Occurrence of 2,4,6-Trichloroanisole in anaerobically stabilised dewatered biosolids emission.

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Abstract.

Odours from biosolids emission are a complicated matrix. Still a little is known about chemical composition of odours from biosolids. Apart from well-known odorants such as sulphur compounds and ammonia participation of other volatile organic compounds (VOCs) in overall odour may be non neglectable. Especially if this chemicals have low odour threshold, exists in low concentrations and their analytical identification is not trival. In this work occurrence of 2,4,6-Trichloroanisole (TCA) into biosolids emission was measure using GC-MS/O system. Thirty six anaerobically stabilised dewatered biosolids samples from wastewater treatment plant were stored over a 35 days under ambient conditions. Emissions from samples were collected onto Tenax TA sorbent tubes using a U.S. EPA flux hood method on days 1, 3, 7, 10, 14, 21 and 35. Odour intensities classified on a scale of 1 to 4 and character were specified by three ODP operators. TCA was identified in all biosolids cake emission. Intensities levels of TCA do not shown any increasing or decreasing trend as the biosolids were aged. However the intensities of TCA as samples were stored varied.

Keywords: biosolids, 2,4,6-trichloroanisole TCA, odour, GC-MS/ODP

1. Introduction

Odours are a common occurrence at wastewater treatment plants, biosolids processing facilities and biosolids recycling locations (Visan and Parker 2004). In order to develop strategies for minimizing malodors, it's necessary to identify odorous compounds and their fate during the biosolids processing, storage and land application. Odours from biosolids emission are a complicated matrix. Anaerobic digestion of sludge produces gases such as, hydrogen sulfide, methane, as well as odorous nitrogen, sulfur, and fatty acid compounds from the degradation of organic matter resulting in sulfidic and putrid/rancid odours (Agus *et al*. 2012, Suffet *et al*. 2009). Odours from sludge digestion have been described as putrescent, greasy, and cabbage-like odors (Agus *et al*. 2012), while the resultant biosolids odours have moldy, musty, fecal, fishy, and rancid odour characters or qualities (Suffet *et al*. 2009). Apart from well-known odorants associated organic matter degradation, such as sulfur compounds and ammonia, participation of other volatile organic compounds (VOCs) in the overall odour matrix cannot be ignored. Even low impact odorants which are generally considered unimportant in odour perception could have the great significance in global odour perception (Ryan *et al*. 2008). However, there is a knowledge gap regarding the chemical composition of biosolids odors contributing to musty type characters. For the management of biosolids odours, the identities of the main odorants need to be known and methods need to quickly and efficiently identify compounds of concern (Agus *et al*. 2012). The odour problem caused by chloroanisoles are well documented in drinking water, food materials such as wines, eggs and poultry, chickens, pulp chips, dried fruits, and coffee (Coque *et al*. 2003, Zhang *et al*. 2016). Chromatographic and electrochemical methods are commonly used for the determination of TCA, however its detection at low concentrations remains a technical challenge (Varelas *et al*. 2011). Mass spectrometry detectors (MSD) are frequently used detector in combination with GC due to their sensitivity and selectivity. However, for analysis of tastes and odor compounds at pg mL^{-1} levels, the sensitivity of GC–MSD may still be insufficient (Ma *et al*. 2012). TCA may be present at low concentrations (even ppt) and will need to be isolated from high concentrations of matrix components. Moreover, TCA is volatile, care must be taken to avoid losses during sampling and analysis, in particular during any solvent removal step, particularly if concentrating to small volumes (Jakobsen *et al*. 2003, Ridgway *et al*. 2010). Combining sensorial methods, such as odour detection ports (ODP) with GC-MSD systems can overcome some drawbacks as assessors directly sniff the GC effluent identifying where sensorial relevant compounds occur in the chromatogram. Agus *et al*. (Agus *et al*. 2011) used a GC-MSD/ODP system and flavor profile analysis (FPA) to effectively characterize the occurrence and fate of odorants from six full-scale advanced water treatment plants operated with surface waters that receive municipal wastewater effluent. This paper will detail the identification of TCA, responsible for musty type odour characters, in biosolids odour emissions using a combination of analytical and sensorial approaches. In addition, this research investigate whether

chloroanisoles such as TCA contribute to musty/moldy type of odours from biosolids.

