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Citation for published version:

De Munari, A., Semiao, A.J.C. & Antizar-Ladislao, B 2013, 'Retention of pesticide Endosulfan by nanofiltration: Influence of organic matter-pesticide complexation and solute-membrane interactions', *Water Research*, vol. 47, no. 10, pp. 3484-3496. <https://doi.org/10.1016/j.watres.2013.03.055>

Digital Object Identifier (DOI):
[10.1016/j.watres.2013.03.055](https://doi.org/10.1016/j.watres.2013.03.055)

Link:
[Link to publication record in Edinburgh Research Explorer](#)

Document Version:
Peer reviewed version

Published In:
Water Research

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Retention of pesticide Endosulfan by nanofiltration: Influence of organic matter-pesticide complexation and solute-membrane interactions

Submitted to *Water Research*

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1 **Abstract**

2 Nanofiltration (NF) is a well-established process used in drinking water production to effectively
3 remove Natural Organic Matter (NOM) and organic micropollutants. The presence of NOM has
4 been shown to have contrasting results on micropollutant retention by NF membranes and removal
5 mechanisms are to date poorly understood. The permeate water quality can therefore vary during
6 operation and its decrease would be an undesired outcome for potable water treatment. It is hence
7 important to establish the mechanisms involved in the removal of organic micropollutants by NF
8 membranes in the presence of NOM. In this study, the retention mechanisms of pesticide
9 Endosulfan (ES) in the presence of humic acids (HA) by two NF membranes, TFC-SR2 and TFC-
10 SR3, a "loose" and a "tight" membrane, respectively, were elucidated. The results showed that two
11 mechanisms were involved: (1) the formation of ES-HA complexes (solute-solute interactions),
12 determined from solid-phase micro-extraction (SPME), increased ES retention, and (2) the
13 interactions between HA and the membrane (solute-membrane interactions) increased membrane
14 molecular weight cut-off (MWCO) and decreased ES retention. HA concentration, pH, and the ratio
15 between micropollutant molecular weight (MW) and membrane MWCO were shown to influence
16 ES retention mechanisms. In the absence of HA-membrane interactions at pH 4, an increase of HA
17 concentration increased ES retention from 60% to 80% for the TFC-SR2 and from 80% to 95% for
18 the TFC-SR3 due to ES-HA complex formation. At pH 8, interactions between HA and the loose
19 TFC-SR2 increased the membrane MWCO from 460 to 496 g/mol and ES retention decreased from
20 55% to 30%, as HA-membrane interactions were the dominant mechanism for ES retention. In
21 contrast, for the "tight" TFC-SR3 membrane the increase in the MWCO (from 165 to 179 g/mol),
22 was not sufficient to decrease ES retention which was dominated by ES-HA interactions.
23 Quantification of the contribution of both solute-solute interactions and solute-membrane
24 interactions is hence fundamental in understanding the removal mechanisms of micropollutant by
25 NF membranes in the presence of NOM in order to optimize the treatment process.

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27 **Keywords:** nanofiltration, micropollutant, natural organic matter, solute-solute interactions, solute-
28 membrane interactions

29

30

31 **1. Introduction**

32 Removal of organic micropollutants from water intended for human consumption is a growing
33 concern for the drinking water industry due to increasing occurrence of these compounds in surface
34 water and groundwater, as well as their adverse effects on human health (Schwarzenbach et al.
35 2006). Application of nanofiltration (NF) processes for the removal of micropollutants has become
36 widespread due to an effective rejection achieved by full scale plants (Cyna et al. 2002) and the
37 extensive research carried out in explaining the micropollutant removal mechanisms (Bellona et al.
38 2004, Van der Bruggen et al. 2006).

39

40 Natural organic matter (NOM) is ubiquitously present in water and it influences the fate and the
41 behaviour of micropollutants and their removal by NF (Plakas and Karabelas 2009, Salvaterra et al.
42 2011). NOM has shown to increase, decrease or have negligible effect on micropollutant removal
43 by NF (Agbekodo et al. 1996, Devitt et al. 1999, Jin et al. 2007, 2010, Plakas et al. 2006, Xu et al.
44 2005). Contrasting results have been attributed to the different types of micropollutants, membranes
45 and organic matter used in previous studies and to the complexity of the retention mechanisms
46 (Bellona et al. 2004, Boussahel et al. 2002, Jin et al. 2007, Sanches et al. 2011).

47

48 The increase of micropollutant retention in the presence of NOM has been attributed to the
49 formation of micropollutant-NOM complexes of bigger size and higher charge compared to the
50 micropollutant on its own (Agbekodo et al. 1996, Boussahel et al. 2002, Devitt et al. 1999, Jin et al.

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52 removal by NF in the presence of humic acids (HA) using the percentage of the fraction of estrone
53 bound to HA from literature. Poor estimation was attributed to the difference in estrone
54 concentration between the experiments and the literature. Jin et al. (2007) also inferred that most of
55 the estrone-HA interactions took place on the membrane rather than in solution, explaining further
56 the poor removal estimation. Neale and Schäfer (2012) were able to quantify the contribution of
57 hormone-HA interactions on increased hormone removal by ultrafiltration (UF) in the presence of
58 HA by determining organic matter-water partition coefficients. Increasing HA concentration led to
59 more hormone partition onto HA and in turn to greater hormone removal by UF, demonstrating the
60 role of micropollutant-NOM interactions on micropollutant removal. Increase of micropollutant
61 removal by NF in the presence of NOM was also attributed to the modification of the membrane
62 surface caused by adsorption of NOM. NOM deposition can cause pore clogging and change
63 membrane surface charge, resulting in improved retention by steric and electrostatic mechanisms
64 (Jin et al. 2007, Xu et al. 2005).

65

66 Several mechanisms have been inferred to explain reduced or similar retention of micropollutants in
67 the presence of NOM. Lack of binding between the studied micropollutants and NOM was
68 considered the reason for unchanged retention (Boussahel et al. 2002, Jin et al. 2007, 2010).
69 Reduced micropollutant retention was attributed to increased membrane molecular weight cut-off
70 (MWCO) caused by the presence of organic matter (Xu et al. 2005, Xu et al. 2006). Organic matter
71 has been shown to enhance the negative charge of NF membranes, so it was inferred that the
72 increased electrostatic repulsion within the membrane pores increased membrane MWCO
73 (Braghetta et al. 1997, Childress and Elimelech 1996). Schäfer et al. (2010) inferred that membrane
74 hydrophilization might be responsible for the observed reduction in estrone removal when organic
75 matter was present and for the increase in pure water flux after organic matter filtration. The
76 decrease in micropollutant retention in the presence of organic matter was observed for "loose"

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77 membranes (*i.e.* membrane whose MWCO is bigger than micropollutant molecular weight, MW)
78 (Schäfer et al. 2010, Xu et al. 2005, Xu et al. 2006). From the literature, it can be hypothesized that
79 a correlation might exist between micropollutant removal mechanisms in the presence of NOM and
80 micropollutant MW/membrane MWCO ratio. In the cited studies, the mechanisms responsible for
81 reduced micropollutant retention in the presence of NOM were presented as hypotheses without
82 being quantified, indicating the need to perform thorough investigations to demonstrate for which
83 conditions the mechanisms apply.

84

85 For micropollutants that adsorb onto the membranes, retention decreases with time until the
86 membrane is saturated with the compound and real retention is reached (Kimura et al. 2003,
87 Nghiem et al. 2004, Semião and Schäfer 2011). In some case studies there is no indication that
88 membrane saturation was achieved. If the membrane is not saturated with the compound, retention
89 can therefore be overestimated and the comparison of retention results with and without NOM can
90 lead to erroneous conclusions. For example, lower micropollutant retention in the presence of NOM
91 has been linked to adsorption competition on the membrane between the micropollutant and NOM.
92 When NOM is present, it adsorbs on the membrane and decreases the membrane adsorption sites
93 available for the micropollutant. It was therefore inferred that the decrease in micropollutant
94 adsorption in the presence of NOM caused a lower retention of the same micropollutant (Yoon et al.
95 2006). Vice versa, higher micropollutant adsorption was inferred to cause lower retention because
96 adsorbed micropollutants might experience higher diffusion to the permeate side (Boussahel et al.
97 2002). These two opposing results might be linked to the above-mentioned lack of saturation of the
98 membrane by the micropollutant. It is hence important to ensure membrane saturation during the
99 experiments in order to be able to compare retention results in the presence and absence of NOM.
100 These findings reflect the complexity of the mechanisms involved in the removal of micropollutants
101 by NF membranes in the presence of NOM and invite a systematic investigation of NOM influence
102 on micropollutant removal.

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104 Three main mechanisms can influence micropollutant retention by NF in the presence of NOM:
105 solute-solute interactions, solute-membrane interactions and solute-foulant interactions. The impact
106 of fouling by NOM on micropollutant retention has been extensively studied (Hajibabania et al.
107 2001, Ng and Elimelech 2004, Plakas et al. 2006, Xu et al. 2006), so it was not further investigated
108 in this study.

