Real time monitoring of soil contamination with diesel fuel using photoionization detectors

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ABSTRACT

Soil contamination is a very relevant environmental problem, which is directly connected with both groundwater and air contamination. Petroleum products represent often a major source of soil contamination. In this sense, leakage of diesel fuel can cause important environmental problems due to the persistence of it in contaminated soils and to its toxicity at low concentrations. Photoionization detectors (PID) have the ability to evaluate the ampleness of contamination by detection and quantification in real time of diesel fuel vapours. Finally, this achievement can lead to a rapid evaluation (in minutes) of soil contamination and will facilitate the application of most suitable remediation technologies. The purpose of this study was to simulate an accidental spill of diesel on the ground, with the aim to monitor the degree of volatilization of chemical compounds during six weeks. Thus, the reasons behind the low volatility of diesel fuel in the investigated soil samples, based on the trend of volatilization and on soil characteristics as well.

1. Introduction

Soil represents the most fertile part of geosphere. It is simultaneously the field where food for living organisms is produced, and the environment for a continuous development of biological processes (Cuadros et al., 2013). All agricultural activities take place in the soil. In addition, the soil is the receptor of large amounts of pollutants; since it may act as a filter and place of storage for environmental pollutants which can contaminate water and air as well. Industrial and agricultural activities are most important sources of soil pollution. Oil extraction areas are significant pollution points containing waste oil and wastewater (Ratiu, Beldean-Galea, Bocos-Bintintan, & Costea, 2018). The crude oil has the potential to radically alter soil properties, both physical and chemical, as well as biological processes. Sometimes, the impact of oil pollution on ecosystems is far exceeding the intensity of other anthropogenic actions. Diesel fuel is a complex mixture of linear chain alkanes, branched chain alkanes, cycloalkanes and aromatics, mixture that presents a lower volatility compared with gasoline (Clayton & Joseph, 2003).

Various specific and nonspecific analytical methods were used for detection and quantification of petroleum hydrocarbons from soil. Gas-chromatography with flame ionization detector (GC-FID), gravimetric determination and infrared spectrometry (IR), thin layer chromatography with mass spectrometry (TLC-MS) and high performance liquid chromatography (HPLC) were used and modified for decades to minimize the interferences, to reduce the amount of solvents and to simplify analytical procedures. For example, it was demonstrated that GC-FID and IR were suitable for detection and quantification of petroleum hydrocarbons from soil samples containing different contamination levels (Clayton & Joseph, 2003; Paiga, Mendes, Albergaria, & Delerue-Matos, 2012).

However, the same researchers concluded in case of gasoline detection, that the performance of GC-FID was much better than IR, due to less interferences occurring. Moreover, in case of IR, the target component losses during volatilization were noticed. A method based on headspace chromatography together with photoionization detector and flame ionization detector (HS-GC-PID-FID) was for the first time developed for water samples in Brazil (Cavalcante, de Andrade, Marins, & Oliveira, 2010). The basic idea of this method was the rapid sampling process, plus no expensive materials or intense laboratory activity needed.

Most of the methods applied for soil contamination control are based on extraction of volatiles...
organic compounds (VOCs) from soil and further quantification using GC-MS. Head-space analysis, purge and trap analysis, thermal desorption or solvent extraction can be used in this step. In all cases, sampling step is the critical factor in VOCs analysis, because it can lead to the loss of components due to their vaporization during sampling, sample transport, or storage (Meney, Davidson, & Littlejohn, 1998). However, a good alternative is a direct, fast detection of the VOC vapours using PID detectors. Thus, the efficiency of a PID-GC-MS system was confirmed (Robbat, Considine, & Antle, 2010). PID detector was able to detect the presence or absence of pollutants in real time, while GC-MS quantified the target components from samples in about 5 min. It is worth mentioning that the present study describes direct analysis of pollutants retained inside the soil, without extraction.

