Research Article

Light Hydrocarbon Geochemistry of Oils in the Alpine Foreland Basin: Impact of Geothermal Fluids on the Petroleum System

Ł. Pytlak,¹ A. Leis,² W. Prochaska,¹ R. F. Sachsenhofer,¹ D. Gross,¹ and H.-G. Linzer³

¹*Applied Geosciences & Geophysics, University of Leoben, Peter-Tunner-Str. 5, 8700 Leoben, Austria*

²*JR-AquaConSol GmbH, Steyrergasse 21, 8010 Graz, Austria*

³*Rohöl-Aufsuchungs AG, Schwarzenbergplatz 16, 1015 Vienna, Austria*

Correspondence should be addressed to Ł. Pytlak; lukasz.pytlak@onet.pl

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Oil is produced in the Austrian sector of the Alpine Foreland Basin from Eocene and Cenomanian reservoirs. Apart from petroleum, the basin hosts a significant geothermal potential, which is based on the regional flow of meteoric water through Malmian (Upper Jurassic) carbonate rocks. Oils are predominantly composed of *n*-alkanes, while some samples are progressively depleted in light aromatic components. The depletion in aromatic components relative to abundant *n*-alkanes is an effect of water washing. Waters coproduced with oils that are affected by water washing show a progressive reduction in salinity and depletion in ²H and ¹⁸O isotopes, indicating that the degree of water washing is mainly controlled by the inflow of meteoric water from the Malmian aquifer. In some fields with Cenomanian reservoir rocks, a hydraulic connectivity with the Malmian aquifer is evident. However, water washing is also recognized in Eocene reservoirs and in areas where the Malmian aquifer is missing. This shows that existing flow models for the regional Malmian aquifer have to be modified. Therefore, the results emphasize the importance of combining data from the petroleum and geothermal industry, which are often handled separately.

1. Introduction

The Alpine Foreland Basin (AFB) is a minor oil and moderate gas province in central Europe (Figure 1). The cumulative production of oil + condensate was about 9 mio. tons and 1.647 mio. Nm³ of associated gas (RAG production until 2015, industrial data). Main oil reservoirs are found in Cenomanian and Eocene horizons, whereas gas is mainly trapped in Oligomiocene rocks (Figure 2). Many studies have been performed to understand the petroleum systems in the basin. Within this context, organic geochemical, biomarker, and stable isotope data have been used to characterize organic matter type and source rock maturity, as well as oil migration and alteration processes (e.g., Schulz et al. (2002) [1–3]). However, all previous geochemical studies were based on the C₁₅₊ hydrocarbon fraction. In contrast, light hydrocarbons (C₁₅₋ fraction) remained uninvestigated, although they are important proxies for facies and maturity of source rocks and migration and alteration processes (e.g., [4]).

The AFB not only is an important hydrocarbon province but also hosts a major geothermal potential (e.g., [5]), which is related to an active aquifer in Upper Jurassic carbonates (“Malmian aquifer” sensu [6]). The general characteristics of the Malmian aquifer such as charge and discharge area and residence time are reasonably well understood (e.g., [7]; Figure 3). In hydrogeological models, the Malmian aquifer is typically considered as separated from aquifers in overlying stratigraphic units [8]. However, Andrews et al. [7], Goldbrunner [9], and Gross et al. [10] suggested hydraulic connections between the Malmian aquifer and oil-bearing rocks. The interaction of water with hydrocarbons may result in the removal of relative water-soluble compounds (e.g., light aromatics: benzene, toluene, ethylbenzenes, and xylenes (BTEX)) from oil. In the petroleum industry, this process is generally called “water washing” (e.g., [11]). Simple numerical models of Lafargue and Thiez [12] showed that the removal of BTEX is limited by water velocity, if the water flow beneath the oil-water-contact is below 10 cm/year, and by rate of diffusion, if the water flow is higher. Meteoric water can also

FIGURE 1: ((a) and (b)) Map of Europe with location of the study area in the Alpine Foreland Basin. (c) Distribution of oil fields together with the location of investigated samples. The B-B' cross section is presented in Figure 8.

introduce microbial communities into an oil reservoir and provide oxygen or electron acceptors and inorganic nutrients necessary for microbial activity (e.g., [13, 14]). Therefore, under suitable geological conditions, both processes are concomitant.

Hence, the main aim of this study is to reveal any effect of waters from the Malmian aquifer on the composition of oil in Cretaceous and Eocene reservoirs. In addition, information on the regional and stratigraphic distribution of water washing can help to refine and constrain the hydrogeological model.

To increase the regional coverage of the sample set, selected chemistry/isotope data of water from industry and Andrews et al. [7] are included in the present study. The comparison of these old data (often determined at the

beginning of oil production) and data obtained after years of oil production may also reveal any influence of hydrocarbon production on water composition.

