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Non-target screening of organic compounds in offshore produced water by GC×GC-MS

Sofie N Bergfors [1], **Khoa Huynh** [1], **Annette E Jensen** [1], **Jonas Sundberg** [Corresp. 1]

[1] Danish Hydrocarbon Research and Technology Centre, Technical University of Denmark, Kgs. Lyngby, Denmark

Corresponding Author: Jonas Sundberg
Email address: jonsun@dtu.dk

Produced water is the largest by-product of oil and gas production. At off-shore installations, the produced water is typically reinjected or discharged into the sea. The water contains a complex mixture of dispersed and dissolved oil, solids and inorganic ions. A better understanding of its composition is fundamental to 1) improve environmental impact assessment tools and 2) develop more efficient water treatment technologies. The objective of the study was to screen produced water sampled from a producing field in the Danish region of the North Sea to identify any containing organic compounds. The samples were taken at a test separator and represent an unfiltered picture of the composition before cleaning procedures. The analytes were isolated by liquid-liquid extraction and derivatized using a silylation reagent to increase the volatility of oxygenated compounds. The final extracts were analyzed by comprehensive multi-dimensional gas chromatography coupled to a high-resolution mass spectrometer. A non-target processing workflow was implemented to extract features and quantify the confidence of library matches by correlation to retention indices and the presence of molecular ions. Approximately 120 unique compounds were identified across nine samples. Of those, 15 were present in all samples. The main types of compounds are aliphatic and aromatic carboxylic acids with a small fraction of hydrocarbons. The findings have implications for developing improved environmental impact assessment tools and water remediation technologies.

1 **Non-target screening of organic compounds in**
2 **offshore produced water by GC×GC-MS**

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5
6 [1] Danish Hydrocarbon Research and Technology Centre, Technical University of
7 Denmark, Kgs. Lyngby, Denmark
8
9 Corresponding author:
10 Jonas Sundberg[1]
11
12 Email address: jonsun@dtu.dk

Introduction

Produced water is by volume the largest byproduct in oil and gas production. For reservoirs on the Danish continental shelf, where production is often supported by water flooding, the volume of produced water typically exceeds the volume of oil (The Danish Energy Agency, 2014). This water contains a complex mixture of inorganic and organic compounds. Implementation of offshore water management strategies is challenging due to the large volumes and practical limitations on infrastructure. Current procedures consist of cleaning of the produced water, followed by discharge into the sea or reinjection in producing or disposal wells (Lyngbaek & Blidegn, 1991; Røe & Johnsen, 1996; Røe Utvik, 1999; Durell et al., 2004). For discharge, the OSPAR Convention, which was set in to force in 1998, sets a limit of 30 mg of dispersed oil per liter of water as an annual average (OSPAR Commission, 2001). There is currently no limit on the dissolved compounds. Furtthermore, detailed knowledge on their structure and abundance is lacking.

In simplified terms, produced water can be seen as the product of aqueous extraction of crude oil by mixing within the reservoir and during production. In reality, the process is complex and the composition is highly dependent on reservoir properties, field history and water injection strategies (Bergfors, Schovsbo & Feilberg, 2020). For example, studies have shown that salinity influences to the organic content, likely caused by a salting-out effect (Barth, Borgund & Riis, 1990; Barth, 1991; Barth & Riis, 1992; Endo, Pfennigsdorff & Goss, 2012; Dudek et al., 2020). At the producing platform, a gravitational separation of oil, water and gas is carried out. The resulting water phase contains dissolved and dispersed oil droplets. The latter is largely removed by physical methods, i.e. separators, hydrocyclones and gas flotation tanks/degassers implemented in series on the platform, typically resulting in levels below 10 mg/L at the discharge point (Meldrum, 1988; Saththasivam, Loganathan & Sarp, 2016; Durdevic & Yang, 2018). In contrast, the removal of dissolved organics requires chemical treatment, e.g. degradation via advanced oxidation processes (AOPs) (Jiménez et al., 2019; Lin et al., 2020; Liu et al., 2021). This is challenging to implement on offshore installations due to safety and the requirement of low residency times. Furthermore, the current generation of AOPs are mainly based on Fenton's reagent which produces toxic chlorinated byproducts when applied to saline water (Kiwi, Lopez & Nadtochenko, 2000; De Laat & Le, 2006; Sirtori et al., 2012). The goal of produced water management is not necessarily zero discharge but zero *harmful* discharge. Improved knowledge of its composition is thus not only beneficial to develop environmental impact assessment tools. The information may also be used to develop improved and targeted treatment methods, i.e specific removal of harmful components, and not total organic content. This has the potential to increase efficiency and reduce the cost of water management strategies.

53

54 Ultimately, the toxicity of the produced water is a complex function based on the
55 structure and concentration of both the dispersed and dissolved oil components
56 (Strømgren et al., 1995; Bakke, Klungsøyr & Sanni, 2013; Niu et al., 2016; Lofthus et
57 al., 2018). Furthermore, inorganic species such as heavy metals should be taken into
58 consideration. We argue that to fully understand the effect of organic compounds in
59 produced water discharge, we must 1) carry out full structural characterization studies
60 and 2) differentiate between dispersed and dissolved species and 3) develop methods
61 to integrate the data into environmental impact assessment tools. Although numerous
62 compounds in produced water have been identified as part of ongoing water quality
63 studies, a large part of the chemical space remains unknown. Recent advances in
64 analytical technology (i.e. multi-dimensional chromatography, high-resolution mass
65 spectrometry) have allowed more in-depth studies of the organic composition
66 (Samanipour et al., 2019, 2020; Sørensen et al., 2019; Dudek et al., 2020). However,
67 these studies mainly focus on general classes of naphthenic acids and are based on
68 formula calculations of exact masses without further structural elucidations. Sørensen
69 et. al. (2019) described a non-target screening study but did not provide details beyond
70 compound classes (i.e. phenols vs. naphthalenes). Thus, a large knowledge gap in the
71 identity of dispersed and dissolved organics still exists.

