University of Wollongong

Research Online

Faculty of Engineering and Information
Sciences - Papers: Part A

Faculty of Engineering and Information
Sciences

1-1-2014

Rejection and fate of trace organic compounds (TrOCs) during membrane distillation

Kaushalya Wijekoon

University of Wollongong, kcw998@uowmail.edu.au

Faisal Ibney Hai

University of Wollongong, faisal@uow.edu.au

Jinguo Kang

University of Wollongong, jkang@uow.edu.au

William E. Price

University of Wollongong, wprice@uow.edu.au

Tzahi Cath

Colorado School Of Mines

See next page for additional authors

Follow this and additional works at: <https://ro.uow.edu.au/eispapers>

Part of the [Engineering Commons](#), and the [Science and Technology Studies Commons](#)

Research Online is the open access institutional repository for the University of Wollongong. For further information contact the UOW Library: research-pubs@uow.edu.au

Rejection and fate of trace organic compounds (TrOCs) during membrane distillation

Abstract

In this study, we examined the feasibility of membrane distillation (MD) for removing trace organic compounds (TrOCs) during water and wastewater treatment. A set of 29 compounds was selected to represent major TrOC groups, including pharmaceuticals, steroid hormones, phytoestrogens, UV-filters, industrial chemicals, and pesticides that occur ubiquitously in municipal wastewater. Results reported here suggest that rejection and fate and transport of TrOC during MD are governed by their volatility and, to a lesser extent, hydrophobicity. All TrOCs with $\text{pK}_\text{H} > 9$ (which can be classified as non-volatile) were well removed by MD. Among the 29 TrOCs investigated in this study, three compounds (i.e. 4-tert-octylphenol, 4-tert-butylphenol and benzophenone) possess moderate volatility ($\text{pK}_\text{H} < 9$) and therefore had the lowest rejection efficiencies of 54, 73 and 66%, respectively. The results suggest that the rejection of TrOCs with $\text{pK}_\text{H} < 9$ may be governed by the interplay between their hydrophobicity and volatility. In addition, the fate and transport of the TrOCs during the MD process was also investigated. Hydrophilic TrOCs having negligible volatility were concentrated in the feed, while hydrophobic compounds with moderate volatility were substantially lost due to evaporation or adsorption. When MD treatment was integrated with a thermophilic membrane bioreactor (MBR), near complete removal (> 95%) of all 29 TrOCs investigated in this study was achieved despite their diverse physicochemical properties (i.e. hydrophobicity, persistency and volatility). The results suggest that MD could be a promising post-treatment to be used in conjunction with thermophilic MBR for TrOC removal.

Keywords

membrane, during, trocs, distillation, compounds, rejection, organic, trace, fate

Disciplines

Engineering | Science and Technology Studies

Publication Details

Wijekoon, K., Hai, F. Ibney., Kang, J., Price, W. E., Cath, T. & Nghiem, L. D. (2014). Rejection and fate of trace organic compounds (TrOCs) during membrane distillation. *Journal of Membrane Science*, 453 (March), 636-642.

Authors

Kaushalya Wijekoon, Faisal Ibney Hai, Jinguo Kang, William E. Price, Tzahi Cath, and Long D. Nghiem

Rejection and fate of trace organic compounds (TrOCs) during membrane distillation

Revised Manuscript Submitted to

Journal of Membrane Science

Nov 2013

Kaushalya C. Wijekoon ^a, Faisal I. Hai ^a, Jinguo Kang ^b, William E. Price ^b, Tzahi
Cath ^c, and Long D. Nghiem ^{a,*}

^a Strategic Water Infrastructure Laboratory, School of Civil Mining and Environmental
Engineering, University of Wollongong, Wollongong, NSW 2522, Australia

^b Strategic Water Infrastructure Laboratory, School of Chemistry
University of Wollongong, Wollongong, NSW 2522, Australia

^c Colorado School of Mines, Golden, CO, USA

* Corresponding author: Long Duc Nghiem, Email: longn@uow.edu.au; Ph +61 2 4221 4590

Abstract

In this study, we examined the feasibility of membrane distillation (MD) for removing trace organic compounds (TrOCs) during water and wastewater treatment. A set of 29 compounds was selected to represent major TrOC groups, including pharmaceuticals, steroid hormones, phytoestrogens, UV-filters, industrial chemicals, and pesticides that occur ubiquitously in municipal wastewater. Results reported here suggest that rejection and fate and transport of TrOC during MD are governed by their volatility and, to a lesser extent, hydrophobicity. All TrOCs with $pK_H > 9$ (which can be classified as non-volatile) were well removed by MD. Among the 29 TrOCs investigated in this study, three compounds (i.e. 4-tert-octylphenol, 4-tert-butylphenol and benzophenone) possess moderate volatility ($pK_H < 9$) and therefore had the lowest rejection efficiencies of 54, 73 and 66%, respectively. The results suggest that the rejection of TrOCs with $pK_H < 9$ may be governed by the interplay between their hydrophobicity and volatility. In addition, the fate and transport of the TrOCs during the MD process was also investigated. Hydrophilic TrOCs having negligible volatility were concentrated in the feed, while hydrophobic compounds with moderate volatility were substantially lost due to evaporation or adsorption. When MD treatment was integrated with a thermophilic membrane bioreactor (MBR), near complete removal ($> 95\%$) of all 29 TrOCs investigated in this study was achieved despite their diverse physicochemical properties (i.e. hydrophobicity, persistency and volatility). The results suggest that MD could be a promising post-treatment to be used in conjunction with thermophilic MBR for TrOC removal.

Keywords: Trace organic compounds (TrOCs), direct contact membrane distillation (DCMD), volatility, fate and transport, hydrophobicity/hydrophilicity.

1. Introduction

Membrane distillation (MD) is a low temperature distillation process that involves the transport of water in the vapour phase from a feed solution through a microporous and hydrophobic membrane to the distillate (product) side. Direct contact membrane distillation (DCMD) is probably the most widely studied MD system configuration due to its simple operation [1-2]. In DCMD, the feed solution is maintained at a higher temperature than the distillate; thus, creating a vapour pressure difference between the feed and distillate. The membrane separates the liquid phase of the feed and distillate streams but allows water vapour to transport freely through its dry micro porous pores. In MD, the membrane material must be hydrophobic to prevent flooding of the pores by liquid feed or distillate under standard operating conditions. Because mass transfer can occur only in the gas phase, MD can offer complete rejection of all non-volatile solutes such as inorganic salts and pathogenic agents. As a result, to date, much of the effort in MD research has focused on desalination applications [2-5].