PID devices combined with GC/MS were involved in the analysis of environmental pollutants as well. Thus, an integrated system for detecting pollutants on-line in real-time by PID followed by quantitation using GC/MS was described (Siegrist, 1992) for volatile coal tar and petroleum hydrocarbons. In another experiment, chronic exposure of the workers in shoe shops to volatile organic compounds contained by adhesives and leatherette was monitored by a PID detector (Bocos-Bintintan, Smolenschi, & Ratiu, 2016). Moreover, Ghira, Ratiu, and Bocoș-Bintințan detected very low levels of pyridine vapours in controlled atmospheres from indoor air (2013), using both PID and IMS (Ion Mobility Spectrometry), which, as well as GC-MS are sensitive and powerful analytical techniques with multiple applications in trace detection (Buszewski, Raifu, Milanowski, Pomastowski, & Ligor, 2018; Moll, Bocoș-Bintințan, Rațiu, Ruszkiewicz, & Thomas, 2012; Ratiu, Bocoș-Bințințan, Turner, Moll, & Thomas, 2014; Ratiu, Ligor, Bocos-Bintintan, & Buszewski, 2017; Ratiu, Ligor, Bocos-Bintintan, Al-Suod, et al., 2017; Ratiu, Bocos-Bintintan, et al., 2017; Ratiu et al., 2019). Clayton and Clark, developed a comparative study dedicated to the evaluation of the relationship between a FID and a PID (2003). To evaluate performances of both instruments, the analysis of two clay soil sites contaminated with diesel fuel were realized. The authors concluded that both instruments can be used in the diesel fuel contamination monitoring and that the results can be comparable based on a previously calculated correlation between the two instruments (Clayton & Clark, 2003). The difference between our work, and the previous one (Ratiu et al., 2019), is that in our study we monitored a trend decreasing profile of contaminated soil samples during 40 days of experimentally campaign, in order to verify the persistence of contamination, while they evaluated comparatively two different analytical instruments with potential to be used in the same field.

As discussed above, soil contamination caused by diesel fuel is of serious concern, for its strong connection to groundwater and air contamination. Moreover, persistence of diesel fuel in soil is higher than in case of gasoline. Because PID devices have the potential to evaluate the amleness of a contamination with diesel fuel in real time (minutes), this makes it the perfect tool to be used for monitoring of accidental contaminations. In the present study, five different levels of contamination of soil caused by diesel fuel were investigated via simulation, with the aim to monitoring the volatilization process during six weeks. Thus, we succeeded to identify the reasons for the low volatility of diesel fuel in the contaminated soil samples, based on the trend of volatilization and on soil characteristics as well.

2. Materials and methods

The soil was collected from Cluj-Napoca, Romania, sampled from the top soil layer (0–20 cm) using a hand shovel and contaminated with diesel fuel bought from a gas station. Diesel volumes (hence amounts) were accurately measured (using a graduated cylinder) for each container with soil. Subsequently, the diesel fuel in each sample was well mixed to ensure homogeneity. The containers were kept open during the 40 days of experiment, except the time periods of closure for static headspace procedure. For this procedure, for only 30 min before PID analysis containers were sealed with aluminium foil and capped with a metallic lid to reach equilibrium inside the container.

The concentration of volatiles was measured for five different containers (glass jars with a volume of 740 cm$^3$, having a screw metallic lid), with different levels of contamination, using the sensitive PID instrument ppbRAE Plus device model PGM-7620 (made by RAE Systems Inc., USA), during forty days (in May and June). The measurement time in each container was about 30 s, and the equilibration period was 30 min at room temperature.

The used PID has a highly compact design (size 21.8 $\times$ 7.62 $\times$ 5.0 cm), is weighing only 553 g, and is equipped with a standard UV lamp with the photon energy of 10.6 eV. The lamp consists of a glass body, provided with a window transparent to UV radiation at the end; this body is filled with a noble gas (Kr) at reduced pressure. The PID sensor is positioned in the top of the UV lamp. PID uses a pump with a flow rate of 450–550 cm$^3$ min$^{-1}$. Once the vapours of organic compounds are passing through the sensor and are exposed to the UV photons from the lamp, they are ionized quickly if the energy of the UV photons exceeds the ionization energy of the...
molecules $M$; the electrons $e^-$ and positive molecular ions $M^+$ generate an ion current, which is then amplified and displayed on the device’s display directly in concentration units (ppbv). The air drawn by the pump is then evacuated through an outlet after passing through the PID sensor (RAE Systems Inc., 2003). Figure 1 is a diagram that illustrates both PID detector structure and the occurrence of photoionization process.

Prior to the measurements the PID instrument was calibrated using a standard atmosphere containing 10 ppmv of isobutene in purified air (from a pressure gas cylinder, provided by the manufacturer RAE Systems). PID sensor was cleaned two times during experimental campaign, using anhydrous methanol and an ultrasonic bath. All data, initially stored in the internal memory of the instrument, were transferred to a PC computer using a RS-232 interface and the appropriate software.