2. Geological Background

The asymmetric Alpine Foreland Basin (AFB) stretches along the northern margin of the Alps and dips below the Alpine nappes (Figure 1(b)). In the Upper Austrian sector of the Alpine Foreland Basin, the sedimentary succession overlies crystalline basement of the Bohemian Massif and comprises the following from bottom to top: Permo-Carboniferous graben sediments, Jurassic and Upper Cretaceous mixed carbonate-siliciclastic shelf sediments, and Eocene to Upper Miocene Molasse sediments (Figure 2).

FIGURE 2: Time stratigraphic table of the Austrian part of the Alpine Foreland Basin; source rock and oil and gas occurrences are indicated (after [15–17]).

FIGURE 3: Thickness map of the Malmian horizon. Simplified thermal water system, regional water flow (modified from [8]), and location of oil fields are indicated. Inset presents location of map. Faults have been omitted to clarify the look of the map. The A-A' cross section is presented in Figure 4.

Autochthonous Jurassic and Cretaceous sediments form the basin floor. The Upper Jurassic carbonate group (Figure 2), comprising limestones and dolostones, is up to 500 m thick (Figure 3). These fractured and karstified carbonates are the most important deep aquifer for thermal water (Malmian aquifer) but are absent in the northern and eastern part of the study area due to erosion [5]. Because Malmian connate brines have been replaced by meteoric water (average total mineralization is 2.2 g/l [9]), the Malmian water differs hydrochemically and isotopically from waters in overlying horizons. High salinity water in Malmian rocks is found only in the southern part of the basin, indicating stagnant conditions in this area ([7], Figure 3). Recharge and discharge of the Malmian aquifer take place mainly at the basin edges, often through permeable Cenozoic sediments or fractured basement rocks [8, 27].

Main oil and associated gas reservoir rocks are Cenomanian and Eocene shallow marine sandstones (Figure 2).

Minor hydrocarbon deposits are also found in Jurassic clastic rocks and Upper Eocene algal limestones (Lithothamnium limestone). The main source rocks for thermogenic hydrocarbons are deep marine Lower Oligocene pelitic rocks (Schöneck Fm. and Eggerding Fm. [1, 28]), which became mature beneath the Alpine nappes in Miocene time [29]. The lateral migration distance of oil in the Austrian part of the Alpine Foreland Basin varies from less than 20 to more than 50 km [2, 3]. Hydrocarbon migration commenced simultaneously with hydrocarbon generation and continued until the present day [29]. The hydrocarbon habitat is strongly influenced by Neogene uplift and erosion [30]. Neogene tilting of the basin changed migration pathways and oil-water-contacts ([30, 31]; Linzer, pers. comm.). Heavily biodegraded oils occur along the northern margin of the basin in shallow marine Oligocene sands (Figure 1).

Gratzer et al. [2] recognized two oil families. The western oil family (west of S field) contains more sulfur than

FIGURE 4: Regional cross section from the recharge area in Lower Bavaria to the discharge area west of Linz (Upper Austria) (modified from [6]). Position of cross section is indicated in Figure 3 by a dashed line. Area marked by red rectangle is displayed in Figure 8.

the eastern family (east of S field). Dibenzothiophene/phenanthrene (DBT/Ph) ratios are higher in the western oil family, indicating enhanced availability of reduced sulfur for incorporation into organic matter [32]. These variations reflect differences in the source rock facies beneath the Alpine nappes (see [28]).

Dry gas, traditionally interpreted as microbial in origin (e.g., [33, 34]), prevails in clastic deep water sediments with an Oligocene (Lower Puchkirchen Fm.) or Miocene age (Upper Puchkirchen Fm., Hall Fm. [35–37]).

3. Samples and Methods

38 oil and 15 water samples were collected from producing wells operated by Rohöl-Aufsuchungs AG (RAG, Vienna, Austria) in 2013–2015. The sample code represents the field name by a capital letter. If several wells from a single field have been sampled, these are labelled by numbers; for example, samples D1 to D4 are taken from different wells in the D field (see Figure 1(c)). Special precautions were taken during sampling and laboratory handling to avoid any possible losses of volatile hydrocarbons. Glass bottles were filled with reservoir fluids (oil and water), immediately crimped, and stored at 4°C. In the lab, water and oil were separated and stored in crimped bottles at 4°C for further investigations. In addition, oil and water samples from archives were also investigated.

Fresh and archival water samples (19 in total) were measured by ion chromatography. The samples were filtered through a 0.2 µm nylon filter prior to analysis. The filtrate was diluted and analyzed for cations and anions using two different sets of ion chromatography equipment. The anions were determined on a Dionex DX-3000 system with external suppression. For standard runs, a 25 µl sample loop was used.

