

Testing of Activated Carbon for Water and Non-volatile LNAPL Quantitative Determination in Porous Media under Laboratory Conditions

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Abstract

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Activated carbon is a highly porous form of carbon, which has an exceptionally large surface area. Activated carbon material has been artificially processed as a set of plates, within which two different types of pores are present: micropores (< 2 nm) and transport pores (macropores > 50 nm and mesopores 2–50 nm). The transport pores bring molecules of different substances (organic compounds) into the micropores, which are basically the active centres where the adsorption takes place. Activated carbon, due to its high adsorption potential, is used in many applications such as air, water, wastewater or chemical purification. In this study, the pelletized activated carbon (Silcarbon SC40) was tested for water and non-volatile LNAPL (Light Non-Aqueous Phase Liquid; medicinal mineral oil used in this study) determination in a porous medium (silica sand). The experiments were carried out under controlled laboratory conditions. Three different sets of experiments were carried out: (i) the water or LNAPL adsorption from pure media (water or LNAPL liquids); (ii) the water or LNAPL adsorption from pure media (water or LNAPL vapours); (iii) water and/or LNAPL adsorption from the porous material at different sampling intervals. Furthermore, the water/LNAPL contents of the porous media were determined on the basis of the water/LNAPL contents of sampled Silcarbon SC40. The results confirmed the suitability of the Silcarbon SC40 for water/LNAPL sampling from the porous media under laboratory conditions. The method is suitable for detection of water and/or LNAPL in a liquid or gaseous phase and also for water and/or LNAPL quantitative determination. For the quantitative determination a calibration of this method would be required.

Keywords: activated carbon; LNAPL; silica sand; Silcarbon SC40; sampling interval

Organic contaminants are one of the most common substances contaminating the vadose and saturated zones of soil and rock environments. Light Non-Aqueous Phase Liquids (LNAPLs) represent a group of organic substances that are relatively insoluble in water and are less dense than water (US EPA 2012). The LNAPLs move through the vadose zone towards the ground water level; its lateral movement can start even before the LNAPL reaches the ground water level due to the capillary fringe and saturated conditions above the ground water level (COHEN & MERCER 1990). Quite a lot of effort has

been invested in studies of LNAPL behaviour in homogeneous conditions (LENHARD *et al.* 1993; OSTENDORF *et al.* 1993; ECKBERG & SUNADA 1984). However, LNAPL transport within heterogeneous media has not been investigated thoroughly and requires further research (SCHROTH *et al.* 1998). In the past, research was aimed at applications in the petroleum industry. Recently however preferences have changed, and environmental protection has become an important point of interest. That is why new approaches, technologies and models need to be found and applied to this particular aim.

Multiphase flow models which are capable of simulating LNAPL transport have been developed. Such models have been used in site characterization to simulate potential contaminant distribution and in LNAPL recovery system designs. However, multiphase flow is a complex problem, particularly in a heterogeneous environment. Models incorporate simplifying assumptions to facilitate utility. Recognition of the underlying assumptions and evaluation of the site-specific applicability of the model is required. The models require soil and rock hydraulic properties which are also difficult to obtain, and moreover LNAPL spill history, which is often unknown or poorly defined. The quick and efficient collection of a sufficiently large number of samples in the field may be a key improvement in model calibration (US EPA 1996).

DURNFORD *et al.* (1991) concluded that the only method which can be used to determine the amount of LNAPL in soil is an undisturbed soil sampling with subsequent laboratory analysis of extracted LNAPL/water mixture. CAIN *et al.* (2000) employed chemical tracers for detection and LNAPL content estimations mainly in saturated conditions. It was suggested that this method can also be used in unsaturated conditions; however, this statement was not supported by the research results. HARIDY *et al.* (2005) presented an approach for determination of LNAPL/water on the basis of dielectric constant changes in soil using TDR. This method was shown to be relatively costly needing a large calibration data set. Activated carbon is widely used as a treatment medium in many environmental activities (i.e. MALUSIS *et al.* 2010; ÇEÇEN & AKTAŞ 2012). Methods using activated carbon have been successfully introduced. WALLINGFORD *et al.* (1988) used the carbon adsorption method for sampling volatile contaminants as an alternative to relatively expensive portable gas chromatography.

