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Source: Air, Soil and Water Research, 6(1)

Published By: SAGE Publishing

URL: https://doi.org/10.1177/ASWR.S12406

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Air, Soil and Water Research

The use of ^{1}H-NMR Relaxation Times of Water Adsorbed on Soils to Monitor Environment Pollution

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ABSTRACT: Pursuing the goal to develop an express technique for the characterizing of forest ecology, this paper presents a description of the found dependence of nuclear magnetic resonance (NMR) relaxation times of water in soils on the pollution caused by vehicle exhausts. Test measurements were made in Mari El Republic of Russia where wildwood areas located close to human activity are showing degradation, which has drastically intensified in the resent several years. Samples were collected at distances between 100 m to 1.1 km from the highway towards the direction of virgin forest assuming that their contamination level was naturally varied. The measured spin-spin NMR relaxation time of wetted samples showed a growth of more than 20% with the increase of distance from the pollution source. Here we try to explain this effect. As the conclusion, we propose to use the transverse relaxation time of moisturized soil as an indicator for the environment pollution monitoring.

KEYWORDS: Forest pollution, soil contamination, NMR relaxation times, monitoring

CITATION: Grunin et al. The use of 1H-NMR Relaxation Times of Water Adsorbed on Soils to Monitor Environment Pollution. *Air, Soil and Water Research* 2013:6 115–119 doi:10.4137/ASWR.S12406.

TYPE: Short Report

FUNDING: This research was done under grants from the Russian Ministry of Education and Sciences.

COMPETING INTERESTS: Authors disclose no potential conflicts of interest.

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Introduction

Due to drastic effects of human activity on the environment, the effective monitoring of the current ecological situation has become highly necessary. As an undesirable side effect of energy generation and the production of new materials, the environment is being continuously polluted by chemicals that are alien to the natural circumstance. In the past decade, it has been noticed that the Mari El Republic of the Russian Federation, which was previously known as a good ecological territory, has rapidly become a relatively insecure region as the diversity of wildlife and average human health quality has been observed to degrade.[1] One of the readily observable negative changes was the recession of forest flora and fauna along highways. Some efforts were undertaken to investigate the sources and consequences of pollution as well as to find out the reasons causing the degradation of the environment. The increase of traffic with high contents combustible products, particularly diesel, is one suggested reason. Another possible reason is the impact of residual radiation of transported goods. This effect should be subject to a more detailed analysis as part of the industrial activity in the Mari El Republic consists of technologies which are converted from the military industrial heritage of the Soviet Union. There are only a few available studies on this topic and they are conducted in a poor scientific manner.[1]

One of the essential procedures for environmental monitoring is an estimation of heavy metals content in soils. Anthropogenic pollution elements such as Cd, Cr, Pb, Zn, Fe, and Cu are indestructible through natural means and yield negative consequences on the health of humans and animals. Heavy metals are deposited on the soil surface by industrial activity, vehicles exhausts, or can be the result of background radiation. When analyzing, radiation it is often necessary to not only measure the intensity of particle flow but also obtain information on the average radiation dose over a continuous period. For high radiation levels, this problem can be solved by analysis of the residual emission of material samples taken

from the regions of investigation. However, if the active particles flow intensity is comparable to the natural background, such a measurement yields unintelligible results.

According to multiple previous investigations, some types of soil microbiota (actinomycetes, rhizobacteria) are very sensitive to even low radiation levels[2–4] which reveal their presence by increasing metabolic activity, effecting the growth of colonies, and enhancing levels of mutation of the soil bacteria. This also causes such fungal features as radiotropism, the ability to move the population towards the source of radioactive particles. Unfortunately, natural content of fungi and bacteria biomass in soils usually rarely exceeds several grams per one kilogram of raw sample[5,6] making direct observation of their activity difficult. Nevertheless, even at such low concentrations, these microorganisms, together with glycoproteins and aminosaccharides of plants residuals, influence the water adsorption by soil.

Rapid and reliable estimation of the listed contamination types always remains of high actuality. Unlike conventional chemical analysis, isotope methods, mass spectrometry, and chromatography, one of the promising techniques for this analysis is time-domain nuclear magnetic resonance (NMR). NMR normally requires simple procedures of samples preparation and the measurement hardware in recent years has become fairly portable and accurate. Additionally, the measurement itself usually takes not more than several minutes.

