Groundwater
Monitoring&Remediation

^{222}Rn as Natural Tracer for LNAPL Recovery in a Crude Oil–Contaminated Aquifer

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Abstract

The objective of this study was to investigate whether ^{222}Rn in groundwater can be used as a tracer for light non-aqueous phase liquid (LNAPL) quantification at a field site treated by dual-phase LNAPL removal. After the break of a pipeline, 5 ha of soil in the nature reserve Coussouls de Crau in southern France was contaminated by 5100 m^3 of crude oil. Part of this oil seeped into the underlying gravel aquifer and formed a floating oil body of about 3.9 ha. The remediation consists of plume management by hydraulic groundwater barriers and LNAPL extraction in the source zone. ^{222}Rn measurements were performed in 21 wells in and outside the source zone during 15 months. In uncontaminated groundwater, the radon activity was relatively constant and remained always >11 Bq/L. The variability of radon activity measurements in wells affected by the pump-and-skim system was consistent with the measurements in wells that were not impacted by the system. The mean activities in wells in the source zone were, in general, significantly lower than in wells upgradient of the source zone, owing to partitioning of ^{222}Rn into the oil phase. The lowest activities were found in zones with high non-aqueous phase liquid (NAPL) recovery. LNAPL saturations around each recovery well were furthermore calculated during a period of high groundwater level, using a laboratory-determined crude oil-water partitioning coefficient of 38.5 ± 2.9. This yielded an estimated volume of residual crude oil of 309 ± 93 m^3 below the capillary fringe. We find that ^{222}Rn is a useful and cheap groundwater tracer for finding zones of good LNAPL recovery in an aquifer treated by dual-phase LNAPL removal, but that quantification of NAPL saturation using Rn is highly uncertain.

Introduction

Light non-aqueous phase liquids (LNAPLs) such as crude oil or the products derived from it form long-lasting sources of groundwater pollution in many aquifers worldwide. Remediation of source zones usually involves the extraction of LNAPLs from the groundwater surface by dual-phase extraction or skimming. The removal efficiency depends on LNAPL characteristics (viscosity, density, and interfacial tension) and on aquifer characteristics (porosity, hydraulic conductivity, hydraulic gradient, capillary rise, and the position of water table). These aquifer characteristics are not easily measurable and are often spatially variable. Furthermore, LNAPL recovery depends on the LNAPL saturation in the pore space. Estimation of free LNAPL volumes is carried out traditionally by measurement of oil heights in wells (Lenhard and Parker 1990; API 2001).This requires temporary cessation of LNAPL recovery facilities, and it may not always reflect saturation in surrounding aquifer matrix. For the evaluation of LNAPL removal efficiency, baildown tests have been proposed (Huntley 2000). However, the data evaluation is not straightforward (Batu 2012), and at crude oil spill sites, the time for observing fluid level restoration in wells can be long. In summary, present theory and models for the prediction of LNAPL extraction efficiency from porous media are available (API 2007a, 2007b), but need a number of input parameters which are difficult to obtain. Therefore, at real sites LNAPL is often extracted without knowing the efficiency and the time frame of future operation.

^{222}Rn has been introduced as a natural tracer for the quantification of LNAPL saturation in porous media (Hunkeler et al. 1997). After an adequate period of time, the activity in groundwater of this gaseous radionuclide reaches equilibrium with its production from ^{226}Ra in the dissolved phase and within minerals. If residual non-aqueous phase liquid (NAPL) is present, the ^{222}Rn activity will be lower because of its higher affinity for NAPL (Hunkeler et al. 1997; Semprini et al. 2000; Schubert et al. 2007b). Laboratory batch experiments with diesel-fuel contaminated sand quantified this relationship between radon activity and NAPL saturation, and experiments in columns as well as modeling showed that 6 to 12 d of groundwater residence time in contact with NAPL is required for the establishment of equilibrium partitioning (Hunkeler et al. 1997). Several applications of this tracer technique at real LNAPL-contaminated sites were reported. Hunkeler et al. (1997) established a link between the presence of floating diesel fuel and radon activity in groundwater in an aquifer in Switzerland undergoing in situ bioremediation. Fan et al. (2007) showed in a Taiwanese aquifer that the ^{222}Rn activity of 7.4 Bq/L measured upgradient in groundwater decreased to 2.3 Bq/L in a zone contaminated by gasoline as LNAPL. The authors found a reasonable agreement of the local radon decrease in comparison with independent local LNAPL quantifications by coring and chemical analysis.

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Garcia-Gonzalez et al. (2008) showed that ^{222}Rn activity in groundwater was negatively correlated with LNAPL thickness on a site with mixed gasoline/diesel-fuel contamination in Spain. Schubert et al. (2007b) aimed at localizing gasoline LNAPL below a service station in Germany by correlating dissolved volatile organic compounds (VOCs) to radon measurements in groundwater. They found a good inverse correlation between radon activities and dissolved VOCs, and ^{222}Rn was thus recommended for NAPL mapping. Also, radon measurements in soil gas were recommended for mapping of LNAPLs (Schubert et al. 2002) and even dense nonaqueous phase liquids (DNAPLs) (Yoon et al. 2013; Yang et al. 2014). However, in most of these field studies, the aquifers were at natural gradient flow conditions, and no LNAPL recovery operation was active. To the best of our knowledge, no studies have investigated large contaminated sites as a whole and with an operating LNAPL recovery system.

