



## Productivity and oil fingerprinting: Application of analytical chemistry in the assessment of reservoir quality

Nielsen, Julie; Poulsen, Kristoffer G.; Christensen, Jan H.; Lassen, Charlotte; Sølling, Theis I.

*Published in:*  
Journal of Petroleum Science and Engineering

*Link to article, DOI:*  
[10.1016/j.petrol.2020.107914](https://doi.org/10.1016/j.petrol.2020.107914)

*Publication date:*  
2020

*Document Version*  
Peer reviewed version

[Link back to DTU Orbit](#)

*Citation (APA):*  
Nielsen, J., Poulsen, K. G., Christensen, J. H., Lassen, C., & Sølling, T. I. (2020). Productivity and oil fingerprinting: Application of analytical chemistry in the assessment of reservoir quality. *Journal of Petroleum Science and Engineering*, 195, Article 107914. <https://doi.org/10.1016/j.petrol.2020.107914>

---

### General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

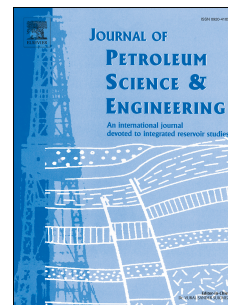
- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

# Journal Pre-proof

Productivity and oil fingerprinting: Application of analytical chemistry in the assessment of reservoir quality

Julie Nielsen, Kristoffer G. Poulsen, Jan H. Christensen, Charlotte Lassen, Theis.I. Sølling



PII: S0920-4105(20)30970-0

DOI: <https://doi.org/10.1016/j.petrol.2020.107914>

Reference: PETROL 107914

To appear in: *Journal of Petroleum Science and Engineering*

Received Date: 9 March 2020

Revised Date: 8 September 2020

Accepted Date: 9 September 2020

Please cite this article as: Nielsen, J., Poulsen, K.G., Christensen, J.H., Lassen, C., Sølling, T.I., Productivity and oil fingerprinting: Application of analytical chemistry in the assessment of reservoir quality, *Journal of Petroleum Science and Engineering* (2020), doi: <https://doi.org/10.1016/j.petrol.2020.107914>.

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2020 Published by Elsevier B.V.

1 Productivity and Oil Fingerprinting: Application of Analytical  
2 Chemistry in the Assessment of Reservoir Quality

3

4 Julie Nielsen<sup>a</sup>, Kristoffer G. Poulsen<sup>b</sup>, Jan H. Christensen<sup>b</sup>, Charlotte Lassen<sup>a</sup>,  
5 Theis. I. Sølling<sup>c,\*</sup>

6 <sup>a</sup> *The Danish Hydrocarbon Research and Technology Centre, Technical University of Denmark (DTU),  
7 Elektrovej, 2800 Kgs. Lyngby, Denmark*

8 <sup>b</sup> *Department of Plant and Environmental Sciences, University of Copenhagen, Thorvaldsensvej 40, 1871  
9 Frederiksberg C, Denmark*

10 <sup>c</sup> *Center for Integrative Petroleum Research, College of Petroleum Engineering & Geoscience, King Fahd  
11 University of Petroleum and Minerals, Dhahran 31261, Kingdom of Saudi Arabia*

12

13 \*To whom correspondence should be addressed theis.solling@kfupm.edu.sa

14

15 ABSTRACT

16 The ability to understand and possibly even predict the productivity of wells across a field is an  
17 important accomplishment in a production setting. In the tight Lower Cretaceous chalk field  
18 Valdemar, 5 wells have been observed to produce significantly larger oil volumes compared to  
19 nearby wells. This study was conducted to map the inter-well differences in the oil composition  
20 to better understand the productivity differences. This was done by analyzing any chemical  
21 differences of 21 samples from 16 different wells by GC-MS and principal component analysis  
22 of summed extracted ion chromatograms (SICs) using the chemometric analysis of selected ion  
23 chromatograms (CHEMSIC) method. The sterane (m/z 217 and m/z 218) and C4 (m/z 234)  
24 biomarker SICs were found to have chemically meaningful features described by principal  
25 component 1 (PC1). The association between these markers and the relative production was  
26 modeled to provide a better understanding of the productivity of the different wells. A  
27 correlation between oil saturation and productivity was established in the sense that the more

28 mature and thus less viscous oil seem to have charged certain favorably placed reservoir sections  
29 first; these locations coincide with the location of the 5 wells in question.

30

## 31 **1. Introduction**

32 The Valdemar Field was discovered in 1977 by the Bo-1 well. The Lower Cretaceous  
33 reservoir is thin (usually less than 300 ft thick) with high porosities but very low permeabilities  
34 (Jakobsen *et al.*, 2005). The reservoir is developed in two areas with long horizontal wells with  
35 sand-propped fracs that vertically connects to other reservoir layers. The North Jens area had  
36 first production in 1994 and the Bo area in 2007. The field is operated by Total and has 16  
37 producing wells (2018). In the North Jens area four wells and one well in the Bo area  
38 outperforms the other wells in the area. The comparison is simply based on the number of  
39 barrels of oil produced each day from the time of well completion.

40 Therefore, we set out to determine if the productivity differences could be (at least partially)  
41 correlated to chemical composition of the oils. Oil samples were taken at the well heads on the  
42 platforms and their “chemical fingerprint” obtained by a gas chromatography-mass spectrometry  
43 (GC-MS) followed by principal component analysis (PCA) using a modified chemometric  
44 analysis of selected ion chromatograms (CHEMSIC) method (Christensen & Tomasi, 2007,  
45 Christensen *et al.*, 2005) where the preprocessed selected ion chromatograms (SICs) were  
46 correlated to productivity by a partial least squares regression (PLS) as detailed in the Method  
47 section.

48 The present study, however, focuses on assessing the chemical composition of the oil in  
49 relation to the reservoir as a valuable avenue of investigation for early prediction of well  
50 performance. The approach of analyzing additional petrochemical information can be considered  
51 complementary to the traditional studies of diagenesis (and depositional history) and thus a way

52 to yield a more detailed picture of factors affecting oil production (Peters & Fowler, 2002). We  
53 employ chemical fingerprinting of closely related crude oils from all 16 producing wells in the  
54 Lower Cretaceous reservoir in Valdemar, linking reservoir quality to the chemical composition  
55 of the crude oil. Specifically, we assess the thermal maturity through the analysis of hopane and  
56 sterane biomarkers in the oil and relate these fingerprints with the average cumulative  
57 production.

