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Removal of trace organics by MBR treatment: the role of molecular properties

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Abstract

This study examined the relationship between specific molecular features of trace organic contaminants and their removal efficiencies by a laboratory scale membrane bioreactor (MBR). Removal efficiencies of 40 trace organic compounds were assessed under stable operating conditions. The reported results demonstrate an apparent correlation between chemical structures and the removal of trace organic contaminants by the laboratory scale MBR system. The removal of all 14 very hydrophobic trace organic compounds (Log D > 3.2) selected in this study was consistently high and was above 85%. The occurrence and types of electron withdrawing or donating functional groups appears to be another important factor governing their removal by MBR treatment. In this study, all hydrophilic and moderately hydrophobic (Log D < 3.2) compounds possessing strong electron withdrawing functional groups showed removal efficiency of less than 20%. In contrast, high removal efficiencies were observed with most compounds bearing electron donating functional groups such as hydroxyl and primary amine groups. A qualitative framework for the assessment of trace organic removal by MBR treatment was proposed to provide further insights into the removal mechanisms of trace organic contaminants by MBR treatment.

Keywords: membrane bioreactor (MBR), trace organic contaminants, sorption, biodegradation molecular structure, hydrophobicity.

1 Introduction

Major driving forces toward water recycling today are the growing demand for water from an increasing population, changing lifestyle patterns, urbanisation, and diminishing natural water resources. In addition, better public awareness about environmental protection has resulted in progressively more stringent wastewater quality discharge regulations. Despite the growing interest in water recycling, our predictive capacity regarding the ability of treatment technologies to remove specific trace organic contaminants remains very limited. This is reflected by the public reluctance to accept reclaimed water for potable reuse and the fact that most water recycling applications are currently still restricted to non-potable purposes.

Membrane bioreactors (MBRs) have recently emerged as an important technology for water recycling, capable of transforming wastewater to high quality effluent suitable for various water recycling applications (Atkinson, 2006). Becoming commercially available only around two decades ago, MBR technology has already been well proven and can provide a superior rating for most bulk water quality indicators such as pathogens, suspended solids and nutrient removal compared to conventional activated sludge (CAS) treatment processes (Melin et al., 2006; Visvanathan et al., 2000). However, the efficiency of MBR technology as a barrier for a range of trace organic contaminants such as endocrine disrupting chemicals (EDCs), pesticides, and pharmaceutically active compounds (PhACs), as well as the specific removal mechanisms involved remain unclear (Clara et al., 2005; De Wever et al., 2007; Kimura et al., 2005; Qu et al., 2009; Visvanathan et al., 2005; Wintgens et al., 2004). Previous studies have indicated significant variation in the removal of trace organics by MBRs, ranging from near complete removal for some compounds (e.g. ibuprofen and bezafibrate) to almost no removal for several others (e.g. carbamazepine and diclofenac) (Clara et al., 2005; Kimura et al., 2005; Tadkaew et al., 2010; Urase et al., 2005). The reasons for such variation are not yet fully understood.

Physicochemical properties of trace organics have been reported to significantly govern the removal efficiency by MBR treatment. Biosorption of trace contaminants driven primarily by hydrophobic interaction appears to be one of the key mechanisms controlling removal efficiency in MBR. For instance, apparent improvement in removal efficiency of certain acidic trace organics such as ibuprofen, ketoprofen, and diclofenac has been observed when MBRs are operated under acidic conditions rather than neutral conditions (Tadkaew et al., 2010; Urase et

al., 2005). This phenomenon was explained by the speciation of the compounds from hydrophilic ionic forms to much more hydrophobic forms at pH lower than their pK_a values.

A limited number of studies has shed some light on the effect of chemical structures on the removal efficiency of trace chemicals during biological treatment processes. For example, Kimura *et al.,* (2005) attributed the poor removal of clofibric acid, diclofenac, and dichloprop to the presence of chlorine in their molecular structure or their relatively complicated aromatic rings. Several studies have utilised the US-EPA-developed Biodegradation Probability Program for Windows (BIOWIN) software package which is one of the most widely used quantitative structure biodegradability relationship (QSBR) computer-based programs to estimate the biodegradability of organic compounds under aerobic conditions. Lapertot and Pulgarin investigated the biodegradability of 17 priority hazardous substances and suggested that the primary and ultimate BIOWIN models were generally suitable for removal assessment of these compounds in industrial wastewater treatment processes (Lapertot and Pulgarin, 2006). On the other hand, Yu *et al.,* (2006) reported some inconsistency between the likelihood of biodegradability predicted by BIOWIN and experimental data when they investigated the removal efficiency of 18 pharmaceutical and personal care products at a conventional municipal wastewater treatment plant (Yu et al., 2006).

Although the connection between chemical structure and removal efficiency seems highly plausible, studies to develop a capacity to predict the removal efficiency of trace organic contaminants by MBR treatment processes based on a range of molecular parameters are still limited. Because of the involvement of the many diverse and complex functional groups, the connection between chemical structure and removal efficiency has not yet been thoroughly examined in the literature. In fact, several previous attempts to identify a definitive relationship between the structures of trace organic contaminants and their removal efficiencies during CAS and MBR treatment have been unsuccessful (Joss et al., 2005; Radjenovic et al., 2007).

This study aimed to elucidate the connection between specific molecular features of trace organic contaminants and their removal efficiencies by a laboratory scale MBR. The MBR system was operated under stable conditions for an extended period to allow for a systematic examination of the removal of 40 trace organic contaminants at environmentally relevant concentrations. Hydrophobicity and molecular structures of the selected trace organic

compounds were carefully delineated and correlated to their removal efficiencies. Key factors governing the removal efficiencies of trace organic contaminants were identified and reported.

2 Materials and methods

2.1. Laboratory scale MBR system

A laboratory-scale MBR system was used in this study. Detailed description of this MBR system is available elsewhere (Tadkaew et al., 2010). The system consisted of a glass reactor, a continuous mixer, two air pumps, a pressure sensor, and influent and effluent pumps. Two ZeeWeed-1 (ZW-1) submerged hollow fibre ultrafiltration membrane modules supplied by Zenon Environmental (Ontario, Canada) were used in this set-up. The membrane has a nominal pore size of 0.04 μm. Each module has an effective membrane surface area of 0.047 m^2. A Neslab RTE 7 equipped with a stainless steel heat exchanging coil was used to maintain a constant temperature in the MBR. A personal computer was used to control the permeate peristaltic pump to operate on a 14 minute suction and 1 minute off cycle to provide relaxation time to the membrane modules. Flow rate of the influent pump was matched with that of the permeate pump to maintain a constant reactor volume. The continuous mixer was used to ensure homogeneous conditions of the mixed liquor and to prevent the settling of biomass.

2.2. Synthetic wastewater

A synthetic wastewater simulating municipal sewage was used to ensure a stable feeding rate throughout the experiment. Concentrated stock solution was prepared and stored in a refrigerator at 4 ^{o}C. It was then diluted with MilliQ water on a daily basis to make up a feed solution containing glucose (400 mg/L), peptone (75 mg/L), KH_2PO_4 (17.5 mg/L), $MgSO_4$ (17.5 mg/L), $FeSO_4$ (10 mg/L), and sodium acetate (225 mg/L). This composition was based on a previous study (Zhang et al., 2006).

2.3. Trace organic compounds

In this study, 40 organic compounds were selected to represent four major trace organic groups of concern in water reuse applications – namely pesticides, pharmaceutically active compounds, steroid hormones, and other endocrine disrupting chemicals. The selection of these model trace

120 organic compounds was also based on their widespread occurrence in domestic sewage and their
121 diverse physicochemical properties (e.g. hydrophobicity and molecular weight). The effective
122 hydrophobicity of these compounds varies significantly as reflected by their Log D values at pH
123 8 (see supplementary data) which is typical of an activated sludge reactor (Wells, 2006). The
124 most hydrophilic compound is enalapril with Log D at pH 8 of –1.21 and the most hydrophobic
125 compound is nonylphenol with Log D at pH 8 of 6.19. All selected trace organic compounds
126 were of analytical grade. A combined stock solution was prepared in pure acetonitrile. The trace
127 organic stock solution was kept in a freezer and was used within less than a month.

128 ## *2.4. Analytical techniques*

129 The analysis of the model trace organics was based on a previously reported method (Tadkaew et
130 al., 2010; Vanderford and Snyder, 2006). Analytes were extracted using 5 mL, 500 mg solid
131 phase extraction hydrophilic/lipophilic balance (HLB) cartridges (Waters, Millford, MA, USA).
132 Samples were spiked with a solution containing 50 ng of an isotopically labeled version of each
133 analyte. The sample was then loaded onto the cartridges at 15 mL/min, after which the cartridges
134 were rinsed with 5 mL of reagent water and dried with a stream of nitrogen for 30 min. Loaded
135 cartridges were stored at – 4 °C in sealed bags until elution and analysis.

