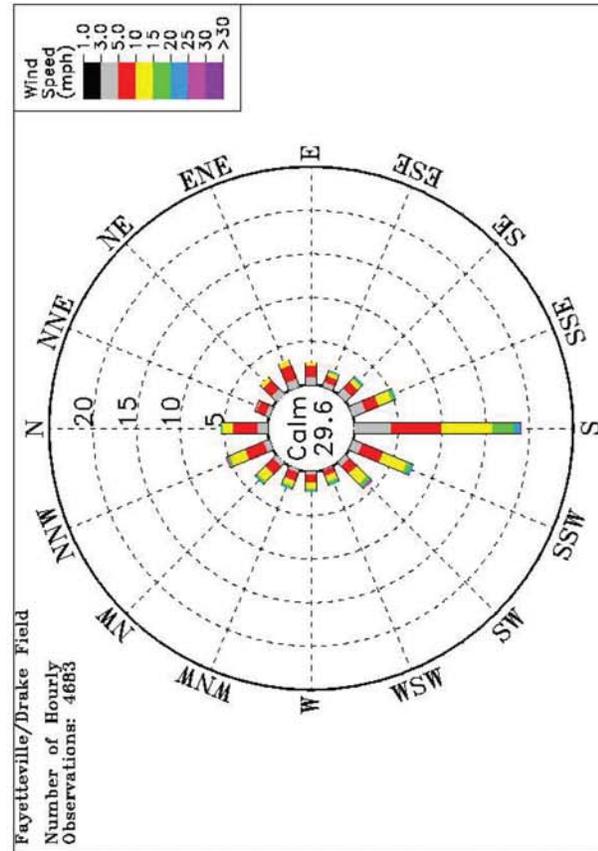
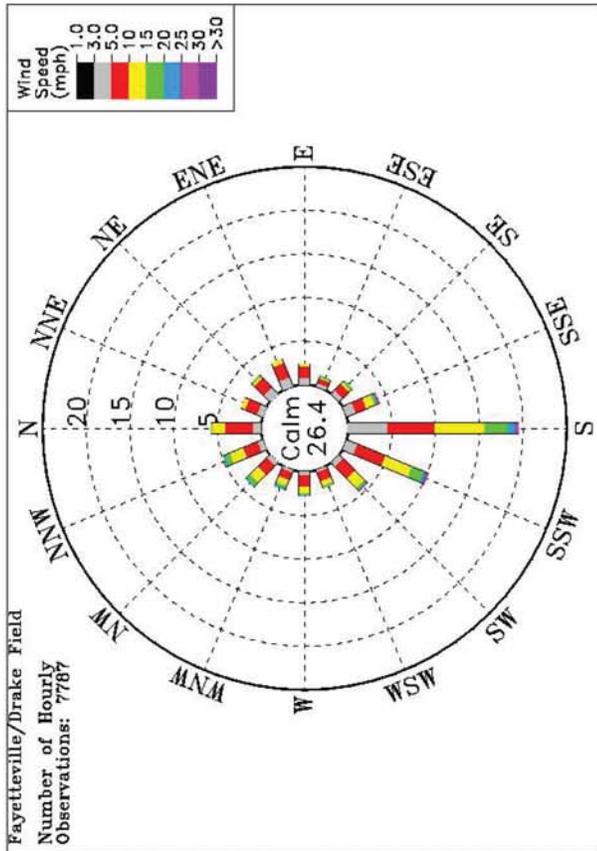


Figure 2. Washington, AR County Air Patterns. Courtesy of Steven E. Cole, Principia Mathematica, Inc., Lakewood, CO.

**CHRONIC AIR ARSENIC LEVELS NEAR LITTER APPLICATIONS**

The community of Prairie Grove, Arkansas lies a few miles from Fayetteville in a rural area heavily impacted by broiler litter applications. Of particular concern is the north central section of town in which several homes and schools are very close to fields to which broiler litter was typically applied at an average rate of 2.0 tons per acre, two or three times per year, as illustrated in Figure 1. In order to estimate the air arsenic levels in this high-impact area, soil and dust samples were collected at a set of homes near schools, as shown in Figure 3. The results of soil and dust analyses are given in Table 3.

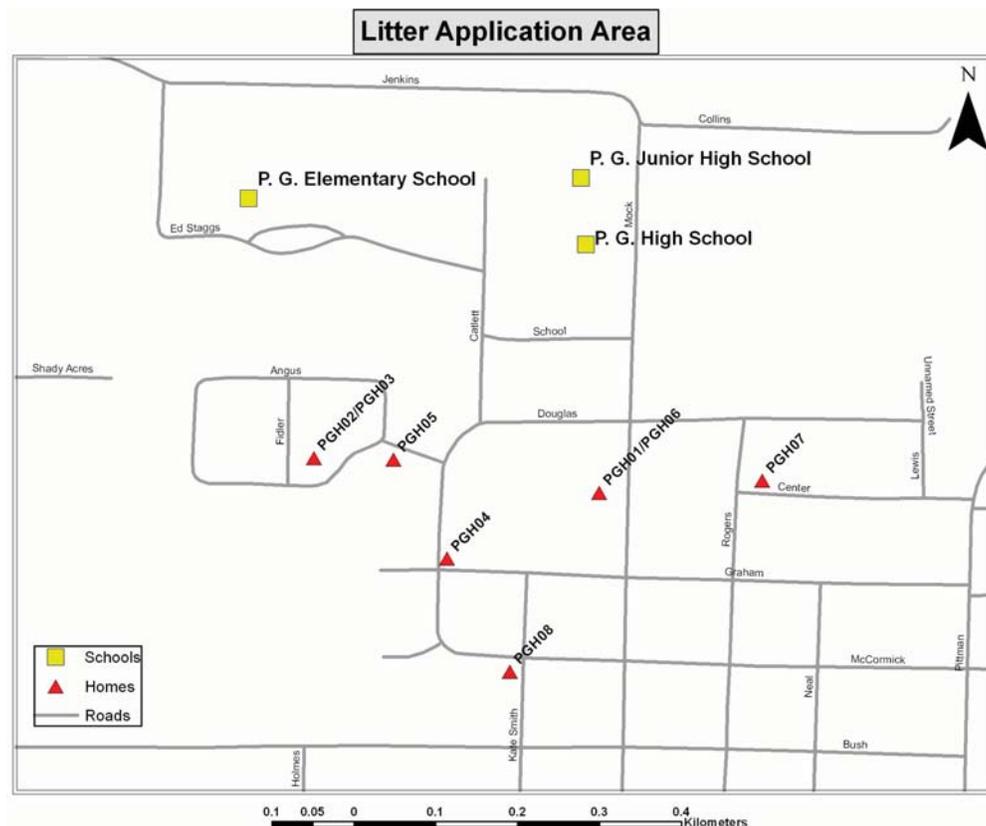
Using the calculated value for the air-volume-to-dust-sample-mass ratio (*R*) from Equation (12) and the dust and soil averages from Table 3, the average (chronic) air arsenic level for the high-impact area is estimated from Equation (8) as:

$$31.0 \text{ mg kg}^{-1} - 5.9 \text{ mg kg}^{-1} = 9.1 \text{ mg m}^3 \text{ ng}^{-1} \text{ kg}^{-1} \times C_{\text{As from air (avg.)}} \quad (13)$$

**Table 3. Homes and Schools Area, Prairie Grove, AR.**

Code	Dates Tested	Dust 1 (mg kg <sup>-1</sup> )	Dust 2 (mg kg <sup>-1</sup> )	Dust 3 (mg kg <sup>-1</sup> )	Soil (mg kg <sup>-1</sup> )
PGH01	09/02	7.2	3.5	18.0	6.1
	01/03	6.8			
PGH02	09/02	34.5	50.5		11.5
	01/03	38.3			
	06/03	41.1			
PGH03	09/02	10.8	46.4		15.9
	09/02				
PGH04	01/03	14.7			
	06/03	11.6			
PGH05	09/02	97.1	130.0		1.1
	09/02	10.0			
PGH06	01/03	18.9	8.7		
	06/03	66.9			
PGH07	09/02	14.4			2.4
PGH08	09/02	13.7	8.9		5.7
		dust average: 31.0 mg kg <sup>-1</sup> soil average: 5.9 mg kg <sup>-1</sup>			

$$C_{\text{As from air (avg.)}} = 25.1 \text{ mg kg}^{-1} \div 9.1 \text{ mg m}^3 \text{ ng}^{-1} \text{ kg}^{-1} = 2.8 \text{ ng m}^{-3} \quad (14)$$



**Figure 3. Locations of Schools and Tested Homes.**

## SOURCE APPORTIONMENT

Arsenic is ubiquitous and any attempt to estimate acute exposure levels, or to assign a principal source, from house dust analyses must take into account alternative sources of arsenic in the dust and in the indoor air. In addition to industrial operations, for which emission information may be available from governmental reports such as Toxic Release Inventory (TRI) data (available on the internet from the U.S. EPA), other sources may require additional chemical testing and extensive questionnaires seeking information on exposures to recognized outdoor and indoor sources such as:

- track-in or blowing dust from local soil containing natural-occurring or anthropogenic levels of arsenic [15]
- blowing dusts from application of arsenic containing poultry litter to nearby agricultural land [12]
- blowing dusts from nearby cotton or rice fields [16], from nearby orchards or potato fields [17], or from a nearby golf course [18] to which arsenicals had been applied
- smoke or ash from coal-fired power plants [19]
- sawdust from CCA-treated (or other arsenical-treated) wood, or smoke from the burning of such wood [20]
- arsenical herbicides or pesticides [21]
- tobacco smoke [14]
- natural gas or its combustion products [22]

Most U.S. uses of arsenicals have been banned or severely limited in recent years, so that current exposures to arsenical rat poisons, weed sprays, CCA-treated lumber sawdust or smoke, or cigarette smoke from tobacco that had been treated with arsenical pesticides are unlikely to have contributed significantly to recent house dust samples. Nonetheless, each of the above-identified potential arsenic sources had to be considered in order to make a reasonable estimate of acute exposure levels in the high-impact area of Prairie Grove.

In identifying the spreading of arsenic-containing broiler litter as the principal source of arsenic in the high-impact area of Prairie Grove, all of the possible contributors listed above were considered. A key factor was the finding of roxarsone and several of its degradation products in most of the homes tested [12].

There were no cotton or rice fields, arsenical-treated orchards or potato fields, or golf courses in the area. The closest coal-fired power plant was more than 20 miles

away, and there was no burning of arsenical-treated wood at nearby facilities, or within the homes for this study. No evidence was found that arsenical herbicides, rodenticides or pesticides had been used within recent years in any of the homes tested for this study and, as previously mentioned, other studies found no correlation between cigarette smoking and household dust levels of inorganic components of cigarette smoke. The arsenic content of natural gas samples studied was so low that any significant contribution to house dusts from that source would have resulted in occupant asphyxiation from the gas or its combustion products. No significant other emission sources of arsenic were identified from TRI reports within 20 miles of the area.

## ESTIMATION OF ACUTE EXPOSURE LEVELS

A second basic equation utilizes the definition of “time-weighted average” (TWA) to estimate peak air exposure concentrations.

$$\text{TWA} = [(\text{exposure}_A \times \text{time}_A) + (\text{exposure}_B \times \text{time}_B) + \dots] \div \text{total time} \quad (15)$$

Once again, use of such an equation would preferably involve specific knowledge of exposure times and exposure levels, but such information is generally unavailable because of the lack of adequate records and of area-wide monitoring data. However, for cases in which a one-time or periodic peak exposure scenario can be identified, Equation (15) can be used to estimate peak (acute) exposure levels.

Given that broiler litter applications just north of the schools in the high-impact area occurred two-to-three times per year, for an hour or less each time, a conservative estimate of the annual peak exposure period would be 0.125 day (3/24 day). It is then reasonable to assume that the non-peak exposures averaged about the total suspended arsenic levels as estimated from measurements at the Fayetteville air monitoring station, namely 0.88 ng m<sup>-3</sup>, during the remaining 364.875 days per year. Accordingly, the peak exposure levels can be calculated by Equation (15) from the chronic exposure (TWA) of 2.8 ng m<sup>-3</sup> found in Equation (14) as:

$$2.8 \text{ ng m}^{-3} = [(0.88 \text{ ng m}^{-3} \times 364.875 \text{ days}) + (\text{peak exposure} \times 0.125 \text{ day})] \div 365 \text{ days} \quad (16)$$

from which

$$\text{peak exposure} = 5,600 \text{ ng m}^{-3} \quad (17)$$

As a check on the reasonableness of this estimate, it is possible to calculate the arsenic content of a dust cloud similar to those shown in Figure 1, as follows:

*Assumptions:*

1. The dust cloud has a volume of about 40,000 m<sup>3</sup>, corresponding to an air volume 10 meters high over an area of one acre (4,047 m<sup>2</sup>).
2. The dust contains only 1.0% of the particulate matter in the 2.0 tons (1,816 kg) of litter being spread per acre, i.e., 18 kg of airborne dust.
3. The litter contains only an average of 30 mg kg<sup>-1</sup> of arsenic. (Litter samples tested in the area actually averaged 38.1 mg kg<sup>-1</sup> of arsenic [12].)

