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The influence of atmospheric conditions on the migration of diesel fuel spilled in soil

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Abstract: The most common chemical's spills in typical transportation accidents are those with petroleum products such as diesel fuel, the consequence of which is an extensive pollution of the soil. In order to plan properly fuel recovery from the soil, it is important to gain information about the soil depth which may be affected by pollutant and to predict the pollutant concentration in different soil layers. This study deals with the impact of basic atmospheric conditions, i.e. air temperature and humidity on the diesel fuel migration through the soil. The diesel fuel was spilled into columns (L = 30 cm; D = 4.6 cm) filled with sandy and clay soil samples, and its concentrations at various depths were measured after 11 days under various air temperature (20 and 40°C) and relative humidity (30–100%) conditions. The effects observed were explained by understanding physical processes, such as fuel evaporation, diffusion and adsorption on soil grains. The increase in temperature results in higher fuel evaporation loss and its faster vertical migration. The relative humidity effect is less pronounced but more complex, and it depends much on the soil type.

Introduction

Oil derivatives, besides pesticides, represent the main pollutants in all three aspects of living environment: water, air and soil. One of the most important crude oil derivatives is diesel fuel, widely used in most types of transportation. Diesel fuels are complex mixtures of a large number of hydrocarbons with C_8 to C_{26} carbon molecules, as well as organic compounds of sulfur, nitrogen and oxygen. According to the Globally Harmonized System of classification and Labeling of Chemicals (GHS), diesel fuels are considered as environmentally hazard materials, since they are expected to be harmful for water organisms in concentrations of 1–100 mg l^{-1} (Islam et al. 2015).

Among all aspects of the environment, soil is certainly the most complex, due to its composition and physico-chemical characteristics, as well as the interactions with pollutants. Previous research was mainly directed towards the impact of petroleum derivatives on water and air, and to a lesser extent on soil (Zawierucha et al. 2014, Halmemies et al. 2003).

Diesel fuel may be found in the soil as a result of accidental spills. After the spillage, there is a vertical transport of the fuel under the influence of gravity and diffusion forces. Before it reaches the water-saturated zone, part of the fuel is adsorbed to soil particles, part dissolves in water retained between particles, and a part evaporates (Szymański and Janowska 2016, Mao et al. 2015, Rosik-Dulewska et al. 2012). If the appropriate remediation is not implemented immediately in the first few days after the spilling, there is little chance for degradation of fuel by natural microbiological or chemical degradation. Instead, the fuel loss mainly occurs due to evaporation, when the concentration of penetrated fuel may be decreased by even 5–70% (Leij et al. 2011, Roon et al. 2005).

Therefore, it is clear that atmospheric conditions, such as air temperature, humidity and rainfall, exert a significant influence on the pollutant behavior in the soil. However, there is scarce information about the correlation between climate conditions and fuel penetration in soil, in temperate climatic zone, such is Balkan Peninsula. For this reason, the scope of this article is to determine the effect of air temperature and humidity on the migration of diesel fuel through the soil.

Materials and methods

Soil characterization

Two soil types were considered in the investigation, namely sand and clay, both collected in the vicinity of Belgrade, Serbia. The sand was of medium grade, quality "0" under construction numeration, with the average grain size of 0.1 mm. The clay after collecting was powdered to a particle size less than 0.001 mm.

The organic content of the soil was determined as a difference between the mass of the dry soil and the mass of the ashed soil after burning for 12 h at 440°C, according to ASTM D 2974 – Standard test methods for moisture, ash, and organic matter of peat and organic soils. The soil was collected at the depth of 100 cm from the surface, so the organic matter content was very low: approximately 200 mg kg^{-1} for sand

and 300 mg kg^{-1} for clay, and it could not influence the soil properties significantly.

Soil column preparation

In order to prepare soil samples (Fig. 1), pipes with 30 cm length and 4.6 cm diameter (500 cm^3 volume) were filled with soil, which had been previously dried at 105°C for 8h in the drying oven. Both sand and clay were filled using the same pressure, so that the bulk density of the soil in each column was 1.7 g cm^{-3}, i.e. weight of the soil samples was 850 g. The pipes were made of chlorinated PVC designed for chemical waste drainage systems, to avoid possible interactions with oil hydrocarbons.

