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Characterization of water-soluble organic compounds released from black shales and coals

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Abstract: Knowledge of the composition of dissolved organic compounds as well as the main controls on their mobilization from natural organic matter is prerequisite for a comprehensive understanding of the fluid-rock interactions taking place in shale environments and coal seams over both geological and human timescales. In this study, black shales and coals from five different geological settings and covering the maturity range Ro = 0.3 – 2.6% were extracted with deionized water. The dissolved organic carbon (DOC) yields were found to decrease rapidly with increasing diagenesis and remain low throughout catagenesis. Four different fractions of DOC have been qualitatively and quantitatively characterized in the study using size exclusion chromatography (SEC). Acetate is the dominant low molecular weight organic acid (LMWOA) in all extracts of shales and coals of bituminous rank. The concentrations of individual LMWOA also decrease with increasing maturity of the samples except for acetate extracted from the overmature Posidonia shale from the Haddessen well, which was influenced by hydrothermal brines. The positive correlation between the Oxygen Index (OI) and respective LMWOA yield indicates that OI is a significant factor influencing the extraction of organic acids from shales. The yields of both DOC and individual organic acids normalized to TOC are in the same order of magnitude for coals and shales with the same maturity. However, the extracts of coals tend to contain more aromatic compounds and the molecular masses of most constituents included in macromolecular fractions are higher than for shale extracts. These results suggested that different kerogen types show comparable amounts of DOC being extracted, but different DOC composition. Thus, both the origin of organic matter and thermal maturation progress during deposition has significant influence on water extract composition.

Key words: Dissolved organic carbon; Low molecular weight organic acids; Maturity; Size-exclusion chromatography; Shales; Coals

Highlights:

- Maturity of samples affects the concentration of DOC in water extracts.
- Composition of dissolved organic matter is influenced by the kerogen types.
- Acetate is the dominant LMWOAs in the water extracts of shale samples.
- The concentration of LMWOAs in extracts is constrained by OI of shales and coals.
- Hydrothermal processes might enhance the generation of acetate.

1. Introduction

Dissolved organic carbon (DOC) is defined as the fraction of organic matter in water that passes through a filter with pore size 0.45µm (Herbert and Bertsch, 1995). DOC in near-surface groundwater and natural formation waters like oil field brines has been studied for years (Leenheer and Croué, 2003; Lepane et al., 2004; Schmidt et al., 2009) and the first insights into the molecular composition have been provided. Special attention has been paid to the abundance and origin of low molecular weight organic acids (LMWOAs) in subsurface brines (Means and Hubbard, 1987). LMWOAs have been proposed as tracers or proximity indicators of hydrocarbons (Zinger and Kravchik, 1973), and Kharaka et al. (1983) argued that acid anions are important precursors of natural gas via thermal cracking. LMWOAs are assumed to create secondary porosity in the subsurface by increasing the dissolution of aluminosilicates and carbonates (Surdam et al., 1984). Additionally, LMWOAs can act as feedstock for the deep terrestrial biosphere (Horsfield et al., 2006; Vieth et al., 2008). As far as oil and gas production is concerned, it has been reported that LMWOAs make up a dominant fraction of DOC in waters utilized during oil shale retorting (Dobson et al., 1985; Leenheer et al., 1982). High concentrations of formate and acetate in flowback waters were previously reported in fracturing flowback (Lester et al., 2015; Olsson et al., 2013). The amount and composition of other organic compounds in flowback and produced waters from hydraulic fracturing of shales have been reported in recent years (Maguire-Boyle and Barron, 2014; Orem et al., 2014). Although the occurrence of DOC and LMWOAs in different types of natural waters is well documented, only little work has been done to elucidate the relation between their quantitative and qualitative occurrence in water and the properties of the rock they have been in contact with.

Black shales and coals usually contain high concentrations of organic matter. During progressive burial over geological times, reactive functional groups within the organic material are thermally degraded. It is well known that during diagenesis, with vitrinite reflectance (Ro) below 0.5%, biopolymers such as polysaccharides, proteins and amino sugars are initially degraded by microorganisms in the water column and in young sediments, after which a loss of hydrolysable moieties takes place during continuing subsidence (Tissot and Welte, 1984). Catagenesis (R_O = 0.5 –

2.0%) is characterized by the progressive cracking of carbon-carbon and carbon-oxygen bonds accompanied by aromatization and condensation of the kerogen (Kelemen et al., 2007; Lis et al., 2005; Petersen et al., 2008; Robin and Rouxhet, 1978; Werner-Zwanziger et al., 2005). The generation of LMWOAs in sedimentary basins has been attributed to the cleavage of kerogen fragments containing carboxylic functional groups during the early stage of thermal maturation (Cooles et al., 1987). Decreasing yields of ester-bound LMWOA generated with increasing maturity of coals has been reported (Glombitza et al., 2009). In addition, oxidation reactions involving mineral oxidants may also produce organic acids during thermal maturation (Borgund and Barth, 1994; Seewald, 2001a, b; Surdam et al., 1993).

Knowing the composition, molecular size and structure of the DOC as well as the main controls on the release of DOC are prerequisites for a better understanding of the fluid-rock interactions taking place in shale environments over both geological and human timescales. Soxhlet extraction of marine sediments accesses a larger and more complex pool of organic matter than that contained in interstitial pore water (Schmidt et al., 2014). Hot water extraction of organic matter has also been previously applied to soils to examine the labile organic fractions (Bu et al., 2010; Ghani et al., 2003; Gregorich et al., 2003; Sarkhot et al., 2011). Thus, water extraction is an appropriate tool for studying the soluble organic matter released during the interaction between water and rock. As far as we are aware, leaching experiments have only rarely been applied to black shales and coals (Bou-Raad et al., 2000; Vieth et al., 2008) and little attention has been paid to how DOC composition varies as a function of organofacies, organic matter type and maturity. In the present contribution, we report the composition of DOC in water extracts from shales and coals not only of different geological ages and depositional settings, thereby covering different kerogen types, but also different thermal maturation levels, enabling the controls of progressive thermal maturation on composition of water extracts to be documented.

2. Materials

Thirty-two organic-rich black shales and coals from around the world, representing a wide range of depositional settings and ages (Paleozoic through Cenozoic age) were selected for this study (Table 1).

The samples cover a maturity range from immature (R_O = 0.29; T_{max} = 409°C) to overmature (R_O = 2.6; T_{max} = 602°C) with TOC contents of shales and coals extending up to 15% and 67%, respectively. The chain length distribution of *n*-alkyl moieties (C_{1-5} total, *n*-C_{6-14}, *n*-C_{15+}) in pyrolysates of the original samples is illustrated in the ternary diagram of Horsfield (1989) (Fig. 1). The pyrolysate compositions of shale samples indicate Paraffinic-Naphthenic-Aromatic Low Wax Oil petroleum type as well as Gas and Condensate petroleum type organofacies. The chain length distributions of the macromolecular organic matter in shale samples are closely similar despite their diverse origins. The three bituminous coals (C3, C4 and C5) fall in the High Wax, Paraffinic-Naphthenic-Aromatic Oil petroleum type and the two lignites C1and C2 fall in Paraffinic Oil High Wax organofacies. Relative percentages of the three main minerals of the shale samples are shown in Fig. 2. The Posidonia and Duvernay shales are dominated by carbonate, whereas the Bakken and Alum shales are characterized by higher contents of quartz and clays, respectively.

2.1 Posidonia shale

The Lower Toarcian Posidonia shale samples are from three shallow boreholes (Wickensen, Harderode, Haddessen) located in the Hils Syncline of Northwest Germany and cover a large maturity range from immature to overmature (Rullkötter et al., 1988). The shale was deposited in a restricted epicontinental sea with prevailing anoxic conditions, and the organic matter originates mostly from marine phytoplankton with minor terrigenous input (Littke et al., 1991). Comprehensive studies on the Posidonia shales have been presented by several authors, on nanoscale structure (Bernard et al., 2010; Bernard et al., 2012), petrophysical characteristics (Mann and Müller, 1988) and biogeochemistry (Wilkes et al., 1998). The depositional conditions and the preservation of organic matter are considered to be uniform for the three sampling sites (Littke et al., 1988; Littke et al., 1991; Rullkötter et al., 1988).