The objective of this study was to investigate the use of ^{222}Rn as a tracer for LNAPL quantification at a field site where a dual-phase LNAPL recovery system is active. The following specific questions were addressed: (1) Can ^{222}Rn be reliably measured in wells with continuous water extraction combined with LNAPL removal? (2) Is there a relationship between ^{222}Rn activity and LNAPL recovery efficiency? and (3) Can ^{222}Rn measurements give an accurate areal-integrated prediction of residual LNAPL?

Field Site, Sampling, and Analytical Methods

Field Site

The site is in a nature reserve of restricted access at 16 m above sea level in the "La Crau" alluvial plain formed by the former river Durance (Figure 1) during the Pleistocene (Naudet et al. 2004). Locally, these deposits are about 15 m thick (Blondel et al. 2014) and consist of coarse gravel of various alpine rocks, with fine gravel and sand in the interstices, overlaying silt or sandy-silt deposits of low permeability. The coarse gravels are cemented in the upper portion by calcareous concretions formed by evaporation, in the form of a Puddingstone with fractures. The deeper parts of the gravel deposits are free from concretions (hydraulic conductivities of 0.5 to 1 × 10^{-3} m/s) and form the most important regional aquifer. The ground water table is 8 to 11 m below surface and shows important seasonal variations of up to 3 m caused by local rainfall and irrigation upgradient. On August 7, 2009, a pipeline transporting crude oil buried at 1 m depth broke suddenly, and about 5100 m^3 of oil under pressure was projected to the surface where it spread across 5 ha. The crude oil then infiltrated the Puddingstone through fractures and formed a floating oil body which covered in fall 2010 about 3.9 ha.

Remediation

The first remedial actions on this site consisted in excavation and off-site disposal of oil-soaked surface soils. Nineteen monitoring wells were installed within 2 months (Figure 1), and the site was characterized in detail by hydrogeological and geophysical methods (Blondel et al. 2014). After the arrival of LNAPL in 3 monitoring wells and after a dissolved plume was observed, 17 new wells devoted to hydraulic plume management and 30 more wells for tentative LNAPL recovery or monitoring were installed (Figure 1). Recovery wells were equipped with an electric submersed pump positioned

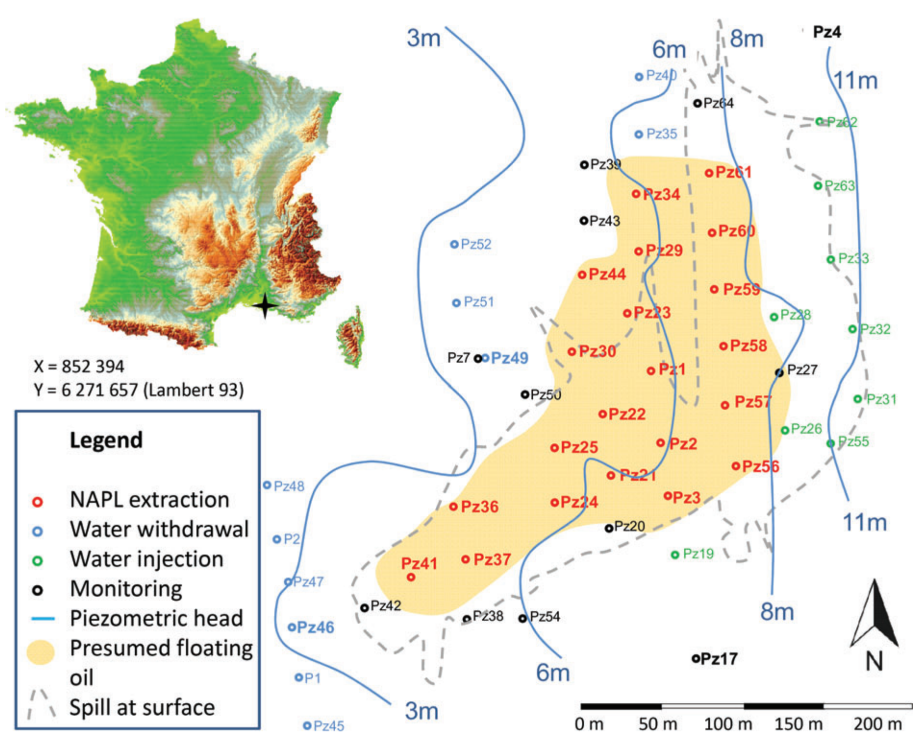

Figure 1. Site map showing the piezometric surface as observed on April 2, 2013 under the influence of pumping and oil recovery. Blue wells belong to the hydraulic barrier and green wells to the injection line upgradient. For wells with floating oil, the water level was corrected using an oil density of 0.86 kg/L.

deep below water table and delivering continuously 0.5 to 2 m^3/h of groundwater, and a pneumatic pump just below the water table filled gravitationally by LNAPL, which was delivered by pressurized air to a recovery tank. Recovery started in January 2010 in three wells and was extended progressively as a function of LNAPL arrival in other wells. At the end of this study, LNAPL recovery was operated in 22 wells producing a total of about 22 m^3 of water per hour. This water, together with water pumped downgradient of the site in wells of the hydraulic barrier (20 to 25 m^3/h), was treated by an activated charcoal filter and reinjected upgradient in seven wells (Figure 1). A total of 32 m^3 of LNAPL were recovered from the aquifer within 4 years. The total volume of oil present in 2014 is unknown; however, the footprint of the floating LNAPL lens had stabilized.