Since the density was constant in all columns, the soil permeability was related to the soil grain size. Empirical equations for predicting permeability from grain size, proposed until now (Cheng and Chen 2007, Odong 2008), have suggested that the coefficient of permeability is proportional to the squared value of grain size. In this work, the average particle size of sand was 100 times higher than for clay, so it may be calculated that the permeability coefficient in sand columns was 10,000 times higher than in clay columns.

Diesel fuel was poured uniformly to the soil surface at a level of 10 dm^3 m^{-2}. This application level was based on previous studies where diesel fuel (10 dm^3 m^{-2}) spilt on soil surfaces was considered as a moderate spill.

For measuring temperature influence, the filled columns were then placed in temperature chamber (Heraeus type) where the air humidity was kept constant (absolute humidity 15.3 g m^{-3}) at various temperatures from 20 to 40°C. On the contrary, when the influence of air humidity was examined, the temperature in chamber was kept constant at 40°C, at different relative humidity values, from 30 to 100%.

Diesel fuel concentration analysis

To analyze the fuel migration in the soil, the samples of contaminated soil were collected 11 days after the spillage, at four different depths: 0–5 cm, 5–10 cm, 10–15 cm, and 15–30 cm. The 11 day period was chosen for sampling because earlier research shows that the most significant physical changes of the pollutant are observed between 10 and 15 days, while after 15 days, a significant biodegradation occurs (Zawierucha et al. 2014). The fuel content was determined by following ISO 16703:2004 – Determination of content of hydrocarbon in the range C_{10} to C_{40} by gas chromatography. Approximately 4g of each contaminated sample was extracted with 20 ml of methylene chloride. The soil-solvent mixture was mixed for 3×15 min with a wrist-action shaker to partition the diesel fuel components to the solvent phase. A 10 ml portion of the solvent was then transferred into a clean glass-barrel syringe for analysis.

The concentration of diesel fuel in soil was determined by a Varian 3400 Gas Chromatograph (GC) with a flame ionization detector using a DB1 capillary column. The sample injection volume was 0.3 µl. The initial oven temperature was 80°C held for 1 min, and ramped to 360°C at 20°C min^{-1}. The total retention time was 10 min. The injector temperature and detector temperature were 300°C and 350°C, respectively. High-purity N_2 gas was used as the carrier gas.

Diesel fuel concentration in the extracted samples was expressed as total petroleum hydrocarbons in soil, TPH, as mg_{fuel} kg_{soil}^{-1} (Markowicz et al. 2016). Quantitative conversion of GC area counts data to TPH was performed by preparing standards of refined diesel fuel and establishing the relationship between the mass of diesel fuel injected and the area count response. The diesel fuel at five different concentrations (800, 1700, 2500, 3700, and 4400 µg ml^{-1}) in methylene chloride was used as the calibration standards for estimating TPH.

Regression analysis

The collected data on the dependence of the fuel concentration in soil on temperature and air humidity were fitted to regression equations using SigmaPlot 11 software. The SigmaPlot curve fitter uses the Marquardt-Levenberg algorithm to find the coefficients of the independent variables that give the best fit between the preselected equation and the data. The coefficient of determination, R^2, was used as a measure of how well a regression model describes the data. The closer R^2 is to one, the better the independent variables predict the dependent variable (Szymański and Janowska 2016).