Then:

$$30 \text{ mg kg}^{-1} \times 18 \text{ kg} \div 40,000 \text{ m}^3 \times 10^6 \text{ ng mg}^{-1} \\ = 13,500 \text{ ng m}^{-3} \quad (18)$$

Thus, a calculation associated with actual dust cloud observations and known application rates indicates that the mass balance and time-weighted average approaches yield reasonable order-of-magnitude results.

## DISCUSSION AND CONCLUSIONS

The calculations in this study, based on previously published sampling and analytical data [12], demonstrate that blowing of dusts from poultry litter containing arsenicals can result in high levels of exposure in nearby areas. For comparison, the U.S. National Institutes for Safety and Health (NIOSH) recommends a maximum 15 minute exposure (CEIL) in the workplace to inorganic arsenic not to exceed 2,000 ng m<sup>-3</sup> [23]. Exposures to the general population, particularly children, pregnant women, and persons with compromised immune systems, should obviously be kept well below any recommended workplace ceiling limits.

There are, of necessity, several assumptions inherent in the methodology of this study, but care has been taken to use reasonable and conservative values. Although broiler litter dusts may contain several different chemical forms of arsenic, all—including residual roxarsone itself [24]—must be considered as significant health risks.

Additionally, this study describes a methodology

that might be utilized in other scenarios for which the composition of nonvolatile contaminants in “long-term” house dusts and the identification of periodic exposure sources and time frames are available.

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# An Evaluation of Maintaining Elevated Oxygen Concentrations in Activated Sludge Systems

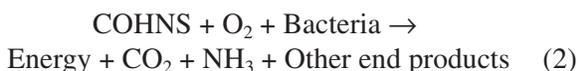
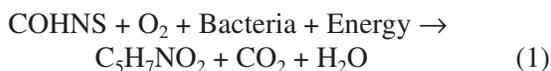
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**ABSTRACT:** The potential of reducing secondary sludge production in activated sludge treatment systems by elevating residual dissolved oxygen (DO) was investigated for a pulp and paper mills. Approximately 10% less sludge was produced by elevating the aeration basin DO concentration from 1 mg/L to 8 mg/L for the three mill effluent types tested. High DO in the aeration basins improved system performance, in terms of COD removal, sludge settling and dewatering properties. However, aeration requirements were at least four times higher for the high DO system as compared to the conventional system operating at a residual DO of 1 mg/L.

## INTRODUCTION

**A**EROBIC biotreatment has long been practiced for the treatment of pulp and paper mill effluents. Two primary biological processes involved within such systems are the synthesis (anabolism) and subsequent degradation (catabolism) of biomass. In aerobic treatment systems oxygen is required for the transformation of organic substrates found in untreated mill effluents into new biological cells, carbon dioxide, nitrogen species and other minor end products as shown in Equations (1) and (2). The energy needed for the biosynthesis by heterotrophic organisms is generated from the bacterial oxidation of organics [Equation (2)]. The endogenous degradation or respiration taking place in aerobic biotreatment systems also requires oxygen as expressed by Equation (3). Assuming that other factors are not limiting, the rates of these anabolic and catabolic processes in aerobic environments are a function of the amount of dissolved oxygen available as oxygen is required to move all reactions to the right.



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COHNS = biologically oxidizable organic substrate commonly known as BOD

$\text{C}_5\text{H}_7\text{NO}_2$  = the empirical formula for biomass

As cell synthesis and degradation of biomass are generally not zero order reactions, one could surmise that the rates of anabolic and catabolic activities within the wastewater treatment system would be dependent on dissolved oxygen (DO) concentration. One can predict that the treatment performance (anabolic activity), at least in terms of BOD removal, would be influenced by the availability of oxygen (aeration). In cases where there is not sufficient oxygen available to oxidize the incoming BOD, there would be a significant reduction in treatment performance (anabolic activity), resulting in residual BOD leaving with treated outflow. Biomass degradation (catabolic activity) in the activated sludge process can also be negatively impacted by the lack of oxygen. Thus, the overall sludge yield of an effluent treatment system, which dictates the sludge wasting rate, would increase in low dissolved oxygen concentration conditions.

In order to understand the effect of dissolved oxygen concentration in the bulk liquid on excess sludge production, Abbassi *et al.* [1] developed a mathematical model taking into account mass transfer of oxygen, biological reactions within floc particles and the endogenous respiration process. Model predictions supported with lab experiments treating a synthetic substrate

showed that the oxygen concentration in the bulk liquid had a significant effect on excess sludge production. They hypothesized that an increased oxygen concentration in the bulk liquid leads to a deep diffusion of oxygen into the floc, which enlarges the aerobic volume inside the floc leading to a deficient situation regarding the organic substrate. According to Monod kinetics, a decreased substrate concentration puts more emphasis on cellular maintenance leading to a reduced growth rate resulting in a lower production of excess sludge. The improved diffusion of oxygen within biological flocs, as a result of higher DO in the liquid phase, has recently been measured and documented [2,3]. The positive impact of elevated DO on floc properties, in regards to their size [4] and settleability [5,6], have also been shown.

Chapman *et al.* [5] surveyed numerous municipal treatment facilities and found evidence to suggest that full-scale systems operating within a DO concentration range of 4–6 mg/L produced significantly less excess sludge than systems operating with DO concentrations between 1–2 mg/L. Consistently, one of the major claims of the suppliers of pure oxygen-based activated sludge systems is that they produce less sludge than the conventional activated sludge systems. Evidence from the developers of the pure oxygen-based systems seems to support it, albeit some with very high DO (15 mg/L) concentrations [7].

This paper investigates the potential of elevating residual DO in the aeration basin to reduce secondary sludge generation in activated sludge treatment systems treating pulp and paper wastewaters. Experiments were performed on laboratory and pilot-scales for evaluating implications of this approach regarding treatment system performance and sludge production.

## MATERIALS AND METHODS

Two identical laboratory-scale activated sludge units were operated in parallel (Figure 1). One of the two units served as control or conventional system while the other operated under experimental conditions. Each unit had a 9.4 L aeration basin which flowed into a 2.1 L secondary clarifier. During the investigation three trials were completed, each treating an effluent collected from a different mill type. Primary treated effluent samples were collected from a newsprint mill henceforth referred as the TMP mill, an integrated kraft pulp and paper mill and a groundwood/kraft (GW/kraft) pulp

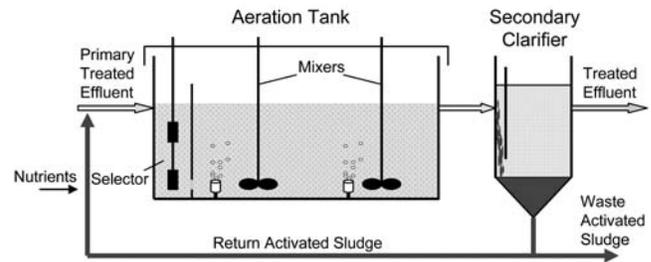


Figure 1. Schematic of the laboratory activated sludge unit.

and specialty paper mill. The samples were stored at 3°C. The reactor temperature was controlled at 34°C throughout the study. Table 1 presents characterization data for the collected primary treated samples.

The control and experimental laboratory units were seeded before each trial with 9.4 L of mixed liquor suspended solids (MLSS) collected from the wastewater treatment facility supplying the primary treated effluent. The laboratory units were operated to mimic the operation of the treatment plant where the effluent samples were collected (Table 2). The only parameter that varied from the mill situation was the aeration basin DO concentration. During each of the three trial periods the control unit was operated under DO conditions of approximately 1.0 mg/L. The experimental unit was operated at a higher DO concentration ranging between 7.7 mg/L and 8.4 mg/L. The control and experimental systems were referred to as conventional activated sludge (CAS) and CAS<sub>O<sub>2</sub></sub> units, respectively. To achieve high DO in the CAS<sub>O<sub>2</sub></sub> system, the reactor feed air was enriched with pure oxygen. This was necessary as a result of high reactor operating temperature which negatively impacts dissolved oxygen saturation concentration. Saturation DO in deionized water at 34°C is 7.1 mg/L as compared to 10.4 mg/L at 20°C at 1 atm. Nutrients were

Table 1. Characterization of primary treated effluent samples. Data in parenthesis are the number of analysis.

Parameter	TMP	Integrated kraft	GW/kraft
pH	6.5 (1)	7.2 (1)	9.1 (2)
BOD, mg/L	725 (23)	495 (26)	610 (16)
COD, mg/L	1955 (26)	1470 (35)	2400 (35)
TSS, mg/L	192 (8)	89 (12)	73 (5)
Colour, CU	870 (12)	1270 (17)	2875 (6)
NH <sub>3</sub> , mg/L	4.6 (2)	0.2 (9)	0.6 (3)
NO <sub>2</sub> <sup>-</sup> , mg/L	NA	< 1 (2)	< 1 (2)
NO <sub>3</sub> <sup>-</sup> , mg/L	NA	< 1 (2)	< 0.5 (2)
PO <sub>4</sub> <sup>-3</sup> , mg/L*	NA	0.30 (2)	0.88 (2)

NA = Not available.

\*Reported as P.

**Table 2. Operating parameters of the treatment units during the three trial steady state periods.**

Parameter	TMP		Integrated kraft		GW/kraft	
	CAS	CAS <sub>O<sub>2</sub></sub>	CAS	CAS <sub>O<sub>2</sub></sub>	CAS	CAS <sub>O<sub>2</sub></sub>
Aeration volume, L	9.4	9.4	9.4	9.4	9.4	9.49.4
HRT, h	12.9	12.8	12.9	12.9	14.0	14.1
pH	7.1	7.3	7.5	7.7	7.7	7.7
Temperature, °C	34	33	33	33	33	34
Residual DO, mg/L	0.8	7.8	1.1	8.4	1.0	7.7
MLSS, mg/L	2640	2730	2540	2835	2790	3045
SRT, d	4.8	4.9	7.2	8.7	8.0	8.4
Trial period, d	39	39	55	55	38	38
Number of sludge ages completed, <i>n</i>	8.1	8.0	7.6	6.3	4.8	4.5

HRT= Hydraulic retention time.

SRT= Solids retention time.

supplied in the form of  $\text{NH}_4\text{HCO}_3$  and  $\text{NaH}_2\text{PO}_4$  at the BOD:N:P ratio of 100:5:1. Consistent COD removal was used to indicate stable treatment system performance at which time data collection began. Acclimatization periods ranged between 6–11 days prior to data collection for the trial periods. The duration of each of the trial is reported in Table 2.

During each trial the reactors' performance was assessed by analyzing for BOD, COD, and colour removal as well as the discharge of suspended solids (TSS) and nutrients (nitrogen and phosphorous) with the treated effluent. The MLSS was characterized in terms of specific oxygen uptake rate (SOUR), settling using the stirred sludge volume index method [8] and microscopic examination (TMP trial only). The waste activated sludge (WAS) dewatering properties were determined using a primary to secondary sludge ratio of 50:50, with standard reference pulp being used as the primary sludge. The sludge was not conditioned with any chemicals before completing the dewatering tests. A pressure filtration timing device was used to produce a 3 g sludge cake using 100 psi pressure. Detailed description of the dewatering procedures can be found in Lo and Mahmood [9]. Sludge inventory in the reactors, volume and concentration of the wasted sludge and TSS discharged with treated effluent were determined for each system on a daily basis. The daily sludge production was calculated, which is the net change in sludge inventory plus the wasted sludge and the sludge lost with the treated effluent. Sludge production was reported as kilogram of TSS produced per kilogram of COD removed from the system over the course of the whole trial period. The microbiological properties of the MLSS were determined at the end of the TMP experiment using an Olympus BX40 phase contrast microscope. Higher life forms were enumerated by

averaging the numbers found within three 7.5  $\mu\text{L}$  samples.

Air flow rate to the aeration basins was monitored throughout the trials. However, due to short contact time available for oxygen transfer from air to the bulk liquid the small laboratory systems would not necessarily estimate the aeration demand of a full-scale facility. To better represent aeration demand of a full-scale activated sludge system, a separate pilot-scale experiment was performed. A 10 cm diameter plexi-glass column with a height of 3.65 m was used to simulate a full-scale activated sludge system. Fine bubble aeration was provided by air blown through a porous stainless steel aerator of five micron pore size situated at the bottom of the column. Acclimatized MLSS in the column was recirculated at a rate of 3 L/min to insure complete mixing within the column. Primary treated effluent was fed at a rate of 2.6 L/h. An YSI Model 54A oxygen meter using an YSI 5740 probe was used to monitor the DO within the column at various depths. Approximately 33 L of acclimatized GW/kraft MLSS was used to fill the column. The MLSS was previously acclimatized over a 10 day period using two separate activated sludge units, each with an aeration volume of 35 L. One unit operated at a DO of 1 mg/L while the other at 7.5 mg/L. The operating parameters were kept practically the same as those for the laboratory trial. The MLSS acclimatized at 1 mg/L was added to the column and the MLSS recirculation and effluent feed system were started. Sufficient air was supplied to the column to maintain a residual DO of approximately 1 mg/L. The air flow rate was monitored to estimate aeration requirement under steady state conditions. Following this the column was filled with MLSS acclimatized at 7.5 mg/L and the procedure was repeated. The column experiments operated between 2.5–3.5 hours.