72

73 To narrow this gap we have carried out a non-target screening study. The objective was
74 not to evaluate the efficiency of implemented cleaning procedures but to obtain an
75 "unfiltered" picture of the water composition immediately after production. Several
76 samples were obtained from the test separator of a producing platform in the Danish
77 North Sea. The organics were extracted by liquid-liquid extraction (LLE) using
78 dichloromethane (DCM). The extracts were derivatized to increase the volatility of
79 oxygenated compounds and analyzed using comprehensive multidimensional gas
80 chromatography (GC×GC) coupled with a high-resolution quadrupole-time of flight mass
81 spectrometer (MS). One advantage of using GC-MS as compared to liquid-
82 chromatography (LC)-MS is the possibility of identification by spectral matching using
83 commercially available libraries. In contrast, LC-MS is significantly dependent on user-
84 generated libraries based on reference compounds as the ionization efficiency is more
85 dependent on experimental conditions (Schymanski et al., 2015). Approximately 1500
86 compounds were detected per sample, with 120 unique compounds tentatively
87 identified across all samples. To increase the confidence of library matches, a data
88 processing workflow that implemented retention indices and accurate mass matching
89 was implemented. The data were analyzed to obtain a broad knowledge of the types of
90 compounds present, their relative abundance as well as common compounds present
91 across all samples.

92

Materials & Methods

Chemicals and reagents

Benzoic acid, phenol, cycolhexanecarboxylic acid, octanoic acid, dichloromethane (LiChroSolv, Merck), *n*-hexane (SupraSolv for gas chromatography MS, Merck), magnesium sulfate (ReagentPlus, Redi-Dri, Sigma Aldrich), N,O-bis(trimethylsilyl)trifluoroacetamide containing 1% of trimethylchlorosilane (BSTFA+TMCS, Supelco) were used as received. Deuterated internal standards (naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, Supelco analytical standards) were used to monitor retention time shifts. ^{1}D retention index calibration was performed using a linear C7 to C30 saturated alkanes mixture (Supelco, TraceCERT, Sigma Aldrich). High purity water was obtained from a Milli-Q Advantage A10 unit. All chemicals and reagents were used as received.

Sampling and sample preparation

Produced water samples were donated by Mærsk Oil & Gas (now Total E&P). The samples were acquired from a producing field (water-injected) located in the Danish region of the North Sea. The sampling campaign took place between June 2018 and February 2019. The samples were taken at irregular intervals with no replicates. Water samples were collected at the test separator on the production platform following protocols established by the operator. The test separator is a simple gravity-based three-phase separator where the water settles below the oil and can be sampled. No cleaning or further processing of the samples was carried out at the platforms. The samples were received in plastic bottles (1 L), aliquoted (500 mL), and immediately treated with dilute hydrochloric acid (18%, 1 mL per 100 mL sample) for a final pH < 2. Nine samples from the received batch were selected for analysis. The samples were selected due to the absence of dispersed oil droplets as evaluated by visual inspection (using microscope). The samples were stored in the dark at 4 °C until extraction and analysis.

Three aliquots (50 mL) of each produced water sample were extracted using separate glassware. The aliquots were filtered through a 0.45 µm PTFE-filter to remove solids and particles. Each 50 mL aliquot was extracted with DCM (50 mL). The organic phase was washed with saturated aqueous sodium chloride (50 mL) and carefully removed in vacuo. The residue was reconstituted in *n*-hexane (1.5 mL) and dried over $MgSO_4$. An aliquot (1000 µL) of the sample was transferred to a 2 mL vial, combined with deuterated internal standards (for monitoring of retention time stability), combined with BSTFA+TMCS (50 µL) and incubated at 70 °C for 30 minutes, whereafter, it was allowed to return to room temperature. The derivatized sample was further diluted ten-fold with *n*-hexane and immediately analyzed on the GC×GC-MS.

133 **Extraction recovery and reproducibility**
134 A model produced water containing five representative model compounds (benzoic
135 acid, phenol, 2-naphthoic acid, cyclohexanecarboxylic acid, and octanoic acid, each at 5
136 ppm, total organics 25 ppm) in synthetic formation water (see supplemental information)
137 was prepared to establish variability in the sample preparation protocol and instrumental
138 analysis. The concentration of total organics was chosen to emulate typical levels
139 encountered at production platforms. The model water was extracted four times in two
140 batches following an identical procedure as for the produced water samples. Three
141 procedural blanks were prepared to establish background levels and experimental
142 sources of contamination.
143
144 **GC×GC-MS Analyses**
145 GC×GC-MS data were acquired using an Agilent 7890B GC coupled to a 7200B QTOF
146 high-resolution mass spectrometer (Agilent Technologies, Palo Alto, CA, USA). The
147 system was equipped with a Zoex ZX-2 thermal modulator (Zoex Corporation, Houston,
148 TX, USA). The separation was achieved using a combination of an Agilent DB-5MS UI
149 (^{1}D, 30 m, 0.25 mm i.d., 0.25 μm d_f) and a Restek Rxi-17Sil MS (^{2}D, 2 m, 0.18 mm i.d.,
150 0.18 μm d_f) capillary columns connected using a SilTite μ-union. The oven was
151 temperature programmed as follows; 1 min hold-time at 50 °C, ramp to 320 °C, 3 °C
152 min^{-1} in constant flow mode (1 mL/min). The modulation period was set to 3 s with a 400
153 ms hot-jet duration. The MS transfer line was held at 280 °C. The MS acquired spectra
154 in electron ionization mode (70 eV) with a mass range of 45 – 500 and an acquisition
155 speed of 50 Hz. The instrument was operated in its 2 GHz sampling rate mode to
156 increase the dynamic range. Automatic mass calibration was performed for every 5th
157 sample (approximately 7.5 hours).
158
159 **Data processing**
160 Baseline correction (Reichenbach et al., 2003), peak detection and library search were
161 performed using GC Image v2.8.3 (Zoex, Houston, TX). Mass spectra were matched
162 against the NIST Mass Spectral Library (National Institute of Standards and
163 Technology, 2017 edition) with a minimum match factor of 700. All compound tables
164 were exported as comma-separated texts for external processing. A data processing
165 workflow was implemented in Python (Python Software Foundation. Python Language
166 Reference, version 3.7.4. Available at http://www.python.org). The script is available as
167 supplementary information deposited in a Zenodo repository (doi://
168 10.5281/zenodo.4009045).
169
170 # Results
171 **Sample preparation and analyses**