Unlike pressure driven membrane processes, due to the absence of a hydraulic pressure, MD is less susceptible to membrane fouling [3, 6]. Even when membrane fouling does occur, it is expected to be a less compacted layer and can be easily removed [3, 7-8]. The low operating temperature of MD allows for the utilization of solar thermal or low grade heat as the energy source [1-2, 9-13]. Given the advantages of high separation efficiency, low fouling propensity, and potentially low energy consumption (when low grade heat is readily available), MD can be useful for a range of applications beyond those for brackish and seawater desalination. Several studies have explored the use of MD for food processing, such as whey protein recovery in dairy processing [8], polyphenolic antioxidants from olive oil wastewater [14], and orange juice concentration [15], separation of fermentation broth [16] as well as treatment of wastewater from the textile [17] and petrochemical industries [10], and municipal water reuse [11, 18].

Despite the growing interest in using MD for treatment of a range of wastewaters, there is still a lack of understanding of the rejection mechanisms of trace organic compounds (TrOCs) by MD. These TrOCs have been frequently detected in raw sewage and biologically treated effluent at concentrations ranging from several ng/L to several $\mu\text{g/L}$ [19-23]. As a result, the removal of these TrOCs from secondary treated effluent by advanced treatment processes such as

nanofiltration (NF), reverse osmosis (RO), oxidation and activated carbon adsorption has been extensively investigated in recent years [24-28]. Nevertheless, only a few studies have been conducted to elucidate the rejection of specific organic compounds by MD. Moreover, the available studies are mostly concerned with industrial chemicals such as benzene [29] and trichloroethylene [30] at an elevated feed concentration.

Given the concerns associated with human and environmental exposure to TrOCs, it is important to elucidate their fate and transport during MD, particularly in water reuse applications. Examples of these include the investigation by Cath et al. [18] and Cartinella et al. [31] to treat urine and hygiene wastewater by MD for water reuse in long term space missions and the novel membrane distillation membrane bioreactor (MDBR) concept proposed by Phattaranawik et al. [11] and Goh et al. [32].

In this paper, we studied the rejection of a broad range of TrOCs by MD. The potential application of MD as a post treatment for thermophilic MBR to enhance TrOC removal was also investigated. The transport and fate of TrOCs during MD treatment are discussed with respect to compound hydrophobicity and volatility (measured by the log D and the Henry's law constant, respectively). The results provide further insight with respect to TrOC rejection using MD, which is critical for the further development of this technology for wastewater reclamation applications.

2. Materials and Methods

2.1. *Experimental system*

The rejection of TrOCs by MD was evaluated using a hydrophobic microporous polytetrafluoroethylene (PTFE) membrane (GE, Minnetonka, MN) and a laboratory-scale DCMD system [33]. According to the manufacturer, the average pore size and porosity of the MD membrane were 0.22 μm and 70%, respectively. The DCMD system (Fig. 1) comprised a membrane cell, a stainless steel feed tank, a glass distillate tank, two circulation pumps (Micropump Inc., USA), a temperature controller (Coleparmer, USA), and a heating element (Process Technology, USA). The membrane cell was made of acrylic glass, and a flow channel was engraved in each of the two acrylic glass blocks that make up the feed and permeate semi-

cells. The length, width, and height of each channel were 145, 95, and 3 mm, respectively. The feed solution was circulated from a stainless steel reservoir to the membrane cell and then returned back to the feed reservoir. A temperature sensor was placed immediately before the feed inlet to the membrane cell. The heating element and the temperature sensor were connected to a temperature control unit that was used to regulate the temperature of the feed solution. Another temperature sensor was installed immediately at the outlet of the distillate semi-cell. The temperature of the distillate was regulated using a chiller (AquaCooler, Australia) equipped with a stainless steel heat exchanging coil immersed directly in the distillate reservoir. Excess water was allowed to overflow from the distillate reservoir into a glass container, placed and continuously weighed on an analytical balance (Mettler Toledo, Switzerland). All pipework used in the DCMD test unit was covered with insulation foam to minimize heat loss. The feed and distillate tanks were covered with aluminium foil to minimise evaporation loss during the experiment. At the end of each experiment, the solution volume was measured again and the total volume loss was found to be less than 6%.

[FIGURE 1]

One set of MD experiments was conducted using a synthetic feed solution containing approximately 5 µg/L of each TrOC in Milli-Q water. In another set of experiments, effluent obtained from a thermophilic MBR system (Supplementary Data Fig. S1) was used as the feed solution to evaluate the feasibility of combining MD with MBR. The MBR and MD experiments were conducted separately. The MBR system consisted of a 5 L glass reactor immersed in a PID control water bath (Julabo, Germany), three peristaltic pumps (Masterflex L/S, USA) for feeding, recirculation and effluent extraction, and an external ceramic membrane module (NGK, Japan). The ceramic membrane had a nominal pore size of 1 µm and effective area of 0.09 m². Further details of this MBR system are available elsewhere [34].

2.2. *Experimental protocol*

In all MD experiments, the feed and distillate temperatures were 40 and 20 °C, respectively and the cross flow velocity of the feed and distillate circulation flow was 11.7 cm/s. The initial feed volume was 10 L. The experiment was concluded once the water recovery had reached 70% at which stage the feed and distillate samples were collected for TrOC analysis.

The duration of each MD experiment was approximately 24 h. At the beginning of each MD experiment, 3.35 L of Milli-Q water was used as the initial distillate. Thus, TrOC concentration in the distillate was corrected for dilution by taking into account the initial volume of Milli-Q water in the distillate.

The MBR system was operated under thermophilic conditions (40 °C) with an average dissolved oxygen (DO) concentration of 2.9 mg/L, hydraulic retention time of 24 hr, and average mixed liquor pH of 7.7. Excess sludge was withdrawn every week to maintain the mixed liquor suspended solid (MLSS) concentration in the reactor at 5000 mg/L, resulting in a solids retention time (SRT) of 140 days. The system was fed with a synthetic wastewater containing 100 mg/L glucose, 100 mg/L peptone, 17.5 mg/L KH_2PO_4 , 17.5 mg/L MgSO_4 , 10 mg/L FeSO_4 , 225 mg/L CH_3COONa and 35 mg/L urea [35].