109

110 In this work, commercial HA have been chosen as a representative of the bigger fraction of NOM
111 because they have been extensively characterized in the literature and they were shown to have
112 similar organic matter retention properties than real Scottish NOM (Chin et al. 1994, De Munari
113 2012, Shin et al. 1999). Pesticide Endosulfan (ES) has been employed as a model micropollutant
114 because it is believed to interact with NOM and it is neutral over a large pH range (Banasiak 2009,
115 Forman et al. 1965). Moreover, ES is extensively used worldwide, persistent in the environment,
116 toxic to aquatic life and has estrogenic properties similar to DDT (German Federal Environment
117 Agency 2007, Soto et al. 1994). Two commercial NF membranes, TFC-SR2 and TFC-SR3
118 provided by Koch, have been selected as their MWCO is respectively higher and lower than the ES
119 molecular weight (MW).

120

121 The aim of this study is to elucidate the mechanisms responsible for the different retention trends
122 obtained for the micropollutants in the presence of NOM. The objectives were to: (1) quantify the
123 contribution of solute-solute interactions (*i.e.* formation of ES-HA complexes) on ES removal; (2)
124 investigate the contribution of ES-membrane interactions on ES retention; and (3) investigate the
125 contribution of HA-membrane interactions on ES retention for a "tight" and a "loose" membrane.
126 For the first time, the relative contribution of solute-solute interactions and solute-membrane
127 interactions to micropollutant retention by NF membranes in the presence of organic matter will be
128 evaluated to explain micropollutant retention mechanisms.

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129

130 In order to quantify the influence of solute-solute interactions on ES retention, the method
131 developed by Neale and Schäfer for UF (2012) was adapted to NF and applied to quantify the
132 contribution of ES-HA complexes on ES removal. HA-water partition coefficient K_{HA} for ES was
133 determined and the calculated fraction of ES bound to HA was used to estimate ES removal due to
134 complex formation. Neale and Schäfer (2012) did not consider the contribution of solute-membrane
135 interactions since the dominant mechanism for hormone removal by UF was deemed to be solute-
136 solute interactions only. In this study, the contribution of solute-membrane interactions on
137 micropollutant retention was investigated by evaluating ES adsorption to the membranes (ES-
138 membrane interactions) and the influence of HA on membrane characteristics (HA-membrane
139 interactions).

140

141 **2. Materials and methods**

142 **2.1 Stirred cells equipment and filtration protocol**

143 Experiments were performed with a stainless steel stirred cell with a volume of 990 mL and a
144 diameter of 70 mm, resulting in a membrane area of 38.5 cm². The cell was pressurised at 5 bar
145 with filtered lab air to create similar conditions as full scale membrane plants; the pressure was kept
146 constant and automatically measured every minute with a pressure transducer (Omega Engineering,
147 UK). Temperature inside the cell and permeate collected on an electronic balance (Advancer Pro,
148 Ohaus, UK) were measured every minute. A digital magnetic stirrer (Fisher Scientific, UK) was
149 used at a speed of 300 rpm.

150

151 Membrane coupons were compacted for an hour at 15 bar and pure water flux was measured at 5
152 bar, before and after the experiments. A 900 mL feed solution was prepared prior to the experiments
153 and stirred at 150 rpm for 24 hours to ensure formation of ES-HA complexes. The experiments

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154

155 were carried out in concentration mode in two phases. In the first phase, 480 mL of feed were
156 filtered in order to ensure membrane saturation by ES, where a feed, a permeate and a concentrate
157 sample were collected to determine ES sorption by mass balance. Filtration of 480 mL of solution
158 was determined as sufficient to reach ES saturation for both membranes. In the second phase, the
159 permeate was returned to the stirred cell, a feed, a concentrate and four permeate samples of 60 mL
160 each were collected. Mass of ES sorbed to the membranes was determined with a mass balance on
161 the total solution filtered during the experiment and no adsorption of micropollutant occurred
162 during the filtration of the 4x60 mL. Retention was determined with a mass balance on the last
163 permeate collected; retention was constant for the last four permeates since equilibrium had been
164 reached.

164

165 **2.2 Membrane characteristics**

166 TFC-SR2 and TFC-SR3 membranes provided by Koch Membrane Systems (San Diego, USA) were
167 extensively characterized. Membrane MWCO was determined by filtering aqueous solutions
168 containing dioxane, xylose, dextrose and polyethylene glycol (PEG) of different MW (Teixeira et
169 al. 2005). Pore radius was estimated using the hydrodynamic model (Nghiem et al. 2004). Point of
170 zero charge was measured with an electrokinetic analyser (EKA, Anton Paar KG, Austria) with the
171 same background electrolyte used in the experiments. TFC-SR2 and TFC-SR3 membranes are
172 amphoteric, positively charged at acidic pH and negatively charged with increasing pH. Contact
173 angle measurements (CAM 100, KSV Instrument Ltd, US) were performed using the sessile drop
174 method. At least three measurements per membrane were performed and the average of the
175 measurements is reported (standard deviation $\pm 2^\circ$). In the case of membranes with HA deposits,
176 which presented zones of different colour, measurements were repeated in triplicate for different
177 zones and the average was reported. The variation between different zones of the membranes with
178 HA deposit was $\pm 2^\circ$, comparable with the variation obtained by repeated measurements on virgin
179 membranes. Roughness was estimated by atomic force microscopy (AFM) using a multimode AFM

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180 system (VEECO, presently Bruker Corporation, USA) by contact mode in liquid (scan size 2.0×2.0
181 μm). The cantilever (Mikromasch CSC38/AIBS type B) was made of Si with a tip radius of 10 nm.
182
183 Since a new membrane coupon was used for each experiment, the reproducibility of retention and
184 adsorption results was mainly affected by the variability of different membrane coupons. For
185 quality control, only coupons with a pure water flux varying ±15% were employed in the
186 experiments.
187
188 **2.3 Chemicals and solution chemistry**
189 Experiments were conducted in ultra-pure water obtained by PuraLab Ultra (Elga LabWater, UK).
190 All chemicals were of analytical grade. Inert organics for MWCO and pore size determination
191 consisted of 25 mgC/L of dioxane, dextrose PEG 400, PEG 600, PEG 100 (Fisher Scientific, UK)
192 and xylose (Acros Organics, UK). HA (Sigma Aldrich, UK) stock solutions containing 250 mgC/L
193 were conserved in the fridge in the dark for one week maximum. HA was used at a concentration of
194 12.5 mgC/L because it represents typical NOM concentration found in upland natural water in
195 Scotland (De Munari 2012). Experiments with HA ranging from 5 to 250 mgC/L were performed to
196 study the effects of HA concentration on ES-HA complex formation. Background electrolyte
197 solution consisted of 1 mM NaHCO₃ and 20 mM NaCl (Fisher Scientific, UK). pH was adjusted
198 with 1M of HCl or NaOH (Fisher Scientific, UK). Radiolabeled [2,3-¹⁴C] ES (>95% purity; 18.5
199 MBq solid form) was purchased from the Institute of Isotopes Co., Ltd. (Hungary). Feed solutions
200 of 10 μg/L of radiolabeled ES were prepared from stock solutions (10,000 μg/L) made in methanol
201 (CH₃OH) (Fisher Scientific, UK).
202
203 ES is an organochloride insecticide of the cyclodiene group commercially produced as a 7:3
204 isomeric mixture of α and β forms (Table 1). ES isomers degrade by chemical hydrolysis to ES-diols
205 at pH > 8 with half time of less than 12 hours (Peterson and Batley 1993), comparable with the time

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206 used in the filtration experiments. ES-sulfate can also be a hydrolysis product of ES isomers in the
207 presence of microbiological activity or strong chemical oxidants but it was not detected in
208 "artificial" samples after eight weeks (Peterson and Batley 1993). Therefore, it was inferred that
209 ES-sulfate was not present in the solutions prepared for the experiments.

(TABLE 1)

2.4 Analytical methods

214 Radiolabeled ES was measured with a liquid scintillation counter (Beckman LS 6500, USA); 1 mL
215 of sample was analysed in 20 mL scintillation vials containing 7 mL of scintillation liquid (Ultima
216 Gold LLT, UK). Inert organics (dioxane, dextrose PEG 400, PEG 600, PEG 100) were measured
217 with a Total Organic Carbon (TOC) V_{CPH/CPN} Shimadzu analyser with the high sensitivity catalyst
218 in a non-purgeable organic carbon mode. Calibration standards were made using potassium
219 hydrogen phthalate (Acros Organics, UK). Samples were analysed for TOC the same day of the
220 experiments. HA concentration was determined by ultraviolet absorbance at 254 nm measured with
221 an UV Visible Spectrophotometer Cary 100 (Varian, UK). Samples were analysed within a few hours
222 from collection and stored in the dark at controlled room temperature. Conductivity and pH
223 measurements were conducted for the feed, permeate and concentrate samples using a pH/Cond
224 340i meter (WTW, Germany).

