Addition of Permanganate to Biosolids for Odor Control

September 2012

Background

King County (KC) produces class B biosolids for beneficial reuse such as soil amendment and fertilizers. West Point Treatment Plant (WPTP) produces an average of 15,000 dry tons of 25-28% biosolids per year. On daily basis, three to five trucks of biosolids are transported out of WPTP to a staging facility in South Seattle before they are taken to Eastern Washington for land application. The trucks are kept at the staging area due to an agreement with the city of Seattle that trucks are not to be driven into or out of WPTP between the hours of 1600 and 0600. A round trip between Seattle and Eastern Washington is 11 hrs. which requires the trucks leave Seattle early in the morning if they need to make a return trip within the same day.

Occasionally, strong odor was noticed at and around the staging area in South Seattle. KC conducted two biosolids odor characterization studies in 2009 and 2010 where air sample analyses showed high level of reduced sulfur compounds (up to 15,000 ppbv) which peaked around third day of biosolids storage. Nitrogen compounds (amines) were not analyzed in this study.

KC has been evaluating methods to reduce the biosolids odor at the staging area by either chemically or biologically means. Potassium Permanganate ($KMnO_4$) was evaluated in this study due to its strong oxidization capacity and ability to target reduced sulfur compounds. It is also well-documented as an odor control agent.

Objectives

The purpose of this pilot study was to evaluate the effectiveness of Potassium Permanganate ($KMnO_4$) on the reduction of biosolids odor and document the odor characteristics of the biosolids from production through 25 days of storage. The data was collected via both chemical analysis and sensory observation. The study focused on two groups of odorous compounds - reduced sulfur compounds and amine compounds.

Approach

The concentrations of both groups of odorous compounds were compared between a Control batch and Amended batch (dosed with potassium permanganate). The Control batch consisted of biosolids produced under normal operating conditions. The Amended batch consisted of biosolids treated with 10 lbs. per dry ton of 3% $KMnO_4$ solution. The solution was added to the digested sludge at the dewatering feed pump discharge. The sludge and $KMnO_4$ mixture traveled a distance of 50 feet, through a mechanical mixer, and into the dewatering centrifuge.

The Control and Amended batches were produced on two separate, consecutive days due to time constraint. For each batch, the dewatered biosolids were conveyed into a haul trailer. From the trailer, biosolids samples were collected and stored in 5 sealed buckets designated for sample day 1,2,3,8 and 25. On a designated day, a headspace air sample was collected from the corresponding bucket and analyzed for reduced sulfur compounds. A sensory test (odor strength and characterization) of the headspace air was conducted using two treatment plant staff. A sample from the same bucket was also analyzed for total solids (TS), volatile solids (VS), pH, oxidation-reduction potential (ORP), ammonia (NH_3), and total kjeldahl nitrogen (TKN).

After biosolids samples were collected for the buckets, each trailer was covered tightly with tarps and parked at the treatment plant for duration of three days after production. On each day, a 100 L gas sample was collected from the trailer headspace for the amines analysis (detailed sample collection method in SAP).

After 3 days at the treatment plant, the trailers were taken to Eastern Washington and unloaded into piles at the application site. The Control and Amended material were kept in separate piles for further monitoring. A field operator performed sensory tests on both piles approximately 2 times per week through 25 days from dewatering.

<u>Results and Discussions</u>

Twenty total reduced sulfur compounds were analyzed in the Control and Amended batches. The analytical results are shown in Table 1. Of the twenty compounds analyzed, five compounds were consistently detected in both batches.

Table 1: Reduced Sulfur Compounds and Total Reduced Sulfur Compounds Concentrations in Control and Permanganate Amended batches (blank cells in the table represent value less than method reporting limit)