## RESULTS AND DISCUSSION

### Sludge Production

The sludge yield of the high DO unit (CAS<sub>O<sub>2</sub></sub>) was consistently lower than that of the low DO unit (CAS) during each of the three trials (Figure 2). The average decrease in sludge production ranged between 5–13%, with the highest reduction attained during the treatment of GW/kraft effluent. The reductions attained were significantly lower than those which have been reported in the literature. Abbassi *et al.* [1] reported a 26% reduction in sludge yield when comparing a system with a residual DO of 6.0 mg/L with one operating at 2.0 mg/L during the treatment of a synthetic substrate. McWhirter [7] referenced sludge reductions of greater than 50%; however, DO residuals in this municipal wastewater study were in the 15 mg/L range. It appears that the lower yield reductions achieved during this study could have been a result of pulp and paper wastewaters being more difficult to degrade as a result of the presence of lignin and other refractory compounds such as with many chlorinated organics. Such substrates would cause lower sludge production as compared to yields of systems treating easily degradable substrates such as glucose-based synthetic and municipal wastewaters. Reduction in the production of new biomass could result from the higher proportion of energy expended by the bacteria for cellular maintenance when treating hard to degrade wastewaters. In such systems the subsequent sludge reduction strategies would be less effective as the system is already operating under low sludge yield conditions. Another possibility could be that the floc structure of sludge in pulp and paper activated sludge systems is different from that typically found in municipal sys-

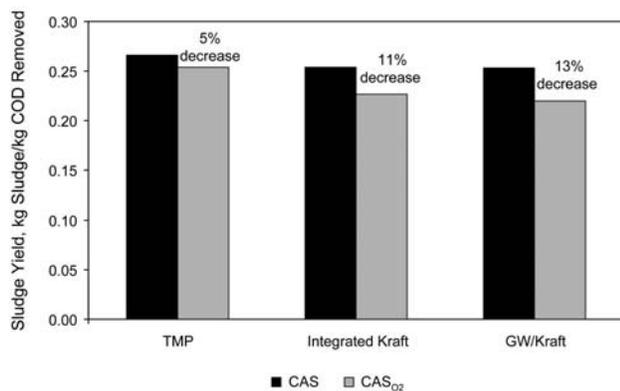


Figure 2. Sludge yield from laboratory units treating TMP, integrated kraft and GW/kraft effluent.

tems. Differences in floc structure, especially those affecting the permeability of oxygen within the floc, would limit catabolic activity within a floc thus compromising sludge yield reduction potential when treating pulp and paper effluents.

As mentioned in the introduction, the likely mechanism for lower sludge yield under high DO conditions is the result of an increase in DO concentration gradient between the liquid phase and the center of the sludge floc. The higher concentration gradient allows for deeper oxygen diffusion into the sludge floc resulting in enlarged endogenous respiration zone. This would inevitably lower the quantity of biomass in the treatment system. Another possible mechanism involves the effect DO has on higher life forms, which play a crucial role in sludge yield reduction through predating on free swimming bacteria and small flocs. In consistently elevated DO environments, oxygen would definitely not be a factor limiting the growth and proliferation of protozoa and metazoa. An increase in predatory pressure on bacteria would result in a reduction in total biomass which is the basis for the low sludge production (LSP) process [10,11]. Support for this additional mechanism was seen with the enumeration of higher life forms during the treatment of TMP effluent. Figure 3 shows approximately double the higher life forms in the oxygen enriched system as compared with the conventional system. Microscopic examinations of the MLSS were not performed during the other trial periods.

### Sludge Properties

There were significant differences in MLSS characteristics between the two systems during each of the three trials (Table 3). Sludge settling, as indicated by

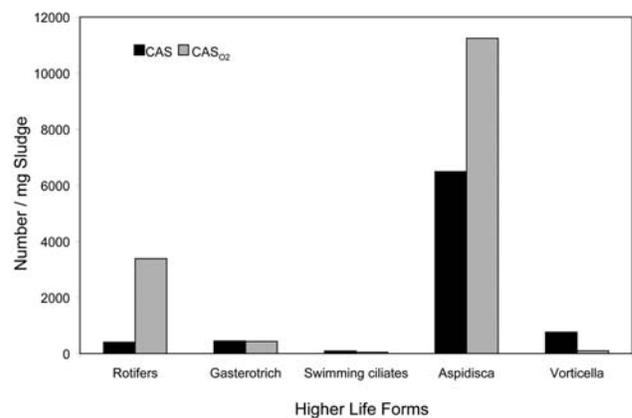


Figure 3. Abundance of higher life forms during the treatment of TMP effluent.

**Table 3. Sludge properties (mean values).**

Parameter	TMP		Integrated kraft		GW/kraft	
	CAS	CAS <sub>O<sub>2</sub></sub>	CAS	CAS <sub>O<sub>2</sub></sub>	CAS	CAS <sub>O<sub>2</sub></sub>
SSVI*, mL/g	224	199	63	51	118	53
Presscake consistency, %	16.4	21.6	30.8	32.2	33.0	37.0
SOUR**, mg/(h.g)	20	18	12	11	13	11

\*Stirred sludge volume index. Data are averages of 17 to 24 analyses.

\*\*Specific oxygen uptake rate. Data are averages of 7 to 9 analyses.

SSVI was positively affected by elevated DO concentrations. The improvement was less evident during the treatment of integrated kraft mill effluent (11%) and greatest (55%) for the GW/kraft mill effluent. The likely reason for the relatively lower percent improvement in settling properties of the integrated kraft MLSS is that this effluent produced well settling sludge in both the CAS and CAS<sub>O<sub>2</sub></sub> systems. These results are consistent with literature results [4,6]. The likely reason for the improved settling is the suppression of the extended growth of filamentous bacteria outside of the flocs which can adversely affect settling [12]. The microscopic examination of the MLSS of the two systems during the TMP period supports this claim as the filament intersectional count for the reference system was 17,500/mg sludge for the CAS system as compared to only 6000/mg sludge for the CAS<sub>O<sub>2</sub></sub> system.

Improvement in dewatering properties of the sludge wasted from the higher DO systems was also realized. Higher final presscake solids were achieved with the CAS<sub>O<sub>2</sub></sub> sludge as compared to the sludge from the CAS system (Table 3). The presscake solids were 5.2, 1.4 and 4 percentage points higher for sludges from the CAS<sub>O<sub>2</sub></sub> systems when treating the TMP, integrated kraft and GW/kraft mill effluents, respectively. These improvements could be related to the reduction in filamentous bacteria as DO limiting conditions can be a cause for their proliferation. Filamentous bacteria are believed to adversely affect dewatering, however direct evidence is

limited [13]. Also, under oxygen limited conditions there can be a loss in hydrophobicity of the bacterial cell surface which reduces sludge dewaterability [14].

The MLSS of the two systems had similar levels of microbiological activity, as was evident from the specific oxygen uptake rate (SOUR) data shown in Table 3. It appears that the TMP effluent was easier to degrade as compared to kraft and GW/kraft effluents as the specific oxygen uptake rate of the sludge using this effluent was approximately 65% greater than the SOUR for the other two effluents.

### Treatment Performance

Both the conventional and oxygen enriched systems were found to remove greater than 95% of incoming BOD (Table 4) when treating all three types of effluents. Despite the high BOD removal efficiency, the GW/kraft effluent was the most difficult to treat as COD removals were only 53% and 55% for the CAS and CAS<sub>O<sub>2</sub></sub> systems, respectively. The COD removal was consistently, albeit marginally (1–3%), better with the CAS<sub>O<sub>2</sub></sub> system as compared to the CAS system, during all three trials. It was surprising to find that the oxygen enriched system reduced colour when treating TMP effluent. However, this was not demonstrated during the treatment of the other two effluents which had substantially more colour (Table 1). The non-settleable solids

**Table 4. Treatment performance during the three trial periods.**

Parameter	TMP		Integrated kraft		GW/kraft	
	CAS	CAS <sub>O<sub>2</sub></sub>	CAS	CAS <sub>O<sub>2</sub></sub>	CAS	CAS <sub>O<sub>2</sub></sub>
BOD removal, %*	95	97	98	98	98	99
COD removal, %*	76	79	68	69	53	55
Colour removal, %**	-4 <sup>‡</sup>	30	19	22	0	1
Overflow TSS, mg/L*	24	17	22	34	23	20

\*Mean of at least 15 analyses during steady state.

\*\*Mean of 2–5 analyses during steady state.

<sup>‡</sup>The negative sign represents a net increase.

**Table 5. Nutrient discharge from the two systems during the three trial periods. Number of analysis is in parenthesis.**

Parameter	TMP		Integrated kraft		GW/kraft	
	CAS	CAS <sub>O<sub>2</sub></sub>	CAS	CAS <sub>O<sub>2</sub></sub>	CAS	CAS <sub>O<sub>2</sub></sub>
NH <sub>3</sub> , mg/L	1.1 (2)	1.2 (2)	1.1 (2)	0.9 (2)	4.2 (2)	0.3 (2)
NO <sub>2</sub> <sup>-</sup> , mg/L	NA	NA	< 1 (2)	< 1 (2)	< 1 (2)	< 1 (2)
NO <sub>3</sub> <sup>-</sup> , mg/L	NA	NA	7.7 (2)	26.1 (2)	4.0 (2)	30.9 (2)
PO <sub>4</sub> <sup>-3</sup> , mg/L*	NA	NA	2.3 (2)	2.7 (2)	6.0 (2)	6.8 (2)

NA, Not available.

\*Reported as P.

(TSS) concentration in the treated effluent (overflow TSS) remained low for both systems during all trials.

Although not investigated in this study, one may speculate that the higher residual DO system would perhaps be better in handling organic shock loading which results in a rapid increase in oxygen demand. The high residual DO in the aeration basin would, at least partially, satisfy this demand preventing incomplete effluent treatment.

Nutrients discharged from the oxygen enriched systems had substantially higher nitrate concentrations than found in the CAS overflows (Table 5). This observation is consistent with the findings reported in literature. Satch *et al.* [15] reported that nitrification rates in activated sludge systems increase proportionally with increasing DO. During the treatment of GW/kraft effluent the nitrate discharge was relatively low but the residual ammonia concentration in the treated overflow from the CAS system was substantially higher than that from the CAS<sub>O<sub>2</sub></sub> system. Elevated ammonia concentrations, especially in higher pH environments, are linked to fish toxicity which is regulated in Canada [16]. The ammonia and nitrate data for the GW/kraft trial in Table 5 suggest that an added benefit of maintaining elevated DO concentrations in systems treating hard to degrade effluents is that residual ammonia concentrations could perhaps be lowered. Additional experimental evidence is, however, needed to confirm this finding.

## Aeration Demand

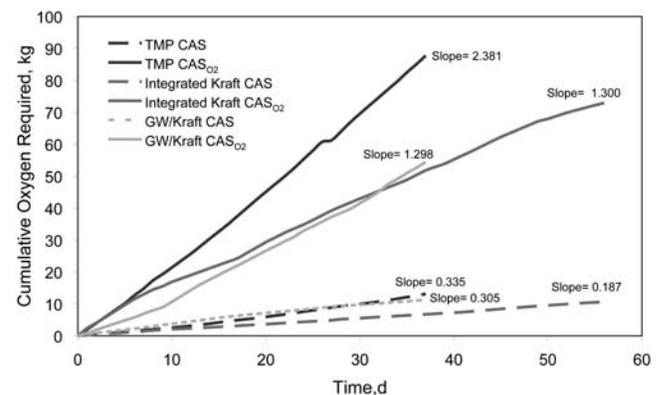
### Laboratory-scale

As one would expect, the aeration required to maintain residual DO between 7.7 mg/L and 8.4 mg/L was found to be significantly higher than that needed to maintain 1.0 mg/L residual (Figure 4). These data illustrate that the type of effluent used also has an influence on aeration demand, as is evident from the diverging

lines. Particularly, when treating the TMP effluent the increase in aeration demand was highest, this correlates well with the SOUR data reported in Table 3. Comparing slopes of the lines of the low and high residual DO systems, fold increases of 7.1, 6.9 and 4.1 for the TMP, integrated kraft and GW/kraft mill trials were found, respectively.