2.5 Calculation of HA-water partitioning coefficient K_{HA}

227 HA-water partitioning coefficient K_{HA} for ES was determined as a function of pH and HA
228 concentration using the negligible-depletion solid phase micro-extraction (nd-SPME) method
229 developed by Neale et al. (2008). The SPME method allows estimating the fraction of
230 micropollutant bound to NOM, irrespective of the specific interactions (e.g. hydrophobic, hydrogen
231 bonding, etc.) between micropollutant and NOM. The method measures the freely dissolved

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concentration of a micropollutant in water at equilibrium and it is based on the valid assumption

that only the freely dissolved micropollutant and not the fraction bound to the organic matter is measured by the SPME fibre (Poerschmann and Kopinke 2001).

The SPME fibres were calibrated to establish the time necessary to reach equilibrium and calculate the fibre-water partition coefficient K_{fw} for ES as a function of pH. Seven polyacrylate (PA) fibres (Polymicro Technology, US) of 5 cm length each were introduced in 100 mL solutions containing 10, 25, 50, 100 $\mu\text{g/L}$ of ES and background electrolyte (1 mM NaHCO_3 and 20 mM NaCl) with pH varying from 4 to 12. The fibres were shaken at 200 rpm at 25 °C in a Certomat BS-1 incubator shaker (Sartorius, Germany) and extracted at regular time intervals. The fibres were cut into three pieces, added to a scintillation vial with 7 mL of scintillation liquid, manually shaken and left overnight to desorb before being analysed by scintillation counter to determine m_F , the mass of ES in the fibre.

A kinetic approach was used to quantify K_{fw} :

$$K_{fw} = \frac{C_F}{C_W} = \frac{m_F}{m_W} \cdot \frac{V_W}{V_F} \quad (1)$$

where C_F ($\mu\text{g/L}$) is the concentration of ES in the fibre, C_W ($\mu\text{g/L}$) is the concentration of freely dissolved ES in aqueous solution, m_w (μg) is the mass of freely dissolved ES in aqueous solution as sampled at the end of the experiments, V_w (L) is the volume of the aqueous solution, V_F (L) is the volume of the fibre (0.77 μL). $\log K_{fw}$ was calculated from the linear regression of $\log C_F$ as a function of $\log C_w$ obtained with the four different concentrations of ES in solution.

In order to determine the HA-water partitioning coefficient K_{HA} for ES as a function of pH and HA concentration, 100 mL solutions containing 10, 25, 50, 100 $\mu\text{g/L}$ of ES, 5, 12.5, 50, 125, 250 mgC/L of HA and background electrolyte were prepared at pH varying from 4 to 12 and shaken for 24

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hours at 200 rpm to allow complex formation. Fibres were then introduced in the solution and

shaken for 96 hours, chosen as equilibrium time. Following, the fibres were extracted, cut into three pieces, added to a scintillation vial with 7 mL of scintillation liquid, manually shaken and left overnight to desorb before being analysed by scintillation counter to determine m_F .

In the presence of HA, m_w was determined from the ES-fibre partitioning coefficient, K_{fw} , obtained during fibre calibration as follows:

$$m_w = \frac{m_F}{K_{fw}} \cdot \frac{V_W}{V_F} \quad (2)$$

K_{HA} (L/kg) was then calculated as:

$$K_{HA} = \frac{c_{HA}}{C_W} = \frac{m_{HA}}{m_{DOM}} \cdot \frac{V_W}{m_w} \quad (3)$$

where c_{HA} ($\mu\text{g/kg}$) is the concentration of ES sorbed to HA, m_{HA} (μg) is the mass of ES sorbed to HA, m_{DOM} (kg) is the total mass of HA dissolved in solution.

In order to estimate m_{HA} a full mass balance was carried out:

$$m_{HA} = m_{TOT} - m_F - m_w \quad (4)$$

where m_{TOT} is the initial mass of ES in solution before the fibre is added.

The fraction of ES bound to HA f_{HA} (%) was determined as (Neale and Schäfer 2012):

$$f_{HA} = \frac{1}{\frac{V_W}{m_{DOM} \cdot K_{HA}} + 1} \quad (5)$$

The error in the determination of K_{fw} , K_{HA} and f_{HA} was calculated from the instrumental error in the determination of m_F , m_w , m_{TOT} and m_{DOM} using the error propagation rule (Miller and Miller 2000).

3 Results and discussion

3.1 ES-HA complex formation

The formation of ES-HA complexes was quantified as a function of pH and HA concentration in order to evaluate the influence of solute-solute interactions on ES retention in the presence of HA. The HA-water partition coefficient K_{HA} for ES was determined using the nd-SPME method described in Section 2.5 and the fraction of ES bound to HA, f_{HA} hence complex formation, was calculated with equation 5. In order to determine K_{HA} , the SPME fibres were calibrated to obtain the fibre-water partition coefficient K_{fw} for ES as a function of pH.

3.1.1. Fibre calibration and determination of fibre partitioning coefficient

SPME has been largely employed as a technique for extracting organic micropollutants from aqueous solutions and values of K_{fw} for α -ES and β -ES are available in the literature (Valor et al. 2001). However, there are no data published on the variation of K_{fw} with pH for ES. Moreover, the free-standing fibre method used in this study differs from the traditionally employed techniques using fibre holders. Fibre calibration was therefore required to establish equilibrium time and determine K_{fw} . PA fibres reached equilibrium after 48 hours and 96 hours were chosen for determination of the partitioning coefficients. No adsorption of ES to the glass was measured in control samples.

PA fibre uptake was constant with pH up to pH 8 and then decreased rapidly (Figure 1). Since ES does not dissociate, this was attributed to the hydrolysis of α -ES and β -ES to ES-diol, which has lower log K_{ow} and therefore less affinity to the fibres (DiFilippo and Eganhouse 2010). However, the decrease at pH 10 and 12 can be considered negligible once the logarithm is calculated, since the difference was less than 0.5 log units, and log K_{fw} for ES can be considered constant with pH

(Figure 1). For the pH range studied the negligible-depletion condition $K_{fw} \cdot \frac{V_F}{V_W} \lll 1$ was fulfilled

(Vaes et al. 1997). Values of log K_{fw} obtained for ES are in agreement (maximum difference 0.3 log units) with the values obtained in the literature for PA coated fibres at neutral pH (Valor et al. 2001), confirming the validity of the nd-SPME technique employed in this study.

(FIGURE 1)

3.1.2. Determination of HA partition coefficient and percentage of ES bound to HA

The HA partition coefficient for ES, K_{HA} , was estimated as a function of pH and HA concentration. While K_{oc} values for ES have been determined for various soils (Hillenbrand et al. 2006, Ministerio de Agricultura Pesca Y Alimentacion 1999, Organization for Economic Cooperation and Development 1995), there are no published data on partitioning coefficient of ES and aquatic organic matter. Values obtained for soil organic carbon cannot be used for aquatic HA as partition coefficients in water could be 2-3 orders of magnitude greater (Devitt and Wiesner 1998). It is fundamental to quantify the partition coefficients at the same conditions used during the experiments with membranes as environmental conditions have shown to influence considerably the K_{HA} values (DiFilippo and Eganhouse 2010).

As shown in Figure 2, the partitioning coefficient for ES between HA and water and the fraction of ES bound to HA can be considered constant with pH. Albeit HA deprotonates at pH above 4, the complexation of ES and HA did not decrease at high pH as ES is neutral in the whole pH range, in agreement with findings for other organochloride pesticides (Prosen et al. 2002). Log K_{HA} decreased with increasing HA concentration indicating that complexation is limited by the mass of ES available. The percentage of ES bound to HA, calculated with equation 5, increased with HA concentration.

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(FIGURE 2)

3.2 Influence of pH and HA concentration on ES retention

The influence of HA on the removal of ES for different micropollutant MW/membrane MWCO ratio was investigated. Firstly, ES retention was determined with and without HA for TFC-SR2 and TFC-SR3 as a function of pH and secondly, ES retention was determined for the TFC-SR2 and TFC-SR3 as a function of HA concentration. The study of ES retention as a function of pH is important because, while pH was shown not to influence ES-HA complex formation and the percentage of ES bound to HA (Figure 2a), it can influence membrane charge within the pores (Braghetta et al. 1997, Dalwani et al. 2011, 2010). ES retention in the presence of HA was expected to be affected by HA concentration since HA concentration influenced the formation of ES-HA complexes and the percentage of ES bound to HA (Figure 2b).

3.2.1. Influence of pH on ES retention

The permeate flux J_v/J_0 ratio, an indicator of membrane fouling, the ES mass adsorption on the membrane and the ES retention were determined for a pH range between 4 and 12, as shown in Figure 3. The use of new membrane coupons with pure water flux varying $\pm 15\%$, resulted in $\pm 8\%$ variability in retention results and $\pm 0.02 \mu\text{g}/\text{cm}^2$ variability in adsorption results as determined by repeating some experiments in duplicate and triplicate with different membrane coupons. The determined variability was used for all the experiments in this study.