136 Analytes were separated using an Agilent (Palo Alto, CA, USA) 1200 series high performance
137 liquid chromatography (HPLC) system equipped with a 150 x 4.6 mm, 5 μm particle size, Luna
138 C18 (2) column (Phenomenex, Torrence CA, USA). Mass spectrometry was performed using an
139 API 4000 triple quadrupole mass spectrometer (Applied Biosystems, Foster City, CA, USA)
140 equipped with a turbo-V ion source employed in both positive and negative electro-spray modes.
141 Steroid hormones were analysed using an atmospheric pressure chemical ionisation method and
142 all other compounds were analysed using an electro-spray ionisation method. For each analyte
143 and internal standard a precursor ion and two product ions were monitored for reliable
144 confirmation. Relative retention times of the analyte and isotopically labeled internal standard
145 were also monitored to ensure correct identification (Vanderford and Snyder, 2006).

146 Standard solutions of all analytes were prepared at 1, 5, 10, 50, 100, 500 and 1000 ng/mL. A
147 relative response ratio of analyte/internal standard over a 1 – 1000 ng concentration range was
148 generated enabling quantification with correction for losses due to ion suppression and

incomplete SPE recovery. All calibration curves had a correlation coefficient of 0.99 or better. The limit of reporting was determined using an s/n ratio of greater than 10.

Conductivity and pH were measured using an Orion 4-Star Plus pH/conductivity meter. Total organic carbon (TOC) and total nitrogen (TN) were analysed using a Shimadzu TOC/TN-V_{CSH} analyser. TOC analysis was conducted in non-purgeable organic carbon (NPOC) mode. Samples were kept at 4°C until analysed and calibrations were performed in the range between 0 and 1000 mg/L and 0 to 100 mg/L for TOC and TN, respectively. Mixed liquor suspended solid (MLSS) and mixed liquor volatile suspended solid (MLVSS) contents in the MBR were measured in accordance to the Standard Methods for the Examination of Water and Wastewater (Clescerl et al., 2005).

2.5. MBR experimental protocol

The MBR was seeded with activated sludge from the Wollongong sewage treatment plant, NSW, Australia. After the initial start-up process, which lasted about 2 months, a small amount of sludge was regularly extracted from the reactor to keep the sludge age at approximately 70 days. The hydraulic retention time was set at 24 hours, corresponding to a permeate flux of 4.3 L/m^{2}h. The MBR temperature and dissolved oxygen content were kept constant at 20.0±0.1^{o}C and 2±1 mg/L, respectively. Performance of the MBR system with regard to basic water quality parameters was then monitored for an extended period of more than four weeks.

Once stable operation had been achieved, trace organic contaminants were continuously introduced into the feed solution to make up a concentration of approximately 2 µg/L of each selected compound. The investigation with trace organics was over a period of four weeks during which no sludge was withdrawn from the reactor. The feed solution was kept in a stainless steel reservoir at controlled room temperature (20±2 ^{o}C). Feed and permeate samples were taken twice a week in duplicate and solid phase extraction was conducted immediately for subsequent trace organic analysis. Removal efficiency was calculated as $R = 100 \times \left(1 - C_{Eff} / C_{Inf}\right)$, where C_{Eff} and C_{Inf} are effluent (permeate) and influent concentrations (ng/L) of the trace organic compound, respectively. It is noted that complete degradation of an organic compound may follow different pathways and undergo several steps. Therefore, the term removal here does not necessarily indicate complete degradation of the trace organics, but rather a loss of the specific trace

chemical molecule. In many cases, stable intermediates or 'metabolites' may be produced, but detailed consideration of these intermediates is beyond the scope of the current study.

3 Results and discussion

3.1. Performance stability of the MBR

In this study, synthetic feed solution was used to ensure a consistent influent composition. The MBR showed stable and good performance with respect to all key water quality parameters. The stable performance continued even following the introduction of the trace organic contaminants to the feed solution. A notable exception, however, was a significant decline in the removal of total nitrogen (TN) immediately after the introduction of the trace organic contaminants from almost complete removal to as low as 60%. The decrease in TN removal can be explained by the introduction of acetonitrile, the solvent used to introduce the trace organics, to the influent. The MBR system used in this study was operated under aerobic conditions and therefore is not expected to have any biological denitrification capacity. The synthetic feed solution was deficient in nitrogen, and therefore, the initial high TN removal observed here could be attributed to the conversion of dissolved organic nitrogen to biomass, which would then be retained by the membrane. Because acetonitrile was used as a carrying solvent for the introduction of the trace organic contaminant cocktail into the feed solution, the introduction of trace organic contaminants into the feed solution resulted in a significant increase in TN in the influent from 12 mg/L to approximately 49.5 mg/L. This was assumed to be the main reason for the observed decrease in TN removal. The increase in nitrogen content of the feed water did not exert any discernible impact on any other biological performance indicators of the MBR system. There was a slight increase in the MLSS content in the reactor from 8.6 g/L to 10.0 g/L over the duration of the experiment of approximately one month while the MLVSS/MLSS ratio remained constant at approximately 0.9. Other basic performance parameters including TOC removal efficiency (98%), pH of the MLSS (7.5±0.1), effluent conductivity (559±19 µS/cm) were also relatively stable during the entire experiment . In addition, no abnormal transmembrane pressure increase was observed following the introduction of the trace contaminants to the feed solution (data not shown).

Stable performance of the MBR system could also be observed with respect to the removal of trace organic contaminants (Figure 1). It is noted that the error bars shown in Figure 1 represent the standard deviations of eight influent and effluent samples, regularly collected in replicate throughout the experiment. It is also notable that the removal efficiencies of the 40 compounds investigated in this study vary significantly ranging from negligible removal (e.g.: atrazine, carbamazepine, dilatin, and trimethoprim) to removal to below the analytical detection limit (e.g.: 17β-estradiol, testosterone, and triclocarban), indicating a removal of at least 98%. The observed significant variation in the removal efficiency of the trace organic contaminants by MBR treatment indicates that improved understanding of the key factors that govern the elimination of specific chemicals is required to enable prediction of MBR treatment performance for any particular chemical or class of chemicals.

[FIGURE 1]

3.2. Removal of trace organic contaminants

A logical approach to qualitatively predict the effectiveness of MBR treatment for the removal of a wide range of trace organic contaminants is to evaluate their removal efficiency according to the intended applications or origins of these compounds. Accordingly, Table 1 summarises the removal efficiencies of the 40 compounds selected in this study. Data previously reported in other studies, whenever available, are also included for comparison purposes. With caffeine being the only noteworthy exception, results reported here are in good agreement with the literature data. The mean removal efficiency of caffeine observed in our study is 49.6 %, which is substantially lower than the previously reported values (Kim et al., 2007; Snyder et al., 2007). In a recent study, Santos et al., (2009) examined the performance of four CAS wastewater treatment plants in Seville city (Spain). They reported a highly variable caffeine removal efficiency among these four treatment plants with the mean value ranging from as low as 44% up to 75% (Santos et al., 2009). Given the similarity between MBR and CAS treatment, it is possible that this discrepancy can be explained by the differences in operating conditions. The literature data presented in Table 1 are from a range of sources with different operating conditions and system arrangements. The reported experimental results confirm that the MBR system used in this study behaved well within the range of typical performance data from other systems. Therefore, the results presented in this study and the conclusion drawn from them

would be broadly applicable and generalisable to most typical MBR systems. In fact, data presented in Table 1 suggest that some generalisation can be made about certain groups of compounds.

[TABLE 1]

All the three pesticides investigated in this study showed very low removal efficiencies. Atrazine, a chloro-triazine herbicide, was removed at a rate of less than 5%. It has been reported to be poorly removed both in CAS and MBR (Bernhard et al., 2006) and that a major removal mechanism was sorption onto withdrawn sludge (Bouju et al., 2008). Linuron is a dichloro-phenylurea herbicide. Despite being a widely used herbicide, no reports on the removal of Linuron in CAS or MBR could be found. However, its slow natural attenuation rate in various soils and the evolution of more toxic and persistent chloroaniline intermediates in the process have been reported (Dejonghe et al., 2003). A mean removal of 21% of linuron as achieved in our MBR, therefore, appears to be consistent with the reported recalcitrance of this compound. DEET is a toluamide compound and is the most common active ingredient in insect repellants. In this study, a mean removal of 4.6% of DEET was recorded during MBR treatment. This removal efficiency is at the lower end of range reported in other published studies. Bernhard et al., (2006) reported nil to over 50% removal of DEET by MBR treatment and suggested that DEET removal efficiency was dependent on the sludge retention time. Kim et al. (Kim et al., 2007) reported no removal of DEET in their study; however, no information about the SRT was provided. The highest removal efficiency of DEET of 78% was reported by Snyder et al., calculated from a one off sampling event at a pilot scale treatment facility (Snyder et al., 2007).

