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Research Paper

Sorption behaviour of targeted volatile organic compounds on airborne particulate matter using selected ion flow tube mass spectrometry

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Intensive agriculture emits air pollutants such as inorganic gases, volatile organic compounds (VOC) and airborne particulate matter. The public can suffer from severe odour nuisance caused by these emissions, particularly in areas with high population densities. Odorous compounds are not only present in the free gas phase but undergo a partitioning between the gas phase and particulate matter making particles possible odour carriers. In order to investigate this partitioning behaviour, an advanced analytical method was developed using selected ion flow tube mass spectrometry (SIFT-MS). This method was used to determine the particle-to-air partitioning coefficients of 4 important organic odorants (acetic acid, butanoic acid, phenol and dimethyl disulphide). An air stream with constant VOC concentration was generated in a home-made system and was injected as a step function onto a chromatographic column packed with particles (PM_{10}) collected from a pig stable using high volume sampling. From the registered breakthrough curves, dimensionless particle-to-air partitioning coefficients were calculated. They ranged from $13 \times 10^3 \pm 3.1 \times 10^3$ for dimethyl disulphide to $16 \times 10^5 \pm 1.7 \times 10^5$ for phenol. Partitioning coefficients can be estimated using octanol–air partitioning coefficients available from the literature ($r^2 = 0.94$). The results show that particles were enriched in VOC but the fraction of sorbed volatiles was low (<0.11%) at a PM_{10} concentration of 1 mg m^{-3}.

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Nomenclature

BP	Boiling point (°C)
CDS	Capillary diffusion system
C_{GF}	Concentration in the gas phase (ng VOC m^{-3} air)
C_{in}	Concentration of the VOC in the inlet gas stream (μg m^{-3})
C_{ou}	Concentration of the VOC in the outlet gas stream (μg m^{-3})
C_{PM}	Concentration particulate matter (g [PM] m^{-3})
C_{PP}	Concentration in the particulate phase (ng VOC m^{-3} air)
DMDS	Dimethyl disulphide
f	Fraction of the compound in the particulate phase (–)
F_i	Gas flow (m^3 min^{-1}), where i can be 1 to 5
H	Henry coefficient (–)
K_{oa}	Octanol-to-air partitioning coefficient (–)
K_{ow}	Octanol–water partitioning coefficient (–)
K_p	Particle-to-air partitioning coefficient (m^3 μg^{-1})
$K_{PM/air}$	Dimensionless particle-to-gas partitioning coefficient (–)
MFC_i	Mass flow controller, where i can be 1–5
m_{PM}	Mass of particulate matter in the column (g)
MW	Molecular weight (g mol^{-1})
P_1	Pressure measuring point (hPa)
PDMS	Polydimethylsiloxane
PM	Particulate matter
PM_{10}	Particulate matter with an aerodynamic diameter < 10 μm
$PM_{2.5}$	Particulate matter with an aerodynamic diameter < 2.5 μm
PTFE	Polytetrafluoroethylene
r	Pearson correlation coefficient
RSD	Relative standard deviation (%)
$SCOT$	Single compound threshold value (μg m^{-3})
SEM	Scanning electron microscope
$SIFT_i$	Measuring point for SIFT-MS, where i can be 1–2
SIFT-MS	Selected ion flow tube mass spectrometry
SPME	Solid phase micro extraction
TSP	Total suspended particles concentration (μg m^{-3})
V_i	Valve, where i can be 1–3
V_{air}	Volume air (1 m^3)
VOC	Volatile organic compound
vp	Vapour pressure (Pa)
ws	Water solubility (mg m^{-3})
WWB	Warm water bath
ρ_{PM}	Density of the particulate matter (g m^{-3})

1. Introduction

Data from the Food and Agriculture Organisation of the United Nations (FAO) show that the member states of the European Union reared 147 million pigs in 2013 (FAO, 2013). Geographically, the major pig production basin in the European Union extends from Denmark to the Flemish region in Belgium and accounts for 30% of the sows in the EU (Marquer, 2010). In this production area, the density of pigs (pigs km^{-2}) is the highest of Europe being 294, 282 and 216 pigs km^{-2} for The Netherlands, Denmark and Belgium respectively (EC, 2013).

Intensive agriculture results in the emission of air pollutants which can be categorised into inorganic gases, volatile organic compounds (VOC) and airborne particulate matter (Faulkner & Shaw, 2008; Hendriks et al., 2013; Rumsey, Aneja, & Lonneman, 2012; Van Ransbeeck, Van Langenhove, & Demeyer, 2013a; Wang, Cardenas, Misselbrook, & Gilhespy, 2011). In Flanders (Northern region of Belgium), the agricultural emissions of carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) amounted to respectively 5%, 77% and 56% of the total gas emissions in 2011 (MIRA, 2012). These data show that agricultural activities are important sources of greenhouse gases and thus contribute to global warming. Ammonia (NH_3), can cause soil and water acidification. The agricultural sector amounted to 93% of the total ammonia emissions in 2011 (MIRA, 2012). The agricultural emission for the group of the volatile organic compounds (VOC) was estimated at 2100 t or 2.8% of the total emission in Flanders in the year 2011. Although the contribution of the agricultural sector towards total VOC emission is rather low, it can nevertheless be important. Some VOC have a low single compound odour threshold values (SCOT), this is the lowest concentration of a single compound in air that can be detected by the human olfactory sense, and can therefore be responsible for severe odour nuisance (Parker et al., 2012). This is particularly important for countries such as The Netherlands with 404 inhabitants km^{-2} and Belgium with 366 inhabitants km^{-2} which rank among the nations with the highest population densities in the 28 EU member states (EC, 2013). Several studies have identified and quantified volatile organic compounds in pig stables (Blanes-Vidal et al., 2009a, 2009b; Feilberg, Liu, Adamsen, Hansen, & Jonassen, 2010) and the review by Ni, Robarge, Xiao, and Heber (2012) provides a good overview of recent research on VOC at pig rearing facilities (Ni et al., 2012). Many of the VOC are formed by microbial degradation of high molecular weight constituents (i.e. fats, proteins, fibres) (Spoelstra, 1980).

Particulate matter emissions are also significant for the agricultural sector and were estimated at 6700 t [PM_{10}] and 2200 t [$PM_{2.5}$] in 2011, this is respectively 20% and 39% of the total emissions in Flanders (MIRA, 2012). In addition to the contribution of incomplete fossil fuel combustion to particulate emission resulting from the use of agricultural vehicles and heating of infrastructure, there is also a contribution from the animal production inside animal rearing buildings (Ni et al., 2012). Particles produced in the pig rearing buildings originate from the feed, hair, skin flakes, and faecal material of the animals and may also contain moulds, bacteria, mites, pollen grains and insect parts. It has to be noted that research on particulate matter is mainly focused on the determination of mass concentrations (Van Ransbeeck, Van Weyenberg, Van Langenhove, & Demeyer, 2013b; Ulens et al., 2014).