2.2 Bakken shale

The Devonian-Mississippian Bakken shale samples from six wells located in the Williston Basin in North Dakota, USA and covering the immature to mature range, were supplied by the North Dakota

Geological Survey. The Bakken shale was deposited in an epicontinental setting (Jiang et al., 2001) under anoxic and uniformly quiet conditions, judging by the widespread occurrence of planar and thin laminations (Webster, 1984). Amorphous organic matter derived from marine algae dominates, and terrestrial contributions are minor (Smith and Bustin, 1998). The detailed petroleum system has been investigated in previous studies (Jiang and Li, 2002; Kuhn et al., 2010; Kuhn et al., 2012; Leenheer, 1984; Muscio et al., 1994).

2.3 Duvernay shale

Six samples were taken from the Upper Devonian Duvernay Formation in the Western Canada Sedimentary Basin, and supplied by the Geological Survey of Canada. They follow a progressive trend in maturity from northeast to southwest. Two principal interbedded lithofacies are present: the nodular to nodular-banded lime mudstones exhibit varying degrees of bioturbation and indicate relatively oxygenated conditions; the dark bituminous laminated lime mudstones were deposited in deep water under oxygen-starved conditions (Chow et al., 1995; Creaney and Allan, 1990; Dieckmann et al., 2004; Li et al., 1997). The organic matter is mainly of marine planktonic origin as indicated by, for example, the biomarker value of pristane/n-C_{17} versus phytane/n-C_{18} (Li et al., 1997) and petrographic composition (Dieckmann, 1999).

2.4 Alum shale

The Alum shale samples were collected from a shallow well located in the south of the island of Bornholm, Denmark, which covers stratigraphic ages from Middle Cambrian to Lower Ordovician (Schovsbo et al., 2011). The shale formation is considered to have been deposited in a predominantly anoxic marine environment as the TOC content of the Alum shale is very high (Buchardt et al., 1986; Buchardt and Lewan, 1990). The Alum shale comprises homogeneous fine-grained mudstone and a low proportion of limestone occurring as beds and nodules, which indicate a uniform depositional environment (Buchardt et al., 1986). All the Alum shale samples, having evolved from an alginate-rich Type II kerogen (Horsfield et al., 1992), have a very high thermal maturity with the reflectance of "vitrinite-like" particles being about 2.3% (Buchardt and Lewan, 1990).

2.5 New Zealand coal

The Cenozoic coal samples were gathered from one drilled core and two coal mines in New Zealand. Three samples were taken from the DEBITS-1 well located in the Waikato Coalfield, two of which were lignites from above an unconformity and one of sub-bituminous rank from below the unconformity (Kallmeyer et al., 2006). The sample from Rotowaro Mine in Waikato Basin represents sub-bituminous coal and the one from Welcome Mine in West Coast Basin is a coal of High Volatile Bituminous rank (Vu et al., 2009).

Table 1: Sample origin and Rock-Eval pyrolysis characteristics. Hydrogen Index (HI) and Oxygen Index (OI) are measured in mg hydrocarbons/g organic carbon and mg CO_2/g organic carbon, respectively. TOC and Rock-Eval data of Duvernay shales and New Zealand coals were taken from (Dieckmann, 1999) and Glombitza (2011), respectively. Posidonia, Bakken and Alum shale samples were analyzed in this study. Ro values of Posidonia, Bakken, Alum and New Zealand samples were taken from Rullkötter et al. (1988), Dembicki and Pirkle (1985), Buchardt and Lewan (1990), and Glombitza (2011) respectively. Ro of Duvernay shales was calculated using the empirical formula %Ro = 0.018 * T_{max} - 7.16 (%) (Jarvie et al., 2007).

ID	Well	Depth (m)	TOC (%)	Tmax (°C)	OI	HI	Ro (%)
(A) Black shale, Posidonia Formation, Germany, Lower Jurassic, Type II							
P1	Wickensen	58.2	9.9	430	14	664	0.53
P2*	Wickensen	42.2	9.0	432	16	658	0.53
P3	Wickensen	30.2	11.4	433	14	634	0.53
P4	Harderode	77.3	4.8	447	7	340	0.88
P5*	Harderode	42.5	7.2	449	7	384	0.88
P6	Harderode	55.7	11.0	449	5	282	0.88
P7	Haddessen	36.6	9.2	466	9	87	1.45
P8*	Haddessen	51.0	5.0	466	16	79	1.45
P9	Haddessen	60.6	7.7	469	8	66	1.45
(B) Black shale, Bakken Formation, USA, Mississippian, Type II							
B1*	Daniel Anderson 1	1012.1	9.4	409	28	360	0.35
B2	Dobrinski 18-44	2631.7	14.9	423	12	420	0.45
B3	Nordstog 14-23-161-98H	2651.6	12.1	440	3	462	0.7
B4	Loucks 44-30	2350.8	15.0	440	2	460	0.75
B5*	Titan E-Gierke 20-1-H	3351.6	11.9	452	3	118	0.86
B6	BR 12-29	3253.7	8.4	452	4	93	1.1
(C) Black shale, Duvernay formation, Canada, Late Devonian, Type II							
D1*	Sarcee et al Pibroc	1395.9	6.4	418	19	619	0.36
D2	Imperial Kingman	1404.2	2.4	427	32	412	0.53

D3	Bangg Imperial	1677.9	5.5	431	6	621	0,6
D4	Tomahawk	2337.5	4.8	435	7	620	0.67
D5*	Imperial Cynthia	2976.1	1.9	447	12	92	0.89
D6*	Banff Aguit Ram River	4623.9	2.0	542	17	4	2.6
(D) Black shale, Alum Formation, Denmark, Lower Ordovician to Middle Cambrian, Type II							
A1	Skelbro-2	39.6	6.3	564	2	3	2.3
A2*	Skelbro-2	27.0	10.1	591	8	4	2.3
A3	Skelbro-2	38.7	8.1	591	2	3	2.3
A4	Skelbro-2	15.0	11.2	599	1	7	2.3
A5	Skelbro-2	11.8	7.7	600	4	3	2.3
A6	Skelbro-2	21.1	11.4	602	34	10	2.3
(E) Coal, New Zealand, Cenozoic, Type III							
C1*	DEBITS-1	18.9	45.1	414	95	192	0.29
C2*	DEBITS-1	62.5	35.9	414	80	366	0.29
C3*	DEBITS-1	140.5	58.2	419	26	172	0.39
C4*	Rotowaro Mine	Outcrop	61.2	422	32	154	0.45
C5*	Welcome Mine	Outcrop	67.4	424	15	209	0.52

*: Samples selected for display in Figures 4 and 5 are covering the whole range of maturity from each location.

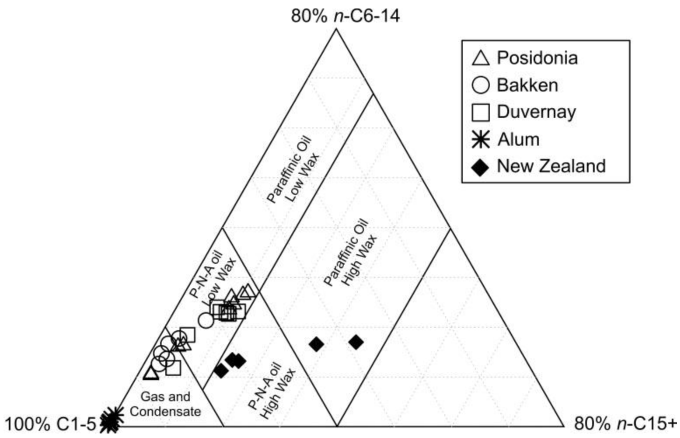

Figure 1: Bulk properties of the sediment pyrolysates concerning alkyl chain length distribution and petroleum type organofacies using the ternary diagram of Horsfield (1989).