2. Methodology

The 36 dewatered biosolids cakes (~10L) were grab-sampled from the WWTP and processed for emission analysis within 6 hours of sampling. Emission samples were captured on day 1, 3, 7, 10, 14, 21 and 35 as the biosolids were stored. In total 218 emissions samples from dewatered WWTP biosolids cakes were captured using US EPA dynamic flux hoods. Sample analysis was performed using a gas chromatograph equipped with a mass spectrometer detector (MSD) and an olfactory detection port (ODP). Three ODP assessors were two males – RB & XW and one female – RF complying with panelist requirements according to European Dynamic Olfactometry standard (EN 13725:2003), were used for the olfactory analysis. A simplified direct intensity method was employed to record odour descriptors and intensities (Van Ruth 2001, Delahunty *et al*. 2006). Each ODP assessor analysed one of each triplicate sorbent tubes. Intensities of odours detected from the ODP were recorded using a controller device or by hand with a scale from 1 to 4 (with 4 being the strongest and 1 the weakest odour intensity) according to Gerstel ODP Recorder system (Gerstel GmbH & Co., Germany). Moreover, the assessor RB extended the scale for additional halves points: 0.5, 1.5, 2.5 and 3.5. During the sample analysis, odour descriptors were recorded with voice-recognition software. ODP assessors used their own odour descriptors based on their own experience and referenced descriptors on published compost and wastewater odour wheels (Suffet & Rosenfeld 2007). Additionally assessors RB and RF had assessed suitable odour descriptors of raw biosolids cakes samples prior to emission sampling. An ODP result recorded as odorous VOCs was assumed to be valid if at least one assessor detected an odour signal at a similar retention time and similar odour character across all 656 samples. TCA was distinguished from the rest of the odorants based on the similar retention time and similar odour characters and additionally, based on commercial mass spectral library NIST 11 (Agilent Chemstation software, Santa Clara, CA) with matches between the fragment sizes greater than 75%, and finally compare with the authentic standard.TCA was tentatively identified by comparing its odour character with descriptors available in the literature and additionally, based on commercial mass spectral library NIST 11 (Agilent Chemstation software, Santa Clara, CA) with matches between the fragment sizes greater than 75%. Finally fragments and retention time were compared with the authentic standard with 99% purity purchased from Sigma Aldrich (Sigma-Aldrich Co.).

3. Results and Discussion

The raw biosolids cakes odour emission was characterized by assessors RB and RF as sewery, rotten egg and vegetable type characters during the first two measurement days, whilst moldy/musty/wet cloth odour character was dominant from day 7.Using the GC-MSD/ODP system the TCA odour was detected 182, 184 and 104 times respectively by the assessors RB, RF and XW. The typical descriptor used by the assessors RB and RF was “musty”, for respectively 95% and 73% of all their responses. Other descriptors periodically used at the identical retention time for assessor RB were “gasoline”, “machine oily”, “chemical oily”; for assessor RF were “gasoline/petrol”, “chemical musty”, “astringent”, , “chemical glue”, “plastic”, “napthalene”. While assessor XW used “machine” as the most frequent descriptor, 80% of all his responses, as well as “hospital”, “alcoholic/soybean sauce” periodically. The presence of TCA at the retention time corresponding to the assessor responses was confirmed using an analytical standard of TCA. Although the odour character of TCA was detected by assessors via ODP in the above samples, the presence of TCA in the biosolids emissions was only identified 16 times by MSD as a result of mass spectral fragments comparison with NIST database. The intensities of TCA over storage time for all 36 biosolids cakes are reported in Figure 1. TCA was detected in every biosolids cake. The odour intensity of TCA detected by the operators was typically lower than 2.5. TCA was detected continuously as most cakes were aged, however in some cakes (no. 1, 2, 4, 7 and 19) it was not detected in the first days of storage, whilst in others (no. 10, 12, 15, from 23 to 30 and from 33 to 36) it wasn’t present until later. In cakes no. 23 to no. 30 and no. 33 to no. 36 it was no longer detectable after day 14 and 21, respectively. This absence may be related to the source reduction of the likely TCA precursor, TCP, or decreased emission rates, resulting in concentrations below the odour detection threshold of the assessors. Figure 2 presents a view on overall odour intensity trend of TCA occurrence in dewatered biosolids cakes. It shows the consistent intensity of TCA emissions throughout cake storage. Taking into consideration 36 different biosolids cakes at the different age of storage it could be concluded that due to its intensity and frequency of detection by ODP operators TCA should be consider as odorant of concern in biosolids emission.