(FIGURE 3)

Figure 3a shows that, for both membranes, J_v/J_0 was constant with pH when ES was filtered alone, showing no effect of pH on the membrane permeate flux. When ES and HA were both filtered, fouling (i.e. J_v/J_0 decline) was not observed for both membranes when compared to J_v/J_0 with ES

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only. For the "tighter" TFC-SR3 (Table 2) the presence of HA did not influence the flux ratio, while for the "looser" TFC-SR2 (Table 2) HA increased the flux ratio at pH 6, 8 and 10 up to 40%. Increased permeate flux in the presence of NOM at pH > 4 has been previously observed for "loose" NF membranes (Braghetta et al. 1997, Schäfer et al. 2010). Since NOM enhances the negative charge of the NF membranes, which increases the electrostatic repulsion within the membrane pores, it was inferred that NOM might increase membrane MWCO (Braghetta et al. 1997, Childress and Elimelech 1996).

(TABLE 2)

ES adsorption onto the TFC-SR3 was low (average over pH: $0.01 \mu\text{g}/\text{cm}^2$) and independent of pH and the presence of HA (Figure 3b). ES adsorption was higher (average over pH: $0.03 \mu\text{g}/\text{cm}^2$) for the more hydrophobic TFC-SR2 (Table 2) compared to the TFC-SR3. At pH > 8, ES adsorption decreased with and without HA for the TFC-SR2. In this pH range ES hydrolyses to ES-diol, which is less hydrophobic than α -ES and β -ES (Table 1) and might adsorb less on the membrane (Banasiak 2009).

For both membranes in the absence of HA ES retention varied with pH (Figure 3c). It is inferred that the variation of membrane surface characteristics with pH (i.e., negative surface charge increase with increase of pH) combined with hydrolyzation of ES isomers to ES-diol, which has a lower molecular weight and lower hydrophobicity, decreased ES retention by the TFC-SR3 membrane with increasing pH. The same occurred for the TFC-SR2 membrane with the exception of pH 12. At this pH it is possible that some of the ES diol is dissociated (pKa value in Table 1) which might have an enhanced retention by the negatively charged membrane.

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379 For TFC-SR3 (micropollutant MW/membrane MWCO ratio > 1) HA increased ES retention at
380 every pH. This increase in retention is not caused by pore clogging from HA, since J_v/J_o did not
381 decrease when HA was present compared to filtration without HA (Figure 3a). A possible
382 explanation for the increase in ES retention is the formation of ES-HA complexes: as HA is highly
383 retained by the NF membrane, ES molecules that complex with HA will also be retained. The
384 influence of complexation on ES retention will be studied in detail in the next section.

385

386 In contrast, ES retention in the presence of HA decreased at pH 6, 8 and 10 and was similar at pH 4
387 and 12 for the TFC-SR2 (micropollutant MW/membrane MWCO ratio < 1). Decrease in ES
388 retention in the presence of HA was observed for the "loose" membrane, confirming the inferred
389 correlation between micropollutant MW/membrane MWCO ratio and micropollutant removal in the
390 presence of NOM. Decreased ES retention in the presence of HA at pH 6, 8 and 10 for TFC-SR2
391 corresponded to an increase in flux ratio (Figure 3a), as observed in previous studies (Boussahel et
392 al. 2002, Schäfer et al. 2010), and to an increase in ES adsorption (Figure 3b). At pH 12, the flux
393 was unchanged (Figure 3a) and the ES adsorption on the membrane was lower, translating into an
394 increased retention of ES.

395

396 Two mechanisms of ES removal in the presence of HA can be identified so far: (1) for TFC-SR3
397 the presence of HA increased ES retention, potentially caused by the formation of ES-HA
398 complexes (2) for TFC-SR2 the presence of HA decreased ES retention and increased J_v/J_o for
399 certain pH conditions (pH 6 to 10), indicating a change of membrane performance when HA is
400 present, whilst for others (pH 4 and 12) it increased ES retention, potentially caused by the
401 formation of ES-HA complexes.

402

403 3.2.2. Influence of HA concentration on ES retention

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404 In order to carry out a more in depth investigation of the role of ES-HA complexes on ES removal,
405 retention of ES as a function of HA concentration was studied. For both membranes ES retention as
406 a function of HA concentration was studied at pH 4 because membranes and HA are neutral and
407 charge effects are minimal. ES retention was also investigated at pH 8 for the TFC-SR2, where the
408 presence of HA was found to decrease ES retention (Figure 3c). ES retention as a function of HA
409 concentration at pH 8 was not studied for the TFC-SR3 as ES retention in the presence of HA is
410 independent of pH (Figure 3c).

411

412 At pH 4, flux ratio decline occurred for both membranes for HA > 50 mgC/L (Figure 4a). For these
413 experimental conditions the high concentrations of HA caused the membrane to foul by pore
414 blocking (Xu et al. 2005). In this case, ES retention can be affected by pore blocking, competition
415 of adsorption sites between HA deposits and ES (Yoon et al. 2006), and interactions between ES
416 and the fouling layer. The complexity of the mechanisms when the HA fouling layer is present does
417 not allow the study of the impact of ES-HA complexes on ES retention. Therefore, the mechanisms
418 of ES retention in the presence of HA when the HA fouling layer is present will not be discussed in
419 detail further since an investigation of the impact of fouling mechanisms in micropollutant retention
420 is outside the scope of this study. For HA ≤ 50 mgC/L there was no effect on the flux ratio J_v/J_o for
421 both TFC-SR2 and TFC-SR3.

422

(FIGURE 4)

424

425 For the TFC-SR2 at pH 8, the flux ratio increased from 0.97 to 1.21 for HA > 5 mgC/L confirming
426 what was observed previously in Figure 3a. Some studies in the literature have reported an increase
427 in permeate flux after NOM filtration and inferred that it could be linked to increase in MWCO
428 (Braghetta et al. 1997, Childress and Elimelech 1996, Xu et al. 2005, Xu et al. 2006). The influence
429 of HA filtration on MWCO will be studied in detail in the next section.

430

431 ES adsorption was independent of HA concentration for TFC-SR3, while for TFC-SR2 it increased
432 with HA concentration up to HA 50 mgC/L and then decreased for a concentration higher than 50
433 mgC/L (Figure 4b). The decrease in ES adsorption for HA > 50 mgC/L might be caused either by a
434 higher percentage of ES bound to HA (Figure 2 b) leaving less freely dissolved ES to adsorb on the
435 membrane or due to fouling of the membrane by HA (Figure 4 a) which competes for adsorption
436 sites on the membrane (Yoon et al. 2006). An increase in ES adsorption for HA > 5 mgC/L can be
437 caused by the inferred increase in the MWCO of the membrane due to HA filtration.
438 Micropollutants have been shown to adsorb inside the NF membrane pores (Kimura et al. 2003,
439 Semião and Schäfer 2012). Hence whilst HA fouling blocks the pores and does not allow for the ES
440 to adsorb inside the TFC-SR2, an increase of MWCO increases the internal area for more ES
441 adsorption to occur.

442

443 At pH 4 ES retention increased with HA concentration for the looser TFC-SR2 from 60.0% to
444 84.4% while it was constant for the tighter TFC-SR3 with a retention of 96.0%. (Figure 4c). For
445 TFC-SR2 at pH 8 ES retention decreased with HA concentration up to HA 50 mgC/L from 55% to
446 30%, confirming what was observed for HA 12.5 mgC/L at pH 6, 8 and 10 (Figure 3c).

447

448 These results confirmed that the presence of HA increased the retention of pesticide ES for TFC-
449 SR3, whose MWCO is smaller than ES MW, and decreased ES retention for TFC-SR2 at pH 8,
450 whose MWCO is bigger than ES MW. However, ES retention by TFC-SR2 was found to increase
451 at pH 4 with increase of HA concentration. HA concentration and pH played a role in the different
452 ES retention in the presence of HA. HA concentration influenced ES-HA interactions and pH
453 affected HA-membrane interactions.

454

455

456 ES adsorption on the membranes (ES-membrane interactions) was not believed to influence ES
457 retention in the presence of HA. ES adsorption values on TFC-SR2 were similar at pH 4 and at pH
458 8 (Figure 4b) for HA concentrations <12.5 mgC/L while ES retention in the presence of HA
459 increased at pH 4 and decreased at pH 8 (Figure 4c). To elucidate the mechanisms responsible for
460 increase/decrease of ES retention in the presence of HA, the contributions of solute-solute
461 interactions (ES-HA complexes) and solute-membrane (HA-membrane) interactions on ES removal
462 have been investigated and described in Section 3.3.

462

463 **3.3 Mechanisms of ES retention in presence of HA**

464 In order to quantify the contribution of ES-HA interactions on ES removal, ES retention in the
465 presence of HA was estimated from the calculated partition coefficient, K_{HA} , and the fraction of ES
466 bound to HA, f_{HA} . The approach developed by Neale and Schäfer (2012) for UF was modified for
467 NF. Neale and Schäfer (2012) determined hormone retention in the presence of HA as proportional
468 to the retention of HA and to the fraction of micropollutant bound to HA only, due to the low
469 retention of hormones by UF membranes. In the case of NF, micropollutant retention cannot be
470 ignored and the method was modified and improved by carrying out a mass balance in order to take
471 this term into account.