Sampling

In monitoring wells without floating LNAPL and not equipped for LNAPL removal, groundwater samples were obtained using a submersible electric pump (Twister, SDEC, Reignac-sur-Indre, France) and a polyethylene tube. Care was taken that these pumps never were in contact with oil. At least two well volumes were pumped at rates of 4 to 6 L/min, recording continuously electric conductivity, temperature, pH, and oxygen (probes from WTW, Weilheim, Germany). Samples were taken only after stabilization of these parameters. For ^{222}Rn analysis, 250 mL flasks were gently filled at flow rates <1 L/min, including an ample period for overflow, and were capped thereafter without permitting air bubbles. In recovery wells, water samples were obtained at each well from a tap on the PVC tubing used for pumping groundwater to the treatment facility. Likewise, the flasks were filled gently with low flow rates by submersed tubing and capped without air bubbles.

In order to study the temporal variation of ^{222}Rn activities in this aquifer, wells were studied from November 2012 to February 2014. However, within the LNAPL source zone, two distinct periods were chosen: in 2012 + 13 (low water level), and in February 2014 (high water level).

Measurement of LNAPL-Water Partitioning Coefficient

Crude oil was sampled in April 2013 on the site from the recovery storage tank and stored for 1 month in order that all ^{222}Rn decayed. Six glass bottles with calibrated volumes of about 1.1 L were filled with uncontaminated groundwater from well Pz4 without headspace. In the laboratory, three of the bottles were opened, equipped with a stirring bar, and 30 mL of water were replaced by crude oil. The bottles were capped and stirred gently for 24 h, and thereafter 250 mL of water were transferred to radon flasks via stainless steel tubing. The partitioning coefficient K between LNAPL and water was calculated from the average reference ^{222}Rn activity in three bottles without NAPL (A_{ref}), the activity in the LNAPL-amended bottles (A_{NAPL}) and the volumes of LNAPL (V_{NAPL}) and water (V_{w}) using:

$$K_{\mathrm{NAPL\text{-}w}} = \frac{\left(A_{\mathrm{ref}} - A_{\mathrm{NAPL}}\right)}{A_{\mathrm{NAPL}}} \frac{V_{\mathrm{w}}}{V_{\mathrm{NAPL}}} \quad (1)$$

^{222}Rn Analysis and Statistical Tests

The 250 mL flasks were transported to the laboratory and analyzed within 3 to 36 h using a RAD-H_2O system connected to an air radon detector (RAD7-Durridge, Co. Inc., Billerica, Massachusetts). The protocol involved four periods of 5 min each for counting. Results were corrected for humidity using *Capture* software (Durridge) and for decay after sampling. To check the reliability of repeated sampling, Levene's tests were calculated using SPSS 14.1 for Windows (IBM, Dublin, Ireland)

Results

Field Results—Wells Without LNAPL

The temporal evolution of the piezometric heads of two selected uncontaminated and unpumped wells from upgradient and two pumping wells >50 m downgradient the floating oil phase is shown in Figure 2A. Piezometric heads followed the same trend in all four wells although wider variations are noticeable in the pumped wells. Following the spill, the groundwater table rose by more than 2 m and reached a historic maximum in January 2010. At that time, the first arrival of crude oil occurred in some monitoring