58 Biomarkers are organic molecules of biological origin that are present in crude oil, which  
59 have (partially) resisted degradation throughout formation and migration of oil reservoirs  
60 (Eglinton & Calvin, 1967). The surviving biomarker molecules are therefore useful in relating  
61 crude oil to its source (Welte *et al.*, 1997), indicate oil maturity (Peters & Moldowan, 1993,  
62 Philp, 1985, Seifert & Michael Moldowan, 1978, Seifert & Moldowan, 1981, Waples &  
63 Machihara, 1991), and tracking weathered/biodegraded samples from oil spills (Wang *et al.*,  
64 1999, Wang & Fingas, 2003, Wang *et al.*, 2006). A large number of biomarkers have been  
65 investigated via GC-MS techniques (Philp, 1985) and especially steranes and terpanes are often  
66 studied (Seifert & Michael Moldowan, 1978, Seifert & Michael Moldowan, 1979) as they  
67 degrade and interconvert at an adequate rate to provide useful information within the oil-  
68 generative window in between catagenesis and metagenesis (Peters & Moldowan, 1993).

69 The CHEMSIC methodology applied here has been applied previously to several cases,  
70 including assessment of bioremediation of oil contaminated soil (Soleimani *et al.*, 2013),  
71 weathering effects (Kristensen *et al.*, 2015), and source differentiation relating to hydrocarbons  
72 in soil and oil spills (Al-Kaabi *et al.*, 2017, Gallotta & Christensen, 2012). Here we present a  
73 novel use of this method in order to determine the potential applications of chemical  
74 fingerprinting for predictions of well production.

75

76 *1.1. Geological setting*

77 The Valdemar Field in the Danish Central Graben produces from two separate reservoirs, the  
78 Upper Cretaceous and the Lower Cretaceous. This study only covers the Lower Cretaceous  
79 reservoir. The reservoir part of Lower Cretaceous consists of the Sola and Tuxen formations  
80 with layered heterogeneous chalks and marly chalks (see Fig. 1). The field is a saddle-shaped  
81 anticline structure with the North Jens area located higher than the Bo area (see Fig. 2).

82 Samples were taken at a range of different locations and their productivity and geographical  
83 location is outlined in Table 1.

84

85 **2. Methodology**

86 The methodology of the crude oil samples involved: Chemical analysis of the crude oils  
87 using GC-MS measuring PAHs and petroleum biomarker in Selected Ion monitoring (SIM)  
88 mode; PCA of preprocessed SICs to screen PAHs and petroleum biomarkers for significant  
89 chemical variation; and PLS to model and predict the average cumulative oil production between  
90 day 900 and 1000 using the chemical descriptive SICs.

91

92 *2.1. Gas chromatography-mass spectrometry (GC-MS)*

93 Crude oil samples were diluted with dichloromethane to a total oil concentrations of approx.  
94 2 mg/ml. Samples were analyzed on an Agilent 5975C inert XL MSD with electron ionization  
95 operating in selected ion monitoring mode. The GC parameters were as follows: 1  $\mu$ l sample was  
96 injected in splitless mode (inlet: 300 °C) to a 60 m HP-5 capillary column with 0.25 mm inner  
97 diameter, 0.25  $\mu$ m film thickness. The flow rate was 1.1 ml/min. The initial temperature (40 °C)  
98 was held for 2 minutes, ramped with 25 °C/min to 100 °C, followed by 5 °C/min to 315 °C and

99 held for 14 minutes (total run time: 61.4 minutes). Temperatures: transfer line: 315 °C, ion  
100 source: 230 °C, quadrupole: 150 °C. 55 m/z values were monitored in 12 groups with 13 m/z's  
101 each, with a dwell time of 25 ms.

102

## 103 2.2. CHEMSIC

104 The selected ion chromatograms (SICs) data was processed according to the CHEMSIC  
105 method as described previously (Christensen & Tomasi, 2007, Christensen *et al.*, 2005). A  
106 detailed account of the analysis methodology is given in the SI (11 pages, methodsX). In brief,  
107 the SIC data was corrected by baseline removal, retention time alignment and normalization. A  
108 Savitzky-Golay function using a 1st order differentiation was used for baseline removal  
109 (Savitzky & Golay, 1964), while the correlation optimized warping (COW) algorithm was used  
110 for retention time alignment (Nielsen *et al.*, 1998). The PLS regression analysis included  
111 dividing the data into a calibration set of source oils, a set of reference oils and a test set. The  
112 PLS was then applied to the calibration set using the reference set to achieve the best possible fit.  
113 The quality of the model was then tested by predicting the test set. In the final model a small  
114 subset of samples (12-19 %) were excluded from the calibration set and the prediction target was  
115 based on the oil volume produced between day 900 to 1000 for each well as the information  
116 within this time span was available for all analyzed samples.

117

## 118 3. Results and discussion

119 The biomarkers were selected for analysis based on the compounds being some of the most  
120 commonly suggested relevant biomarkers in literature (Peters & Moldowan, 1993, Philp, 1985,  
121 Waples & Machihara, 1991). The following petroleum biomarkers were analysed in detail using

122 the CHEMSIC method: Hopanes (m/z 191), sesquiterpanes (m/z 123), triaromatic steranes (m/z  
123 231), steranes (m/z 218), C<sub>4</sub>-phenanthrenes/anthracenes/C<sub>0</sub>-benzonaphthothiophene (m/z 234).

124 The PCA was performed using four principal components (PCs) and the resulting PCs  
125 subsequently analyzed to identify any significant chemical differences displayed in the SICs  
126 associated with each PC. No significant chemical variation was observed in PC1 to PC4 loading  
127 coefficients for any of the analyzed biomarkers, except for PC1 for steranes (m/z 218) and PC1  
128 for C<sub>4</sub>-phenanthrene/anthracene/C<sub>0</sub>-benzonaphthothiophene (m/z 234).