Prior to the commencement of this study, the MBR system had been acclimatized at 40 °C and operated for more than two months to produce constant effluent quality (Supplementary Data Fig. S2). TrOCs were introduced to the MBR feed to obtain approximately 5 µg/L of each compound and the MBR system was operated continuously at similar operating conditions. Then, the effluent was collected and used as MD feed. In good agreement with the previous studies [24, 36-37] no significant difference in the biological performances of the MBR was observed following the introduction of TrOC. Key operational parameters including MLSS, mixed liquor volatile suspended solid (MLVSS), DO, TOC and TN removal, and permeate turbidity were continuously monitored to ensure the biological stability of the MBR. The performance of the MBR system was stable throughout this study with respect to these parameters. TOC and TN removal were stable at 91 and 47%, respectively. The turbidity of the MBR permeate was always below 0.9 NTU. The MLVSS/MLSS ratio of the sludge remained constant at approximately 0.76 throughout the experimental period. In addition, the MBR system was operated at a transmembrane pressure (TMP) below 90 kPa (13 psig) to maintain a constant permeate flux, and no abnormal variation in TMP was observed over the entire study (Supplementary Data Fig. S3).

TrOC removal or rejection (R) is defined as:

$$R = 100 \times \left(1 - \frac{C_p}{C_F}\right) \quad (1)$$

where C_p and C_F are concentration of the specific compound in the permeate and feed, respectively. The term rejection was used for the MD process while the term removal was used for MBR and the combined treatment of MBR and MD to take into account the fact that TrOC can also be biologically degraded. Losses of TrOCs during the MD process were calculated by considering the mass balance of each compound in the feed, concentrate and distillate as given in Equation 2.

$$C_F \times V_F = (C_D \times V_D) + (C_C \times V_C) + \text{total loss} \quad (2)$$

In Equation 2, C_F , C_D and C_C are concentration in the feed, distillate and concentrate, respectively. Similarly, V_F , V_D and V_C are the volume of the feed, distillate and concentrate, respectively.

2.3. Trace organic contaminants

A set of 29 TrOCs was selected to represent pharmaceuticals, steroid hormones, phytoestrogens, UV-filters (i.e., active ingredients of sunscreens), industrial chemicals, and pesticides that occur ubiquitously in municipal wastewater [19-23]. Analytical grade samples of these compounds were obtained from Sigma-Aldrich (Saint Louis, MO, USA). A combined stock solution of all the TrOCs was prepared in pure methanol and kept at -18 °C in the dark. Log D values of these compounds were obtained from the SciFinder Scholar database (<https://scifinder.cas.org/scifinder>) at pH 9 (Table 1). Vapour pressure, molecular weight (MW), and water solubility of each selected compound were also obtained from the SciFinder Scholar database (Supplementary Data Table S1) to calculate the Henry's law constant as: H (atm.m³/mol) = Vapour pressure × MW / water solubility. The pK_H value presented in Table 1 is defined as $pK_H = -\log_{10}H$. It is important to note that because the water solubility used to calculate the Henry's law constant was obtained at 25 °C, the actual pK_H values at 40 °C (which was used during the MD experiment) could deviate slightly from those values presented in the Table 1.

The pH of the synthetic feed solution was 8.5 and 8.6 at the beginning and the end of the MD experiment, respectively. The initial pH value of the MBR effluent was 7.8 and it increased to pH 9.1 by the end of the experiment. Accordingly, the log D and pK_H values of the TrOCs investigated in this study were obtained at pH 9 (Table 1).

[TABLE 1]

2.4. Analytical methods

2.4.1 Basic water quality parameters

Total organic carbon (TOC) and total nitrogen (TN) were analysed using a Shimadzu TOC/TN-V_{CSH} analyser (Shimadzu, Kyoto, Japan). TOC analysis was conducted in non-purgeable organic carbon mode. Electrical conductivity and pH of the feed and distillate were monitored using an Orion 4 Star Plus portable pH/conductivity meter (Thermo Scientific, Waltham, MA).

2.4.2 TrOC analysis

TrOC concentrations were determined using an analytical method previously reported by Hai et al. [38]. This method consisted of a solid phase extraction procedure followed by gas chromatography separation and quantitative determination using a mass spectrometry detector with electron ionization. Feed and distillate samples (500 mL each) were extracted using 6 mL 200 mg Oasis HLB cartridge (Waters, Milford, MA, USA). First, the cartridges were preconditioned with 7 mL dichloromethane and methanol mixture (1:1 v/v), 7 mL methanol, and 7 mL reagent water (Milli-Q water). The samples were acidified to pH 2-3 and loaded onto the cartridges at a flow rate of 1-5 mL/min. The cartridges were then rinsed with 20 mL Milli-Q water and dried in a stream of nitrogen for 30 min. The extracted TrOCs were eluted from the cartridge using 7 mL of methanol followed by dichloromethane and methanol mixture (1:1 v/v) at a flow rate of 1-5 mL/min. The eluents were subsequently evaporated using a water bath (40 °C) under a gentle stream of nitrogen. The extracts were dissolved with 200 µL methanol which contained 5 µg bisphenol A-d₁₆ and transferred into 1.5 mL vials, and then further evaporated under a gentle stream of nitrogen. Finally, the extracts were derivatized by adding 100 µL of N,O-Bis(trimethylsilyl)trifluoroacetamide (1% trimethylchlorosilane) and pyridine (dried with

KOH solid), then heated in a heating block (60–70 °C) for 30 min. The derivatives were cooled to room temperature and analysed using a Shimadzu QP5000 GC–MS (Shimadzu, Kyoto, Japan) equipped with a AOC20i autosampler and a Phenomenex Zebron ZB-5 (5% diphenyl–95% dimethylpolysiloxane) capillary column (30 m × 0.25 mm ID, $d_f = 0.25 \mu\text{m}$). The detection limit of the selected compounds was in the range of 1 to 20 ng/L [38].

3. Results and discussion

3.1 *Basic Performance of the MD Process*

The MD experiments were analyzed considering the distillate flux, water recovery, pH and conductivity variation (Supplementary Data Table S1). The distillate flux was continuously monitored to assess the stability (Fig. 2). There was no notable difference in the performance of the MD process with respect to the water flux and conductivity rejection when either the synthetic solution or MBR effluent was used as the feed. Both experiments achieved satisfactory water recovery at 70%. The average TOC and TN concentrations of the MBR effluent were 15 ± 6 and 17 ± 4 mg/L, respectively. However, this high residual organic content in the MBR effluent did not exert any negative impact on the MD process. TOC and TN concentrations of the distillate were consistently less than 1 mg/L. When either the synthetic solution or the MBR effluent was used as the feed to the MD process, the water flux was stable at approximately 17.5 L/m².h and no flux decline was observed during the entire experimental period (Fig. 2). The conductivity of the distillate was consistently below 10 $\mu\text{S}/\text{cm}$ regardless of the salinity level in the feed (Supplementary Data Table S1).