Proton NMR (^{1}H-NMR) relaxation rates are considered to be very sensitive to water molecule mobility.[7,8] Moreover ^{1}H-NMR relaxation times T_1 and T_2 significantly depend on presence of paramagnetic particles such as the ions of some heavy metals absorbed from ionizing radiation, as has been shown in experiments made on fungi.[9] The presence of specific centers of relaxation intensifies the exchange between ^{1}H protons and speeds up the relaxation due to interactions between the nuclear magnetic dipoles of protons and the magnetic dipole moments of the electrons in these paramagnetic ions.[8] This leads to an effective reduction of both spin-lattice and spin-spin relaxation times.[10]

Biofilms formed in macro pores of soils[11] contain a large variety of microbiological organisms including bacteria, algae, and fungi. During their life cycle, while filtering rain water and consuming atmospheric vapor, their cell walls adsorb a perceptible amount of metal ions arising from pollution agents that are dissolved in water flowing through the soil humus. Thus, soil microbiota can be distinctly considered as a reservoir for the collection of pollution agents.

In this research, we aim to propose a simple technique to monitor the average radiation background together with the concentration of chemical pollutants. This technique is based on two effects—the fungal growth stimulated by external radiation and the influence of adsorbed chemicals on the NMR relaxation parameters. To illustrate this, we are showing the experimentally found dependence of proton NMR relaxation times of wetted forest soils on the distance between sampling place and the road with intensive traffic. We are supposing that the contamination effect reduces as the distance to the pollution source increases.

Materials and Methods

For development of a method applicable to different types of landscapes, it was decided to investigate an A2 soil horizon where pollution agents were thought to be accumulated over a long period of time. Once the NMR relaxation signals of this horizon showed very low intensity, samples were enriched with water to boost the ^{1}H-NMR response and to simultaneously yield structural information from interactions of H_2O molecules with both the inorganic and biochemical components of samples. Thus, the general strategy of measurements was to investigate the NMR relaxation behavior of water adsorbed on soils with different levels of heavy metal contamination.

In order to simulate the variation of soil pollution, the distance from the contamination source (highway) to the sampling point was varied, assuming an attenuation of the pollutant concentrations with increasing distance to the road. Four series (from a to d) of samples were taken according to the sampling pattern demonstrated in Figure 1. Sampling in each series was done at eight different distances between 100 and 1100 m from the road and into the forest area. All 32 samples were taken between the 8 km and 9 km milestones of the straight part of the road leading from Yoshkar-Ola to Volzhsk. This road carries heavy traffic of various vehicles types, including the periodic transportation of potentially radioactive materials, which are also able to contribute to environmental contamination effects. The distance between each series along the road was 200 m, therefore the sampling covered an approximately rectangular area with one side of a total length of 600 m along the road and the other side of 1100 m perpendicular to the road.

At each sampling position, a volume of 600 cubic centimeters (cc) of soil was taken from the A horizon (top soil) from a depth between 10 and 20 cm. All samples were collected within 6 hours of each other and 2 days after the last rain.

The collected soil samples were sifted through a 4 mm sieve to remove stones, plant materials, and large soil particles. All samples were then thoroughly stirred and dried at 40°C to avoid the growth of fungi and to prepare the soils to an equal condition before the adsorption of water vapor.

At the next stage of preparation, samples were carefully wetted under identical conditions. Soil samples of approximately 1 gram were put on plates and weighed. Then plates were placed into a desiccator over a salt solution at 98% relative humidity (0.98 relative water vapor pressure) at 20 ± 0.2°C. All samples had been kept in a desiccator for 10 days until a constant weight was reached. For further NMR analysis, each soil sample was portioned out into three parts and placed in three NMR test tubes of 9 mm diameter.

