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Evaluation of an electronic nose for odorant and process monitoring of alkaline-stabilized biosolids production

Adrian Romero-Flores [a], Laura L. McConnell [a], Cathleen J. Hapeman [b], Mark Ramirez [c], Alba Torrents [a, *]

[a] *University of Maryland, College Park, Civil and Environmental Engineering Department, College Park, MD, USA*
[b] *USDA Agricultural Research Service, Hydrology and Remote Sensing Laboratory, Beltsville, MD, USA*
[c] *District of Columbia Water and Sewer Authority, Washington, D.C., USA*

HIGHLIGHTS

- Odorants in emissions from biosolids were analyzed by GCMS and the enose.
- The enose differentiated under dose from over dose alkaline stabilized biosolids.
- Small increase in calcium oxide dose was not differentiated by the electronic nose.
- Odorants monitoring by GCMS better differentiated process conditions.

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ABSTRACT

Electronic noses have been widely used in the food industry to monitor process performance and quality control, but use in wastewater and biosolids treatment has not been fully explored. Therefore, we examined the feasibility of an electronic nose to discriminate between treatment conditions of alkaline stabilized biosolids and compared its performance with quantitative analysis of key odorants. Seven lime treatments (0–30% w/w) were prepared and the resultant off-gas was monitored by GC-MS and by an electronic nose equipped with ten metal oxide sensors. A pattern recognition model was created using linear discriminant analysis (LDA) and principal component analysis (PCA) of the electronic nose data. In general, LDA performed better than PCA. LDA showed clear discrimination when single tests were evaluated, but when the full data set was included, discrimination between treatments was reduced. Frequency of accurate recognition was tested by three algorithms with Euclidan and Mahalanobis performing at 81% accuracy and discriminant function analysis at 70%. Concentrations of target compounds by GC-MS were in agreement with those reported in literature and helped to elucidate the behavior of the pattern recognition via comparison of individual sensor responses to different biosolids treatment conditions. Results indicated that the electronic nose can discriminate between lime percentages, thus providing the opportunity to create classes of under-dosed and over-dosed relative to regulatory requirements. Full scale application will require careful evaluation to maintain accuracy under variable process and environmental conditions.

1. Introduction

Improved monitoring of gases, especially volatile organic compounds (VOCs) is needed in a wide range of fields from the food industry, to disease detection in the medical arena, to agricultural and environmental engineering applications (Lebrero et al., 2011; Liu et al., 2012; Loutfi et al., 2015; and Ram et al., 2015). The electronic nose technology has evolved over the past decades as a promising approach for applications which require a continuous monitoring of specific VOCs or patterns of odorants. These sensors can provide rapid and automated detection of volatile compounds with low operational costs when compared to other analytical techniques such as GC-MS or olfactometry measurements. The

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* Corresponding author.
E-mail address: alba@umd.edu (A. Torrents).

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sensor data can then be processed and used to discriminate between air samples containing complex mixtures of compounds to determine progress of process or treatment (Feng et al., 2011).

Electronic noses have been used in the food industry to monitor quality of decaying fruits (Brezmes et al., 2000) and meats (Ghasemi-Varnamkhasti et al., 2009) as well as processed food such as rice extrudes (Feng et al., 2011). Application of electronic nose technologies in the environmental engineering field has been reported for the quantification of odors from composting facilities (Sironi et al., 2007a, 2007b; and Delgado-Rodríguez et al., 2012), within wastewater treatment plants (Stuetz and Fenner, 1999 Bourgeois and Stuetz, 2002; and Sohn et al., 2009) and at receptor locations downwind from treatment facilities (Sironi et al., 2008). Challenges still exist, however, as electronic nose sensors can exhibit drift in response due to changing environmental conditions over time (Romain and Nicolas, 2010). Sampling techniques (*i.e.*, static and dynamic) and sample characteristics (*i.e.*, temperature and humidity) have limited their performance in full scale applications (Knobloch et al., 2009). Moreover, the concept of using sensor arrays for odor measurements has recently been evaluated by Boeker (2014) concluding in part that the response of an electronic nose should not be correlated to that of human perception of odors.

Reuse of biosolids recovered from wastewater treatment facilities has proven to be a sustainable practice where nutrients can be safely recycled into the environment while providing municipalities with an economical and socially-responsible disposal method (Obreza and O'Connor, 2003; Singh and Agrawal, 2008). However, biosolids that have not been sufficiently stabilized prior to field application can create nuisance odors for nearby residents, leading to complaints and resistance to biosolids application programs. Thus, an engineering application where an electronic nose technology could be conceptually useful is in biosolids production for both process monitoring and odor management to support of field application programs.

