Purification of hydrocarbon-contaminated soils by silicon-rich substances

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Abstract. Hydrocarbon (HC) contamination of soil occurs during oil extraction, transportation and treatment. To enhance the efficacy of HC-polluted soil restoration is an important challenge. In greenhouse and field experiments, two silicon (Si)-rich substances were tested for reduction of HC content in diesel + used motor oil contaminated soil. Over 3 months the HC content decreased from 3 to 2.8; 1.1 and 0.8% in control, calcium silicate slag- and amorphous Si dioxide-treated soils, respectively. Silicon-rich substances remarkably increased the catalase and dehydrogenase activities in the contaminated soil. Several mechanisms underlying the Si-mediated purification of HC-contaminated soil are suggested: a) changing soil physical properties; b) capsulation of HC molecules by polysilicic acid; c) adsorption of monosilicic acid by HCs leading to enhanced hydrophilicity; d) direct effect on soil microbial activity. Many types of Si-rich materials are cheap and available in large volumes (industrial by-products) that potentially could be used for the purification of HC-polluted environment after ecological expertise of the absence of inorganic pollutants.

1. Introduction
Soil contamination with crude oil and oil products is widespread problem because of rapidly rising production, refining, and transportation [1]. Increasing use of petroleum products globally leads to an immense increase in environmental contamination by diesel, spent engine oil or jet fuel [2]. Soil contamination with hydrocarbon (HC)-based products has a negative impact on public health, being a source of acute and chronic diseases, such as: poisoning, cardiovascular diseases, cancer, and others [3].

Selection of the strategy applicable for soil restoration primary depends on a level of pollution. If the content of HCs is higher than 3%, oil and oil products are recommended to remove mechanically from soil [4]. If soil contains 0.3-3% of HCs, it is classified as contaminated and special techniques are required to reduce their content. Various remediation strategies have been elaborated, for instance, application of soil amendments such as peat, fertilizers, manure, microbial preparations, specific chemicals (enzymes), special plant cultivation and others [5; 6; 7].

Microorganisms possess the ability to transform or mineralize naturally occurring organic molecules, and this can be utilized in the in situ remediation of oil-contaminated areas [2; 8]. Numerous remediation-related studies have been aimed at the selection of microorganisms able to degrade petroleum HCs [7; 9]. Because of inhibitory effect of HC on microbial community, the efficiency of bioremediation processes are often low [4; 8; 10].
Over the last decades, beneficial impacts of Si-rich compounds on various soil properties and fertility level have been well documented [11; 12]. Silicon fertilizers and soil amendments provide increased adsorption and water holding capacity; improved plant availability of P, K, Fe, Zn and other nutrients; decreased toxicity of organic and inorganic pollutants; strengthened texture stability and others [13; 14]. It should be noted that some types of industrial wastes can be classified as Si fertilizers [11]. Due to numerous Si-mediated favourable effects on soil, plant and biota, Si-rich substances could be a promising agent for involvement in the HC-polluted soil restoration. There is data that application of Si-rich substances increases the soil microbial activity [13].

A lot of studies are available regarding soil contamination by diesel or oil-products, while their combined presence is rarely studied [7; 9]. The aim of the current study was to determine the effect of Si-rich substances on HCs content and enzymatic activity in diesel+spent motor oil contaminated soil.

2. Materials and Methods

Two Si-rich substances (calcium silicate slag and amorphous silicon dioxide) were tested in greenhouse and field experiments. Calcium silicate slag was obtained from the Kosogorsky metallurgical enterprise (Tula region, Russia). This slag was mostly comprised of CaSiO$_3$. Heavy metals or other inorganic pollutants (As, Cd, Hg, Pb et al.) were not detected. Amorphous silicon dioxide (SiO$_2$) (Aerosil A-300) (Ltd Silica, Russia) is chemically pure substance contained 99.8% of SiO$_2$. The content of water-soluble Si was 4.6 ± 0.5 and 48.5± 1.5 mg kg$^{-1}$ of Si, accordingly in CaSiO$_3$ and SiO$_2$.

Greenhouse experiment was conducted on Grey Forest Soil in the Institute Basic Biological Problems Russian Academy of Sciences. The field test was conducted on Soddy Podzolic Soil in the north of Moscow region. Soil chemical properties are presented in Table 1. The scheme of both experiments was the following:

1) Control;
2) HC pollution;
3) HC pollution + CaSiO$_3$ 5 t ha$^{-1}$;
4) HC pollution + CaSiO$_3$ 10 t ha$^{-1}$;
5) HC pollution + SiO$_2$ 5 t ha$^{-1}$;
6) HC pollution + SiO$_2$ 10 t ha$^{-1}$.

