INHIBITING THE PRODUCTION OF ODORS FROM DEWATERED RESIDUALS USING NITRATES AND ANTHRAQUINONES

Article *in* Proceedings of the Water Environment Federation · January 2002

DOI: 10.2175/193864702784248458

Mohammed Abu-Orf
Hazen and Sawyer, P.C.
137 PUBLICATIONS **1,708** CITATIONS

Chris Peot
District of Columbia Water and Sewer Authority
45 PUBLICATIONS **74** CITATIONS

Laura L. McConnell
Bayer CropScience
64 PUBLICATIONS **1,118** CITATIONS

Hyunook Kim
University of Seoul
237 PUBLICATIONS **9,190** CITATIONS

INHIBITING THE PRODUCTION OF ODORS FROM DEWATERED RESIDUALS USING NITRATES AND ANTHRAQUINONES

Mohammad Abu-Orf, Chris Peot, Mark Rameriz, Mark Laquidara, Laura L. McConnell,
Hyunook Kim, and David Hunniford

Director - Biosolids R&D Program
Vivendi Water/USFilter North American Technology Center
1901 West Garden Road
Vineland, NJ 08360

ABSTRACT

This paper reports on the use of chemical addition to dewatered residuals for odor control. Odor is the number one obstacle to land application of biosolids and residuals. The chemicals used were calcium nitrate solution and anthraquinone particles. Nitrate salt was evaluated alone and in combination with anthraquinone. Both chemicals are commercially available and are used to control hydrogen sulfide in sewer systems. Experiments were conducted on both limed and unlimed samples of dewatered residuals from the Blue Plains Facility. Odor characterization for these experiments was conducted using a simplified plant panel and analytical determination using a solid phase microextraction technique. Other experiments were conducted on unlimed dewatered biosolids from the Philadelphia Water Department Facilities. These experiments used only a mixture of nitrate and anthraquinone particles. This paper will report only on the Blue Plains results. The results from PWD are available in Higgins et al paper also presented in this conference.

Results showed that nitrate salt addition is capable of significantly reducing sulfur odor compounds. The use of the anthraquinone particles with the nitrate salt resulted in further odor reduction. This effect was more pronounced on the limed residuals. However, the determination of the odor compounds did not correlated, however, with the odor detection from the simplified panel. Therefore, the use of these chemicals should be tested at more facilities with different residuals in order to document success and the exact conditions of use. Future research that includes controlled addition on different biosolids and residuals coupled with long term full scale documentation is also warranted.

KEY WORDS

Odor Control, Biosolids, Residuals, Nitrate; Anthraquinones

INTRODUCTION

The drivers for treatment and/or disposal of biosolids and municipal residuals for any environmental management process are regulatory compliance and cost effectiveness. However, this is not true for biosolids odors, which are still unregulated. Public acceptance of land application to land, the disposal method favored by the current Part 503 regulations, hinges on adequate odor control. Moreover, these odor issues will continue to influence both in-plant and off-site biosolids processing and practices.

According to EPA (2000), odor is the most important factor limiting public acceptance of biosolids. The bottom line remains: as long as the odors are objectionable, the pathogen classification of biosolids (Class A or B) has no merit. This opposition to land application caused biosolids use to be banned in many counties, and caused restrictive ordinances to be set in others. The result is an overall increase in biosolids disposal costs.

The methods described in this paper propose to reduce odor production from residuals downstream of dewatering through the use of chemical additives. These chemical additives reduce and ultimately inhibit odor production. The overall objective of the research described in this paper is to demonstrate the effectiveness of nitrate salts and anthraquinones solutions in reducing present and future generated odors from dewatered solids. This objective may be achieved through characterization and quantification of odors from limed and unlimed residuals in the presence and absence of nitrate salt; comparison of odor characteristics of residuals with nitrate alone and with nitrate and anthraquinone (AQ); evaluation of changes and persistence of odors from residuals samples over time; and finally comparison of results between analytical measurements and odor panel results from identical samples.

Results are presented for limed and unlimed residuals from the Blue Plains Facility and anaerobically digested biosolids from the Philadelphia Water Department (PWD). Two types of testing were conducted at the Blue Plains Facility, laboratory and large scale mixing. This paper will present the results from the Blue Plains facility only. The results from the PWD are presented in Higgins et al (2002) paper, also presented in this conference.