[FIGURE 2]

3.2 *Rejection and fate of TrOCs during MD*

3.2.1 *TrOC rejection*

Most of the 29 TrOCs investigated were effectively removed by MD (Fig. 3). However, it is important to note that only a moderate rejection efficiency was observed for several compounds. In particular, 4-tert-octylphenol showed the lowest rejection (54%). In MD, mass transfer occurs only in the gas (vapour) phase. Thus, the transport of TrOCs from the feed to the

distillate solution depends on their volatility. Not surprisingly, all TrOCs with pK_H value higher than 9 (low volatility) were well removed by the MD process. Oxybenzone is the only exception. Compared to other TrOCs, the relatively lower rejection (81%) of oxybenzone in relation to its pK_H value as plotted in Fig. 3 could be attributed to the strong dependence of its pK_H value on pH. pK_H values at pH 9 have been plotted in Fig. 3. However, it is noteworthy that the pK_H value of oxybenzone changes from 9.23 to 8.39 when the solution pH decreases from 9 to 8 (Supplementary Data Table S2). Because in this study the feed solution pH was 8.5 and 8.6 at the beginning and the end of the MD experiment, respectively, the interpolated pK_H (8.6) value of oxybenzone is actually below 9. The three TrOCs with the lowest rejection (i.e., 4-tert-octylphenol, 4-tert-butylphenol and benzophenone) also have the highest volatility (or lowest pK_H values) amongst the 29 TrOCs studied. Low rejection of volatile organic compounds such as benzene [29] and trichloroethylene [30] by MD have been previously reported in the literature. However, in this study, there was no obvious correlation between rejection efficiencies and pK_H values for TrOCs possessing a pK_H value of less than 9. The data presented in Fig. 3 suggest that in addition to volatility, other physicochemical properties such as hydrophobicity (which can be obtained from $\log D$) may also influence the transport of TrOCs during MD. In fact, octocrylene, which has the fourth lowest rejection value of 81%, is also the most hydrophobic compound of the 29 TrOCs. In addition, in this study most of the TrOCs with pK_H of less than 9 were also hydrophobic (i.e., $\log D > 3$) and their rejection efficiency varied widely from as low as 54% (i.e., 4-tert-octylphenol) to near complete rejection. Significant adsorption of hydrophobic organics to the MD membrane has been previously reported by Zuo and Wang [39]. The results reported in Fig. 3 suggest that the rejection of TrOCs may be governed by the interplay between their volatility and hydrophobicity.

[FIGURE 3]

3.2.2 Fate of TrOCs in the MD process

The fate of TrOCs during the MD experiments is presented in Fig. 4. Considering each experiment as a closed system, any loss of TrOCs could be attributed to either evaporation or adsorption to the membrane. The former is governed by the volatility and the latter is governed by the hydrophobicity. Both of these physicochemical properties could be important in determining the fate of TrOCs during MD (Fig. 4). Results reported in this study reveal that the

hydrophilic TrOCs with low volatility ($pK_H > 9$) can be concentrated in the feed. On the other hand, significant losses through either evaporation or adsorption could be observed for moderately volatile (i.e. pK_H value < 9) and hydrophobic (i.e. $\log D > 3$) compounds. As a result, moderately volatile and hydrophobic compounds such as triclosan, propoxur, amitriptyline, octocrylene and 17 β -estradiol-17-acetate did not accumulate in the feed. Indeed, concentrations of all three compounds (i.e. 4-tert-octylphenol, 4-tert-butylphenol and benzophenone) with the lowest pK_H in the concentrate at the end of the experiment were lower than the initial values (Supplementary Data, Table S3). In addition, the rejections of these compounds by MD were also the lowest amongst the 29 TrOCs investigated here (Fig. 4).

[FIGURE 4]

3.3 MBR-MD system

MD can be operated with feed temperature compatible to that in thermophilic MBR, these two processes can complement each other for an enhanced performance. TrOC concentrations in the feed and after each of these treatment steps are shown in Supplementary Data Table S4. MBR treatment effectively removed most of the 29 TrOCs investigated in this study. High removal of these compounds during MBR treatment has also been reported elsewhere [25, 36-37, 40]. However, several compounds including propoxur, atrazine, ametryn, clofibric acid, diclofenac, carbamazepine, naproxen and fenoprop were found to be persistent to MBR treatment, and their residual concentrations in the MBR effluent were relatively high. Low removal efficiencies of these compounds have also been reported in several previous studies [36, 41-42]. It is noted that the removal efficiency of these compounds under thermophilic conditions in this study were comparatively lower than that observed in our previous study under mesophilic conditions [37]. The low removal of most of the persistent compounds can be attributed to the disturbed metabolic activity generally associated with the biological treatment at elevated temperatures [38]. Nevertheless, as illustrated in Fig.5, all TrOCs including those that were resistant to MBR treatment were effectively removed by the MD process. In this study, complete or near complete ($> 95\%$) removal efficiency of all 29 TrOCs was achieved by the combined MBR-MD treatment.

TrOC removal by MD as a post treatment step following an MBR has not been reported in the literature. On the other hand, the use of other post treatment processes such as NF and RO

desalination subsequent to MBR has been previously demonstrated [24-25, 43-44]. Tam et al. [43] reported near complete removal of estrogens and disinfection by-products (trihalomethanes and halo-acetic acids) by a pilot MBR/RO system. Alturki et al. [24] also demonstrated the benefits of coupling MBR treatment and NF/RO desalination for removing 40 TrOCs with a diverse range of physicochemical properties. Results reported in the current study suggest that an MBR-MD hybrid system could be as effective as an MBR-NF/RO system for removing TrOCs. In addition, high removal of TrOCs by a combination of MBR and MD treatment can be achieved regardless of the diversity of their volatility, persistency, and hydrophobicity.

The results shed light on the prospective of integrating MD with MBR for TrOC removal (e.g., MBR coupled MD (multi pass) system and MD bioreactor), and the salinity affected complexities on removal performance would be vital to investigate. However, it was not within the scope of the current study. Overall, the high water flux, excellent distillate quality and the near complete removal of TrOCs reported here suggests that MBR-MD system could be used to ensure safe water reuse.