			Control					Permanganate Amended				
			Concentrations (ppbv)					Concentrations (ppbv)				
		Day#	1	2	3	8	25	1	2	3	8	25
		Date	10/16/12	10/17/12	10/18/12	10/23/12	11/7/12	10/17/12	10/18/12	10/19/12	10/24/12	11/8/12
Compounds	Odor Threshold ppbv	MRL ppbv										
Hydrogen Sulfide	0.07-130	5.0	72,000	89,000	10,000	3,600		20,000	13,000	82	3,100	
Carbonyl Sulfide	-	5.0	66			14		460	220			
Methyl Mercaptan	0.00015-42	5.0	100,000	150,000	2,300	210	7.0	23,000	46,000	580	1,700	15
Ethyl Mercaptan	0.013-36	5.0	76	200								
Dimethyl Sulfide	0.1-20	5.0	34,000	130,000	110,000	700	7.1	22,000	49,000	72,000	78,000	89
Carbon Disulfide	7.7-74000	2.5				3.4	3.6	73	43			5.3
Isopropyl Mercaptan	-	5.0	130	630		13						
tert-Butyl Mercaptan	0.5	5.0										
n-Propyl Mercaptan	0.0008-0.5	5.0		170					73			
Ethyl Methyl Sulfide	-	5.0			170	9.5					120	
Thiophene	-	5.0										7.1
Isobutyl Mercaptan	2000	5.0										
Diethyl Sulfide	-	5.0										
n-Butyl Mercaptan	0.02-1100	5.0										
Dimethyl Disulfide	0.026-160	2.5	940	4,200	3,000	1,300	18	2,100	11,000	18,000	1,600	150
3-Methylthiophene	-	5.0										
Tetrahydrothiophene	-	5.0										
2,5-Dimethylthiophene	-	5.0										
2-Ethylthiophene	-	5.0										
Diethyl Disulfide	-	2.5										
Total Reduced Sulfur (as Hydrogen Sulfide equivalent)			230,000	400,000	140,000	7,900	63	77,000	150,000	120,000	93,000	460

MRL – method reporting limit

On day 1, hydrogen sulfide (HS), methyl mercaptan (MM) and dimethyl sulfide (DS) were detected at higher concentrations in the Control batch. Carbonyl sulfide (CS) and dimethyl disulfide (DMDS) were detected at higher concentration in the Amended batch (Figure 1). All of the detected compounds concentrations were higher than their odor thresholds. The exception was CS, which the odor threshold concentration is not available.

The concentrations in the Control batch increased and appeared to peak on day 2 and 3, then, dropped dramatically by day 8 (Figure 2). The Amended batch started with lower concentration on Day 1 (Figure 3). HS continue to decrease after day 1, but MM and DMDS increased and peak between day 2 and 3. DMS continue to increase through day 8. Since there was no sampling between day 8 and day 25, therefore, we are not able to tell if DMS peaked at day 8 or not. The concentration reduced significantly by day 25.

Total reduced sulfur compounds concentrations in the Control batch was higher than the Amended batch on day 1:230,000 ppbv vs. 77,000 ppbv (Figure 4). The TRS in both batches increased and peaked on day 2. By day 8, the TRS concentration of the Control batch was significantly less than that of the Amended batch. On day 25, TRS of the Control batch was 43 ppbv and Amended batch was 460 ppbv.

The data indicated that the permanganate addition reduced the reduced sulfur compounds concentrations in the headspace initially and altered the peaking pattern of some compounds.

Figure 1: First Day Concentration of Selected Compounds and Their Odor Threshold Concentration Ranges in Control and Amended Batches