The amount of oxygen supplied to the laboratory systems as a function of BOD removed was 30.7, 24.2 and 31.0 kg O<sub>2</sub>/kg BOD for the TMP, integrated kraft and GW/kraft trials, respectively. These values are substantially higher than those for full-scale systems. A mean value of 1.6 kg O<sub>2</sub>/kg BOD removed was found from a survey of 10 pure oxygen-based activated sludge systems [17]. The majority of the oxygen delivered during the laboratory trials can be assumed to have been vented from the system without being transferred to the liquid phase. The primary reason for this is the shallow depth of the aeration chamber which affects solubility in two ways; minimal contact time of gas bubble as it rises in the water column and lack of pressure which can be found at the lower depths of full-scale treatment basins.

The oxygen transfer rate from the gas phase to the liquid phase is generally described in terms of interfacial



**Figure 4.** Oxygen supplied to maintain target DO concentrations in laboratory units during the three trial periods.

mass transfer coefficient ( $K_L a$ ). There are many factors that influence this transfer rate. The alpha factor ( $\alpha$ ) relates to how well oxygen can diffuse into wastewater as compared to water. The beta factor ( $\beta$ ) provides information on the impact dissolved solids has on the transfer efficiency. Temperature changes will also affect the transfer of oxygen (theta factor ( $\theta$ )). Biological activity, particularly with high-rate systems such as activated sludge, can play an important role in determining transfer efficiency. Other factors include oxygen partial pressure, oxygen deficit and saturation concentration. In other words, the residual DO level in a wastewater treatment system is not a simple function of air supplied. Many factors must be taken into consideration when predicting aeration required for ascertaining elevated levels of DO.

Another factor in determining the aeration requirement with existing air diffusion systems is the coalescence of air bubbles reducing the interfacial area for the transfer of oxygen from the gas to liquid phase. Hui and Duff [18] described how increasing the air flow rate from 1 to 5 sLpm in water only increased the  $K_L a$  by 67%.

Thus, predicting the actual increase in aeration demand to achieve high residual DO levels for a full-scale system from these laboratory data would be difficult. Differences between laboratory-scale and full-scale activated sludge systems include mixing intensity, bubble size, pressure and the gas/liquid contact time. To better simulate aeration in a full-scale treatment system an experiment was conducted using a column reactor which had a water column height similar to that of full-scale facilities.

#### Pilot-scale

The MLSS from the GW/kraft mill (acclimatized at 1 mg/L) had a SOUR of 8.2 mg/(g.h). During the 3.5 hour test an average airflow of 0.11 L/min was required to maintain a residual DO of 2.5 mg/L (Figure 5). The 7.5 mg/L acclimatized MLSS, which had a SOUR of 8.2 mg/(g.h), required an airflow of 0.43 L/min to maintain a residual DO of 7.5 mg/L. These data appear to support the laboratory GW/kraft trial results that aeration demand would increase to about four fold if the residual DO were to be increased to 7.5 mg/L. However, as mentioned earlier extrapolating from laboratory data what the actual aeration demand and its associated costs would be for a treatment system implementing this sludge reduction methodology is challenging. Building on these foundations, site-specific investigations are

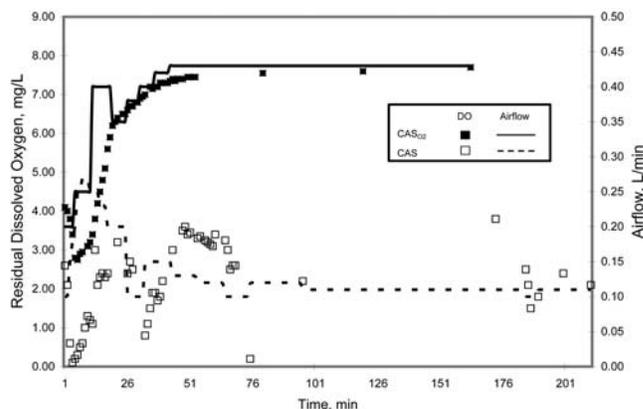


Figure 5. Aeration required for the two DO scenarios during column experiments with GW/kraft effluent.

recommended to accurately estimate increased aeration demand to maintain high residual DO in commercial treatment systems. Economic evaluation could then be completed to assess the net benefits of sludge reduction via increased DO concentration.

It appears unlikely that a conventional air-based activated sludge system would be capable of increasing residual DO to near saturation levels without the addition of liquid oxygen. A more likely fit for this sludge reduction technology would be with pure oxygen treatment systems which have the on-site capabilities to elevate the residual DO to higher concentrations. Particularly important is to elevated DO concentrations at the back end of the systems where degradation of biomass is more pronounced due to limited soluble substrate.

## CONCLUSIONS

Sludge yield reduction values reported in literature for domestic wastewaters (under high DO conditions) were not demonstrated in this study. Approximately 10% less sludge was found to be produced when elevating the residual DO from 1 mg/L to 8 mg/L. This high DO level was attained by increasing aeration at least four fold. Site specific evaluations are recommended to estimate the increase in airflow/energy requirement for achieving such high DO levels.

The increase in DO concentration in the aeration basin of a laboratory activated sludge system showed improvements in COD removal (albeit marginally), sludge settling and dewatering properties. However, due to its limited benefits and relative high cost it appears unlikely that this sludge reduction method is transferable to the pulp and paper industry.

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# Assessment of Sewage Sludge Characteristics in Tehran Municipal Wastewater Treatment Plants

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**ABSTRACT:** The application of sewage sludge to agricultural land has become a common practice over the past several decades. The practice, however, raises a number of concerns because sludge contains pathogenic microorganisms, which pose a threat to public health. The aims of this study were (1) to assess important characteristics of dried sewage sludge in three wastewater treatment plants (WWTPs) in Tehran, Iran and to compare these characteristics with international standards and (2) to find a probable statistical relationship between different parameters of the sludge. Samples were collected during a year (2006–07) from drying beds of the WWTPs and main parameters like Parasite eggs; Fecal coliform (FC), Total Coliform (TC) of the samples were examined. The results showed that the average amounts of FC for sludge of the Tehran's WWTPs, "Shahrak-e-Gharb", "Shoosh" and "Mahallati" were found to be  $1.3 \times 10^4$ ,  $1.05 \times 10^4$  and  $2 \times 10^4$  MPN/g DS<sup>1</sup>, respectively. According to the obtained data, the sludge of all these wastewater treatment plants is classified into Class B of USEPA 40 CFR Part 503 regulations. Strong statistical relationships were found between parasite eggs and Fecal Coliform of the samples with the Pearson correlation factor of 0.952.

## INTRODUCTION

**T**HE application of sewage sludge to agricultural land has become a common practice over the past several decades. Sewage sludge is an organic waste which usually contains high levels of nitrogen and phosphorous as well as significant concentrations of micronutrients (Kucukhemek *et al.*, 2007). The practice, however, raises a number of concerns because sludge, by its nature, is teaming with microbes and also contains pathogenic microorganisms, which pose a threat to public health (The Fundamental Microbiology of Sewage, 2007).

Hence there is a risk, albeit small, that the use of such sludge may cause outbreaks of disease due to the transmission of these organisms through the food chain. For these reasons, there is a need to control the levels of pathogens in sludge and its application to agricultural land (The Microbiology of Sewage Sludge, 2003). Ob-

viously, in order to treat and dispose of the sludge that is produced in a wastewater plant effectively, and to decrease the health risk of using sludge, it is crucial to know the characteristics of the sludge that will be processed (Fytili and Zabaniotou, 2006).

Presently, wastewater treatment plants (WWTPs) in Iran use their sludge in agriculture field without any proper treatment. Several studies in different cities of Iran were carried out in order to investigate the sludge characteristics (Bina *et al.*, 2004; Farzadkia and Taherkhani, 2005; Mesdaghinia *et al.*, 2004). Whereas dried sludge is applying in agricultural lands in Tehran city, there was a need to study the characteristics of Tehran WWTPs' sludge. The main aims of this study are (1) to assess some important characteristics of dried sewage sludge in three WWTPs including Sharhrak-e-Gharb, Shoosh and Mahallati WWTPs, Tehran, Iran and to compare these characteristics with the international standards in order to evaluate the ap-

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<sup>1</sup>Most Probable Number per gram of Dry Solids.

plicability of these sludge for using in agriculture fields and (2) to find a probable statistical relationship between different parameters of the sludge.

## MATERIALS AND METHODS

This study was carried out from October 2006 to August 2007 in four seasons. In Tehran, the capital and largest city of Iran, there are seven WWTPs. Presently, of these seven WWTPs, just three of them including “Sharhrak-e-Gharb”, “Shoosh” and “Mahallati” are producing dried sludge, some of which is used on agricultural lands. The sludge samples were taken from drying beds of these three WWTPs, preserved and transferred to the laboratory in an appropriate temperature according to the standard methods and U.S.EPA procedure (US EPA, 1983 and Standard Methods, 1992). Samples were collected during four seasons (fall, winter, spring and summer (2006–07)) and different parameters including Total Coliform (TC), Fecal Coliform (FC), Parasite eggs (ova), Solids (total solids (TS), volatile solids (VS), Fixed solids, VS/TS and Total Dissolved Solids), pH, and Electrical conductivity (EC) were examined using standard methods (Standard Methods, 1992; USEPA, 1992, 2000 and European standards, 2005). In addition, in order to find a possible statistical relationship between the obtained data, SPSS as statistical software was used.

## RESULTS AND DISCUSSION

Some important parameters of the sewage sludge including TC, FC, parasite eggs (ova), sludge solids, pH, Electrical conductivity (EC) and Total Dissolved Solids (TDS) were examined and the possible statistical relationship between these parameters were checked in this study. The results are discussed below.

### Important Characteristics of Sludge

#### Total Coliform and Fecal Coliform

The results of enumeration of TC and FC for sludge

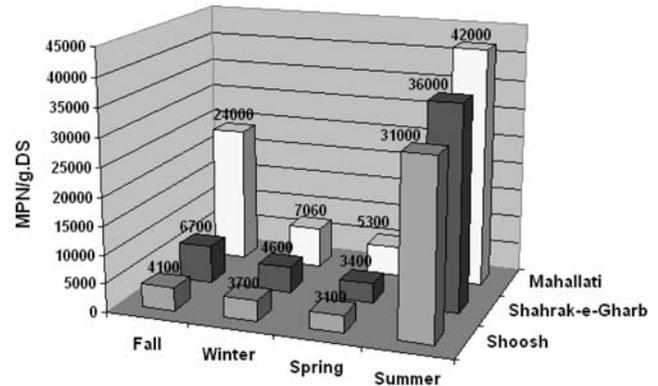


Figure 1. Amounts of Fecal Coliform in the WWTPs during four seasons.

are usually expressed as Most Probable Number per gram of Dried Solids (MPN/g.DS) according to the available procedures (Standard Methods, 1992; USEPA, 1992). The obtained results of enumeration of TC and FC of the samples are summarized in Table 1 and Figure 1, respectively. The results showed that the average amounts of FC for sludge of Shahrak-e-Gharb, Shoosh and Mahallati WWTP's were  $1.3 \times 10^4$ ,  $1.05 \times 10^4$  and  $2 \times 10^4$  MPN/g.DS, respectively. In comparison to U.S.EPA standards (EPA 40 CFR Part 503 regulations), all the sludge samples are classified as Class B. Therefore, direct human exposure to these sludges would still pose a significant health risk and its application would be restricted. As is reported in Table 1 and Figure 1, the maximum and minimum values of FC and TC were observed in summer and spring, respectively for all WWTPs. The lowest and highest amounts of FC were belonged to Shoosh and Mahallati WWTP, respectively.

In comparison to the available data from other WWTP's in Iran such as Isfahan WWTPs (south of Isfahan, north of Isfahan and ShahinShahr WWTPs), Serkan and Shoosh WWTP in 2004 (Bina *et al.*, 2004; Farzadkia and Taherkhani, 2005; Mesdaghinia *et al.*, 2004), lower amounts of FC were found in the selected WWTPs in Tehran. These amounts for south of Isfahan, north of Isfahan and ShahinShahr WWTPs were reported as  $1.8 \times 10^6$ ,  $2.3 \times 10^6$  and  $1.6 \times 10^6$  MPN/g.DS

Table 1. Amounts of Total Coliform in the WWTPs during Four Seasons.

Wastewater Treatment Plants	Fall	Winter	Spring	Summer
	TC (MPN/g.DS)	TC (MPN/g.DS)	TC (MPN/g.DS)	TC (MPN/g.DS)
Shahrak-e-Gharb	$2 \times 10^5$	$5.6 \times 10^4$	$4.2 \times 10^3$	$4.7 \times 10^5$
Shoosh	$2 \times 10^5$	$4.8 \times 10^4$	$2 \times 10^4$	$2.3 \times 10^5$
Mahallati	$3.5 \times 10^5$	$9.6 \times 10^4$	$5.7 \times 10^4$	$5.2 \times 10^5$

(Bina *et al.*, 2004). The value was  $8.97 \times 10^7$  MPN/g.DS for Serkan WWTP (Farzadkia and Taherkhani, 2005) and  $2 \times 10^6$  MPN/g.DS for Shoosh WWTP in 2004 (Mesdaghinia *et al.*, 2004).