MATERIALS AND METHODS

Chemicals Used. Two different additives were used, Calcium Nitrate (60% active, 3.5 lbs NO3-O per gallon), which is commercially available as Bioxide®, and Calcium Nitrate AQ, which contains 1 lb of anthraquinones/10 gallons bioxide, commercially available as Bioxide®-AQ, respectively.

Literature indicated that there are no known safety issues with the use of anthraquinones. In fact, some of these chemicals have been sold commercially as a laxative, and many are naturally occurring in a number of plants such as rhubarb (Weimer et al., 1995).

The mechanisms for the overall effectiveness of both nitrate salts and anthraquinones particles are described in detail in Ballinger et al. (2001), Hunniford and Davis (2001), and Weimer et al. (1995). Weimer et al (1995) offer excellent review of the different biocides used for bacterial inhibition as well as anthraquinones. The nitrate simulates the growth of hetrotrophic denitrifiers and anaerobic thiobacillus species that outcompete SRB (sulfate reducing bacteria) and thus reduce their activity. Hunniford and Davis (2001) also reported that addition of nitrate provides an oxygen source, which promotes the growth of naturally occurring bacteria, which utilize the sulfur in their metabolism. Nitrite, the intermediate product of nitrate reduction, may inhibit microbes. Biocide use is aimed at killing SRB. The polycyclic quinines, however, which represent the material used for this study, only inhibit the SRB activity due to the blocking of production of adenosine triphosphate (ATP) by the bacteria. This action, therefore, removes the bacteria's ability to respire by sulfate reduction. Thus, when the two reactants (nitrate and quinines) are used together a synergistic effect leads to a higher degree of sulfate reducing bacterial inhibition.

The use of these chemicals for reduced sulfuric compounds odor reduction and control for wastewater collection and treatment systems is well documented. This paper is the first to address its use in municipal, biosolids and residuals applications.

Laboratory Experiments. The laboratory testing was designed to qualitatively assess odor reduction. Testing was conducted May 2001. A bulk sample of centrifuged dewatered residuals was collected in order to eliminate variations within solids. For quality control, the lime was mixed with the dewatered biosolids in the laboratory chemical treatment followed in the mixer. This assured the same amount of lime used for all samples. Plant records indicated cake solids to be about 25% and the polymer dose was kept constant during sample collection (since previous research results indicated that polymer can impact odor from dewatered residuals at the same facility (Kim et al, 2001a). The samples were transferred into 5-gallon buckets; each bucket contained a constant amount of residuals (10 lbs). A constant lime dosage was used (the same as in full-scale at a ratio of 1 lb. of lime per 4 lbs. of dry solids) and mixing using a kitchen mixer. The initial time required to achieve adequate mixing of the lime was determined to be about 2 minutes, the same mixing time was used for all samples. The various samples were mixed in three batches and stored in covered buckets at room temperature. Table 1 (see below) provides the overall testing matrix used to assess the effect of Bioxide and Bioxide-AQ on both limed and non-limed biosolids.

Table 1. Sample matrix used for the initial laboratory testing at the Blue Plains.

Sample ID	Control	BL	BM	BH	BL-AQ	BM-AQ
No lime	X	X	X	X	X	X
With lime	X	X	X	X	X	X

BL, low dosage of bioxide that is equivalent to 0.1 gallons per ton of dewatered sludge (wet basis)
BL, medium dosage of bioxide that is equivalent to 0.5 gallons per ton of dewatered sludge (wet basis)
BH, high dosage of bioxide that is equivalent to 1.0 gallons per ton of dewatered sludge (wet basis)

Analysis of Samples. Odor analysis of the different samples was conducted using a simplified 5-person panel from the plant staff, and Gastec Detector Tubes. The sample identification was not disclosed to the plant's panel to avoid influencing the results.

Full-Scale Testing. Full scale laboratory testing, which was intended to verify the results obtained, was conducted during the month November 2001. In order to better control the mixing of the residuals, lime and bioxide products, a pilot scale mixing unit was transported to the plant. The mixing unit (Figure 1, USFilter/Asdor) was located outside the dewatering building. The throughput of the mixer was estimated at 3-7 m^3 of wet residuals per hr. Dewatered unlimed residuals were conveyed to the mixer's upper hopper as needed from the centrifuge. The throughput was adjusted to ~ 4.3 wet tons per hour and accordingly the lime addition was calibrated to match the plant dosage, approximately 20% on dry basis. Different amounts of bioxide (See Table 2) were added to the residuals as they moved through the mixer using a hand held pump sprayer with a variable speed nozzle. The amount of chemical addition was calibrated to the mixer throughput, which assured the dosages in Table 2.