172 Previous studies on dissolved organics in oilfield produced water have employed LLE or
173 solid-phase extraction (SPE) (Thomas et al., 2009; Kovalchik et al., 2017; Barros et al.,
174 2018; Samanipour et al., 2019). For produced water, LLE using DCM has been shown
175 to have a similar recovery as SPE (Samanipour et al., 2019). The main difference was
176 observed in the size distribution, where larger species tend to have a higher recovery
177 using SPE due to their low solubility in DCM. LLE is non-discriminative in comparison to
178 SPE which is used to fractionate compound classes based on adsorption
179 characteristics. Thus, it allowed us to extract the broad range of organics present in
180 produced water. Furthermore, the Norwegian Oil and Gas specialist network
181 recommends LLE for the quantification of phenols in produced water (Norwegian Oil
182 and Gas, 2012). Thus, it would allow us to 'see' what is missing using routine targeted
183 analyses. Approximately 30 samples were received as part of the campaign.
184 The water samples had varying levels of oil, likely due to the sampling and status of the
185 test separator. Samples that contained a clear separate layer of oil, including smaller
186 amounts, were excluded from the study to minimize the risk of contamination (Figure 1).
187 Optical inspection of these samples showed that they contained large amounts of
188 dispersed oil droplets, even when sampling below the oil layer (Figure 2). After
189 exclusion, 9 samples were chosen to be included in the study with extraction and
190 characterization. All samples were filtered through a 0.45 µm PTFE-filter to remove
191 insoluble material and particles. A small aliquot (50 mL) of each sample was extracted
192 in triplicate using an equivalent volume of DCM.
193
194 The dissolved components of produced water were largely expected to be oxygenated
195 organics, i.e. alcohols (mainly phenols) and acids. To increase the volatility of the
196 aforementioned compounds, the samples were silylated. After removal of the solvent in-
197 vacuo, each sample was reconstituted in 1.5 mL of n-hexane. A 1 mL aliquot of the
198 reconstituted extract was treated with BSTFA-TMCS and incubated at 70 °C for 30
199 minutes. After derivatization, the samples were further diluted ten-fold, meaning that the
200 samples ultimately were concentrated approximately three-fold (from 50 mL to 15 mL).
201 The final concentration factor was chosen as a compromise between the detection of
202 trace compounds and avoiding column and detector overload. Due to the large
203 concentration range of our analytes, it would be beneficial to run each sample at
204 multiple dilution factors. However, due to the long run time (90 minutes) and the number
205 of extraction replicates (3) this was not feasible due to time constraints. It is important to
206 remember that this strategy has two effects; 1) high concentration compounds may
207 overload the detector with spectral skewing and poor library match as result, and 2)
208 trace-compounds may be diluted to a level below the limit of detection.
209
210 Three procedural blanks were extracted and analyzed to determine background levels
211 and potential sources of contamination. Minor amounts of fatty acids were detected in

212 addition to a series of polysiloxanes (discrete peaks, not common column bleed). The
213 source of the latter could not be identified but as it lacked retention in the ^{2}D it did not
214 interfere with our analytes of interest. To establish recovery and repeatability, a model
215 produced water was prepared by spiking four organic acids and phenol into synthetic
216 formation water (see Experimental section and supplemental data). All model
217 compounds were detected in one or more produced water samples. The model water
218 was extracted in four replicates. The recovery values were calculated based on peak
219 volumes in comparison to those obtained by analyzing pure stock solutions (Table 1).
220 The recovery varied from 36% for benzoic acid up to 90% for phenol. Considering the
221 multi-step sample extraction, including a derivatization reaction, this was deemed
222 acceptable. The relative standard deviation of the peak volumes (measured after
223 baseline correction using the GC Image package) of model compounds as detected in
224 a representative produced water sample varied from 2% to 23% (calculated from three
225 extraction replicates).
226
227 **Chromatography**
228 Crude oil is an ultracomplex mixture of saturated and aromatic hydrocarbons with a
229 smaller fraction of N,S,O-containing compounds (Marshall & Rodgers, 2004; Hsu et al.,
230 2011; Palacio Lozano et al., 2020). This complexity will be reduced but reflected in the
231 produced water. Based on previous studies of Danish oils we know that the dominant
232 oxygenated species belong to the O1 and O2 classes with a large diversity in
233 aromaticity (Sundberg & Feilberg, 2020). Thus, the compositional variation in the
234 produced water was assumed to be dominated by carbon number and level of
235 saturation. Ultimately, the boiling point range was assumed to be larger than the
236 variation in saturated versus aromatic structures. Therefore, we choose to use a non-
237 polar column in the ^{1}D (providing the highest separation power) with a shorter medium
238 polarity column in the ^{2}D. Conventional polar columns are based on polyethyleneglycol
239 (PEG) chemistry and are incompatible with silylation reagents. Therefore, we choose to
240 use a 50%-phenyl-type column where aromaticity is the largest factor affecting
241 retention. By using this column combination, the retention in both dimensions will
242 increase with aromaticity. For example, cyclohexane acetic acid has a retention of 17.2
243 min/0.84 s in ^{1}D/^{2}D as compared to 24.6 min/1.33 s for benzeneacetic acid (measured
244 as the corresponding trimethylsilyl esters). In contrast, alkylation of a core aromatic or
245 saturated structure will only affect retention in the ^{1}D. For example, phenol and its
246 alkylated homologs (methyl, ethyl and propyl) have ^{1}D retention times of 13.4, 16.9,
247 19.9 and 23.3 minutes, respectively, where the retention in ^{2}D is within 0.89 to 0.95
248 seconds. By investigation of a typical chromatogram, two things become obvious; 1) the
249 desired separation of saturates, mono- and diaromatics is achieved and 2) a large
250 portion of the ^{2}D space is relatively uncopied due to the small number of polycyclic