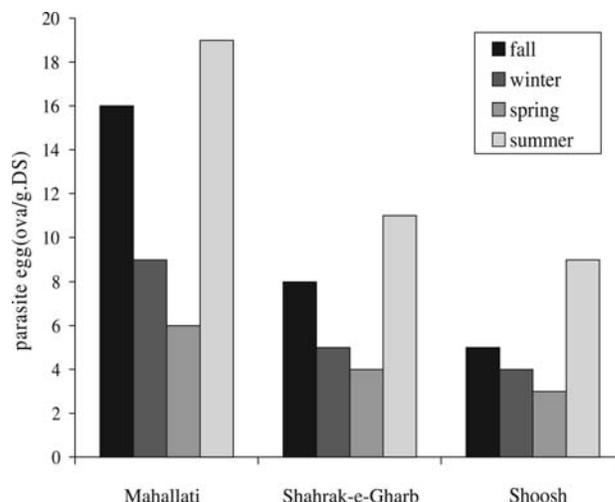
#### Parasite Eggs (ova)

One of the important parameters in sludge is parasite eggs that can cause serious diseases. The results of counting parasite eggs are illustrated in Figure 2. The results showed that the average amounts of parasite eggs (ova) for sludge of Shahrak-e-Gharb, Shoosh and Mahallati WWTP's were found to be 7, 5 and 13 ova/g.DS, respectively. According to Figure 2, the maximum and minimum values of parasite eggs (ova) were observed in summer and spring, respectively for all WWTPs. In addition, Shoosh WWTP has the lowest amounts and Mahallati WWTP has the highest amounts of parasite eggs. Amounts of parasite eggs (ova) for all samples were more than the acceptable amount of 1 ova per gram of dried solids EPA regulations (Class A of USEPA 40 CFR Part 503 regulations).

Lower amounts of parasite eggs were found in Tehran WWTPs in compared with those of Isfahan (south of Isfahan, north of Isfahan and ShahinShahr WWTPs) and Serkan WWTP. The amounts of Parasite eggs were determined to be 12, 16, 58 and 63 ova/g.DS for south of Isfahan, north of Isfahan, ShahinShahr and Serkan WWTPs, respectively (Bina *et al.*, 2004. Farzadkia and Taherkhani, 2005).

#### Solids (The ratio of Volatile Solids to Total Solids and Total Dissolved Solids)

Total solids, volatile solids and fixed solids are important parameters which were determined in this study. The volatile solid to total solid ratio is one the important criteria for evaluating stabilization of sludge. Therefore, VS/TS values were calculated. The expression, "total dissolved solids" (TDS), refers to the total amount of all inorganic and organic substances—including minerals, salts, metals, cations or anions in a



**Figure 2.** Amounts of Parasite eggs in the WWTPs during four seasons.

liquid. Total dissolved solids are normally discussed for freshwater systems, since salinity comprises some of the ions constituting the definition of TDS, but the reason we determined this parameter for sludge samples was to study the possible statistical relationship between TDS and other parameters such as EC with SPSS statistical software. Fixed solids were also determined for this reason.

Values of total and dissolved solids are summarized in Table 2. Average amounts of total solids and volatile solids of Isfahan WWTPs were 66.9% and 45.5%, respectively. (Bina *et al.*, 2004). In this study, the average amounts for Tehran were 56.99% and 54.02% for total and volatile solids respectively. The percentage of total solids in Isfahan WWTPs is more than Tehran WWTPs and the percentage of volatile solids is less. Maximum and minimum values for Total solids in Tehran WWTPs were observed in Shoosh and Shahrak-e-Gharb WWTPs, respectively.

As it is shown in Figure 3, the average amounts of VS/TS ratio for Shahrak-e-Gharb, Shoosh and Mahallati WWTPs were 0.52, 0.46 and 0.64, respectively. The amount of VS/TS ratio for Mahallati WWTP

**Table 2.** The Ratio of VS/TS in the WWTPs during Four Seasons.

Wastewater Treatment Plants	Fall	Winter	Spring	Summer	Average	Typical Values*
	VS/TS	VS/TS	VS/TS	VS/TS	VS/TS	VS/TS
Shahrak-e-Gharb	0.56	0.57	0.56	0.40	<b>0.52</b>	< 0.6
Shoosh	0.56	0.39	0.42	0.47	<b>0.46</b>	
Mahallati	0.78	0.63	0.56	0.59	<b>0.64</b>	

\*Adopted from (Bina *et al.*, 2004).

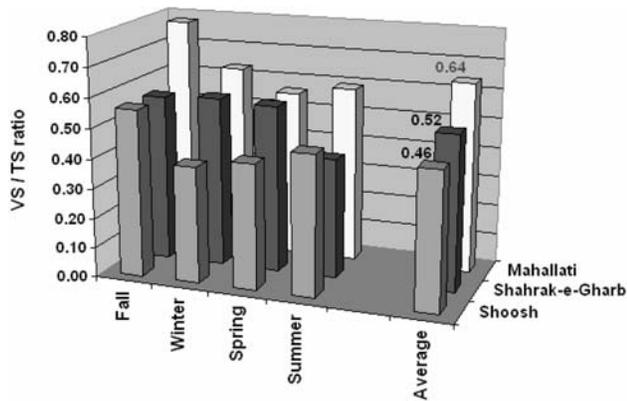


Figure 3. Amounts of VS/TS ratio in the WWTPs during four seasons.

is more than acceptable ratio (0.6) that is needed for stabilized sludge. The VS/TS ratio was determined as 0.754 for Serkan WWTP (Farzadkia and Norieh, 2005), which is higher than amounts which were found in Tehran WWTPs.

#### pH and Electrical Conductivity (EC)

In this study, the pH of all samples was measured as one of the stability criteria and also because pH is one of the most important measurements of soil fertility (USEPA: SW-846 Method 9045, 2000). When sludge is applied to agricultural lands as a fertilizer it can change the pH of soil. The pH of the soil changes ability of plants to take nutrients from the ground, and some plants will not grow in acidic or basic soils that may be perfect for other plants.

Value of pH are shown in Figure 4. As can be seen, pH values of collected samples were in the rang of 6–9 that is a typical value for pH (Bina *et al.*, 2004). The maximum and minimum values were for Mahallati and Shoosh WWTP, respectively. The pH in Serkan WWTP and Isfahan WWTPS was found to be 7.57 and 7.5, respectively (Bina *et al.*, 2004; Farzadkia and Norieh, 2005).

Sewage sludge contains large quantities of salts which may increase the soil solution electrical conductivity (EC). Increasing the EC increases the osmotic po-

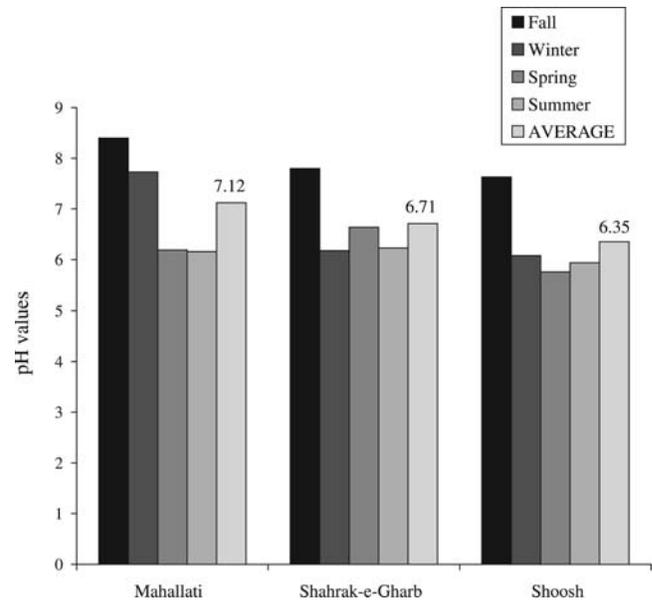


Figure 4. Values of pH in the WWTPs during four seasons.

tential of the soil solution, which may reduce the ability of plants to absorb water at high water suctions. (Johnsson *et al.*, 2005).

Amounts of EC in all samples are summarized in Table 3. Average values of EC for Shahrk-e-Gharb, Mahallati and Shoosh were found 1396  $\mu\text{s/cm}$ , 1197  $\mu\text{s/cm}$  and 1794  $\mu\text{s/cm}$ , respectively. All the values are in the range of typical values of 700–2000  $\mu\text{s/cm}$ . (Industry Standards of DWAF, 2007).

#### Probable Statistical Relationship between Different Parameters of the Sludge

There are some experiments which are time consuming, need high accuracy, need expensive experimental apparatus or some are very hard to carry out especially in determining microbiological characteristics of sewage sludge. If there is a statistical relationship between different parameters, it will be possible to determine the easiest one and then according to the relationship between them, estimate the other.

Table 3. Values of Electrical Conductivity in the WWTPs during Four Seasons.

Wastewater Treatment Plants	Fall	Winter	Spring	Summer	Average
	EC( $\mu\text{s/cm}$ )				
Shahrak-e-Gharb	1225	1242	888	2230	1396
Shoosh	1682	1649	1424	2420	1794
Mahallati	1364	1200	813	1410	1197

**Table 4. Pearson Correlation Coefficient Between Different Parameters of Sludge.**

Parameters	Fecal Coliform	Total Coliform	Parasite egg (ova)	Electrical Conductivity	Fixed Solids	TDS/TS
Fecal Coliform	1	—	0.952	—	—	—
Total Coliform	—	1	0.867	—	—	—
Parasite egg (ova)	0.952	0.867	1	—	—	—
Electrical Conductivity	—	—	—	1	—	0.813
Fixed Solids	—	—	—	—	1	—
TDS/TS	—	—	—	0.813	—	1

In this study, probable statistical relationship between different parameters of the sludge like fecal coliform and parasite eggs (ova) were investigated. For this purpose, the statistical software (SPSS) was used. By using this software, correlation coefficient can be calculated which will show the power of linear relation between parameters (Fotoohi and Asghari, 2003). In this study, Pearson correlation coefficients between different parameters were calculated. The results are summarized in Table 4.

Pearson correlation coefficient between fecal coliform and parasite eggs was 0.952 ( $R^2 = 0.906$ ) which is close to +1 and shows a strong statistical relationship between these two parameters. Pearson correlation coefficient between total coliform and parasite eggs was found to be 0.867 which also shows a relatively strong relationship between these parameters. In addition, Pearson correlation coefficient of 0.813 was found between electrical conductivity and total dissolved solids.

Other correlation coefficients were less than 0.5; therefore there is no linear relationship between the other parameters. The maximum Pearson correlation coefficient was observed between fecal coliform and parasite eggs.

## CONCLUSION

In this study, some important characteristics of dried sewage sludge of “Sharhrak-e-Gharb”, “Shoosh” and “Mahallati” WWTPs, were assessed. Conclusions of this study are summarized as below:

- The maximum values of TC and FC were found in Mahallati WWTP which the amounts are  $5.2 \times 10^5 \times 10^5$  MPN/g.DS and  $4.2 \times 10^4$  MPN/g.DS, respectively. According to obtained data, the sludge of all these wastewater treatment plants is classified into Class B of USEPA 40 CFR Part 503 regulations.

Therefore, more attention should be considered for using the sludge for application in agriculture.

- The maximum value of parasite eggs (ova) was observed in Mahallati WWTP which is 19 ova/g.DS which is more than the regulatory level of 1 ova/4gr.DS (USEPA 40 CFR Part 503 regulations).
- The VS/TS ratio for Mahallati WWTP was an acceptable ratio (0.6).
- Other parameters like Total Solids, Volatile Solids, pH and Electrical conductivity (EC) were usually in the range of acceptable values.
- Linear relationships were observed between “fecal coliform and parasite eggs”, “total coliform and parasite eggs” and “electrical conductivity and total dissolved solids”, with Pearson correlation coefficients of 0.952, 0.867 and 0.813, respectively.

Therefore, according to the obtained results, the treatment processes of these WWTPs need to improve in order to produce sludge with higher quality for agriculture fields. Also, more researches are needed study the statistical relationship between different sludge parameters.

