Geochemical and environmental geological assessment of experimental hydrocarbon contamination modeling results

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Research backgrounds and aims of the dissertation

Hydrocarbon contaminations which are occurring in the geological environment are very complex, since the hydrocarbons undergo numerous changes in the subsurface media. Identifying possible source of the pollution is getting more and more difficult by time, due to various natural attenuation processes. These are under different factor’s influence depending on the contamination transport processes. Degree of the changes considerably depends on the composition of the hydrocarbon and the environmental circumstances. Alterations in the concentration of hydrocarbon components, in their mobility and quantity are basically determined by the age of the pollution and the distance from the source.

Remarkably large numbers of researchers are focusing on hydrocarbons in raw material point of view, while substantially less deal with geochemical and environmental geological investigations of contaminations, which are derives mostly from oil industrial activities (e.g. production and transportation). Organic geochemical methods of pollution examinations, application possibilities of light hydrocarbon analyses and national practical methods of site investigations in case of hydrocarbon contaminations are summarized in my dissertation. I have paid significant attention to systematization of the preliminary knowledge of natural attenuation processes connecting to my research, namely volatization and sorption of organic compounds, hydrocarbons and gasoline type hydrocarbons.

Most publication which can be found in the literature is not qualified for modeling natural attenuation processes, only for monitoring the contaminant transport. Majority of these is short term and is directed towards observation of biodegradation. Generally natural attenuation processes have been noticed under natural circumstances, significantly less laboratory experiment have been conducted, because simulation of the contaminant transport of unsaturated zone is very difficult in laboratory. Important advantage of laboratory experiments over field modeling is the knowledge of initial hydrocarbon composition, which makes drawing more exact and reliable conclusions easier.

Volatilization and gas transport of VOCs are the basis for remediation technologies, such as soil vapor extraction, soil venting and air sparging (Kim et al. 2005), consequently knowledge of the volatility of the organic compounds is important for understanding their fate in subsurface media. Gas phase migration of hydrocarbons can be very hazardous threat for the subsurface geological surroundings, because their diffusion in air is on the order of more times larger than their diffusion in water. Little is known about sorption of VOCs, since most of the hydrocarbon sorption studies are concerned with fluid-mineral interaction and natural clay sorbents are only rarely applied. There is very little information about sorption during upward migration of gas phase components. Preliminary researches are deficient in observations and modeling in low relative humidity environments, particularly in case of multicomponental hydrocarbon contaminations. Less information about the natural attenuation processes can be obtained with regard to the volatility of hydrocarbons, nevertheless together with biodegradation mainly are responsible for natural attenuation of the hydrocarbons.

Gasoline type hydrocarbons in the subsurface geological media often mean serious problems, due to their high mobility and numerous high health-risky compounds contained. On grounds of problems arise up in connection with site investigations and remediation, as well as preliminary knowledge about natural attenuation processes of polluted areas have been account for working out a laboratory model, which can give new detailed information regarding gaps of literature and natural attenuation of gasoline type hydrocarbons.
Considering the importance of volatility in processes proceeding in the nature and the very little knowledge about linking long term modeling, I have regarded reporting new results about volatility of gasoline type hydrocarbons as main research aim. Moreover I have endeavored providing new information about sorption features and hereby contribute to possible solutions of the problems coming up during site investigations and remediation of light hydrocarbon contaminated geological media.

Main research aims of the dissertation were the followings:

- Design and execution of a special long term column experiment, which can provide continuous leaving of volatile components of the selected gasoline type hydrocarbon, without any other attenuation processes having effect on changing of the fluid phase.
- Ensure the systematic sampling with minimal loss of material during the column experiment, from fluid phase and if required from vapor-space, air-space and soil.
- Determine the quantity of total hydrocarbons, which have left the fluid phase, as a function of the quality and quantity of the filling materials.
- Design volatility trends with reference to every hydrocarbon component, that is measurable in the initial composition or probable will be measurable due to their relative enrichment.
- Gain information regarding to the composition changing of the selected hydrocarbon type in the fluid phase as a function of time.
- Ensure the possibility of sorption of hydrocarbon components by alternate materials and design the quantitative analysis of the sorbed hydrocarbons.
- Determine the quantity of sorbed hydrocarbons and assess it as a function of time, quality and quantity of the filling materials.
- Determine layer by layer the quantity of sorbed hydrocarbons of the filling materials placing above the fluid phase, and investigate their correlations.
- Measure and quantify the components that leaved the fluid phase and are not sorbed on the filling materials.
- Determine layer by layer the quantity of free gas phased hydrocarbons of the filling materials placing above the fluid phase, and investigate their correlations.
- Comparative assessment of the results derived from analyses of samples of different phases (fluid, gas and solid).
Materials and methods