Figure 1. Biosolids and Lime Mixing Unit (USFilter/Asdor)

Table 2. Sample Matrix used for the full-scale testing at the Blue Plains.

Sample ID	Control	BL	BM	BL-AQ	BM-AQ
Dosage of Bioxide*	0	0.1	0.5	0.1	0.5
Dosage of Bioxide**	0	1.4	7.0	1.4 + 0.04	7.0 + 0.2

* Units are gallon/ton of dewatered sludge (wet basis).

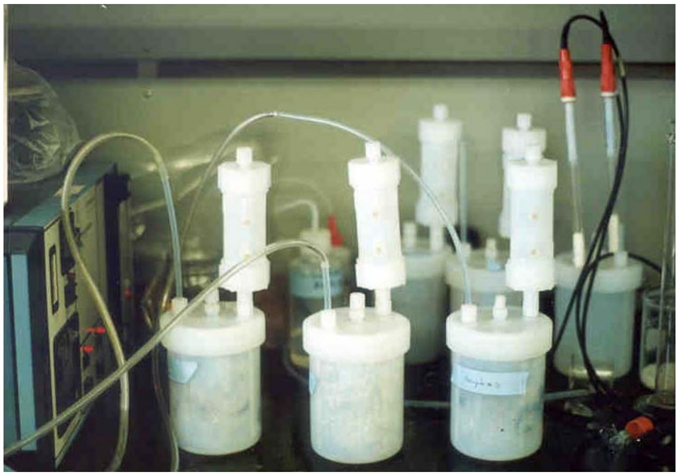
** Units are in lb per dry tone.

Analysis of the Samples. Samples of the residuals were collected every 5 minutes to assure representative sampling during mixing. One set of sub-samples from the mixed residuals was transferred into 5-gallon buckets that were stored at the plant's laboratory. These samples (Figure 2) were used in assessing odors by plant's simplified odor panel. Another set of sub-samples (600 g) was transferred to five different 1-L Teflon jars. The sample matrices collected are provided in Table 2. The samples were transported to the US Department of Agriculture (USDA) laboratory and stored at 25°C for 20 days. Different odorants concentrations, i.e., carbon disulfide (CS_2), dimethyl sulfide (DMS), dimethyl disulfide (DMDS), methyl mercaptan (MSH), and total reduced sulfur (TRS) were measured using solid phase microextraction (SPME) coupled with gas chromatography with mass spectrometer (GC-MS). The odorants were measured at 6 different times for a period of 20 days to monitor the dynamic change of the odorants from the samples over time. These measurements were coordinated with plants' odor panel testing.

Figure 2. Samples of limed biosolids treated with bioxide products stored for Blue Plains's panel testing.

The experimental set-up for the odor analysis at the USDA is illustrated in Figures 3. The headspace of the jar was flushed with nitrogen gas at a constant rate of 72 mL/min. This set-up is configured so that the air flow from five of these 1-L Teflon chambers connects to a single nitrogen cylinder using a flow splitting system. The odors from the five samples were collected simultaneously.

Figure 3. Samples at the USDA laboratory for odorant analysis.