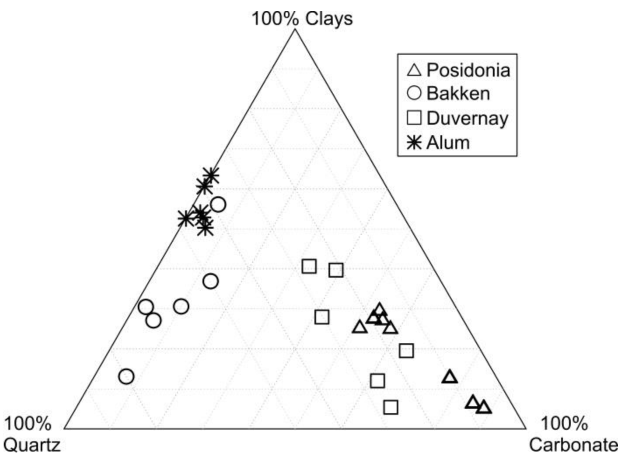

Figure 2: Ternary diagram showing the relative contents of clays, quartz and carbonate minerals for the studied shale samples.

3. Methods

3.1 Sample extraction

The experimental set up consisted of reaction vessels, equipped with a reflux condenser, in which the samples (10g; previously freeze-dried and ground) were extracted with deionized water (125ml) by heating to 100°C for 48 hours. The water had been treated via UV-photooxidation (Simplicity 185, Millipore) to remove organic compounds prior to the experiments. The extracts were vacuum filtered using 0.45 µm polypropylene filters. The samples were stored at 4°C in the refrigerator and later analyzed by different chromatographic methods. The reproducibility of the extraction was evaluated by running 6 parallel extractions. The standard deviation of the concentration of individual organic acids from the six extracts is below 10% (data not shown).

3.2 Analytical methods

3.2.1 Determination of total organic carbon (TOC) and Rock-Eval Pyrolysis

Determination of the total carbon content (TOC) was achieved by measuring the carbon dioxide formed by combustion at 1350°C using a Leco SC-632 IR-detector. Finely crushed rock samples were treated with diluted HCl at 60°C to remove inorganic carbon. The Rock-Eval analyses were performed using a Rock-Eval 6 instrument and following the procedure described in NIGOGA 4th edition (Weiss et al., 2000).

3.2.2 Open-system pyrolysis gas chromatography (Py-GC)

Open-system Py-GC was applied to all the shale and coal samples. Depending on TOC, up to 35 mg of each crushed sample was placed into a small glass tube, which was sealed and inserted into a Quantum MSSV-2 Thermal Analyzer (Horsfield et al., 1989; Horsfield et al., 2015). The sample was heated in a flow of helium at 300°C for 5 min to get rid of volatile constituents and pollutants. Afterwards, the sample was pyrolyzed at the rate of 50°C min^{-1} from 300°C to 600°C. Pyrolysis products were collected in a cryogenic trap from which they were later liberated and directly transferred into an Agilent GC 6890A gas chromatograph. Boiling ranges (C_{1-5}, n-C_{6-14} and n-C_{15+}) and individual compounds were quantified by external standardization using *n*-butane.

3.2.3 X-ray Diffraction (XRD)

The mineral composition of the shale samples was determined by X-ray diffraction (XRD) followed by Rietveld refinement for a quantitative evaluation. XRD analyses were performed using a PANalytical Empyrean. The software EVA (Bruker) was used to identify the minerals and the program AutoQuant for Rietveld calculations was used to determine the amount of the identified minerals (detection limit ~1 wt %).

3.2.4 Ion chromatography (IC)

Extracts were analyzed in replicate by ion chromatography (IC) using conductivity detection (ICS 3000, Dionex) to determine the content of organic acids (formate, acetate, propionate, butyrate, valerate and oxalate) and different anions (F^-, PO_4^{3-}, NO_3^-, Cl^- and SO_4^{2-}); the detection limit was about 0.1mg L^{-1}. The equipment used an ASRS Ultra II 2 mm suppressor and a Dionex conductivity detector. For chromatographic separation of the anions the analytical column AS 11 HC (Dionex Corp.) was used at a constant temperature of 35 °C. Samples were eluted using KOH solution of varying concentrations over time. The initial KOH concentration was 0.5 mmol L^{-1} and held for 8 min. After 10 min, a concentration of 15 mmol L^{-1} KOH was reached and kept constant for 10 min. After 30 min analysis time, a concentration of 60 mmol L^{-1} KOH was reached, followed by a rapid increase to 100 mmol L^{-1} reached after 30.2 min analysis time. At 32 min, the KOH concentration was again at the initial level of 0.5 mmol L^{-1} and kept there for an additional 15 min to equilibrate the system. For quantification of organic acids, standards containing all investigated compounds were measured in different concentrations every day. The standard deviation of sample and standard quantification is below 10% (determined by at least two measurements).

3.2.5 Liquid chromatography- Dissolved organic carbon (LC-OCD)

The characterization and quantification of the dissolved organic carbon (DOC) and its fractions were conducted by size-exclusion-chromatography (SEC) with subsequent UV (λ=254 nm) and IR detection by LC-OCD (Huber and Frimmel, 1996). Phosphate buffer (pH 6.85; 2.7 g L^{-1} KH_2PO_4, 1.6 g L^{-1} Na_2HPO_4) was used as mobile phase set to a flow of 1.1 mL min^{-1} (Huber et al., 2011). The chromatographic column was packed with Toyopearl HW-50S resin and had a size of 250 × 20 mm. The solid phase separates the components according to their molecular mass, where increasing retention time indicates decreasing molecular mass (Pelekani et al., 1999). With LC-OCD the organic matter can be separated into five different fractions referred to as Macro-1 (>10000 Da), Macro-2 (~1000 Da), Macro-3 (350-500 Da), Acids (<350 Da) and Neutrals (<350 Da) (Huber et al., 2011) (Table 2). Constituents of Macro-3 fraction are assumed to reflect breakdown products of constituents of Macro-2 fraction and are described alternatively as material similar to humic substances but with lower molecular masses (Huber et al., 2011). The properties and origins of each fraction are shown in Table 2. The amount of DOC was quantified by IR-detection of released CO_2 after UV-oxidation (λ=185 nm) in a Gräntzel thin-film reactor. For molecular mass calibration, humic and fulvic acid standards of the Suwannee River, provided by the International Humic Substances Society (IHSS), were used.

Table 2 Description of LC-OCD fractions. Modified from Huber et al. (2011) and Penru et al. (2013).

Fraction (This study)	Fraction (Huber et al., 2011)	Molecular mass range	Properties	Description
Macro-1	Biopolymers	>10000 Da	Not UV-absorbable, hydrophilic	Polysaccharides and proteins
Macro-2	Humic substances	~1000 Da	Highly UV-absorbable, hydrophobic	Calibration based on Suwannee River standard from IHSS
Macro-3	Building blocks	350-500 Da	UV-absorbable	Breakdown products of humic substances
Acids	Low molecular weight acids	<350 Da	Negatively charged	Low molecular weight aliphatic acids
Neutrals	Low molecular weight neutrals	<350 Da	Weakly or uncharged hydrophilic, amphiphilic	Alcohols, aldehydes, ketones, amino acids

4. Results

4.1 Extraction of DOC

The concentrations of DOC versus maturity (T_{max}) for the five series under study are shown in Figure 3. In general, the concentrations of DOC decreased steeply with progressive maturation and then remained at low values for samples with T_{max} higher than 435°C. The DOC concentrations ranged from 0.01 to 2.1 mg/g rock (Fig. 3a) or 0.03 to 15.1 mg/g TOC (Fig. 3b), respectively. The amounts of DOC were comparable in the extracts of Posidonia, Bakken, and Duvernay shales, while the Alum extracts had the lowest concentrations of DOC and the New Zealand coal extracts showed the highest DOC concentrations. When the DOC concentration was normalized to TOC of the extracted shales and coals, the Alum extracts still showed the lowest DOC concentrations but the DOC concentrations of the New Zealand coal extracts were no longer outstanding (Fig. 3b).