The cations were analyzed using a Dionex DX-120 system with electrochemical micromembrane suppression and a 25 µl sample loop. Standards were made from commercially available reference material (Merck, Certipur®). The samples were diluted with Milli-Q® 1:100 before analysis. For all steps in the analytical procedure, Milli-Q water was used, the analyzed components in the blank were always below detection limit. The detection limits [ppb] were established as follows: Li, 0.1; Na, 5; K, 5; Ca, 10; Mg, 10; Cl, 100; Br, 5; F, 5; J, 0.1; and SO₄, 10.

The oxygen isotopic composition ($\delta^{18}\text{O}$) of the water samples was measured by the CO₂–H₂O equilibrium technique [38] with a fully automated device adapted from Horita et al. [39] coupled to a Finnigan DELTAplus mass spectrometer. Horita et al. [39] designed an automated operating procedure to analyze hydrogen and oxygen isotope ratios of the same water samples without sample change. However, in this operating procedure, the equilibrium unit with the sample vials was shaken laterally at a few Hz for 4 h to enhance the isotopic exchange reaction. In the EQ-device used in this study, the water sample is stirred individually in each vial. This leads to a higher precision of the isotope measurements. The temperature of the water bath was 24°C ± 0.1°C during water–CO₂ equilibration. Measurement reproducibility of duplicates was better than ±0.05‰ for $\delta^{18}\text{O}$. Deuterium ($\delta^2\text{H}$) was measured with a Finnigan DELTAplus XP continuous flow stable isotope ratio mass spectrometer by chromium reduction using a ceramic reactor slightly modified from Morrison et al. [40]. The analytical precision of the $\delta^2\text{H}$ measurements was better than 1.5‰. Normalization of the raw results versus the V-SMOW-SLAP scale was achieved by using a four-point calibration of in-house water standards that have been calibrated against

the international reference materials V-SMOW, GISP, and VSLAP. No further corrections were applied. Stable hydrogen and oxygen isotopes of water are expressed against V-SMOW.

Oils were separated from water and treated to remove asphaltenes: 50 mg of oil was diluted in *n*-pentane and the insoluble fraction was separated by centrifuging. The pentane-soluble fractions were analyzed using a gas chromatograph (GC) equipped with a J&W DB-1 PONA (50 m length, ID 0.2 mm, 0.5 μ m film thickness) fused silica capillary column. The sample was injected in split mode at 270°C. The GC oven temperature was programmed as follows: 32°C hold for 5 min followed by heating 2.5°C/min to 310°C and hold for 30 min. Helium was used as carrier gas with a constant flow of 1.3 ml/min. A flame ionization detector was operated at 320°C with gas flows of 350 ml/min and 35 ml/min for air and hydrogen, respectively.

4. Results

4.1. Water Samples. Total mineralization (total dissolved solids) of samples measured in the frame of this study varies between 1893.1 mg/l (sample U2; Cenomanian reservoir) and 18103.3 mg/l (sample N6; Eocene reservoir; Table 1). Notably, the average salinity of waters from Eocene reservoir (10559.7 mg/l) is higher than that of Cenomanian waters (2958.5 mg/l). This observation is also supported by data from industry (Eocene: 14164.5 mg/l; Cenomanian: 6222 mg/l) and Andrews et al. ([7]; Eocene: 11738.1 mg/l; Cenomanian: 2333.5 mg/l; Tables 1 and 2). However, unusually low salinity water from Eocene reservoir is found in oil field D (samples D1-2; Tables 1 and 2) in the northeastern part of the study area. The most important dissolved ions are Na^+ and Cl^- . In connate brines, these constituents are mainly derived from dissolved halite.

$\delta^2\text{H}$ [V-SMOW] and $\delta^{18}\text{O}$ [V-SMOW] values of water (measured in the frame of this study) from Eocene reservoir range from -48.3‰ to -12.9‰ and from -7.1‰ to 0.6‰ for hydrogen and oxygen, respectively (Table 1). The isotopic composition of water from Cenomanian reservoir ranges from -51.4‰ to -41.4‰ and from -5.8‰ to -4.8‰ for hydrogen and oxygen, respectively.

4.2. Oil Samples. Oil samples are characterized by abundant *n*-alkanes up to C_{36} . Because detailed information on biomarkers and stable isotopes based on the C_{15+} fractions has already been presented by Gratzer et al. [2] and Bechtel et al. [3], the present paper focuses on light hydrocarbons. The dominant light hydrocarbons are *n*-alkanes, although cycloalkanes and aromatics are also abundant. However, some oils are characterized by progressive depletion or almost entire removal of benzene, toluene, ethylbenzene, and xylenes (BTEX). To illustrate this phenomenon, the methylcyclohexane/toluene (Mch/Tol) and cyclohexane/benzene (Ch/B) ratios have been calculated (Table 1), which vary widely from 1.7 to 98.2 and from 2.3 to 904, respectively.

FIGURE 5: Cross-plot of Na^+ against Cl^- dissolved in the water coproduced with oil. For comparison, data from this study are plotted together with industry and literature data. Deviation of the water from the seawater dilution line is probably caused by reservoir additives.