251 species where the majority of aromatics are benzene derivatives. A representative
252 chromatogram with selected analytes marked is presented in Figure 3.
253
254 A 3 °C min^{-1} temperature gradient was found to be the optimal compromise between
255 peak width, resolution and run time. At this rate, the typical peak width was 10 s in the
256 first dimension. Thus, using a modulation period of 3 s allowed us to obtain the
257 recommended minimum of three modulations per peak (Murphy, Schure & Foley, 1998).
258 Due to instrumental complexity and long run times, retention time shifts are commonly
259 observed both in inter-sample and inter-batch runs. Deuterated PAH standards were
260 used to monitor retention times over time. The ^{1}D/^{2}D retention time variability is
261 presented in Table 1. Both ^{1}D and ^{2}D were shown to be stable over the whole analyses
262 run, covering 27 seven injections (9 samples with three extraction replicates) and 7
263 days.
264

265 **Non-target screening and compound identification**
266 Approximately 1500 compounds were detected in each sample. A data processing
267 workflow was implemented to sort, organize and score the data. A schematic
268 representation is presented in Figure 4. The associated files are available as
269 supplementary information. The detected features were matched against the NIST EI
270 Mass Spectral Library (2017). All compounds with a match factor below 700 were
271 removed. To increase the annotation confidence, two additional factors were included;
272 retention index (Kovats) and the presence of the molecular ion. To quantify the
273 identification confidence the following scoring rules were implemented:
274
275   1. A match factor above 800 gives a score of 10 points.
276   2. A match factor between 700 and 800 gives a score of 5 points.
277   3. A retention index match within 50 units gives a score of 5 points.
278   4. The detection of the molecular ion within 20 ppm mass accuracy gives a score of
279   5 points.
280
281 A total score of above 10 was (i.e. match factor of a minimum of 700 and either a
282 retention index and or molecular ion match) was classified as a probable match,
283 whereas a total score below 10 was classified as a tentatively identified structure
284 (Schymanski et al., 2014). To reduce experimental errors, only features that were
285 present in all three replicates were included in the final table of compounds.
286 Furthermore, all duplicate compounds were removed. This is a crude step that
287 inherently removes, for example, isomeric species which would not be differentiated
288 using automatic library search. However, for our purpose the identification of isomers is
289 not an inherent goal. The aim of the study was to identify the presence of broad
290 compound-class types and dominant species. The correct identification of isomeric

291   species or species with highly similar fragmentation patterns requires manual
292   intervention and is beyond the scope of this study.
293
294   The workflow reduced the number of features from approximately **1)** 1500 detected to **2)**
295   200 library hits with match factor > 700, to **3)** 50 - 70 when with duplicates based on
296   name were removed. Ultimately, the merging of inter-sample features resulted in 120
297   unique hits across all samples. Of those, 42 had the maximum score of 20 (i.e. match
298   factor > 800, molecular ion detected and retention index within 50 units). Near all (87%)
299   identified compounds are oxygen-containing, with amines, sulfides and hydrocarbons
300   being the remaining constituents. Only 15 compounds (after removal of internal
301   standards and background species) were present in all samples (Table 2).
302

Discussion

304   A few papers have previously described non-target screening of produced water,
305   primarily from the Norwegian continental shelf. Sørensen et. al. described the
306   characterization of unpurified DCM extracts with comparisons to the polar and non-polar
307   fractions as isolated by SPE (Sørensen et al., 2019). In their study, a high concentration
308   of hydrocarbons including naphthalenes and linear alkanes was detected in the
309   produced water. This is in contrast to our study, where only a few hydrocarbons, in
310   relative trace amounts, were observed as measured by extracted ion chromatograms of
311   known species. The aqueous solubility of saturated hydrocarbons is low. However,
312   BTEX-type (benzene, toluene and xylene) compounds have relatively high solubility but
313   were still not identified. Furthermore, hydrocarbons could be present in the water phase
314   as dispersed oil droplets. We observed that the presence of such droplets in a water
315   sample is heavily dependent on the oil-water ratio and that optical inspection using a
316   microscope was required for their detection. Oil droplets were not observed in the
317   samples included in our study which we believe explain why only small amounts of
318   hydrocarbons were detected. A second explaination could be losses during sample
319   transport and storage, either via volatilization/diffusion through the plastic container or
320   microbial degradation. However, this cannot be validated without further sampling with
321   more control of the process.
322
323   Only a small fraction of the detected compounds were identified with an acceptable
324   confidence level. 36 unique compounds (across all samples) received the maximum
325   identification score, i.e. a match factor > 800, retention index match and detection of the
326   molecular ion. The match factor had the most severe impact on feature reduction.
327   Lowering the match factor limit to >600 increased the number of tentatively identified
328   features by approximately 40% (compared to match factor > 700). A manual evaluation
329   showed that although several hits were chemically reasonable based on structure and
330   retention index, the lower limit also led to multiple apparent false positives. Added