MATULA *et al.* (2008) presented a relatively simple and inexpensive method of LNAPL/water sampling by adsorption on a suitable adsorbent. The amount of adsorbed liquid is detected by weighing and water is separated by evaporation in an oven at 105°C. The main aim of this study is to examine the possibilities of this method by exploring properties of the adsorbent, which is Silcarbon SC40.

MATERIAL AND METHODS

Materials. Medicinal grade white oil Marcol 82 (Esso, Ltd., Irving, USA) was used as a suitable representative of LNAPL substances. It is a colourless,

transparent, odourless and tasteless oily liquid with a superior chemical inertness. Marcol 82 can be used in a variety of applications, cosmetics, food-related and pharmaceutical products. The basic properties of Marcol 82 are as follows: kinematic viscosity (40°C) min 14.5 and max 17.5 mm²/s, dynamic viscosity (20°C) min 27 and max 37 mPa · s, density (20°C) min 842 and max 855 kg/m³, and flash point min 182°C. It was proven by the preceding study of MATULA *et al.* (2008) that this oil is stable within an oven drying temperature of 105°C, thus the ratio of adsorbed LNAPL and water can be determined by weighing after the evaporation of water in the oven (the observed error was < 0.9%). The water used for the experiments was tap water of drinking quality.

Activated carbon Silcarbon SC40 (Brenntag, Ltd., Prague, Czech Republic) is a pelletized carbon with a pellet diameter of approximately 4 mm and a length of approximately 12 mm. The size of the pellets was measured with an accuracy of 0.1 mm using a digital sliding gauge (EXTOL® Premium, Všetaty, Czech Republic) providing an accuracy of ± 0.04 mm. Diameter and length measurements were taken two times, while weighing was repeated five times for each pellet. The basic descriptive statistics for 80 tested pellets is presented in Table 1. The apparent density of activated carbon pellets is 450 ± 25 kg/m³ and the specific surface area is approximately 1100 m²/g. The mass of one pellet is about 0.1 g (depending on its size). Drying out the pellets in the oven to the constant mass preceded all experiments. Enlarged photographs of a Silcarbon SC40 pellet are displayed in Figure 1 (taken by the optical microscope Advance ICD, Bresser Optik, Springdale, USA).

Silica sand with the commercial name ST56 (Sklopísek Střeleč, a.s., Újezd pod Troskami, Czech Republic) was selected as a porous medium. It has a very high content of SiO₂ (98.9%) with small portions of Fe₂O₃, K₂O, Na₂O, CaO and MgO. The middle grain size (*d* 50) is

Table 1. Basic descriptive statistics for 80 pellets of activated carbon Silcarbon SC40

	Diameter (mm)	Length (mm)	Mass of dry pellets (g)
Arithmetic mean	3.97	11.99	0.1096
Standard deviation	0.21	1.91	0.0304
Minimum	3.30	8.60	0.0612
Maximum	4.90	17.75	0.2190
Range	1.60	9.15	0.1578
Median	3.98	11.83	0.1091
Mode	4.00	10.55	0.0927

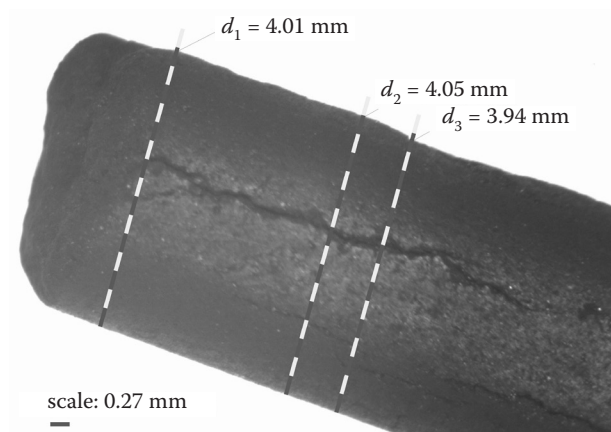


Figure 1. Detailed picture of the activated carbon pellet Silcarbon SC40, enlarged 10×

0.15 mm and the particle density is 2.65 g/cm^3 . All the artificially packed columns for experiments were prepared with the same dry bulk density of 1.48 g/cm^3 , thus with a total porosity of 44.15%.

Test of weighing accuracy and reproducibility.