3. Results and discussions

PID is a very sensitive, non-expensive, compact and robust instrument, extremely useful for real time detection of volatile organic compounds. However, the major drawback of PID devices is that in case of mixture of components we cannot predict which components are providing the answer displayed on the screen. In fact, in case of mixtures what is measured by a PID instrument is the total amount of photo-ionizable components, and therefore the correction factors in order to obtain the real recorded concentration cannot be used as in the case of a single, known analyte. However, in our experiment we have realized a simulation of controlled contamination with diesel fuel. Knowing the identity of pollutant, the appropriate correction factor (for diesel fuel) was used and consequently the quantities of diesel vapours expressed in ppmv were calculated.

When the containers were filled with the soil sample, about half of the container was kept empty, in order to allow static headspace procedure. Headspace technique was used for sampling vapours of diesel fuel, by covering the container (glass jar) with aluminium foils (0.1 mm thick, in double layer) and then closed with the original metallic lid. Equilibration time of 30 min was given, to allow vapours of diesel fuel to pass from soil matrix into the headspace air (Figure 2(B)). Finally, the metallic lid was removed, the aluminium foil was carefully to open an orifice of about 8 mm diameter (Figure 2(C)), through which the PID’s sampling probe was introduced into the container directly, recording the VOCs concentrations in ppmv, for about 30 s (Figure 2(D)). In Figure 2, PID instrument (A), sealed containers ready for analysis together with

![Figure 1. Schematic of the photoionization detector PID.](image-url)
the tools used for sample collection (B) and head-space sample sniffing (C and D) can be observed.

The highest concentration of diesel fuel vapours was recorded after about 30 s of air sampling. As described in the materials and methods part, the containers were kept open to air during the six weeks of experiments and covered just before sample collection. The ambient storage temperature was between 18 and 22 °C. The mass of each empty container was 330 g.

Granulometric analysis and soil classification were realized in order to obtain information about soil properties, which can influence persistence of diesel fuel. For example, the density will influence some physical properties such as: water retention capacity, porosity, soil aeration, permeability. Based on the standard procedure SR EN ISO 14688-2/2005, soil samples were classified using an automatic Excel Program (2010). The values of investigated parameters are presented in Table 1.

According to the granulometric analysis the investigated soil samples were classified into the group of clay with powdery sand. Based on $i$ and $p$ it is soft clay characterized by an average absorption capacity (85%). The degree of humidity indicates a dry ground.

In Table 2 and Figure 3, the obtained experimental results from PID are presented. For each sampling day, temperature and the date of sample collection were presented as well. By direct observations it was noticed that both the quantity of diesel fuel added and ambient temperature may have influences on the vapour concentrations recorded. Consequently, using IBM SPSS statistical software package (version 21), a Pearson product-moment correlation analyses was conducted to examine the relationships between quantity of fuel initially added, ambient temperature and concentration of vapours detected. Correlation test highlighted that the quantity of fuel initially added to the samples was strongly positively related to vapour concentration detected: $r(17) = 0.955$, $p = .01$, and strongly negatively correlated with ambient temperature $r(17) = 0.848$, $p = .01$. These findings indicated that in case of investigated soil samples, the quantity of fuel added explains more variability that does the temperature.

In Figure 3, a decreasing trend of vapour concentration may be observed for each container, independent by the amount of diesel fuel initially added.
Table 2. Concentrations of diesel fuel recorded during experimental champagne.