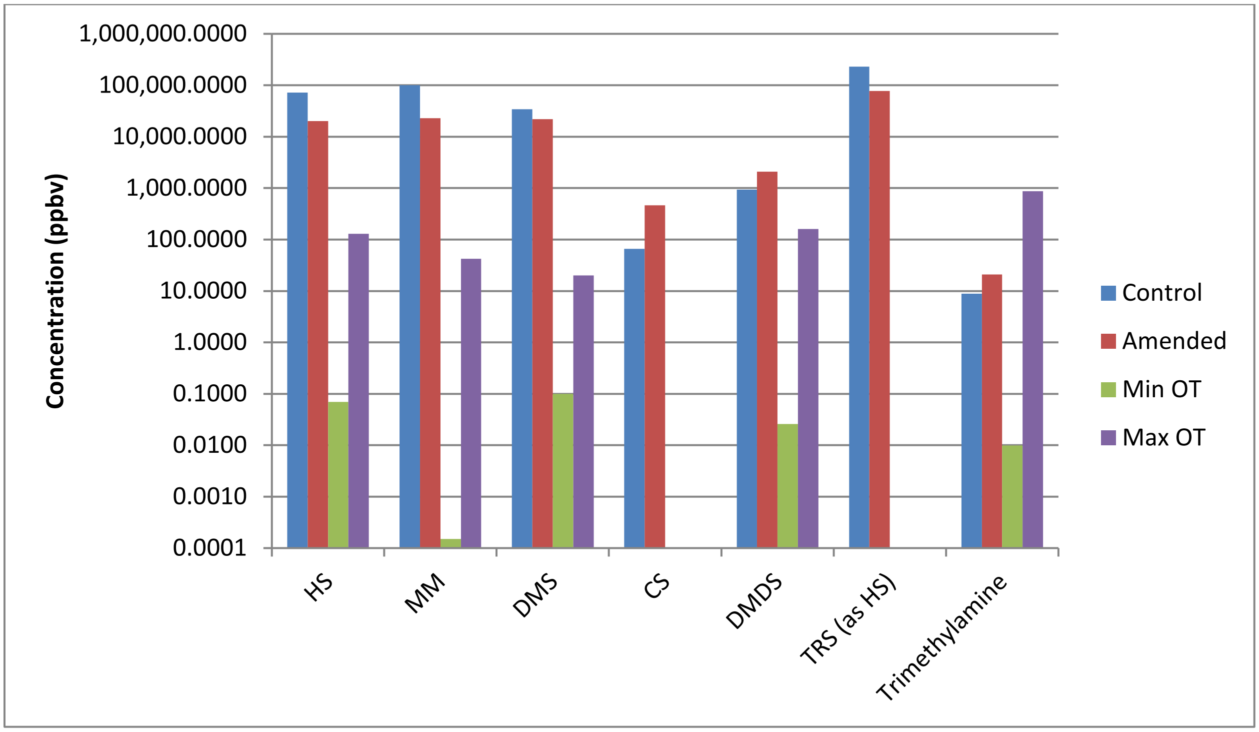


Figure 2: Selected Reduced Sulfur Compounds Concentrations in Control batches