129

### 130 3.1 PCA loading coefficients for the sterane biomarker.

131 In the case of the steranes, PC1 is associated with the separation of  $\alpha\alpha$  vs.  $\beta\beta$   
132 stereoisomers of steranes, specifically the  $5\alpha,14\alpha,17\alpha(20R+20S)$  and  $5\alpha,14\beta,17\beta(20R+20S)$   
133 isomers of steranes (see Fig. 3). These are identified by opposite PC1 loading coefficients (blue  
134 line) with comparisons to the average chromatogram (dotted line in black) in Fig. 3. The relative  
135 depletion of  $\alpha\alpha$  to  $\beta\beta$  stereoisomers has previously been associated with thermal maturity of  
136 crude oil (Curiale, 1986, Mackenzie *et al.*, 1980, Sakata *et al.*, 1988). The stereoisomers are  
137 generally easy to separate in the chromatogram but the non-specific steranes considered here  
138 (C<sub>26</sub>-C<sub>30</sub> (20S+20R)) are not recommended for evaluation of thermal maturity by themselves  
139 (Peters & Moldowan, 1993, Waples & Machihara, 1991).

140 PC1 scores for the sterane PC model is shown in Fig. 5 with distinction between the wells  
141 from the two locations (North Jens and Bo area, respectively) and mixture samples (Quality  
142 Control) indicated by purple, orange and blue color, respectively. We note that there is a large  
143 overlap and thus no significant difference in chemical composition between the two areas of  
144 drillings. Additionally, Fig. 5 provides information on the fingerprint of the different wells with a



145 negative PC1 loading coefficient being associated with higher relative ratio of  $\beta\beta$  stereoisomers  
146 (indicating a higher thermal maturity).

147 In the case of  $C_4$ -phenanthrenes/anthracenes/ $C_0$ -benzophthothiophene (234 m/z), PC1 is  
148 primarily associated with the presence of retene. This is identified by the large positive loading  
149 coefficient for retene, while the remaining compounds are associated with minor negative  
150 coefficients (see **SI** Fig. S4).

151

### 152 3.2. PLS regression of steranes and retene vs. average cumulative oil production

153 The association between average cumulative production (taken between day 900 and  
154 1000) and the chemical fingerprint was explored by PLS regression analysis. Fig. 6 shows the  
155 observed oil volume produced (x-axis) plotted against the predicted oil volume produced based  
156 on the final PLS model using the sterane biomarker with samples W11, W16 and W16-2 being  
157 excluded as outliers. The PLS regression coefficients (Fig. 7) reflects thermal maturity through  
158 the  $\alpha\alpha$ - /  $\beta\beta$ -isomer pattern with an increase in production with a high relative  $\alpha\alpha$  levels, which  
159 indicates a clear relation between thermal maturity associated and production. This findings  
160 pertaining to maturity is unlikely to be the sole explanation and most likely the combined root  
161 cause for the observed correlation with production contains contributions from diagenesis,  
162 maturation, migration, and biodegradation effects.

163 Additionally, we note that the highest producing wells are geographically located together  
164 and any difference in thermal maturity could potentially be affecting the viscosity and density of  
165 the oil making the lighter oil cumulate in the Western area of the crest. The maturity potentially  
166 associated with the sterane biomarkers link high production with high relative amount of  $\alpha\alpha$ -

167 isomer and thus low maturity, i.e. heavy oil. The same observation is made for the retene  
168 biomarkers.

169 The sampling duplicates (W01, W03, W04, W15,) illustrate the inherent uncertainty  
170 associated with the analysis as a result of chemical differences the samples in between. These  
171 are caused by factors such as different sampling times or poor storage. The difference is minor  
172 (<10 %) for W01, W04, and W15 samples, whereas the W03 and W16 samples display much  
173 larger variations.

174 PLS regression analysis of m/z 234 SIC mainly described by retene yield a less significant  
175 correlation between predicted and observed oil production. A Pearson correlation coefficient of  
176 0.82 can be obtained by removal of W11, W14, and W16 (3/16 ~19 %) from calibration dataset  
177 (see **SI** Fig. S6). The sterane fingerprint thus appears as the better marker for prediction of the  
178 well production although the complex and potentially opposing contributions to the  $\alpha\alpha/\beta\beta$   
179 stereoisomerism will likely not be transferable to other oil fields.

180

### 181 3.3. Oil saturation

182 Additional analysis of central factors associated with increased cumulative production  
183 reveals a trend between oil saturation and production. An estimate for total oil saturation (TOS)  
184 based on the total water saturation averaged over the entire well-profile (SWT) can be expressed  
185 as:

$$186 \quad TOS = 1 - SWT \quad (1)$$

187 In Fig. 8 a linear trend between SWT and oil production is presented. The trend relies on the  
188 exclusion of some outliers (6/16 ~ 38%) associated with middle-range performing wells although  
189 the trend appears valid for the majority of wells (12/16 ~ 75%). A clear trend is observed

190 between total water saturation and average cumulative oil production between day 900 and 1000;  
191 the lower the water saturation, the higher the production. This is equivalent to a trend associating  
192 high oil saturation with high oil production. The correlation is consistent with *a priori*  
193 assumptions of potential factors underlying high relative production but a correlation which is  
194 rarely (if ever) demonstrated.

195 In summary our findings point to three key areas of investigation that critically influence the  
196 relative productivity of the analyzed wells; the location of the well on the geological structure,  
197 the maturity of the oil, and the oil saturation averaged over the entire well profile. The highest  
198 production is associated with geographical location, high oil saturation, and a specific fingerprint  
199 associated with high relative levels of  $\alpha\alpha$ -steranes and retenes to  $\beta\beta$ -steranes and other C<sub>4</sub>-  
200 phenanthrenes/anthracenes, respectively. We speculate that the oil located at the Western side of  
201 the crests may be a lighter, less viscous oil associated with a high thermal maturity expressed by  
202 the increased retene levels. The oil at this area may additionally have been affected by more  
203 recent charging events resulting in the high levels of  $\alpha\alpha$ -steranes.

#### 204 **4. Conclusion**

205 We have applied oil fingerprinting analysis in the form of chemometric analysis of selected  
206 ion chromatograms (CHEMSIC) to closely related oil samples from the North Sea. Indeed, the  
207 results clearly show that all the oils under study here arise from the same source and therefore is  
208 its highly unlikely that production takes place from different reservoirs and that this is the reason  
209 for the high production from certain wells. CHEMSIC analysis of SICs from a GC-MS analysis  
210 showed that the  $\alpha\alpha$  vs.  $\beta\beta$  stereoisomerism of steranes as well as the presence of retene in the  
211 chromatograms were the most defining features of the SICs. The major component from the  
212 four-component PCA were subsequently used for prediction of average cumulative production of

213 the 16 investigated wells, yielding a clear correlation between the sterane marker and the  
214 production.