472

473 Some assumptions were made to determine the fraction of ES bound to HA and therefore estimate
474 retention due to complex formation:

475 (1) The total mass of ES in solution (m_{ES}) is either freely dissolved (m_{fES}) or complexed to HA
476 (m_{ES-HA}) after the membrane saturation has been reached:

$$477 m_{ES} = m_{ES-HA} + m_{fES} \quad (6)$$

478 (2) ES complexed with HA is retained together with the HA to which it is partitioned

479 (3) ES freely dissolved in HA solution has the same retention as ES during experiments without
480 HA carried out at the same conditions of pH, pressure and background electrolyte.

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481

482 While the first two assumptions can be considered generally valid, the last assumption will not be
 483 true if the presence of HA influences the retention of freely dissolved ES. HA-membrane
 484 interactions can influence the retention of freely dissolved ES in the HA solution and result in
 485 different overall ES retention than the estimated retention. HA can adsorb to the membrane surface
 486 resulting in pore blocking (Xu et al. 2005) and increasing membrane charge (Hong and Elimelech
 487 1997, Xu et al. 2005), membrane MWCO (Xu et al. 2006) and membrane hydrophilicity (Hong and
 488 Elimelech 1997, Schäfer et al. 2010).

489

490 The total ES retention due to the retention of ES complexed with HA and freely dissolved ES has
 491 been estimated by mass balance from the total mass of ES in the feed (m_{ESfeed}) and in the permeate
 492 (m_{ESperm}):

$$m_{ESfeed} = m_{ES-HAfeed} + m_{IESfeed} = f_{HA} \cdot m_{ESfeed} + (1 - f_{HA}) \cdot m_{ESfeed} \quad (7)$$

$$m_{ESperm} = m_{ES-HAperm} + m_{IESperm} = (1 - R_{HA}) \cdot m_{ES-HAfeed} + (1 - R_{ES}) \cdot m_{IESfeed} \quad (8)$$

495

496 where R_{HA} is the retention of HA and R_{ES} is the retention of ES during experiments without HA.

497 For TFC-SR3, R_{HA} was 99% and could be considered constant with pH and HA concentration (\pm
 498 2% variability); for TFC-SR2, the average HA retention over the pH was 88%, increasing from
 499 75.8% at pH 4 to 98.5% at pH 12 and from 71.5% for HA concentration 5 mgC/L to 99.1% for HA
 500 250 mgC/L.

501

502 The retention estimated with this methodology is indicated with a dotted line in Figure 3c and
 503 Figure 4c, and was compared with the retention obtained during ES-HA experiments. Similar
 504 experimental and estimated retention would indicate that solute-membrane interactions are
 505 negligible (i.e. the third hypothesis is verified) and solute-solute interactions are dominant. When

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506

507 solute-membrane interactions are important the retention predicted from K_{HA} is expected to be
 508 different from the retention obtained experimentally. This methodology depends on the fraction of
 509 micropollutant bound to NOM, on micropollutant retention and on NOM retention and it can be
 510 applied to any micropollutant that forms complexes with NOM to estimate the contribution of
 511 micropollutant-NOM interactions on micropollutant retention by NF, irrespective of the type of
 512 interactions and the compound properties.

512

513 As shown in Figure 3c, ES retention in the presence of HA estimated with K_{HA} was similar
 514 (maximum 10% difference) to the experimental retention for the TFC-SR3, showing that for this
 515 membrane solute-solute interactions (i.e. the formation of ES-HA complexes) are the dominant
 516 mechanism affecting ES retention. For TFC-SR2 the estimated retention was higher than the
 517 experimental retention for all the pH range studied, with the exception of pH 4 and 12, indicating
 518 that solute-membrane interactions (i.e. HA-membrane interactions) played a role. For both
 519 membranes at pH 4 the estimated ES retention was similar to the experimental retention (Figure 4c),
 520 indicating that at this pH solute-solute interactions are the dominant mechanism.

521

522 For TFC-SR2 at pH 8 ES retention obtained experimentally was lower than the estimated ES
 523 retention for any HA concentration (Figure 4c). At this pH the role of solute-membrane interactions
 524 on ES removal was more predominant than the formation of ES-HA complexes. The U-shape of the
 525 retention curve indicated that solute-membrane interactions were dominant for lower HA
 526 concentrations while at high HA concentrations both ES-HA interactions and pore blocking by HA
 527 fouling (evidenced from a decrease in permeate flux in Figure 4a) became more important.
 528 However, even at high HA concentrations ES retention was lower than the estimated retention
 529 (dotted line) since solute-membrane interactions could not be considered negligible.

530

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531 In order to establish how solute-membrane interactions affected ES retention in the presence of HA,
532 the characteristics of both membranes were evaluated for membranes pre-filtered with 900 mL of
533 ultra-pure water and background electrolyte and membranes pre-filtered with 900 mL of solution
534 containing 12.5 mgC/L of HA and background electrolyte at pH 8. Membrane MWCO and contact
535 angle were determined in order to evaluate change in membrane pore size and hydrophilicity caused
536 by the presence of HA (Table 3).

(TABLE 3)

540 HA deposited preferentially on the TFC-SR3, forming a visible yellowish layer on the membrane,
541 while visible HA deposits were not observed on the TFC-SR2. This different behaviour does not
542 seem to be linked with the different roughness of the two membranes (Table 2), as the membrane
543 with the highest roughness had no visible deposits on its surface. MWCO increased in the presence
544 of HA for both membranes, confirming what was inferred in previous studies (Xu et al. 2005, Xu et
545 al. 2006). The increase in MWCO for TFC-SR3 did not influence ES retention as the higher
546 MWCO (179 g/mol) was still lower than ES MW (407 g/mol). In the case of TFC-SR2, for which
547 micropollutant MW/membrane MWCO ratio < 1 and ES is partially retained, the increase in
548 MWCO from 460 to 496 g/mol decreased the ratio further, in turn decreasing ES retention.

550 After HA were filtered the observed contact angle decreased for TFC-SR2 and increased for TFC-
551 SR3 (Table 3). For membranes fouled by NOM, contact angle measurements have been shown to
552 be representative of the fouling layer: in the case of fouling by HA, contact angles indicated the
553 adhesion of a layer of intermediate hydrophobicity (Jucker and Clark 1994, Lee et al. 2004, Palacio
554 et al. 1999, Xu et al. 2006). For TFC-SR3 the contact angle is thought to be determined by the HA
555 layer visibly deposited on the membrane after filtration; the roughness of the HA deposits were also
556 likely to increase the observed contact angle (de Gennes 1985). For TFC-SR2, for which HA

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557 deposits were not visible after filtration, the contact angle is thought to reflect membrane
558 hydrophilization due to filtration of charged HA (Hong and Elimelech 1997). Increase in
559 hydrophilization can also explain the observed increase in permeate flux (Figure 4a).

560
561 A schematic of the proposed mechanisms is presented in Figure 5. At pH 4, when membranes and
562 HA are neutrally charged, size exclusion and solute-solute interactions (i.e. ES-HA interactions)
563 dominated ES retention. At neutral pH, both HA and the membranes are negatively charged and
564 solute-membrane interactions (i.e. HA-membrane interactions) influence membrane MWCO and
565 hydrophilicity. The filtration of HA increased the MWCO for both membranes (Table 3), but
566 different trends were obtained. For TFC-SR3, whose micropollutant MW/membrane MWCO ratio
567 > 1, the small increase in MWCO from 165 to 179 g/mol was not sufficient to allow for increase in
568 ES passage. This low HA impact in MWCO increase was further evidenced by a lack of increase in
569 permeate flux (Figure 3 a and Figure 4 a). For TFC-SR3, the formation of ES-HA complexes was
570 the dominant mechanism responsible for the increase of ES retention and it overcame the increase
571 in MWCO (Figure 3 c). For TFC-SR2, interactions between charged HA and the membrane also
572 resulted in an increase of the MWCO (Table 3), which is further evidenced from an increase in
573 permeate flux (Figure 3 a and Figure 4 a). As TFC-SR2 has a micropollutant MW/membrane
574 MWCO < 1, a further increase in the MWCO had a high impact in ES retention by decreasing it
575 considerably. For TFC-SR2, HA-membrane interaction was the dominant mechanism responsible
576 for the decrease of ES retention when HA are present since the formation of HA-ES complexes did
577 not overcome the increase of membrane MWCO.

(FIGURE 5)

580

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581 **4 Conclusions**

582 The mechanisms involved in the removal of micropollutants by NF membranes in the presence of
583 NOM were identified and evaluated in this study. For the first time, the contribution of both solute-
584 solute interactions and solute-membrane interactions were evaluated to explain micropollutant
585 retention mechanisms.