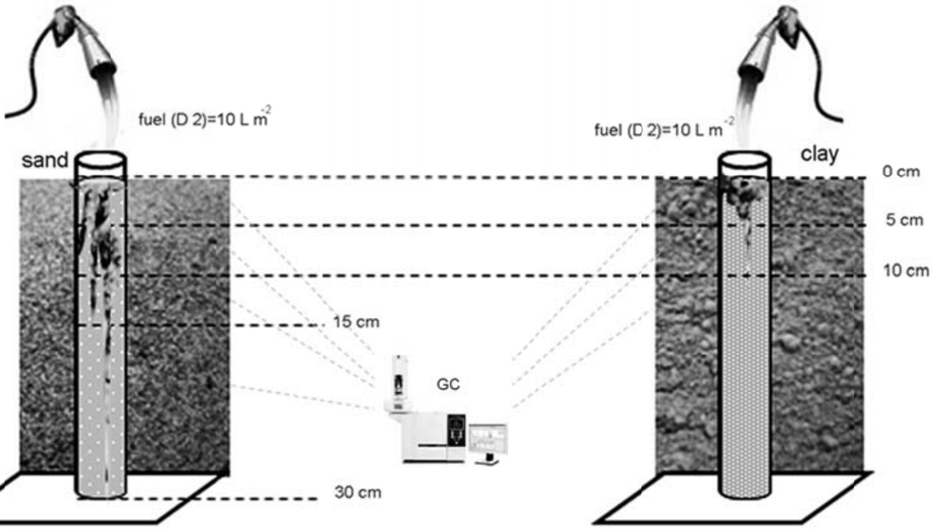

Fig. 1. The soil column setup

Results and discussion

Air temperature influence on fuel migration

Eleven days after the spillage, the concentration of diesel fuel was measured for various temperatures and air humidity values at different depths in sand and clay, and the calculated results are presented in Fig. 2. For all test conditions, on the eleventh day after the spill, the fuel in sand reached the layer 15–30 cm from the surface (although fuel did not reach the bottom of the column in any experiment), while in clay the fuel was found only in layers 0–5 cm and 5–10 cm from the surface, and no diesel fuel was found in sections below this depth. Such different depths reached by the fuel are related to the retention capacity of the soils. The retention capacity is defined as the maximum concentration of diesel fuel (mg kg^{-1}) that can be retained in the soil under the influence of gravity after certain period of free drainage, usually 72 h (Ma et al. 2015). It means that the concentration of fuel in the surface section of soil (0–5 cm) measured after 11 days, may be regarded as a maximum concentration that may be adsorbed on the soil particles, bearing in mind that the real retention capacity is even higher because there was constant evaporation loss. The maximum saturation level seen in Fig. 2, as a concentration in the surface layer, was app. 24000 mg kg^{-1} in sand and 68000 mg kg^{-1} in clay. Although the literature data for retention capacity differ widely for different testing methods, soil and fuel types, etc., according to the summary of the research results from the American Petroleum Institute (Brost and DeVaull 2000), the range of retention capacity for sand with average particle size of 0.1 mm is 20,000–35,000 mg kg^{-1}, while for clay it is in the range of 55,000–70,000 mg kg^{-1}, and this is in accordance with our observations in surface layer.

The influence of air temperature on fuel distribution in different sand layers is given in Fig. 3. For the top two layers of sand (0–5 cm and 5–10 cm), with the increase in air temperature from 20 to 40°C, the concentration of spilled fuel decreases by approximately 5000 mg kg^{-1}. In the section of sand depth of 10–15 cm reduction is twice less, about 2500 mg kg^{-1}, while for the layer 15–30 cm, with a rise in air temperature from 20 to 40°C, the pollutant concentration increases for about 1500 mg kg^{-1}.

Regression analysis of experimental results shows that the change in concentration of spilled fuel in the upper sections of sand is best described with the exponential function, whereas in deeper layers (10–15 cm and 15–30 cm) a second order polynomial function is more suitable (equations 1–4 in Table 1).

The distribution of spilled fuel in the clay layers for various temperatures was recorded in the same manner as for the sand, and the results are shown in Fig. 4.

In both clay sections, it is evident that with the temperature increase, the pollutant concentration decreases. For the upper layer, when the temperature was changed from 20 to 40°C, the fuel concentration fell down for 5000 mg kg^{-1}, and there is an exponential dependence between these two parameters, as shown in equation 5. On the other hand, in the second clay layer, 5–10 cm, the contaminant concentration changed for 5400 mg kg^{-1} with the temperature increase, and this relation cannot be approximated with the exponential function (equation 6).

