HYDROCARBON CONTAMINATION OF AQUIFERS BY SNMR DETECTION

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ABSTRACT

Surface NMR can be used to unambiguously detect subsurface water in suitable geological formations to a depth of 100 meters and more depending on the presence of natural and cultural electromagnetic noise. Mathematical routines yield depth distributions of the liquid, provided that the liquids are present in horizontal layers and not in pores that are too small to be detectable at present. Furthermore, determination of pore size distributions is now possible with relaxation time measurements.

Experiments were performed at shallower depths to detect signals from deposits of subsurface gasoline and diesel fuel near Abakan, Siberia. Surface NMR signals were observed with multiple T_2^* relaxation times at sites containing both gasoline and water. The identification of gasoline and water signals were made on the basis of making measurements much farther from the apparent source of contamination and obtaining only one T_2^* component, presumed to be water. We are not aware of any other surface NMR experiments that have detected subsurface organic contaminants, especially in the presence of water.

INTRODUCTION

Aquitards and aquifers often have different ranges of electrical resistivity and density. Nevertheless, surface electrical and density technique is often (but not always) able to indirectly delineate the coarse-grained alluvial deposits, which have potential of being aquifers. The SNMR method, on the other hand, allows direct and noninvasive (remote) sounding of groundwater distribution versus depth. Moreover other proton-containing liquids such as hydrocarbons can also be studied.

An earlier study [1] discusses some aspects of the surface nuclear magnetic resonance (SNMR) sounding signal of bulk water detected below the ice surface of Ob reservoir near Novosibirsk. Such SNMR experiments of bulk water are useful for calibration and testing the method. As it was partly reported earlier in [2], investigation of spin relaxation times T_2^*, T_2, T_1 is important for information about the microstructure of pores as well as diamagnetic, paramagnetic, and

hydrocarbon contamination. The present study identifies hydrocarbon contamination based on SNMR relaxation.

Basic principles of the SNMR method

Figure 1 sketches the typical scheme of SNMR groundwater sounding and contamination detection. The method is based on the principle of observation of the proton magnetic resonance in the geomagnetic field of hydrogen ^1H nuclei of groundwater molecules H_2O.
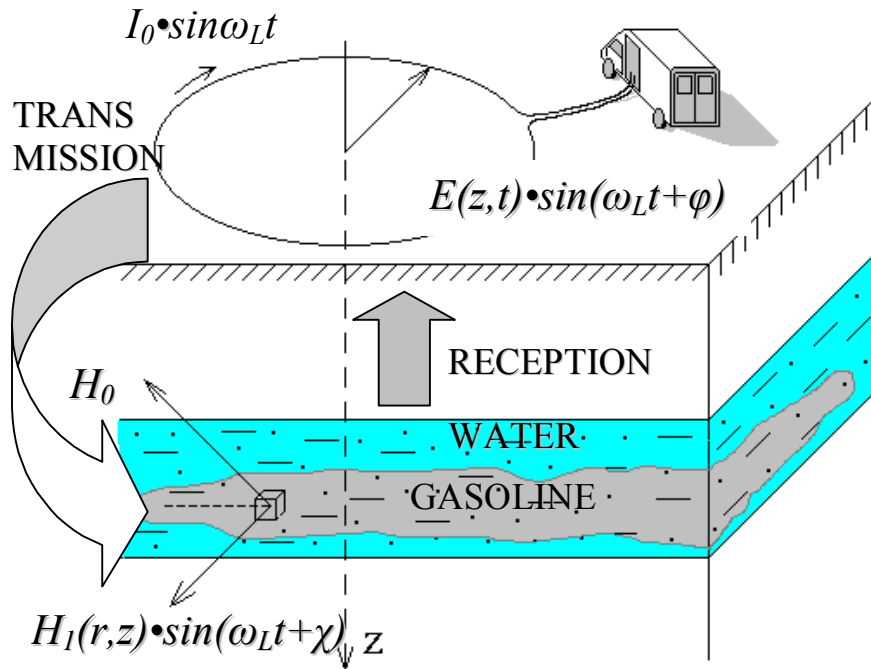

Fig. 1. A scheme of SNMR groundwater sounding and hydrocarbon contamination detection.