215 Additionally, we linked the productivity and potentially reservoir quality to the average oil  
216 saturation, thus providing two analytical tools for the investigation and prediction of oil well  
217 productivity. The investigated biomarkers have traditionally been linked to thermal maturity, yet  
218 in our analysis yielded contradictory conclusion in terms of the thermal maturity of the majority  
219 of the wells. This apparent discrepancy may be explained by the complex contributions  
220 underlying the sterane biomarker, including diagenesis, biodegradation, and migration.

221 Finally, we noted that the highest producing wells have a geographically very similar  
222 position field-wise, indicating that the reservoir height and thus potentially viscosity are  
223 important factors to consider for production. We speculate that the high-lying reservoirs may be  
224 associated with accumulation of less viscous oil yielding higher productivity.

## 225 **References**

- 226 Al-Kaabi, N. S., Kristensen, M., Zouari, N., Solling, T. I., Bach, S. S., Al-Ghouti, M. &  
227 Christensen, J. H. (2017). Source identification of beached oil at Al Zubarah, Northwestern  
228 Qatar. *Journal of Petroleum Science and Engineering* **149**, 107-113.  
229
- 230 Christensen, J. H. & Tomasi, G. (2007). Practical aspects of chemometrics for oil spill  
231 fingerprinting. *Journal of Chromatography A* **1169**, 1-22.  
232
- 233 Christensen, J. H., Tomasi, G. & Hansen, A. B. (2005). Chemical Fingerprinting of Petroleum  
234 Biomarkers Using Time Warping and PCA. *Environmental Science & Technology* **39**, 255-260.  
235 Curiale, J. A. (1986). Origin of solid bitumens, with emphasis on biological marker results.  
236 *Organic Geochemistry* **10**, 559-580.  
237
- 238 Eglinton, G. & Calvin, M. (1967). Chemical Fossils. *Scientific American* **216**, 32-43.  
239 Fabricius, I. L. (2003). How burial diagenesis of chalk sediments controls sonic velocity and  
240 porosity. *AAPG Bulletin* **87**, 1755-1778.  
241
- 242 Fabricius, I. L. (2007). Chalk: composition, diagenesis and physical properties. *Bulletin of the*  
243 *Geological Society of Denmark* **55**, 97-128.  
244

- 245 Gallotta, F. D. C. & Christensen, J. H. (2012). Source identification of petroleum hydrocarbons  
246 in soil and sediments from Iguaçú River Watershed, Paraná, Brazil using the CHEMSIC method  
247 (CHEMometric analysis of Selected Ion Chromatograms). *Journal of Chromatography A* **1235**,  
248 149-158.
- 249  
250
- 251 Jakobsen, F., Ineson, J. R., Kristensen, L., Nytoft, H. P. & Stemmerik, L. (2005). The Valdemar  
252 Field, Danish Central Graben: field compartmentalization and regional prospectivity of the  
253 Lower Cretaceous chalk play. *Geological Society, London, Petroleum Geology Conference*  
254 *series* **6**, 177-186.
- 255
- 256 Kristensen, M., Johnsen, A. R. & Christensen, J. H. (2015). Marine biodegradation of crude oil  
257 in temperate and Arctic water samples. *Journal of Hazardous Materials* **300**, 75-83.
- 258
- 259 Mackenzie, A. S., Patience, R. L., Maxwell, J. R., Vandembroucke, M. & Durand, B. (1980).  
260 Molecular parameters of maturation in the Toarcian shales, Paris Basin, France—I. Changes in  
261 the configurations of acyclic isoprenoid alkanes, steranes and triterpanes. *Geochimica et*  
262 *Cosmochimica Acta* **44**, 1709-1721.
- 263
- 264 Nielsen, N.-P. V., Carstensen, J. M. & Smedsgaard, J. (1998). Aligning of single and multiple  
265 wavelength chromatographic profiles for chemometric data analysis using correlation optimised  
266 warping. *Journal of Chromatography A* **805**, 17-35.
- 267
- 268 Peters, K. E. & Fowler, M. G. (2002). Applications of petroleum geochemistry to exploration  
269 and reservoir management. *Organic Geochemistry* **33**, 5-36.
- 270
- 271 Peters, K. E. & Moldowan, J. M. (1993). *The Biomarker Guide - Interpreting Molecular Fossils*  
272 *in Petroleum and Ancient Sediments*: Prentice-Hall International Ltd.
- 273
- 274 Philp, R. P. (1985). *Fossil Fuel Biomarkers - Applications and Spectra*: Elsevier Science  
275 Publishing Company Inc, 294 pages.
- 276
- 277 Sakata, S., Suzuki, N. & Kaneko, N. (1988). A biomarker study of petroleum from the Neogene  
278 Tertiary sedimentary basins in Northeast Japan. *GEOCHEMICAL JOURNAL* **22**, 89-105.
- 279 Savitzky, A. & Golay, M. J. E. (1964). Smoothing and Differentiation of Data by Simplified  
280 Least Squares Procedures. *Analytical Chemistry* **36**, 1627-1639.
- 281
- 282 Scholle, P. A., Albrechtsen, T. & Tirsgaard, H. (1998). Formation and diagenesis of bedding  
283 cycles in uppermost Cretaceous chalks of the Dan Field, Danish North Sea. *Sedimentology* **45**,  
284 223-243.
- 285
- 286 Seifert, W. K. & Michael Moldowan, J. (1978). Applications of steranes, terpanes and  
287 monoaromatics to the maturation, migration and source of crude oils. *Geochimica et*  
288 *Cosmochimica Acta* **42**, 77-95.
- 289