The total concentration of spilled fuel may be obtained by calculation, as an average value for concentrations in different layers, of depth to 30 cm. The change of the total concentration of spilled diesel fuel with air temperature, after

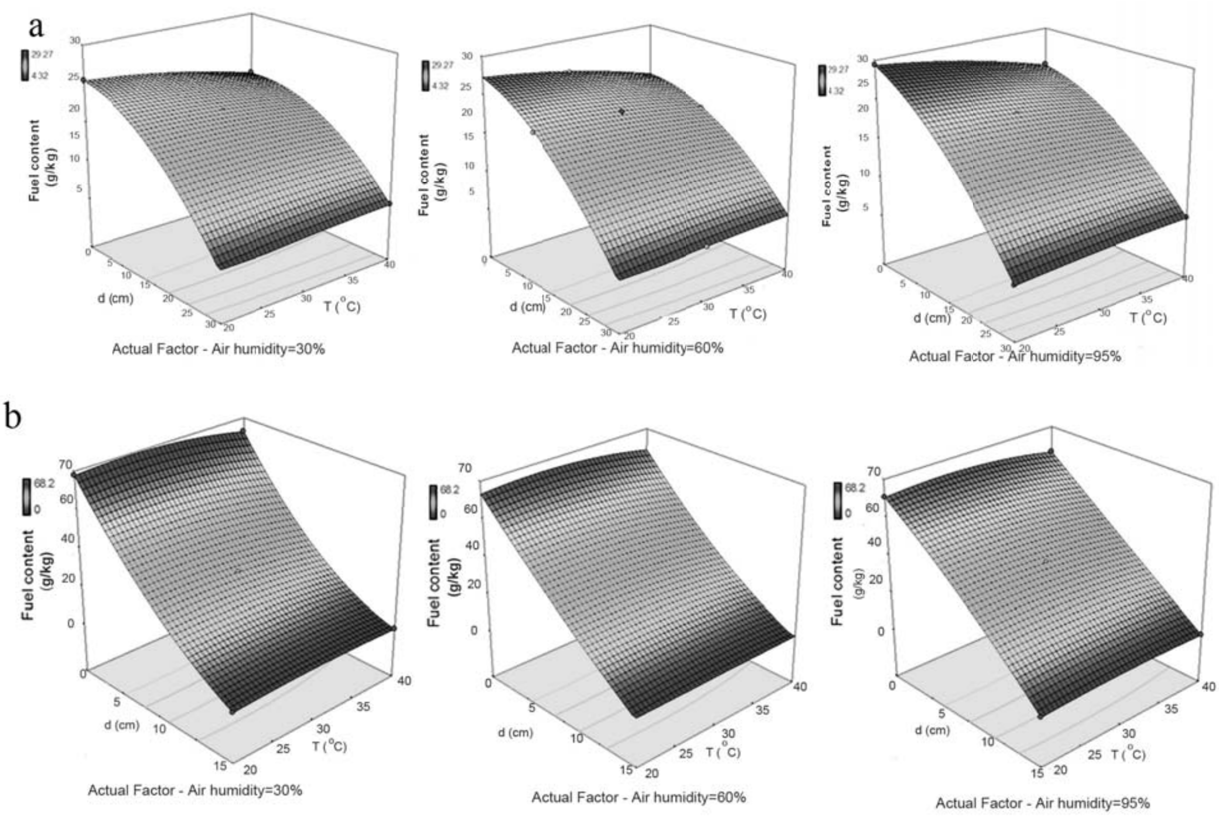

Fig. 2. Distribution of the spilled fuel in the profile at various air temperatures and humidity values: a) in sand; b) in clay

11th day, is presented in Fig. 5. The equations 7 and 8 show that the total concentration decreases exponentially with the temperature.