Time-domain NMR measurements were done with the Spin Track NMR analyzer of Resonance Systems Ltd. at a

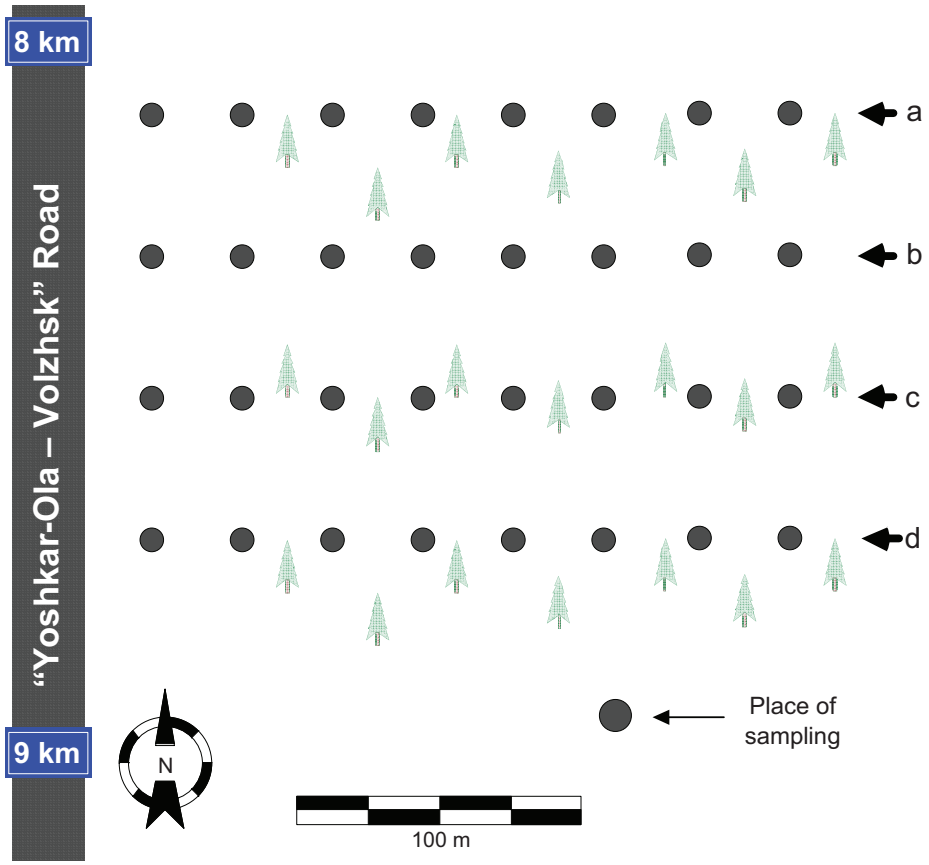

Figure 1. Schematic location map of the studied areas.

^{1}H resonance frequency of 19.2 MHz.[12] Data was collected using a simple pulse and acquire sequence to obtain a free induction decays (FID). The spin-spin (T_2) relaxation time of water in the soil samples was measured by the Hahn Echo method[13] as conventional CPMG sequence could not be applied due to the fast relaxing decays with T_2 values that could be as low as 200 microseconds.[14] For each relaxation curve 20 points were measured with the echo time varied between 30 and 2000 microseconds.

The transverse relaxation times were calculated using the single exponent best fit least squares method. The maximal relative standard deviation was below 8%. All statistical functions such as deviations, errors, and mean values were calculated using conventional expressions.[15]

Results and Discussion

FID on the original dry soil samples were of very low intensity and the observable magnetization was seen to disappear at around 23–30 microseconds after the excitation pulse. The magnitude of the FIDs collected on the soil samples did not show a dependence on distance from the pollution source. The most likely reason for such fast decaying NMR signals is dry residual organics, as both polysaccharides and proteins yield very short proton relaxation times of around 10–20 microseconds.[16] After the moisturizing of samples (described above) the NMR signal response was increased making the measurement of longer relaxation times by echo sequences possible (Fig. 2).

All measured T_2 values of the acquired soil samples fell within a range of values between 200–350 microseconds (Fig. 3). Apart from some results reported earlier,[8,10] these data showed that the water permeated into the samples at the desiccator atmosphere was not free bulk water but an effectively adsorbed surface water, as aqueous transverse relaxation in pore volumes normally gives T_2 from tens of milliseconds up to several seconds.[17,18] This fact was also confirmed by the relatively minor water uptake that was less than 5% of th urizing. The most likely condition of this water was to be adsorbed by both the organic and inorganic (mostly silica) content of soils. All observed relaxation decays showed an exponential behavior (Fig. 2) characteristic of a fast spin exchange between ^{1}H nuclei.[13,19] In other words, the signals of the water bound by the organic and silica surfaces contributed to a single relaxation time T_2. Samples that had not been moisturized in a vapor atmosphere gave no satisfactory ^{1}H-NMR Hahn Echo response, confirming the low concentration and water in these samples.