- 290 Seifert, W. K. & Michael Moldowan, J. (1979). The effect of biodegradation on steranes and  
291 terpanes in crude oils. *Geochimica et Cosmochimica Acta* **43**, 111-126.
- 292 Seifert, W. K. & Moldowan, J. M. (1981). Paleoreconstruction by biological markers.  
293 *Geochimica et Cosmochimica Acta* **45**, 783-794.
- 294
- 295 Soleimani, M., Farhoudi, M. & Christensen, J. H. (2013). Chemometric assessment of enhanced  
296 bioremediation of oil contaminated soils. *Journal of Hazardous Materials* **254-255**, 372-381.
- 297 Wang, Z., Fingas, M. & Page, D. S. (1999). Oil spill identification. *Journal of Chromatography*  
298 *A* **843**, 369-411.
- 299
- 300 Wang, Z. & Fingas, M. F. (2003). Development of oil hydrocarbon fingerprinting and  
301 identification techniques. *Marine Pollution Bulletin* **47**, 423-452.
- 302
- 303 Wang, Z., Stout, S. A. & Fingas, M. (2006). Forensic Fingerprinting of Biomarkers for Oil Spill  
304 Characterization and Source Identification. *Environmental Forensics* **7**, 105-146.
- 305
- 306 Waples, D. W. & Machihara, T. (1991). *Biomarkers for Geologists - A Practical Guide to the*  
307 *Applications of Steranes and Triterpanes in Petroleum Geology*: The American Association of  
308 Petroleum Geologists (AAPG).
- 309
- 310 Welte, D. H., Horsfield, B. & Baker, D. R. (1997). *Petroleum and Basin Evolution - Insights*  
311 *from Petroleum Geochemistry, Geology and Basin Modeling*: Springer.
- 312

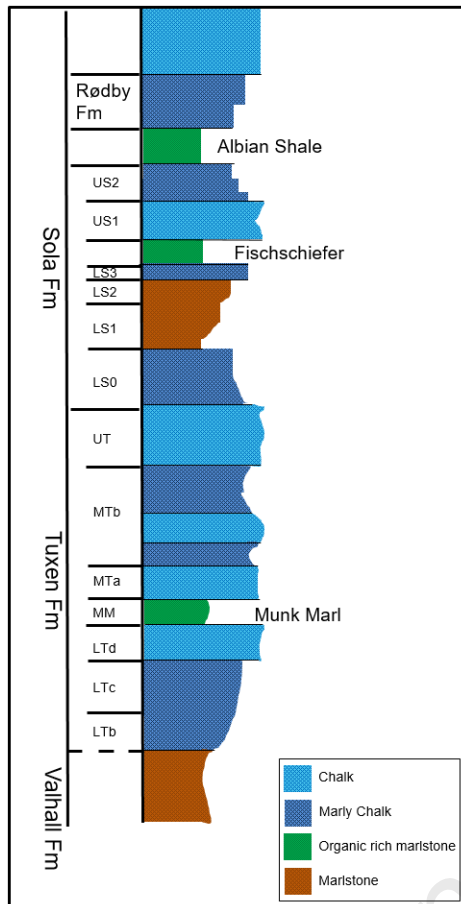
1 **Table 1.**

- 2 Sample numbers (chronological), their abbreviations, and relative rank in terms of production  
 3 (duplicate samples are marked by an asterisk).

Sample No.	Well	Date	Production Rank
1	W01	25-02-1994	5
2	W02	03-09-2001	1
3	W03	02-08-2006	7
4	W04	30-12-2006	3
5	W05	04-08-2007	9
6	W06	30-03-2008	16
7	W07	24-08-2008	4
8	W08	13-09-2008	10
9	W09	19-10-2008	6
10	W10	15-12-2008	12
11*	W01-2	05-07-2009	5
12	W11	01-04-2010	14
13*	W03-2	01-04-2010	7
14	W12	01-04-2010	2
15*	W04-2	01-04-2010	3
16	W13	01-04-2010	11
17	W14	19-05-2010	15
18	W15	27-01-2012	13
19*	W15-2	28-01-2012	13
20	W16	18-06-2012	8
21*	W16-2	Start 2013	8

4

5



6

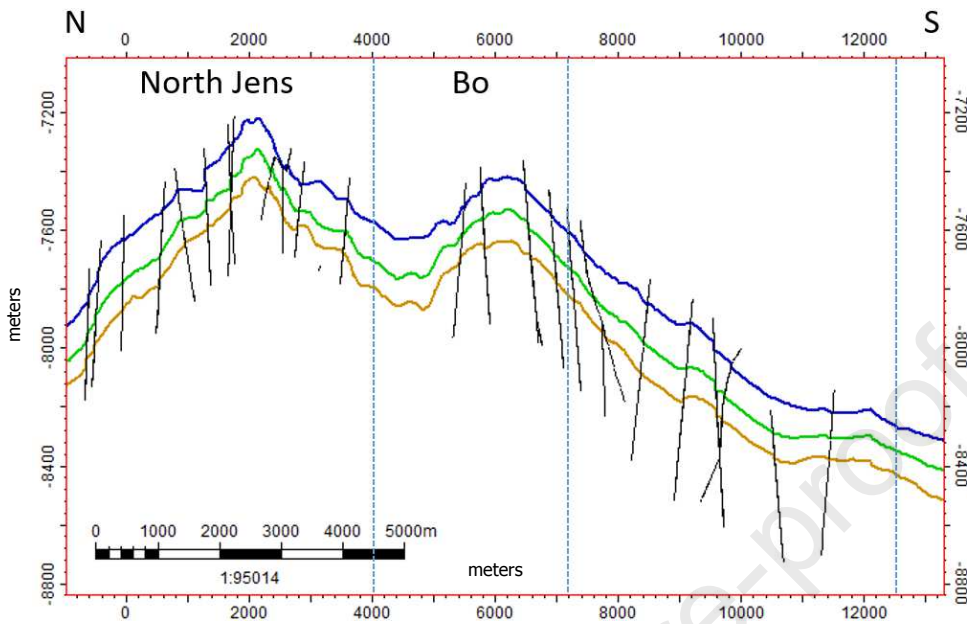
7 **Fig. 1.** Lithology of the Sola and Tuxen formations.

8 (Fabricius, 2003, Fabricius, 2007, Scholle et al., 1998).