4. Conclusions

Very little is known about TCA emissions from biosolids. Apart from well-known odorants such as sulphur compounds and ammonia, the participation of other VOCs in overall odour mixture should not be neglected. However, the detection of compounds with low odour threshold that are present at low concentrations is difficult with basic gas-chromatography coupled with common chemical detectors like MS or FID. Instead approaches using combined analytical and sensorial methods are useful in identifying the presence of odorants in emission mixtures. TCA was identified in all analysed samples of dewatered biosolids after anaerobically stabilization process. Intensities levels of TCA do not shown any increasing or decreasing trend as the biosolids were aged, showing TCA is consistently present in stored biosolid samples. TCA seems to be an odorant of importance in biosolids emission due to its low odour threshold and frequent detection by ODP assessors. TCA has previously not been quantitatively detected in biosolids emission and very limited data on qualitative analysis of musty type odours. TD-GC-MSD/ODP systems are a powerful tool for the identification and tracking of TCA in biosolids emissions.

Acknowledgement

This work was supported by a Marie Curie International Outgoing Fellowship under the grant PIOF-GA - 2013-

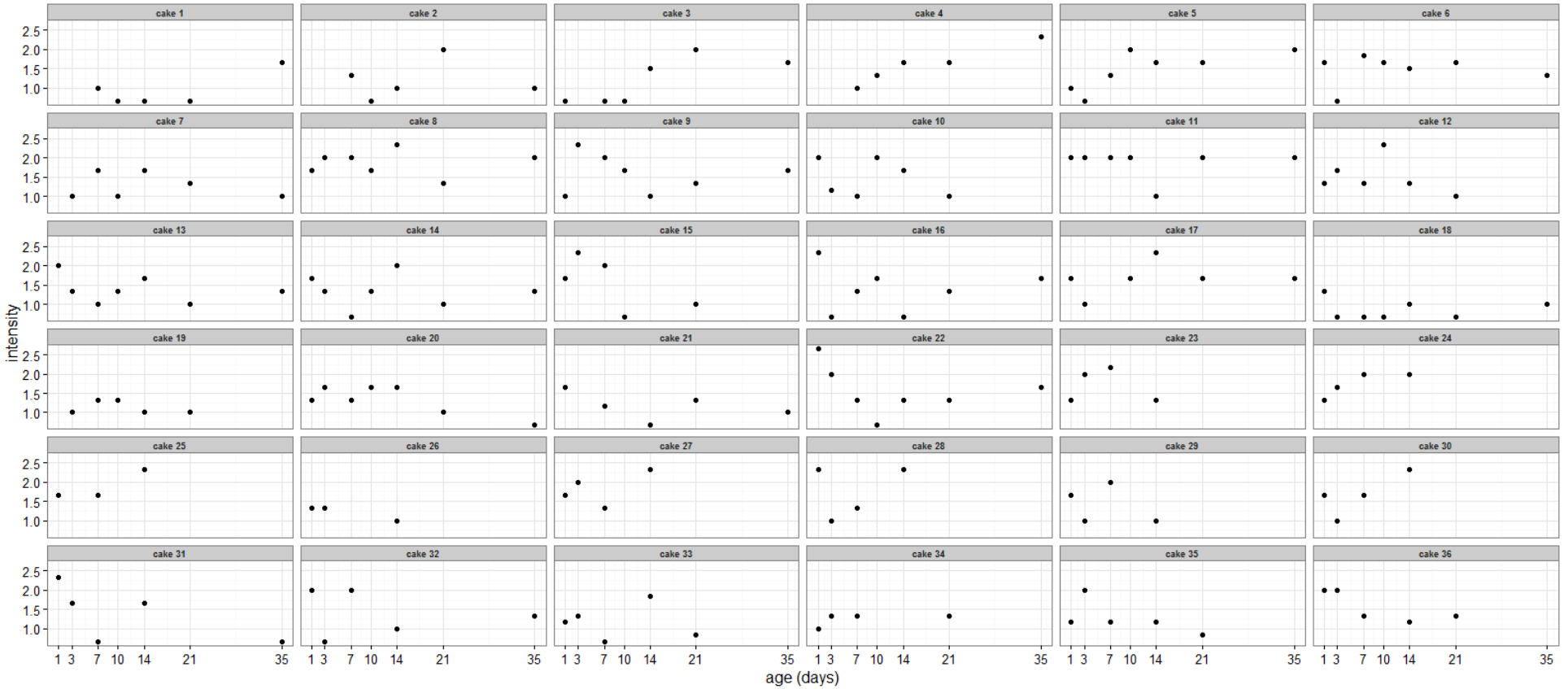

Figure 1. 2,4,6-Trichloranisole odour intensity from biosolids cake emissions over storage time

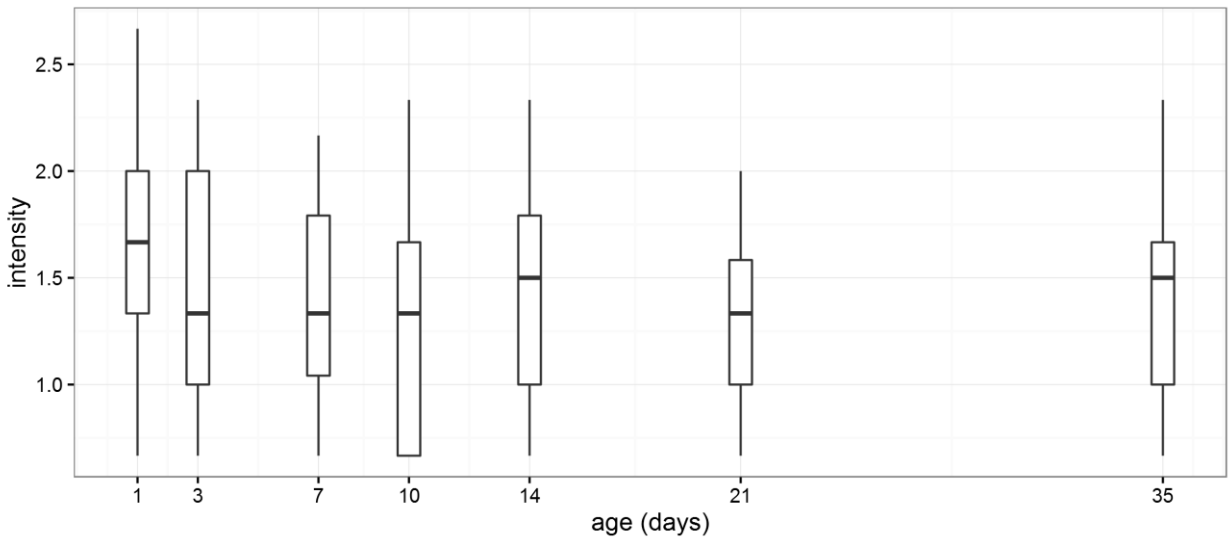

Figure 2. Odour intensity of Trichloroanisole into aged biosolids emission

622523 OdourCOB within the seventh European Community Framework Programme, an Australian Government APA scholarship and by the CRC for Low Carbon living project RP2008 'Beneficial Re-use of Biosolids'.