First of all, a weight test was carried out in order to realize any uncertainty of the following experiments caused by the method itself. All experiments were carried out under laboratory conditions with a constant temperature of 21°C , the weighing was carried out with a precision of 0.0001 g (balance Denver Instrument SI-234A, Orville, USA). 20 randomly chosen dry pellets of activated carbon were weighed; each pellet was weighed 20 times. The pellets were placed into small glass beakers and metal forceps were used for handling the pellets. A variable analysis for deviation from the mean value was carried out within the observed dataset. The average deviation from the mean was 0.000 002 g; the deviations from the mean ranged from -0.0004 g to 0.0005 g for the pellets of cca 0.1 g.

Effect of pellet irregularity. Small irregularities were observed within each particular pellet. The

diameter was not exactly the same throughout the whole length of the pellet and the pellets also quite often had uneven edges (Figure 1). During the following experiments (section 2.4.1) a rather high range of adsorbed liquid was observed: from 55.7% to 100.8%. The diameter of the tested activated carbon pellets (40 pieces) ranged from 3.3 mm to 4.3 mm. An analysis of variance determined a significant decrease in the amount of adsorbed liquid correlated with an increased pellet diameter (Figure 2).

Experiments. Three different sets of experiments were carried out: (i) the water or LNAPL adsorption from pure liquid media (water or LNAPL) in order to observe the maximum water or LNAPL content to be adsorbed; (ii) the water or LNAPL adsorption from water or LNAPL vapours; and (iii) water and/or LNAPL adsorption from the porous material at different sampling intervals in order to observe how the sampling interval can affect the amount of adsorbed water or LNAPL.

Water or LNAPL adsorption from liquid media. An air tight plastic container was prepared in a way that the lower half of the container was filled with water or LNAPL, and 20 pellets of activated carbon were placed within the lower third of the container and were held immersed in water or LNAPL (Figure 3, left part). Initially dry pellets were left in the water or LNAPL for 20 h. After opening the container, the pellets were taken out of the water or LNAPL and the excessive water or LNAPL was drained naturally within a few minutes. This time period was left as short as possible due to possible water or LNAPL evaporation from the pellet. Afterwards the mass of the water or LNAPL contents was determined as a ratio of mass of water or LNAPL to mass of dry pellet of activated carbon.

At the same time, an experiment was carried out in order to observe how the time of exposure could affect the adsorbed amount of water or LNAPL. Ten sampling intervals were chosen (5, 10, 15, 20, 30,

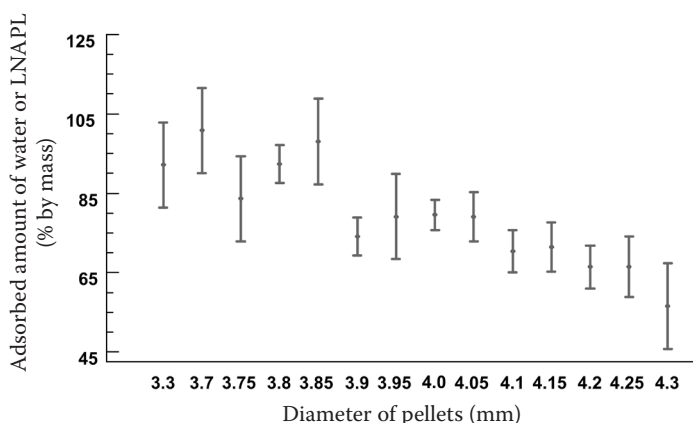


Figure 2. Results of one way ANOVA confirming significant effect of diameter of the activated carbon pellets; means and 95.0% LSD intervals for diameter factor affecting amount of adsorbed water or LNAPL from liquid media

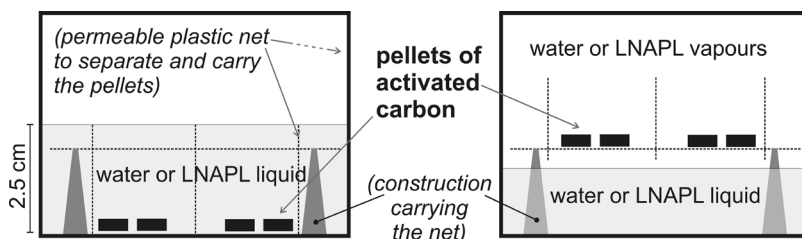


Figure 3. Schema of water or LNAPL adsorption from liquid media (left part) and from vapours (right part)

45 and 60 min; 24, 65 h and 7 days) and 5 pellets of activated carbon for each sampling interval were processed as described above (thus 50 pellets for water and 50 pellets for LNAPL).