[FIGURE 5]

4. Conclusion

In this study, we have investigated the rejection of 29 trace organic compounds (TrOCs) and their fate in a membrane distillation (MD) system. Results reported here suggest that rejection and fate and transport of TrOC during MD would be mainly governed by the volatility and partially governed by the hydrophobicity of the compound. All TrOCs with $pK_H > 9$ (which can be classified as non-volatile) were highly removed by MD. However, three compounds (i.e., 4-tert-octylphenol, 4-tert-butylphenol and benzophenone) with $pK_H < 9$ and thus classified as partially volatile showed relatively low rejection efficiencies (i.e., 54, 73 and 66%, respectively). The results also suggest that the rejection of TrOCs with $pK_H < 9$ may be governed by the interplay between their hydrophobicity and volatility. In addition, the reported results show that hydrophilic TrOCs having negligible volatility were concentrated in the feed, while hydrophobic compounds with moderate volatility were substantially lost due to evaporation or adsorption to membrane. Membrane bioreactor followed by MD treatment resulted in near complete ($> 95\%$)

removal of all 29 TrOCs despite their diverse physicochemical properties (i.e., hydrophobicity, persistency and volatility).

5. Acknowledgement

The authors would like to thank the University of Wollongong for the PhD scholarship support to Kaushalya C. Wijekoon.

6. References

- [1] K.W. Lawson, D.R. Lloyd, Membrane distillation, *Journal of Membrane Science*, 124 (1997) 1-25.
- [2] E. Curcio, E. Drioli, Membrane distillation and related operations—A review, *Separation & Purification Reviews*, 34 (2005) 35-86.
- [3] A. Alkhudhiri, N. Darwish, N. Hilal, Treatment of saline solutions using air gap membrane distillation: experimental study, *Desalination*, 323 (2013) 2-7.
- [4] C.R. Martinetti, A.E. Childress, T.Y. Cath, High recovery of concentrated RO brines using forward osmosis and membrane distillation, *Journal of Membrane Science*, 331 (2009) 31-39.
- [5] T.Y. Cath, V.D. Adams, A.E. Childress, Experimental study of desalination using direct contact membrane distillation: a new approach to flux enhancement, *Journal of Membrane Science*, 228 (2004) 5-16.
- [6] F. He, J. Gilron, H. Lee, L. Song, K.K. Sirkar, Potential for scaling by sparingly soluble salts in crossflow DCMD, *Journal of Membrane Science*, 311 (2008) 68-80.
- [7] S. Srisurichan, R. Jiraratananon, A.G. Fane, Humic acid fouling in the membrane distillation process, *Desalination*, 174 (2005) 63-72.
- [8] A. Hausmann, P. Sanciolo, T. Vasiljevic, M. Weeks, K. Schroën, S. Gray, M. Duke, Fouling of dairy components on hydrophobic polytetrafluoroethylene (PTFE) membranes for membrane distillation, *Journal of Membrane Science*, 442 (2013) 149-159.
- [9] P.A. Hogan, Sudjito, A.G. Fane, G.L. Morrison, Desalination by solar heated membrane distillation in *Proceedings of the Twelfth International Symposium on Desalination and Water Re-use*, in, Malta, (1991), pp. 81-90.
- [10] T.-H. Khaing, J. Li, Y. Li, N. Wai, F.-s. Wong, Feasibility study on petrochemical wastewater treatment and reuse using a novel submerged membrane distillation bioreactor, *Separation and Purification Technology*, 74 (2010) 138-143.
- [11] J. Phattaranawik, A.G. Fane, A.C.S. Pasquier, W. Bing, A novel membrane bioreactor based on membrane distillation, *Desalination*, 223 (2008) 386-395.
- [12] J.-P. Mericq, S. Laborie, C. Cabassud, Evaluation of systems coupling vacuum membrane distillation and solar energy for seawater desalination, *Chemical Engineering Journal*, 166 (2011) 596-606.

- [13] F. Suárez, S.W. Tyler, A.E. Childress, A theoretical study of a direct contact membrane distillation system coupled to a salt-gradient solar pond for terminal lakes reclamation, *Water Research*, 44 (2010) 4601-4615.
- [14] A. El-Abbassi, H. Kiai, A. Hafidi, M.C. García-Payo, M. Khayet, Treatment of olive mill wastewater by membrane distillation using polytetrafluoroethylene membranes, *Separation and Purification Technology*, 98 (2012) 55-61.
- [15] V.D. Alves, I.M. Coelho, Orange juice concentration by osmotic evaporation and membrane distillation: A comparative study, *Journal of Food Engineering*, 74 (2006) 125-133.
- [16] M. Gryta, A. Markowska-Szczupak, J. Bastrzyk, W. Tomczak, The study of membrane distillation used for separation of fermenting glycerol solutions, *Journal of Membrane Science*, 431 (2013) 1-8.
- [17] V. Calabro, E. Drioli, F. Matera, Membrane distillation in the textile wastewater treatment, *Desalination*, 83 (1991) 209-224.
- [18] T.Y. Cath, D. Adams, A.E. Childress, Membrane contactor processes for wastewater reclamation in space: II. Combined direct osmosis, osmotic distillation, and membrane distillation for treatment of metabolic wastewater, *Journal of Membrane Science*, 257 (2005) 111-119.
- [19] A.S. Stasinakis, G. Gatidou, Micropollutants and aquatic environment, in: J. Virkutyte, S. Varma R, V. Jegatheesan (Eds.) *Treatment of micropollutants in water and wastewater: Integrate environmental technologies series*, International Water Association, London, (2010), pp. 1-51.
- [20] K. Kümmerer, The presence of pharmaceuticals in the environment due to human use - present knowledge and future challenges, *Journal of Environmental Management*, 90 (2009) 2354-2366.
- [21] P. Gago-Ferrero, M.S. Díaz-Cruz, D. Barceló, Occurrence of multiclass UV filters in treated sewage sludge from wastewater treatment plants, *Chemosphere*, 84 (2011) 1158-1165.
- [22] J. Kang, W.E. Price, Occurrence of phytoestrogens in municipal wastewater and surface waters, *Journal of Environmental Monitoring*, 11 (2009) 1477-1483.
- [23] Y.S. Liu, G.G. Ying, A. Shareef, R.S. Kookana, Occurrence and removal of benzotriazoles and ultraviolet filters in a municipal wastewater treatment plant, *Environmental Pollution*, 165 (2012) 225-232.
- [24] A.A. Alturki, N. Tadkaew, J.A. McDonald, S.J. Khan, W.E. Price, L.D. Nghiem, Combining MBR and NF/RO membrane filtration for the removal of trace organics in indirect potable water reuse applications, *Journal of Membrane Science*, 365 (2010) 206-215.
- [25] L.N. Nguyen, F.I. Hai, J. Kang, W.E. Price, L.D. Nghiem, Removal of trace organic contaminants by a membrane bioreactor-granular activated carbon (MBR-GAC) system, *Bioresource Technology*, 113 (2012) 169-173.
- [26] K. Lekkerkerker-Teunissen, A.H. Knol, L.P. van Altna, C.J. Houtman, J.Q.J.C. Verberk, J.C. van Dijk, Serial ozone/peroxide/low pressure UV treatment for synergistic and effective organic micropollutant conversion, *Separation and Purification Technology*, 100 (2012) 22-29.