586

587 Results showed that in the absence of HA-membrane interactions, ES-HA complexation was the
588 governing mechanism in ES removal, enhancing ES removal. ES-membrane interactions did not
589 contribute to the variation of ES retention in the presence of HA. In contrast, HA-membrane
590 interactions affected membrane performance by increasing the MWCO and decreasing ES retention.

591

592 This work improves the understanding of the fundamentals involved in the removal mechanisms by
593 NF and demonstrates that the evaluation of the contributions of both solute-solute interactions and
594 solute-membrane interactions is fundamental for understanding micropollutant removal
595 mechanisms by NF

596 **Acknowledgments**

597 The authors would like to thank Koch Membranes Systems for kindly providing the membranes
598 used during the experiments, Dr. Alexander Bismarck and Dr. Kingsley Ho, Imperial College, UK,
599 for assistance with zeta potential measurements, Dott. Flaminia Gallo and Dr. Alberto Figoli ITM-
600 CNR, Italy, for contact angle measurements, Ime Akanayeti and Dr. Nhan T Pham, The University
601 of Edinburgh, UK, for AFM measurements, Dr. Peta Neale, The University of Queensland, for
602 useful discussions and proof reading and Dr. Helfrid Schulte-Herbrüggen, The University of
603 Edinburgh, for paper proof reading. Special thanks are given to the Drinking Water Quality
604 Regulator for Scotland (DWQR) and the School of Engineering of The University of Edinburgh for
605 funding the PhD studentship for De Munari.

606

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607 **References**

608 Agbekodo, K.M., Legube, B. and Dard, S. (1996) Atrazine and simazine removal mechanisms by
609 nanofiltration: Influence of natural organic matter concentration. *Water Research* 30(11), 2535-
610 2542.

611 Banasiak, L.J. (2009) Removal of inorganic and trace organic contaminants by electrodialysis. PhD
612 Thesis, The University of Edinburgh.

613 Bellona, C., Drewes, J.E., Xu, P. and Amy, G. (2004) Factors affecting the rejection of organic
614 solutes during NF/RO treatment - a literature review. *Water Research* 38(12), 2795-2809.

615 Boussahel, R., Montiel, A. and Baudu, M. (2002) Effects of organic and inorganic matter on
616 pesticide rejection by nanofiltration. *Desalination* 145(1-3), 109-114.

617 Braghetta, A., Di Giano, F.A. and Ball, W.B. (1997) Nanofiltration of natural organic matter: pH
618 and ionic strength effects. *Journal of Environmental Engineering* 123(7), 628-641.

619 Childress, A.E. and Elimelech, M. (1996) Effect of solution chemistry on the surface charge of
620 polymeric reverse osmosis and nanofiltration membranes. *Journal of Membrane Science* 119(2),
621 253-268.

622 Chin, Y., Aiken, G. and O'Loughlin, E. (1994) Molecular weight, polydispersity, and spectroscopic
623 properties of aquatic humic substances. *Environmental Science and Technology* 28(11), 1853-1858.

624 Cyna, B., Chagneau, G., Bablon, G. and Tanghe, N. (2002) Two years of nanofiltration at the Méry-
625 sur-Oise plant, France. *Desalination* 147(1-3), 69-75.

626 Dalwani, M., Benes, N.E., Bargeman, G., Stamatialis, D. and Wessling, M. (2011) Effect of pH on
627 the performance of polyamide/polyacrylonitrile based thin film composite membranes. *Journal of*
628 *Membrane Science* 372(1-2), 228-238.

629 Dalwani, M., Benes, N.E., Bargeman, G., Stamatialis, D. and Wessling, M. (2010) A method for
630 characterizing membranes during nanofiltration at extreme pH. *Journal of Membrane Science*
631 363(1-2), 188-194.

De Munari, A., Semiao, A.J.C., Antizar-Ladislao, B. (2013) "Retention of pesticide Endosulfan by nanofiltration: Influence of organic matter-pesticide complexation and solute-membrane interactions", *Water Research* 47(10):3484-3496. doi:10.1016/j.watres.2013.03.055

632 de Gennes, P.G. (1985) Wetting: statics and dynamics. *Reviews of Modern Physics* 57(3), 827-863.

633 De Munari, A. (2012) Removal mechanisms of organic and inorganic solutes in raw, upland
634 drinking water by nanofiltration: Influence of solute-solute and solute-membrane interactions. PhD
635 Thesis, The University of Edinburgh.

636 Devitt, E.C., Ducellier, F., Côté, P. and Wiesner, M. (1999) Effects of natural organic matter and
637 the raw water matrix on the rejection of atrazine by pressure-driven membranes. *Water Research*
638 32(9), 2563-2568.

639 Devitt, E.C. and Wiesner, M.R. (1998) Dialysis investigations of atrazine-organic matter
640 interactions and the role of a divalent metal. *Environmental Science and Technology* 32(2), 232-
641 237.

642 DiFilippo, E.L. and Eganhouse, R.P. (2010) Assessment of PDMS-water partition coefficients:
643 Implications for passive environmental sampling of hydrophobic organic compounds.
644 *Environmental Science and Technology* 44(18), 6917-6925.

645 Forman, S., Durbetaki, A., Choen, M. and Olofson, R.A. (1965) Conformational equilibria in cyclic
646 sulfites and sulfates. The configurations and conformations of the two isomeric thiodans. *Journal of*
647 *Organic Chemistry* 30(1), 169-175.

648 German Federal Environment Agency (2007) Draft dossier prepared in support of a proposal of
649 endosulfan to be considered as a candidate for inclusion in the annexes of the Stockholm
650 Convention.

651 Hajibabania, S., Verliefe, A., McDonald, J.A., Khan, S.J. and Le-Clech, P. (2001) Fate of trace
652 organic compounds during treatment by nanofiltration. *Journal of Membrane Science* 373(1-2),
653 130-139.

654 Hansch, C., Leo, A. and Hoekman, D. (1995) Exploring QSAR: hydrophobic, electronic and steric
655 constants, American Chemical Society, Washington DC, USA.

656 Hillenbrand, T., Marscheider-Weidemann, F., Strauch, M. and Heitmann, K. (2006) Prioritäre
657 Stoffe der Wasserrahmenrichtlinie Datenblatt Nr. 14: Endosulfan (in German).

De Munari, A., Semiao, A.J.C., Antizar-Ladislao, B. (2013) "Retention of pesticide Endosulfan by nanofiltration: Influence of organic matter-pesticide complexation and solute-membrane interactions", *Water Research* 47(10):3484-3496. doi:10.1016/j.watres.2013.03.055

658 Hong, S. and Elimelech, M. (1997) Chemical and physical aspects of natural organic matter (NOM)
659 fouling of nanofiltration membranes. *Journal of Membrane Science* 132(2), 159-181.

660 Jin, X., Hu, J. and Ong, S.L. (2007) Influence of dissolved organic matter on estrone removal by NF
661 membranes and the role of their structures. *Water Research* 41(14), 3077-3088.

662 Jin, X., Hu, J. and Ong, S.L. (2010) Removal of natural hormone estrone from secondary effluents
663 using nanofiltration and reverse osmosis. *Water Research* 44(2), 638-648.

664 Jucker, C. and Clark, M.M. (1994) Adsorption of aquatic humic substances on hydrophobic
665 ultrafiltration membranes. *Journal of Membrane Science* 97, 37-52.

666 Kimura, K., Amy, G., Drewes, J. and Watanabe, Y. (2003) Adsorption of hydrophobic compounds
667 onto NF/RO membranes: an artifact leading to overestimation of rejection. *Journal of Membrane*
668 *Science* 221(1-2), 89-101.

669 Lee, N., Amy, G., Croué, J.-P. and Buisson, H. (2004) Identification and understanding of fouling
670 in low-pressure membrane (MF/UF) filtration by natural organic matter (NOM). *Water Research*
671 38(20), 4511-4523.

672 Miller, J.N. and Miller, J.C. (2000) *Statistics and chemometrics for analytical chemistry*, Pearson
673 Education Limited, Harlow.

674 Ministerio de Agricultura Pesca y Alimentacion (1999) Endosulfan - Vol 1 - Monograph prepared
675 in the context of the inclusion of the following active substance in Annex I of the Council Directive
676 91/414/EEC.

677 Neale, P.A., Escher, B.I. and Schäfer, A.I. (2008) Quantification of solute-solute interactions using
678 negligible-depletion solid-phase microextraction: measuring the affinity of estradiol to bulk organic
679 matter. *Environmental Science and Technology* 42(8), 2886-2892.

680 Neale, P.A. and Schäfer, A.I. (2012) Quantification of solute-solute interactions in steroidal
681 hormone removal by ultrafiltration membranes. *Separation and Purification Technology* 90, 31-38.

De Munari, A., Semiao, A.J.C., Antizar-Ladislao, B. (2013) "Retention of pesticide Endosulfan by nanofiltration: Influence of organic matter-pesticide complexation and solute-membrane interactions", *Water Research* 47(10):3484-3496. doi:10.1016/j.watres.2013.03.055

682 Ng, H.Y. and Elimelech, M. (2004) Influence of colloidal fouling on rejection of trace organic
683 contaminants by reverse osmosis. *Journal of Membrane Science* 244(1-2), 215-226.