Water or LNAPL adsorption from fully saturated water or LNAPL vapours. An air tight plastic container was prepared in a way that the lower third of the container was filled with water or LNAPL, while 20 pellets of activated carbon were placed within the upper part of the container, which was saturated with the water or LNAPL vapours (Figure 3, right part). The dry pellets of known mass were left in the vapours for 72 h and after opening the container they were weighed immediately. The mass of the water or LNAPL contents was determined as a ratio of mass of water or LNAPL to mass of dry pellet of activated carbon; the procedure was the same as in the first type of experiment.

Water and/or LNAPL adsorption from the porous material at different sampling intervals. The silica sand of known water, LNAPL and water + LNAPL content was carefully prepared, well mixed and packed into three plastic containers (dry bulk density 1.48 g/cm^3). The liquid content was 20% by mass and for the mixture of water + LNAPL a ratio of 1:1 was used. The methodology and materials follow MATULA *et al.* (2008). The chosen material (silica sand) and the way of preparation ensure homogeneity and prevent any preferential flow. The scheme of the experimental

setup is in Figure 4. The pellets of activated carbon were placed into the sampling point using a metal lab-built sampler and left there for the time of the preset sampling interval (5, 10, 15, 20, 30, 45 and 60 min). Five replications for each sampling interval in each container were carried out. Additionally, this set of experiments enables the checking of whether the activated carbon is sampling the given water and/or LNAPL content.

RESULTS AND DISCUSSION

Water or LNAPL adsorption from liquid media. The capacity of activated carbon pellets to adsorb water or LNAPL was tested. The 20 pellets of activated carbon immersed in water for 20 h reached 80.5% by mass on average, while those immersed in LNAPL reached 75.1% by mass. Basic statistics for the adsorption from pure liquid media is presented in Table 2. The pellets can adsorb both liquids in a similar way; however, the adsorption of LNAPL from pure media is slightly lower and with a higher range than the adsorption from water. The high range of observed values can be caused by different diameters of pellets which ranged from 3.3 to 4.3 mm (described above).

Figure 5 shows how the time of exposure can influence the adsorbed amount of water or LNAPL. The pellets of activated carbon which were immersed in water adsorbed about 91% of the maximum water

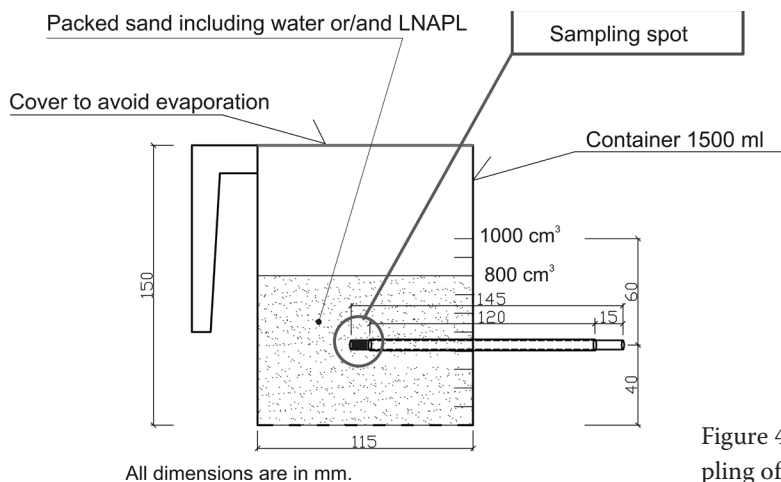


Figure 4. Schema of the experimental setup for sampling of water and/or LNAPL from porous material

Table 2. Basic statistics processed for adsorption of water or LNAPL from pure liquid media or vapours (in % by mass)

	Adsorption from liquid media		Adsorption from vapours	
	water content	LNAPL content	water content	LNAPL content
Arithmetic mean	80.5	75.1	37.3	2.7
Standard deviation	10.9	11.6	8.7	1.2
Median	81.0	73.9	36.3	2.2
Minimum	55.7	56.0	20.0	1.5
Maximum	94.7	100.8	55.5	5.6
Range	39.0	44.8	35.5	4.1

content within 5 min. The maximum water content was 73% by mass and was reached after 24 h. It is slightly less than what was observed in the previous experiment (with 20 pellets for 20 h); however, there were only 5 replicates carried out for each time interval and the value is within the borders of the standard deviation (see in Table 2). The pellets which were immersed in LNAPL adsorbed about 62% of the maximum LNAPL content within 5 min. The maximum LNAPL content was 78% by mass and was observed after 7 days of continual exposure to the LNAPL liquid. However, after 24 h 75% by mass of the LNAPL content was observed, which is in agreement with the previous experiment. The slower adsorption of LNAPL can be explained by the general characteristics of this liquid, mainly due to its higher viscosity.