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# Assessment of Fenton Process as a Minimization Technique for Biological Sludge: Effects on Anaerobic Sludge Bioprocessing

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**ABSTRACT:** Sludge minimization is becoming a more important issue in sludge treatment for many reasons regarding the improved processing of sludge, transportation, and landfilling. Many techniques on sludge minimization have been developed recently. Among these techniques, advanced oxidation processes have taken place as efficient methods in the area of sludge minimization. To determine the effects of the oxidative treatment on anaerobic sludge digestion for sludge minimization purpose, the Fenton process was used in this study. This process was applied to biological sludge samples preceding anaerobic sludge digestion. The samples were taken from a municipal wastewater treatment plant located in Izmir, Turkey. Sludge digestion studies were carried out using six 8.5 L lab-scale anaerobic reactors. Three of them were operated as control reactors without Fenton's application, while the others were fed with Fenton processed sludge. The reactors were operated in mesophilic conditions for 30 days of operation period. Two reactors were operated as batch, while the others were operated as semi batch system. Two different sludge retention times as 5 and 10 days were applied during the operation. A ratio of 0.067 gram Fe(II) per gram H<sub>2</sub>O<sub>2</sub>, and 60 g H<sub>2</sub>O<sub>2</sub>/kg Dried Soil were chosen as a result of an optimization study on Fenton processing of sludge. Experimental results showed higher volatile solids reductions and higher biogas productions for the digesters fed with Fenton processed sludge as positive effect of Fenton's application on anaerobic sludge biodegradability. Significant reductions in protein concentrations indicating the effective floc disintegration were also obtained in Fenton processed digesters compared to the control reactors. These results were also consistent with the particle size distribution results. On the other hand, the Fenton process led to decrease in the biosolids' resistance to dewatering in terms of capillary suction time (CST), but did not have a positive effect on sludge dewatering performance on a belt press simulation.

## 1. INTRODUCTION

The biological treatment of wastewater results in the generation of a considerable amount of waste activated sludge (WAS) that has to be treated. Sludge treatment and disposal represents a decisive factor for design, operation and costs of wastewater treatment especially for large treatment plants. Since the costs of sludge treatment are high, representing 50–60% of the total operating costs of the wastewater treatment (Egemen *et al.*, 2001), much attention has been focused on advanced sludge treatment processes to reduce the amount of sludge produced and to improve the dewaterability of the sludge. In order to improve hydrolysis and anaerobic digestion performance, disintegration was devel-

oped as the pretreatment process of sludge to accelerate the anaerobic digestion and to increase degree of stabilization (Bougrier *et al.*, 2005; Weemaes *et al.*, 2001). An increase of stabilization degree of sludge with disintegration process provides less sludge production, more stable sludge and more biogas production comparing the classical anaerobic digestion (Wang *et al.*, 2005). Ultrasonic treatment (Tiehm *et al.*, 2001; Nickel *et al.*, 2007; Zawieja *et al.*, 2008), ozone oxidation (Bougrier *et al.*, 2006; Magdalena *et al.*, 2007; Weemaes *et al.*, 2000), mechanical disintegration (Lehne *et al.*, 2001), alkaline treatment (Chang *et al.*, 2002; Lin *et al.*, 2007), thermal treatment (Barjenbruch *et al.*, 2003) and biological hydrolysis with enzymes (Lai *et al.*, 2001; Ayol *et al.*, 2007) were investigated for sludge disintegration purpose by several researchers in half-scale and lab-scale plants.

The Fenton process is one of the commonly used ad-

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vanced oxidation techniques. Fenton's reagent is a mixture of  $H_2O_2$  and ferrous iron. The ferrous iron initiates and catalyses the decomposition of  $H_2O_2$ , resulting in the generation of highly reactive hydroxyl ( $\cdot OH$ ) radicals (Kitis *et al.*, 1999). The  $\cdot OH$  radical is the main reactant in the process capable of decomposing a number of organic substances via oxidation. The rate and extent of the Fenton reactions are dependent on system parameters including, iron and hydrogen peroxide concentration, and solution pH. The application of the Fenton process for disintegration of WAS may cause two phenomena, solubilization and mineralization of sludge solids. Part of activated sludge is mineralized to carbon dioxide and water while part of sludge is solubilized to biodegradable organics, which are easily accessible and can be digested much faster in later biological process than sludge in a particular phase. Takumura *et al.*, 2007 applied the similar advanced oxidation method of photo-Fenton reaction to WAS in a batch photo reactor for disintegration purposes. Soluble chemical oxygen demand (SCOD) was achieved at highest level in the presence of 4 g  $H_2O_2/L$ , 40 mg  $Fe(II)/L$ , 3000 mg MLSS/L, pH = 3 for 6 h reaction time and effective disintegration was obtained. At longer times than 6 h, COD was decreased and mineralization occurred. Neyens *et al.*, 2003 applied the Fenton Process to thickened sludge and they noted that the optimum activity was in the presence of 25 g  $H_2O_2/kg$  DS, 1.67 g  $Fe(II)/kg$  DS, pH = 3 at ambient temperature and pressure. In these conditions, the Fenton Process resulted in a considerable reduction of dry solids (DS) and organic dry solids (ODS) contents in the filter cake of approximately 20%, an improved dewaterability with a 30% reduction of the sludge volume, and a 30% increase of the cake DS-content when compared with the untreated sludge sample. Dewil, *et al.*, 2005 investigated the influence of the Fentons Process on the drying performance of two different waste activated sludges and found that one increased the DS content from 22.5% to 40.3% and the other increased the DS from 18.7% to 35.2%. In another study, Buyukkamaci, 2004 was evaluated the effect of Fenton's reagent on dewatering capacity of biological sludge for various  $Fe(II)$  (1000–6000 mg  $L^{-1}$ ) and  $H_2O_2$  (2000–6000 mg  $L^{-1}$ ) dosages using specific resistance to filtration (SRF) and CST parameters and these values of conditioned sludge decreased with increasing  $H_2O_2$  and  $Fe(II)$  concentrations in almost all cases.

The major objectives of this study were to investigate the effects of Fenton process on sludge properties and

to evaluate performance of Fenton processed sludge on the anaerobic sludge digestion process. This paper will present significant experimental results for enhanced anaerobic degradability of sludge using Fenton process. The applicability of this process in practice for sludge minimization will be also debugged in this paper.

## 2. MATERIALS AND METHODS

### 2.1. Sludge Characterization

Waste activated sludge was sampled from the municipal wastewater treatment plant in Izmir, which has extended aeration activated sludge plant with nutrient removal facilities. At the start-up of the reactors, granular anaerobic sludge taken from a full-scale upflow anaerobic sludge blanket (UASB) reactor treating beer industry wastewater, Efes Pilsen Inc., was used as the inoculum for anaerobic reactors. Total dried solids (TDS), volatile solids (VS), pH, electrical conductivity (EC), and CST analyses were done to determine the physico-chemical characteristics of sludges and presented in Table 1. All analysis were done according to procedures given in Standard Methods (2005). pH and electrical conductivity measurements were carried out with a 890 MD pH meter and a YSI Model 33 conductivity-meter, respectively.

**Table 1. Properties of waste activated sludge and anaerobic inoculum sludge.**

Parameters	Activated Sludge	Anaerobic Inoculum Sludge
pH	7 ± 0.17	8.04 ± 0.1
Electrical Conductivity (EC, $\mu S/cm$ )	7.22 ± 1.73	3.4 ± 0.3
Redox Potential (ORP, mV)	35 ± 2	-195 ± 3
Dried solids (DS, %)	1.82 ± 0.43	7.2 ± 0.1
Volatile Solids (VS, %)	56.72 ± 2.02	84.2 ± 1.7
Suspended Solids (SS, $mgL^{-1}$ )	14650 ± 700	72750 ± 4975
Volatile Suspended Solids (VSS, $mgL^{-1}$ )	9367 ± 441	64225 ± 4365
Soluble Chemical Oxygen Demand (SCOD, $mgL^{-1}$ )	420 ± 35	1893 ± 46
Capillary Suction Time (CST, s)	120.6 ± 11.24	248.5 ± 1.9
Particle size ( $\mu m$ )		
Surface weighted mean D[3,2]	38.307	93.705
Volume weighted mean D[4,3]	81.217	526.432
d (0.1)	22.374	37.299
d (0.5)	73.269	433.559
d (0.9)	151.651	

## 2.2. Experimental Procedure and Analytical Methods

Box-Wilson statistical design which is a response surface methodology used for evaluation of a dependent variable as functions of independent variables (Mantha *et al.*, 1998) was used for optimization of major process variables of hydrogen peroxide and Fe(II) concentrations before the anaerobic digestion studies. This is an empirical modeling technique, devoted to the evaluation of the relationship of a set of controlled experimental factors and observed results. Basically this optimization process involves three major steps: performing the statistically designed experiments, estimating the coefficients in a mathematical model, and predicting the response and checking the adequacy of the model. Disintegration degree (DD) (Muller, 2000) was chosen as system response for evaluation of sludge disintegration.  $\text{H}_2\text{O}_2$  concentration ( $X_1$ ) varied between 10 and 100 g/kg dried solids (DS), while Fe(II) concentration ( $X_2$ ) was ranged from 1 to 5 g/kg DS. Fenton process was applied to 1.5 L sludge sample. This method was carried out by first adjusting the pH of the sludge to 3 using  $\text{H}_2\text{SO}_4$ . The second step was the addition of Fe(II) at certain concentrations. After this period, different  $\text{H}_2\text{O}_2$  concentrations were added to the sample. The mixed sample was stirred at 100 rpm for 60 min. After the reaction, the sample was neutralized with  $\text{Ca}(\text{OH})_2$ . In Fenton experiments, analytical grade  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  was used as source of Fe(II) and purchased from Merck. Hydrogen peroxide solution (37% (w/w)) in stable form,  $\text{H}_2\text{SO}_4$  (98–99%) and NaOH were all provided from Merck. After the optimization study, sludge digestion studies were carried out using six 8.5 L lab-scale anaerobic reactors. Three of them were operated as control reactors without Fenton's application, while the others were fed with Fenton processed sludge. The reactors were operated at  $37 \pm 3^\circ\text{C}$  under mesophilic conditions for 30 days. The reactors were heated and the temperature was kept constantly by heat transfer oil jacket and constructed from stainless-steel and, operated with PLC. Mechanical mixers were used in the reactors to provide adequate mixing. Two reactors were operated as batch system, and the others were operated as semi-batch systems. Different sludge retention times such as 5 and 10 days were applied during the operation in order to determine optimum retention time. Control reactors were coded as  $\text{CR}_B$ ,  $\text{CR}_5$ ,  $\text{CR}_{10}$  and the reactors fed with Fenton processed sludge were

coded as  $\text{FPR}_B$ ,  $\text{FPR}_5$ ,  $\text{FPR}_{10}$  (subscripts in here represents the sludge retention times). At the start-up phase, inoculum sludge was fed to reactors. After that, 1/2 volume of the reactor content was withdrawn and the same volume of activated sludge was fed to the reactors. For batch system, no feed and no withdrawal from the reactors was applied during the operation period, only small volume of sludge was taken from reactors for analyses. 1.7 L and 0.85 L of sludge were fed and the same volumes of sludge were withdrawn from the reactors for 5 days and 10 days of sludge retention time, respectively each day during the operation period. For system evaluations, pH and temperature were monitored daily while alkalinity, VFA, and redox potential values were measured three times in a week. For performance evaluations, total dried solids (DS), volatile solids (VS), suspended solids (SS), volatile suspended solids (VSS), protein contents, particle size distribution, daily total gas and methane productions, and CST were measured during the operation period. DS, VS, SS and VSS analyses were regularly done according to Standard Methods (2005). CST values were analyzed with a Triton A-304 M CST-meter. Particle size distributions were monitored using a Malvern Mastersizer 2000QM analyzer. The belt press simulator of crown press supplied from Phipps and Bird, Richmond, VA was used for evaluation of dewatering properties of sludge. Sludge slurry (200 mL) was drained through a screen and the volume collected after 2 min was measured. The solids remaining on the screen were then pressed and the final cake solids determined. Methane production was determined by the liquid displacement method in which gas passes through distilled water including 3% (w/v) NaOH (Kuscu *et al.*, 2005). Due to the lack of any digital device coupled to the reactor to measure the amount of gas produced, gas valves of the reactors were first closed about one hour and then they were opened. The liquid displacements were converted to daily production. Gas components ( $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{S}$ ) were analyzed using a Dräger model X-am 7000 multi gas analyzer. Volatile fatty acid (VFA) measurements were done using a HPLC Agilent 1100 with C18 column. Extracellular polymeric substances (EPS) were extracted from the samples using the heat extraction technique originated by Goodwin and Forster (1985) and Frolund *et al.* (1996). The protein contents of EPS samples were analyzed using protein assay kits (Procedure No. TP0300 Micro Lowry, Sigma).