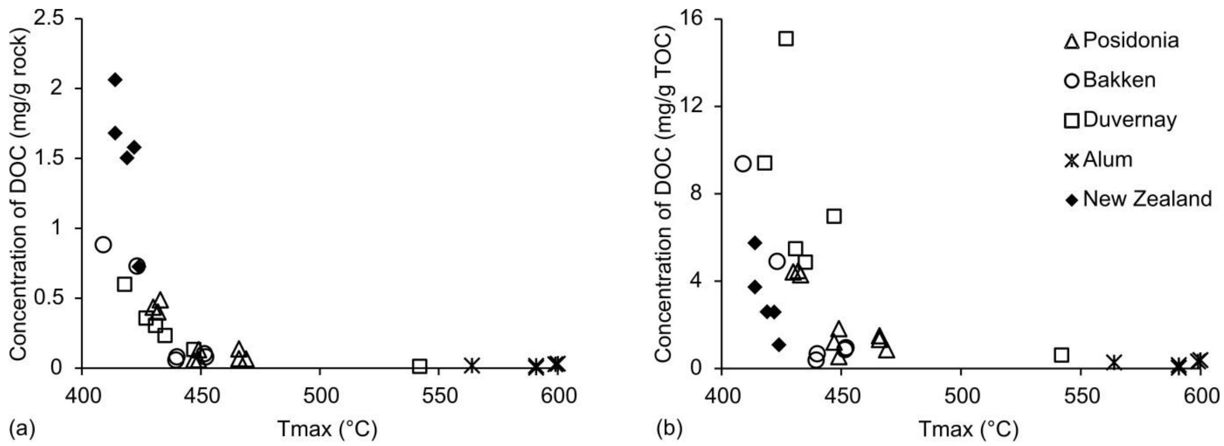

Figure 3: DOC concentrations of shale and coal extracts plotted over T_{max} in mg/g rock (a) and in mg/g TOC (b).

4.2 Composition of DOC

Using size-exclusion chromatography (SEC), DOC can be separated into different fractions according to their molecular masses. The chromatograms of selected shale extracts are shown in Fig. 4. These shales have been selected as they represent the whole range of maturity occurring at the different locations. The DOC of the shale extracts was characterized by one prominent peak (peak 1) at an elution time of 47.2 min in the IR-chromatogram. This peak was considered to represent the Acid fraction based on the elution order of authentic standards. Peak 2 was characteristic of the Macro-3 fraction and appeared at a retention time of 42.5 min, except for the extracts of immature samples B1 and D1 where it appeared a little later at 43.1 min. A small peak 3 appearing at 39.8 min represented the Macro-2 fraction, which is of higher molecular mass than the Macro-3 fraction. The compounds eluting at a later retention time than 50 min correspond to the Neutral fraction. We identified some peaks belonging to the Neutral fraction in both Bakken and Duvernay shale extracts. There is no indication of the Macro-1 fraction in any shale extract.

Most UV-chromatograms showed two prominent peaks with retention times of 47.2 min (peak 1) and 42.5 min (peak 2) except for the extract from B1 that showed a small shift in peak 2 to retention time of 43.1 min. This extract showed an additional peak (peak 3) at retention time of 39.8 min. The peak 3 is not observable for the extracts from shales with higher maturity than B1 (Fig. 4b). These parallel peaks indicate the UV-activity of the extracted organic compounds. As the fractions Macro-2 and Macro-3 contain aromatic and unsaturated structures, they have a good UV response (Jacquemet et al., 2005).

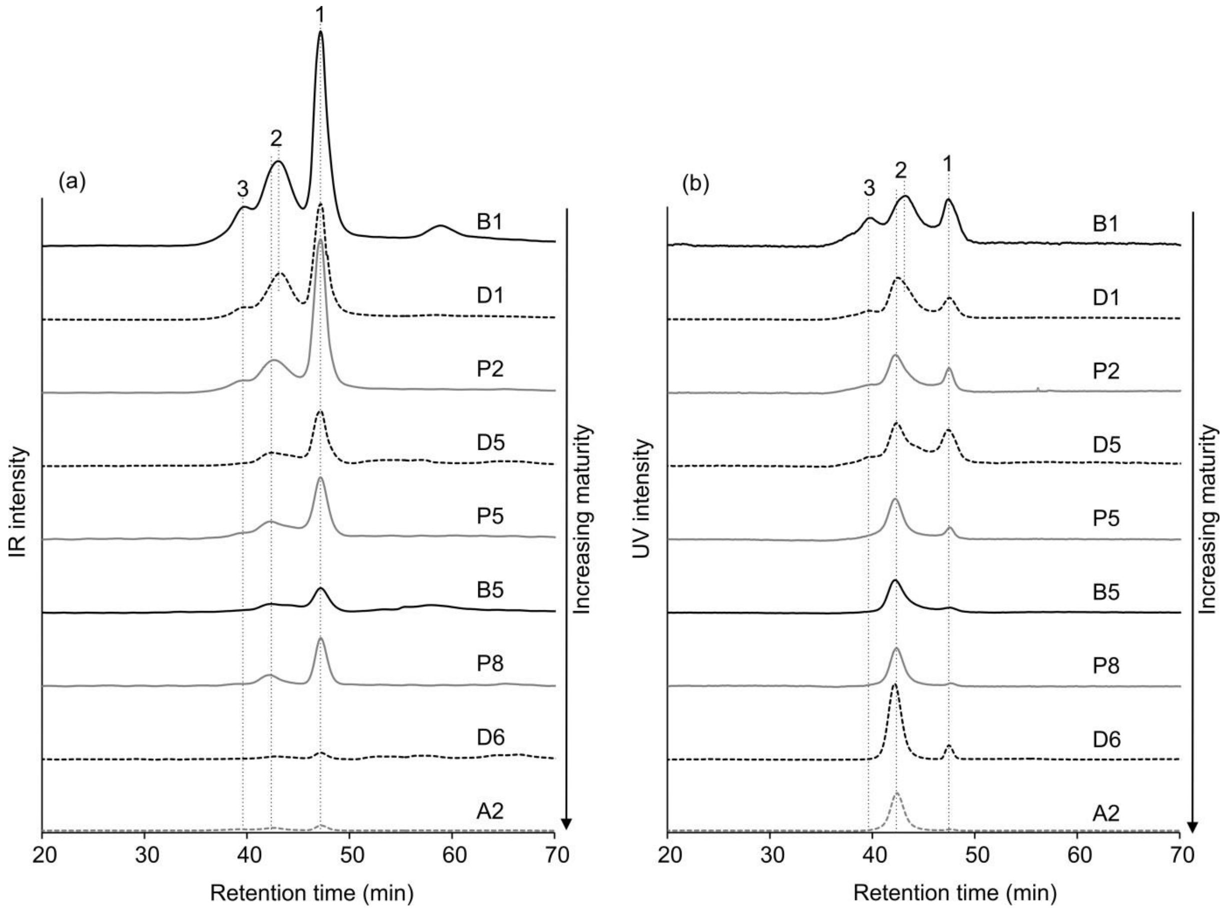

Figure 4: SEC chromatograms giving intensity of (a) IR-signal and (b) UV-signal over run time of the analytical separation of shale extracts.

Figure 5a shows the IR-intensities of DOC compositions in coal extracts. Generally, the extracts of coals with $T_{max} \geq 419°C$ (C3, C4 and C5) showed comparable chromatograms to the shale extracts, but the retention times of the peaks were not exactly identical. Peak 1, indicating the Acid fraction, also eluted after 47.2 min. The peak 2, belonging to the Macro-3 fraction, appeared after 42 min, except for the two lignite extracts of C1 and C2 with retention time of 41.7 min. In general, peak 2 eluted a little earlier than in the shale extracts (42.5min). Peak 3, evaluated as belonging to the Macro-2 fraction, showed a shoulder at retention time of 39 min, which was about 1 min earlier than the peak 3 in the shale extracts. The chromatograms of lignite extracts of C1 and C2 were quite different to the other three extracts from coals of bituminous rank. Here, the Macro-2 was the prominent fraction and an additional peak 4 existed, representing the Macro-2 of higher molecular mass. In general, the extracts show decreasing intensities of the IR-signals with increasing T_{max} for both shale and coal samples.