Near complete removal or removal to below the analytical limit of all eight steroid hormones and three other EDCs selected for investigation (bisphenol A, nonylphenol, and t-octylphenol) were observed in this study. These results are consistent with other published studies (Table 1). It is noteworthy that all of these compounds possess significant hydrophobicity and bear a similar molecular backbone structure; which may, in part, explain the similarities of their removal efficiencies.

No generalistion can be inferred for any of the six therapeutic classes of pharmaceuticals investigated in this study (Table 1). Their removal efficiencies by MBR treatment vary widely even within the same class of compounds. The removal efficiencies of the five non-steroidal

anti-inflammatory drugs (NSAIDs) differ remarkably from one another. For example, ibuprofen registers a removal efficiency of 97% whereas the removal efficiency of diclofenac is only 17%. Unlike the other NSAIDs, diclofenac is a chlorinated compound, which can possibly explain its recalcitrant behavior in MBR treatment. Significant variation in the removal efficiency can also be observed among compounds used as anti-depressants and mood stabilizers. Dilantin, primidone and carbamazepine were poorly removed, whereas the removal efficiencies of clozapine, risperidone, and amitriptyline were 85% and higher. Given the considerable dissimilarity in the molecular structure among these anti-depressants and mood stabilizers, differences in their removal efficiencies can be expected. Further analysis of the molecular structures of these compounds is presented in section 3.3.2. Significant variation in removal efficiency was observed among the other pharmaceutical groups (cardiovascular and other drugs) and can again be attributed to their diverse molecular structures (Table 1 and supplementary data 1). Among the hypolipidemic agents (lipid lowering drugs) investigated in this study, simvastatin is a hydrophobic compound with Log D (at pH 8) of 4.41 and the compound registers a removal efficiency of 98% (Table 1). Simvastatin hydroxyacid) shares the same molecular backbone structure with that of simvastatin. However, the 3, 5–dihydroxy–heptanoic acid functional group of simvastatin hydroxyacid renders the compound much more hydrophilic (Log D at pH 8 of 0.64). Consequently, simvastatin hydroxyacid shows a much lower removal efficiency of 60% in comparison to that of the related compound simvastatin.

Results reported in Table 1 suggest that the classification of trace organics according to their intended use or origin can only be used to qualitatively predict the removal efficiencies of compounds of similar molecular structure, having similar molecular features or physicochemical properties. In fact, certain molecular features and physicochemical properties of the trace organic contaminants appear to be the underlying factors governing their rate of removal during MBR treatment.

3.3. Role of molecular features

Attempts to fit the removal efficiency data obtained in our study and the corresponding available biodegradability scores from BIOWIN model did not result in any meaningful correlations (data not shown). Although this result is somewhat surprising, it does not necessarily invalidate the model. BIOWIN is essentially a statistical model and the discrepancies may have arisen to some

296 extent due to the fact that the BIOWIN scores were derived from batch tests, which cannot
297 effectively replicate the biological conditions of an MBR. It is also noteworthy that only three
298 out of 40 compounds investigated in this study were included in the database which has been
299 used for the development of BIOWIN. Furthermore, BIOWIN would not account for the
300 adsorption of trace organics to biosolids which can be an important removal mechanism along
301 with biodegradation. Given the poor correlation between the removal efficiencies experimentally
302 obtained in this study and the BIOWIN biodegradability scores, it is necessary to further
303 examine the key physicochemical properties and molecular features that can govern the removal
304 efficiency of trace organic compounds.

305 *3.3.1 Effects of hydrophobicity*

306 The removal of trace organic contaminants by an activated sludge treatment process is a complex
307 function of both sorption and biological degradation. In a CAS treatment process, the sludge-
308 bound contaminants can be subsequently removed via sludge withdrawal. In addition, sorption of
309 trace organic contaminants to biosolids results in a longer residence time in the reactor, which
310 may lead to further removal via biodegradation. Because the MLSS content and sludge retention
311 time of typical MBR processes are much higher than those of CAS treatment, sorption has been
312 suggested as a major removal mechanism for the removal of trace organic contaminants by MBR
313 treatment. In a systematic survey of the literature data, Wells suggested that the sorption of a
314 trace organic contaminant to the activated sludge could be assessed by considering the Log D
315 value of the compound at a given pH (Wells, 2006). Experimental results presented in Figure 2
316 indicate that this finding can be extended to MBR treatment. There appears to be a 'removal
317 envelop' that can be defined by the hydrophobicity of the trace organic contaminants (Figure 2).
318 Removal of the very hydrophobic (Log D > 3.2) compounds is probably dominated by sorption
319 to the activated sludge facilitating enhanced biological degradation in some cases. Therefore,
320 these compounds consistently showed high removal efficiency (above 85%). As the Log D value
321 of the compounds decreased to below 3.2, sorption of these trace organic contaminants onto the
322 activated sludge was no longer a dominating removal mechanism and the removal efficiency of
323 these compounds is much more strongly influenced by their intrinsic biodegradability. As a
324 result, the removal efficiency of trace organics with low Log D values (at pH 8) varies
325 significantly from less than 20% to removal to below the analytical detection limit
326 (corresponding to a removal of at least 98%). Of particular note in Figure 2 is a cluster of five

327 compounds that show very low removal efficiencies despite their moderately high
328 hydrophobicity (Log D in the rage from 2 to 3.2). It is also noteworthy that all five compounds
329 possess one or several electron withdrawing functional groups, such as a chlorine atom or amide
330 group. Results reported here suggest that individual molecular features can also be an important
331 factor governing the removal efficiency of trace organics during MBR treatment.

332 **[FIGURE 2]**

333 *3.3.2 Effects of molecular weight*

334 The molecular weights of the trace organics studied here ranged from 151 g/mol (paracetamol) to
335 455 g/mol (verapamil). There appears to be a weak but nevertheless discernible correlation
336 between the removal efficiency of these trace organics and their molecular weights (Figure 3).
337 Compounds with molecular weight of more than 300 g/mol were relatively well removed
338 (>60%), while the removal efficiencies those with molecular weight of less than 300 g/mol
339 varied from almost no removal to more than 98% (removal beyond the analytical detection
340 limit). A plausible explanation for this observation could be the relative hydrophobicity (log D at
341 pH 8 in the range from 2.03 to 5.74, see supplementary data) of the compounds having molecular
342 weight of more than 300 g/mol. In addition, in this study, removal efficiency does not necessarily
343 represent a complete mineralisation of the compound. Compounds with higher molecular weight
344 may have more branches, which would offer more opportunities for the microbes to selectively
345 cleave a certain target site and initiate degradation.

346 **[FIGURE 3]**

347 *3.3.3 Effect of chemical structure*

348 Experimental results obtained in this study confirm the possible role of molecular functional
349 groups in governing the removal of moderately hydrophobic and hydrophilic trace organic
350 compounds by MBR treatment. The 40 trace organic compounds investigated in this study can
351 be systematically categorized into three groups. Group A consists of compounds with Log D at
352 pH 8 of above 3.2. As discussed above, sorption was a dominant removal mechanism for these
353 hydrophobic compounds and the removal efficiencies of all compounds of group A were above
354 85% (Figure 2). To further elucidate the role of different molecular features, the rest of the
355 compounds can be categorised in terms of ring structure (heterocyclic/ non-heterocyclic, mono
356 or polynuclear) and functional groups (electron withdrawing/donating moieties). Figure 4 shows

357 the removal efficiency as a function of ring structure, whereas Figure 5 presents the compounds
358 under three distinct categories (B, C and C*) based on the presence and types of electron
359 withdrawing or donating functional groups.

360 **[FIGURE 4]**

361 **[FIGURE 5]**

362 No clear distinction between heterocyclic or non-heterocyclic compounds removal could be
363 observed in this study (Figure 4). Similarly, no discernible trend in terms of mononuclear or
364 polynuclear compound could be observed. It is generally considered that simple aliphatic and
365 monocyclic aromatic compounds are readily degradable, while polycyclic structures may be
366 more persistent (Jones et al., 2005). However, irrespective of the mono or polynuclear structure,
367 degradation can initiate by the mere cleavage of a side chain structure and then further
368 mineralisation may depend on the complexity of the nucleus. In this study, removal indicates the
369 loss of the parent structure, and not complete mineralisation. Therefore, the absence of any
370 discernible correlation between the removal efficiency and ring structure is not entirely
371 unexpected.