| Date   | Temperature (°C) | Sample 1 (500 g soil, 100 mL fuel added, initial concentration 14.40%) | Sample 2 (445 g soil, 75 mL fuel added, initial concentration 12.40%) | Sample 3 (425 g soil, 50 mL fuel added, initial concentration 9%) | Sample 4 (405 g soil, 25 mL fuel added, initial concentration 4.93%) | Sample 5 (440 g soil, 10 mL fuel added, initial concentration 1.87%) |
|--------|------------------|------------------------------------------------------------------------|------------------------------------------------------------------------|------------------------------------------------------------------|------------------------------------------------------------------|------------------------------------------------------------------|
| 11.05  | 21               | 144                                                                     | 132                                                                    | 163.2                                                            | 155                                                             | 154                                                             |
| 14.05  | 20               | 132                                                                     | 150                                                                    | 130.4                                                            | 126.4                                                            | 106                                                             |
| 15.05  | 19               | 128                                                                     | 156                                                                    | 184                                                             | 116                                                             | 88                                                              |
| 16.05  | 20               | 124                                                                     | 148                                                                    | 150.4                                                            | 107                                                             | 84                                                              |
| 17.05  | 18               | 109.6                                                                   | 113.6                                                                  | 116                                                             | 76.8                                                             | 60                                                              |
| 18.05  | 22               | 114.4                                                                   | 136                                                                    | 116                                                             | 70.4                                                             | 57                                                              |
| 20.05  | 18               | 68.8                                                                    | 76.8                                                                   | 69.6                                                             | 48.8                                                             | 36                                                              |
| 21.05  | 19               | 56.8                                                                    | 65.6                                                                   | 53.6                                                             | 41.6                                                             | 28                                                              |
| 22.05  | 19               | 45.6                                                                    | 52.8                                                                   | 44                                                              | 29.6                                                             | 21                                                              |
| 23.05  | 20               | 42.4                                                                    | 51.2                                                                   | 46.4                                                             | 30.4                                                             | 22.4                                                            |
| 24.05  | 22               | 49.6                                                                    | 50.4                                                                   | 36.8                                                             | 27.2                                                             | 19.2                                                            |
| 26.05  | 22               | 49.6                                                                    | 55.2                                                                   | 46.4                                                             | 28.8                                                             | 20                                                              |
| 28.05  | 20               | 45.6                                                                    | 39.2                                                                   | 36                                                              | 24                                                              | 16.8                                                            |
| 31.05  | 22               | 52.8                                                                    | 44                                                                     | 43.2                                                             | 31.2                                                             | 17.2                                                            |
| 04.06  | 19               | 37.6                                                                    | 39.2                                                                   | 31.2                                                             | 20.8                                                             | 12.8                                                            |
| 08.06  | 22               | 49.6                                                                    | 47.2                                                                   | 38.4                                                             | 26.8                                                             | 16.8                                                            |
| 13.06  | 18               | 42                                                                     | 39.2                                                                   | 29.8                                                             | 20                                                              | 11.4                                                            |
| 17.06  | 21               | 47.8                                                                    | 45.8                                                                   | 35.4                                                             | 22.2                                                             | 13.2                                                            |
| 20.06  | 19               | 42.8                                                                    | 42.4                                                                   | 33.2                                                             | 23.6                                                             | 13.6                                                            |

Figure 3. The temporal evolution of diesel fuel vapours profile.
In the first part of the experiment a sharp decline with small fluctuations was observed, followed by a slight and continuous decreasing trend in the second period of the experiment. The recorded fluctuations may be caused by the temperature variations in the room where the containers with contaminated soil were kept, which certainly will increase or decrease the volatilization process, or by headspace sample collection process.

After 40 days of experimental campaign, we noticed that fuel vapours still could have been detected in the contaminated soil (from ca. 40 ppmv, for the highest initial concentration of diesel fuel, to ca. 10 ppmv, for the lowest initial concentration of diesel fuel in soil). This denotes a relatively high persistence of diesel fuel in this specific type of soil (clay with powdery sand) in case of an accidental contamination. This persistence is given by both low volatility of diesel and soil type, which present a high absorption capacity: about 85%. It was found that the soil used as sample (clay with powdery sand) is composed by fine fractions that may retain most of the toxic VOCs. The coexistence of the sandy fraction together with the fine fraction results in an average absorption capacity by 85%. Without the sandy fraction, the volatilization capacity by 85%. Without the sandy fraction, the volatilization would have taken longer time. However, following the decreasing trend of vapour concentration we can estimate that null values may be obtain in more than several years postcontamination.

4. Conclusions

Soil, defined as a complex physical and biological system, cannot cope with a contamination that exceeds its ability to restore its ecological balance. The experiment presented in this study is a simulation which offers a general view of diesel fuel volatilization in time, without any intervention, conducted under laboratory conditions at a relatively stable temperature. The fast screening method used (PID detection) may offer valuable information about the presence or absence of contamination in real life scenarios, as well as an assessment of pollution amplitude in case of an accidental contamination. In case of facing this situation, a real time response of the order of minutes can be achieved.

Disclosure statement

No potential conflict of interest was reported by the authors.

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