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# Hydrophobic organic compound (HOC) partitioning behaviour to municipal wastewater colloidal organic carbon

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## ABSTRACT

The sorption behaviour of hydrophobic organic compounds (HOCs) 1,2,4,5-tetrachlorobenzene (TeCB), pentachlorobenzene (PeCB) and hexachlorobenzene (HCB) to Aldrich humic acid (AHA) and municipal wastewater treatment plant (MWTP) influent colloidal organic carbon (COC) was investigated using the gas-stripping technique. Gas stripping assumptions of gas/water equilibrium and a constant volatilization rate were validated prior to calculation of partitioning parameters. The  $\log K_{\text{COC}}$  coefficients determined for MWTP influent COC were 3.86, 3.89 and 3.19 for TeCB, PeCB and HCB, respectively. Due to the presence of COC, the mass transfer of TeCB, PeCB and HCB with the primary effluent to the secondary biological stage was predicted to increase 8.7%, 9.6% and 1.2%, respectively, based on the measured COC concentration and  $\log K_{\text{COC}}$  values. The calculated increases in apparent solubility for TeCB, PeCB and HCB in the primary effluent were 14.4%, 22.0% and 6.5%, respectively. This partitioning did not follow the expected trend (TeCB < PeCB < HCB) based on hydrophobicity predicted by octanol/water partitioning. The trend observed differed from the current AHA standard and correlation-based trends derived from natural COCs. More experiments with other HOCs are needed to better understand and predict the magnitude and significance of MWTP influent COCs on the fate and transport of HOCs during the MWTP process.

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## 1. Introduction

Organic carbon in aquatic environments impacts the fate and transport of hydrophobic organic chemicals (HOCs). HOCs are widely distributed in these environments as both freely-dissolved chemical and bound chemical to colloidal and particulate organic matter. The importance of partitioning of HOCs to colloidal organic carbon (COC: defined as organic matter passing a 1.5  $\mu\text{m}$  filter) and particulate organic carbon (OC: defined as organic matter captured on a 1.5  $\mu\text{m}$  filter) in natural environments has been widely studied in surface and ground waters, soils and sediment, and commercially available isolates such as Aldrich humic acids. More specifically for

COC, this partitioning behaviour between COC and water is represented by the partition coefficient  $K_{\text{COC}}$  (unitless) with the analogous expression  $K_{\text{OC}}$  used for the partitioning between water and OC used in the literature.

Literature on partitioning of HOCs to natural environment OC compared with COC indicates large differences in their partitioning coefficients which highlights the need to study COC separately. The HOC partitioning to OC ( $K_{\text{OC}}$ ) has been shown to be strongly dependent upon the chemical hydrophobicity as indicated by the octanol–water partition coefficient ( $K_{\text{OW}}$ ). For example, an evaluation of the  $K_{\text{OC}}$  data by Seth et al. (1999) found the relationship of  $K_{\text{OC}} = 0.35K_{\text{OW}}$  with 95% confidence limits of a factor of 2.5. In contrast, based on an

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extensive dataset on HOC partitioning to natural environment COC a much weaker and more variable predictive relationship of  $K_{COC} = 0.08K_{OW}$  with 95% confidence limits of a factor of 20 was developed by Burkhard (2000).

Municipal wastewater treatment plants (MWTs) are widely recognized as important sources for HOCs into the environment including those of emerging concern such as polybrominated diphenyl ethers (PBDEs) (Song et al., 2006). In contrast to natural environment COC, HOC partitioning to MWTP COC has received much less attention in terms of significance assessment (Holbrook et al., 2004a, 2004b; Neale et al., 2011) and has not been included in fate and transport modelling (Seth et al., 2008). HOCs have been found to interact differently with MWTP COC as compared to both natural environment COC and OC since they originate from different sources with widely varying physico-chemical parameters (Neale et al., 2011; Holbrook et al., 2004a, 2004b). More importantly, recent studies have highlighted the potential importance and significance of HOC binding to MWTP COC for chemicals including pyrene (Holbrook et al., 2004a; Borisover et al., 2006), 17β-estradiol and 17α-ethinylestradiol (Holbrook et al., 2004b), and various atrazine herbicides and PAHs (Ilani et al., 2005). Holbrook et al. (2004a; 2004b) indicate that municipal effluent COC provides a significant transport mechanism for HOCs to aquatic environments with ca. 30% of aqueous pyrene and up to 60% of aqueous 17β-estradiol and 17α-ethinylestradiol potentially associated with effluent COC. Despite  $K_{OW}$  correlations being commonly used to define HOC partitioning for both natural and wastewater OC and natural COC, a universal  $K_{COC} - K_{OW}$  relationship has not yet been investigated for wastewater-derived COCs. Although natural environment COC differs from MWTP COC, the weak  $K_{COC} - K_{OW}$  correlation for natural COC indicates the need for assessment of other surrogate parameters which may be more accurately correlated with partitioning behaviour. However, attempts to find other universal surrogate parameters such as aromatic, protein and polysaccharide contents have not been successful (Holbrook et al., 2004b).