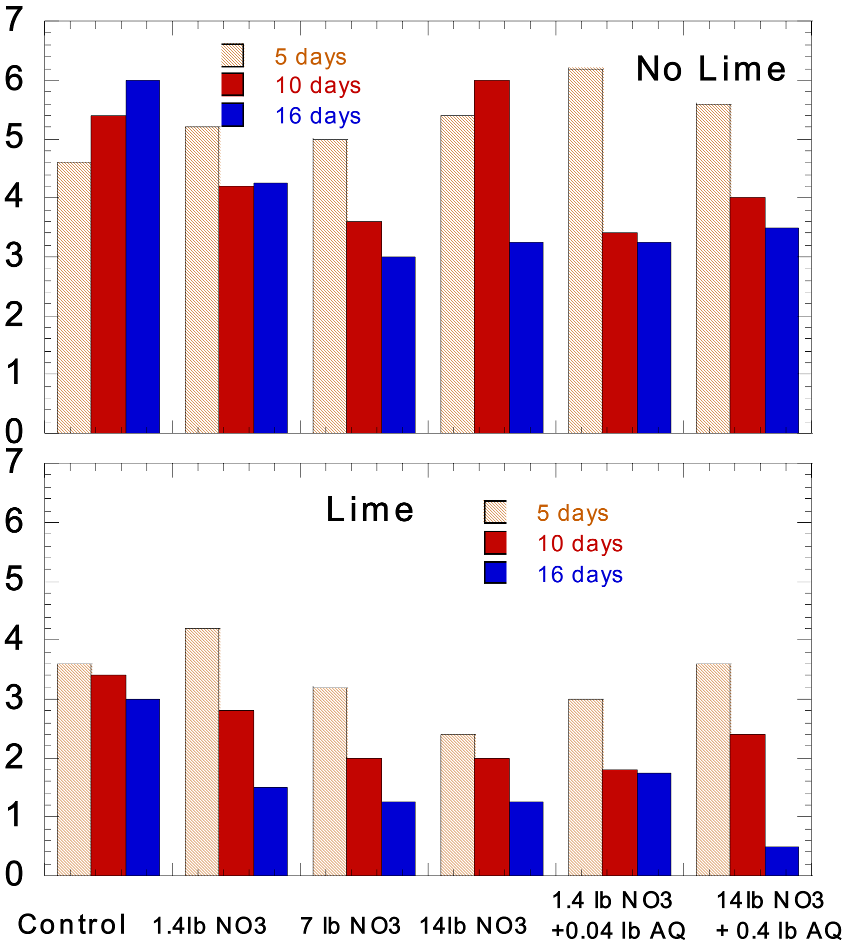


The odorous compounds, excluding hydrogen sulfide, from the headspace of the collecting chamber were extracted by SPME fibers to the off gas for 1 hr in the laboratory. After the extraction was complete, the fibers were injected into GC/MS system for the analysis. The exact details of the analysis, calibration, temperature program etc., can be found elsewhere (Kim et al., 2001b). Hydrogen sulfide was analyzed with Jerome 631X hydrogen sulfide analyzer (Arizona Instrument, Phoenix AZ).

RESULTS AND DISCUSSION

Laboratory Results. Plant staff organized an internal odor panel to test the samples. The panel tested the residuals in terms of odor intensity and hedonic tone as shown in Figures 4 and 5, respectively. The reported results are five persons averages. With no lime and no bioxide, the odor intensity and hedonic tone increased with time. In almost every case, the lime reversed this trend, and the bioxide product amplified this reversal.

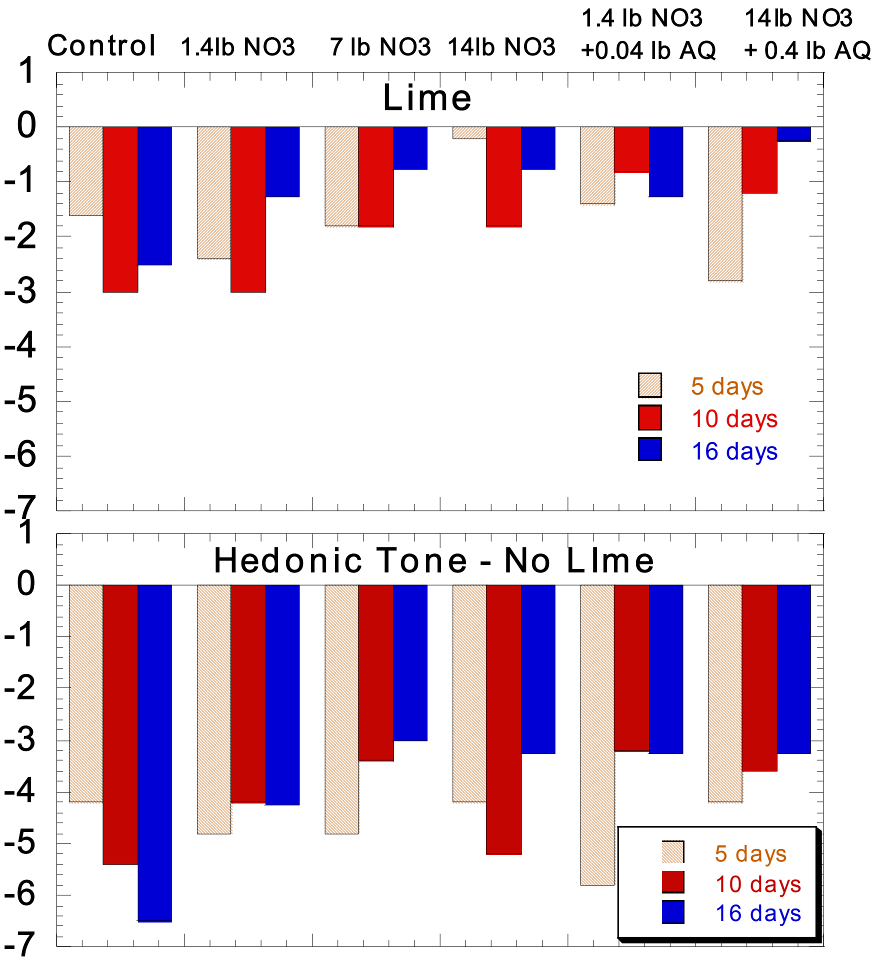
Figure 4. Odor intensity from the different treated samples – simplified odor panel.