During the design and execution of the special column experiment lasting for near two year, aim was to provide continuous leaving of volatile components of the selected gasoline type hydrocarbon, without any other attenuation processes having effect on changing of the fluid phase. For the sake of the aim, special glass columns have been constructed.

Clays from the Kiscell Clay Formation and commercial sands were applied for filling materials. The modeled contaminant was a gasoline type hydrocarbon. The special glass columns were placed in an isolated room, where modeling was done in constant pressure and temperature circumstances.

The applied geological methods were the followings:

- Geological field survey, sampling for modeling
- Testing for selecting the most suitable research materials
- Gas chromatographical analyses (GC-FID and ATD-GC-MS)
- XRD investigations
- Pyrolysis analyses
- Thermal analyses
- Carbonate-content measuring (with autocalcimeter)
- Mangane-content measuring (after sample preparation in accordance with MSZ-21470-50 standard, on grounds of MSZ-1484-3: 2006 standard, with F-AAS technique)
- Adsorption capacity investigations (with modified Mehlich method, on grounds of MSZ-08-0215-78 standard)
- Size distribution analyses
- Investigations with stereo- and polarizing microscope
- Density determination of fluid phase samples (with areometric method, on grounds of MSZ AN ISO 3675:2000 standard)
- Determination of distilling characteristics (with automatic distillator, on grounds of MSZ EN ISO 3405:2000 standard)
- Determination of total sulfur (on grounds of MSZ-12697-2002 standard).

Quantities of the sampled materials were determinate by applied techniques. These were identical quantities during the whole time of modeling. 500 ml from air space, 100 µl from vapor space, 0.3 µl from fluid phase and 0.4 g from fillings were collected for analyses.

I registered the level of fluid in the course of the modeling lasting for 640 days. Samples were collected from fluids every week at the first period, than one or more occasion every month, on the basis of analytical results. Vapor space, air and filling sampling were done biannually. Air and filling samples were collected layer-by-layer at the end of modeling, as well.
New scientific results

1. I succeeded in planning and executing a special column experiment. The experiment rendered continuous leaving of the volatile components of the gasoline type hydrocarbon possible, during close two years. Altering of the fluid phase was not influenced by any natural attenuation processes apart from volatilization. The available soil models for modeling were as follows: 50 cm sandy, 50 cm sandy with clay-cap, 100 cm sandy, 100 cm sandy with clay-cap, 150 cm sandy, 150 cm sandy with clay-cap, 200 cm sandy and 200 cm sandy with clay-cap. The volatile components of the used hydrocarbon could be transported only in one direction (upward through the fillings), therefore the investigation of the sorption of components was also possible. In the course of the modeling, which was done in constant pressure and temperature circumstances, the systematic sampling with minimal loss of material was ensured.

2. I have determined the volatilized and the remainder hydrocarbon quantities with volumetric calculation by altering the fluid levels. I have found that the quantity of filling materials placed above fluid phases (i.e. “thickness” of the layer) has greater effect on volatilization, than their material characteristics. I have established that at the end of the experiment more than half of the initial hydrocarbon volatilized, due to the volatility of the individual constituents. I have found that the volatilization was very effective in the first year; significant loss of the fluid phase was seen mainly in the first quarter. More than half of the total loss occurred during the first six months. By this time, differences caused by diverse fillings decreased and length of the columns (i.e. thickness of different fillings) became an increasingly determinative factor of volatilization. Decreasing the quantity of more volatile compounds significantly affected the total loss.