5. Discussion

5.1. Quality Control of Water Samples. To control the quality of samples with respect to possible influence of any reservoir additives used during oil production, the Na^+ and Cl^- concentrations are cross-plotted in Figure 5. No significant deviation from the sea water dilution line is observed, suggesting no influence from reservoir additives. Nevertheless, chlorine, which is considered as a conservative constituent, is used in further interpretation.

Lécuyer et al. [41] emphasized that the isotope fractionation factor between CO_2 and H_2O is salinity-dependent and that increasing salt contents (KCl or NaCl) results in an increasing overestimation of oxygen isotope ratios. Because water samples investigated in the frame of this study are characterized by varying salinities, the potential effect on the study results has to be reviewed. The most saline water sample is sample N6 (18103.3 mg/l; Table 1), resulting in an overestimation of $\delta^{18}\text{O}$ by less than 0.1‰ , which is rather small but significant relative to analytical uncertainties. However, the quantification of the mixing between end-member waters from Malmian aquifer and Cenomanian/Eocene reservoirs performed by using $^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$ as natural traces will be negligently affected by lack of salinity-dependent corrections. In addition, it is unknown if the published isotopic compositions of samples were corrected. Therefore, the correction is not applied for the samples measured in the frame of this study.

5.2. Possible Processes Influencing the Light Hydrocarbon Fraction. The methylcyclohexane/toluene (Mch/Tol) and cyclohexane/benzene (Ch/B) ratios are cross-plotted in Figure 6

TABLE 1: Sample list with selected reservoir conditions, chemistry, and isotopic composition of reservoir water.

Sample code		Sample type	Res. age	Depth ^a [m]	Res. temp. [°C]	°API	Mch/Tol	Ch/B	Cl5−/ Cl5 ⁺ ^b	Li ⁺	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	F [−]	Cl [−]	Br [−]	I [−]	NO ₃ [−]	SO ₄ ^{2−}	Water [V-SMOW] ^c δ ² H δ ¹⁸ O	
A	OA	EO				31.8	85.7	257.1	2.6													
B1	OA	EO					19.1	72.1	4.2													
B2	OA	EO					23.3	174.2	3.3													
B3	OA	EO					15.5	98.4	3.5													
C	O, W	EO		1151		36.1	10.2	28.2	4.3	0.2	1965	12	12	44	8.5	2910	22.2	5.2	0	11		
D1	OA	EO		1059			83.7	904.0	2.7													
D2	O, W	EO		1142	55	32.6	79.9	517.3	3.3	0.2	1335	7	7	36	10.0	1945	13.1	2.2	1	5		
D3	OA	EO					98.2	40.1	2.2													
D4	O, W	EO		1048	48	32.6	82.7	209.7	2.8	0.6	1626	12	9	25	9.0	2104	15.2	3.7	0	1		−7.1
E1	OA	EO					4.5	6.3	3.6													
E2	O	EO		1869	65	33.1	3.3	3.8	3.4													
F1	O	EO + Ce		2030		34.8	3.3	4.2	4.2													
F2	O	Ce		2381		33.1	3.8	5.2	4.0													
G1	OA	Ce					5.1	8.9	3.5													
G2	OA	EO					2.4	2.6	4.0													
H	OA	EO					3.3	3.3	3.3													
I1	O, W	EO		2463	86	32.1	2.4	3.2	3.4	3.2	4357	47	25	215	2.7	6862	59.8	9.9	3	45	−24.6	−0.6
I2	O	EO		2465	86	32.1	2.8	3.6	4.2													
J1	O	EO		2058	68	35.3	1.7	3.0	3.8	1.3	6337	51	38	472	6.1	9498	102.4	24.3	0	75		
J2	O	EO		2118	80	37.1	1.8	2.3	0.5													
J3	WA	EO								1.2	4002	58	24	194	2.1	6562	50.4	9.3	1	1	−39.6	−4.3
J4	WA	EO								0.9	4073	53	20	168	2.3	6769	38.2	7.1	1	22	−39.5	−2.7
J5	O	EO		2067	79	35.3	1.9	3.0	3.9													
J6	O	EO		2106	69	35.8	1.9	2.4	4.0													
J7	WA	EO								1.2	5028	74	29	365	2.8	8804	43.0	7.6	1	128	−29.1	−3.45
K	O	Ce		2341	71	33.2	6.8	6.4	3.4													
L1	OA	EO					2.8	4.1	3.5													
L2	O, W	EO		2059	69	36.6	2.0	2.7	4.9												−23.1	−1.3
L3	O, W	EO		2038	69	36.6	2.2	2.7	5.2												−12.9	0.6
M	OA	EO					3.0	6.4	3.1													
N1	O	EO		1700	62	36.4	2.1	3.6	3.2													
N2	O	EO		1754	62	36.4	2.6	3.4	4.7													
N3	O	EO		1752	62	36.4	2.7	3.5	4.8													
N4	O, W	EO		1683	62	36.4	2.4	3.3	5.6	2.4	5926	45	53	212	1.5	9299	74.6	18.2	2		−30.6	−2.2
N5	O	EO		1694	62	36.4	2.3	3.7	3.6													
N6	O, W	EO		1761	62	36.4	2.4	3.3	4.9	3.0	6758	47	84	338	2.1	10748	96.5	24.7	1	2	−23.0	−0.4
O	O	EO		1620	60	37.8	3.0	4.4	5.3													
P	O	EO		1706	58	37.2	2.5	5.2	8.1													
Q	OA	Ce				34.4	5.8	9.4	3.8													