For the unlimed samples, both odor intensity and hedonic tone decreased with storage time and the effect was observed to be more intense at the longer storage time of 16 days. However, in this case higher dosages of nitrate and/or AQ did not show much effect.

The chemical treatment of the biosolids was effective for the limed residuals. Increasing the nitrate dosage reduced odor intensity significantly, and this reduction was amplified as a function of storage time. The use of combined nitrate and anthraquinone further reduced the odor intensity. This same trend was observed for the hedonic tone. Overall, the combination of nitrate salt and anthraquinone appear to produce the best results with long storage times. This corresponds well with the mechanisms discussed earlier. Testing with the Gastic tubes showed no significant results with the limed samples.

Figure 5. Hedonic tone for the different samples – simplified odor panel.



Balinger et al. (2001) theorized the why anthraquinones are more effective at higher pH. The active species of anthraquinone appears to be in insoluble form. The activity of the ionic form of the anthraquinone appears to be due to the conversion from form to non-ionic. At the higher pH, the insoluble (non-ionic) anthraquinone becomes soluble and allows it to diffuse into the biofilm and contact the SRB more easily. As the pH decreases with time, the ionic form precipitates as very fine particles from solution within the biofilm, which increase the efficiency of the treatment.

Full-Scale Results: Quantitative analysis of the odor compounds. The results of the odor analysis conducted at USDA laboratory are presented in Figures 6 through 9. As shown in the figures, odor measurements for the samples began after 2 days of treatment and continued for 20 days. Figure 6 and 7 show the measured amount of total reduced sulfur and the methyl mercaptan for the different samples as a function of time. As expected, increasing the nitrate concentration led to reduction in total reduced sulfur and methyl mercaptan in all samples as well as at the different sampling times. The addition of anthraquinone to the nitrate resulted in further decrease in the measured total reduced sulfur and methyl mercaptan. However, after 8 days of storage, no decrease in either odorant was observed in the samples with time when treated with anthraquinone. It should be noted that this was observed at the higher anthraquinone doses for both compounds.

Dimethyl sulfide and carbon disulfide generated from the residuals during this experiment are shown in Figures 8 and 9, respectively. These figures show that the chemical treatment did not result in significant reduction in these odorants. However, it should be further noted that only small amounts of the odorants were present in the systems at the start.

Figure 6. Total reduced sulfur (ppm) for samples treated with different amounts of nitrate and anthraquinones.

