Comparative laser-induced fluorescence evolution analysis of different oil pollution on the terrestrial surface

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Abstract. We have studied the time evolution of the laser-induced fluorescence spectra of oil pollution on the terrestrial surface at a fluorescence excitation wavelength of 355 nm. The paper presents a block-diagram of the experimental laboratory setup and data processing results of the laser-induced fluorescence spectra for the oil-polluted soil and sand and conducts a comparative analysis of the fluorescence spectra evolution of pollution due to spilling crude oil and heavy and light petroleum products.

1. Introduction
Oil and petroleum products are high on the list of pollutants in the environment. Penetration of oil and its components into the soil, air or water entails a change in their physical, chemical, biological properties and disturbs natural biochemical processes. Therefore, development of methods and means to control the oil and petroleum product pollution of water and terrestrial surfaces is a challenge.

Currently, the problem of oil pollution on the terrestrial surface is especially relevant due to leaks of oil during its transfer through pipelines because of their wear-out or mechanical damages [1,2]. Now available current oil pipeline control systems have a detection limit ranging from units to one-tens of a percent of the pipeline capacity. Existing control systems do not detect the lower rate leakages.

The most efficient techniques to control oil pollution are laser-induced fluorescence (LIF) methods [3]. However, presently, a great majority of papers on the experimental study of the oil pollution LIF deal with measuring the fluorescence spectra of oil pollution on the water surface (films of oil and petroleum products on the water surface, “oil-in-water” or “water-in-oil” emulsions) or the LIF spectra of pure petroleum products [4-9]. There are a few papers [10,11], which show the experimental study results concerning the oil and petroleum products spilled on the terrestrial surfaces.

One of the promising laser wavelengths (in terms of laser pulse power and eye-safety) to excite the fluorescence of petroleum products is the wavelength of 355 nm (third harmonic of Nd: YAG laser).

The paper deals with the time evolution of the LIF spectra of different oil pollution on the terrestrial surface at the fluorescence excitation wavelength of 355 nm.

2. Experimental setup
To measure LIF spectra of oil and oil pollution on various terrestrial surfaces, was used an experimental laboratory setup a schematic diagram of which is shown in figure1.
Third harmonic of a diode pumped Nd:YAG laser is used as an excitation source. A fluorescence detection system is designed on the basis of a spectrometer and a highly sensitive ICCD. Calibration of equipment involved a wavelength calibration of the polychromator and registration system calibration.

Table 1 presents basic parameters of the laboratory setup.

| Parameter                                | Value   |
|------------------------------------------|---------|
| Laser energy pulse, mJ                   | 0.8     |
| Excitation wavelength, nm                | 355     |
| Laser pulse width, ns                    | <8      |
| Repetition rate, Hz                      | Up to 500 |
| Band of spectral registration, nm        | 290 –750     |
| Spectral resolution, nm                  | 5      |
| Receiving lens diameter, mm              | 15     |
| Distance to the sample under study, m    | ~ 1.4 |
| Laser beam diameter in the sample plane, mm | ~ 20   |
| Detector viewing field diameter in the sample plane, mm | ~ 20 |

For laboratory setup control, the LabVIEW software in visual development environment was used. In the course of measurements, a laser output power value was under control. The measured laser output power value was used when processing the measurement data, i.e. a correction factor was introduced thereby leading the intensity level of detected fluorescence emission to the single laser output power value of 100%.

To control the experimental laboratory setup calibration a Raman-scattering spectrum of distilled water was used. The curves 1-3 in figure 2 are examples of the Raman-scattering spectra of distilled water measured during two weeks’ experiments. It is seen from the figure that a laboratory setup measurement error of the signal of the Raman-scattering of distilled water is ~ 10 % (of the measured signal value). Thus, though the laboratory setup does not provide absolute measurements of the fluorescence intensity value, it allows, however, taking quantitative measurements and judging the

![Figure 1. Schematic diagram of the experimental laboratory setup.](image)
relative value of the fluorescence signals, obtained at different times from the various samples under investigation.

![Figure 2](image-url)  
**Figure 2.** Raman-scattering spectrum of water.

Figure 3 allows us to estimate a measurement error of the LIF spectra of the samples under investigation arising from the detection system noise. Here we represent an example of the background noise measurements of the detection system with the laser source being switched off.

![Figure 3](image-url)  
**Figure 3.** Detection system background noise.

The curve in figure 3 as compared to the measurement data given bellow shows that detection system noise is low and therefore, its impact on the measuring fluorescence spectrum is negligible.

3. **Experiment description**

The experimental laboratory setup measurements for a fluorescence excitation wavelength of 355 nm enabled us to obtain LIF spectra of various oil pollution at different times after spilling petroleum products on a diversity of terrestrial surfaces (black soil, river sand, sandy soil, garden soil, forest soil, clay, a mixture of black soil and clay, a mixture of soil and sand, etc.).

As soil pollutants, the following petroleum products were used: crude oil (Almetyevsk); stock-tank oil of the Moscow and Ryazan refineries; diesel fuel (some types); gasoline (some types); engine oil (some types); used engine oil, gas-condensate.

4. **Results**

Figures 4 – 6 below illustrate examples of the typical LIF spectra measured in the laboratory setup at different times after spillage of various petroleum products and gas-condensate on the sand. The peak at the wavelength of 532 nm in the spectra corresponds to the second harmonic of the YAG-laser emission. Figures 4 – 6 show a pollution spectrum detected immediately (curve 1), after 5 days (curve 2) and 12 days (curve 3) upon spilling petroleum product and gas-condensate on the sand.
Figures 4 – 9 below illustrate examples of the typical LIF spectra measured in the laboratory setup at different times after spillage of various petroleum products on the garden soil. Figures 7-9 show the spectrum of pollution detected upon the spillage of petroleum products as follows: immediately (curve 1); in two hours (curve 2 in figures 7, 8) and after 8 days (curve 2 figure 9); after 9 days (curve 3 figures 7,8); after 16 days (curve 4 in figures 7,8).

The time evolution analysis of the LIF spectra shows that for light petroleum products (gasoline), a fluorescent signal value is reduced with time considerably faster than for oil and heavy petroleum products and in a few days becomes insignificant.
For oil and heavy petroleum products, a nature of decreasing fluorescent signal value with time is approximately of the same order (though there is, certainly, a dependency on the type of an petroleum product and a soil) - after 12-16 days upon spilling petroleum product on the terrestrial surface the fluorescent signal value is about 2-6 times less.
Comparison between our measuring results and those presented in the papers on the time evolution of the LIF spectra of the oil spill on the water surface can be conducted using the data of the paper [8].

Figure 10. Fluorescence spectra of oil spill.

The curves (1 … 16) in figure 10 [8] are the numbers of days upon spill. It shows that the fluorescent signal value is decreased with time considerably faster upon spilling oil on the water surfaces than on the terrestrial ones: on expiry of 16 days upon spilling oil on the water surface the fluorescent signal value becomes more than 20 times less.

5. Conclusion
The LIF evolution of oil pollution on the terrestrial surface with time (after contamination) depends heavily on the type of a petroleum product. For petroleum product pollution on the terrestrial surface, the fluorescent signal value is decreased with time considerably faster than for oil and heavy petroleum products and in a few days becomes negligible. For oil and heavy petroleum product pollution, the nature of decreasing fluorescent signal value with time is the same: after 12-16 days the value becomes approximately 2-6 times less.

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