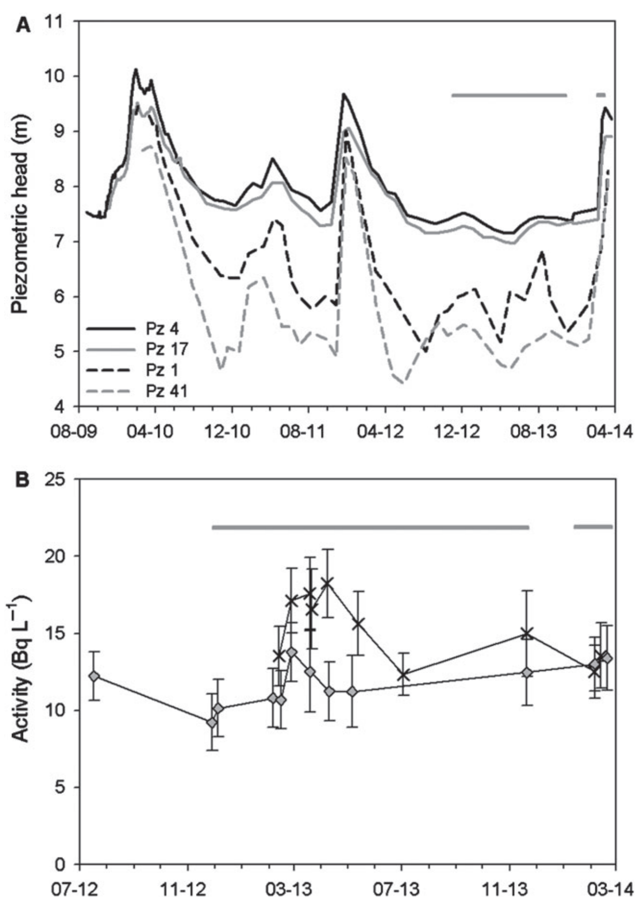

Figure 2. (A) Temporal evolution of piezometric level in two unpumped wells (Pz4 and Pz17) and two pumped wells (Pz1 and Pz41), and (B) temporal evolution of ^{222}Rn activity in Pz4 (black crosses) and Pz17 (gray diamonds). The gray bars represent the two periods of radon monitoring. Pz1 and Pz41 were drilled and equipped for pumping and skimming in January 2010.

Table 1

Summary of Field Measurements in Background Groundwater Samples, Period December 2012 to February 2014

Well	Number of Samples	Temp. Mean (°C)	Conductivity Mean (µS/cm)	O2 Saturation Mean (%)	pH Mean (—)	Radon Activity Mean (Bq/L)	Standard Deviation (Bq/L)
Pz17	12	17.4	607	80	7.3	11.7	0.6
Pz4	10	17	564	97.7	7.4	15.2	0.8
Pz46	4	18.5	623	45.9	7.1	12.6	0.8
Pz49	4	17.8	522	44.2	7.3	15.4	0.9

wells, and oil recovery was progressively developed. The groundwater table decreased during each summer to about pre-spill level, and increased during each winter, but was variable: whereas the groundwater table almost reached its maximum measured in 2010 during the winter 2011 to 2012, the rise was very limited during the following winter, when most of the radon measurements were made (periods of sampling displayed in Figure 2A). In early 2014, the water level rose again to near the historic maximum of January 2010, which gave the opportunity to measure ^{222}Rn at high water levels.

The ^{222}Rn activities in two selected uncontaminated wells from upgradient of the source zone are shown in Figure 2B. Both activities show little seasonal variation. The mean activity in Pz4 was 15.2 Bq/L, about 3 Bq/L higher than the mean activity in Pz17 (Table 1). Oxygen saturation in Pz4 was >97%, whereas in Pz17 it was only 80%. Samples were also taken from two pumping wells from the hydraulic barrier downgradient, Pz46 and Pz49 (Table 1, location in Figure 1). The mean activity in Pz46 was 12.6 Bq/L and 15.4 Bq/L in Pz49. These wells were at about equal distance downgradient from the floating LNAPL and had intermediate oxygen saturation.

Field Results—Wells with LNAPL

The ^{222}Rn activities in 21 NAPL-contaminated wells in the source zone were monitored during a long period of stable and low water level in 2013 (first period), and by some measurements in February 2014 (second period) after the water level rose (Table 2). Each well was sampled at least three times during the first period. During the second period one sample was taken for each well except for three wells for which two samples were analyzed 1 week apart (Table 2). Temperature and electrical conductivity were recorded and in case of strong anomalies, single ^{222}Rn activities were discarded. During the first period ^{222}Rn activities ranged from 1.2 Bq/L ± 0.4 to 16.1 Bq/L ± 1.6. During the second period activities ranged from 0.5 Bq/L ± 0.2 to 14.2 Bq/L ± 2.6 (Table 2).

The mean ^{222}Rn activities showed an interesting relation with the mean oxygen saturation in groundwater (Figure 3). All wells with ^{222}Rn activites <6.5 Bq/L had hypoxic to anoxic conditions, with oxygen saturation <7% (Figure 3). In wells with ^{222}Rn activities higher than 6.5 Bq/L, no relationship was noted and O_2 saturation was comprised between 0.1% and 98%.

Both ^{222}Rn activities and O_2 saturation were poorly correlated with the maximum oil heights measured in wells during the first period (Figure S2A and S2B, Supporting Information).

Discussion

Reliability of ^{222}Rn Measurements

Radon measurements within the source zone were made on samples taken from the wells continuously pumped with high rates, without disruption of LNAPL removal, whereas samples from wells upgradient from the source zone were taken after purging two well volumes with a pump with lower flow rate. Statistical tests were performed to assess whether pumping or oil skimming affects the variability of ^{222}Rn activity. The Levene's test was chosen to test variances in data from pumped and skimmed wells against variances in unpumped and uncontaminated wells. Several combinations were tested: unpumped wells (Pz4 and Pz17) vs. pumped but non-skimmed wells (Pz46 and Pz49; test 1), pumped but non-skimmed wells vs. pumped and skimmed wells (data from Pz1/3/37/58, test 2), and finally unpumped wells vs. pumped and skimmed wells (same series as before, test 3). All Levene's tests showed that variances of data series tested were not significantly different (p-values for test 1: 0.438; test 2: 0.939 and test 3: 0.268 for $\alpha = 1\%$). Oil recovery does not seem to introduce greater variability in measured ^{222}Rn activities; however, this observation is subject to low number of data in each series tested (<20).