The results observed in Figs. 2–5 may be explained by the temperature effect on two different physical processes: fuel evaporation and mobility in soil. At higher temperatures, the volatility of fuel increases and thus the total amount of contaminants in the soil is reduced. Also, with the increase in temperature the viscosity of the fuel is reduced, allowing easier fuel transport into deeper soil sections (Tzovolou et al. 2009). The influence of temperature on fuel viscosity is clearly seen in sand (Fig. 3), due to its higher permeability in comparison to clay. While fuel content decreases at higher temperatures in the upper layers in both sand and clay due to faster evaporation, there is an accumulation of fuel in the lowest sand layer, because of its faster movement at high temperatures.

Additionally, it is evident that the soil type significantly influences the fuel migration, as well. As seen in Fig. 5, the total concentration of spilled fuel after eleven days is higher in clay at all temperatures. Low permeability and large specific surface area of clay significantly affect the retention of all phases of petroleum pollutants (Adam et al. 2005). So, although the fuel does not penetrate into clay more than 10 cm after eleven days, one cannot observe higher evaporation loss in clay as compared to sand. This is because the fuel molecules are more strongly absorbed in clay particles with high contact surface (Roon et al. 2005).

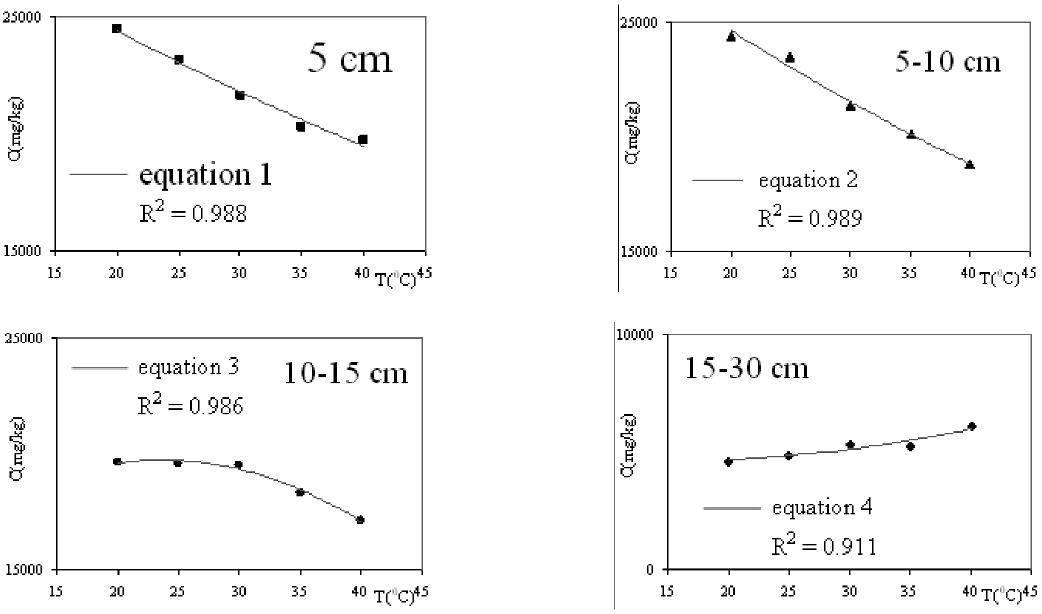

Fig. 3. Changes in fuel concentrations at different sand layers with air temperature

Table 1. Equations describing the dependence of diesel fuel migration through the soil profile under diverse atmospheric conditions

Temperature influence	
Depth (cm)	Equation
Sand	
0–5	1. $C = 30227 \cdot e^{-0.011 \cdot T}$
5–10	2. $C = 32565 \cdot e^{-0.014 \cdot T}$
10–15	3. $C = 14150 + 470 \cdot T - 10 \cdot T^2$
15–30	4. $C = 4600 - 42 \cdot T + 2 \cdot T^2$
Total 0–30	7. $C = 15502 \cdot e^{-0.0059 \cdot T}$
Clay	
0–5	5. $C = 72728.5 \cdot e^{-0.0035 \cdot T}$
5–10	6. $C = 13300 + 1100 \cdot T - 22{,}6 \cdot T^2$
Total 0–30	8. $C = 21370 \cdot e^{-0.056 \cdot T}$
Air humidity influence	
Depth (cm)	Equation
Sand	
0–5	9. $C = 15500 + 156 \cdot RH - 0{,}735 \cdot RH^2$
5–10	10. $C = 13000 + 251 \cdot RH - 1{,}92 \cdot RH^2$
Total 0–30	11. $C = 10200 + 88 \cdot RH - 0{,}6 \cdot RH^2$