The corresponding UV-response of the coal extracts is shown in Figure 5b. It is obvious that the UV-chromatograms of shale and coal extracts are quite distinct and the intensity of UV-chromatograms decreases with increasing maturity of the coals. The two lignite extracts of C1 and C2 were comparable with one another in UV-peak distribution and shapes. They both showed a dominant peak at 37 min and a shoulder at 39 min. The two coal extracts of C3 and C4 showed a peak at 39 min and two small shoulders (retention times of 37 and 42 min) on both sides while the coal extract of C5 showed the lowest UV-signal. All the coal and shale extracts exhibited a peak at 47.2 minute in the UV-chromatograms, which might correspond to the breakdown products of the Macro-3 fraction or comprise colloidal material where the UV-signal resulted from light scattering rather than absorption (Allpike et al., 2007).

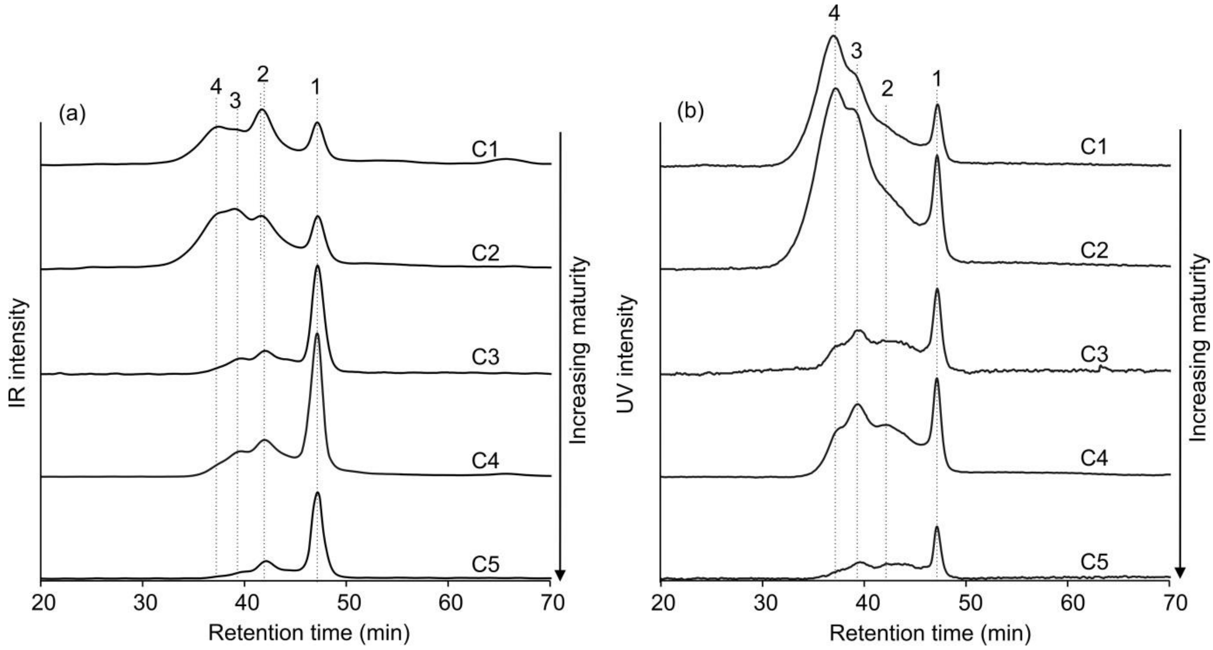

Figure 5: SEC chromatograms giving intensity of (a) IR-signal and (b) UV-signal over run time of the analytical separation of coal extracts.

The relative percentages of DOC in the different fractions (Acids, Macro-2+3 and Neutrals) are shown in Figure 6. As the boundary between the fractions Macro-2 and Macro-3 was difficult to identify, these two fractions were grouped together. For the Posidonia extracts, the percentages of the Acids decreased with progressive shale maturation up to peak oil window (T_{max} = 447°C - 449°C) and reversed afterwards. The percentages of the Neutral fraction showed the opposite tendency and the percentages of the Macro-2+3 fraction showed slight but steady decrease with increasing maturity of the shales (Fig. 6a). The DOC fractions extracted from the Bakken and Duvernay shales showed comparable variation (Fig. 6b+c). With increasing maturity of the Bakken and Duvernay shales, the relative percentages of the Neutral fraction showed a progressive increase, the percentages of the Macro-2+3 fraction decreased and the Acid fraction decreased only slightly. However, the percentages of the different fractions were different for Bakken and Duvernay shale extracts. The extracts of the overmature Alum shales generally showed high percentages of the Neutral fraction and low percentages of the Acid fraction. As the total amounts of DOC in the leachates of Alum shales were extremely low, the variations in percentages of different fractions should not be over-interpreted. For New Zealand coals, the fractions of the two lignite extracts of C1 and C2 showed similar relative distributions of DOC fractions (Neutrals around 15%, Macro-2+3 around 80%, Acids around 5%) while the percentage of the Acid fraction increased up to 37% and the percentage of the Macro2+3 fractions decreased to 47% for the extracts of the other three bituminous coal samples.