In the Earth's magnetic field $\mathbf{H_0}$ a macroscopic magnetization $\mathbf{M_0}(\mathbf{r})$ of a unit volume in thermal equilibrium is described by the equation [4]:

$$\mathbf{M_0}(\mathbf{r}) = n(\mathbf{r})\frac{\gamma^2 \hbar^2}{3kT} S(S+1) \cdot \mathbf{H_0} \qquad\qquad \text{(Eq. 1)}$$

where $n(\mathbf{r})$ is the number of magnetic nuclei per unit volume, $S=1/2$ is the nuclear spin, $\hbar$ and k are Planck and Boltzmann constants, and T is the temperature.

After the pulse, which generates the oscillating field $\mathbf{H_1}(\mathbf{r}) \cdot e^{-i\omega t}$, in resonant case the frequency ω is equal to the Larmor precession frequency in geomagnetic field $\omega_L = \gamma_H \cdot H_0$, the vector $\mathbf{M_0}(\mathbf{r})$ is tilted away from the vector $\mathbf{H_0}$ by the angle:

$$\theta(\mathbf{r}) = 0.5 \cdot \gamma_H \cdot H_{1\perp}(\mathbf{r}) \cdot \tau_p \tag{Eq. 2}$$

where γ_H is the gyromagnetic ratio of protons, $\mathbf{H}_{1\perp}(\mathbf{r})$ is the alternating field component that is normal to $\mathbf{H_0}$ and τ_p is the pulse duration.

The emf induced in the loop by the magnetic field of groundwater nuclear magnetization is determined by the equation [1]

$$E_0(Q) = (\omega/I)\int_V M_\perp(\mathbf{r})H_{1\perp}(\mathbf{r})dV(\mathbf{r}) \tag{Eq. 3}$$

where $M_\perp(\mathbf{r}) = M_0(\mathbf{r}) \cdot \sin\theta(\mathbf{r})$, I is the amplitude of the excitation current, $Q = I \cdot \tau_p$ is the excitation pulse intensity (pulse moment), and $E_0(Q)$ is the NMR signal amplitude that is measured.

The depth of water-saturated layers can be determined from the NMR signal amplitude dependence on the excitation-current pulse intensity (pulse moment) Q.

Experimental and test sites

The SNMR experiments were performed using the Hydroscope-3 equipment made in the Institute of Chemical Kinetics and Combustion of Siberian branch of the Russian Academy of sciences, Novosibirsk. The technique uses maximal pulse moment up to 20000 A*ms (at 40 ms pulse duration), the battery capacitance 0.2 F, and possibility of two-pulse sequence. The 2 17m diameter three-turn loops were connected in a figure-eight configuration [3] to detect hydrocarbon pollution.

A team from Siberian Branch of Russian Academy of Sciences (SBRAS), Yuzhno-Minusinsk Hydrogeological Enterprise (YMHE), and New Mexico Resonance studied leaky underground storage (LUST) near Abakan. Anatoly Krivosheev and Vladimir Yashchuk of YMHE had monitored numerous LUST sites near Abakan and south of Krasnoyarsk region from borehole measurements. Figure 2 exemplifies a borehole measurement of a 27-cm thick gasoline layer over water at a site in Abakan.
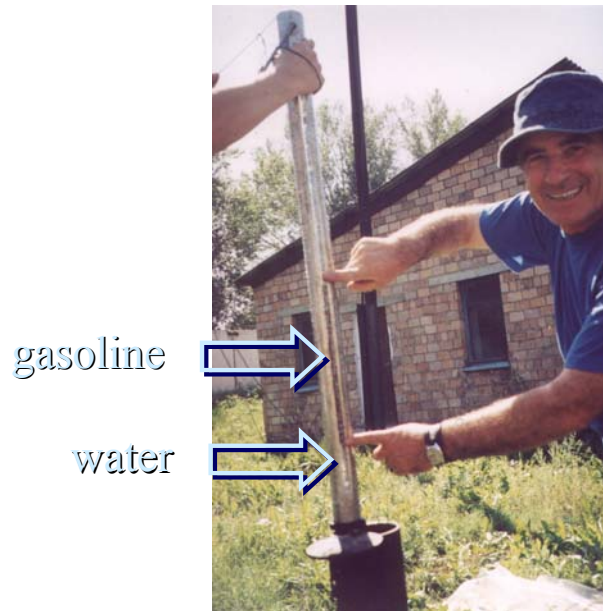
Fig. 2. An example of hydrocarbon pollution of groundwater (Abakan).

At another location, Borehole #52 near a leaking tank of gas station (Abakan), the depth of the gasoline layer was 1.15 m. The dissolved hydrocarbon content in groundwater was 7.15 mg/l. The lithological log of Borehole #52 is clay sand 1-4 m, medium-grained sand 4-5 m, clay and pebbles 5-9 m, and gravel 9-11 m.