Measures of ^{226}Ra (parent nuclide of ^{222}Rn) in the aquifer solids were not possible due to the nature of their matrix (puddingstone) and regulations that forbid any new drilling. Given the scale of investigated zone, radium concentration in the matrix is likely not homogeneous but any intrinsic heterogeneity in radon emission was hidden by the depletion induced by the presence of LNAPL. Wells surrounding the source zone showed relatively close and constant ^{222}Rn activity with time regardless of water level (Table 1 and Figure 2B).

Spatial and Temporal Variations of ^{222}Rn

Let us recall again the conceptual model for the distribution of ^{222}Rn in a NAPL-contaminated aquifer developed by Hunkeler et al. (1997), which was experimentally confirmed in laboratory columns: upgradient of NAPL, water with a residence time of >3 half-lives of ^{222}Rn (>12 d) approaches closely steady-state equilibrium activity. Knowledge of this background activity will be used for NAPL quantification in Equation 2. When this water flows into a zone with residual NAPL, a new equilibrium is reached within 6 to 12 d,

Table 2

Summary of Field Measurements in Groundwater Samples

Well	Number of Samples	Temp. Mean (°C)	Conductivity Mean (µS/cm)	O_2 saturation Mean (%)	pH Mean (—)	Radon Activity Mean (Bq/L)	Standard Deviation (Bq/L)	LNAPL Saturation (%)		Maximum Oil Height[1] (cm)	Oil Volume Based on ^{222}Rn L/m²
Pz1	5	19.0	541	25.5	7.3	12.2	1.1	0.8	±0.4	52	0.5
	2	19.0	703	0.4	6.9	4.2	1.2	5.7	±4.1	28	8
Pz2	6	19.8	603	11.6	7.1	11.9	0.9	0.9	±0.4	6	0.5
	1	20.2	703	1.3	6.8	6.3	1.5	2.8	±2.1	5	7.2
Pz3	3	18.7	617	14.9	7.2	13.6	1.4	0.4	±0.4	1	0.4
Pz21	4	19.2	598	7.5	7.2	10.7	1.1	1.3	±0.6	2	2.1
	2	21.8	665	0.3	6.8	2.3	0.9	12.2	±11.4	1	40
Pz22	3	19.2	580	2.3	7.3	3.8	0.8	8.4	±3.7	7	8.3
	1	18.4	694	2.5	6.8	4.2	1.3	5.5	±4.2	12	16.4
Pz23	5	20.4	566	2	7.4	3.0	0.5	11.3	±3.9	24	0.8
Pz24	3	17.0	606	2.1	7.4	6.1	1.0	4.2	±1.9	1	6.0
	1	23.0	681	4.7	6.8	4.9	1.2	4.4	±2.9	1	12.2
Pz25	5	21.5	625	2.5	7.0	3.1	0.5	10.8	±3.9	1	6.4
	1	21.7	824	0.2	6.6	4.6	1.9	4.8	±6.1	1	7.7
Pz29	4	25.0	532	5.3	7.4	11.7	1.1	0.9	±0.5	53	0.4
	1	18.8	590	5.1	7.0	9.0	1.6	1.2	±1.0	14	2.6
Pz30	3	22.3	521	44.1	7.3	10.5	1.4	1.3	±0.8	1	0
	1	18.7	597	31.4	7.1	13.1	2.1	0.0	±0.5	1	0
Pz34	3	21.0	600	30.7	7.2	14.5	1.5	0.2	±0.4	68	0
Pz36	4	23.5	601	0.9	7.3	2.5	0.5	13.9	±6.0	9	7
	1	18.8	757	0.2	6.7	4.9	1.2	4.4	±2.9	6	14
Pz37	5	19.2	609	5.5	7.3	14.0	1.0	0.3	±0.3	1	0
	1	17.6	714	0.5	6.8	14.2	2.6	0.0	±0.6	1	0
Pz41	3	19.0	596	8.7	7.3	15.9	1.7	0.0	±0.3	4	0
Pz44	3	19.1	557	1.2	7.3	16.1	1.6	0.0	±0.3	5	0
Pz56	5	19.0	602	12.8	7.2	11.7	1.0	0.9	±0.4	15	0.4[2]
	1	18.3	611	0.1	7.1	12.2	2.0	0.2	±0.6	4	0.3[2]
Pz57	3	20.0	593	9.5	7.4	15.6	1.5	0.0	±0.3	85	0.1[2]
	2	19.3	672	0.7	6.9	4.8	1.3	4.5	±3.3	4	16.5[2]
Pz58	3	20.5	587	12.9	7.3	11.8	1.5	0.9	±1.6	1	0.5[2]
	1	23.9	635	0.8	7.0	3.9	1.4	6.3	±5.8	1	18.0[2]
Pz59	3	20.2	585	4.4	7.3	11.7	1.5	0.9	±0.7	72	2.1[2]
	1	19.4	750	6.5	6.8	4.6	1.3	4.9	±3.6	39	22.2[2]
Pz60	5	19.5	593	1.4	7.3	1.2	0.4	32.7	±20.5	19	31.0[2]
	1	19	626	0.3	7.0	0.5	0.2	67.9	±32.1	47	167[2]
Pz61	3	17.6	632	72.9	7.2	14.3	1.6	0.3	±0.4	18	0.1[2]