As concerning the effect of temperature change on the total fuel loss, the diagrams in Fig. 5 as well as the equations 7 and 8, reveal that the effect is stronger in clay. For instance, the difference between the fuel concentrations at 20 and 40°C is 2000 mg kg^{-1} in clay, and only 1400 mg kg^{-1} in sand. Once again, this is a result of the slower fuel evaporation in clay at lower temperatures, so that the temperature increase is needed to provide energy for desorption of fuel molecules from clay aggregates (Roon et al. 2005).

Air humidity influence on fuel migration

Similarly to air temperature, the air humidity also influences the fuel movement through the soil. First of all, at higher humidity, the possibility of water condensation in the soil increases, changing the conditions of fuel transition into the gas phase, as well as its transport and distribution in soil layers. This establishes a different mode of fuel transport, based on the capture of free space between the soil grains by water molecules, water sorption on the grains, and partial mixing of polar fractions of fuel with water (Cabbar and Bostanci 2001).

The effect of the relative air humidity on the diesel fuel concentration after 11 days in different depth sections of sand is presented in Fig. 6.

In the layer closest to the atmosphere, the amount of contaminant increases with increasing humidity, for all relative humidity values, probably due to the more difficult fuel

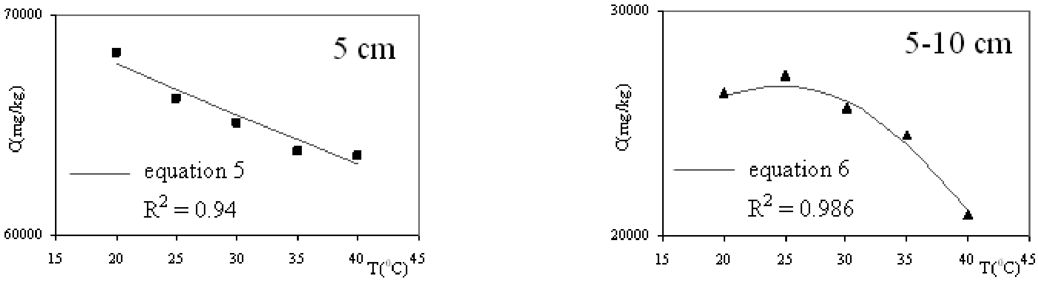

Fig. 4. Changes in fuel concentrations at different clay layers with air temperature

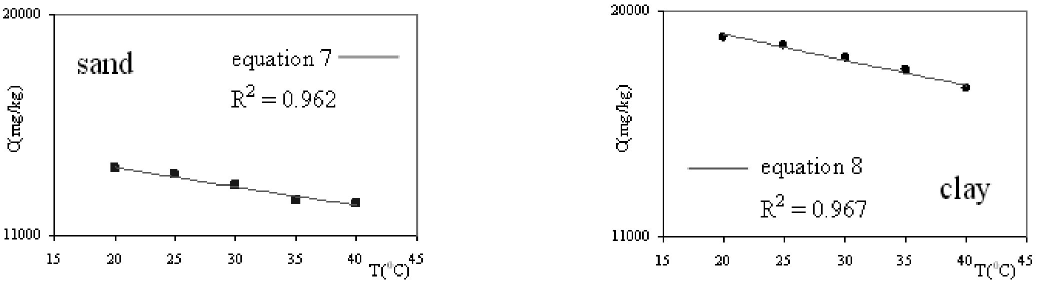

Fig. 5. Changes in fuel concentrations, calculated as an average value for the depth of 30 cm, with air temperature