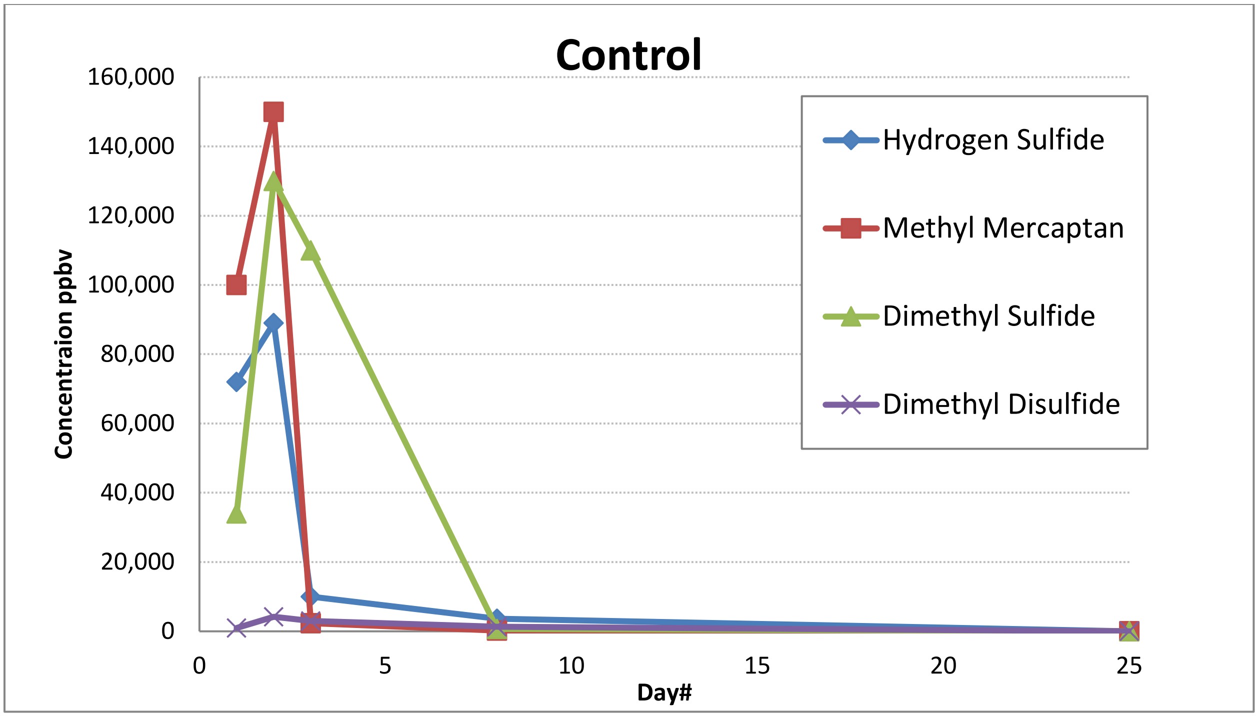


Figure 3: Selected Reduced Sulfur Compounds Concentrations