Environ. Eng. Res. Vol. 8, No. 5, pp. 252~258, 2003
Korean Society of Environmental Engineers

QUANTIFICATION AND TREATMENT OF SLUDGE ODOR

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(received August 2003, accepted October 2003)

Abstract : Nuisance odors from municipal sludge are problematic at municipal treatment plants. The breakdown of organic and inorganic materials leads to the production of sulfur containing gases. Hydrogen sulfide has been perceived as the primary cause of odors associated with municipal sludges. Head space analyses of municipal sludges with the Drager Chip Measuring System and GC/MS show hydrogen sulfide is important to the sludge odor signature. However, methanethiol quickly becomes the most dominant odor causing gas emanating from the sludge. Dimethyl sulfide and dimethyl trisulfide are also found in the headspace at greater concentrations as the sludge ages. The effectiveness of the odor treatment method was determined using an odor concentration index, defined herein. The odor concentration index allows quantifiable reproductions in odor based upon the chemical composition of the headspace. An alternative sludge treatment method was evaluated with the odor concentration index for potential use at solid waste disposal facilities. The 3% hypochlorite solution destroyed sludge odor for up to thirty days. Hypochlorite is relatively inexpensive and readily available, especially at water treatment facilities. Chlorination of sludge should be considered for particularly noxious odors in the wastewater treatment facility or for selective odor control of incoming noxious sludge at solid waste disposal facilities.

Key Words : odor, sludge, landfill, hydrogen sulfide, methanethiol (methyl mercaptan)

INTRODUCTION

The human olfactory system is sensitive to a variety of odorous chemical compounds. The intensity, detectability, concentration and character of the chemical influences the human perception of an odor. Odorous compounds in sludge include both inorganic and organic compounds, many of which are produced by biological activity. These compounds may be formed through aerobic or anaerobic decomposition of proteins and carbohydrates in sludges. Table 1 presents a list of odorous compounds and their odor thresholds associated with domestic wastewater and sludge. The odor threshold refers to the minimum concentration required for an individual to perceive the odor, although the exact type of odor may not be identifiable.1)

Hydrogen sulfide emissions from wastewater treatment plants have been widely studied. Research efforts have been directed towards preventing hydrogen sulfide emissions from wastewater treatment plants.2,3) Odors associated with sludge disposal are also a problem at solid waste disposal facilities. These odor problems have commonly been associated with hydrogen sulfide, while in fact the odors may be attributed to a complex mixture of organic and inorganic compounds.

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Table 1. Odorous Compounds Found in Sewage and Sludge[1-3]

Compound	Odor Threshold (ppm)	Characteristic Odor
Acetaldehyde	0.067	Pungent, fruity
Allyl mercaptan	0.0001	Disagreeable, garlic
Ammonia	17	Pungent, irritating
Amyl mercaptan	0.0003	Unpleasant, putrid
Benzyl mercaptan	0.0002	Unpleasant, strong
Butylamine	0.080	Sour, ammonia
Cadaverine	---	Putrid, decaying fresh
Chlorine	0.080	Pungent, suffocating
Chlorophenol	0.00018	Medicinal, phenolic
Crotyl mercaptan	0.000029	Skunk-like
Dibutylamine	0.016	Fishy
Diisopropyamine	0.13	Fishy
Dimethylamine	0.34	Putrid, fishy
Dimethyl sulfide	0.001	Decayed cabbage
Diphenyl sulfide	0.0001	Unpleasant
Ethylamine	0.27	Ammonialike
Ethyl mercaptan	0.0003	Decayed cabbage
Hydrogen sulfide	0.0005	Rotten eggs
Indole	0.0001	Fecal, nauseating
Methylamine	4.7	Putrid, fishy
Methyl mercaptan	0.0005	Rotten cabbage
Propyl mecaptan	0.0005	Unpleasant
Putrescine	---	Putrid, nauseating
Pyridine	0.66	Pungent, irritating
Skatole	0.0001	Fecal, nauseating
Tert-butyl mercaptan	0.00008	Skunk, unpleasant
Thiocresol	0.0001	Skunky, irritating
Thiophenol	0.000062	Putrid, garlic-like
Triethylamine	0.0004	Pungent, fishy

Sludge stabilization processes are essential to the performance of any wastewater treatment plant. The type of sludge stabilization plays an important role in the odor signature of the sludge when it is disposed. Sludge stabilization has two purposes: to substantially reduce pathogenic organisms minimizing the health hazards associated with the sludge; and to reduce odorroducing organisms minimizing nuisance conditions. The sludge must be nonhazardous, biologically inactive, free of offensive odors and aesthetically acceptable. Commonly used sludge stabilization processes includes anaerobic digestion, aerobic digestion, composting and chemical stabilization.[1)]

Biological stabilization converts organic matter to water, carbon dioxide and methane by anaerobic or aerobic digestion.[4)] This process reduces the volatile and biodegradable organic content and the mass of the sludge by converting it to soluble material and gas. It may also reduce pathogen levels and odors.