Water or LNAPL adsorption from fully saturated water or LNAPL vapours. The pellets of activated carbon were able to adsorb water from the water vapours quite well; the mass water content of the pellets was determined to be 37.3% by mass on average (see the basic statistics in Table 2). The adsorbed

amounts of LNAPL vapours were significantly lower, only 2.7% by mass. This fact reflects the inert and non-volatile properties of the tested representative of LNAPLs. More importantly, it was proven that even very small amounts of LNAPL can be sampled by adsorption on the activated carbon. The graphical overview of sampled liquid contents is provided in Figure 6.

Water and/or LNAPL adsorption from the porous material at different sampling intervals. The influence of exposure time of the activated carbon pellets on the sampled liquid was observed. Furthermore, there is the idea that the real liquid content can be measured in a low-cost manner using activated carbon pellets. Activated carbon is being used for this purpose, for example, FACT (FLUTE Activated Carbon Technique) is a method developed by FLUTE (Flexible Liner Underground Technologies, Ltd.L.C.) for mapping the distribution of contamination in the porous and fracture system of a borehole wall (FLUTE 2010).

However, the results show a significant effect of selected sampling intervals on the amount of ad-

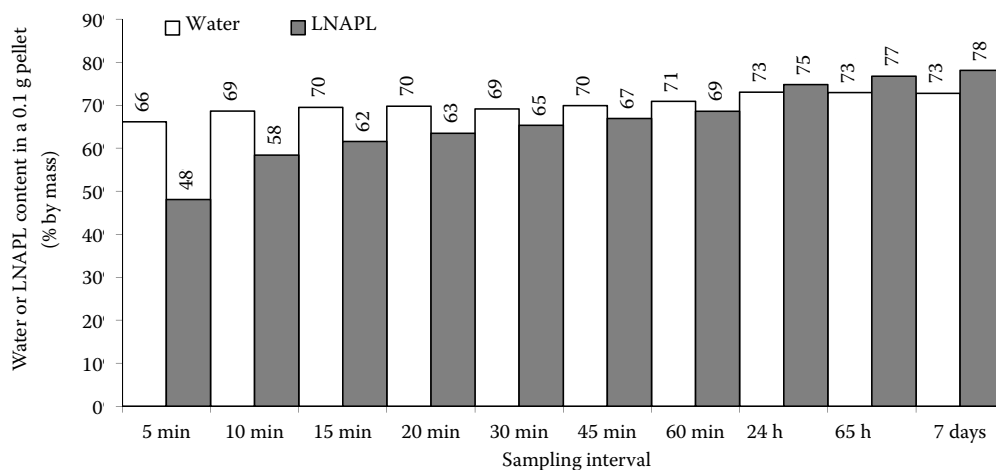


Figure 5. Adsorbed water or LNAPL from pure liquid media after different time of exposure