684 Nghiem, L.D., Schäfer, A.I. and Elimelech, M. (2004) Removal of natural hormones by
685 nanofiltration membranes: Measurement, modeling, and mechanisms. *Environmental Science and*
686 *Technology* 38(6), 1888-1896.

687 Organization for Economic Cooperation and Development (1995) Environment Monograph No.
688 108: Final report on the OECD project to compare pesticides data reviews.

689 Palacio, L., Calvo, J.I., Prádanos, P., Hernández, A., Väisänen, P. and Nyström, M. (1999) Contact
690 angles and external protein adsorption onto UF membranes. *Journal of Membrane Science* 152(2),
691 189-201.

692 Peterson, S.M. and Batley, G.E. (1993) The fate of endosulfan in aquatic ecosystems.
693 *Environmental Pollution* 82(2), 143-152.

694 Plakas, K.V. and Karabelas, A.J. (2009) Triazine retention by nanofiltration in the presence of
695 organic matter: The role of humic substance characteristics. *Journal of Membrane Science* 336(1-
696 2), 86-100.

697 Plakas, K.V., Karabelas, A.J., Wintgens, T. and Melin, T. (2006) A study of selected herbicides
698 retention by nanofiltration membranes - the role of organic fouling. *Journal of Membrane Science*
699 284(1-2), 291-300.

700 Poerschmann, J. and Kopinke, F.-D. (2001) Sorption of very hydrophobic organic compounds
701 (VHOCs) on dissolved humic organic matter (DOM). 2. Measurement of sorption and application
702 of a Flory-Huggins concept to interpret the data. *Environmental Science and Technology* 35(6),
703 1142-1148.

704 Prosen, H., Troha, A. and Zupančič - Kralj, L. (2002) Studies of interaction between some
705 organochlorine insecticides and humic acid using solid-phase microextraction and gas
706 chromatography. *Acta Chimica Slovenica* 49(3), 561-573.

De Munari, A., Semiao, A.J.C., Antizar-Ladislao, B. (2013) "Retention of pesticide Endosulfan by nanofiltration: Influence of organic matter-pesticide complexation and solute-membrane interactions", *Water Research* 47(10):3484-3496. doi:10.1016/j.watres.2013.03.055

707 Salvaterra, A.F., Sarmiento, G., Minhalma, M. and de Pinho, M.N. (2011) Nanofiltration of surface
708 water for the removal of endocrine disruptors. *Desalination and Water Treatment* 35(1-3), 54-61.

709 Sanches, S., Penetra, A., Granado, C., Cardoso, V.V., Ferreira, E., Benoliel, M.J., Barreto Crespo,
710 M.T., Pereira, V.J. and Crespo, J.G. (2011) Removal of pesticides and polycyclic aromatic
711 hydrocarbons from different drinking water sources by nanofiltration. *Desalination and Water*
712 *Treatment* 27(1-3), 141-149.

713 Schäfer, A.I., Nghiem, L.D., Meier, A. and Neale, P.A. (2010) Impact of organic matrix compounds
714 on the retention of steroid hormone estrone by a "loose" nanofiltration membrane. *Separation and*
715 *Purification Technology* 73(2), 179-187.

716 Schwarzenbach, R.P., Escher, B.I., Fenner, K., Hofstetter, T.B., Johnson, C.A., von Gunten, U. and
717 Wehrli, B. (2006) The challenge of micropollutants in aquatic systems. *Science* 313(5790), 1072-
718 1077.

719 Semião, A.J.C. and Schäfer, A.I. (2011) Estrogenic micropollutant adsorption dynamics onto
720 nanofiltration membranes. *Journal of Membrane Science* 381(1-2), 132-141.

721 Semião, A.J.C. and Schäfer, A.I. (2012) Removal of adsorbing estrogenic micropollutants by
722 nanofiltration membranes. Part A - experimental evidence. *Journal of Membrane Science* 431: 244-
723 256.

724 Shin, H.-S., Monsallier, J.M. and Choppin, G.R. (1999) Spectroscopic and chemical
725 characterizations of molecular size fractionated humic acid. *Talanta* 50(3), 641-647.

726 Soto, A., Chung, K. and Sonnenschein, C. (1994) The pesticide endosulfan, toxaphene and dieldrin
727 have estrogenic effects on human estrogen-sensitive cells. *Environmental Health Perspectives*
728 102(4), 380-383.

729 Teixeira, M.R., Rosa, M.J. and Nyström, M. (2005) The role of membrane charge on nanofiltration
730 performance. *Journal of Membrane Science* 265(1-2), 160-166.

731 Vaes, W.H.J., Ramos, E.U., Hamwijk, C., van Holsteijn, I., Blaauboer, B.J., Seinen, W., Verhaar,
732 H.J.M. and Hermens, J.L.M. (1997) Solid phase microextraction as a tool to determine

De Munari, A., Semiao, A.J.C., Antizar-Ladislao, B. (2013) "Retention of pesticide Endosulfan by nanofiltration: Influence of organic matter-pesticide complexation and solute-membrane interactions", *Water Research* 47(10):3484-3496. doi:10.1016/j.watres.2013.03.055

733 membrane/water partition coefficients and bioavailable concentrations in vitro systems. *Chemical*
734 *Research in Toxicology* 10(10), 1067-1072.

735 Valor, I., Perez, M., Cortada, C., Apraiz, D., Molto, J.C. and Font, G. (2001) SPME of 52 pesticides
736 and polychlorinated biphenyls: Extraction efficiencies of the SPME coatings
737 poly(dimethylsiloxane), polyacrylate, poly(dimethylsiloxane)-divinylbenzene,
738 carboxenpoly(dimethylsiloxane) and carbowaxdivinylbenzene. *Journal of Separation Science* 24(1),
739 39-48.

740 Van der Bruggen, B., Verliefde, A., Braeken, L., Cornelissen, E., Moons, K., Verberk, J., Van Dijk,
741 H. and Amy, G.L. (2006) Assessment of a semi-quantitative method for estimation of the rejection
742 of organic compounds in aqueous solution in nanofiltration. *Journal of Chemical Technology and*
743 *Biotechnology* 81(7), 1166-1176.

744 Xu, P., Drewes, J.E., Bellona, C., Amy, G.L., Kim, T.U., Adam, M. and Heberer, T. (2005)
745 Rejection of emerging organic micropollutants in nanofiltration–reverse osmosis membrane
746 applications. *Water Environment Research* 77(1), 40-48.

747 Xu, P., Drewes, J.E., Kim, T.-U., Bellona, C. and Amy, G. (2006) Effect of membrane fouling on
748 transport of organic contaminants in NF/RO membrane applications. *Journal of Membrane Science*
749 279(1-2), 165-175.

750 Yoon, Y., Westerhoff, P., Snyder, S.A. and Wert, E.C. (2006) Nanofiltration and ultrafiltration of
751 endocrine disrupting compounds, pharmaceuticals and personal care products. *Journal of Membrane*
752 *Science* 270(1-2), 88-100.

753

754

De Munari, A., Semiao, A.J.C., Antizar-Ladislao, B. (2013) "Retention of pesticide Endosulfan by nanofiltration: Influence of organic matter-pesticide complexation and solute-membrane interactions", *Water Research* 47(10):3484-3496. doi:10.1016/j.watres.2013.03.055

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Figure 1 Mass of ES in the nd-SPME fibre for different ES concentrations and Log K_{fw} values for ES as function of pH. ES 10, 25, 50, 100 $\mu\text{g/L}$, background electrolyte 1 mM NaHCO_3 and 20 mM NaCl.

Figure 2 HA-water partition coefficient and fraction of ES bound to HA (a) as a function of pH, HA 12.5 mgC/L and (b) as a function of HA concentration. ES 10, 25, 50, 100 $\mu\text{g/L}$, background electrolyte 1 mM NaHCO_3 and 20 mM NaCl.

Figure 3 (a) Ratio of permeate flux J_v and initial pure water flux J_0 (b) ES adsorption (c) and ES retention as a function of pH for TFC-SR2 and TFC-SR3. Dotted lines indicate ES retention in presence of HA estimated using the calculated partition coefficient K_{HA} . ES 10 $\mu\text{g/L}$, HA 12.5 mgC/L, pressure 5 bar, background electrolyte 1 mM NaHCO_3 and 20 mM NaCl.

Figure 4 (a) Ratio of permeate flux J_v and initial pure water flux J_0 (b) ES adsorption and (c) ES retention as a function of HA concentration for TFC-SR2 and TFC-SR3. Dotted lines indicate ES retention in presence of HA estimated using the calculated partition coefficient K_{HA} . ES 10 $\mu\text{g/L}$, pressure 5 bar, HA 5, 7.5, 12.5, 25 50, 125 250 mgC/L, background electrolyte 1 mM NaHCO_3 and 20 mM NaCl.