9



10

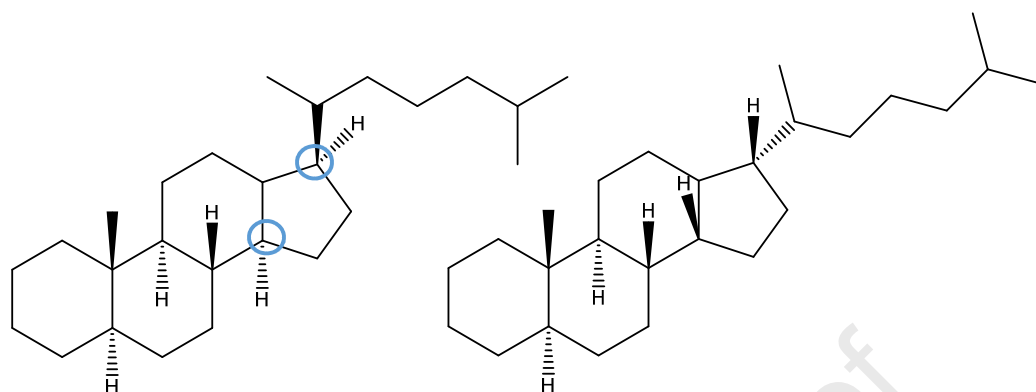


11

12 **Fig. 2.** North-South cross-section of the Lower Cretaceous structure in the Valdemar Field. The  
13 structure is a saddle-shaped anticline with the North Jans area located higher than the Bo area.

14

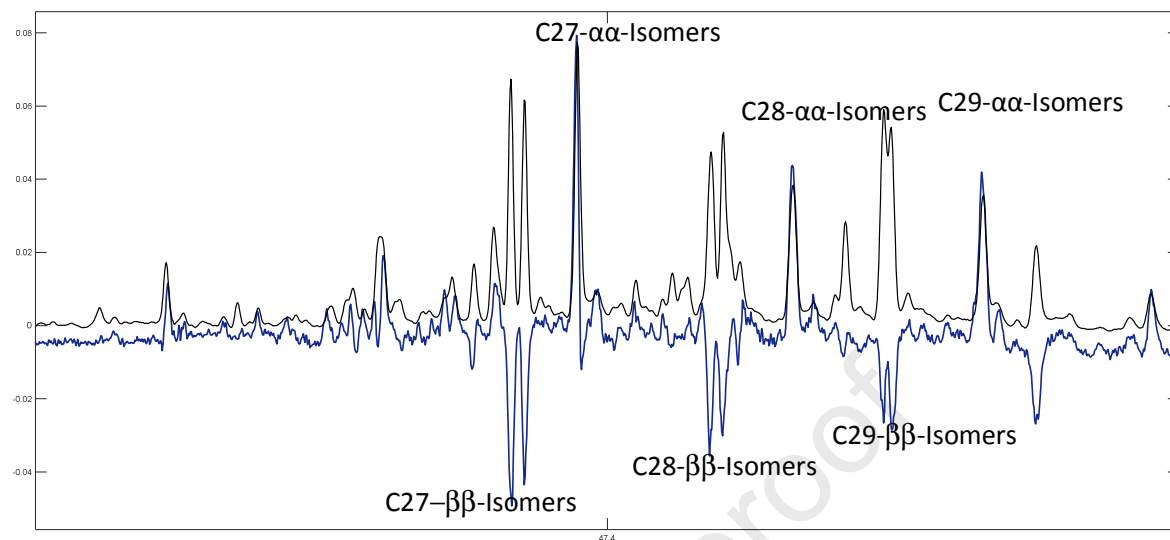
15



16

17 **Fig. 3.** Structure of an  $\alpha$ - $C_{27}$  sterane species ( $5\alpha(H), 14\alpha(H), 17\alpha(H)$ -cholestane) with the 14 and  
18 17 positions highlighted by open circles to illustrate the difference between  $\alpha$ - (left) and  $\beta$   
19 ( $\beta$ ) isomerism. Note that the 20R/S stereoisomerism is not indicated but appears as a straight  
20 line.

21

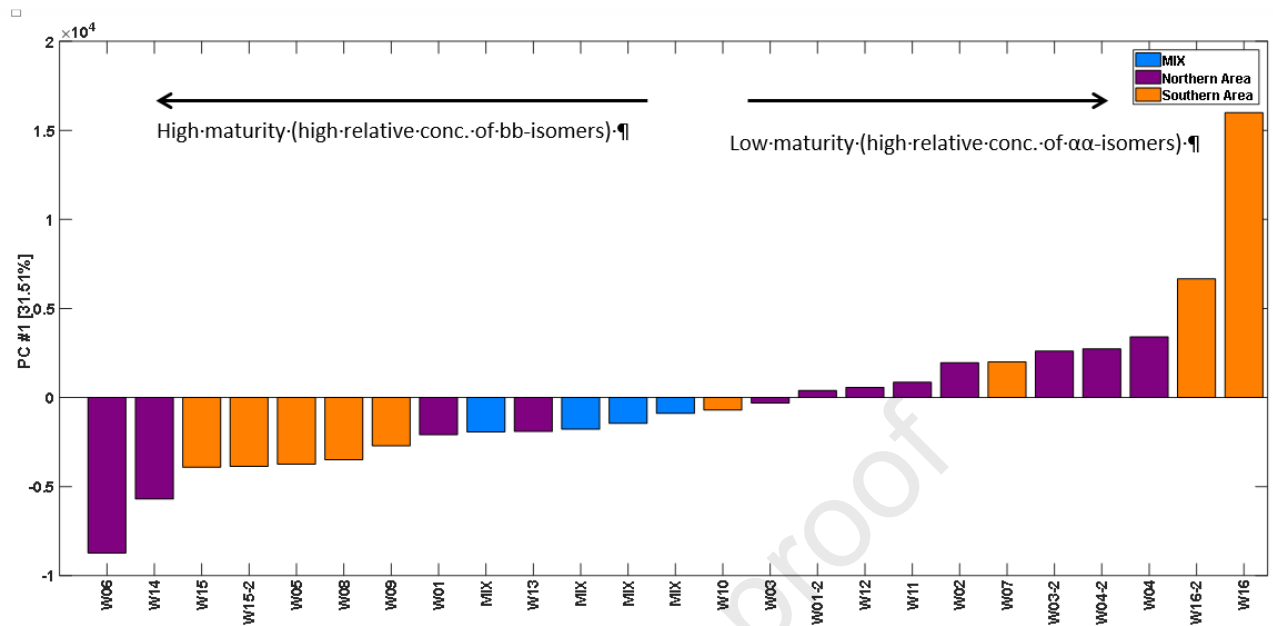


22

23 **Fig. 4.** PC1 loading coefficient (blue line) compared to the average chromatogram (black dotted  
24 line) with specific peaks and dips associated to  $\alpha\alpha$ - to  $\beta\beta$ -isomers marked