in $KMnO_4$ Amended batch

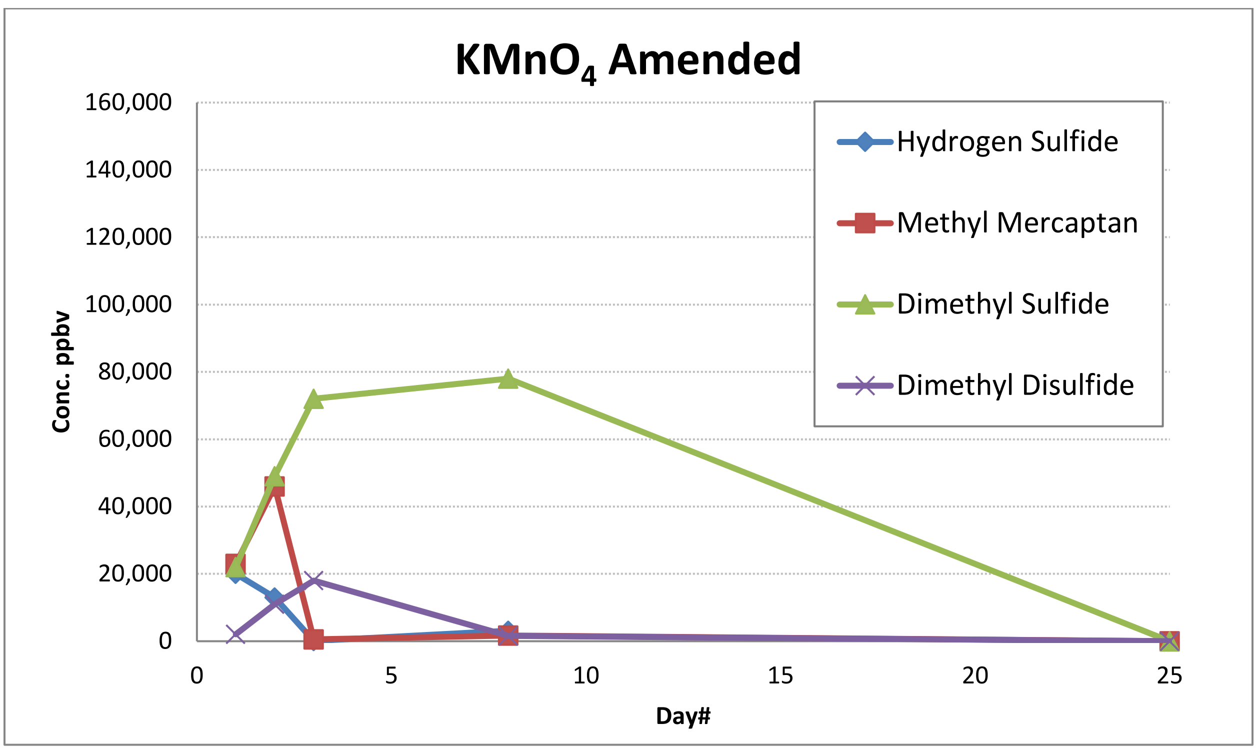
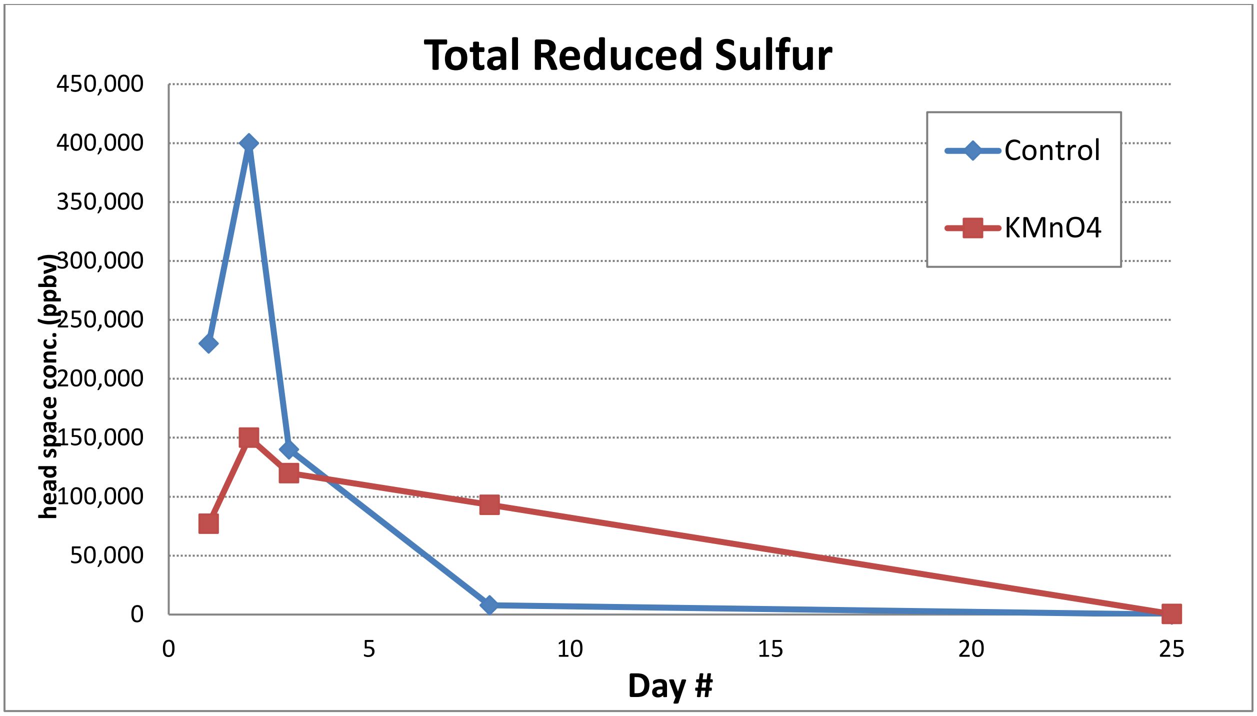