TABLE I: Continued.

Sample code	Sample type	Res. age	Depth ^a [m]	Res. temp. [°C]	°API	Mch/Tol	Ch/B	Cl5+ ^b	Li ⁺	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	F ⁻	Cl ⁻	Br ⁻	J ⁻	NO ₃ ⁻	SO ₄ ²⁻	Water [V-SMOW] δ ² H	Water [V-SMOW] δ ¹⁸ O
R	OA	EO			33.4	3.8	6.0	3.0													
S1	OA	EO				6.5	15.7	3.0													
S2	O	Ce	2754	90	31.7	6.4	4.4	2.6													
S3	O	EO	2230	85	31.9	9.6	7.7	3.4													
T	O	EO				8.3	11.4	4.5													
U1	OA	Ce				59.3	130.2	1.6													
U2	O, W	Ce	1611	62	30.2	45.9	30.2	2.1	0.2	929	19	5	17	8.4	888	4.7	1.2	1	19	-51.4	-5.8
U3	O, W	Ce	1577	57	30.2	56.5	38.9	2.4												-41.4	-4.8
U4	O, W	Ce	1574	57	30.2	43.1	30.6	2.2	0.5	1990	30	5	24	0.6	1821	5.0	1.7	116	30		
V	OA	Ce				50.4	88.8	1.9													
W	O	EO	2780	87	34.7	1.7	2.7	3.0													
X	O	EO	3342	110	31.4	2.2	2.9	3.3													
Y	O, W	EO	2240	85	32.8	3.5	4.4	2.7	1.7	4994	41	30	70	1.8	7557	51.2	6.5		159		
Z	OA	EO			33	4.6	15.1	4.1													
AA1	O, W	EO	1819	70	35.5	3.3	9.8	3.4	2.0	2681	40	18	49	4.1	3433	26.1	6.8	3	192	-36.5	-2.5
AA2	O, W	EO	1810	73	35.6	2.8	4.9	3.1												-48.3	-4.2
AA3	O, W	EO	1855	71	35.3	3.3	10.3	4.1	2.0	3117	33	12	20	4.7	4155	31.8	9.1	18	76		
AA4	OA	Ce				6.1	18.5	2.6													
AB	O, W	EO	1408	63	35.5	4.5	15.0	3.0	1.1	4143	83	55	139	2.0	5823	54.0	15.1	1	3		
AC	O	EO	2197	85	34.5	3.1	9.3	4.3													
AD	O	EO	2503	86	33.5	2.0	4.9	4.1													

^aTrue vertical depth subsurface. ^bRatio calculated based on all peaks above chromatographic baseline. O, oil; OA, oil archival; W, water; WA, water archival; Res. age, reservoir age; Ce, Cenomanian; EO, Eocene; Res. temp., reservoir temperature; Mch, methylcyclohexane; Tol, toluene; Ch, cyclohexane; B, benzene.

TABLE 2: Sample list with chemistry and isotopic composition of reservoir water (industry and literature data).