References

Agus, E., Lim, M.H., Zhang, L. and Sedlak, D.L. (2011) Odorous Compounds in Municipal Wastewater Effluent and Potable Water Reuse Systems. Environmental Science & Technology 45(21), 9347-9355.

Agus, E., Zhang, L. and Sedlak, D.L. (2012) A framework for identifying characteristic odor compounds in municipal wastewater effluent. Water Research 46(18), 5970-5980.

Coque, J.-J.R., Álvarez-Rodríguez, M.L. and Larriba, G. (2003) Characterization of an Inducible Chlorophenol O-Methyltransferase from Trichoderma longibrachiatum Involved in the Formation of Chloroanisoles and Determination of Its Role in Cork Taint of Wines. Applied and Environmental Microbiology 69(9), 5089-5095.

Curren, J., Hallis, S.A., Snyder, C.L. and Suffet, I.H. (2016) Identification and quantification of nuisance odors at a trash transfer station. Waste Management 58, 52-61.

Decottignies, V., Huyard, A., Kelly, R.F. and Barillon, B. (2013) Development of a diagnostic tool: The wastewater collection network odour wheel. Water Science and Technology 68(4), 839-847.

Jakobsen, H.B., Nørrelykke, M.R., Christensen, L.P. and Edelenbos, M. (2003) Comparison of methods used for pre-concentrating small volumes of organic volatile solutions. Journal of Chromatography A 1003(1–2), 1-10.

Ma, K., Zhang, J.N., Zhao, M. and He, Y.J. (2012) Accurate analysis of trace earthy-musty odorants in water by headspace solid phase microextraction gas chromatography-mass spectrometry. Journal of Separation Science 35(12), 1494-1501.

Ridgway, K., Lalljie, S.P.D. and Smith, R.M. (2010) Analysis of food taints and off-flavours: a review. Food Additives & Contaminants: Part A 27(2), 146-168.

Rosenfeld, P.E., Clark, J.J.J., Hensley, A.R. and Suffet, I.H. (2007) The use of an odour wheel classification for the evaluation of human health risk criteria for compost facilities, pp. 345-357.

Ryan, D., Prenzler, P.D., Saliba, A.J. and Scollary, G.R. (2008) The significance of low impact odorants in global odour perception. Trends in Food Science & Technology 19(7), 383-389.

Suffet, I.H., Burlingame, G.A., Rosenfeld, P.E. and Bruchet, A. (2004) The value of an odor-quality-wheel classification scheme for wastewater treatment plants, pp. 25-32.

Suffet, I.H., Decottignies, V., Senante, E. and Bruchet, A. (2009) Sensory Assessment and Characterization of Odor Nuisance Emissions during the Composting of Wastewater Biosolids. Water Environment Research 81(7), 670-679.

Suffet, I.H. and Rosenfeld, P. (2007) The anatomy of odour wheels for odours of drinking water, wastewater, compost and the urban environment. Water Science and Technology 55(5), 335-344.

Varelas, V., Sanvicens, N., Marco, M.P. and Kintzios, S. (2011) Development of a cellular biosensor for the detection of 2,4,6-trichloroanisole (TCA). Talanta 84(3), 936-940.

Visan, M. and Parker, W.J. (2004) An evaluation of solid phase microextraction for analysis of odorant emissions from stored biosolids cake. Water Research 38(17), 3800-3808.

Zhang, K., Luo, Z., Zhang, T., Mao, M. and Fu, J. (2016) Study on formation of 2,4,6-trichloroanisole by microbial O-methylation of 2,4,6-trichlorophenol in lake water. Environmental Pollution 219, 228-234.