Lime stabilization temporarily raises the pH of the raw sludge to decrease biological activity and reduce pathogen levels.[5)] However, it increases the dry solids percentage of the sludge. Because pH effects are temporary, decomposition, leachate generation, and release of gas, odors, and heavy metals may occur after initial treatment.

Composting is an aerobic process involving the biological stabilization of sludge in a windrow, aerated static pile or vessel.[4,5)] Composting lowers the biological activity and destroys most pathogens. Composting also degrades sludge to humus like material. However, composting increases sludge mass due to the addition of bulking agents.

Heat drying is used to kill pathogens and reduce the water content of sludge.[1,2,4] Thermal disinfection destroys most pathogens and odors. However, thermal disinfection is very costly.

It is difficult to quantifiably define noxious odors. Odor intensity is the strength of the odor sensation. For most odorant the intensity of the odor sensation, I, increases with the concentration, C, in accordance with Steven's Psychophysical Law[2]:

$$I=K(C)^n \qquad (1)$$

Where:

I = intensity of the odor sensation

C = the odor concentration, ppb

K = a constant

n = slope of the psychophysical function, an exponent whose value may vary from 0.2 to 0.8 depending on the odorant.

According to EPA documents, odor compounds that have higher threshold values have higher slope (n) values. Odor compounds which have lower threshold values have lower slope (n) values.[4] Dravnieks showed that the slope of the concentration versus odor intensity line varies with n.[6]

Unfortunately, not enough reliable information about K and n values of the major odor compounds from sludge (hydrogen sulfide, methanethiol, dimethyl sulfide, dimethyl disulfide, and dimethyl trisulfide) is available for the psychophysical law to be useful in engineering design calculations. Steven's Law could not be accurately applied to the odor intensity from sludge. Methods for quantifying odors associated with sludge disposal are needed. Therefore, instead of using Steven's Law, we developed an odor concentration index method, which shows relative odor intensity values rather than Steven's Law.

Treatment methods to reduce nuisance odors at solid waste disposal facilities during sludge disposal are also needed. Odor abatement processes must be quantifiable and long lasting. Alternative methods applicable to both wastewater and solid waste disposal facilities were investigated. The results of this investigation to find alternative odor treatment techniques and a quantifiable method for odor evaluation are discussed within this paper.

METHODS AND MATERIALS

Sludge samples were collected in one gallon sealed containers. These samples were transported from the solid waste facility and stored at 4°C within a secondary sealed 5 gallon plastic container. The initial headspace analysis was performed within 24 hours.

240 mL septic bottles were used as reactors. The control contained 100 g of sludge. The second reactor contained 50 g of water along with the 100 g of sludge. The other reactor contained 50 g of 3% hypochlorite solution added to 100 g of sludge.

Initially, air samples were collected from the one gallon sludge container in a one liter Tedlar sample bag. The Drager Chip Measuring System (CMS) was used to detect and measure hydrogen sulfide and to calibrate the GC/MS for hydrogen sulfide concentration. Drager CMS consists of two key components: the gas selective chips and the analyzer. Approximately 0.2 to 0.5 liters of air from the sample was passed through the Drager CMS. The GC/MS was calibrated for hydrogen sulfide from the results of the Drager CMS tests.

Other headspace products were quantified and identified with a Hewlett Packard 5890 Series II gas chromatograph (GC) with a 5972 mass selective detector (MS). Five hundred microliters of the headspace air was injected into the GC/MS to determine the concentration and speciation of odor causing agent in the headspace. The air sample was separated with a 0.32 mm × 60 m VOCOL capillary column purchased from Supelco, Inc. All samples were quantified using single point calibrations after linearity in the concentration range of interest had been verified. Comparing the spectra generated by the MS detector to standard library spectra allowed identification of compounds in the headspace.

RESULTS AND DISCUSSION

Gas chromatography and mass spectrometry were used to detect and quantify the odorous compounds generated from a lime stabilized sludge. Hydrogen sulfide, methyl mercaptan, dimethyl sulfide, dimethyl disulfide, and dimethyl trisulfide were found to be the major odor generating compounds in the sludge.