**Table 2. Experimental Data Points used in Box–Wilson Statistical Design and Observed and Predicted Values for Response Functions.**

Experimental No	X <sub>1</sub> (g H <sub>2</sub> O <sub>2</sub> /kg DS)	X <sub>2</sub> (g Fe(II)/kg DS)	Predicted DD, %	Observed DD, %
Axial points				
A <sub>1</sub>	100	3	14.31	14.29
A <sub>2</sub>	10	3	4.92	4.76
A <sub>3</sub>	55	5	20.61	19.05
A <sub>4</sub>	55	1	5.76	7.14
Factorial points				
F <sub>1</sub>	86.8	1.6	9.34	8.33
F <sub>2</sub>	23.2	1.6	3.30	2.38
F <sub>3</sub>	86.8	4.4	20.33	21.43
F <sub>4</sub>	23.2	4.4	13.10	14.29
Center point				
C <sub>1</sub>	55	3	23.81	23.81
C <sub>2</sub>	55	3	23.81	23.81
C <sub>3</sub>	55	3	23.81	23.81

### 3. RESULTS AND DISCUSSION

#### 3.1. Examination of Floc Disintegration by Fenton Process

Experimental points for Box–Wilson statistical design are shown in Table 2. The experiments consist of four axial (A), four factorial (F), and central points (C). The central point was done in triplicate resulting as 11 experiments in total. Experimental data was used for determination of the response function coefficients for each independent variable by iteration. The estimated coefficients of the response functions are presented in Table 3. Predicted values of DD using the estimated coefficients are compared with the experimental results in Table 4. Response function predictions were in good agreement with the experimental data.

The performance of the system was described by the following response function:

$$E = b_0 + b_1X_1 + b_2X_2 + b_{12}X_1X_2 + b_{11}X_{12} + b_{22}X_{22} \quad (1)$$

where  $E$  is the predicted response function,  $b_0$  is the constant,  $b_1$ – $b_2$  are the linear coefficients,  $b_{12}$  is the cross product coefficient, and  $b_{11}$  and  $b_{22}$  are the quadratic coefficients. The coefficients of the response functions were determined by using the experimental

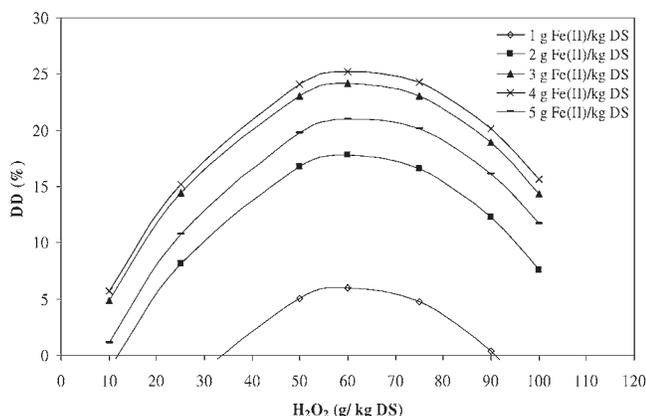
data and the Statistica 5.0 computer program for regression analysis.

The increase of DD is determined as the substance that can be readily used to produce methane in the anaerobic digestion (Wang *et al.*, 2005). Variations in disintegration degree with H<sub>2</sub>O<sub>2</sub> at different Fe(II) concentrations are depicted in Figure 1. The correlation coefficient ( $R^2$ ) between the observed and predicted values was 99.95%.

As shown in Figure 1, maximum DD of 25.2% was achieved at 60 g H<sub>2</sub>O<sub>2</sub>/kg DS and 4 g Fe(II)/kg DS, and optimum Fe(II)/H<sub>2</sub>O<sub>2</sub> ratio was found as 0.067. This ratio is in agreement with Neyens *et al.*, 2003. Up to 60 g H<sub>2</sub>O<sub>2</sub>/kg DS concentration, hydroxyl radicals preferentially attack the organic substances and destruct the activated sludge microorganisms cell walls in biomass and oxidized them to dissolved organic substances and these substances released to the liquid phase and increased the DD, at higher H<sub>2</sub>O<sub>2</sub> concentrations, decreases in DD may be explained with two phenomena, (1) that a competition between the organic substances and H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> acts as a scavenger of the highly potent hydroxyl radicals, and inhibits the disintegration or (2) high H<sub>2</sub>O<sub>2</sub> concentrations may cause the mineralization of organic substances to water and carbon dioxide. These were observed in other studies for waste activated sludge (Bougrier *et al.*, 2006) and wastewater (Catalkaya *et al.*, 2007).

**Table 3. Coefficients of the response function.**

Coefficients	b <sub>0</sub>	b <sub>1</sub>	b <sub>2</sub>	b <sub>12</sub>	b <sub>11</sub>	b <sub>22</sub>
Values	-37.078726	0.855438	19.283546	0.006685	-0.007010	-2.656420

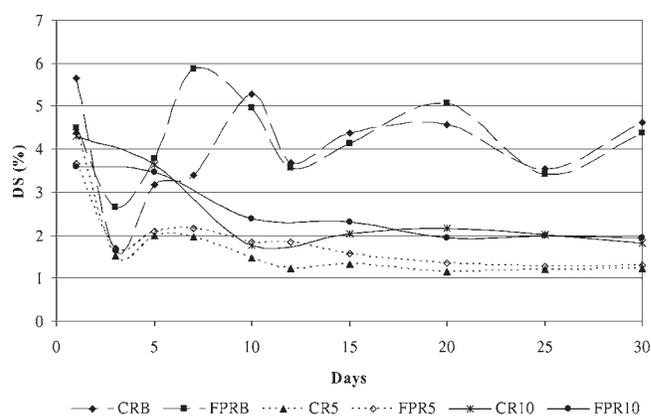


**Figure 1.** Variations of DD with the  $H_2O_2$  concentration at different  $Fe(II)$  concentrations.

### 3.2. Anaerobic Sludge Digestion Following Floc Disintegration by Fenton Process

In digestion studies, pH and temperature parameters were monitored daily while alkalinity, redox potential, and volatile fatty acids (VFA) parameters were analyzed three times in a week for evaluation of anaerobic digester performance. The pH values varied from 6.80 to 8.80 in the reactors. The temperature was kept at  $37 \pm 2^\circ C$  in all the reactors. Redox potentials of reactor contents were in the very negative range of  $-300$  mV and  $-500$  mV. Total alkalinity values were measured regularly as a measure of the stability of the digestion unit. An alkalinity range of 1580–5917 mg  $CaCO_3/L$  was measured during the operation period. The VFA content was also checked for reactor stability and VFA values did not exceed 1000–1500 mg/L which is recommended for anaerobic methogens (Malina and Pohland, 1992). VFA values did not exceed this recommended range even in the first operation days. Dried solids concentrations varied between 3% and 5% for the reactors operated as a batch system while they ranged from 1% to 5% for reactors operated with 5 and 10 days sludge retention times. DS changes in reactors as a function of operation time are given in Figure 2. DS concentrations in reactors fed with Fenton reagents were lower than those in control reactors for all sludge retention times. Lower DS values were obtained for reactors operated with 5 and 10 days sludge retention times than those in batch reactors were DS values decreased drastically especially during the first ten days in these reactors.

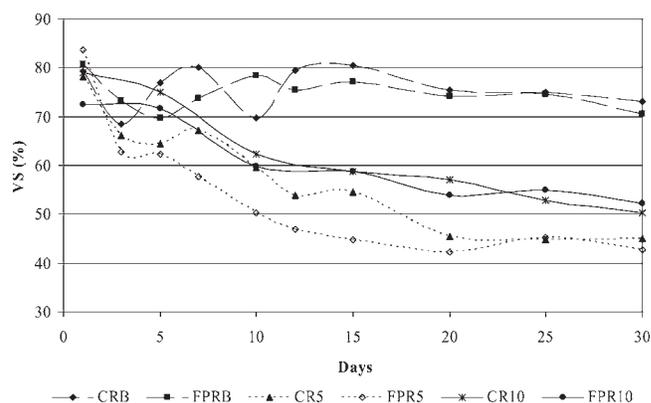
Dried solids concentrations varied between 3% and 5% for reactors operated as batch system while those ranged from 1% to 5% for reactors operated with 5 and



**Figure 2.** Dried solids changes in the reactors as a function of operation time.

10 days sludge retention times. DS changes in reactors as a function of operation time are given in Figure 2. DS concentrations in reactors fed with Fenton reagents were lower than those in control reactors for all sludge retention times. Lower DS values were obtained in the reactors operated with 5 and 10 days sludge retention times when compared to batch reactors and DS values decreased drastically especially during the first ten days in these reactors.

VS measurement results are shown in Figure 3. Better volatile solids reductions were observed for reactors operated with 5 and 10 days SRT comparing to reactors operated as batch system. VS concentrations in reactors fed with Fenton reagents were lower than those in control reactors for all sludge retention times. The highest reductions in VS were obtained in the reactor coded as FPR5 while the lowest reductions in VS were observed in the reactor coded as CRB. Very close DS and VS reductions were observed among the reactors fed with Fenton processed sludge and control ones.



**Figure 3.** Volatile solids changes in reactors as a function of operation time.

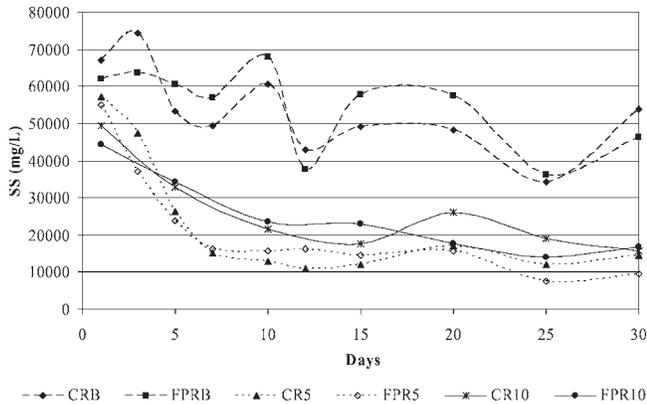


Figure 4. Suspended solids changes in reactors as a function of operation time.

Figure 4 and Figure 5 demonstrate the changes of SS and VSS as a function of operation time, respectively. The disintegration of the sludge cells was also reflected in decreasing SS contents of the sludge. SS and VSS decreased quickly especially in first week of operation period in reactors operated with 5 and 10 days of sludge retention times. After ten days of operation SS and VSS had no change significantly and nearly same values of SS and VSS were observed for 5 and 10 days of SRT.

Higher reductions in SS and VSS were observed in reactors fed with Fenton processed sludge than in control reactors. The minimum SS and VSS were achieved by the FPR5. The minimum SS value of 7700 mg/L was achieved at 25th day of operation period, while the value was 55100 at the end of the first operation day. Similarly, the minimum VSS value of 5100 mg/L was obtained at the end of 25th day of operation and the value was 47700 mg/L at the end of the first operation day. Here, the efficiency of the Fenton process in

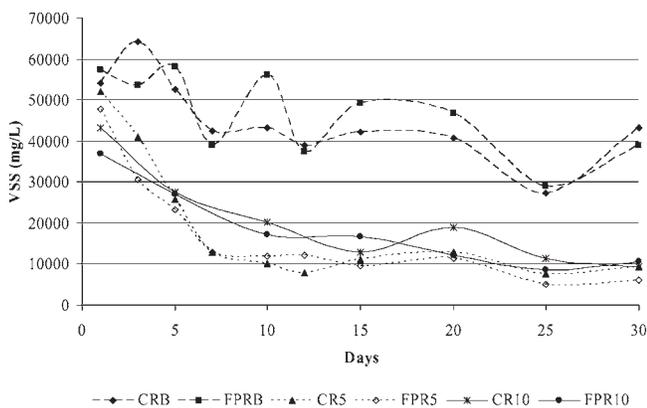


Figure 5. Volatile suspended solids changes in reactors as a function of operation time.

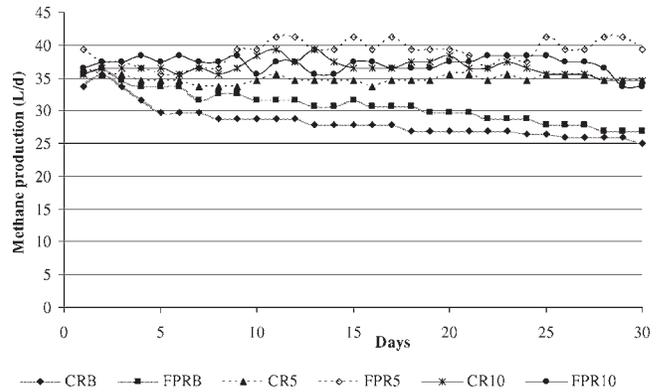


Figure 6. Methane productions during the operation period.

sludge solubilization has been confirmed by the laboratory data.

Figure 6 shows the methane production during the operation period. Minimum methane productions were obtained in CRB and FPRB. Reactors operated with 5 and 10 days of SRT gave nearly same oscillation during the operation period for methane. Especially for 5 days of SRT, very narrow oscillation was observed and the highest biogas productions were also obtained. For batch systems, methane gas decreased during the operation period. Reactors fed with Fenton processed sludge gave higher methane production comparing to the control reactors. For reactors in FPR5 and FPR10, H<sub>2</sub>S values higher than 100 ppm were recorded during the operation period. For batch system, and control reactors, H<sub>2</sub>S values were lower than 100 ppm. The Fenton process led to increase in H<sub>2</sub>S levels in the reactors. The reason might be the reduced methanogenic activity and improvement in sulphidogenic conditions.