Notes: For each well, the first line represents period from December 2012 to November 2013 and the second line February 2014 if data were available.
[1]Maximum value of dynamic oil height during dual-phase operation, without discontinuation of pumping.
[2]Low estimate since travel time to wells may not be sufficient for reaching equilibrium.

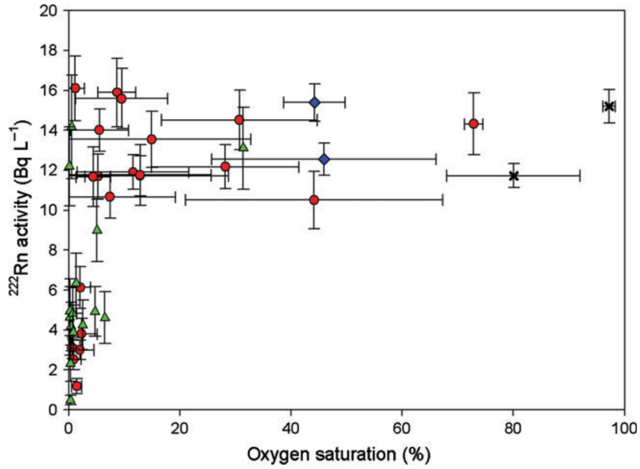

Figure 3. ^{222}Rn activity vs. oxygen saturation in all sampled wells. Red circles: pumped wells with NAPL, values from first period; green triangles: pumped wells with NAPL, values from second period; blue diamonds: pumped wells without NAPL from downgradient; black crosses: unpumped wells from upgradient (the well displaying the highest oxygen saturation is Pz4).

depending on NAPL saturation (Hunkeler et al. 1997). Finally, when the groundwater leaves a NAPL-contaminated source zone, the upgradient equilibrium will be approached again within a residence time of 12–15 d. At this site, groundwater flow velocities range from 5 m/d in the central source zone to >10 m/d at the upper and lower margins near the injection or pumping wells of the hydraulic barrier. The residence time of water in the central source zone is sufficiently high to reach a new equilibrium. However, the water from the wells Pz57-61 at the upper margin of the source zone may not fully be in equilibrium where the NAPL saturation is low. The travel time of water from the NAPL zone to the pumped well Pz46 downgradient is about 8 d and may be too short to reach background activity again.

Correlation of ^{222}Rn Activity with Oxygen Saturation

Figure 3 showed that groundwater can be rich in both oxygen and radon, depleted in both or depleted only in oxygen. There is no well displaying high oxygen content and low ^{222}Rn activity. Oxygen is consumed by aerobic bacteria at locations where LNAPL is present, and thus a correlation is expected between O_2 and NAPL. Oxygen is not resupplied within the source zone once it has been consumed while radon is produced everywhere by the aquifer matrix. If the NAPL smear zone goes deep enough to reach a low permeability layer, sampled water will have low oxygen saturation and low radon activity. Wells downgradient with screens reaching deep below the NAPL smear zone will yield higher radon activity but still low oxygen saturation. LNAPL-contaminated wells displaying oxygen saturation >30 % and ^{222}Rn activity >8 Bq/L are located on the assumed margin of floating oil body (Pz61, Pz30, and Pz34, Figure 1).

^{222}Rn Activity and LNAPL Extraction Efficiency

For technical reasons, it was not possible to monitor oil recovery rates specifically for each well with time. However, distinct zones of oil recovery efficiency were determined with tests that required discontinuation of LNAPL extraction. These tests were performed in each pump-and-skim well to assess their oil productivity and were made during a low water period. Two central zones of relatively high productivity were identified, bounded by a zone of intermediate recovery and three margins of low recovery (Figure 4A). The northern high productivity zone corresponds to the pipeline breakpoint and the southern zone to an area lacking puddingstone.

The mean radon activities in the groundwater of source zone wells during the first period were generally correlated inversely to LNAPL recovery efficiency (Figure 4B): all wells with less than 6.5 Bq/L ^{222}Rn were in the highly productive central zones (except for Pz22). They also exhibited the lowest oxygen contents. However, the three wells Pz1,

Figure 4. (A) Zones of oil recovery efficiency: red areas show wells high recovery efficiency at this site, yellow areas wells with intermediate recovery efficiency and green areas wells with low recovery efficiency; (B) mean radon activities in source zones wells and background wells during first period; (C) mean radon activities in source zones wells and background wells during second period. Green triangles represents wells with ^{222}Rn activity >13 Bq/L, yellow squares wells with activity comprised between 8 and 13 Bq/L and red circles wells with activity <6.5 Bq/L.