The five major odor compounds are sulfur containing compounds. As mentioned previously, hydrogen sulfide is the key odor compound at wastewater treatment facilities. Animal waste treatment facilities also identified the same major odor compounds (hydrogen sulfide, methanethiol, dimethyl sulfide, and dimethyl disulfide) for their odor problems.[7-9] Composting facility odors are dominated by dimethyl disulfide.[1]

The relative strength of an odor is dependant upon both the conversion of that compound in the air and the sensitivity of the human olfactory system. The sensitivity of the human olfactory system was assumed to be directly related to the odor threshold of each compound. The threshold values of these sulfur related compounds are very low (0.5-3 ppb). Therefore the n values of these major compounds are nearly equivalent. The total odor intensity from the sludge is directly related to the threshold values and concentration.

A unitless odor concentration index (ODI) was used to compare the strengths of the sludge odors by dividing the concentration of the compound in the headspace, $C_{headspace}$ in ppb, by the odor threshold, $C_{threshold}$ in ppb, given in Table 1:

$$ODI = C_{headspace}/C_{threshold} \tag{2}$$

In the samples analyzed, Figure 1 shows the concentration of odor compounds over time and Figure 2 shows the corresponding equivalent values by odor concentration index method. Initially, hydrogen sulfide is the most odorous and highly concentrated compound. However, after two days, methyl mercaptan dominated the odor

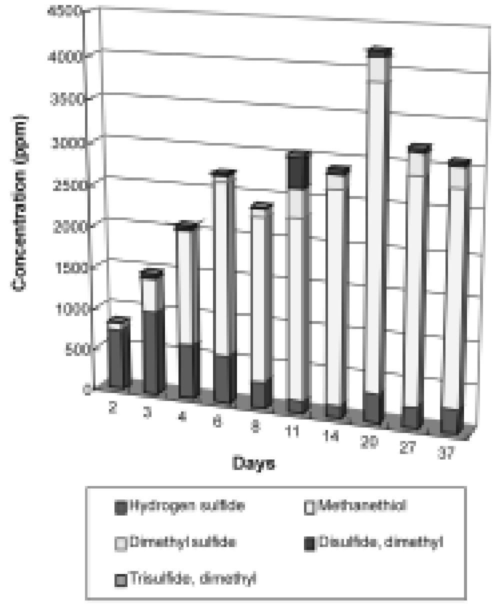

Figure 1. Concentration composition of odor compounds emanating from a lime stabilized sludge.

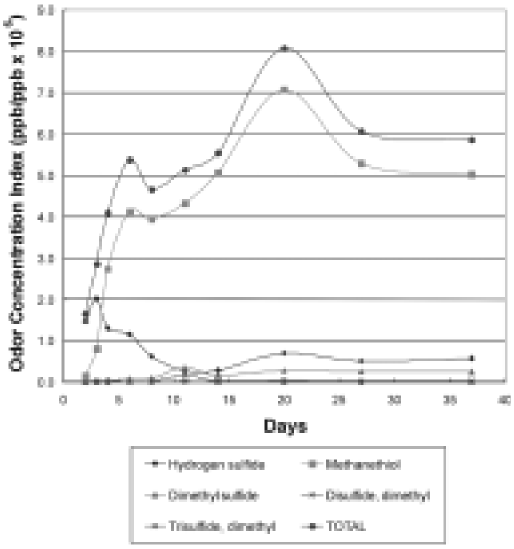

Figure 2. Odor concentration index values of odor compounds emanating from a lime stabilized sludge.

concentration index. Hydrogen sulfide continued to contribute to the overall odor of the sludge along with dimethyl sulfide, dimethyl disulfide and dimethyl trisulfide.

The generation mechanism of the five odorous compounds from the sludge is not clear. These odor compounds may be generated when organic matter is decomposed and oxidized or through a reduction process.

Hydrogen sulfide is generated when sulfate is reduced and from protein decomposition.[3,5] Cysteine and methionine are two sulfur containing amino acids which compose protein.[10] Sulfate is a major end product of cysteine metabolism. However, in soil an alternative pathway for cysteine oxidation is provided by the combined activities of various microorganisms. Cysteine is largely desulfurated under these conditions to hydrogen sulfide by a wide range of bacteria.

