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Modelling of the fate of selected endocrine disruptors in a municipal wastewater treatment plant in South East Queensland, Australia

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Abstract

The aim of this study was to develop a fugacity-based analysis of the fate of selected industrial compounds (alkylphenols and phthalates) with endocrine disrupting properties in a conventional activated sludge wastewater treatment plant (WWTP A) in South East Queensland, Australia. Using mass balance principles, a fugacity model was developed for correlating and predicting the steady-state-phase concentrations, the process stream fluxes, and the fate of four phthalates and four alkylphenols in WWTP A. Input data are the compound's physicochemical properties, measured concentrations and the plant's operating design and parameters. The relative amounts of chemicals that are likely to be volatilized, sorbed to sludge, biotransformed, and discharge in the effluent water was determined. Since it was difficult to predict biotransformation, measured concentrations were used to calibrate the model in terms of biotransformation rate constant. Results obtained by applying the model for the eight compounds showed <40% differences between most of the estimated and measured data from WWTP A. All eight compounds that were modelled in this study had high removal efficacy from WWTP A. Apart from benzyl butyl phthalate and bisphenol A, the majority is removed via biotransformation followed by a lesser proportion removed with the primary sludge. Fugacity analysis provides useful insight into compound fate in a WWTP and with further calibration and validation the model should be useful for correlative and predictive purposes.

Keywords: Phthalate; Alkylphenol; Fugacity modelling; Wastewater treatment plant; Biosolids; Water

1. Introduction

There is increasing evidence that endocrine disrupting compounds (EDCs) can have harmful effects on aquatic organisms. Some of the compounds with high estrogenic activity include natural and synthetic estrogens as well as chemicals from household or industrial processes such as alkylphenols and phthalates. These endocrine disruptors from domestic, agricultural or industrial sources may be released directly or indirectly to the aquatic environment (Birkett and Lester, 2003). Wastewater treatment plants (WWTPs) appear to be one of the major secondary sources of pollution because these compounds may not be totally removed or degraded by chemical, physical and biological treatment processes within the plants.

The removal of endocrine disruptors in wastewater treatment processes is dependent on the inherent

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physicochemical properties of the compounds and on the nature of the treatment processes involved (Birkett and Lester, 2003). There are four major removal pathways for organic compounds during conventional wastewater treatment; namely (i) adsorption onto suspended solids or association with fats and oils, (ii) biodegradation, (iii) chemical (abiotic) degradation by processes such as photolysis and hydrolysis and (iv) volatilization. The hydrophobic nature of many EDCs causes them to sorb onto particulates. This suggests that the general effect of wastewater treatment processes would be to concentrate organic pollutants, including EDCs in the wastewater sludge. Mechanical techniques, such as sedimentation would result in significant removal from the aqueous phase to primary and secondary sludges (Birkett and Lester, 2003).

A compound's physicochemical characteristics can be used to predict physical processes, such as sorption, volatilisation and dissolution. Knowledge of chemical partitioning between the aqueous and solid phases is needed to assess pathways of EDC transport and transformation. A conventional WWTP is typically a three-stage process consisting of preliminary treatment, primary sedimentation and secondary treatment (Hamer, 1997; Birkett and Lester, 2003). More recent technologies include advanced tertiary treatments i.e. ozonation, ultrafiltration, sand/carbon filtration, ultraviolet (UV) disinfection and reverse osmosis. Wastewater sludge is a complex mixture of fats, proteins, amino acids, sugars, carbohydrates, lignin, celluloses, humic material and fatty acids (Birkett and Lester, 2003). In secondary sludge, the large amounts of live and dead microorganisms provide a large surface area (0.8–1.7 $m^2\ g^{-1}$) for interaction with the compound (Rogers, 1996). Those EDCs that preferentially adsorb onto the suspended particulates do so because of their hydrophobic properties. The K_{ow} values often correlate with the degree of association between an organic compound and the solid phase (Dobbs et al., 1989; Byrns, 2001). $\log K_{ow}$ values increase with increasing lipophilicity and correlate inversely with aqueous solubility.

Chemical factors, such as structure, together with environmental factors influence biodegradation which is not as predictable as processes such as volatilization and sorption (Meakins et al., 1994; Alcock et al., 1999). Molecular mass or size can limit active transport, solubility can result in competitive partitioning, and toxicity can result in cell damage or enzyme inhibition. Unlike naturally occurring compounds, anthropogenic compounds tend to be relatively resistant to biodegradation. This is partly due to the fact that microorganisms lack the necessary enzymes required for transformation, so a longer acclimation period may be required. The importance of biotransformation increases with sludge retention time and increasing $\log K_{ow}$ of the selected compound. Biotransformation rates have been found to increase to a maximum at $\log K_{ow}$ 3–3.5 and then decline rapidly as sorption to sludge dominates the removal mechanisms for more hydrophobic compounds (Danielsson and Zhang, 1996).

Apart from biodegradation, abiotic chemical reactions can also be responsible for the transformation of compounds. Photolysis, exposure to (UV) sunlight, may degrade certain compounds to simpler compounds, rendering them more susceptible to biodegradation (Birkett and Lester, 2003). Suspended particulates are responsible for a large amount of turbidity in the watercourse. They decrease the proportion of irradiating light to the target compounds, as a high clarity of the water is usually required in order for UV to reach compounds in the water column (Birkett and Lester, 2003). Hydrolysis is usually the most important chemical transformation. Hydrolysis is a nucleophilic displacement reaction that can occur when molecules have linkages separating highly polar groups (Rogers, 1996). Factors such as pH, temperature, moisture and inorganic matter can also have an effect on chemical degradation rates (Meakins et al., 1994; Alcock et al., 1999). Volatilization is the transfer of a compound from the aqueous phase to the atmosphere from the surface of open tanks such as clarifiers. However in practice, the majority of volatilization losses occur through air stripping in the aeration tank. A proportion may be lost during sludge treatment at the dewatering or thickening stage, particularly if the sludge is aerated or agitated. Low molecular mass, non-polar compounds with low aqueous solubilities and high vapour pressures are known to be transferred to the atmosphere during aeration in wastewater treatment (Byrns, 2001).

A number of studies have proposed and reported mathematical fugacity models which can be used to quantify the distribution and fate of xenobiotic compounds in WWTPs (Clark et al., 1995; Byrns, 2001; Khan and Ongreth, 2002; Johnson and Williams, 2004; Khan and Ongreth, 2004). These models consider the major abiotic and biotic processes which influence the intermedia distribution and eventual fate of the organic compounds. Under optimal operating conditions, a WWTP may remove a large percentage for example, 70–100%, of many organic pollutants from the wastewater, but treatment efficiency varies (Clark et al., 1995). Apart from these few cited literatures there are even fewer reported studies on the fugacity modelling of compounds that are estrogenic mimics within a WWTP. The complexity of wastewater sampling and analysis coupled with the intricate design of the WWTP fugacity model and its various unknowns could be one of the reasons for the lack of published studies.

The purpose of this current research was to test a simple fugacity-based model's ability to predict the fate of selected phthalates and alkylphenols in a conventional activated sludge WWTP (WWTP A) located in South East Queensland. This major WWTP (people equivalent capacity of 240 000) receives its influent from both domestic and industrial discharges; and its configuration is typical of those currently found in South East Queensland. To date, none of the reported fugacity modelling studies has previously investigated the fate and behavior of phthalates and alkylphenols commonly found in WWTPs. Phthalates have a