372 As shown in Figure 4, the compounds containing strong electron withdrawing groups (B)
373 consistently showed very low (<20%) removal efficiency. According to Knackmuss
374 (Knackmuss, 1996), the initial electrophilic attack by oxygenases of aerobic bacteria is often a
375 rate-limiting step and the first of a chain of reactions responsible for the biodegradation of many
376 organic compounds. As a result, the presence of electron withdrawing functional groups
377 generates an electron deficiency and thus renders the compounds less susceptible to oxidative
378 catabolism. Electron donating functional groups, on the other hand, render the molecules more
379 prone to electrophilic attack by oxygenases of aerobic bacteria. Consequently, the removal
380 efficiencies of organic compounds bearing strong electron donating functional groups were, in
381 most cases, much higher than those of group B in Figure 4. The removal of the compounds
382 containing both electron withdrawing and donating groups however showing less than 70%
383 removal have been placed in group C*.

384 The elucidation of the overall influence of these functional groups and particularly their
385 opposing effects on the biodegradability of trace organic compounds is a complex task and
386 would generally require extensive exercise involving simultaneous application of quantitative

387 structure activity relationship and biochemical interpretation, as demonstrated for a particular
388 compound class (N-heterocycles) by Philipp et al. (2007) . Because a large number of diverse
389 compound classes were studied here, such a rigorous approach falls beyond the scope of this
390 paper. Nevertheless some general inference, can be drawn from the results in the light of
391 metabolic pathway information retrieved from the sparse literature and also from biodegradation
392 prediction tools such as UM-BBD PPS (Wackett and Ellis, 1999).

393 The biodegradation of amide-only compounds needs to proceed from conversion of the amide
394 group to primary amine (Hart and Orr, 1975). As suggested by the low removal of
395 carbamazepine and dilantin, this pathway appears to be extraordinarily recalcitrant. All the tested
396 compounds possessing only methyl (weak electron donor) and amide (strong electron
397 withdrawing) groups including primidone, DEET and meprobamate were very poorly removed.
398 The presence of methyl groups means that the degradation could initiate from conversion of the
399 methyl group to alcohol (Shaw and Harayama, 1992), bypassing the recalcitrant amide
400 conversion. However, methyl and other aliphatic groups have very weak electron donating
401 capacity, and thus in presence of a strong electron withdrawing group they may have limited
402 activating effect.

403 All three compounds (i.e. atenolol, enalapril and caffeine) containing both the amine (strong
404 electron donating) and the amide (strong electron withdrawing) functional groups were quite
405 well removed (50-97%). Degradation of compounds with amine group may proceed by
406 converting the existing amine to a less substituted form of amine and aldehyde/ketone (Hakil et
407 al., 1998). Comparing the performance of these three compounds (containing amide and amine
408 groups) with that of primidone, DEET and meprobamate (containing amide and methyl groups),
409 it appears that the co-existence of the amine, and not the methyl group, with the amide group
410 may make these compounds more amenable to biodegradation. The excellent removal of another
411 amide-containing compound paracetamol can be attributed to the presence of the hydroxyl group
412 which is also a strong electron donating functional group. In this context, it is noteworthy that the
413 entire set of hydroxyl group-containing compounds tested in this study showed high removal.
414 Such positive impact of hydroxyl group on biodegradation is in line with the literature reports
415 (Tunkel et al., 2000).

Halogenated organics comprise a superset which has many antimicrobial as well as human toxic and carcinogenic industrial chemicals as members (Häggblom and Bossert, 2004). Linuron contains both halogen and amide groups and accordingly demonstrated low removal. Interestingly, of the halogenated compounds with amine group, risperidone (containing amine, methyl and amide) and hydroxyzine (containing amine and hydroxyl) showed good removal while diclofenac (containing amine and carboxylic) and atrazine (containing amine and methyl) showed poor removal. Literature review regarding the metabolic pathways of these compounds provided further insights but could not resolve the paradox. It is suggested in the literature that the metabolism of hydroxyzine can proceed simultaneously through the conversion of amine to aldehyde/ketone or through oxidation of the alcohol moiety to a carboxylic acid (Campoli-Richards et al., 1990). In case of risperidone the degradation may initiate via 9-hydroxylation and/or via N-dealkylation at the piperadine nitrogen (Mannens et al., 1993). Diclofenac has been suggested to be degraded by hydroxylation of the 1-amino-2-unsubstituted aromatic fragment (Marco-Urrea et al., 2010). The degradation of atrazine, on the other hand, has been reported to be initiated through N-monodealkylation, hydroxylation of the isopropyl or tert-butyl moiety (Lang et al., 1996) or in the rare case via oxidation of the s-triazine ring to hydroxy-s-triazine (De Souza et al., 1995). While it is certain that the aerobic oxidation of the halogenated compounds initiate from the co-existing electron withdrawing groups and not via dehalogentaion, it is not clear why despite seemingly similar metabolic pathways (e.g., hydroxylation, dealkylation) the compounds exhibit different extents of recalcitrance.

Notably hydroxylation of the vicinal unsubstituted aromatic fragment and the mono-carbon-substituted benzenoid are the predominant initial degradation pathways (Quintana et al., 2005) for the well removed compounds ibuprofen (97%) and ketoprofen (70%), respectively. It is, however, not clear why despite possessing the similar metabolic pathway as ketoprofen, triamterene registered a rather low removal of 28%. The absence of any literature data regarding triamterene removal by CAS or MBR restricts further clarification regarding this matter. The only possible distinction that can be offered at this stage is that triamterene is a heterocyclic compound.

It is known that the degradation of compounds with an aromatic-aliphatic ether fragment can proceed by ether cleavage, producing phenol derivative and aldehyde (Bernhardt et al., 1988). Of the tested compounds that fit into this category gemfibrozil (98%) and verapamil (87%) were

447 well removed while omeprazol (62%) and naproxen (40%) demonstrated moderate removal, and
448 trimethoprim was poorly removed (16%). The predominant biodegradation route of naproxen
449 and trimethoprim appears to be via ether cleavage (Quintana et al., 2005); however, the
450 degradation can potentially proceed via conversion of tertiary/secondary aliphatic to
451 corresponding alcohol. On the other hand, in addition to the ether cleavage verapamil may be
452 degraded by N-demethylation (Unadkat et al., 2008). The degradation of omeprazole can also
453 initiate from the conversion of di-[C,O]-substituted sulfoxide to sulfone (Kanazawa et al., 2003),
454 and gemfibrozil can be degraded also through conversion of aromatic methyl to primary alcohol
455 (Hermening et al., 2000). The discrepancy in the removal rates of these compounds may,
456 therefore, be attributed to the distinct alternate routes of biodegradation, which may govern the
457 overall removal.

458 The combined effect of functional groups and hydrophobicity on the removal of trace organic
459 compounds by the MBR is shown in Figure 6. It is evident from the above discussion that all the
460 aspects of chemical structure i.e., aromatic moiety, ring composition, substituent groups, side
461 chain and associated metabolic pathway need to be taken into account in conjunction with
462 physical parameters namely hydrophobicity and molecular weight to explain observed
463 variabilities in trace organic removal by MBR.

464 As noted earlier, in an MBR, adsorption and biodegradation may simultaneously play important
465 roles. However, for the compounds with low hydrophobicity, properties such as molecular
466 weight, ring structure and functional groups may influence the biodegradability and consequently
467 govern the overall removal. Although some similarities can be expected, the purpose of this
468 section is clearly not to describe the biodegradability of trace organics in biological wastewater
469 treatment in general. The comprehensive discussion on biodegradability and metabolic pathway
470 as furnished here serves the important purpose of explaining the removal of compounds with low
471 hydrophobicity in the MBR.

472 **[FIGURE 6]**

473 *3.3.4 A framework to predict removal efficiency*

474 Notwithstanding a few exceptions which will be subjected to further investigation, results
475 reported in this study indicate a clear link between molecular features and the removal of trace
476 organic compounds by MBR treatment. Figure 7, based on the data presented in this study,

outlines a qualitative and schematic framework for the prediction of the removal efficiency of any given compound by an aerobic MBR treatment process. Given the similarities between CAS and MBR treatment, the framework proposed here may also be applicable to CAS treatment processes to some extent. However, differences in operational conditions between MBR and CAS must be carefully considered. For example, because MBR usually operates at a much longer sludge retention time and can offer complete retention of the biomass, hydrophobicity of the trace organic compounds would have a more profound impact on their removal efficiency by MBR than that by CAS. For the compounds with low hydrophobicity, where biodegradability is likely to govern the overall removal, the performance of CAS operated under the same loading and sludge retention time may be comparable to MBR (Clara et al., 2005). However it also needs to be noted that MBR may facilitate growth and maintenance of special degrading microbes (Hai et al., 2010) which may contribute to enhanced removal of compounds with low hydrophobicity. To derive further insight into this matter long-term investigation with the same set of data comparing the performance of CAS and MBR will need to be carried out. That, however, is beyond the scope of this study. It is prudent to note that this proposed framework has been based on a limited set of data of only 40 compounds. Nevertheless, this framework has the potential to provide significant insights to the removal of trace organic contaminants by MBR treatment. With ongoing scientific and dedicated efforts in this field, the framework can be a foundation for a future quantitative model for the prediction of trace organic removal by MBR and CAS treatment.