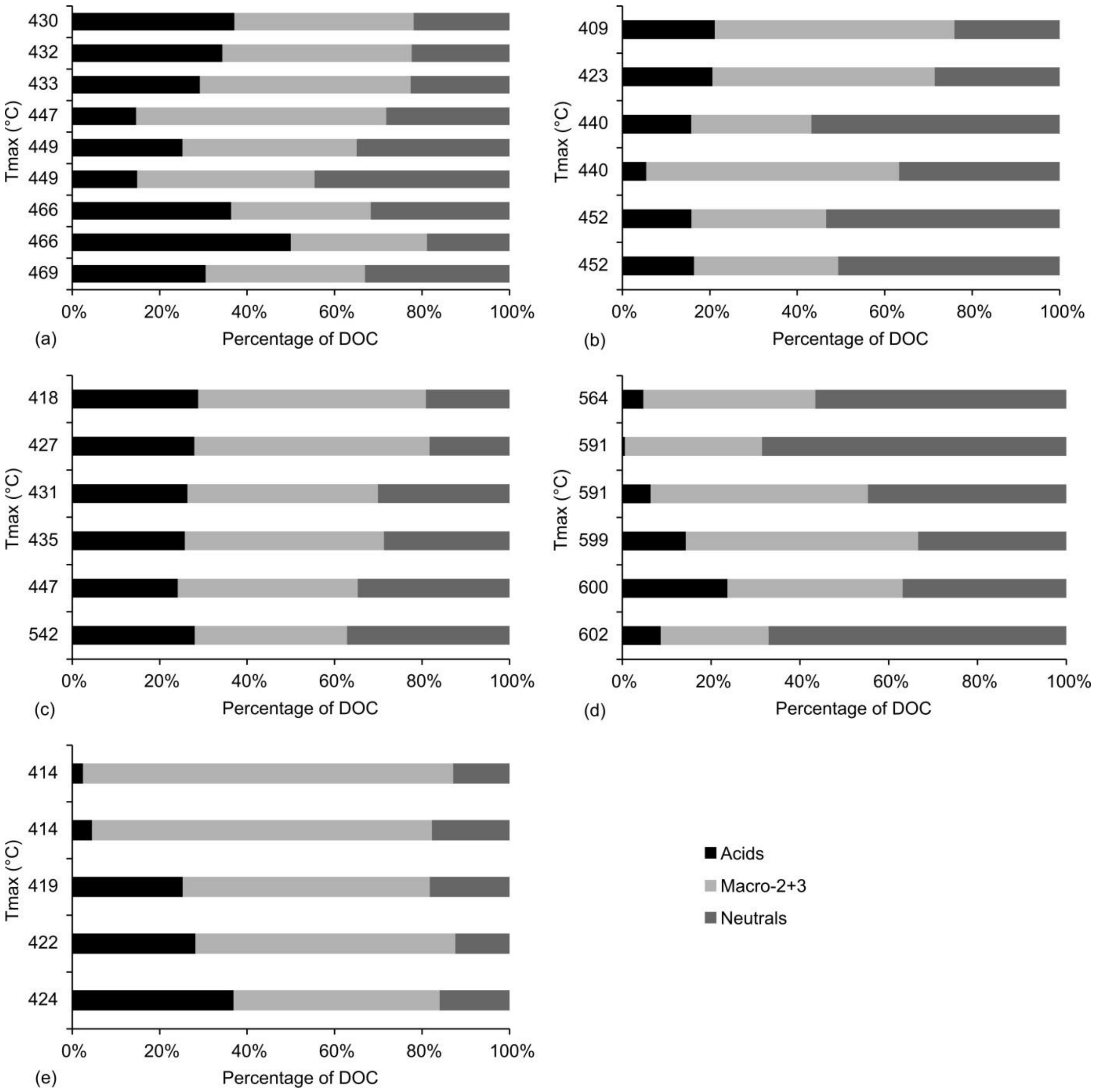

Figure 6: The relative percentages of the different DOC fractions extracted from shales and coals, (a) Posidonia shales; (b) Bakken shales; (c) Duvernay shales; (d) Alum shales; (e) New Zealand coals.

4.3 Occurrence of individual organic acids in the extracts

4.3.1 The organic acids in shale extracts

Formate and acetate were the dominant LMWOAs detected in the water extracts of all shale samples followed by oxalate. Propionate, butyrate and valerate were present in low concentrations in the extracts of immature and some mature samples; none of them were detected in the overmature samples.

The Posidonia shales from the wells Wickensen, Harderode and Haddessen are immature, mature and overmature, respectively (Rullkötter et al., 1988). The concentrations of LMWOAs in the extracts are comparable for samples from the same well, while significant differences can be observed between wells (Fig 7). The concentrations of formate decreased remarkably with increasing maturation of the shales and then remained at a low level for shales reaching the oil window. The concentrations of acetate also decreased with maturity of the shales but surprisingly showed a reversal for shales reaching the gas window – possible explanations for the reversal are discussed later in this paper.

The Bakken shale samples were immature to mature and the concentrations of formate and acetate in the extracts were both negatively correlated to thermal maturity, as was the case for the early mature to mature Posidonia samples. No overmature Bakken shale samples were available. The Duvernay shale samples, which were either immature or mature except for one extremely overmature sample, also showed a trend of decreasing carboxylic acid concentrations with increasing maturity. The extracts of the overmature Alum shale had extremely low concentrations of both formate and acetate, which ranged from 0.02 to 0.5 mg/g TOC and 0.02 to 0.10 mg/g TOC, respectively. The reversal in acetate concentration at high maturity as noted for the Posidonia shale extracts was not seen for either the Alum or the Duvernay extracts.

4.3.2 Organic acids in coal extracts

The concentrations of formate were higher than the concentration of acetate in the extracts of the two lignites while in the extracts of three bituminous coals the concentrations of acetate were higher than formate. Except for oxalate showed much high concentration in the extracts of the two lignites, other acids (e.g. propionate, butyrate, valerate) showed only trace amount or were below the detection limit in all coal extracts. Due to the narrow range of the maturity of the coal samples, the concentration of formate and acetate in the coal extracts was not so obviously correlated with thermal maturity compared to the shale extracts. When normalized to TOC, the concentrations of formate ranged from 0.5 to 1.76 mg/g TOC for coals and from 0340.02 to 2.44 mg/g TOC for all shale extracts (Fig. 7a). The concentrations of formate in the extracts of coals and shales with same maturity were comparable (Fig. 7a). The concentrations of acetate in the coal extracts were also within the range detected in the shale extracts, but acetate concentrations were much lower in coal extracts compared to extracts from shales with the same maturity (Fig. 7b).

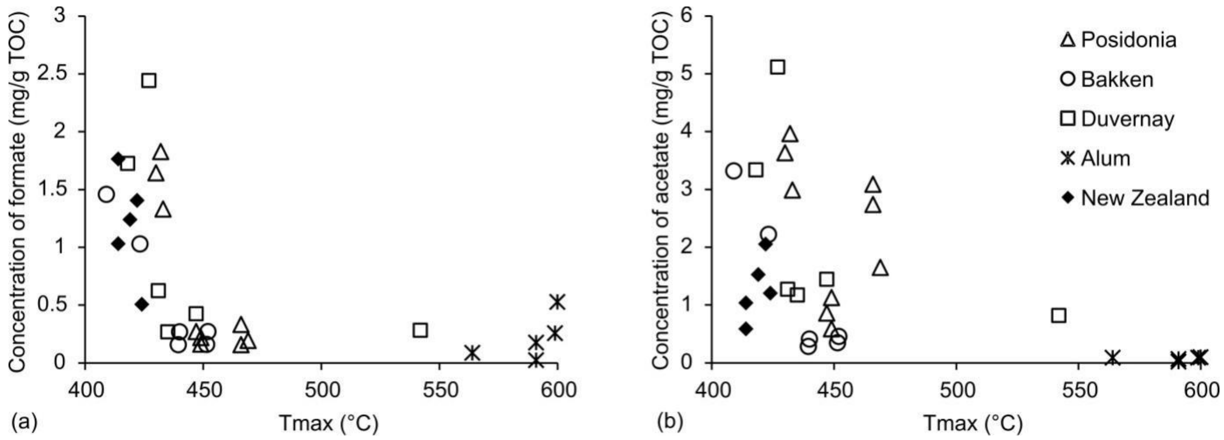

Figure 7: The concentrations of formate (a) and acetate (b) extracted from shales and coals of different maturities.

5. Discussion

5.1 Effect of shale and coal organic matter composition on water extracts

5.1.1 Bulk DOC and DOC fractions

As shown in Fig 3b, only a few permil of the TOC was extracted as DOC in our experiments. However, the coal samples with higher contents of TOC show higher amount of extracted organic carbon than the shale samples (Fig. 3a). When normalized to TOC, the concentrations of DOC in the coal extracts are within the range of the DOC concentrations of the immature shale leachates (Fig. 3b). From these experimental results, we can conclude that the total amount of extractable organic compounds from shales and coals was influenced by the amount of TOC and probably not by the kerogen type of the organic matter. Nevertheless, the DOC compositions of shale and coal extracts are clearly influenced by the kerogen types, as shown by the differences in IR-chromatograms of the extracts. The two lignite extracts of C1 and C2 are characterized in their IR-chromatograms by high intensities of the Macro-2+3 fractions while the IR-chromatograms of the other three coal extracts (C3, C4 and C5) show high peaks of the Acid fraction, which are similar to the chromatographic patterns of the immature shale extracts. The organic matter of coals C4 and C5 contains mainly terrestrial higher plant material with a significant contribution of microbial biomass (Vu et al., 2009) and it can be as *previous* sumed that the organic matter of C3 also has a significant contribution of microbial biomass as it belongs to a similar petroleum type organofacies as coals C4 and C5 (Fig. 1). Also all selected shales have organic matter that is derived from a mixture of planktonic and microbial sources. Therefore, the similarity of the chromatographic patterns is plausible. However, the retention times of the peak maxima of the Macro-2 and Macro-3 fractions from the coal extracts are shorter than for the shale extracts, which points to the differences in the molecular masses of these DOC fractions from shales and coals. The molecular masses of most constituents included in the fractions Macro-2 and Macro-3 in the coal extracts are heavier than in shale extracts. Even more notable differences between shale and coal extracts can be observed in the UV-chromatograms where coal extracts showed higher intensities. These higher intensities may be related to the presence of aromatic structures in the DOC of coal extracts. Coals with type III kerogen mainly originate from terrigenous higher plant material of lignocellulosic origin while the shales with type II kerogen originate from marine planktonic material which is comprised of aliphatic structures.