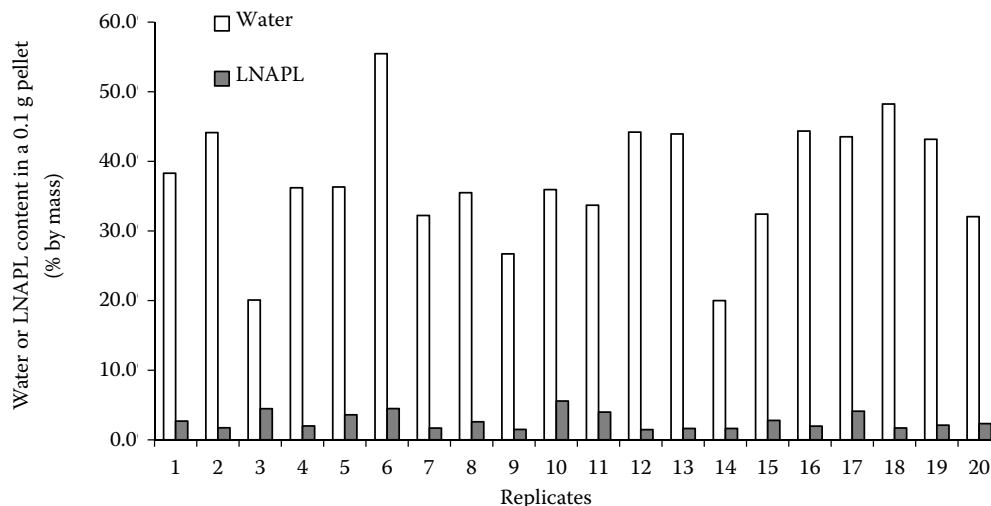


Figure 6. Adsorbed water or LNAPL from water or LNAPL vapours

sorbed water and/or LNAPL from porous media. Firstly, the adsorption from porous media with 20% by mass of water or LNAPL content was evaluated. This means a 3-phase unsaturated system including a solid, gaseous and liquid phase. Although an unsaturated system including only a solid, gaseous and LNAPL phase is not found in natural contaminated porous systems, it was included in this detailed testing. The sampling from unsaturated porous media shows different results than the sampling from water or LNAPL liquid media (Figure 7). For all sampling intervals, less water than LNAPL was sampled. A linear trend was observed during the first 60 min for both liquids. The real LNAPL content of 20% by

mass was reached after cca 35 min, while the real water content of 20% by mass was reached after cca 50 min. The graph shows averaged values of 5 replicates with a standard deviation and it is apparent that the standard deviation of LNAPL adsorption is rather high. This may be caused by the very small data set and higher variability within the LNAPL data observation.

The experiment with the water and LNAPL mixture had rather different results from those with a pure medium of water or LNAPL (Figure 8). The amount of water in the water + LNAPL mixture (10 + 10% by mass) was sampled 3–4 times more than the amount of LNAPL. The level of water saturation (10% by

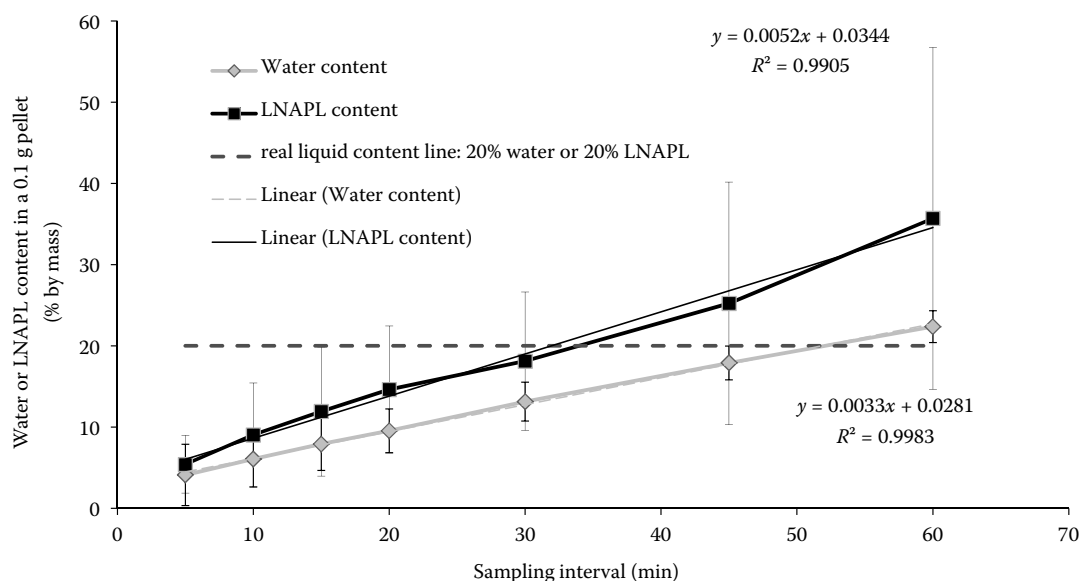


Figure 7. Amount of adsorbed water or LNAPL from the porous material: 20% by mass of total liquid content (2 separate experiments). Average values; bars are standard deviations