Pz29, and Pz59 which were highly productive showed ^{222}Rn activities >10 Bq/L. Pz59 is near the upgradient boundary of NAPL, and the groundwater residence time may not have been sufficient for partitioning equilibrium to be established. For Pz1 and Pz29 that are more central this equilibrium should be established. Pz1 was drilled deeper than other wells and equipped with a screen two times longer, which means that a deeper layer of the aquifer is assessed by pumping and that water not in equilibrium with LNAPL was pumped This explained that ^{222}Rn activities were higher (see bore cores construction; Figure S1). The high activity in Pz29 is presently not understood.

During the second period, all wells in the highly productive central zones had less than 6.5 Bq/L ^{222}Rn, except for Pz29 (Figure 4C). Some wells in zones of intermediate recovery also exhibited low ^{222}Rn activity. This depletion is related to the high water level: in 2014, an important part of the oil smear zone was below the water table and dissolved radon activities were thus lower. Wells having a ^{222}Rn activity higher than 14 Bq/L were not all located outside the source zone or in low productivity zones (Figure 4B and 4C). However, they were all along the lateral margins of the source zone, and continuous pumping may have attracted radon-rich groundwater from outside to these wells.

It is interesting to note that the maximum oil heights were neither correlated with ^{222}Rn activities nor with extraction efficiency. The two wells Pz57 and Pz34 which had very thick maximum floating LNAPL (85 and 68 cm respectively) were reported only as producing intermediate recovery rate.

Quantification of LNAPL Saturation

For the quantification of LNAPL saturation, an accurate partitioning coefficient is required. The partitioning coefficient between crude oil and water was determined to be 38.5 (standard deviation 2.9). Partitioning coefficients for ^{222}Rn between petroleum products or constituents and water depend on the Hildebrand parameter and vary from about 33 to 60 (Schubert et al. 2007a). Our value for crude oil is somewhat lower than that for diesel fuel (40 ± 2.3, Hunkeler et al. 1997) and similar to that for gasoline (38.9 ± 0.9, Schubert et al. 2007a), but higher than the value for petroleum (32) estimated by (Semprini et al. 2000). Partitioning between hexadecane and water would yield a K of 33 (Abraham et al. 1994).

LNAPL saturation S in percent of saturation of pores space was calculated using Equation 2 from Hunkeler et al. 1997 and the $K_{\text{NAPL-w}}$ of 38.5:

$$S(\%) = \left(\frac{\frac{A_{\text{Bg}}}{A_{\text{Well}}} - 1}{K_{\text{NAPL-w}} - 1} \right) \times 100 \quad (2)$$

where A_{Bg} is the ^{222}Rn activity in the background (groundwater upgradient of the source zone), and A_{Well} is the activity of any source zone well. The well Pz4 was chosen as background reference, based on Figure 3, which shows that Pz4 is both rich in radon and in oxygen, suggesting that water in this well is uncontaminated and that radon is in equilibrium with aquifer solids. It should be noted that the saturation S is an average across the whole screen depth of each sampling well. Wells with screens reaching deep below the NAPL smear zone will therefore yield low apparent NAPL saturations. Results for apparent NAPL saturation calculation for each well are in Table 2 and in Figure 5. A sensitivity analysis of Equation 2 using typical standard deviations for A_{Bg} and A_{Well} and using the uncertainty of K_{NAPL} (38.5 ± 2.9) showed that saturations are affected by about 20% uncertainty. Contour maps of oil saturation for the first and second period of sampling are shown in Figure 5A and 5B, respectively. Maps for both periods confirm two zones of high productivity for both periods. However, the outer contour line of the whole source zone is highly uncertain, especially at the upgradient source boundary where equilibrium may not be

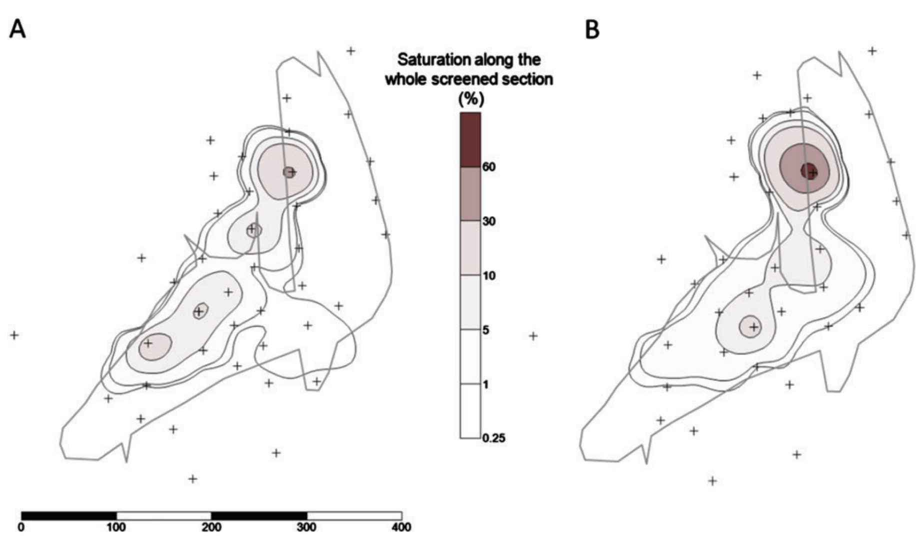

Figure 5. Contour maps of calculated oil saturation for 2013 data series (A) and 2014 data series (B). Crosses represent wells and gray line limits the spill in surface. Contour maps were plotted based on the interpolation of oil saturation calculation for each sampled well.