Compared to the spin-spin relaxation of pure water[17,18] (on the order of 2 seconds) the observed short T_2 below 350 microseconds could also be explained by the presence of

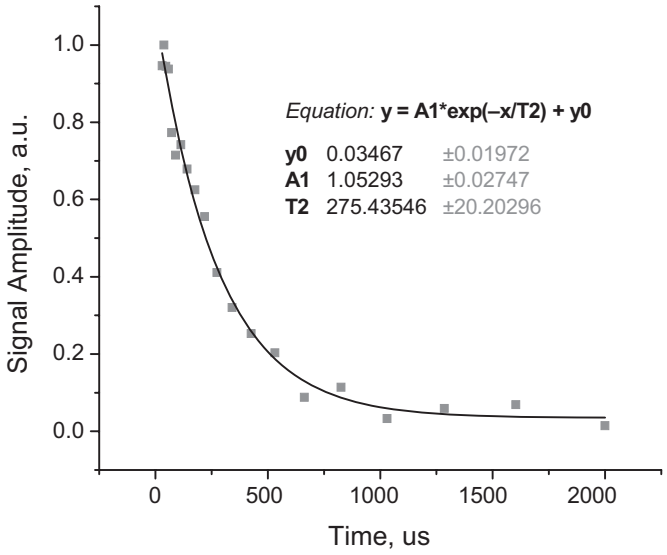

Figure 2. Experimental spin-echo decay for a wetted soil sample (grey squares) and its exponential fit (solid line).

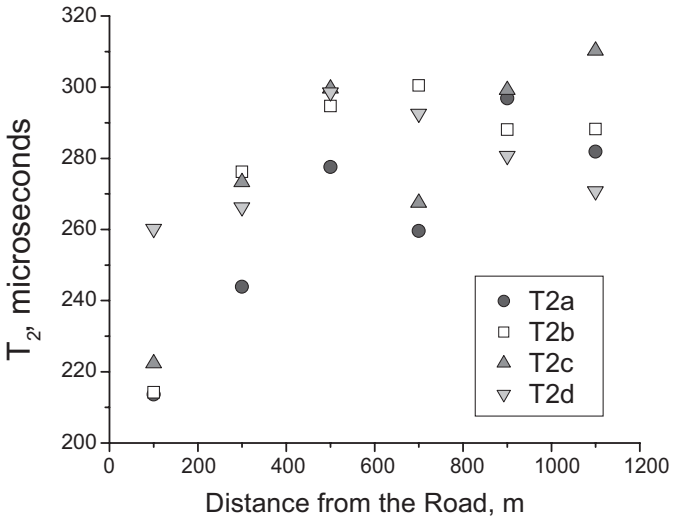

Figure 3. Spin-spin relaxation times for different sampling rows and their dependence on distance from the source of pollution.

specific paramagnetic relaxation centers, such as the ions of some heavy metals, pore surface defects, short broken polymer chains and free radicals.[9,13,18]

Although paramagnetic heavy metals that increase the rate of NMR relaxation are present in soils naturally at a trace concentration, they can also be continuously accumulated by penetrating to soils from the air.[20] Soils in close proximity to highway areas contain a wide range of heavy metal ions such as Pb, Mn, Fe, Zn, Cu, Cr, Ni, and Cd.[3,4]

Free radicals including superoxide ($O_2^{\cdot-}$), hydrogen peroxide (H_2O_2), hydroxyl (HO·), peroxyl (ROO·), and alkoxyl (RO·) in soils exist predominantly in the humin fraction and can be produced by ionizing radiation,[21] oxidation of water,[22] or by the formation of secondary partially reduced oxygen species[23] as a consequence of radiation.