Figure 4: Total Reduced Sulfur in Control and Amended

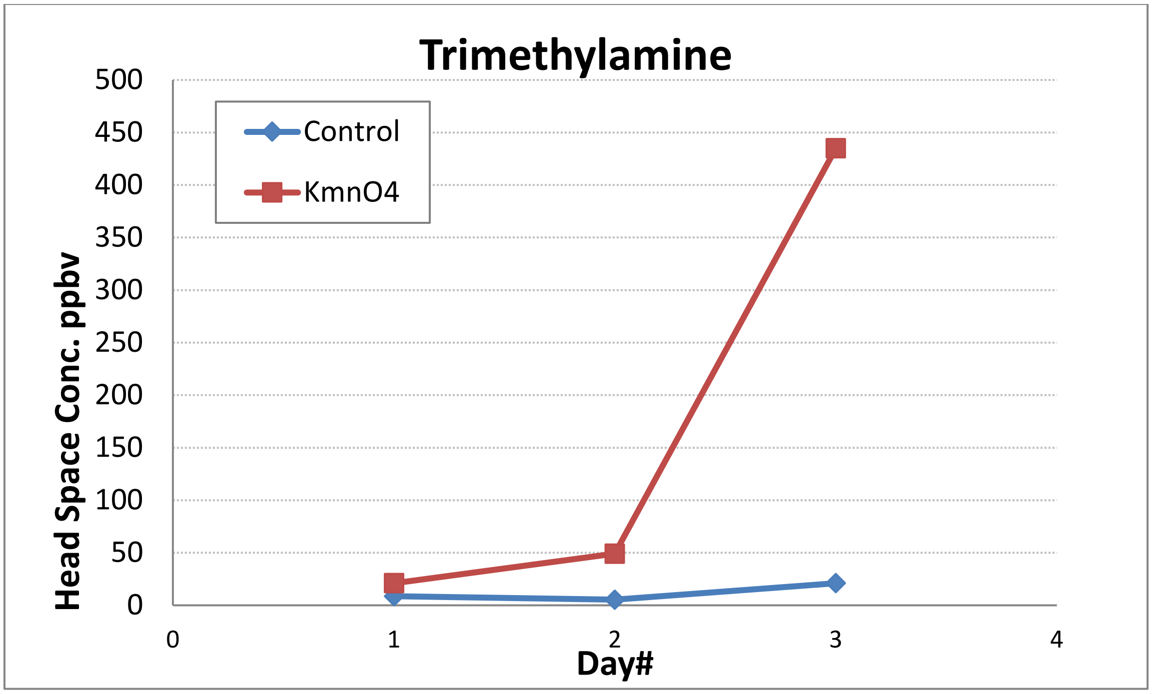


The amines compounds samples were collected from head space air in the truck. Of the thirteen compounds analyzed, only one, Trimethylamine, was detected in both Control and Amended batches (Table 2). The concentration started out at 8.3 ppbv in Control batch and 22 ppbv in Amended batch. By day 3, the concentration in the Control batch increased to 22 ppbv while that of the Amended batch increased to 435 ppbv. The samples were collected for 3 days, due to method limitation. Trimethylamine concentration in the Amended batch started out higher than that of the control batch and increased more rapidly, resulting in significantly higher concentration at day 3 (Figure 5).

Table 2: Amines Compounds Concentration in Control and Permanganate Amended batches

			Amine Compounds Concentrations (ppbv)							
			Control			Amended				
	Day #		1	2	3	1	2(1)	2(2)	3(1)	3(2)
	Date		10/16/2012	10/17/2012	10/18/2012	10/17/2012	10/18/2012	10/18/2012	10/19/2012	10/19/2012
Compounds	Odor Threshold range (ppbv)	MRL (ppbv)								
Dimethylamine	0.9-1895	3.0								
Ethylamine	9.6-4,144	3.1								
Trimethylamine	0.1-1,029	2.2	8.8	5.4	21	21	13	85	430	440
Isopropylamine	1421	2.2								
tert-Butylamine	-	3.6								
n-Propylamine	-	2.4								
Diethylamine	24-154	1.8								
sec-Butylamine	-	1.8								
Isobutylamine	-	1.9								
n-Butylamine	95-16,472	1.8								
Diisopropylamine	154-179	1.3								
Triethylamine	119-34,340	1.3								
Dipropylamine	-	1.3								

Figure 5: Triethylamine Concentrations in Control and Amended batches



Sensory observations from the bucket test indicated that the Amended batch had less odor initially, however the odor became stronger with time (Table 3). The Control batch had strong odor which seemed to peak around day 2, coinciding with headspace analysis. The odor characteristics of the Control and the Amended batch appeared to be different. The both batches had fishy smell. The Control batch had strong petroleum smell while the Amended batch had chemical smell.

Field sensory observation showed that the strength of the smell of the Amended batch was slightly less than that of the Control batch (Table 4).

The data indicated that $KMnO_4$ addition altered the odor characteristic.