Sample code	Water chemistry, industrial data [mg/l]					Water chemistry, Andrews et al. (1987) [mg/l]					Water, Andrews et al. (1987) [V-SMOW]							
	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	NH ₄ ⁺	Cl ⁻	HCO ₃ ⁻	SO ₄ ²⁻	SiO ₂	δ ² H	δ ¹⁸ O
C	2660	23	10	67	3673	29	669											
D1	1160	11	3	18	2011	13	436	1130	11	3	16	4	1570	421	5		-57.0	-6.5
D2	1310*	12*	4*	24*	1836.3*	10.7*	479*											
G1	6020	186	20	237	9490	397	668											
I1	4600	186	18	295	6730	18	735											
J1	4790*	75*	31*	383*	7867*	101*	429*											
J2	2400	2100	22	309	6027			3920	68	28	220	9	6494	729	55		-42.0	-4.4
J3																		
J5	4656*	2958*	32*	342*	8456*	102*	521*											
J6	6300			369	9329													
K	3562	70	30	271	5388	424	249											
L3	5450	63	31	242	7764	235	408											
M	4950	54	51	390	7473	153	359											
N1	5211*	3874*	63*	720*	11234*	97*	533*											
N2	7700	66	113	449	12840	9	201											
N3-4	5211*	3874*	63*	720*	11234*	97*	533*											
N5	4675	42	34	140	6576	140	647											
N6	7300	73	45	432	11585	53	273											
P	5622*	76*	62*	325*	8216*	47*	626*	3360	27	20	68	13	4680	1404	110	35	-30.0	-1.6
R	12669	102	112	922	20551	117	414											
S1	11117	71	115	731	18124	18	502											
U1-4	1081*	394*	3*	21*	1499*	249*	800*	690*	15*	2*	8*	23*	462*	1042*	93*		-63.0*	-8.3*
W	3606*	59*	23*	141*	4747*	535*	1142*	2160	62	20	150	11	2720	1019	678	60	-38.0	-2.0
Y	6764	67	45	347	10581	111	440	6548	187	41	209	95	10578	954	55		-21.0	0.2
AA1	6200	86	71	469	9182	132	448											
AA3	6800	96	73	481	9731	79	494											
AA4	2870	55	19	110	3390	324	1260											
AA1-4								5744*	93*	67*	320*	123*	9260*	1444*	102*		-20.5*	-1.5*
AB	3938	42	31	154	5362	7	761											
AC	1794*	86*	30*	185*	2204*	574*	641*	1410	33	7	31	6	1600	1086	14	56	-57.0	-6.1
AD	1800*	38*	8*	27*	1872*	17*	119*											

* Average salinity and isotopic data from adjacent wells produced from the same formation.

FIGURE 6: Cross-plot of the methylcyclohexane/toluene (Mch/T) ratio versus the cyclohexane/benzene (Ch/B) ratio. Ratios are calculated from chromatographic peak areas. Solubilities (mg/l at 20°C) of different compounds in water are given in brackets. Because aromatic compounds are more soluble in water, water washing results in an increase in Mch/T and Ch/B ratios. The theoretical evaporation trend, assuming simple mixtures of two compounds, is indicated (vapor pressure at 20°C for Mch: 48.3 hPa, Tol: 29.1 hPa, Ch: 104 hPa, B: 100 hPa after [18]). *Signature for kerogen type after Schaefer et al. [19]. Note that land plant-rich type III kerogen yields hydrocarbons with high contents of aromatic compounds resulting in very low Mch/T and Ch/B ratios. **Dotted line delineates typical Mch/T and Ch/B values from unaltered oils in the Rocky Mountain area [20], Gulf of Mexico (Pleistocene), California (Miocene), Louisiana (Lower Cretaceous [21]), North Slope (Alaska [22]), Mexican Gulf Coast Basin [23], North Central Sinai [24], and SW Barents Sea [25].

to show the significant variations in the relative contents of light hydrocarbon compounds between different oils. The observed differences may originate from natural primary and secondary processes as well as from poor storage of archival samples (e.g., changes due to evaporation losses). Therefore, it is critical to determine the consequences of each process that can generate compositional differences.

5.2.1. Influence of Source Rock Facies. Significant differences are observed in generation of hydrocarbons from marine and terrestrial organic matter. Type III kerogen yields predominantly aromatic hydrocarbons (e.g., benzene and toluene [19]), while type I/II kerogen produces more *n*-, iso-, and cycloalkanes (e.g., [42]). Moreover, Odden et al. [43] showed that increasing contents of terrigenous organic matter in source rocks results in higher concentration of aromatics,

cyclohexane, and methylcyclohexane compared to cyclopentanes and acyclic hydrocarbons. Because the observed trend leads towards higher Mch/Tol and Ch/B ratios, increasing content of coaly facies in source rock can be ruled out (Figure 6).

5.2.2. Evaporative Fractionation. An alternative process that could influence the pattern of light hydrocarbons is called evaporative fractionation (Thompson, 1987) and describes the loss of light hydrocarbons from an oil phase (in reservoir or during migration) resulting from a later gas charge. During this process, the gas phase of a gas-saturated oil escapes from the oil, leaving behind residual oil strongly enriched in toluene and moderately enriched in cycloalkanes. In contrast, *n*-alkanes (e.g., heptane) will be preferentially dissolved in the escaping gas phase (Thompson, 1987). Therefore, evaporative fractionation would result in a trend opposite to the observed one (Figure 6).

5.2.3. Evaporation Losses of Light Fraction during Sample Handling. The current study is based on the quantification of relative volatile hydrocarbons. Therefore, it is critical to discuss the effect of possible losses caused by evaporation during sampling, storage, or laboratory handling. Evaporation of hydrocarbons depends on different factors like group type (linear, branched, cyclic, and aromatic), isomeric structure, molecular weight, and bulk composition of the sample [44]. However, laboratory controlled evaporation of crude oil showed that this process is primarily controlled by differences in boiling points [23]. Consequently, based on differences in vapor pressure of mixtures of two components (Mch/Tol; Ch/B), it is possible to estimate general evaporation trends. Thus, incidental loss of light hydrocarbons will result in a strong decrease of the Mch/Tol ratio and a small increase in the Ch/B ratio (see Figure 6). Hence, evaporation cannot explain the observed strong increase in Mch/Tol and Ch/B ratios, although a minor effect on samples, which have been stored for a long time (archive samples), cannot be ruled out completely.