Results and discussion

Borehole #52 was located at a gas station on the embankment of Enisei River. Figures 2 and 3 exemplify the hydrocarbon (gasoline) pollution of aquifer detected near the gas station but on the flood plain of the river. Surface NMR signals were observed with two T_2^* relaxation rates at a site, known to contain both gasoline and water and close to the gas station. The identification of gasoline and water signals were made on the basis of making measurements 150 meters farther from the source of contamination, and closer to the Enisei River, and obtaining signals with only one T_2^* component (Fig. 3), presumed to be water [4]
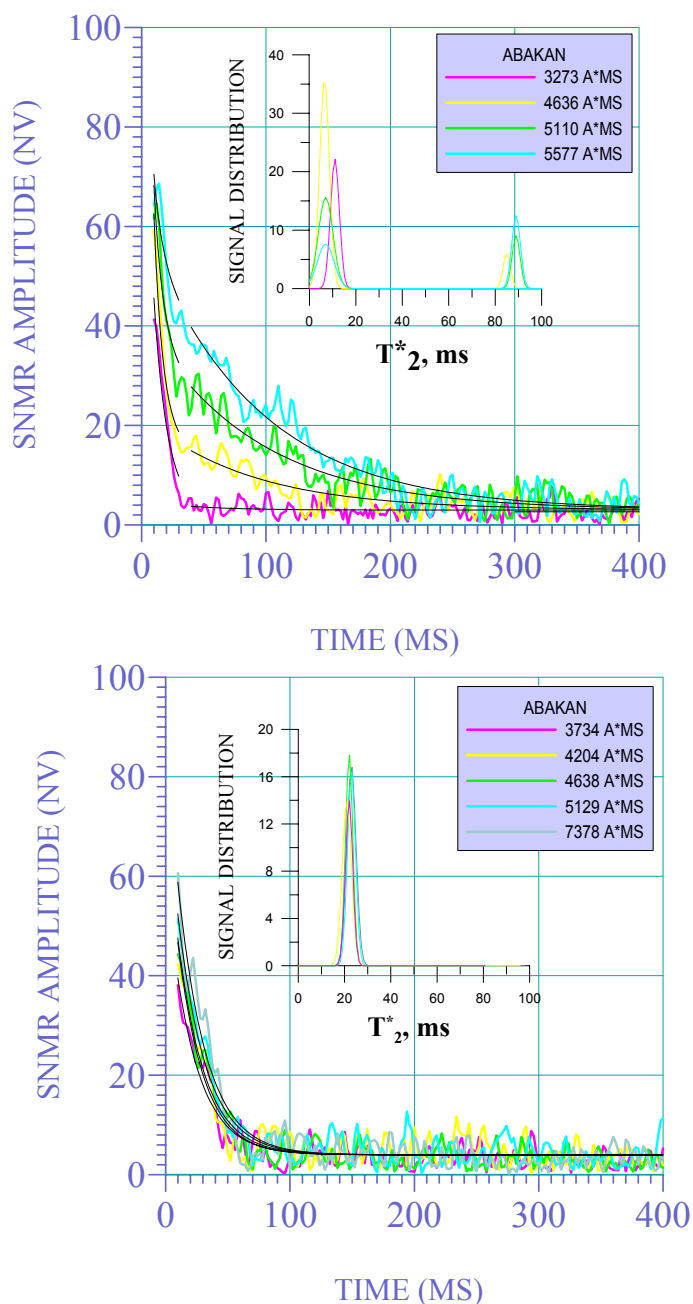
Fig. 3 An example of SNMR amplitude versus time at different pulse
moments. Near Borehole #52 at leaking tank of gas station in Abakan
(top). 150 m away from Borehole #52 (bottom).

Since the rock surface is usually water-wetted and the non-wetting phase remains in the bulk, the NMR signal of wetting phase (water) has much shorter relaxation times (~10 ms), while the non-wetting phase (hydrocarbon) exhibits close-to-bulk relaxation behavior (~90 ms). The surface-NMR results obtained are in good agreement with earlier laboratory and NML measurements [5-7]. The pore-surface water-proton relaxation times of ~10 ms (inset, Fig.2) are shorter than the bulk relaxation times of ~20 ms (inset, Fig 3), also in good agreement with past work [5-7].