Table 3: Conventional Parameters and Sensory Observations

Parameters	Control Samples	Permanganate Amended Samples

	Control day 1	Control day 2	Control day 3	Control day 8	Control day 25	KMnO4 day 1	KMnO4 day 2	KMnO4 day 3	KMnO4 day 8	KMnO4 day 25
TS%	26.44	26.76	26.36	26.29	26.06	27.46	26.69	26.91	26.7	26.04
VS%	70.52	70.48	70.23	69.99	69.04	69.55	69.07	68.91	68.89	68.14
pH	8.23	7.88	8.33	8.1	8.24	8.44	8.39	8.08	8.35	8.27
ORP	-308	-289.3	-303.2	-214.3	-210.5	-290.4	-306.7	-291.7	-226.7	-248.8
NH3	2483	2390	3185	3365	3112	2678	2639	2951	3581	3428.06
TKN	21241	18523.54	19122.6	18949	20549	15259	16461	19408	20053	15718.09
Sensory Observations										
Observation by Phuong Truong	Very strong odor (9 in intensity), heavy fishy smell, pungent, rotten vegetable.	Even stronger than day 1 (10 in intensity), heavy fishy smell, rotten fish, overwhelming, petroleum	Still have the fishy smell, less than day 2 but the petroleum smell is more potent and higher in intensity, also smell more like raw sewage, putrid, urine smell. A 7 in intensity	The same as day 3, heavy petroleum smell, fishy smell, heavy urine smell, fecal smell, putrid. A 7 or 8 in intensity.	Same as the other days just stronger	A little bit of fishy smell but a lot less than the control bucket, earthy smell. 1 in intensity. Sludge is darker in color and appears to be drier than C samples	Worse than day 1, the earthy smell still there but a lot stronger, also some petroleum smell. 5 in intensity. Sludge is darker in color and appears to be drier than C samples	Same as day 2 but with a 7 in intensity	Very pungent chemical smell, fishy smell, strong earthy smell. Scale of 7 or 8 in intensity . A light petroleum smell. Sludge is a lot darker than the C samples .	Worse than C-25, strong fecal smell
Observation by Erin Howell	Strong fishy odor	Still smells fishy,	Strong petroleum odor,			More earthy smell, better than C-2	Still more earthy than C-3 but a little fishy too. worse than P-1	Strong fishy odor, worse than P-2	Strong smell	

Table 4: Field Sensory Observations

Field operator's observations	Control		KMnO4 Amended		Temp/Comments
10/22/2012	Ammonia	6	Ammonia-less sharp	2	65 degrees, Amended is blacker in color
10/23/2012	Less strong	5	Musty	2	65 degrees
10/26/2012	Musty	3	Musty	2	60 degrees
10/30/2012	Musty	3	Musty	3	59 degrees
11/5/2012	Musty	2	Musty	2	71 degrees-better weather
11/9/2012	Musty	3	Musty	2	70 degrees-wet
11/12/2012	Stronger	5	Musty	2	68 degrees-snow on ground
11/17/2012	Biosolids odor	4	Biosolids odor	4	57 degrees-breezy, wet piles on top, lots of rain

Summary

There are 10 reduced sulfur compounds and one amine compound detected in the biosolids gas samples from both control and amended batches. The concentrations throughout the study ranged from 7 – 150,000 ppbv for sulfur compounds and 5-440 ppbv for amines.

The reduced sulfur compounds concentrations in the biosolid gas sample started out at lower concentrations, increased and peaked, then, declined. The Trimethylamine, which was the only amine compound detected, started out at low concentration then continued to increase through day 3. The peaking patterns of Trimethylamine in both batches are unknown beyond day 3, since no sample was collected due to sample collection limitation.

Since many of the compounds have method reporting limit value higher than low range of their odor threshold concentration, they may contribute to the odor strength and characteristic, yet undetected by chemical analyses.

The data showed that $KMnO_4$ addition had the following effects to biosolids:

- Reduced initial concentrations of the majority of reduced sulfur compounds analyzed and detected.
- Did not delay the peaking time significantly, but caused the post-peak concentrations to decrease at a slower rate than the untreated.
- Increased the initial concentration of Triethylamine, which was an only amine compounds detected, and cause the concentration to increase more rapidly.
- Altered the odor characteristic of the biosolids. However, correlating lab analysis results with sensory observation is challenging due to very low odor threshold of most compounds and subjectivity of sensory observation.

If permanganate were to be used as odor suppression agent at WPTP, the cost of chemical would be approximately $470,000 per year, excluding the capital investment of chemical addition; maintenance of the system or operational costs.