331 confidence to questionable identities could be obtained by a corroborative study using
332 soft ionization techniques, i.e. chemical ionization or low voltage electron ionization,
333 where the molecular ion is better observed for non-aromatic species.
334
335 Looking at the obtained data, two conclusions were made; 1) samples were dominated
336 by oxygenated organics, and 2) sample-to-sample variation was large, both in terms of
337 composition and relative abundance. Oxygenated hydrocarbons form during diagenesis
338 but may also be the result of microbial and or chemical processes during oil production
339 (Aitken, Jones & Larter, 2004; Head, Gray & Larter, 2014; Pannekens et al., 2019). The
340 oxygenation leads to high partitioning into the aqueous phase during oil-water
341 separation, and these compounds will likely require attention when developing
342 successful water management technologies. Approximately 50% of the compounds
343 were aromatic, primarily benzene-derivatives with few naphthalenes present. The
344 molecular structure of six representative compounds are presented in Figure 5. Some of
345 the identified compounds are suspected residual production chemicals, e.g.
346 hexadecanol which does not occur naturally in crude oil. Even when comparing two
347 samples that were sampled from the same well and only three days apart, the
348 difference was substantial. As we lack more detailed information on the sampling step, it
349 is difficult to conclude where these differences stem from. The intra-sample variation
350 can be an effect of sampling and oil-to-water ratio in the test separator. The level of
351 dispersed and or layered oil in samples will likely influence the aggregation and
352 solubility of organics in the aqueous phase. A more controlled sampling campaign is
353 required to identify the source of variability.
354

355 ## Conclusions
356 The composition of produced water is highly complex with several unknowns. Our study
357 aimed to narrow this gap by a broad identification of dissolved organics. The
358 implemented identification workflow excluded approximately 95% of the detected
359 compounds (1000 – 1500 per sample), resulting in 50 – 80 tentatively identified
360 compounds per sample. This demonstrates both the power and pitfalls of non-target
361 screening; more than 100 compounds were identified with an acceptable level of
362 confidence, and more than 1000 compounds remain unknown. To our knowledge, this
363 is the most comprehensive list of identified compounds in produced water that has been
364 publicly published. However, being a screening study, quantification was not carried out
365 for any compounds. As this is an important factor for environmental assessment, the
366 obtained compound lists should be used to develop targeted methods to look at
367 absolute concentrations. Furthermore, it would be beneficial to reduce the number of
368 unknowns by using complementary techniques (e.g. HPLC-MS and other soft ionization
369 methods), improved custom libraries and in-silico mass spectral prediction.
370

371 When performing environmental impact assessments, both structure and concentration
372 have to be taken into consideration (Tang et al., 2019). A large part of the detected
373 compounds are present at trace levels. Their concentration will be further reduced at
374 discharge to sea where a rapid dilution to a large body of water occurs. However,
375 potential cocktail effects where the combined effect of a series of micro-pollutants is
376 harmful but not the single species should be accounted for (Di Poi et al., 2018). Here, it
377 would be highly beneficial to link non-target screening studies with toxicological
378 measurements. Ultimately, we hope that our study contributes a small piece of the
379 puzzle, and a stepping stone towards further studies to uncover the full picture.
380

Author contributions

382 J.S conceptualized the study, developed the analytical methodology and sample
383 preparation workflow. S.B and A.J carried out the experimental work and sample
384 extractions. A.K carried out method validation and recovery studies. J.S developed the
385 data processing workflow and wrote the code. S.B and J.S analyzed the data and wrote
386 the manuscript. All authors performed scientific and grammatical revisions of the final
387 draft.
388

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Figure 1

Four representative samples showing the varying oil content.

Photo of four samples after decanting into glass bottles. Only visually clear samples were used in the study (two leftmost), while samples containing oil were excluded (two rightmost). The latter typically contained dispersed oil droplets in the aqueous phase as seen by optical microscopy (Figure 2).

Figure 2

Optical microscope image (10x magnification) of two different produced water samples.

The image shows the lack (A) or presence (B) of dispersed oil in the aqueous phase. Samples containing dispersed oil were excluded from the study.

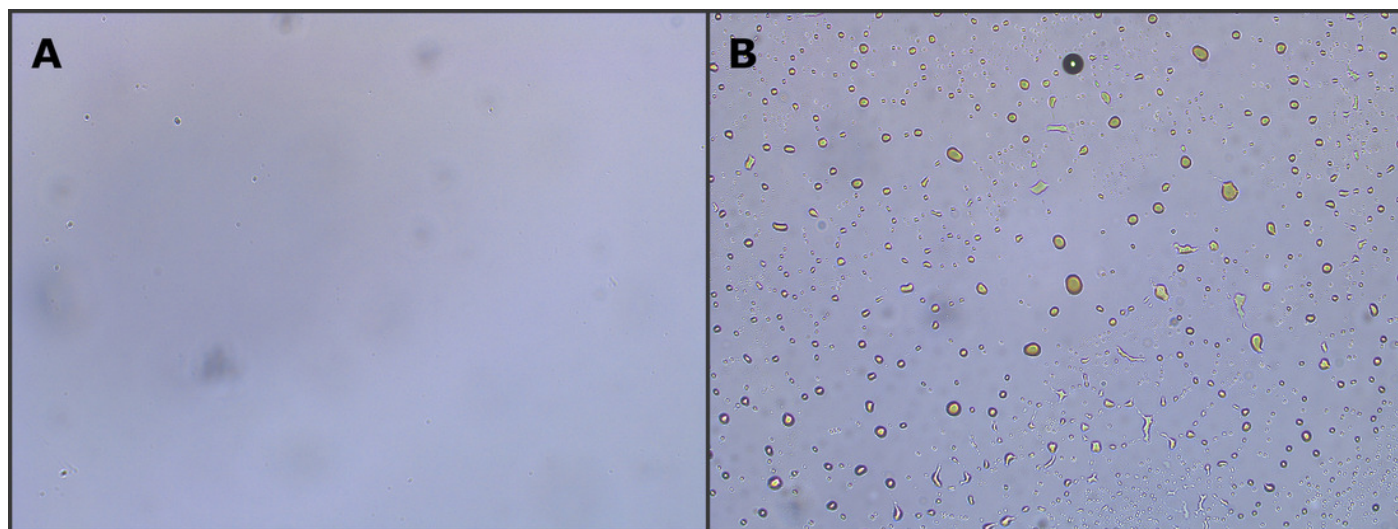



Figure 3

Example 2D chromatogram showing the distribution of peaks with a heavy saturation of compounds between 0.5 and 1.5 s in the 2D.