Taylor described methanethiol (methyl mercaptan) and dimethyl sulfide production from the following reactions[10]:

H_2S + S-adenosylmethionine =
CH_3SH + S-adenosylhomocysteine
CH_3SH + S-adenosylmethionine =
CH_3SCH_3 + S-adenosylhomocysteine

It has also been observed that methanethiol (methyl mercaptan), dimethyl sulfide, and dimethyl disulfide were produced from methionine, a ubiquitous component of proteins, in soil incubations.[10]

Taylor and Kiene show the microbial transformation of methionine.[10] Methanethiol is produced from methionine through methionine γ-lyase. Dimethyl sulfide is generated from methanethiol through thiol S-methyltransferase. Dimethyl disulfide is also produced from methanethiol though chemical and probably biochemical oxidation. Sylvia also identified several possible biochemical precursors to hydrogen sulfide, methanethiol, dimethyl sulfide and dimethyl disulfide.[11]

When water reacts with methanethiol, hydrogen sulfide is produced.[3,5] This is one possible explanation for the increase in hydrogen sulfide levels from sludge containing higher water content, which were observed during the course of sludge evaluation shown in Figure 3.

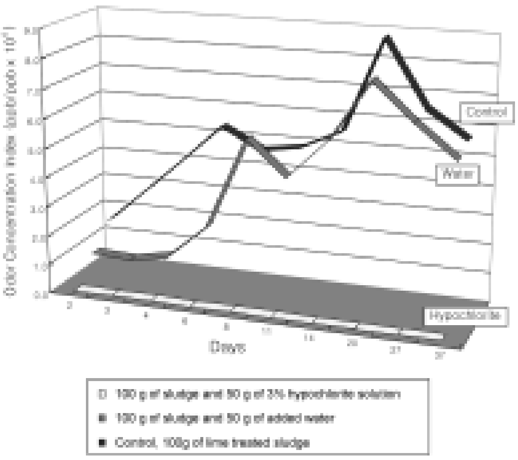

Figure 3. Effects of water and hypochlorite on odor emissions from lime stabilized sludge.

In these experiments, as the sludge aged the odor concentration index increased rapidly for the first five days in the experimental reactor. The data correlate well with reports by personnel at the solid waste disposal facility. Personnel at the facility reported increased odor problems with sludge deliveries which were left in transit over an evening or a weekend. The data also indicate the shortcomings of odor treatment methods at wastewater treatment plants, since the lime treatment did not eliminate the odor problem.

An alternative method was investigated to treat odor emanating from the sludge during disposal. Figure 3 shows the control sample of the sludge in the 250 milliliter reactor. Water was added to a second sample to gain an understanding of how the water content effects the odor concentration index. The third sample was treated with a simple 3% hypochlorite solution. Figure 3 shows the odor concentration index for each test.

The control sample had the highest initial odor concentration index value. As mentioned previously, the odor concentration index increased steadily up until day 6. In the headspace, the initial odor was 1.7 million times greater than the odor threshold. The maximum odor value actually was found 20 days after the sludge was sampled and was almost 9 million times greater than the odor threshold. This represents a significant short term and long term odor problem for the solid waste disposal facility.

The sample with water added had a lower initial odor concentration index value than the control. However, the sample was still approximately 1 million times greater than the odor threshold. After a brief lag period of 3-4 days, the sample with added water soon matched or surpassed the control sample in odor. Its maximum value also occurred 20 days after the sample was received and was nearly 8 million times the odor threshold. The high water content sludge also represents a significant short and long term concern for solid waste disposal facilities.

The third sample treated with a 3% hypochlorite solution showed no measurable odor. More importantly, the characteristic increase in odor was prevented. The short term and long term odor problems associated with this sludge were eliminated with the hypochlorite treatment method.

CONCLUSION

The odors from the sludge are caused primarily by high concentrations of hydrogen sulfide, methanethiol, dimethyl sulfide, dimethyl disulfide, and dimethyl trisulfide. These odors collectively can be measured and the intensity determined by an odor concentration index. An odor concentration index greater than 1 means the odor threshold has been exceeded. Odor strength from lime-stabilized sludge was 1.7 million times greater than the odor threshold. The odor intensity increased rapidly for up to 6 days.

A 3% solution of hypochlorite reduced the odor to below detectable limits immediately after treatment and for a period of up to 30 days thereafter. Monitoring of the odors ceased after the 30 day time period. Hypochlorite is relatively inexpensive and readily available, especially at wastewater treatment facilities. Chlorination of sludge should be considered for particularly noxious odors in the wastewater treatment facility or for selective odor control of incoming noxious sludge at solids waste disposal facilities.

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