[FIGURE 7]

4 Conclusion

Results reported in this study indicate an apparent correlation between molecular features and the removal of trace organic contaminants by a laboratory scale MBR system. The removal efficiencies of all 14 very hydrophobic trace organic compounds (Log D at pH 8 > 3.2) selected in this study consistently showed removal efficiencies in the range between 85% to removal to below the analytical detection limit, indicating a removal of at least 98%. The occurrence of electron withdrawing or electron donating functional groups appears to be another important factor governing their removal by MBR treatment. All hydrophilic and moderately hydrophobic (Log D < 3.2) compounds possessing strong electron withdrawing functional groups consistently

showed removal efficiency of well below 20%. In contrast, high removal efficiency was observed with most compounds bearing electron donating functional groups such as hydroxyl groups and primary amine groups. Nevertheless, further analysis also revealed several exceptions which remained unexplainable given the current lack of biochemical data about these compounds of interest. Based on the reported data, a qualitative framework for the assessment of trace organics removal by MBR treatment was presented.

5 Acknowledgements

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Table 1: Removal efficiencies of the selected trace organic contaminants (n=16) obtained in this investigation and corresponding values recorded in the literature.

Class	Compound	This study (%) (Average ± Std)	Literature (%) (min – max)	References [a]
Pesticides	Atrazine	4.4 ± 3.7	9 – 40	1,2
	Linuron	21.1 ± 4.1	not available	
	DEET	4.6 ± 2.4	0 – 78	1, 3, 4
Non-steroidal anti-inflammatory	Paracetamol	95.1 ± 3.4	≥99	3, 5-7
	Ketoprofen	70.5 ± 0.8	43.9 – 95	5-6, 8-9
	Naproxen	40.1 ± 2.8	36 – 91.6	3, 5-7, 9-10
	Ibuprofen	96.7 ± 0.7	≥90	1,3, 5-7, 9, 11-14
	Diclofenac	17.3 ± 4.2	0 – 87.4	1,3, 5,6, 9, 12, 13, 15, 16
Anti-depressants & mood stabilizers	Clozapine	84.8 ± 5.4	not available	
	Risperidone	95.8 ± 2.2	not available	
	Primidone	12.4 ± 4.3	not available	
	Carbamazepine	13.4 ± 4.3	0 – 13	1,5, 7, 11, 13, 17
	Dilantin	5.4 ± 3.6	0 – 12	4
	Amitriptyline	97.8 ± 0.8	not available	
Antibiotic & antiseptic	Triclosan	>91.8	61 – 95	3, 4
	Triclocarban	>98.4	not available	
	Sulfamethoxazole	91.9 ± 0.6	52 – 80.8	3,5,6, 11-13, 18
	Trimethoprim	16.6 ± 3.7	0 – 90	3, 6, 11, 18
Hypolipidemic agents	Simvastatin	97.9 ± 0.9	not available	
	Gemfibrozil	98.95 ± 0.1	32.5 – 90	5, 6, 11
	Sim-hydroxyacid	59.6 ± 2.8	not available	
Cardiovascular drugs	Atenolol	96.9 ± 0.2	70	5, 9
	Verapamil	88.4 ± 6.1	not available	
	Enalapril	97.1 ± 0.1	not available	
Other drugs	Triamterene	27.9 ± 6.3	not available	
	Hydroxyzine	>92.2	not available	
	Meprobamate	14.5 ± 3.3	not available	
	Caffeine	49.6 ± 4.1	98 – 99	3, 4
	Omeprazole	62.1 ± 3.5	not available	
Steroid hormones	Estrone	98.0 ± 0.2	96.3	13, 19
	17β-estradiol	>99.4	100	13, 19
	Androstenedione	>99.5	not available	
	Estriol	98.2 ± 1.9	>99	13
	Testosterone	>99.4	not available	
	Etiocholanolone	>99.4	not available	
	Androsterone	>99.3	not available	
	17α-ethynylestradiol	93.5 ± 1.2	81.9 – 93.6	19
Other EDCs	Bisphenol A	90.4 ± 3.1	68.9 – 99.0	10, 12, 13, 19, 20
	Nonyphenol	99.3 ± 0.2	0 – 88	12, 13, 21, 22
	t-octylphenol	94.5 ± 1.1	44.9 – 99.0	13

687 [a] References: [1](Bernhard et al., 2006); [2](Bouju et al., 2008); [3](Kim et al., 2007); [4](Snyder et al.,
688 2007); [5](Radjenovic et al., 2007); [6](Radjenovic et al., 2009); [7](Joss et al., 2005); [8](Kimura et al.,
689 2005); [9](Quintana et al., 2005); [10](Urase et al., 2005); [11](Reif et al., 2008); [12](Kreuzinger, 2004);
690 [13](Clara et al., 2005); [14](Smook et al., 2008); [15](Gonzalez et al., 2006); [16](Abegglen et al., 2009);
691 [17](Clara et al., 2004); [18](Göbel et al., 2007); [19](Lyko et al., 2005); [20](Chen et al., 2008); [21](Cirja
692 et al., 2006); [22](Hu et al., 2007).
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LIST OF CAPTIONS

Figure 1: Influent and effluent concentration of the selected trace organic contaminants. Samples were collected twice a week and in duplicate for four weeks. Error bars represent the standard deviation of 16 measurements.

Figure 2: The relationship of removal of trace organic compounds with effective hydrophobicity (Log D). The MLSS pH during the experiment was 7.5±0.1. Log D values were obtained from the SciFinder Scholar (ACS) database. Error bars represent the standard deviation of 16 measurements.

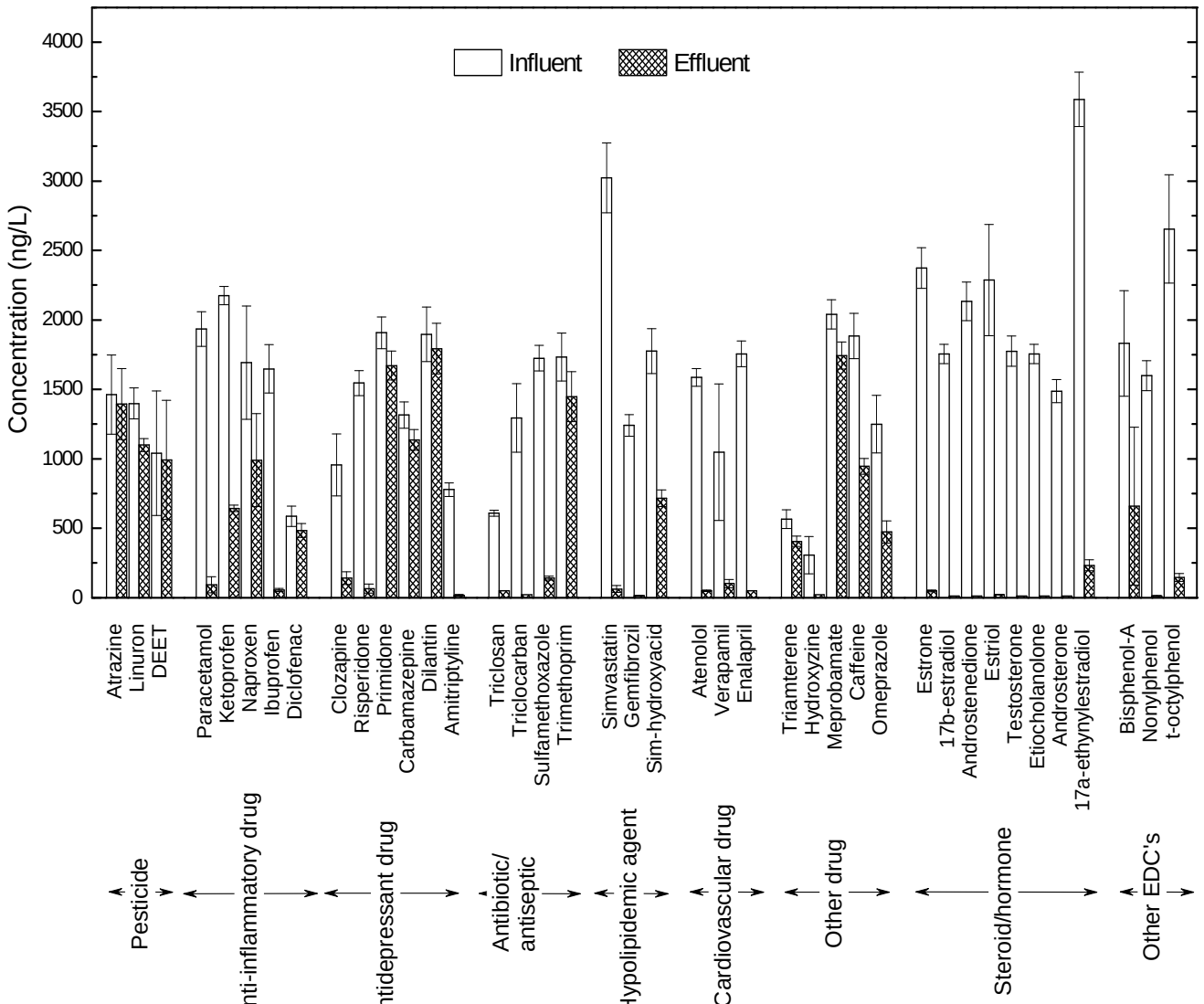
Figure 3: Removal efficiency of trace organic compounds as a function of their molecular weight. Error bars represent the standard deviation of 16 measurements.