| Table 1. Selected properties of experimental soils. |
|-----------------------------------------------|
| pH   | Total C, g kg$^{-1}$ | CEC cmol(+)$^+$ kg$^{-1}$ | Total nitrogen, g kg$^{-1}$ | Total phosphorus, g kg$^{-1}$ | Total potassium, g kg$^{-1}$ |
|-----------------------------------------------|
| Grey Forest Soil    | 7.2 | 24.7 | 12.8 | 3.08 | 0.91 | 22.3 |
| Soddy Podzolic Soil | 6.1 | 9.8  | 8.5  | 2.51 | 0.68 | 15.4 |

Both experiments were performed at the same level of pollution. In greenhouse pot test, 30 mL of diesel and spent motor oil (1:1) mixture was added to 1 L of soil and agitated. In field test, 3 L of diesel and spent motor oil (1:1) per m$^2$ was added and mixed in a 10-cm layer of soil. After this, the Si substances were applied and soil was mixed again. Then barley (*Hordeum vulgare* L. cv Elf) was planted in depth of 2-3 cm. In greenhouse test, 10 seeds were planted in each pot. In field test, 1000 seeds per 1 m$^2$ were planted. Before seeding all seeds were soaked in distilled water for 24 hours. The air temperature in the chamber was kept at 20 ± 2°C during the day time and 12 ± 2°C during the night. The light period was 12 h; the light intensity was 130 µmol photons m$^{-2}$ s$^{-1}$. The relative air humidity was 45 ± 5% during the day and 70 ± 5% during the night. The field test was conducted from June to July, the
Daytime temperature was about 20-25°C and night temperature was 15-20°C. The natural precipitation was 200-300 mm.

In greenhouse test, soil samples were collected weekly over a 4-week period; in field test - every 2 weeks during 8 weeks from 0-5 and 5-10 cm depth. The HC content was analyzed by hexane (C₆H₁₄) extraction method using ST 255 Soxtec system (FOSS). Ten (10) g of soil was placed into Soxtec flask and 100 mL of hexane was added. The extraction temperature was +70°C and time – 24 hours [15].

The biomass of barley was measured 4 weeks after seeding in pot test and in 8 weeks in field test. Considering that microorganisms play a key role in the HC degradation, the soil microbial activity was evaluated by testing the activity of catalase and dehydrogenase.

The catalase and dehydrogenase activities were determined using the methods described by Achuba and Peretitemo-Clarke [16] and Tabatai [17]. Absorbance of solutions was read spectrophotometrically using Shimadzu UV–VIS 160A (Kyoto, Japan). Each treatment and each analysis were conducted in 4 replications. All data obtained was subjected to a statistical analysis based on comparative methods using Duncan’s multiple range tests for mean separation at the 5% level of significance [18].

3. Results and Discussion

The dynamics of HCs in greenhouse experiment is presented in Table 2. In the Si-untreated soil, the HC content insignificantly decreased from 3.1 to 2.8% for 4 weeks. Application of Si-rich substances substantially reduced the soil HCs. The maximum effect was observed under SiO₂ application at 10 t ha⁻¹ (from 3.1% to 0.4%). The minimum reduction was obtained at lower application rate of CaSiO₃ (from 3.1% to 1.8%).

| Treatment                  | Hydrocarbons, %   |
|----------------------------|-------------------|
|                            | 1 week  | 2 weeks | 3 weeks | 4 weeks |
| Control                    | 0.2     | 0.2     | 0.2     | 0.1     |
| Hydrocarbon pollution (HP) | 3.1     | 3.0     | 2.7     | 2.8     |
| HP+ CaSiO₃, 5 t ha⁻¹       | 3.0     | 2.9     | 2.5     | 1.8     |
| HP+ CaSiO₃, 10 t ha⁻¹      | 3.0     | 2.7     | 2.4     | 1.5     |
| HP+SiO₂, 5 t ha⁻¹          | 2.8     | 2.5     | 1.3     | 0.8     |
| HP+SiO₂, 10 t ha⁻¹         | 2.7     | 2.3     | 1.0     | 0.4     |
| LSD₀.₀₅                    | 0.2     | 0.2     | 0.2     | 0.2     |

The used oil products had a toxic effect on barley plants in both greenhouse and field tests. In the contaminated control, all plants have died. The treatment with CaSiO₃ or SiO₂ promoted a reduction in the toxic effect of contaminants on tested plants. Application of the Si-rich substances resulted in increased biomass from 0.5 to 1.8 g of dry weight plant⁻¹ in greenhouse test and from 1.7 to 2.8 g of dry weight plant⁻¹ in field test. Silicon dioxide applied at 10 t ha⁻¹ demonstrated a higher efficacy, whereas CaSiO₃ at 5 t ha⁻¹ was lesser efficient.