5.3. Oil-Water Interaction. In the previous section, it could be shown that source rock facies, evaporative fractionation, and losses during sample storage and handling are not responsible for the observed BTEX depletion. In contrast, the trend in Figure 7 is interpreted to reflect the selective removal of relatively soluble aromatics during contact with water. The oil-water interaction can occur during the migration from the source rock to the reservoir and/or after oil accumulation in the reservoir. The longer the migration distance, the higher the potential interaction between oil and water. Interestingly, there is no correlation between migration distance and BTEX depletion. For example, samples A and P experienced similar migration distance (~35 km according to [3]; see Figure 1(c) for sample location), but only sample A is strongly depleted in aromatic hydrocarbons (MCH/Tol + Ch/B = 342.8). In comparison, the sum of MCH/Tol and Ch/B is only 7.7 for sample P. The same is true for the strongly altered U1–4 samples (average MCH/Tol + Ch/B = 108.7) and the less affected AB sample (MCH/Tol + Ch/B = 19.5) which

FIGURE 7: Cross-plots of the sum of two ratios between cycloalkanes and aromatic hydrocarbons versus (a) chlorine (Cl^-) content in reservoir waters, (b) stable hydrogen isotope ratios of reservoir waters, and (c) stable oxygen isotope ratios of reservoir waters. For sample location, see Figure 1(c).

show similar migration distances. Therefore, the observed water washing phenomenon is most probably not controlled migration distance. Hence, water washing probably occurs in the reservoir.

Significant removal of BTEX from bulk oil composition requires a sufficient volume of BTEX-undersaturated water. Considering hydrostatic conditions, it is unlikely that

the concentration gradient between oil and the volume of associated water would be high enough to explain the observed strong BTEX depletion. This suggests that water washing is related to the Malmian aquifer, which is the only main aquifer, which is under dynamic condition and, thus, may provide sufficient undersaturated water that drives diffusion.

FIGURE 8: Simplified cross section of the oil field and location of U1–U4 samples. Well U is used for reinjection of thermal water produced from Malmian (Upper Jurassic) horizon by a well located 3 km west of the section. Well UU is used as reinjector for reservoir brines coproduced with oil. Init. OWC: initial oil-water-contact at the beginning of oil production. Sec. OWC: secondary oil-water-contact estimated after 40 years of production. TVDSS: true vertical depth subsea.

Because water from this aquifer is characterized by low salinity and light isotopic composition [7], water washing parameters are plotted against Cl^- content, $\delta^2\text{H}$ [V-SMOW] and $\delta^{18}\text{O}$ [V-SMOW] values of water coproduced with oil in Figure 7. Indeed, increasing removal of BTEX components correlates with decreasing Cl^- contents and isotope values (Figure 7). This shows that the original connate brines in water washed Cenomanian/Eocene reservoirs have been mixed with fresh water. The relation between water from the Malmian aquifer and water washed oil is especially obvious in the U field, where Cenomanian reservoir rocks directly overlie fresh water bearing Malmian carbonates (Figure 8). The high permeability of the Malmian carbonate, a prerequisite for significant water flow, is proven by losses of drilling mud (industry data) and allows the reinjection of thermal water in well U (Figure 8, [26]).

5.4. Impact of Water Washing on Oil Properties. Water washing can significantly change oil properties. Lafargue and Barker [11] and Kuo [45] have shown that water washing can affect biomarker ratios, like the methyl phenanthrene index (MPI), a classical maturity parameter [46], and the dibenzothiophene/phenanthrene (DBT/Ph) ratio, a parameter that is often used for oil-source and oil-oil correlations [32]. Remarkably, samples from the water washed U field are characterized by the highest MPI value of all samples in the study area and a DBT/Ph ratio, which is lower than that in comparable oils [2]. Therefore, these parameters have to be used with caution for source rock and maturity evaluations for oil samples, suspected to be water washed.

Water washing reduces API gravity because it is particularly effective for C_{15-} hydrocarbons [11]. To test this hypothesis, the ratio of hydrocarbon fractions with less and

more than 15 carbon atoms, respectively ($\text{C}_{15-}/\text{C}_{15+}$), is cross-plotted versus the sum of two ratios between cycloalkanes and aromatic hydrocarbons in Figure 9(a). It shows that decreasing concentrations of aromatic hydrocarbons correlate fairly well with decreasing contents of light hydrocarbons. This indicates that, to some extent, API gravity of oils from AFB is controlled by water washing. To exclude any effect of losses of light hydrocarbons during sampling or handling, the $\text{C}_{15-}/\text{C}_{15+}$ ratio is plotted against industrial API gravity data, obtained during decades of production (Figure 9(b), Table 1).