- [27] L.N. Nguyen, F.I. Hai, J. Kang, W.E. Price, L.D. Nghiem, Removal of emerging trace organic contaminants by MBR-based hybrid treatment processes, *International Biodeterioration & Biodegradation*, 85 (2013) 474-482.
- [28] A.R.D. Verliefde, S.G.J. Heijman, E.R. Cornelissen, G.L. Amy, B. Van der Bruggen, J.C. van Dijk, Rejection of trace organic pollutants with high pressure membranes (NF/RO), *Environmental Progress*, 27 (2008) 180-188.
- [29] F.A. Banat, J. Simandl, Removal of benzene traces from contaminated water by vacuum membrane distillation, *Chemical Engineering Science*, 51 (1996) 1257-1265.
- [30] S. Duan, A. Ito, A. Ohkawa, Removal of trichloroethylene from water by aeration, pervaporation and membrane distillation, *Journal of Chemical Engineering of Japan*, 34 (2001) 1069-1073.
- [31] J.L. Cartinella, T.Y. Cath, M.T. Flynn, G.C. Miller, K.W. Hunter, A.E. Childress, Removal of natural steroid hormones from wastewater using membrane contactor processes, *Environmental Science & Technology*, 40 (2006) 7381-7386.
- [32] S. Goh, J. Zhang, Y. Liu, A.G. Fane, Fouling and wetting in membrane distillation (MD) and MD-bioreactor (MDBR) for wastewater reclamation, *Desalination*, 323 (2013) 39-47.
- [33] L.D. Nghiem, T. Cath, A scaling mitigation approach during direct contact membrane distillation, *Separation and Purification Technology*, 80 (2011) 315-322.
- [34] K.C. Wijekoon, T. Fujioka, J.A. McDonald, S.J. Khan, F.I. Hai, W.E. Price, L.D. Nghiem, Removal of N-nitrosamines by an aerobic membrane bioreactor, *Bioresource Technology*, 141 (2013) 41-45.
- [35] A. Alturki, J. McDonald, S.J. Khan, F.I. Hai, W.E. Price, L.D. Nghiem, Performance of a novel osmotic membrane bioreactor (OMBR) system: Flux stability and removal of trace organics, *Bioresource Technology*, 113 (2012) 201-206.
- [36] N. Tadkaew, F.I. Hai, J.A. McDonald, S.J. Khan, L.D. Nghiem, Removal of trace organics by MBR treatment: The role of molecular properties, *Water Research*, 45 (2011) 2439-2451.
- [37] K.C. Wijekoon, F.I. Hai, J. Kang, W.E. Price, W. Guo, H.H. Ngo, L.D. Nghiem, The fate of pharmaceuticals, steroid hormones, phytoestrogens, UV-filters and pesticides during MBR treatment, *Bioresource Technology*, 144 (2013) 247-254.
- [38] F.I. Hai, K. Tessmer, L.N. Nguyen, J. Kang, W.E. Price, L.D. Nghiem, Removal of micropollutants by membrane bioreactor under temperature variation, *Journal of Membrane Science*, 383 (2011) 144-151.
- [39] G. Zuo, R. Wang, Novel membrane surface modification to enhance anti-oil fouling property for membrane distillation application, *Journal of Membrane Science*, 447 (2013) 26-35.
- [40] V. Boonyaroj, C. Chiemchaisri, W. Chiemchaisri, S. Theepharakasapan, K. Yamamoto, Toxic organic micro-pollutants removal mechanisms in long-term operated membrane bioreactor treating municipal solid waste leachate, *Bioresource Technology*, 113 (2012) 174-180.
- [41] H. Bouju, G. Buttiglieri, F. Malpei, Perspectives of persistent organic pollutants (POPS) removal in an MBR pilot plant, *Desalination*, 224 (2008) 1-6.

- [42] J. Radjenović, M. Petrović, D. Barceló, Fate and distribution of pharmaceuticals in wastewater and sewage sludge of the conventional activated sludge (CAS) and advanced membrane bioreactor (MBR) treatment, *Water Research*, 43 (2009) 831-841.
- [43] L.S. Tam, T.W. Tang, G.N. Lau, K.R. Sharma, G.H. Chen, A pilot study for wastewater reclamation and reuse with MBR/RO and MF/RO systems, *Desalination*, 202 (2007) 106-113.
- [44] M. Jacob, C. Guigui, C. Cabassud, H. Darras, G. Lavison, L. Moulin, Performances of RO and NF processes for wastewater reuse: Tertiary treatment after a conventional activated sludge or a membrane bioreactor, *Desalination*, 250 (2010) 833-839.

Rejection and fate of trace organic compounds (TrOCs) during membrane distillation

Supplementary Data

Journal of Membrane Science

Nov 2013

Kaushalya C. Wijekoon^a, Faisal I. Hai^a, Jinguo Kang^b, William E. Price^b, Tzahi Cath^c and
Long D. Nghiem^{a,*}

^a Strategic Water Infrastructure Laboratory, School of Civil Mining and Environmental
Engineering, University of Wollongong, Wollongong, NSW 2522, Australia

^b Strategic Water Infrastructure Laboratory, School of Chemistry
University of Wollongong, Wollongong, NSW 2522, Australia

^c Colorado School of Mines, Golden, CO, USA

* Corresponding author: Long Duc Nghiem, Email: longn@uow.edu.au; Ph +61 2 4221 4590

Table S1: MD and MBR-MD experimental conditions.

Parameter	Phase	MD Experiment with Milli-Q as feed	MD experiment with MBR permeate as feed
pH	MD feed	8.5	7.8
	MD concentrate	8.6	9.1
	Initial distillate	7.3	7.3
	Final distillate	7.7	9.6
Conductivity ($\mu\text{S}/\text{cm}$)	MD feed	18 ± 0.3	322 ± 2.0
	MD concentrate	130 ± 17	1026 ± 46
	Initial distillate	1.1 ± 0.1	1.3 ± 0.2
	Final distillate	6.9 ± 0.4	9.3 ± 0.1

Note: 1. Volume loss due to evaporation remained less than 1 L in each test.