The dynamics in the HC soil content is presented in Table 3. Application of the Si-rich substances significantly reduced the content of oil-based products in 0-5 and 5-10 cm soil layers. The maximum effect was obtained at a higher rate of SiO₂ (decreased HCs from 2.5% in control to 0.3%). Additionally, the Si-rich substances reduced the leaching of used motor oil and diesel.
Table 3. Effect of Si-rich substances on HCs in field experiment.

| Treatment                  | Depth, cm | Weeks |
|----------------------------|-----------|-------|
|                            |           | 2     | 4     | 6     | 8     |
| Control                    | 0-5       | 0.2   | 0.2   | 0.2   | 0.2   |
|                           | 5-10      | 0.1   | 0.1   | 0.1   | 0.1   |
| Hydrocarbon pollution (HP) | 0-5       | 2.9   | 2.9   | 2.6   | 2.5   |
|                           | 5-10      | 0.9   | 1.1   | 1.2   | 1.2   |
| HP+ CaSiO₃, 5 t ha⁻¹      | 0-5       | 2.8   | 2.7   | 2.2   | 1.8   |
|                           | 5-10      | 0.9   | 1.0   | 0.8   | 0.6   |
| HP+ CaSiO₃, 10 t ha⁻¹     | 0-5       | 2.8   | 2.5   | 2.0   | 1.4   |
|                           | 5-10      | 0.7   | 0.6   | 0.6   | 0.4   |
| HP+ SiO₂, 5 t ha⁻¹        | 0-5       | 2.5   | 2.0   | 1.8   | 1.0   |
|                           | 5-10      | 1.0   | 0.8   | 1.0   | 0.7   |
| HP+ SiO₂, 10 t ha⁻¹       | 0-5       | 1.6   | 1.3   | 1.1   | 0.3   |
|                           | 5-10      | 0.6   | 0.4   | 0.3   | 0.2   |
| LSDₐₛ                     |           | 0.4   | 0.3   | 0.4   | 0.3   |

Dehydrogenase and catalase together are considered as a sensitive indicator of viable microorganisms and soil quality. Dehydrogenase enzymes take part in oxidation of organic compounds and correlate with HC degradation [5]. Catalase is an antioxidant enzyme providing decomposition of hydrogen peroxide to water and oxygen [16]. The HC pollution led to substantial reductions in the activities of catalase and dehydrogenase (Table 4). Silicon substances, especially SiO₂, promoted a significant increase in the activities of both enzymes. Increased soil dehydrogenase activity evidences enhanced HCs oxidation. The effect of SiO₂ was much higher than that of CaSiO₃, perhaps due to a higher solubility on Si.

Table 4. Effect of Si substances on catalase and dehydrogenase activities in HC-polluted soil.

| Treatment                  | Catalase, O₂ mL | Dehydrogenase, mg of formasana g⁻¹ | Sampling depth, cm of dry soil | Catalase, O₂ mL | Dehydrogenase, mg of formasana |
|----------------------------|-----------------|-----------------------------------|-------------------------------|-----------------|-------------------------------|
|                            | Field test      |                                    |                               | Greenhouse test |                               |
| Control                    | 6.52            | 4.87                              | 0-5                           | 5.83            | 4.11                          |
|                           |                 |                                   | 5-10                          | 4.22            | 2.21                          |
| Hydrocarbon pollution (HP) | 2.30            | 3.60                              | 0-5                           | 1.54            | 1.12                          |
|                           |                 |                                   | 5-10                          | 1.11            | 0.34                          |
| HP+ CaSiO₃, 5 t ha⁻¹      | 2.95            | 3.94                              | 0-5                           | 2.14            | 1.98                          |
|                           |                 |                                   | 5-10                          | 2.43            | 0.95                          |
| HP+ CaSiO₃, 10 t ha⁻¹     | 3.93            | 4.12                              | 0-5                           | 5.12            | 2.21                          |
|                           |                 |                                   | 5-10                          | 3.84            | 1.34                          |
| HP+ SiO₂, 5 t ha⁻¹        | 5.16            | 4.93                              | 0-5                           | 5.34            | 4.02                          |
|                           |                 |                                   | 5-10                          | 4.11            | 2.13                          |
| HP+ SiO₂, 10 t ha⁻¹       | 5.14            | 5.65                              | 0-5                           | 6.34            | 4.23                          |
|                           |                 |                                   | 5-10                          | 5.44            | 2.36                          |
| LSDₐₛ                     | 0.05            | 0.04                              |                               | 0.06            | 0.05                          |

The obtained data has shown that Si-rich substances had a positive influence on the HC-contaminated soil, accelerated HC degradation, and promoted microbial activity. Among two tested Si substances, SiO₂, as having a higher solubility of Si, was more efficient. It is possible to suppose that soluble forms of Si (mono- and polysilicic acids) play an important function in the HC-polluted soil remediation.
Several mechanisms responsible for Si-mediated purification of the HC-contaminated soil can be supposed: a) changing physical soil properties; b) capsulation of HC molecules by polysilicic acid; c) adsorption of monosilicic acid by HCs leading to enhanced hydrophilicity; d) direct effect on soil microbial activity. Some types of Si-rich materials are cheap and available in large volume as being industrial by-products. Therefore, followed ecological expertise on the content of inorganic pollutants, such materials could be involved in soil restoration strategies.

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