Five representative compounds have been annotated in the chromatogram. The annotation corresponds to; a) Cyclopentylcarboxylic acid, TMS derivative b) Octanoic acid, TMS derivative c) 1-Methylnaphthalene d) Benzoic acid, 3-methyl-, trimethylsilyl ester e) 2-Ethyl-1-decanol, TMS derivative

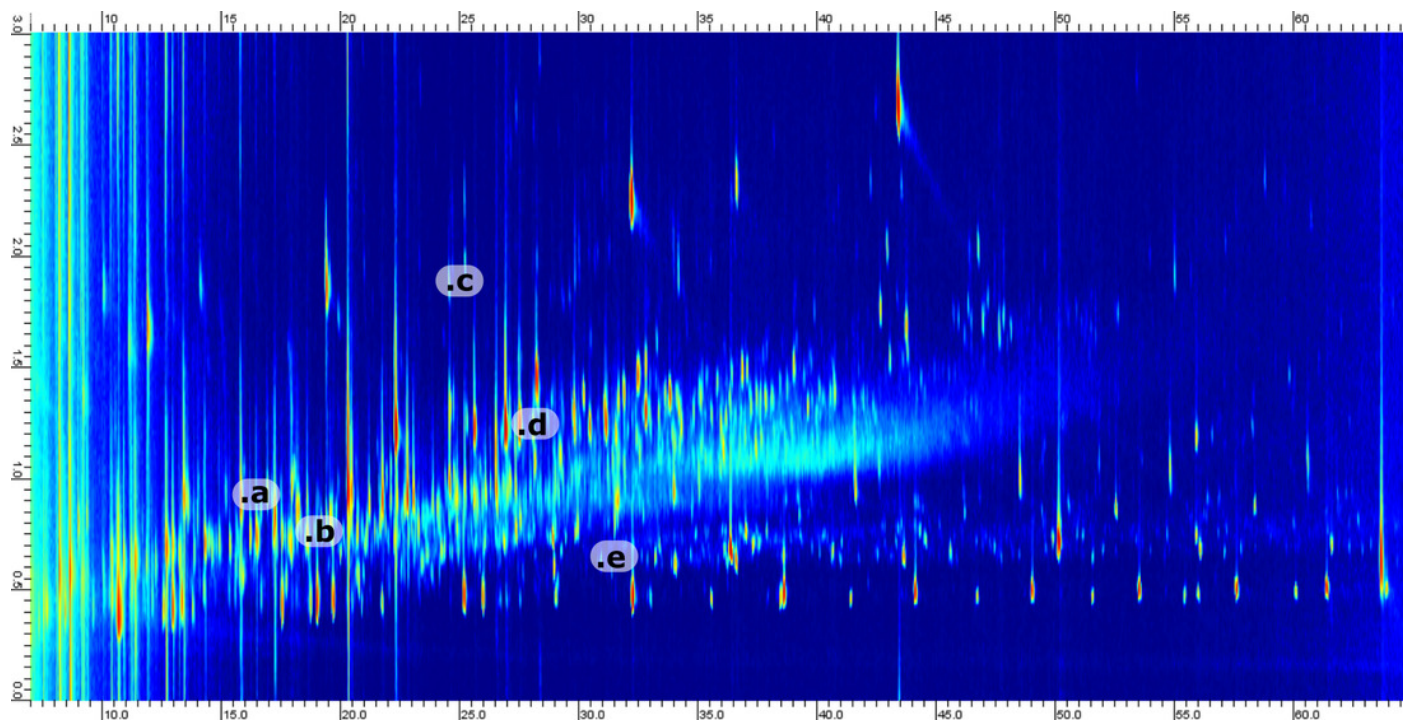



Figure 4

Schematic of the data processing workflow.

Graphic description of how the data processing workflow scores tentatively identified features for added confidence. The scoring was implemented in a Python script and is available as supplementary data.