Figure 4 shows a 3-D stacked plot of the SNMR amplitude versus time and pulse moment, the data of Fig. 2, taken near Borehole #52, Abakan. There are only short lifetimes at low moments while there are both short and longer relaxation times at high moments, as can be seen also in Fig. 2. If the shorter relaxation times are due to water, these results indicate that it is at shallow depths while the gasoline with possibly the longer relaxation times occur only for the larger pulse-moments which imply that they are at greater depths. These results are contrary to the situation at borehole #52 where gasoline was over water.
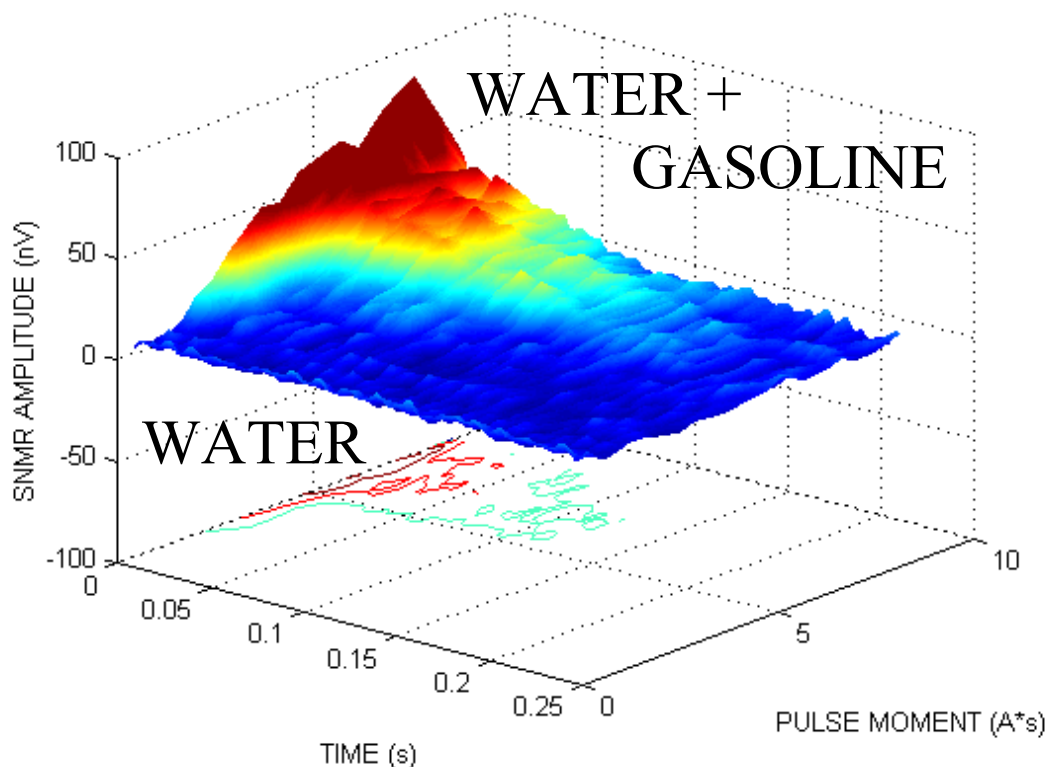

Fig. 4. An example of SNMR amplitude versus time and pulse moment. Near Borehole #52, Abakan.

CONCLUSION

Surface NMR signals were observed with multiple T_2^* relaxation rates at sites with known deposits of subsurface gasoline and water near Abakan. The identification of gasoline and water was made using measurements much farther from the source of contamination and obtaining only one T_2^* component.

REFERENCES

1   Trushkin D.V., Shushakov O.A., Legchenko A.V.: Appl. Magn. Reson., v. 5, 399 (1993).

2   Shushakov O.A.: Magn. Res. Imaging, v. 14, 959 (1996).

3   Trushkin D.V., Shushakov O. A., Legchenko A.V.: Geoph. Prospecting, v. 42, 855 (1994).

4   Shushakov O.A., Fomenko V.M., Yashchuk V.I., Krivosheev A.S., Fukushima E., Kuskovsky V.S.: Proc. ENVIROMIS, Russia, Tomsk, v. 1, 15 (2002, in Russian).

5   Straley C., Morris C.E., Kenyon W.E., Howard J.J.: Log Analyst, v. 36, 40 (1995).

6   Hedberg S.A., Knight R.J., McKay A.I., Whittal K.P.: Water Resour. Res., v. 29, 1163 (1993).

7   Bryar T.R., Knight R.J., Nielsen T.P.: Water Resour. Research, in press.