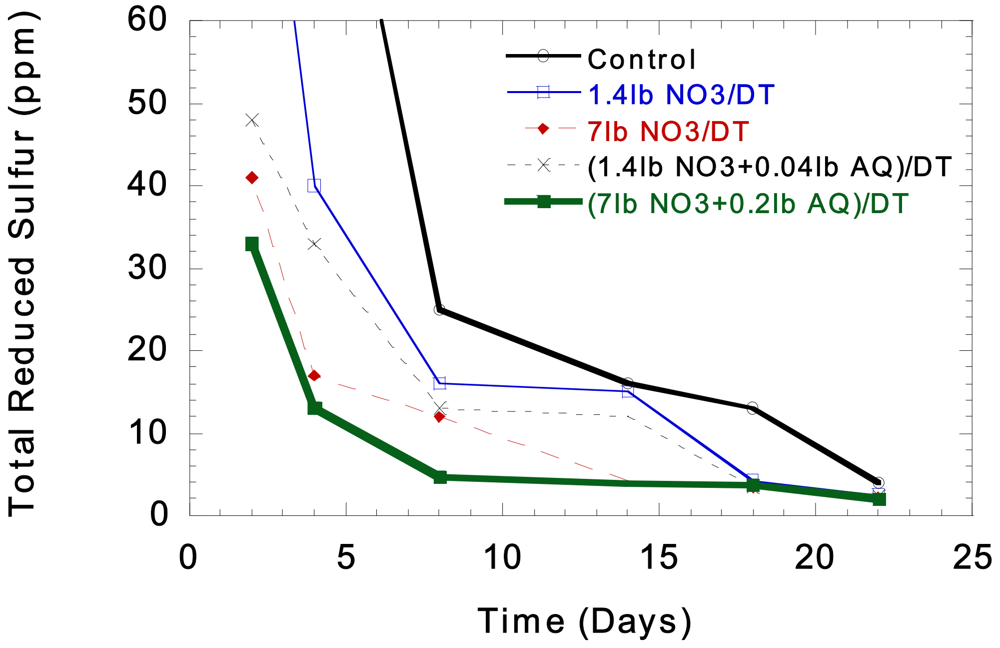


Figure 7. Methyl mercaptan (ppb) for samples treated with different amounts of nitrate and anthraquinones.

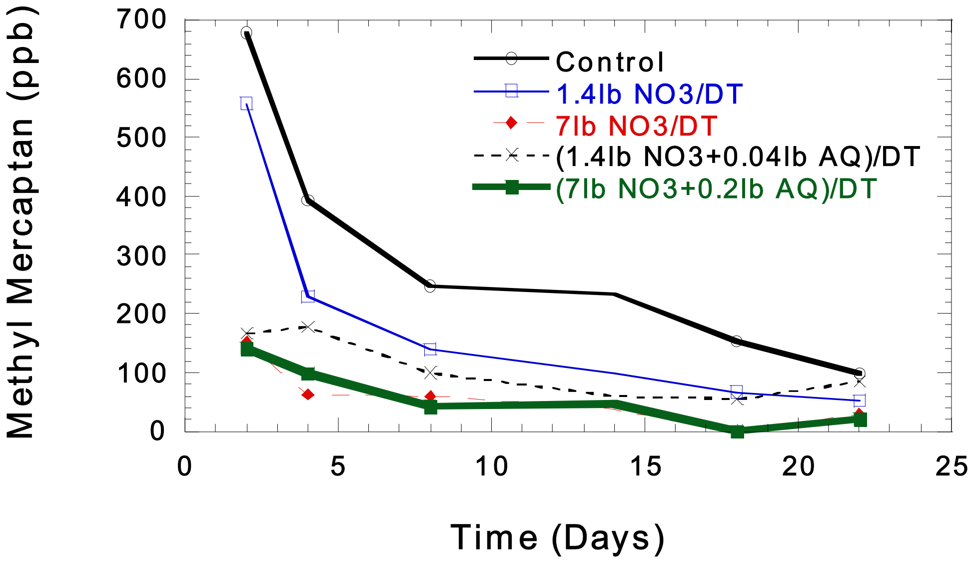


Figure 8. Dimethyl sulfide (ppm) for samples treated with different amounts of nitrate and anthraquinones.

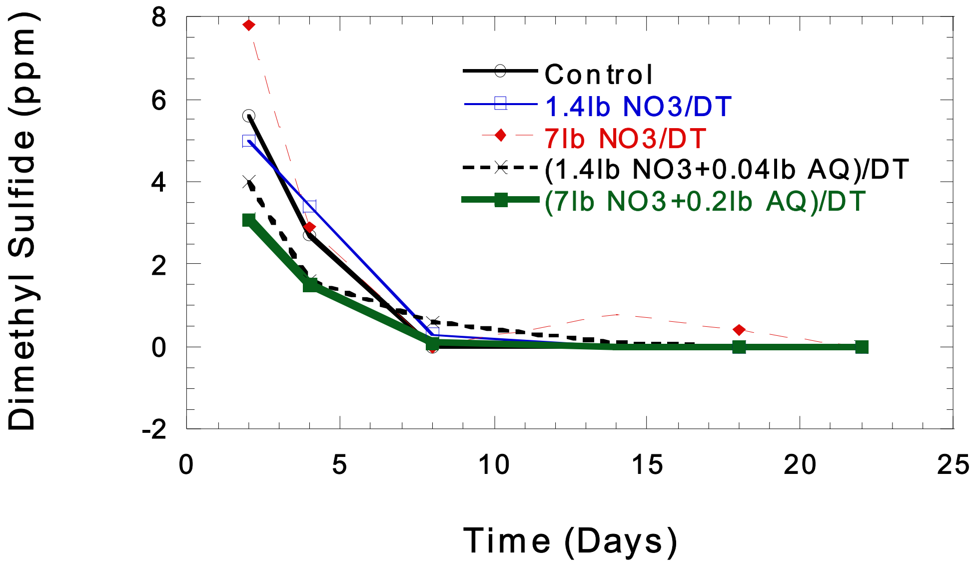


Figure 9. Carbon disulfide (ppb) for samples treated with different amounts of nitrate and anthraquinones.