The United States Environmental Protection Agency (US EPA) regulations require stabilization of biosolids for pathogen reduction and vector control prior to application (US EPA, 1993). Alkaline stabilization, which increases the pH of biosolids to 12, is utilized by approximately 20% of biosolids operations in the U.S (NEBRA, 2007). and changes the odorant profile of biosolids (US EPA, 1993). Hydrogen sulfide, volatile organic sulfur compounds (VOSCs) and trimethylamine (TMA) were found to be among the main odorants emitted from alkaline stabilization (Chang et al., 2005; Kim et al., 2003; Laor et al., 2011; Novak et al., 2002; Rosenfeld, 1999; Rosenfeld et al., 2001). However, limited information exists to correlate alkaline treatment with reduction of specific odorants in biosolids. Thus, more precise control over alkali addition would be useful in reducing nuisance odors in the plant and in the field.

Objectives of this work were to 1) determine the feasibility of utilizing an electronic nose to discriminate between alkaline-stabilized biosolids treated at different doses; 2) examine the odorant profiles of alkaline-stabilized biosolids by GC-MS in an effort to assess the minimum dose required to achieve the key odorant reduction in the plant; and 3) compare the response of the electronic nose with measurements of odorants associated with biosolids to assess its predictive capability and limitations. Results are expected to provide important information on the use of commercially-available electronic nose technologies to increase the effectiveness of biosolids treatment programs and to reduce odor complaints in the field. This approach may also be useful in other industries such as composting operations.

2. Experimental methods

2.1. Biosolids sample collection

Untreated biosolids were collected from the Blue Plains Advanced Waste Water Treatment Plant (Washington, DC, USA). This treatment plant has a capacity of 970 L min^{-1} of domestic wastewater and produces approximately 1089 wet metric tons of alkaline-stabilized biosolids per day. The untreated biosolids utilized in the study consisted of a dewatered 1:1 blend of primary and secondary solids. Samples of approximately 10 kg were collected using a metal shovel from a sampling port in a screw conveyor system and were stored in 22-L plastic buckets. Samples were immediately transported to the laboratory for alkaline stabilization within 1 h after sampling. Total solids (TS) in the untreated sample were determined using the EPA method 1684 (US EPA, 2005).

2.2. Alkaline stabilization

Once in the laboratory, aliquots (~500 g) of untreated biosolids were transferred to 4.7 L stainless steel bowls for mixing with calcium oxide (CaO, dry quick lime) and treated at 0 (untreated control), 5, 10, 15, 20, 25, and 30% CaO by mass. The quick lime utilized in this study is the same industrial grade material utilized in the wastewater plant. Mixing was achieved using a stand mixer (model RKSM500wh, Kitchen Aid, Benton Harbor, MI, USA) at 60 rpm (low speed) for 3 min with an aluminum flat beater. Right after mixing, a stainless steel dome was placed over the mixing bowl for headspace analysis with the electronic nose (Section 2.3.1) and a H_2S sensor (Section 2.3.2). Headspace samples were also collected simultaneously in the last six tests for GC-MS analysis as described in Section 2.3.3. Temperature in the control and treated biosolids was measured in duplicate as minimum using a digital thermometer (4052 Traceable Thermometer, Control Company, Texas, USA) after headspace sampling was completed. pH was measured in duplicate as minimum using standard methods (US EPA Method 9045D, 2004) once the temperature in the cake decreased to 25 C pH was again measured after 72 h to confirm that it met regulations (US EPA, 1993). A total of 10 alkaline stabilization tests were performed over 18 months between October 2013 and April 2015.

2.3. Analytical methods

2.3.1. Electronic nose

The Portable Electronic Nose PEN3 (Airsense Analytics, Schwerin, Germany) was used in this study. It is equipped with ten different heated metal oxide sensors (150–500 °C). While each sensor is responsive to more than one chemical, they are sensitive to specific group of compounds. Sensor affinity and sensitivity to particular test compounds were reported by Baietto et al. (2010) and are listed in Table SI1.

The PEN3 utilized an internal sampling pump at a flow rate of 400 mL min^{-1} and an activated charcoal filter to produce clean air as reference gas to flush and zero the sensors. The method used for all headspace samples was: 60 s of flushing sensor surfaces to a base line; 10 s of zeroing; and 60 s of sampling. Sensor response data were recorded every second and only the final 1-s reading, once the signal proved to be stabilized, was used for statistical analysis and pattern creation. Examples of the PEN3 readings are provided in Fig. SI1. The PEN3 was controlled and sensor data were processed using WinMuster software (Version 1.6.2.15, Airsense Analytics, Schwerin, Germany). For each alkaline stabilization experiment, three readings were collected to evaluate precision and to allow for improved statistical analysis.