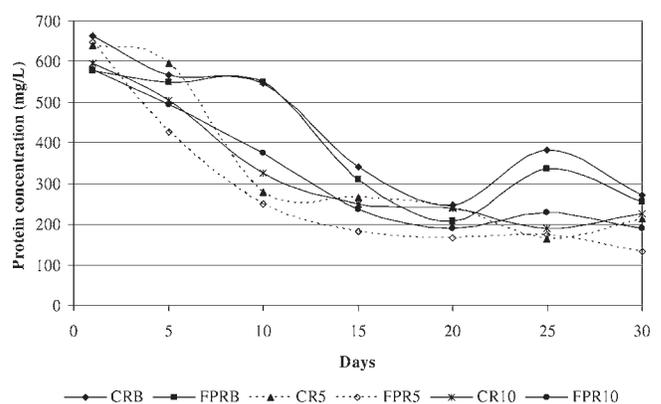
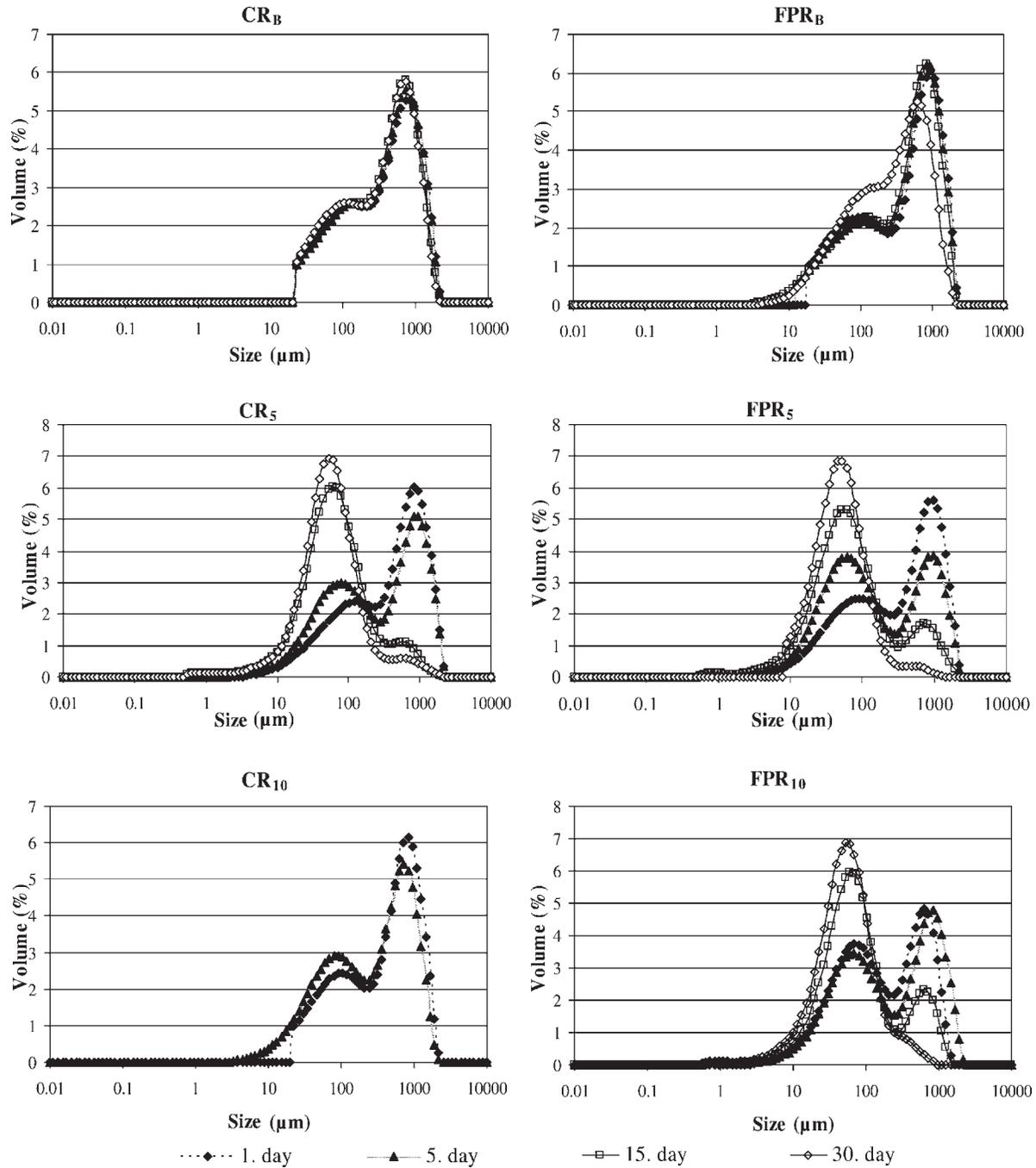


Figure 7. Protein concentrations in reactors content during the operation.



**Figure 8.** Particle size distributions in 1st, 5th, 15th, and 30th operation days for reactor contents.

Cell lysis transforming cell content into the medium is the first stage, and breakdown of the EPS fraction in the sludge is the second stage of floc disintegration. The protein results as depicted in Figure 7 showed that Fenton process enhanced the degradation of extracellular polymeric substances. Protein concentrations of reactor contents decreased with operation time in all reactors and the highest reductions were observed in FPR5.

Particle size distributions reported in Figure 8 indicate floc disintegration stemming from EPS data. Particle size distribution of reactor contents had no significantly change during the operation in CRB and FPRB, and ranged from 10 to 2500  $\mu\text{m}$ . The particle size distribution showed a peak centered around 700 to 800  $\mu\text{m}$  for these reactors. Two peaks were observed, especially in first operation days. The second peak could be explained by a re-flocculation phenomenon, observed by

**Table 4. Particle Size Changes in 1st, 15th, and 30th Operation Days for Reactor Contents.**

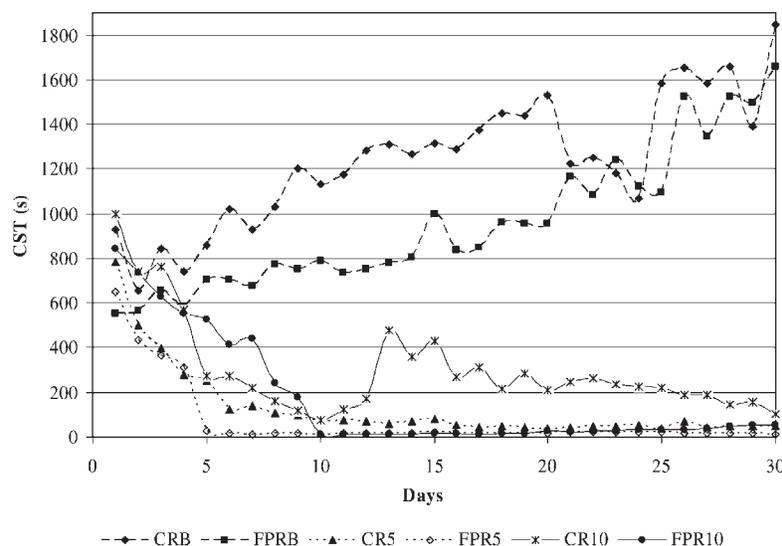
Sludge ID	Surface Weight Mean D(3,2)	Volume Weight Mean (4,3)	d (0.1)	d (0.5)	d (0.9)
CR <sub>B</sub> -1st day	85.888	468.516	34.948	341.848	1120.774
FPR <sub>B</sub> -1st day	81.868	536.41	31.394	429.916	1259.09
CR <sub>5</sub> -1st day	98.801	524.602	39.406	427.091	1201.333
FPR <sub>5</sub> -1st day	78.184	501.129	30.382	365.969	1211.55
CR <sub>10</sub> -1st day	94.083	501.811	36.528	410.931	1149.713
FPR <sub>10</sub> -1st day	58.671	288.394	24.772	141.017	750.275
CR <sub>B</sub> -15th day	97.020	453.577	38.423	353.483	1038.316
FPR <sub>B</sub> -15th day	92.111	513.64	35.545	427.875	1165.602
CR <sub>5</sub> -15th day	24.32	122.067	16.499	59.02	283.737
FPR <sub>5</sub> -15th day	24.657	172.428	14.785	58.735	566.965
CR <sub>10</sub> -15th day	29.693	151.094	19.222	62.547	246.663
FPR <sub>10</sub> -15th day	34.818	165.682	19.204	65.793	544.865
CR <sub>B</sub> -30th day	95.215	426.854	36.527	328.609	985.094
FPR <sub>B</sub> -30th day	94.188	387.303	37.394	274.974	910.391
CR <sub>5</sub> -30th day	22.542	96.052	15.777	50.061	161.351
FPR <sub>5</sub> -30th day	20.152	65.626	12.347	42.494	118.371
CR <sub>10</sub> -30th day	24.116	74.125	17.495	52.94	129.292
FPR <sub>10</sub> -30th day	22.397	73.849	14.199	48.344	144.662

Bougrier *et al.*, 2005. This re-flocculation was obtained especially in the first days due to the release of intracellular or extra-cellular material and the second peak decreased with operation time. Table 4 shows the particle size changes for selected operation days. The designations, d (0.1), d (0.5), and d (0.9) indicate that 10%, 50% and 90% of particles (by volume) are lower or equal to the designated volume in the table. The reduction can be clearly seen in reactors especially operated as a semi-batch system, and higher reductions were obtained in reactors fed with Fenton processed sludge comparing to that in the control reactors. The highest reductions were observed in reactors coded as FPR<sub>5</sub> and

83 % of particle size reduction was recorded at the end of 15 days operation based on d (0.5).

### 3.3. Evaluation of Dewatering Characteristics of Digested Sludge

CST is a quick and simple method to evaluate the filterability of sludge. This method neglects the shear effect on sludge, and it can not determine dewaterability differences between dewatering processes but gives an approach dewatering capacity of sludge. CST variations during the operation period are given in Figure 9. Prior research has shown that anaero-



**Figure 9.** CST variations in reactors as a function of operation time.

**Table 5. Final Cake Solids Obtained from Crown Press Application During the Operation Period.**

Reactor ID/Days	Final Cake Solids, %					
	1	10	15	20	25	30
CR <sub>5</sub>	13.05	11.44	13.15	11.51	13.94	9.63
FPR <sub>5</sub>	10.59	12.88	9.61	10.77	9.98	11.45
CR <sub>10</sub>	11.7	11.50	11.88	12.37	10.50	10.17
FPR <sub>10</sub>	13.6	14.01	13.52	12.09	11.84	11.79

bic digestion leads to increase biopolymers into solution and these biopolymers will cause deterioration of sludge dewatering properties and increase conditioning requirements in batch systems (Novak *et al.*, 2003). Batch digestion studies in this research gave similar results and CST increased with operation time. In contrast, Fenton process enhanced to EPS degradation and led to decrease in the biosolids' resistance to dewatering in semi-batch reactors. Depending on CST data, it can be seen that there was a positive effect of Fenton process before anaerobic digestion on sludge dewatering. In reactors operated as a batch system, this positive effect was not observed.

For evaluation of dewatering characteristics of digested sludge a crown-press was used as a simulator of the belt-press. The reactor contents were regularly processed through a crown-press during the 30 day operation period. The results, listed in Table 5, show a small improvement in cake solids of FPR<sub>5</sub> and FPR<sub>10</sub> contents for 10 days of operation. Final cake solids did not improve with operation time for control reactors. On the other hand, Fenton process before anaerobic digestion did not significantly affect of drainage rate during 60 sec crown-press application as shown in Table 6.

#### 4. CONCLUSIONS

The effect of floc disintegration by Fenton process on anaerobic sludge digestion performance was investigated. From this overall examination, the following major conclusions can be stated.

- A ratio of 0.067 g Fe(II) per gram H<sub>2</sub>O<sub>2</sub>, and 60 g H<sub>2</sub>O<sub>2</sub>/kg DS were found as an optimum for floc disintegration using Box-Wilson experimental design.
- Solubilization of WAS can be effectively performed and better VS reduction (solubilization process plus anaerobic process) was achieved using Fenton process, and the most effective solubilization was observed in reactors operated with 5 days of SRT.
- Significant reductions in EPS were obtained for digested sludge especially pretreated with Fenton process.
- Particle size reductions indicated the floc disintegration.
- Higher methane production was obtained when comparing to that in the control reactor.
- Results of this study showed that anaerobic degradability of sludge can be enhanced using Fenton process.
- Although the Fenton process had a positive effect in terms of the CST, this process did not increase the drainage rate of sludge and led to a small improvement in cake solids on a crown press application.

#### ACKNOWLEDGEMENT

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**Table 5. Drainage volume after 60 sec crown press application during the operation period.**

Reactor ID/Days	Drainage Volume, mL					
	1	10	15	20	25	30
CR <sub>5</sub>	170	170	180	190	170	170
FPR <sub>5</sub>	140	135	170	140	125	145
CR <sub>10</sub>	150	160	175	185	195	175
FPR <sub>10</sub>	115	120	110	120	185	175

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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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