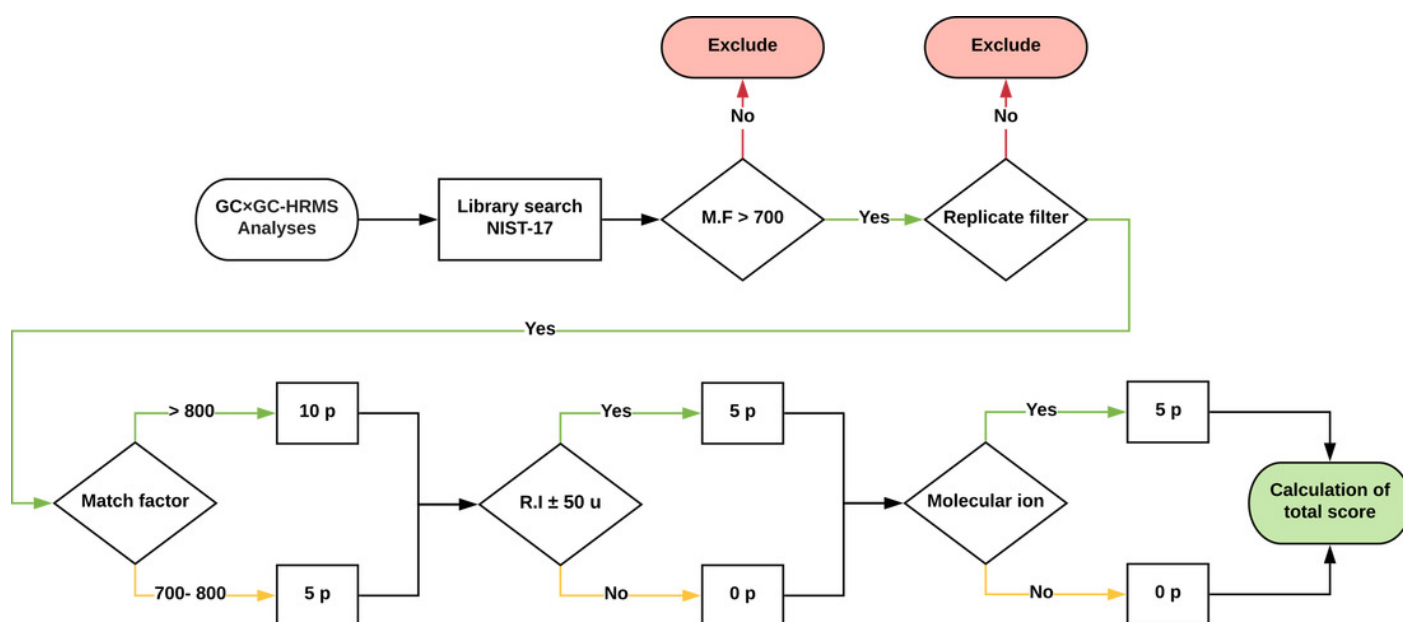
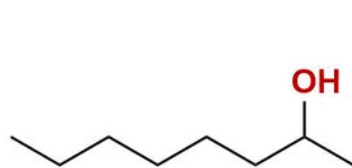
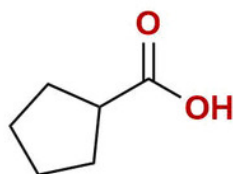
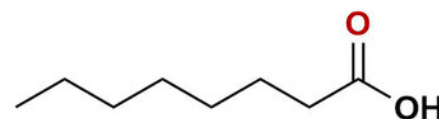
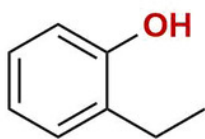
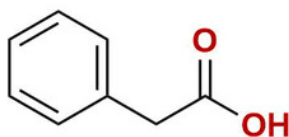
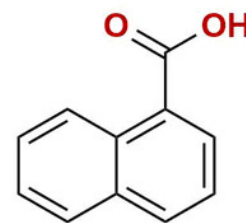



Figure 5

The molecular structures of six representative compounds.

The structures were obtained from the subset of compounds detected in a minimum of 6 out of 9 samples. LogP/XLogP values were obtained from the PubChem database. The reported retention times are of the corresponding trimethylsilyl derivatives.

octanol
LogP 3.0
RT: 14.8 min. / 0.66 s.

cyclopentylcarboxylic acid
XLogP 1.3
RT: 15.8 min. / 0.89 s.

octanoic acid
LogP 3.05
RT: 18.9 min. / 0.69 s.

2-ethylphenol
LogP 2.47
RT: 19.9 min. / 0.93 s.

benzeneacetic acid
LogP 1.41
RT: 24.6 min. / 1.31 s.

naphthoic acid
LogP 3.28
RT: 42.6 min. / 1.75 s.

Extraction recovery and retention time deviations for model and detected compounds

Recovery values are calculated as (peak volume$_{model\ water}$/peak volume$_{standard}$) * 100 (n = 4 for model water and standard, 3 for real-life sample). Retention time deviations were calculated based on the retention of internal standards across all samples (n = 27). [*] Peak volume values were extracted from a representative sample where the compound had been identified.

Model compound	Recovery (%)	%RSD, model water	%RSD, standard	%RSD, real-life sample[*]
Phenol	89.6	23.1	8.9	23.3
Cyclohexanecarboxylic acid	63.8	13.1	5.7	1.8
Benzoic acid	35.9	24.7	1.9	11.3
Octanoic acid	55.0	9.6	4.4	4.2
2-Naphthoic acid	88.4	9.8	3.0	5.2
Internal standard	**Avg. RT I (min.)**	**Avg. RT II (sec.)**	**RT I %RSD**	**RT II %RSD**
Naphthalene-D8	19.399	1.860	0.0004	0.8576
Acenaphthene-D8	32.199	2.236	0.0002	0.6218
Phenanthrene	43.399	2.671	0.0002	0.5178

A list of compounds that were detected in a minimum of 6 of 9 samples.

* The MS-ready name corresponds to the non-derivatized parent compound. Calculated XlogP values were obtained from the PubChem database. #Samples correspond to the number of samples in which the compound was detected. <!--[if !supportLineBreakNewLine]--> <!--[endif]-->