Despite the low concentration of organic material in the soil, the structural organization of the soil matrix will cause changes in the NMR relaxivity of adsorbed and bound water. As reported in other research,[24,25] radiation levels can influence fungi metabolism in soils. Variation of radiation levels leads to variations in the chitin-glucan sequences in the fungal cell walls which then affects the porous formation of the fungal system. Such chemical and porous structural changes can result, for example, in a higher moisture uptake and a decrease of T_2 as the amount of fast relaxing water grows with the increase of the surface area of the microporous structure.[26]

Thus, as discussed above, the diminution of chemical pollution and radiation levels could be the reason for the increase of NMR relaxation times for water adsorbed on soils. The experimentally measured T_2 values for each sampling series as the function of the distance from the road is demonstrated in Figure 3.

In every series, this function increases and the growth range of about 25%–30% exceeds, by at least three times, the maximal measurement error of 8%. The deviations within 10%–15% of the T_2 values observed at similar distances between different series can be explained by the natural difference in the landscape, soil chemistry, and hence the pollution conditions. However these deviations are statistically twice less than the range of the observed and predicted effect.

After averaging of data between the four sampling series, the general trend of the dependence being studied becomes clearly visible and shows the monotonic raise of T_2 as the distance from pollutant is increasing (Fig. 4).

Summarizing the discussion made above, we state that the effect of the wetted soil ^{1}H-NMR transverse relaxation time dependence on the level of some contamination types. If this assumption is correct, that the traffic pollution decreases as function of the distance from the road, then the found effect can be used as a rapid method for the pollution degree estimation.

Conclusion

T_2 relaxation times of moisturized samples of A horizon (top soil) can be considered for use as a quantitative environmental pollution indicator. The spin-spin relaxation time was revealed to be very sensitive to soil content and microstructure changes under possible impact of vehicle exhausts. The reduction of T_2 values correlated to pollution can be explained by the heightened presence of paramagnetic ions and free radicals in the soils, as well as the sensitivity of adsorbed water molecules to changes in micropores surface structures formed by fungal microbiota under an increased radiation background.

Although the observed effect may require additional statistical investigations, the results can form a starting point for

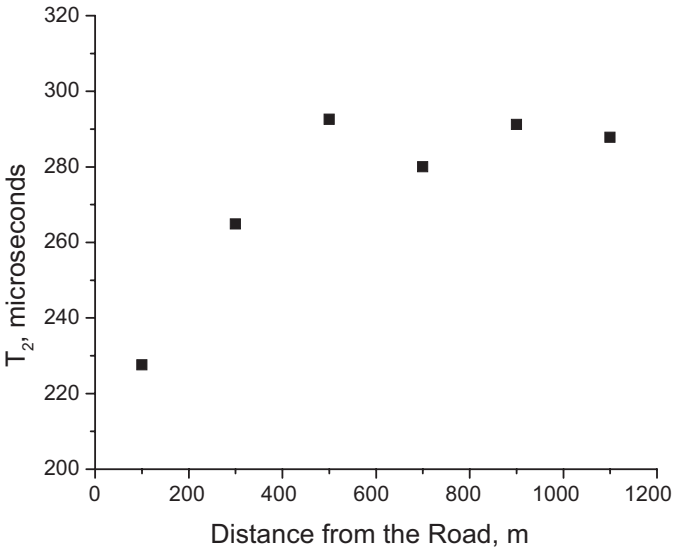

Figure 4. Averaged spin-spin relaxation times and their dependence on distance from source of pollution.

the development of an effective and rapid analysis technique for environmental monitoring.

Acknowledgements

The authors would like to thank Volga State Technology University of Yoshkar-Ola and Resonance Systems Ltd. for the ability to use laboratory equipment and the ecology organization "Чистый" ("Safe Forest") for help with collecting the samples.

Author Contributions

Conceived and designed the experiments: EN, LG. Analysed the data: LG, EN, JE. Wrote the first draft of the manuscript: LG. Contributed to the writing of the manuscript: EN. Agree with manuscript results and conclusions: JE. Jointly developed the structure and arguments for the paper: JE. Made critical revisions and approved final version: LG. All authors reviewed and approved of the final manuscript.

DISCLOSURES AND ETHICS

As a requirement of publication the authors have provided signed confirmation of their compliance with ethical and legal obligations including but not limited to compliance with ICMJE authorship and competing interests guidelines, that the article is neither under consideration for publication nor published elsewhere, of their compliance with legal and ethical guidelines concerning human and animal research participants (if applicable), and that permission has been obtained for reproduction of any copyrighted material. This article was subject to blind, independent, expert peer review. The reviewers reported no competing interests.

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