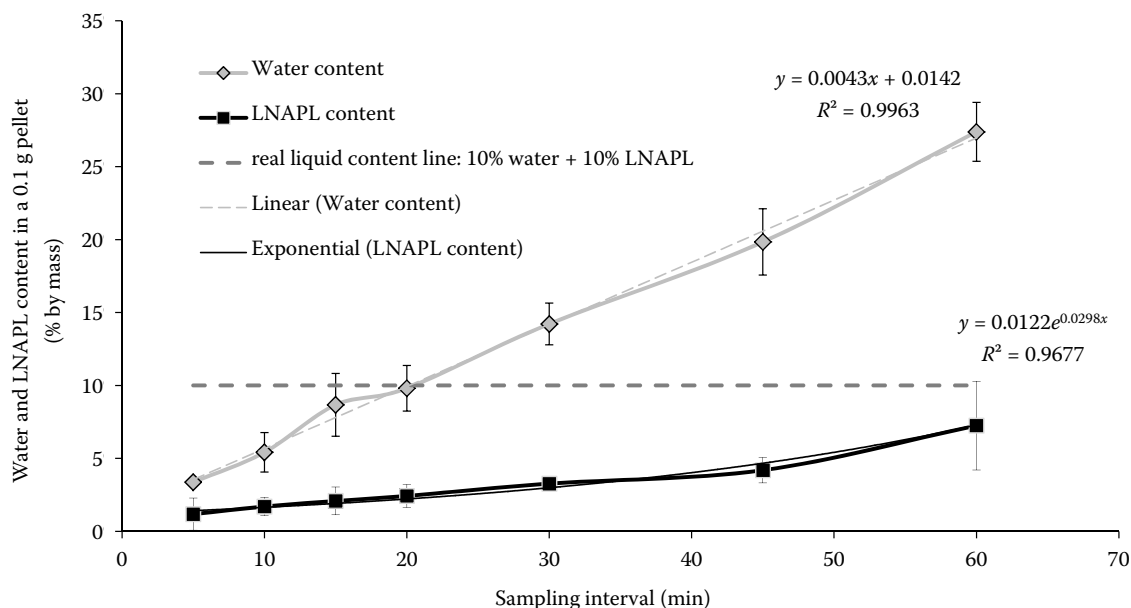


Figure 8. Amount of adsorbed water and LNAPL from porous material: 20% by mass of total liquid content (10% water + 10% LNAPL). Average values; bars are standard deviations.

mass) was sampled after cca 20 min, while the level of LNAPL (10% by mass) was not reached until 60 min. On the other hand, the standard deviation of these observations is acceptably smaller.

CONCLUSIONS

This experimental study investigated in detail an inexpensive method of LNAPL/water sampling by adsorption on a suitable adsorbent as proposed by MATULA *et al.* (2008). The possibilities of this method were widely examined by exploring properties of the adsorbent, which is commonly available: pelletized activated carbon with the commercial name Silcarbon SC40. The amount of liquid adsorbed in the oven-dried pellets was detected by precise weighing and the water was separated by evaporation in an oven at 105°C. Thus this method is applicable for non-volatile LNAPLs only.

The amount of adsorbed liquids was determined as percent by mass. Even though the cylindrical shape of the pellets would suggest a possible recalculation from mass water/LNAPL contents into volumetric content, due to the uneven edges and slightly different diameters in different parts of the pellets, additional error should be incorporated into the water/LNAPL determination. That is why the mass water/LNAPL contents were calculated and discussed.

Different experiments were carried out, as described in section Material and Methods. The experiments dealing with pure media of water or LNAPL are neces-

sary for a better understanding of the whole process of adsorption in the pellets of activated carbon. However, the proposed method is supposed to be used for sampling in porous media, soil. Based on the experimental results, the following conclusions can be declared:

Activated carbon can be considered as a suitable adsorbent for water and LNAPL sampling for the method suggested by MATULA *et al.* (2008). Activated carbon is able to sample even very small amounts of water/LNAPL originating from water/LNAPL vapours. The diameter of the pellets of activated carbon was found to be a significant factor affecting the amount of adsorbed liquids. Thus activated carbon in the form of pellets of exactly the same dimensions is required in order to obtain comparable results. Moreover, specific calibrations need to be carried out, before the method can also be applied to quantitative water/LNAPL determination. The time required for the pellets of activated carbon to adsorb the representative amount of water and/or LNAPL was tested. Based on the results, sampling intervals in further experiments can be optimised.

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