Compound	MS-ready name	Formula	Mol. Weight	XlogP	SMILES	Classification	#Samples
(±)-2-Phenylpropanoic Acid, trimethylsilyl ester	2-phenylpropanoic acid	C9H10O2	150.17	1.9	CC(C1=CC=CC=C1)C(=O)O	Aromatic acid	9
1-Naphthoic acid, TMS derivative	naphthalene-1-carboxylic acid	C11H8O2	172.18	3.1	C1=CC=C2C(=C1)C=CC=C2C(=O)O	Aromatic acid	9
3,4-Dimethylbenzoic acid, TMS derivative	3,4-dimethylbenzoic acid	C9H10O2	150.17	2.7	CC1=C(C=C(C=C1)C(=O)O)C	Aromatic acid	9
Trimethylsilyl 2,3-dimethylbenzoate	2,3-dimethylbenzoic acid	C9H10O2	150.17	2.8	CC1=C(C(=CC=C1)C(=O)O)C	Aromatic acid	9
Trimethylsilyl 4-propylbenzoate	4-propylbenzoic acid	C10H12O2	164.2	3.4	CCCC1=CC=C(C=C1)C(=O)O	Aromatic acid	9
4-tert-Butylphenol, TMS derivative	4-tert-butylphenol	C10H14O	150.22	3.3	CC(C)(C)C1=CC=C(C=C1)O	Aromatic alcohol	9
3-Methyl-1-cyclohexanecarboxylic acid, trimethylsilyl ester (stereoisomer 2)	3-methylcyclohexane-1-carboxylic acid	C8H14O2	142.2	2.1	CC1CCCC(C1)C(=O)O	Saturated acid	9
3-Methylbutanoic acid, TMS derivative	3-methylbutanoic acid	C5H10O2	102.13	1.2	CC(C)CC(=O)O	Saturated acid	9
Cyclohexaneacetic acid, TMS derivative	2-cyclohexylacetic acid	C8H14O2	142.2	2.5	C1CCC(CC1)CC(=O)O	Saturated acid	9
Cyclohexanecarboxylic acid, TMS derivative	cyclohexanecarboxylic acid	C7H12O2	128.17	1.9	C1CCC(CC1)C(=O)O	Saturated acid	9
Cyclopentylcarboxylic acid, TMS derivative	cyclopentanecarboxylic acid	C6H10O2	114.14	1.3	C1CCC(C1)C(=O)O	Saturated acid	9
Heptanoic acid, TMS derivative	heptanoic acid	C7H14O2	130.18	2.5	CCCCCCC(=O)O	Saturated acid	9
Nonanoic acid, TMS derivative	nonanoic acid	C9H18O2	158.24	3.5	CCCCCCCCC(=O)O	Saturated acid	9
Octanoic acid, TMS derivative	octanoic acid	C8H16O2	144.21	3	CCCCCCCC(=O)O	Saturated acid	9
1-Hexadecanol, TMS derivative	hexadecan-1-ol	C16H34O	242.44	7.3	CCCCCCCCCCCCCCCCO	Saturated alcohol	9
Benzenepropanoic acid, TMS derivative	3-phenylpropanoic acid	C9H10O2	150.17	1.8	C1=CC=C(C=C1)CCC(=O)O	Aromatic acid	8
m-Toluic acid, TMS derivative	3-methylbenzoic acid	C8H8O2	136.15	2.4	CC1=CC(=CC=C1)C(=O)O	Aromatic acid	8
2,4-Di-tert-butylphenol	2,4-ditert-butylphenol	C14H22O	206.32	4.9	CC(C)(C)C1=CC(=C(C=C1)O)C(C)(C)C	Aromatic alcohol	8
3-Ethylphenol, TMS derivative	3-ethylphenol	C8H10O	122.16	2.4	CCC1=CC(=CC=C1)O	Aromatic alcohol	8
4-Isopropylphenol, TMS derivative	4-propan-2-ylphenol	C9H12O	136.19	2.9	CC(C)C1=CC=C(C=C1)O	Aromatic alcohol	8
o-Cresol, TMS derivative	2-methylphenol	C7H8O	108.14	2	CC1=CC=CC=C1O	Aromatic alcohol	8
2-Methylbutanoic acid, TMS derivative	2-methylbutanoic acid	C5H10O2	102.13	1.2	CCC(C)C(=O)O	Saturated acid	8
3-Methylvaleric acid, TMS	3-methylpentanoic acid	C6H12O2	116.16	1.6	CCC(C)CC(=O)O	Saturated acid	8
2-Octanol, TMS derivative	octan-2-ol	C8H18O	130.23	2.9	CCCCCCC(C)O	Saturated alcohol	8
Benzeneacetic acid, TMS derivative	2-phenylacetic acid	C8H8O2	136.15	1.4	C1=CC=C(C=C1)CC(=O)O	Aromatic acid	7
Benzenebutanoic acid, TMS derivative	4-phenylbutanoic acid	C10H12O2	164.2	2.4	C1=CC=C(C=C1)CCCC(=O)O	Aromatic acid	7
m-Cresol, TMS derivative	3-methylphenol	C7H8O	108.14	2	CC1=CC(=CC=C1)O	Aromatic alcohol	7
2-Hydroxy-4-methylquinoline, trimethylsilyl ether	4-methyl-1H-quinolin-2-one	C10H9NO	159.18	1.2	CC1=CC(=O)NC2=CC=CC=C12	Aromatic amine/alcohol	7
4-Methylvaleric acid, TMS derivative	4-methylpentanoic acid	C6H12O2	116.16	1.4	CC(C)CCC(=O)O	Saturated acid	7
2-Ethylphenol, TMS derivative	2-ethylphenol	C8H10O	122.16	2.5	CCC1=CC=CC=C1O	Aromatic alcohol	6
4-Trimethylsilylphenol	phenol	C6H6O	94.11	1.5	C1=CC=C(C=C1)O	Aromatic alcohol	6
Benzoic acid, 4-ethoxy-, ethyl ester	ethyl 4-ethoxybenzoate	C11H14O3	194.23	3.2	CCOC1=CC=C(C=C1)C(=O)OCC	Aromatic ester	6
Naphthalene, 1,7-dimethyl-	1,7-dimethylnaphthalene	C12H12	156.22	4.4	CC1=CC2=C(C=CC=C2C=C1)C	Aromatic hydrocarbon	6
3-Methyl-1-cyclohexanecarboxylic acid, trimethylsilyl ester (stereoisomer 1)	3-methylcyclohexane-1-carboxylic acid	C8H14O2	142.2	2.1	CC1CCCC(C1)C(=O)O	Saturated acid	6
Pentanoic acid, TMS derivative	pentanoic acid	C5H10O2	102.13	1.4	CCCCC(=O)O	Saturated acid	6
2-(1-Adamantyl)ethanol, TMS derivative	2-(1-adamantyl)ethanol	C12H20O	180.29	3.4	C1C2CC3CC1CC(C2)(C3)CCO	Saturated alcohol	6