3. I have elaborated volatility rates and trends by the statistical treatment of 29 016 GC-FID analytical data collected during the modeling. I have calculated the volatility rates for every compound with the formula presented in the experiment of CANIPA-MORALES et al. (2003). On the basis of my results, the data of volatility rates, which were thinned out on a quarterly basis, can yield significant information. Three groups could be distinguished by volatility rates and by representing graphically the altering of fluid composition. On the basis of volatility rates and trends pertaining to single components, the length of the fillings (i.e. in fields the depth of contamination) appeared to be very important in the pure volatilization process, while the quality characteristics of fillings (the geological materials) did not prove to be a determining factor. Variations in losses due to volatilization were directed by the individual properties of the constituent compounds.

4. I have provided new information about temporal changes in the composition of the modeled hydrocarbon type. The changes due exclusively to volatilization affect mainly naphthene content, while the quantity of aromatics and paraffins was gradually and relatively enriched to a lesser extent. The quantity of aromatics proved to be more stationary than the quantity of paraffins. Octane and aromatic compounds were found to have changed the most.

5. I have discerned three typical areas of changing by illustrating the changes in the initial composition of the fluid phase in a Thompson diagram (THOMPSON 1987). These areas
referred to changes in volatility rates and the duration of modeling. The volatility of hydrocarbons with a lower carbon number charted out a new direction in the diagram, which is used to classify hydrocarbons according to alteration processes, namely evaporative fractionation, maturation, extraction of aromatics and biodegradation. After the most volatile components disappeared, the proportions were established in accordance with the expected evaporative fractionation vector. On basis of the results, changing the toluene/n-heptane ratio is not sufficiently sensitive in and of itself for volatilization processes. Rather, the loss of components with a lower carbon number resulted rather in altering the n-heptane/methylcyclohexane ratio. Systematic increasing of toluene/n-heptane and methylcyclohexane/ n-heptane ratios with growing loss of light hydrocarbons (Thompson 1987) could be seen only after about a year and a half of volatilization, by which time compounds lighter than pentane volatilized from the fluid phase.

6. I have managed to find the effect of volatilization on altering of main hydrocarbon parameters (density, initial and utmost boiling-points). On the basis of examining the fluid phase, the application of half-lives can be misleading in modeling the transportation of contaminants when planning remediation.

7. A new analytical method with applying ATD-GC-MS was managed to come up, in order to investigate the hydrocarbon content of filling samples. This was necessary because previously only gas phase samples collected onto sorbents were measured, and the clay mineral content of the samples could cause significant problems during the analyses. By adopting the new measuring method, the extraction of samples with organic solvent was avoidable and the determination of components lighter than C9 was also possible. The latter provides great advantage over TPH measuring.

8. I have managed to identify the components of sorbed phase and assessed their distribution in function of modeling time and the properties of fillings. For this purpose I have processed 12,870 ATD-GC-MS data, pyrolysis results of 36 samples, adsorption capacity values of 92 samples, as well as the results of XRD and TPH analyses. On basis of the results I found that sorbed hydrocarbons by top-layers are in inverse proportion to the thickness of fillings. Variations in total sorbed hydrocarbon quantities confirm the assumption of Morrisey and Grismer (1999), that because adsorption rate depends on diffusion, a thin sample will, (in real time) adsorb a greater percentage of material by weight than a system with a larger path length.

9. On the basis of my results, the sorbed hydrocarbons are mainly paraffins and aromatics, while napthenes rarely occur. After half a year, n-C7 was found to be the lightest and C11 the heaviest constituent. The range enlarged continuously, it was possible to measure n-C6 and C12 after one year, while at the end of the modeling n-C5 and C15 were already measurable in some places in clays. It was possible to detect hydrocarbons after half a year only in clay layers and in every sample at the end of modeling. Quantity of sorbed compounds decreased with growing carbon numbers. Models with clay-caps contained larger amounts of hydrocarbons also in deeper layers compared to their sandy pairs (totally three to six times more quantities). The reason for this is presumably the good sealing property of the clay, therefore volatilized components remained in the pores among sand particles or sorbed onto the individual constituents. Quantity of sorbed hydrocarbons is the greatest in the vicinity of the fluid phase. Fine tendencies, dependent on depth, can be seen mostly in case of
cyclohexane, benzene, as well components with slightly larger carbon number (e.g. \( C_{10} \), \( C_{11} \), \( C_{12} \) and \( C_{13} \)). These clearly show the effect of less volatility.