5.1.2 LMWOAs

The observed distribution of the individual organic acid concentrations, where acetate is dominant in the shale and bituminous coal extracts, is in accordance with the results from hydrous pyrolysis of kerogen (Kawamura et al., 1986), crude oils (Borgund and Barth, 1994) and source rocks (Barth and Bjørlykke, 1993; Barth et al., 1988). The observed order in concentrations with acetate >> propionate > butyrate > valerate has also been reported for natural deep subsurface waters (Fisher, 1987; Means and Hubbard, 1987). However, no information about formate concentrations was given in these previous studies.

The relation between the concentrations of formate and acetate, extracted from shales and coals is shown in Figure 8. The results of Alum shale extracts are not included here due to their extremely low concentrations. A linear correlation between the concentrations of formate and acetate can be observed in all shale extracts except for the three Posidonia extracts of P7, P8 and P9 and the coal extracts. This linear trend indicates that the extraction of these acids might be controlled by the same factors. Discussion about the three outlier points representing the three Posidonia extracts of P7, P8 and P9 is given later in this paper. The linear correlation between the concentrations of formate and acetate in the shale extracts cannot be observed in the coal extracts. This may be due to the fact that the five samples already represent two different petroleum type organofacies. Thus, we can deduce that the correlation between the concentrations of formate and acetate in the extracts of samples with the same organofacies might be similar.

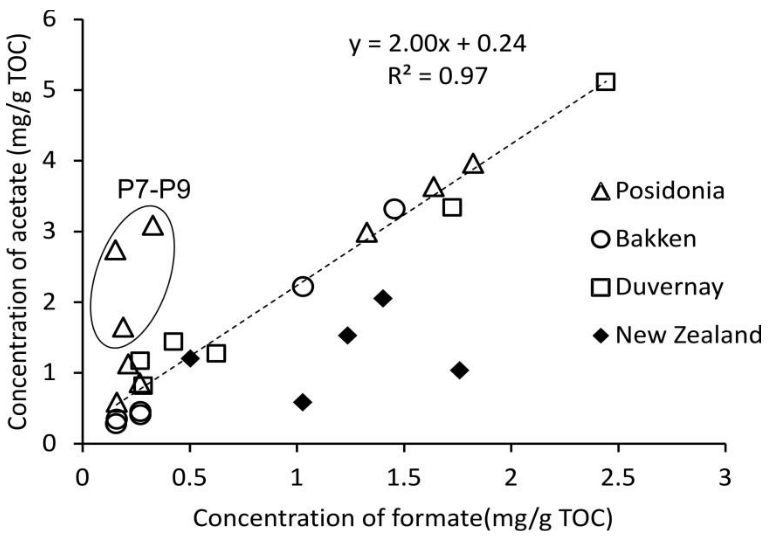

Figure 8: Comparison of formate and acetate concentrations in the water extracts. The linear regression excludes the extracts of P7, P8 and P9 and New Zealand coals.

5.2 Effect of burial processes on composition of water extracts

5.2.1 Influence of maturation on the extracted organic matter

As illustrated in Fig. 3, the concentrations of DOC decreased with maturity until T_{max} reaches 435°C after which low concentrations were maintained. The samples clearly showed a higher potential for DOC extraction at the stage of diagenesis rather than at later stages when thermal cracking reactions became significant. Generally, the concentrations of the individual DOC fractions also decreased with increasing maturity for shale samples from the same formation, which could be indicated by the IR-chromatograms as the intensities of the IR-chromatograms correspond to the concentrations of DOC

(Fig. 4a). But there was no overall trend of decreasing DOC concentration with increasing maturity. This can be illustrated for shale D1 which is less mature (lower T_{max}) than shale P2 but the extract of D1 had a lower DOC concentration (lower IR signal intensity). The similar phenomenon can also be observed for samples B5 and P8. Though the coal samples represent only a very narrow range in maturity, the general trend of decreasing DOC concentrations with increasing T_{max} can also be observed for the coal extracts.

Fig. 7 showed the concentrations of formate and acetate in extracts over T_{max} of the shales/coals. The concentrations of extracted acids decreased with increasing maturity of the samples except for the overmature Posidonia shales from the Haddessen well. Here, acetate concentrations are higher than expected. This similar decreasing tendency of LMWOA concentrations in extracts with ongoing maturation has already been described in the experiments of soxhlet water extraction and alkaline ester cleavage of coals (Glombitza et al., 2009; Vieth et al., 2008). Thus, it may be assumed that a potential equilibrium exists between kerogen bound LMWOAs and free LMWOAs. Kerogen is generally accepted as the source of LMWOAs and their generation is considered to result from kerogen maturation (Eglinton et al., 1987; Kawamura and Kaplan, 1987). The immature kerogen maturation process simulated by hydrous pyrolysis illustrates that the generation of LMWOAs from kerogen resulted from cracking and hydrolysis reactions and continues at high simulated maturation levels (Barth et al., 1988; Kawamura et al., 1986). In the present experiment, the LMWOAs easily extracted during water extraction were assumed to be mainly the free acids, which assimilated into sedimentary organic matter or dissolved in the in-situ pore water during early diagenesis (Pittman and Lewan, 1994). The immature kerogen contains significant amounts of aliphatic components and oxygen. Their functional groups show higher potential to form LMWOAs compared to the overmature kerogen, which contains fewer aliphatic chains and less oxygen (Bernard et al., 2012; Vu et al., 2013). The defunctionalisation reaction of oxygen containing functional groups and oxidation of *n*-alkanes during geological times might lead to the formation of LMWOAs. So the maturity of the samples is a pivotal factor that influences the concentrations of different acids in the extracts. This is supported by the minor amounts of formate and acetate extracted from overmature Alum shale samples.

5.2.2 Influence of OI on the concentration of individual organic acids

The significant decrease of oxygen-containing compounds during diagenesis can be traced using van Krevelen diagram, which shows the preferential decrease of O/C ratio relative to H/C ratio (Tissot and Welte, 1984). Furthermore, the loss of C=O functionalities with increasing maturity can be revealed by infrared spectroscopy (al Sandouk-Lincke et al., 2013; Lis et al., 2005). A general positive correlation between Oxygen Index (OI) and the concentrations of formate and acetate in the extracts could be observed for the Bakken, Posidonia and Duvernay (Fig. 9). This indicates that the amounts of acids extracted from the shales were directly constrained by the initial kerogen oxygen content. When the coals were separated into two groups according to their organofacies, the positive trend between OI of coals and the concentrations of formate and acetate in the extracts also could be observed in each group. The coal samples with type III kerogen, characterized by generally high atomic O/C ratio, were expected to generate a higher concentration of organic acids than type II kerogen (Cooles et al., 1987). But the functionality of the oxygen may be an important factor, i.e. oxygen in carboxylic acids and esters is assumed to contribute more to LMWOAs than the oxygen in ether bonds and ring systems (Borgund and Barth, 1994). Additionally, the type II kerogen contains more aliphatic moieties that can be oxidized to form carboxylic acids.

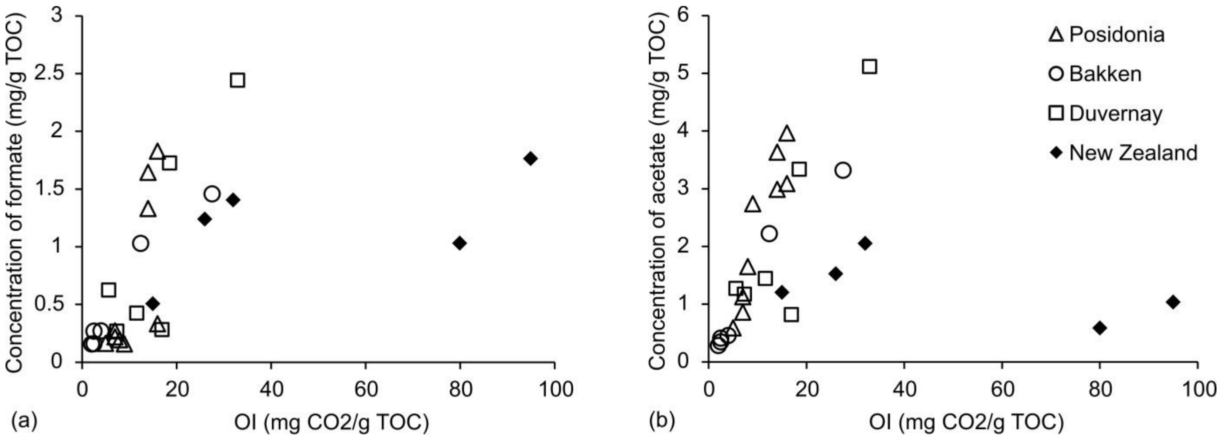

Figure 9: Concentrations of formate (a) and acetate (b) in the extracts are plotted over the oxygen index (OI) values of the shales and coals.