Figure 4: Removal efficiency as a function of ring structure. Error bars represent the standard deviation of 16 measurements.

Figure 5: Compound classification according to the presence of electron donating or withdrawing functional groups.

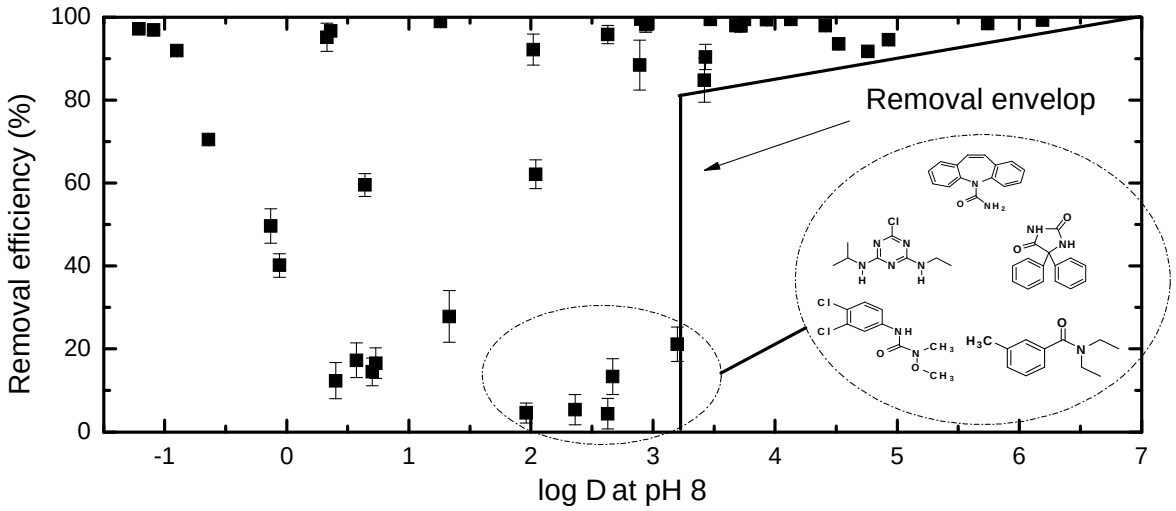
Figure 6: The combined effects of functional group and hydrophobicity on the removal of trace organic compounds by the MBR. Error bars represent the standard deviation of 16 measurements. Group A: all compounds with Log D > 3.2 (at pH 8). Groups B, C, and C* are defined in Figure 5.

Figure 7: A qualitative framework for the prediction of trace organic removal by MBR treatment.



714

715 **Figure 1**



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717 **Figure 2**

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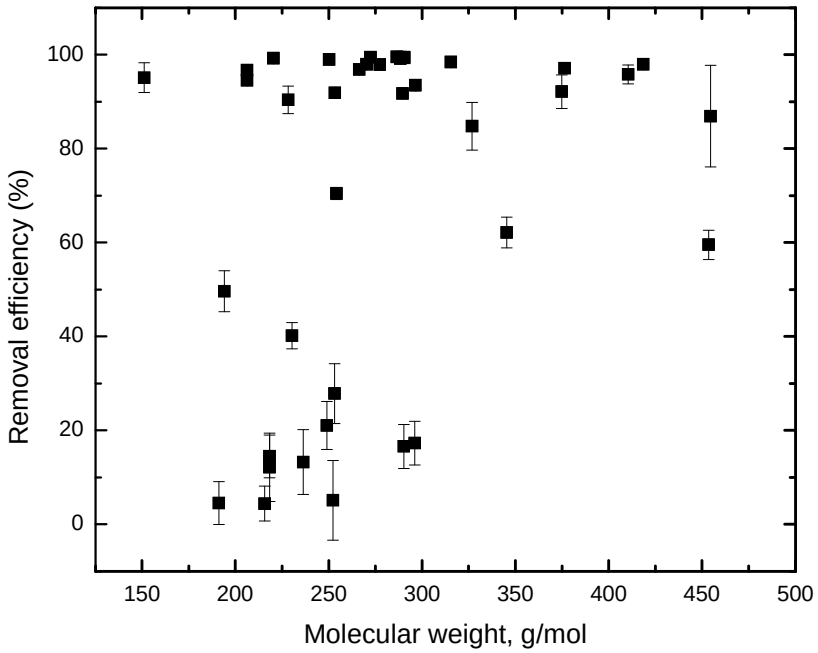

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720 **Figure 3**

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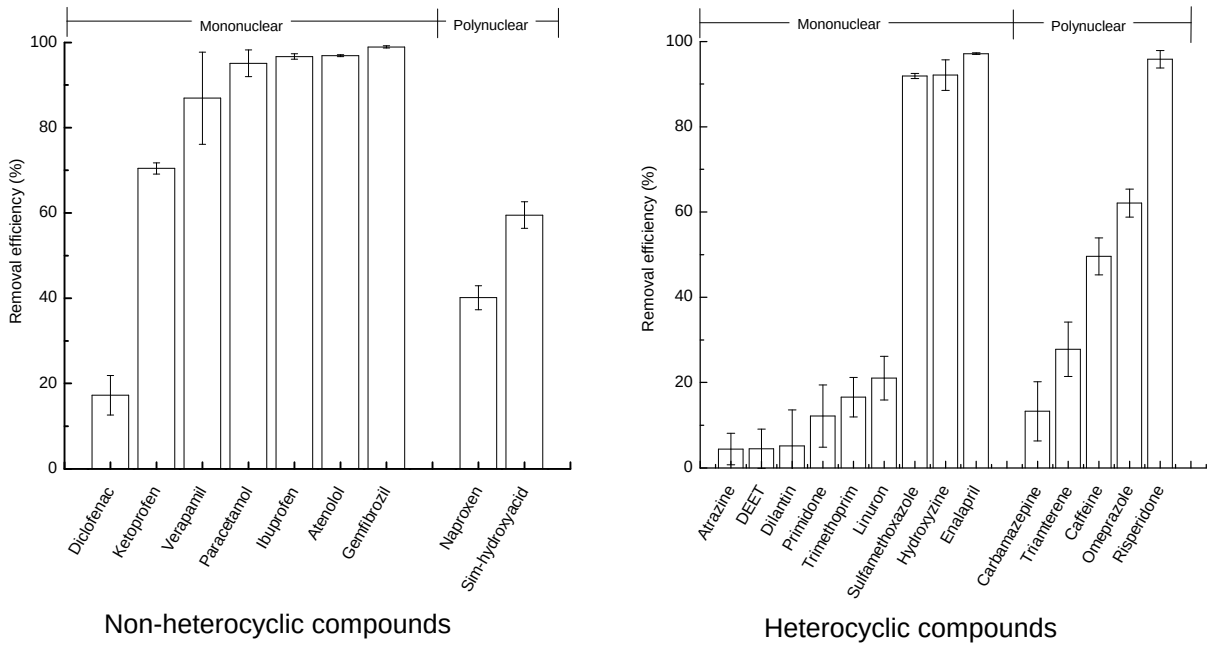