Water washing is often accompanied by biodegradation. In the present case, water washed samples show no signs of biodegradation in the $n\text{-C}_{7+}$ range. However, Gruner et al. [47] detected metabolites of BTEX in reservoir water from water washed fields. This suggests that water washing facilitates biodegradation by making BTEX bioavailable.

5.5. Implication on the Understanding of Hydrological System. The Malmian hydrological system in the AFB is of great economic relevance, because it supplies a high number of hydrogeothermal installations and thermal spas. Assurance of sustainable use of the water is of prime importance and resulted in the establishment of a numeric, thermal hydraulic model ([8]; Figure 3).

The present study shows that heavily water washed fields occur in Cenomanian reservoirs in fields U and V and in Eocene reservoirs in fields A to D. Strong support for mixing of meteoric water and connate brine in these fields, U and D, is provided by the isotopic composition of water. For a simple quantification of mixing, two end-member waters are defined: (i) water from the Malmian aquifer and (ii) sample L3 from an Eocene reservoir (Table 1 and Figure 10). Based on this assumption, it is concluded that up to 77% of connate

FIGURE 9: Cross-plots of the ratio of the sum of hydrocarbons with less than 15 carbon atoms over the sum of hydrocarbons with more than 15 carbon atoms (C_{15-}/C_{15+}) versus (a) the sum of two ratios between cycloalkanes and aromatic hydrocarbons and (b) API oil gravity. Grey arrow indicates effect of water washing. For sample location, see Figure 1(c).

FIGURE 10: Cross-plots of δ^2H [V-SMOW] versus $\delta^{18}O$ [V-SMOW] values. Average isotopic values of Malmian aquifer are indicated after Andrews et al. [7], Goldbrunner [6], and Elster et al. [26]. For sample location, see Figure 1(c). According to Andrews et al. [7] and Goldbrunner [6], the regression line represents the mixing of connate brines and Malmian water.

Cenomanian/Eocene brine has been replaced by Malmian water in field U. The percentage of meteoric water in field D is about 65%.

As discussed above (Figure 8), water washing in the U (and V) fields agrees with the current hydrogeological model.

However, field D is located east of the pinch-out of Malmian rocks and the Eocene reservoir directly overlies crystalline basement (Figure 3, [48, 49]). Moreover, field D is located outside the boundaries of the regional thermal water system, proposed by the Bayerisches Landesamt für Wasserwirtschaft [8] (Figure 3). Within this context, it is noteworthy that an extensive aquifer is indicated by a strong water drive keeping the reservoir pressure constant, despite of decades of oil production. Therefore, the boundaries of the established flow model need modifications. In contrast to oils from the northern part of study area, oils from the southern part typically show no evidence of water washing (e.g., E, I, J, and T fields; Figure 6). This is in agreement with stagnant conditions in the reservoir and the Malmian aquifer in this area (Figure 3).

6. Conclusions

Light hydrocarbon geochemistry of 57 oil samples from Cenomanian and Eocene reservoirs in the Austrian sector of the Alpine Foreland Basin has been investigated in the frame of this study. Strong depletion of BTEX compounds in some oils implies water washing. Additional observed features of water washing include a decrease in API gravity related to depletion in low molecular saturated components.

Water coproduced with water washed oil shows a progressive reduction in chlorine content (min.: 888 mg/l, measured in the frame of this study) and depletion in 2H and ^{18}O isotopes (-51.4 and -5.8 , resp., measured in the frame of

this study), indicating that connate brines have been partly replaced by meteoric water characteristic of the underlying Malmian carbonates, the main aquifer for geothermal water in the basin.

Most strongly affected oils are located in the shallow northern and northeastern part of the study area (fields A, D, U, and V). The U and V fields produce from Cenomanian reservoirs directly overlying the Malmian aquifer. In these fields, a hydraulic connectivity between the reservoir and the aquifer could be proven. Fields A and D are located east of the extension of the Malmian aquifer and produce from Eocene reservoirs. The Eocene reservoir rocks of field D rest directly on crystalline basement. This suggests that Malmian water is discharged (north-eastwards) through crystalline basement rocks and that previous flow models of the regional geothermal aquifer have to be reevaluated.

In contrast to the shallow northern fields, fields in the deep southern part of the basin (e.g., E-J, L-P, R, W-Z, and AD) are apparently not affected by water washing. The water in these fields shows relatively high salinity.

The results emphasize the importance of combining data from the petroleum and geothermal industry, which are often handled separately: recognition of active water flow may help to predict gravity and viscosity anomalies, biodegradation risk, and the presence of hydrodynamic traps. Additionally, identification of water washing helps to improve flow models of the underlying Malmian aquifer.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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