The COC concentration during the MWTP process is highest in the raw influent and remains relatively unchanged during the primary sedimentation process and within primary effluents (Katsoyiannis and Samara, 2007). HOC – COC partitioning can therefore impact HOC removal during primary treatment and increase its mass loading to the secondary biological treatment process where COC-associated HOCs may have reduced bioavailability and volatilization (Holbrook et al., 2004a). To our knowledge the examination of HOC – COC partitioning during the primary treatment process and its significance in HOC fate during the MWTP process has not been studied. To determine  $K_{COC}$ , the estimation of COC-sorbed and freely-dissolved aqueous chemical concentrations is required. A variety of analytical techniques are available to determine freely-dissolved concentrations, some of which attempt to physically separate the freely-dissolved chemical which can create large errors and uncertainties (Burkhard, 2000). Alternatively, the well developed and tested gas stripping technique (Mackay et al., 1979; ten Hulscher et al., 1992; Jantunen and Bidleman, 2006) used currently estimates the freely-dissolved concentration based on head-space analysis eliminating aqueous sample processing.

Currently, the significance of HOC partitioning to COC and its importance for the MTWP primary treatment stage is investigated by examining sorption of three chlorobenzenes (1,2,4,5-tetrachlorobenzene, pentachlorobenzene, and hexachlorobenzene) to raw municipal wastewater COC (<1.5 μm) using the gas stripping technique. Chlorobenzenes (CBs) are persistent HOCs used in industrial and agricultural processes and the use of the three CBs allow for the examination of varying hydrophobicity on partitioning behaviour. Partitioning to the well-defined and extensively studied Aldrich humic acid (AHA) was also examined as reference for comparison to MWTP COC. Objectives of this study were to: (1) examine and quantify  $K_{COC}$  of the three chlorobenzenes to COC present in raw influent municipal wastewater; (2) quantify  $K_{COC}$  of AHA for comparison to historic values and partitioning to colloids; (3) examine the influence of varying hydrophobicity as determined by  $K_{OW}$  on  $K_{COC}$ ; and (4) examine the significance of partitioning to COC on the fate of the three chlorobenzenes during primary treatment by using a modified version of the STP-EX model (Seth et al., 2008).

### 1.1. Theory

HOC binding to OM is considered linear over a wide concentration range (Carter and Suffet, 1982). At equilibrium and assuming first-order kinetics a three phase (vapour, water, COC) closed system can be described by:



Where  $C_{coc}$  is bound concentration ( $ng\ m^{-3}$ ),  $C_{aq}$  is 'freely dissolved' ( $ng\ m^{-3}$ ),  $C_g$  is the vapour phase concentration ( $ng\ m^{-3}$ ), and  $k_{12}$ ,  $k_{21}$ ,  $k_v$ ,  $k_w$  are first-order rate constants ( $d^{-1}$ ) describing mass transfer of chemical between environmental media. In a gas-stripping system containing these three phases an irreversible loss of compound via gas stripping and volatilization occurs negating the  $k_w$  mass transfer rate. Assuming a sparger optimized to create equilibrium between  $C_{aq}$  and  $C_g$  based on bubble/water contact time and further assuming that  $k_{12} \ll k_v$  the expression follows from Eq (1):

$$K_p = \frac{k_{21}}{k_{12}} \quad (2)$$

Where  $K_p$  is the uncorrected COC partitioning coefficient and the total concentration ( $C_T$ ) in the aqueous phase is determined by:

$$C_T = C_{coc} + C_{aq} \quad (3)$$

The change in chemical bound to COC can be determined using the desorption ( $k_{12}$ ) and adsorption ( $k_{21}$ ) rates found in Eq (1) as follows:

$$\frac{dC_{coc}}{dt} = k_{21}C_{aq} - k_{12}C_{coc} \quad (4)$$

Similarly, the change in chemical concentration in the aqueous phase ( $C_{aq}$ ), the total in the aqueous phase ( $C_T$ ) and the gas phase ( $C_g$ ) can be found using Eq (1) as follows:

$$\frac{dC_{aq}}{dt} = k_{12}C_{coc} - (k_{21} + k_v)C_{aq} \quad (5)$$

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