10. On grounds of pyrolysis analyses, samples from different depths did not show measurable hydrocarbon potential besides the clay layers. S1 and S2 peaks are detected in measuring clays, which shows their hydrocarbon sorption and the lowest sorption capacity of sand layers. Results of pyrolysis and ATD-GC-MS analyses were in close correlation in the case of clays. Connection was observable between TOC and hydrocarbon content measured with different methods, between CEC and hydrocarbon content respectively.

11. By comparing the results of detailed analyses, the clay and the sand mainly adsorbed the gas phase hydrocarbon components; while absorption was not verified by X-Ray powder diffraction investigations.

12. I have managed to identify the components that volatilized from the fluid phase and did not sorb onto the fillings. In order to interpret the results of the free gas phase I have processed 12 402 ATD-GC-MS data. In the case of free gas samples also, the detected hydrocarbons in the top-layers are in inverse proportion to the thickness of fillings. A greater concentration of free gases was measurable above clay-caps in general, which can be explained with a higher capillary effect above the clays. On the basis of my results the total amount of free gases increases in direct proportion to the thickness of fillings.

13. I have found a smaller proportion of paraffins in free gas phase than in the initial composition, while the quantity of aromatics and napthenes was slightly larger. I have observed an increase in the proportion of hydrocarbons with larger carbon numbers as time progressed. This is attributable to the more moderately volatile compounds, which go out into the pore air of samples later. The hydrocarbon with the smallest carbon number was the n-pentane during the whole time of modeling. The component with the largest carbon number was \( C_9 \) after half year, \( C_{12} \) after one year and \( C_{14} \) at the end of modeling. Concentrations of the individual hydrocarbons increased continuously with modeling time and as a function of distance from the source of contamination.

14. I have observed good correlation between the distributions and concentrations of free gas components of the columns with different parameters. Layer-by-layer compositions are in agreement, the components are in the range of \( C_5 \) and \( C_{13} \). On the basis of the fingerprints of the samples it is possible to infer the composition of initial fluid phase. Little difference can be seen as a function of the length of fillings, in other words, as a function of the distance from the source of contamination. That is, on the basis of the results, the measurable amount of free gases is influenced by the depth of contamination and the distance from its source.

15. I completed the comparative assessment of the results derived from the analyses of samples from different phases (fluid, gas and solid). On the basis of this assessment, the best practice for identifying the source of a gasoline type contamination is a joint analysis of sorbed and free hydrocarbons of the soil samples, while the best way to monitor a contamination is to analyze free gas components. It is worth applying the analyses together, because a different range of the initial fluid phase can be measured from the free gas and the sorbed phase. The ratio of the lightest hydrocarbons in the total amount of hydrocarbons may indicate the time when the contamination occured.
Application possibilities of the results

The results presented in the dissertation are partly basic researches, partly utilizable directly for industrial purposes, because these can provide new aspects for the research of soils contaminated with light hydrocarbons. The results can contribute to the interpretation of material transport processes of the hydrocarbon contaminated soils and their remediation planning. The concrete industrial application possibilities are very ramifying, so it is practical to showing them in list.

1. The ATD-GC-MS technique is applicable for qualitative and quantitative analyses of gasoline type hydrocarbon contaminated soils. It is particularly suggestible for in order to acceleration of processes of detailed environmental site investigations and/or remediations, after all immediate analyses of the samples decrease time (and cost at the same time) for the laboratories. The analytical results are both fast and both exact, accurate, as well mainly in case of free gas investigations are well comparable.

2. On ground of results presented in the dissertation, good conclusions can be deducted from hydrocarbon composition of air samples collected onto sorbent tubes to the composition of the contaminant.

3. Along spillage from drill pipes, where theoretically we can have knowledge of the initial contaminant composition, we can estimate the age of contaminant by joint analyses of sorbed and free phase of the samples.

4. It is possible to infer source of contamination by analyses of volatile components of subsurface free gasoline type hydrocarbons, derived from subsurface product pipes.