5.2.3 Possible influence of hydrothermal brines

The unexpectedly high concentrations of acetate extracted from these overmature Posidonia shales might be related to the occurrence of hydrothermal fluid migration along the southern rim of the Lower Saxony Basin (Petmecky et al., 1999). The occurrence of authigenic albite with halite inclusions has been used to argue for hydrothermal activity affecting the mineralogy of the Posidonia shale (Bernard et al., 2012). The hydrothermal brines and iron-bearing minerals may have provided a source of available oxygen to partly oxidize bitumen to form acids (Bernard et al., 2012). The oxidation of hydrocarbons may produce LMWOAs during thermal maturation (Barth, 1987; Borgund and Barth, 1994; Eglinton et al., 1987; Seewald, 2001b; Surdam et al., 1993), and this is speculated to be the main control on the high concentration of acetate in the extracts of samples P7, P8 and P9. The higher concentrations of chloride detected in the extracts of shales from the overmature Haddessen well in comparison to the extracts of other Posidonia shales would support an influence of hydrothermal brines (Fig. 10). Hydrothermal activity could have provided both a local heat source to drive the generation reactions which led to the formation of organic acids, and water to act as reaction and transport medium. It should be noted that high geothermal gradients associated with hydrothermal activity might have also increased the rate of acid production from kerogen. The steep gradient in formate/acetate for the Haddessen shales (P7-P9; Fig. 8) might signal the selective generation of acetate from bitumen precursors, possibly accompanied by formate degradation or consumption. Though a heat-flow anomaly existed in the Bakken formation (Kuhn et al., 2012), no obvious influence on the generation of acetate or formate could be observed in our experiments.

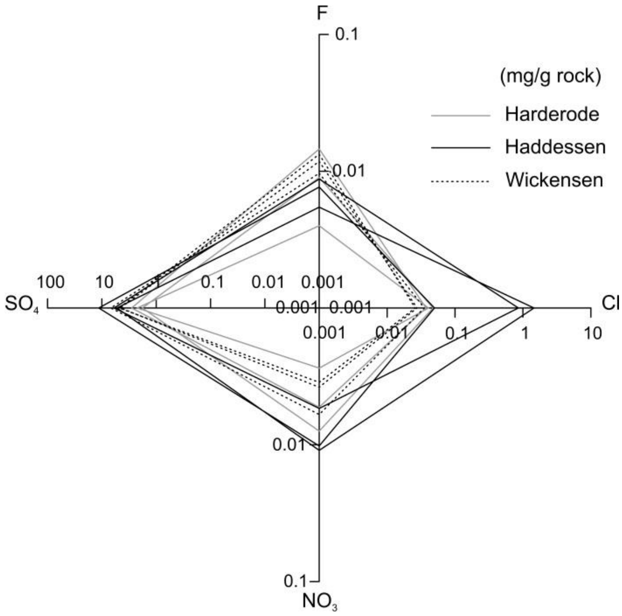

Figure 10: The concentrations of inorganic anions in Posidonia extracts. The concentrations of fluoride, sulfate and nitrate are in the same order of magnitude for most Posidonia samples, only extracts of P8 and P9 show extremely high concentrations of chloride.

5.2.4 Correlation between concentration of acids and porosity

LMWOAs have been shown to be an important potential contributor to generate secondary porosity by dissolution of aluminosilicate and carbonate minerals (Surdam et al., 1984). That type of porosity could provide more space for storage of generated bitumen in shales, which could then act as a source of acetate afterwards. The total porosity of the Posidonia maturity sequence shows a loss of porosity in going from the immature stage (ca. 10-13%) to the oil window (4-6%) and then an increase again in the gas window Haddessen well (9-12%) (Mathia et al., 2013). The pattern in porosity changes with increasing maturity correlates with the concentration of acetate in the water extracts of the respective shales (Fig. 11), but not with formate. According to Bernard et al. (2012), the pores in Posidonia shales of oil window maturity were filled by viscous bitumen during kerogen degradation, and this resulted in the decrease of porosity. In gas window, the porosity increased again because of secondary cracking reactions leading to the generation and exsolution of gaseous hydrocarbons. The creation of nanoporosity within overmature Barnett shale by thermal cracking of retained hydrocarbons has also been reported by Loucks et al. (2009). Based on the lack of porosity data from other shales, no reliable evaluation of the correlation between extracted acetate concentrations and porosity of Posidonia shales is possible. It is assumed that there is no cause-effect relationship between these parameters.

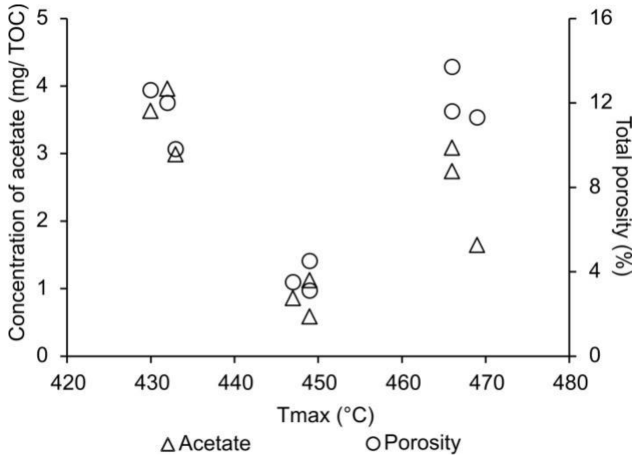

Figure 11: The variation of acetate concentrations in Posidonia extracts (left Y axis) and porosities of the shales (right Y axis) with increasing maturity.

6. Summary and Conclusions

Extraction of black shales and coals using deionized water resulted in the release of water soluble organic compounds. In general, the concentrations of DOC decreased steeply with progressive maturation and then remained at low values for samples with T_{max} higher than 435°C. The coal extracts showed much higher DOC concentrations on a per gram sediment basis, but when normalized to TOC, the concentrations of DOC are within the range observed for the immature shale leachates. From this we conclude that maturity of the kerogen and TOC content are two main factors that influence the amount of DOC extracted from sediments. Macro-2, Macro-3, Acids and Neutrals comprise the four DOC fractions that have been detected in the extracts using SEC. The extracts of immature samples have a high content of the Macro-2 and Macro-3 fractions whereas leachates of mature and overmature samples are dominated by the Neutral fraction, which represent the final degradation products of organic matter during geological maturation. The DOC extracted from coal samples is more aromatic than that extracted from shales, which is documented by the higher intensity of UV-signals. According to the retention times in SEC, it can be deduced that the molecular weight of the constituents included in the fractions Macro-2 and Macro-3 of the coal extracts is higher than for the shale extracts.

Acetate and formate represent the dominant acids extracted from shales and coals. Other LMW mono- and di-carboxylic acids like propionate and oxalate are detected in some of the leachates, but in lower concentrations. The linear trend between the concentrations of formate and acetate extracted from shales indicated that the generation of individual LMWOAs is controlled by the same factor. The concentrations of acids also decreased with increasing maturity of the shales except for the overmature Posidonia shales from the Haddessen well. The reason for the high concentrations of acetate in the extracts of overmature Haddessen shales might be the influence of hydrothermal brines. These brines might provide oxygen and hydrogen to enhance the generation of organic acids.

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