722
723 **Figure 4**

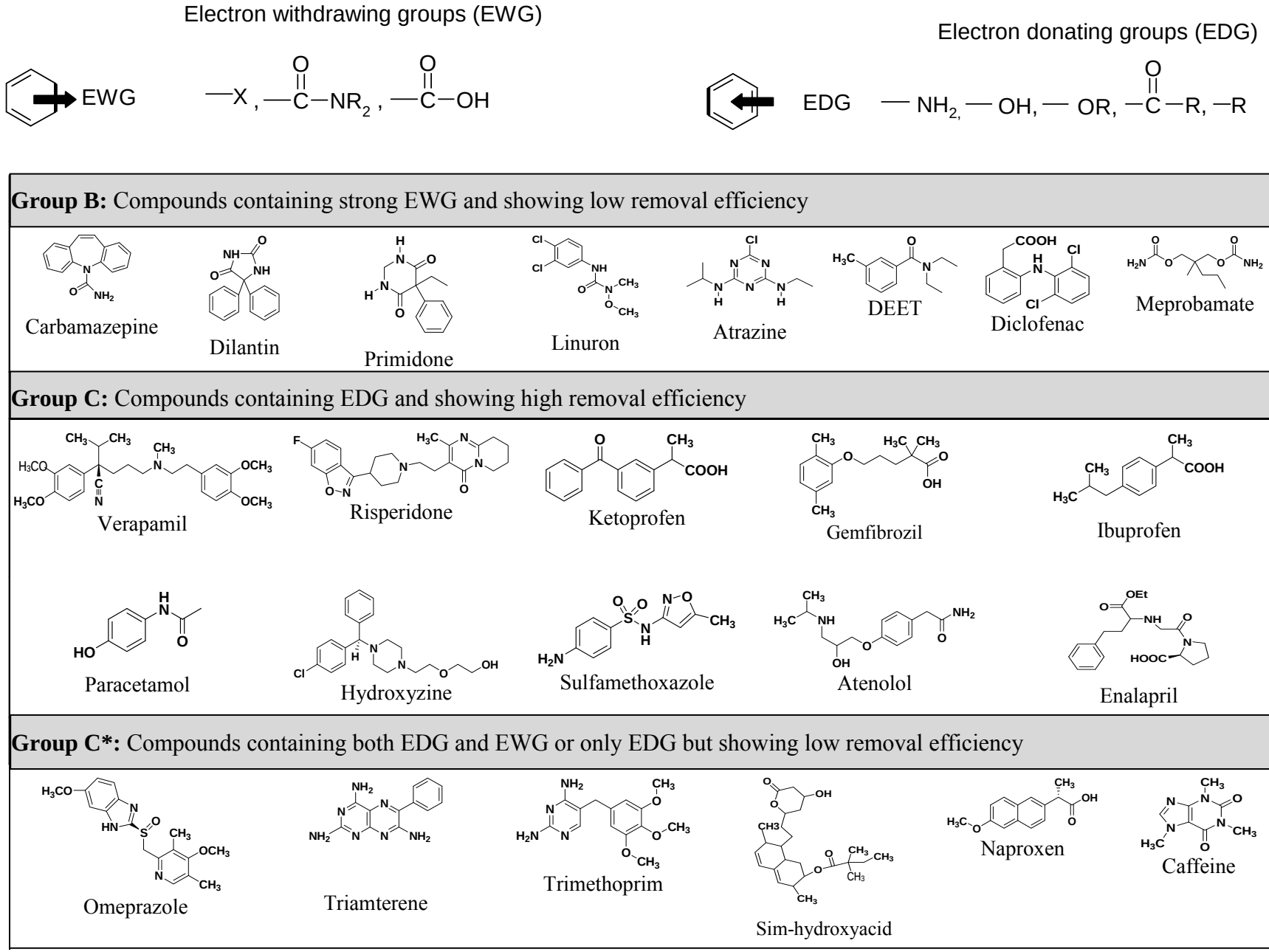
Electron withdrawing groups (EWG)
EWG
—X , —C(=O)—NR2 , —C(=O)—OH
Electron donating groups (EDG)
EDG
— NH2, — OH, — OR, —C(=O)—R, —R
Group B: Compounds containing strong EWG and showing low removal efficiency
Carbamazepine
Dilantin
Primidone
Linuron
Atrazine
DEET
Diclofenac
Meprobamate
Group C: Compounds containing EDG and showing high removal efficiency
Verapamil
Risperidone
Ketoprofen
Gemfibrozil
Ibuprofen
Paracetamol
Hydroxyzine
Sulfamethoxazole
Atenolol
Enalapril
Group C*: Compounds containing both EDG and EWG or only EDG but showing low removal efficiency
Omeprazole
Triamterene
Trimethoprim
Sim-hydroxyacid
Naproxen
Caffeine

Figure 5

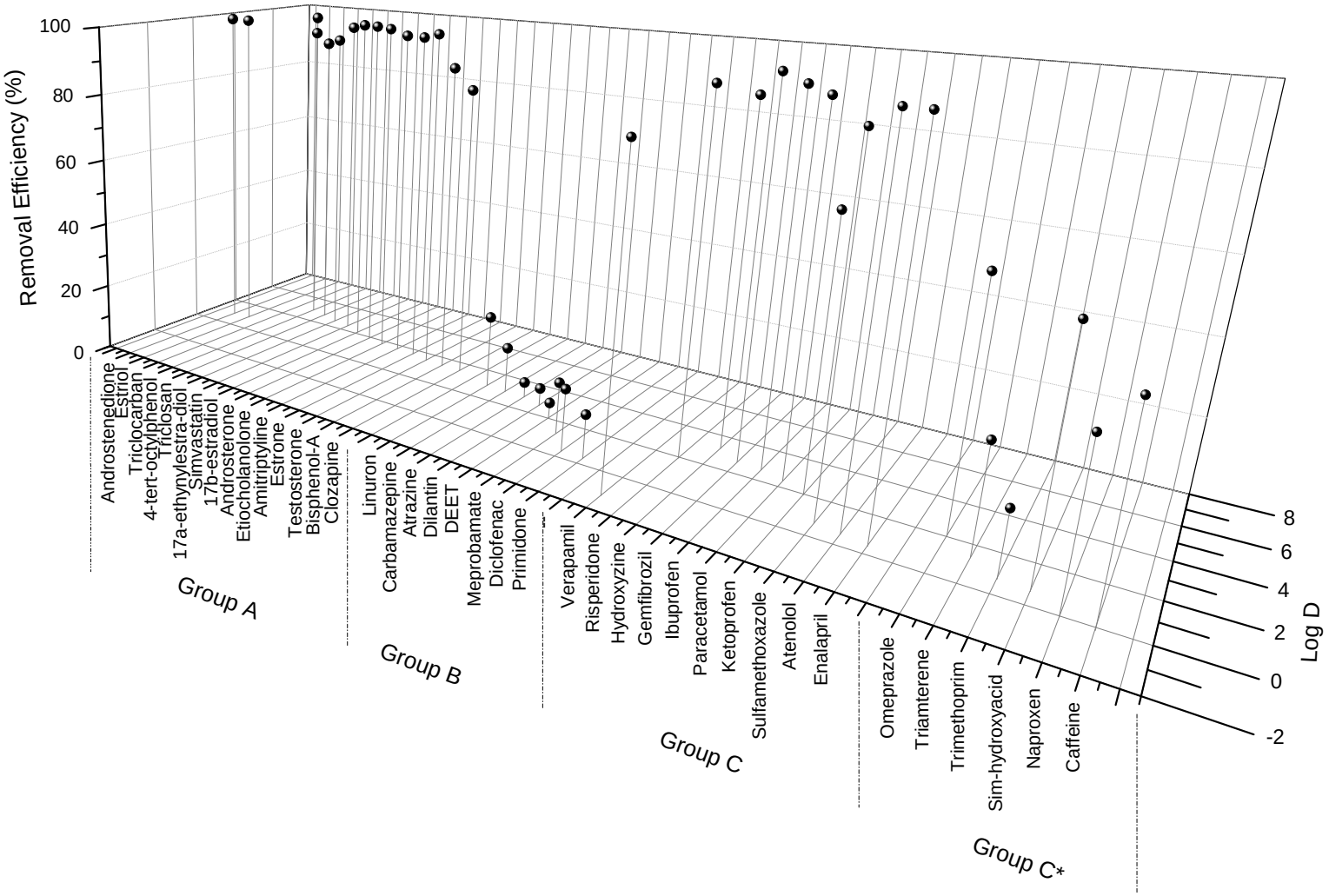
Removal Efficiency (%)
100
80
60
40
20
0
Androstenedione
Estriol
Triclocarban
4-tert-octylphenol
Triclosan
17a-ethynylestra-diol
Simvastatin
17b-estradiol
Androsterone
Etiocholanolone
Amitriptyline
Estrone
Testosterone
Bisphenol-A
Clozapine
Linuron
Carbamazepine
Atrazine
Dilantin
DEET
Meprobamate
Diclofenac
Primidone
Verapamil
Risperidone
Hydroxyzine
Gemfibrozil
Ibuprofen
Paracetamol
Ketoprofen
Sulfamethoxazole
Atenolol
Enalapril
Omeprazole
Triamterene
Trimethoprim
Sim-hydroxyacid
Naproxen
Caffeine
Group A
Group B
Group C
Group C*
Log D
8
6
4
2
0
-2