25

26

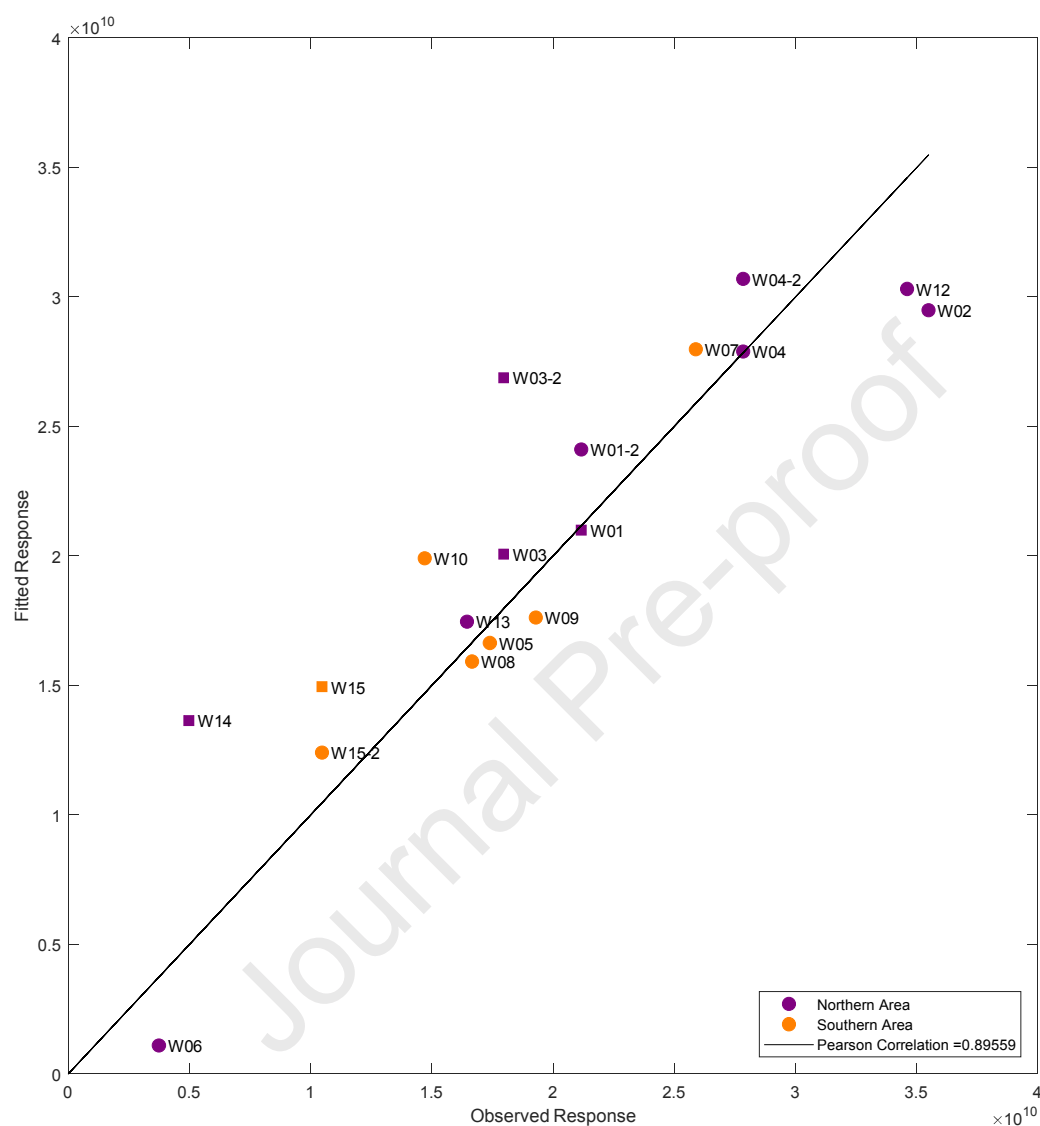


27

28 **Fig. 5.** PC1 score plot for the sterane biomarker (218 m/z). North Jens and Bo wells indicated by  
 29 purple and orange coloration. A clear overlap is observed between the two areas and thus no  
 30 significant variation between the two drilling areas are observed.