Figure 5 Conceptual sketch (to scale) of main retention mechanisms for freely dissolved ES (MW 407 g/mol) and ES-HA complexes by TFC-SR2 and TFC-SR3. The presence of HA increases the MWCO for both membranes at pH 8 (changes indicated by the lighter area on the membranes). For TFC-SR3, MWCO increases from 165 to 179 g/mol but the passage of ES decreases due to the formation of ES-HA complexes: solute-solute interactions are the main mechanism of ES retention

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in the presence of HA. For TFC-SR2, MWCO increases from 460 to 496 g/mol causing an increase

in the passage of ES despite the formation of ES-HA complexes: solute-membrane interactions are the dominant mechanism.

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Table 2 – Characteristics of TFC-SR2 and TFC-SR3

Table 3 – Membrane characteristics for a membrane pre-filtered with 900 mL of ultra-pure water and background electrolyte and a membrane through which 12.5 mgC/L of HA and background electrolyte have been filtered at pH 8

Table 1

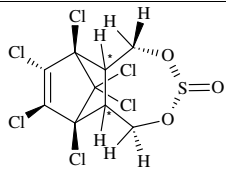
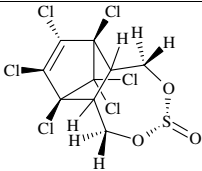
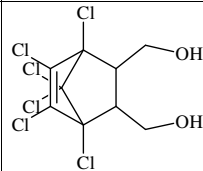
	α -ES	β -ES	Endosulfan diol
			
Formula	C ₉ H ₆ Cl ₆ O ₃ S	C ₉ H ₆ Cl ₆ O ₃ S	C ₉ H ₈ Cl ₆ O ₂
Molecular Weight (g/mol)	406.93	406.93	360.88
Log K _{ow}	3.83 (Hansch et al. 1995)	3.83 (Hansch et al. 1995)	3.68 (Banasiak 2009)
pK _a	-	-	14.62–15.22 (Banasiak 2009)
Dipole Moment	1.02 (Forman et al. 1965)	3.18 (Forman et al. 1965)	Not available

Table 2

	Material	MWCO ¹ (g/mol)	Estimated pore radius (nm)	Point of zero charge ² (pH)	Contact Angle (°)	Roughness ³ (nm)
TFC-SR2	Polyamide on	460	0.52	4.25	57	17.9
TFC-SR3	polysulfone	165	0.38	3.84	44	5.2

¹pressure 5 bar, neutral pH

²Electrolyte solution 1 mM NaHCO₃ and 20 mM NaCl

³ Average roughness, R_a

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Table 3

Pre-filtration Method	TFC-SR2		TFC-SR3	
	Ultra-pure water and electrolyte ¹	HA and electrolyte ¹	Ultra-pure water and electrolyte ¹	HA and electrolyte ¹
MWCO (g/mol)	460	496	165	179
Contact angle	57	49	44	59

¹Electrolyte solution 1 mM NaHCO₃ and 20 mM NaCl

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Figure 1

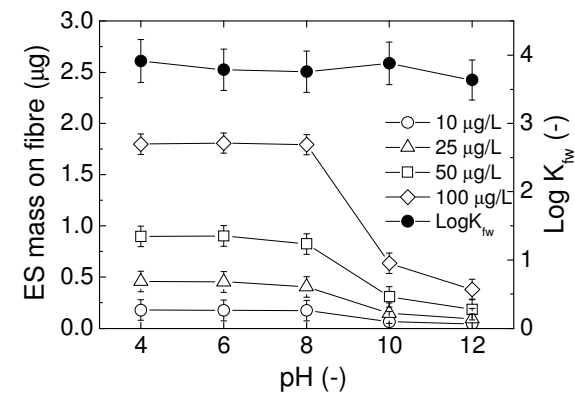


Figure 2

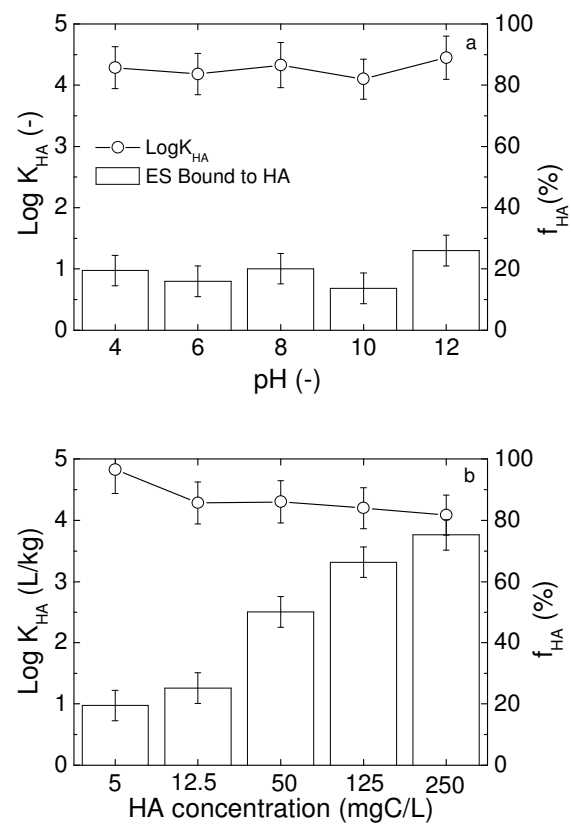


Figure 3

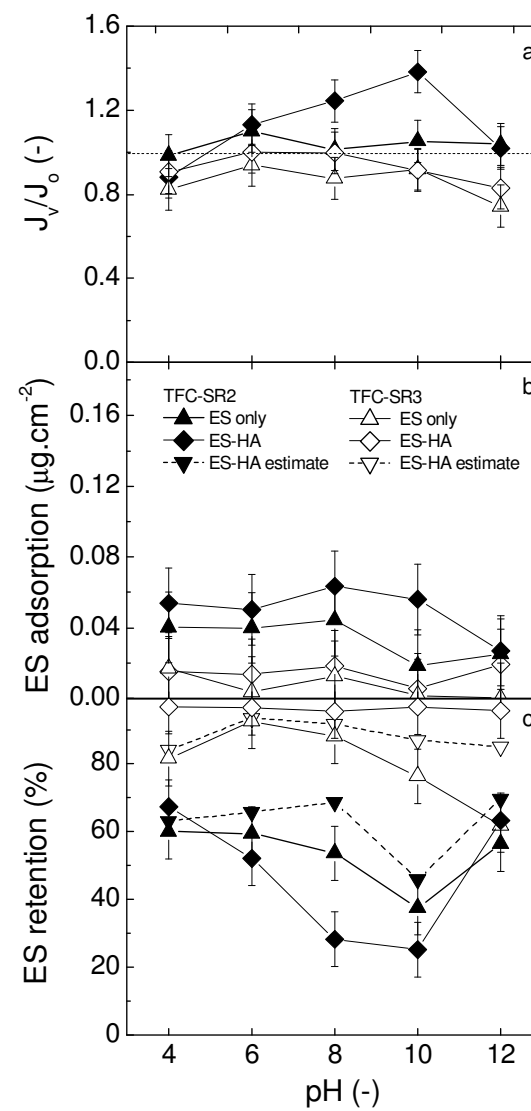


Figure 4

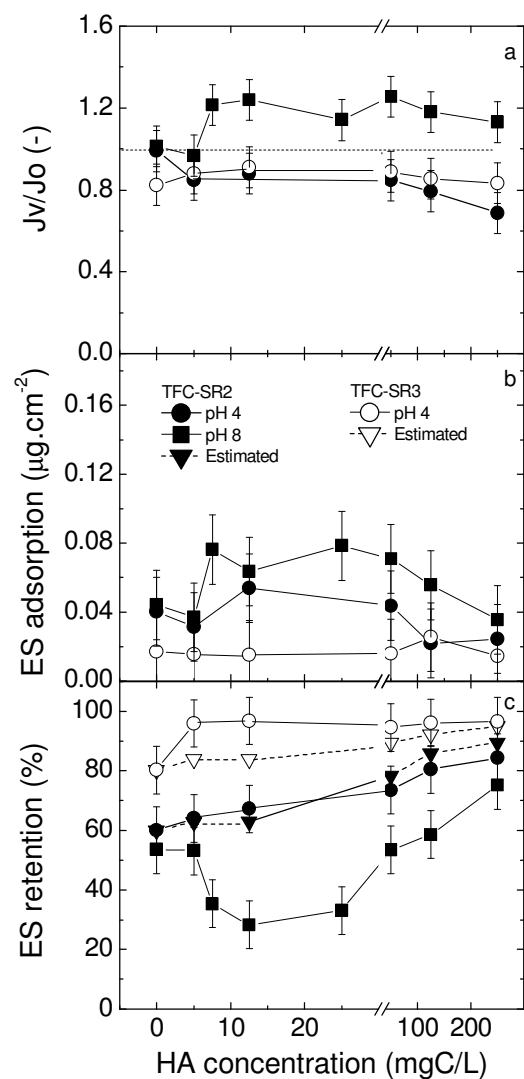


Figure 5