Table 3

Oil Volumes Calculated Based on ^{222}Rn Measurements in Three Zones of Different Productivities

Zone	Wells in Zone Used for Assessment	Area of Zone (m^2)	Volume in Saturated Zone, Period of Low Level[1] (m^3)	Volume in Period of High Level (m^3)
Low productivity	Pz2, 3, 30	10,000	3.2 ± 1	36.4 ± 10.9
Intermediate productivity	Pz21, 22, 34, 37, 41, 44	16,000	27.6 ± 8.3	134 ± 40.3
High productivity	Pz1, 23, 24, 25, 29, 36	13,000	46 ± 13.8	139 ± 42
Total source zone		39,000	77 ± 23.1	309 ± 93

Note: Wells Pz56 to 61 near the upper source boundary were excluded.
[1]Oil volume below the groundwater table during first period (Figure 2A). Error is assumed to be 30%.

reached. Therefore, for oil volume calculations, contours from Figure 4A have been used, together with mean oil saturations based on ^{222}Rn for each zone, and using the height of the wet oil smear zone.

A porosity of 0.1 ± 0.01, estimated from modeling, was used. The extension of the NAPL smear zone was established based on historic highest and lowest water tables in wells contaminated with NAPL. The smear zone of NAPL for each well is sketched in Figure S1. It was assumed that only groundwater flowing through NAPL smear zone was depleted in ^{222}Rn, whereas groundwater flowing below the smear zone displayed background ^{222}Rn activity. Residual oil volumes below the water table traced by ^{222}Rn for each well were calculated and shown in Table 1, and a map with interpolated values is shown in Figure S3. The highest value is predicted for Pz60, where more than 160 L/m^2 of oil might still be present. In contrast, based on ^{222}Rn activity, many wells are affected by very low oil volumes, suggesting that the recovery will soon come to a stop. The total residual oil volume below water table at high water level is estimated to be 309 ± 93 m^3 (Table 3). This value is affected by 30% uncertainty, 20% from saturation estimation, and 10% from uncertainty of porosity.

At this site, the overall recovery performance is not optimal, and pumping tests suggested that the radii of influence of extraction wells are too small. More extraction wells should be added near all wells showing a low ^{222}Rn activity. Furthermore, the radon measurements in the zone of low productivity help to quantify the residual non-extractable oil volume. In Pz2, Pz3, and Pz30, the mean NAPL saturation is around 1.4% and recovery has ended, suggesting that only residual oil remains. Extrapolation to the whole source zone (3.9 ha, smear zone = 2.6 m high, porosity = 0.1), a non-extractable oil volume of 142 ± 43 m^3 can be estimated.

Conclusions and Future Research Needs

This study indicates that ^{222}Rn activity can be measured reliably and quickly in an aquifer with >10 Bq/L where LNAPL recovery is active. Although not common, aquifers with activities lower than 10 Bq/L could also be studied but it is recommended to work with higher volumes of water. This work is the first in which Rn was measured successfully when a pump-and-skim system was active and provides a new perspective for assessing the efficiency of this system. Low radon activities suggest zones of good recovery, while high activities were not always related to poor recovery. It is shown that at the margins of the source zone, especially at the upgradient LNAPL margin, radon-rich water is not necessarily in equilibrium with the NAPL. Well construction is also of importance since wells that are screened below the LNAPL zone may suggest bad recovery. The correlation of oxygen with ^{222}Rn activity is useful for selecting the best well to use as a background reference which is needed to calculate NAPL saturation based on ^{222}Rn activity. The NAPL-water partitioning coefficient between crude-oil and water is slightly lower than coefficients reported for other petroleum products. Finally, the calculation of total residual oil based on ^{222}Rn uses several parameters (activity of background, activity of well, NAPL-water partitioning constant, porosity, and depth of oil smear zone) and the combined uncertainty is very large and hence the standard deviation associated with ^{222}Rn activity is important. The estimation of residual oil is useful for the evaluation of source lifetime. More work is needed for the quantification of LNAPL within the capillary fringe.

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Supporting Information

The following supporting information is available for this article:

Figure S1. Sketches of drill log describing geological layers for each sampled well.

Figure S2. Radon activity vs. maximum oil thickness in 2013 (A) and oxygen saturation vs. oil thickness in 2013 (B).

Figure S3. Interpolation of oil volumes estimated in each well for the period of high water level. Crosses represent wells and gray line limits the spill in surface. Contour maps were plotted based on the interpolation of oil volume calculation for each sampled well.

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