31

32

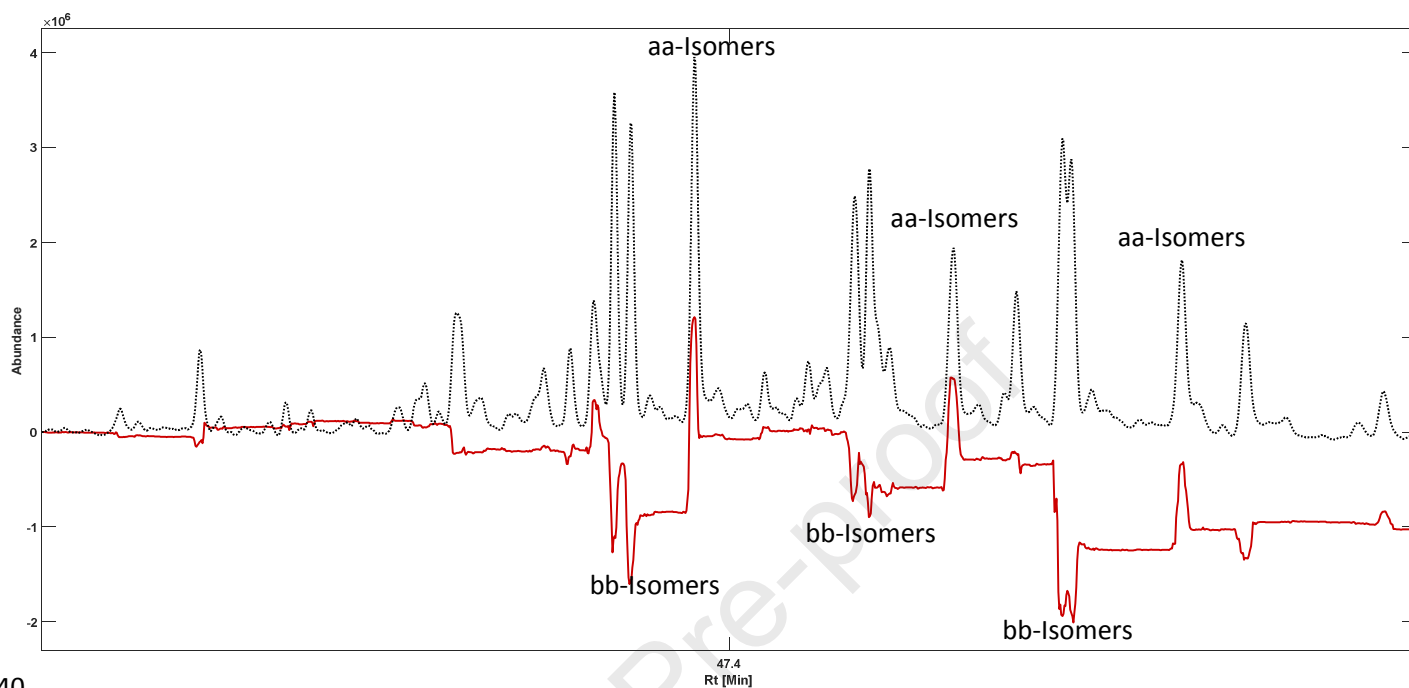


33

34 **Fig. 6.** The observed oil production (x-axis) vs. the production predicted based on the PLS  
 35 model using the m/z 218 SIC (y-axis). Circle sample markers indicate samples included in the  
 36 calibration set. Square sample markers indicate samples included in the test set. A Pearson  
 37 correlation coefficient of 0.89 is then obtained.

38

39

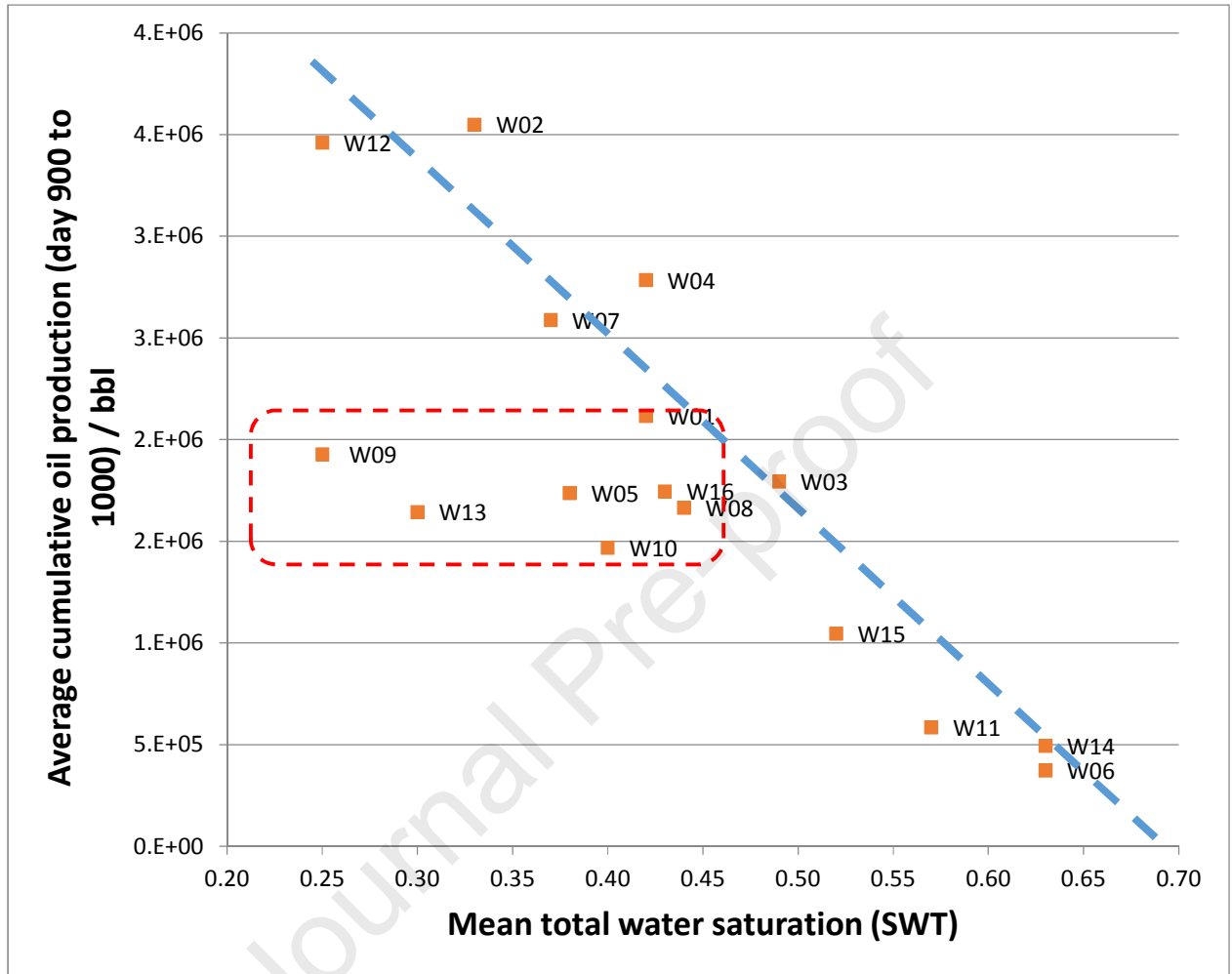


40

41 **Fig. 7.** PLS model regression coefficient (red line) compared to the average chromatogram  
42 (black dotted line) with specific peaks and dips associated to  $\alpha\alpha$ - to  $\beta\beta$ -isomers marked.

43

44



45

46 **Fig. 8.** Mean total water saturation (SWT) (X-axis) compared with Average cumulative oil  
 47 production (day 900 to 1000) (Y-axis).

48

49

50

- Oilfingerprinting can be used as a tool in reservoir characterization
- Maturity correlates with productivity
- High productivity is correlated with low-maturity

Journal Pre-proof



Julie Nielsen: Formal analysis, Investigation, Writing - Original Draft

Kristoffer G. Poulsen: Formal analysis, Software, Investigation, Writing - Original Draft

Jan H. Christensen: Conceptualization, Methodology, Writing - Review & Editing

Charlotte Lassen: Validation, Writing - Review & Editing

Theis. I. Sølling: Conceptualization, Writing - Review & Editing, Project administration

Journal Pre-proof

**Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Journal Pre-proof