5. Sorption of gas phase volatile compounds by soils in vicinity of leakage can be much more than it is assumed by simple models. Consequently results of the modeling can be worth to apply for improving input data of transport models.

6. Results connected to gas phase processes can help both in forecasting of volatile organic compound transport, both in utilization of passive volatilization and planning remediation by soil venting.

7. The presented method can prove possibility for detection light hydrocarbons from surface/subsurface samples, whether from samples containing significant amount of clays.

8. The completed laboratory modeling can ensure considerably quantity of data for correlation of contaminations with different phases, and for working out limit values for the individual hydrocarbon components occurring in soil air.
Published literature

Publications in scientific journals

1. TÓTH, J. 2009: Light hydrocarbon sorption properties of clays from the Kiscell Clay Formation. Mineralogia, in press

2. SZABÓKI-KNAPP, E. - TÓTH, J. 2009: Possibility for investigation of light hydrocarbon content in soil samples: environmental approach. MOL Scientific Magazine, 2009/1, pp. 89-95


Publication in conference proceedings


Abstracts in conference volumes


4. TÓTH J. 2008: Gazolin típusú szénhidrogénnillékonysági és szorpcíos tulajdonságainak vizsgálata. A XXXIX. Ifjú Szakemberek Ankétjának kiadványa, MGE-MFT, Baja, pp. 36-37


**Other publications**

**Publication in scientific journals**


**Chapter of book**


**Publications in conference proceedings**

1. **TÓTH J.** 2005: Földtani tanösvény lehetősége az Orfű környéki karsztterületen. *Adsumus IV. Tanulmányok az VI. Eötvös Konferencia előadásaiból, Argumentum Kiadó, Budapest, pp. 185-204*


**Abstracts in conference volumes**


Conferences related to the topic of the dissertation

1. 19th Annual Goldschmidt Conference, Davos, Svájc, 2009

TÓTH, J.: Assessing Natural Attenuation of Gasoline Range Hydrocarbons Using a Multicomponental Model

2. 2nd Central-European Mineralogical Conference and XV Meeting of the Petrology Group of Mineralogical Society of Poland, Szklarska Poręba, Lengyelország, 2008

TÓTH, J.: Sorption of the volatile hydrocarbons compounds by Oligocene clay

3. X. Bányászati, kohászati és földtani konferencia, Nagyszeben, Románia, 2008

TÓTH, J.: Role of natural attenuation processes in case of hydrocarbon-contaminations (Természetes koncentrációcsökkentő folyamatok szerepe szénhidrogén-szennyeződések esetében)

4. XXXIX. Ifjú Szakemberek Ankétja, Baja, 2008

TÓTH J.: Gazolin típusú szénhidrogén illékonysági és szorpciós tulajdonságainak vizsgálata

5. IV. Geotudományi Ankét, Nagykanizsa, 2007

TÓTH J. – KNAPP E.: ATD-GCMS alkalmazási lehetőségei környezetvédelmi területen

6. IV. Geotudományi Ankét, Nagykanizsa, 2007

TÓTH J. – SZEKSZÁRDI A.: Szénhidrogén megkötési vizsgálatok hazai oligocén korú agyagokon

7. 19th General Meeting of the International Mineralogical Association, Kobe, Japán, 2006

TÓTH, J. – DR. KÁLLAI, M - LUKÁCS, A.: Gasoline pollution modelling in laboratory

8. X. Geomatematikai Ankét, Mórahalom, 2006

TÓTH J. – LUKÁCS A. - DR. KÁLLAI M.: Környezetgeokémiai modellkísérletek eredményeinek statisztikai értékelése

9. XXXVII. Ifjú Szakemberek Ankétja, Balatonkenese, 2006

TÓTH J. – DR. KÁLLAI M.: Gazolin-szennyeződés laboratóriumi modellezése

10. V. Eötvös Konferencia, Budapest, 2004

TÓTH J.: Környezetvédelmi állapotfelmérés készítése szénhidrogén-szennyeződések esetében

11. IX. Bolyai Konferencia, Budapest, 2004

TÓTH J.: Környezeti állapotfelmérés készítése szénhidrogén-szennyeződések esetében