Figure 6

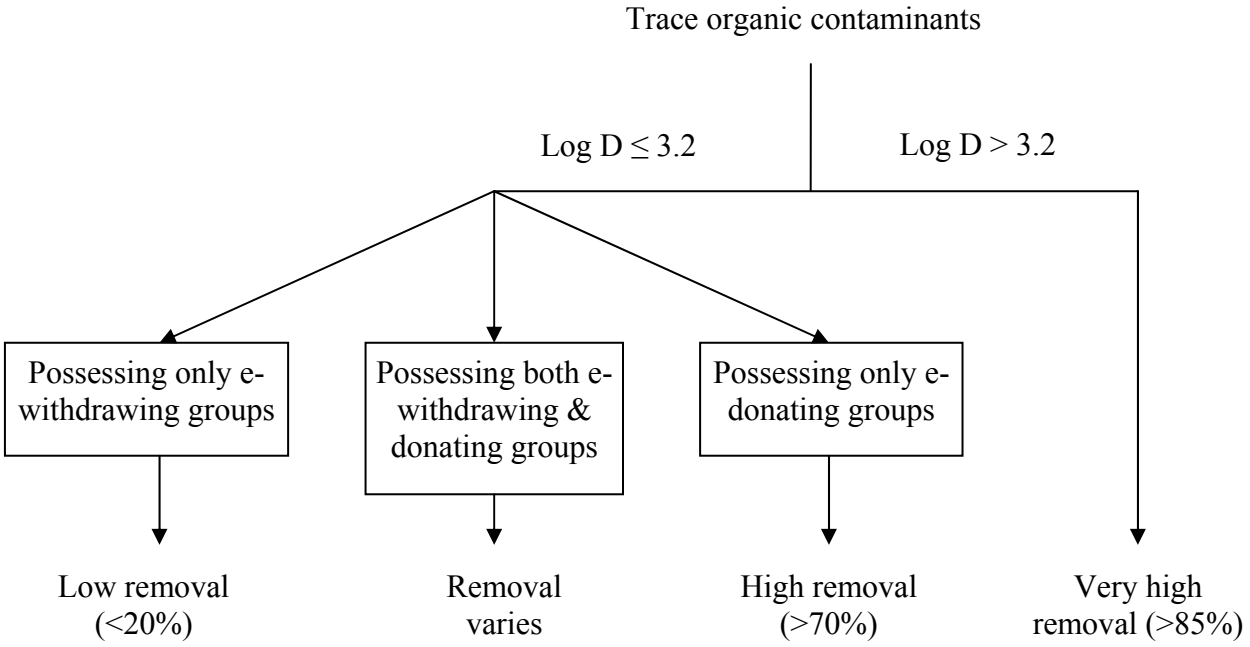
Trace organic contaminants
Log D ≤ 3.2
Log D > 3.2
Possessing only e-withdrawing groups
Possessing both e-withdrawing & donating groups
Possessing only e-donating groups
Low removal (<20%)
Removal varies
High removal (>70%)
Very high removal (>85%)

Figure 7

Removal of trace organics by MBR treatment: the role of molecular properties

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Supplementary data

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Supplementary data: Physicochemical properties of the selected trace organic contaminants.

Compound	CAS number	Formula	MW (g/mol)	Log K_{ow}	Log D (at pH 8)	pK_a
Paracetamol	103-90-2	$C_8H_9NO_2$	151.2	0.33	0.33	9.86; 1.72
DEET	134-62-3	$C_{12}H_{17}NO$	191.3	1.95	1.96	-1.37
Caffeine	58-08-2	$C_8H_{10}N_4O_2$	194.2	-0.13	-0.13	0.73
Ibuprofen	15687-27-1	$C_{13}H_{18}O_2$	206.3	3.72	0.36	4.41
t-Octylphenol	140-66-9	$C_{14}H_{22}O$	206.3	4.93	4.93	10.15
Atrazine	1912-24-9	$C_8H_{14}ClN_5$	215.7	2.63	2.63	2.35
Meprobamate	57-53-4	$C_9H_{18}N_2O_4$	218.3	0.70	0.70	13.09; -1.09
Primidone	125-33-7	$C_{12}H_{14}N_2O_2$	218.3	0.40	0.40	12.26; -1.07
Nonylphenol	104-40-5	$C_{15}H_{24}O$	220.4	6.19	6.19	10.14
Bisphenol-A	80-05-7	$C_{15}H_{16}O_2$	228.3	3.43	3.43	9.73
Naproxen	22204-53-1	$C_{14}H_{14}O_3$	230.3	3.00	-0.06	4.84
Carbamazepine	298-46-4	$C_{15}H_{12}N_2O$	236.3	2.67	2.67	13.94; -0.49
Linuron	330-55-2	$C_9H_{10}Cl_2N_2O_2$	249.1	3.20	3.20	12.13; -1.04
Gemfibrozil	25812-30-0	$C_{15}H_{22}O_3$	250.3	4.39	1.26	4.75
Dilantin	57-41-0	$C_{15}H_{12}N_2O_2$	252.3	2.52	2.36	8.33; -2.81
Triamterene	396-01-0	$C_{12}H_{11}N_7$	253.3	1.34	1.33	6.30
Sulfamethoxazole	723-46-6	$C_{10}H_{11}N_3O_3S$	253.3	0.89	-0.9	5.81; 1.39
Ketoprofen	22071-15-4	$C_{16}H_{14}O_3$	254.3	2.81	-0.64	4.23
Atenolol	29122-68-7	$C_{14}H_{22}N_2O_3$	266.3	0.10	-1.09	13.88; 9.16
Estrone	53-16-7	$C_{18}H_{22}O_2$	270.4	3.69	3.68	10.25
17β-estradiol	50-28-2	$C_{18}H_{24}O_2$	272.4	4.13	4.13	10.27
Amtriptyline	50-48-6	$C_{20}H_{23}N$	277.4	4.92	3.72	9.18
Androstenedione	63-05-8	$C_{19}H_{26}O_2$	286.4	2.90	2.90	8.78
Estriol	50-27-1	$C_{18}H_{24}O_3$	288.4	2.94	2.94	10.25
Testosterone	58-22-0	$C_{19}H_{28}O_2$	288.4	3.47	3.47	15.06
Triclosan	3380-34-5	$C_{12}H_7Cl_3O_2$	289.5	5.17	4.76	7.80
Trimethoprim	738-70-5	$C_{14}H_{18}N_4O_3$	290.3	0.79	0.73	7.20
Etiocholanolone	53-42-9	$C_{19}H_{30}O_2$	290.4	3.75	3.75	15.13
Androsterone	53-41-8	$C_{19}H_{30}O_2$	290.4	3.93	3.93	15.14
Diclofenac	15307-86-5	$C_{14}H_{11}Cl_2NO_2$	296.2	4.06	0.57	4.18; -2.25
17α-ethynylestradiol	57-63-6	$C_{20}H_{24}O_2$	296.4	4.52	4.52	10.24
Triclocarban	101-20-2	$C_{13}H_9Cl_3N_2O$	315.6	5.74	5.74	12.77; -0.34
Clozapine	5786-21-0	$C_{18}H_{19}ClN_4$	326.8	3.48	3.42	7.14
Omeprazole	73590-58-6	$C_{17}H_{19}N_3O_3S$	345.4	2.17	2.04	8.46; 4.72
Hydroxyzine	68-88-2	$C_{21}H_{27}ClN_2O_2$	374.9	2.03	2.02	14.41; 6.12
Enalapril	75847-73-3	$C_{20}H_{28}N_2O_5$	376.5	2.43	-1.21	3.17; 5.43
Risperidone	106266-06-2	$C_{23}H_{27}FN_4O_2$	410.5	2.88	2.63	7.89
Simvastatin	79902-63-9	$C_{25}H_{38}O_5$	418.6	4.41	4.41	13.49
Sim-hydroxy acid	121009-77-6	$C_{25}H_{40}O_6$	436.6	4.05	0.64	4.31
Verapamil	52-53-9	$C_{27}H_{38}N_2O_4$	454.6	3.90	2.89	8.97

Source: SciFinder Scholar, data calculated using Advanced Chemistry Development (ACD/Labs) Software V8.14 for Solaris (1994-2007 ACD/Labs).