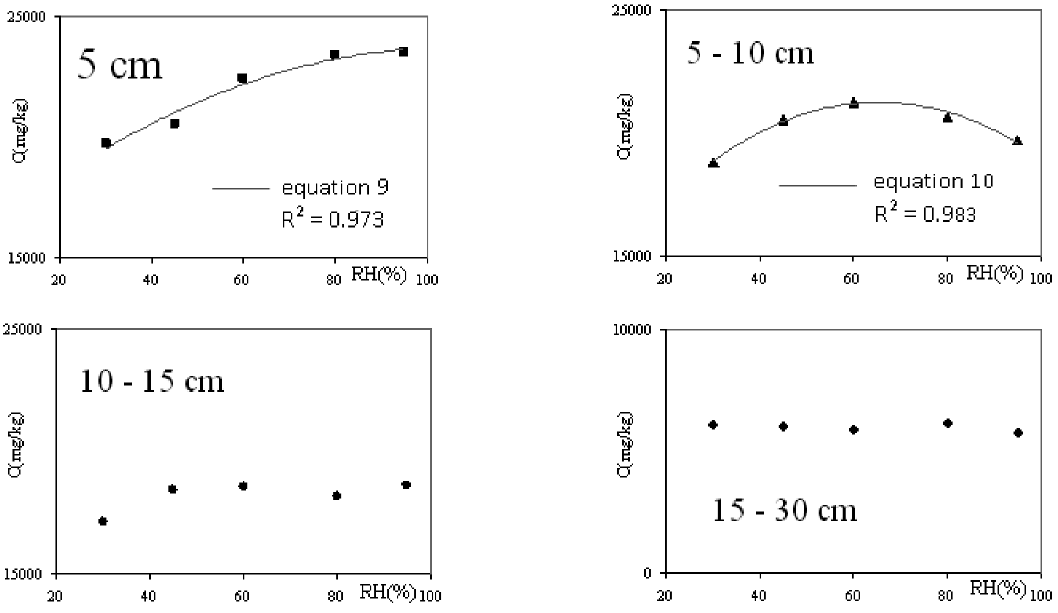

Fig. 6. Changes in diesel fuel concentrations at different sand layers with air humidity

evaporation. On the contrary, in the next sand layer (5–10 cm) the concentration of spilled fuel reaches a maximum value at the transition between dry and humid atmosphere. Until 60% of relative humidity, the amount of fuel in this section increases, again because of inhibited evaporation. However, with further humidity increase, there is probably slower fuel transport towards deeper soil layers as a consequence of the reduced sand permeability, i.e. the capture of free space between the grains by water molecules (Cabbar and Bostanci 2001). In the two deepest sand layers, the correlation between air humidity and fuel content becomes more difficult to understand: for the 10–15 cm layer, there was slight increase in fuel concentration, while there was no change in the final sand section (10–15 cm) with the increase in humidity.

Regression analysis of experimental results enables one to describe the fuel penetration in the upper sand layers by using a second order polynomial function (equations 9 and 10), but the process cannot be mathematically described for the deeper layers.

The change in pollutant concentration with air humidity in the two clay layers is seen in Fig. 7.

In both clay sections, the strongest influence of air humidity is observed at highest humidity values, 80% and above. The relationship between air humidity and fuel penetration is very different in sand and clay. Since clay has a low permeability, its surface layer maintains three times as much fuel as compared to sand. Lower permeability and better absorption ability of clay, hinders fuel evaporation and so humidity of the atmosphere in the surface layer of clay does not significantly affect the loss of spilled diesel fuel by evaporation. On the contrary, there is a significant influence of air humidity on the fuel penetration through the clay. It is seen from Fig. 7 that at high air humidity, a significant amount of fuel migrates from the surface to the lower layer. Due to the higher affinity of clay minerals to the water molecules, at higher humidity there is strong adsorption of water from the atmosphere on clay grains, and this process suppresses fuel molecules whose adsorption forces to the clay are weaker. As a result, fuel fractions migrate to the lower clay sections (Aertsens et al. 2008).