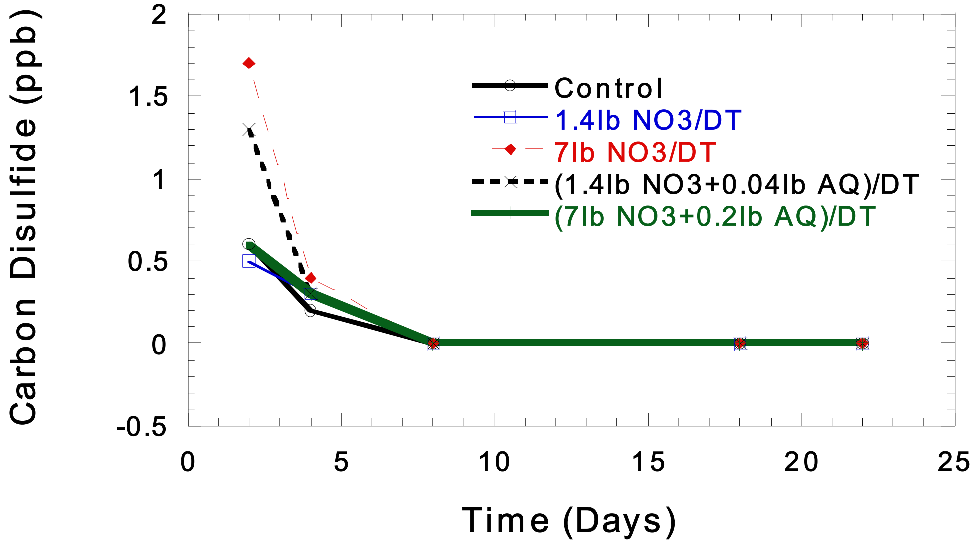
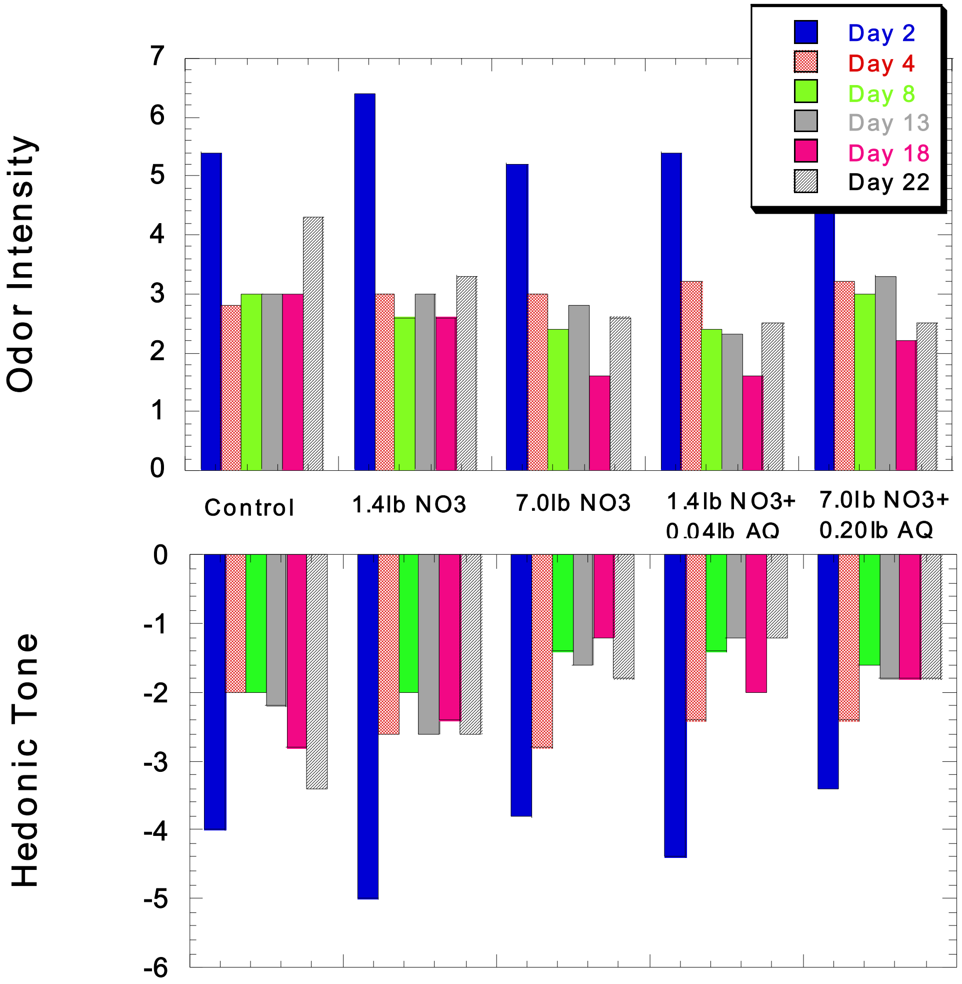