2. The error was calculated from duplicate experiments.

Table S2: pK_H of oxybenzone at different pH values.

pH	Log D	Water Solubility at 25°C and pH 8 (mg/L)	Vapour Pressure at 25°C (mmHg)	pK_H
pH 8	3.42	390	5.26×10^{-6}	8.39
pH 9	2.55	2700	5.26×10^{-6}	9.23

Table S3: Aqueous phase concentration of the selected TrOCs when tested in synthetic feed solution (in Milli-Q water).

Compound	pK _H at pH 9	Log <i>D</i> at pH 9	Feed (ng/L)		Concentrate (ng/L)		Distillate (ng/L)	
			Mean	Error (±)	Mean	Error (±)	Mean	Error (±)
4-tert-Octylphenol	5.06	5.18	2292	828	585	110	631	109
4-tert-Butylphenol	5.15	3.37	1881	0	350	147	245	58
Benzophenone	5.88	3.21	666	0	274	26	128	44
Triclosan	6.19	4.12	3470	242	1019	232	115	26
Propoxur	6.28	1.54	1653	261	81	92	7	5
Atrazine	7.28	2.64	2462	89	10722	387	57	16
Pentachlorophenol	7.59	1.99	2924	459	8223	253	53	17
Amitriptyline	8.18	4.01	2465	455	1569	105	217	84
Ametryn	8.43	2.97	3133	117	10643	420	100	31
Octocrylene	8.47	6.89	888	229	371	76	95	49
Bisphenol A	8.66	3.62	3077	60	9070	266	283	56
17 β – Estradiol- 17- acetate	8.67	5.11	3097	202	1192	278	76	62
17 β – Estradiol	8.93	4.12	3557	20	6944	603	38	24
Estrone	9.03	3.6	4163	34	9231	271	140	79
Carbamazapine	9.09	1.89	1806	105	6053	463	57	20
Oxybenzone	9.23	2.55	3531	333	2877	519	638	41
17 α – Ethinylestradiol	9.43	4.08	3276	145	4468	389	55	28
Clofibric acid	9.54	-1.32	3539	115	11594	72	22	14
Ibuprofen	10.39	-0.19	3555	288	13669	50	12	12
Estriol	10.80	2.5	3124	389	6866	1172	16	16
Fenoprop	11.48	-0.29	2330	42	7873	272	63	45
Diclofenac	11.51	0.83	3527	168	11633	414	123	132
Metronidazole	11.68	-0.14	742	156	3448	486	103	146
Gemifibrozil	12.11	0.67	3941	82	13514	191	34	16
Naproxen	12.68	-0.73	3794	199	13581	500	6	3
Formononetin	13.22	0.88	1432	297	5534	285	7	1
Ketoprofen	13.70	-0.84	3268	141	11493	180	24	2
Primidone	13.93	0.83	1698	121	7280	88	5	4
Enterolactone	15.19	1.89	1213	274	3076	933	2	2

Note: Error represents the standard deviation from four measurements (duplicate samples from two replicate experiments). MD was carried out at the feed and distillate temperatures of 40 and 20 °C, respectively. The feed and distillate circulation flow rate was 2 L/min (corresponding to 11.7 cm/s).

Table S4: Aqueous phase concentration of the selected TrOCs during the MBR-MD experiments with MBR permeate as the MD feed.

Compound	pK _H at pH 9	Log D at pH 9	MBR feed (ng/L)		MBR Permeate (MD feed) (ng/L)		MD Concentrate (ng/L)		Distillate (ng/L)	
			Mean	Error (±)	Mean	Error (±)	Mean	Error (±)	Mean	Error (±)
4-tert-Octylphenol	5.06	5.18	4683	9	147	11	278	69	96	65
4-tert-Butylphenol	5.15	3.37	4240	45	112	19	116	30	51	23
Benzophenone	5.88	3.21	1568	166	205	35	78	25	37	41
Triclosan	6.19	4.12	4496	29	114	17	155	17	26	1
Propoxur	6.28	1.54	4445	68	3011	278	164	53	39	14
Atrazine	7.28	2.64	2800	107	3215	98	10034	1142	28	10
Pentachlorophenol	7.59	1.99	4588	150	441	70	1039	254	13	16
Amitriptyline	8.18	4.01	4143	484	149	42	40	3	36	30
Ametryn	8.43	2.97	4032	24	1655	121	4639	410	25	6
Octocrylene	8.47	6.89	1231	235	31	21	50	18	33	14
Bisphenol A	8.66	3.62	4919	854	56	1	756	17	178	13
17 β – Estradiol- 17- acetate	8.67	5.11	3956	45	12	6	27	27	27	20
17 β – Estradiol	8.93	4.12	4359	22	5	5	0	0	0	0
Estrone	9.03	3.6	4654	26	31	2	40	5	21	17
Carbamazepine	9.09	1.89	3332	142	2093	93	8022	1332	32	12
Oxybenzone	9.23	2.55	5043	8	56	4	31	31	8	5
17 α – Ethinylestradiol	9.43	4.08	4131	339	236	22	125	91	80	11
Clofibric acid	9.54	-1.32	4230	63	2448	156	7245	1092	7	2
Ibuprofen	10.39	-0.19	4915	191	57	16	131	24	5	6
Estriol	10.8	2.5	3680	387	88	22	22	22	16	17
Fenoprop	11.48	-0.29	3940	202	2071	108	5203	600	25	18
Diclofenac	11.51	0.83	3258	39	3916	49	9993	645	19	5
Metronidazole	11.68	-0.14	851	86	127	2	282	86	5	5
Gemfibrozil	12.11	0.67	4628	17	456	29	1473	183	6	1
Naproxen	12.68	-0.73	4746	196	2292	133	6749	296	2	2
Formononetin	13.22	0.88	1081	727	35	10	61	34	27	4
Ketoprofen	13.7	-0.84	4452	107	273	29	757	41	23	6
Primidone	13.93	0.83	2627	181	14	4	82	41	2	2
Enterolactone	15.19	1.89	5530	29	241	78	23	16	114	49

Note: Error represents the standard deviation from four measurements (duplicate samples from two replicate experiments).

Figure S1: Schematic diagram of the MBR system.

Figure S2: Variation of TOC and TN removal of MBR during acclimatization to thermophilic condition (40 °C) and stable operation at 40 °C. Operated HRT, permeate flux, mixed liquor DO concentration and pH were 24 h, 2.36 L/m².h, 2.89 mg/L and 7.68, respectively.