Total concentration of the spilled pollutant, calculated as an average sum of concentrations in different soil layers, is displayed in Fig. 8. For the sand it is even possible, by using regression analysis, to describe this dependence by second order polynomial function with the accuracy of 99.92% (equation 11). The air humidity influence on fuel spillage is less pronounced than it was for the air temperature, but it is more difficult to explain. The maximum fuel content is recorded at 80% air humidity for sand, and at 40% for clay.

Conclusions

In an attempt to understand the effect of atmospheric conditions on the diesel fuel movement through the sand and clay, the concentration of the contaminant in soil was measured 11 days after its spillage. In this period, diesel fuel penetrates 30 cm in sand and only 10 cm in clay.

The polluted soil samples were held at different air temperatures, in the range of 20 to 40°C. The temperature increase reduces the total fuel amount in soil, due to faster evaporation. Nevertheless, the results also show faster fuel movement into deeper soil sections due to lower viscosity at higher temperatures, particularly in sand, because of its higher permeability.

Furthermore, the influence of relative air humidity of various levels, from 30 to 95%, on fuel vertical migration in the soil was investigated. The effect is less emphasized as compared to air temperature influence, but more challenging to explain, due to the fact that in both soil types, there is a maximum total fuel concentration at a certain humidity value: at 80% in sand and 40% in clay. A simple explanation of such dependences cannot be given, because several physical processes on the fuel and soil are involved at the same time. It

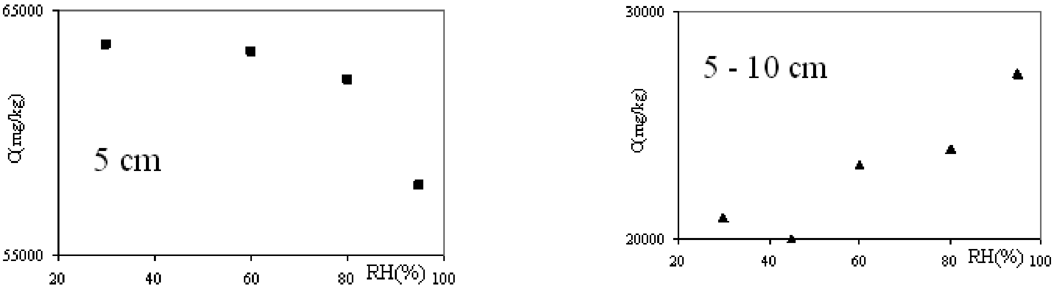

Fig. 7. Changes in fuel concentrations at different clay layers with air humidity

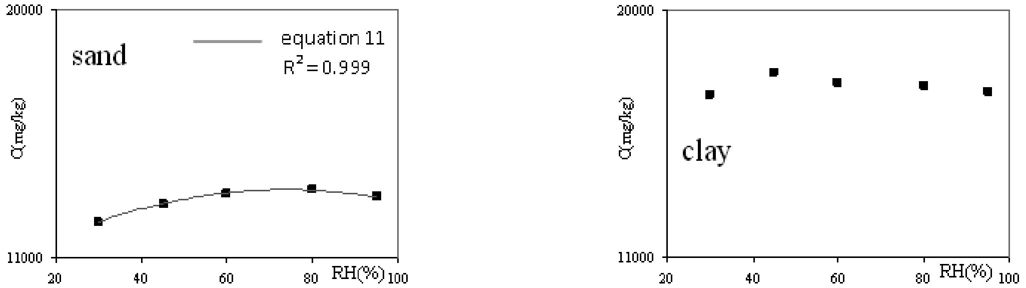

Fig. 8. Changes in fuel concentrations, calculated as an average value for the depth of 30 cm, with air humidity

is only evident that in sand, the air humidity has high influence on fuel content at dry atmosphere, whereas in clay, the most expressed changes are observed at high air humidity.

By using regression analysis, equations are given for mathematical description of the air temperature and humidity influence on diesel movement through the sand and clay. They may be very useful in future for predicting the depth and contamination degree of soil after diesel fuel spillage.

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