Figure 10 shows the odor intensity and the hedonic tone results; which correspond to the results shown in Figures 6 through 9. Again, these numbers are five person averages. In general, odor intensity of the Bioxide treated biosolids was slightly higher during the study period. The other treatments including the control (no additive) showed similar level of odor intensity. A reduction in odor intensity could not be detected over the period of study. There was a slight reduction in the odor intensity with the treated samples at the higher days of storage when compared to the control samples.

The hedonic tone of the odors from the samples was also evaluated (see figure). At the start of the study period, the hedonic tone of the samples was between –5.0 and –3.5. The hedonic tone improved to –3 ~ -2 over the study period. This slight improvement of the odor intensity and hedonic tone should be ignored due to the high level of varribility in the sample (error bars not shown).

Figure 10. Odor intensity and hedonic tone from the simplified plant panel for full-scale testing at Blue Plains. Doses are per dry tone of residuals.



CONCLUSIONS

- The results from this paper provides knowledge on new technologies for reducing and mitigating odours from dewatered biosolids and residuals products prior to storage and/or disposal.
- Nitrate salt addition is capable of significantly reducing reduced sulfur odor compounds. The use of the anthraquinones particles with the nitrate salt resulted in further odor reduction. This is the first study that investigated these chemicals for odor reduction from municipal, lime stabilized and dewatered residuals.
- The effect was more pronounced on the limed residuals; and is believed to be due to the conversion of the anthraquinones to the soluble form, which allows its diffusion within the biofilm of the SRB.
- The determination of the odor compounds did not correlate with the odor detection from the second simplified panel.

- Future research that includes controlled addition on different biosolids and residuals, coupled with long term full scale documentation is needed.

REFERENCES

Ballinger, K; Burger; E.; Knauer; R. (2001) Method for reducing hydrogen sulfide level in water containing sulfate-reducing bacteria and hydrogen sulfide-metabolizing bacteria. US Patent #6,309,597.

Higgins, M.J., S.N. Murthy, J.T. Novak, D.P. Yarosz and D. Glindemann. (2002). Effect of Chemical addition on Production of Volatile Sulfur Compounds and Odor from Anaerobically Digested Biosolids. *Proceedings of Water Env. Fed. 75th Annual Conf.,* Chicago.

Hunniford, D. and Davis H. (2001). Process for removal of dissolved hydrogen sulfide and reduction of sewage BOD in sewer or other waste systems. US Patent# RE37,181.

Kim, H.; S. Murthy; C. Peot.; M. Ramirez; M. Strawn; L. McConnell. (2001a). Examination of Mechanisms for Odor Compound Generation During Lime Stabilization. . *Proceedings of Water Env. Fed. 754th Annual Conf.,* Atlanta.

Kim, H.; Nochetto, C.; McConnell, L. (2001b) Gas Phase Analysis of Trimethylamine, Propionic and Butyric Acid, and Sulfur Compounds using Solid Phase Microextraction." Analytical Chemistry (accepted).

United Stated Environmental Protection Agency. (2002). Summary of States Biosolids Programs. EPA 832-D00-002. December 2000.

Wimer et al., (1995). Anthraquinones as inhibitors of sulfide production from sulfate reducing bacteria. USPatent #5,385,842