Figure S3: TMP profile of the MBR during acclimatization to thermophilic condition (40 °C) and stable operation at 40 °C. HRT and permeate flux were 24 h and 2.36 L/m².h (equivalent to 5 L/d), respectively.

1 **LIST OF FIGURE CAPTIONS**

2 **Figure 1:** Schematic diagram of the DCMD system.

3 **Figure 2:** Permeate flux variation of MD and MBR–MD experiments: MD was carried out at
4 feed and distillate temperatures of 40 and 20 °C, respectively; and feed and distillate
5 circulation flow rate of 2 L/min (corresponding to 11.7 cm/s).

6 **Figure 3:** Rejection of the 29 TrOCs by DCMD and their log D and pK_H values. Log D and
7 pK_H illustrate the values at the pH 9. Error bars represent the standard deviation from four
8 replicate measurements. Synthetic solution containing approximately 5 µg/L of each TrOC in
9 Milli-Q water was used as the feed. The MD was carried out at the feed and distillate
10 temperatures of 40 and 20 °C, respectively. The feed and distillate circulation flow rate was 2
11 L/min (corresponding to 11.7 cm/s).

12 **Figure 4:** The fate of the 29 TrOCs in the DCMD process with their log D and pK_H values.
13 Log D and pK_H illustrate the values at the pH 9. Synthetic solution containing approximately
14 5 µg/L of each TrOC in Milli-Q water was used as the feed. The fate of each compound was
15 analyzed by mass balance considering the total input, mass in concentrate and permeate, and
16 loss due to evaporation or adsorption. Calculation of the fate of TrOCs during the MD
17 process was based on the average value of four measurements (duplicate samples from two
18 replicate experiments).

19 **Figure 5:** Removal of TrOCs by the thermophilic MBR and by the MBR-MD as well as their
20 log D and pK_H values. Log D and pK_H illustrate the values at the pH 9. MBR permeate was
21 used as the feed for MD. Error bars represent the standard deviation from two replicate
22 experiments.

1

2 **Figure 1**

1
2 **Figure 2**

Figure 3

1

2 **Figure 4**

1
2 **Figure 5**

1 LIST OF TABLES

2 **Table 1:** Physicochemical properties of the selected compounds (data from Scifinder Scholar).

Compound	Chemical Formula	Molecular Weight (g/mol)	Log D at pH 9	Water Solubility at 25°C(mg/L)	Vapour Pressure (mmHg)	pK _H at pH 9
Enterolactone	C ₁₈ H ₁₈ O ₄	298.33	1.89	200	3.29 × 10 ⁻¹³	15.19
Primidone	C ₁₂ H ₁₄ N ₂ O ₂	218.25	0.83	1,500	6.08 × 10 ⁻¹¹	13.93
Ketoprofen	C ₁₆ H ₁₄ O ₃	254.30	-0.84	554,000	3.32 × 10 ⁻⁸	13.70
Formononetin	C ₁₆ H ₁₂ O ₄	268.26	0.88	4800	8.17 × 10 ⁻¹⁰	13.22
Naproxen	C ₁₄ H ₁₄ O ₃	230.30	-0.73	435,000	3.01 × 10 ⁻⁷	12.68
Gemfibrozil	C ₁₅ H ₂₂ O ₃	250.30	0.67	263,000	6.13 × 10 ⁻⁷	12.11
Metronidazole	C ₆ H ₉ N ₃ O ₃	171.15	-0.14	29,000	2.67 × 10 ⁻⁷	11.68
Diclofenac	C ₁₄ H ₁₁ Cl ₂ NO ₂	296.15	0.83	20,000	1.59 × 10 ⁻⁷	11.51
Fenoprop	C ₉ H ₇ Cl ₃ O ₃	269.51	-0.29	230,000	2.13 × 10 ⁻⁶	11.48
Estriol	C ₁₈ H ₂₄ O ₃	288.40	2.5	32	1.34 × 10 ⁻⁹	10.80
Ibuprofen	C ₁₃ H ₁₈ O ₂	206.30	-0.19	928,000	1.39 × 10 ⁻⁴	10.39
Clofibric acid	C ₁₀ H ₁₁ ClO ₃	214.64	-1.32	100,000	1.03 × 10 ⁻⁴	9.54
17 α – Ethinylestradiol	C ₂₀ H ₂₄ O ₂	296.48	4.08	3.9	3.74 × 10 ⁻⁹	9.43
Oxybenzone	C ₁₄ H ₁₂ O ₃	228.24	2.55	2700	5.26 × 10 ⁻⁶	9.23
Carbamazepine	C ₁₅ H ₁₂ N ₂ O	236.27	1.89	220	5.78 × 10 ⁻⁷	9.09
Estrone	C ₁₈ H ₂₂ O ₂	270.36	3.6	5.9	1.54 × 10 ⁻⁸	9.03
17 β – Estradiol	C ₁₈ H ₂₄ O ₂	272.38	4.12	3	9.82 × 10 ⁻⁹	8.93
17 β – Estradiol- 17- acetate	C ₂₀ H ₂₆ O ₃	314.42	5.11	1.9	9.88 × 10 ⁻⁹	8.67
Bisphenol A	C ₁₅ H ₁₆ O ₂	228.29	3.62	73	5.34 × 10 ⁻⁷	8.66
Octocrylene	C ₂₄ H ₂₇ N	361.48	6.89	0.36	2.56 × 10 ⁻⁹	8.47
Ametryn	C ₉ H ₁₇ N ₅ S	227.33	2.97	140	1.72 × 10 ⁻⁶	8.43
Amitriptyline	C ₂₀ H ₂₃ N	277.40	4.01	83	1.50 × 10 ⁻⁶	8.18
Pentachlorophenol	C ₆ HCl ₅ O	266.38	1.99	4800	3.49 × 10 ⁻⁴	7.59
Atrazine	C ₈ H ₁₄ ClN ₅	215.68	2.64	69	1.27 × 10 ⁻⁵	7.28
Propoxur	C ₁₁ H ₁₅ NO ₃	209.24	1.54	800	1.53 × 10 ⁻³	6.28
Triclosan	C ₁₂ H ₇ Cl ₃ O ₂	289.54	4.12	19	3.26 × 10 ⁻⁵	6.18
Benzophenone	C ₁₃ H ₁₀ O	182.22	3.21	150	8.23 × 10 ⁻⁴	5.88
4-tert-butylphenol	C ₁₀ H ₁₄ O	150.22	3.37	1000	0.0361	5.15
4-tert-octylphenol	C ₁₄ H ₂₂ O	206.33	5.18	62	1.98 × 10 ⁻³	5.06

3