IMPACT OF SOIL ORGANIC POLLUTANTS ON DIFFERENT TYPES OF CROPS - REVIEW

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Abstract. The organic pollutants of soil like associated petroleum hydrocarbons are a major source of concern for food safety, especially in underdeveloped and developing countries of the world. The increasing concentrations of toxic compounds in agricultural soils contaminated with organic pollutants affect physiology, biochemistry and development and growth of crops, and overall productivity. Organic pollutants can degrade soil structure, disrupt microbial communities, and reduce soil fertility. Due to the difference in the composition and concentration of the different organic pollutants, they have impact on soil, on plant growth and development in different ways and at different rates. The current review aims to give an overview of the response of plants to organic pollution according to factors such as the type, composition, concentration, persistence of organic pollutants, type and characteristics of soil, plant species and climate. Petroleum hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) are part of the most significant classes of organic pollutants, due to their long-term environmental persistence, long-term toxicity, bioaccumulation, and biomagnification properties of living tissues. Up to 90% of all petroleum hydrocarbons are deposited in the soil due to their high hydrophobicity, which improves the rapid interaction with soil particles and their permeability in the lower layers. Thus, this review summarizes the current state of research on the effects of organic pollutants, hydrocarbons especially, on physiology, biochemistry, development and growth of crops.

Keywords: soil pollution, organic pollutants, crops, hydrocarbons.

Introduction

The soil is the fundamental non-renewable resource, which fulfills many vital functions, namely: it provides approximately 95% of global food production for the population, maintains the health and quality of ecosystems, stores, filters and transforms essential substances (water, carbon, nitrogen), is a source of raw materials, carboniferous basin [1]. Consequently, its pollution has particularly serious effects on the ecosystem functions, food security and human health, contributes to the loss of terrestrial and aquatic biodiversity. Soil pollution has become a general environmental problem and one of the world's greatest challenges to food security and human health. Therefore, studies on soil pollution risk assessment and remedial strategies are particularly important.

Organic pollutants in soil can originate from various sources such as industrial activities, transportation, agriculture, waste disposal. The most common organic pollutants in soil are petroleum hydrocarbon contaminants. The oil industry has experienced significant growth over the last decades due to the world' s population growth, industrialization and urbanization, technological advancements, and economic development. All these factors involve an extensive high consumption of petroleum products and therefore that has resulted in serious environmental issues [2-4]. Romania has a long history of oil production, dating back to the mid-19th century, therefore the oil industry has played a crucial role in Romania's economic development. The activities in the oil sector have impact on the soils in Romania: exploration and production of oil, oil refining, transportation, distribution, and consumption of oil.

Petroleum hydrocarbons (PHs) and polycyclic aromatic hydrocarbons (PAHs) are part of the most significant classes of organic pollutants, due to their long-term environmental persistence, long-term toxicity, bioaccumulation, and biomagnification properties of living tissues. Up to 90% of all petroleum hydrocarbons are deposited in the soil due to their high hydrophobicity, which improves rapid interaction with soil particles and their permeability in the lower layers [5; 6]. Petroleum hydrocarbons are compounds derived from mineral sources, crude oil, including various forms of hydrocarbons such as alkanes, alkenes, and aromatics (polycyclic aromatic hydrocarbons). Petroleum hydrocarbons are ubiquitous in the environment due to spills, leaks, industrial discharges, and combustion processes. PAHs are a group of organic compounds composed of multiple fused aromatic rings. They are formed during incomplete combustion of organic materials, such as fossil fuels, wood. Petroleum hydrocarbon

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contamination of soil is often associated with industrial activities (stacking of oil slag and sludge, wastewater from oil extraction, oil spill, exploitation of petroleum), vehicle emissions, and urban runoff. In addition, petroleum hydrocarbon polluted soil causes chemical contamination of groundwater, which limits its use and causes health and economic damage, environmental problems, and decreased agricultural soil productivity. Petroleum in the soil pollutes the groundwater environment through diffusion and migration. The increasing concentrations of toxic compounds in agricultural soils contaminated with organic pollutants affect physiology, biochemistry, development and growth of crops, and overall productivity [7]. Due to the difference in the composition and concentration of the different organic pollutants, they have impact on soil, on plant growth and development in different ways and at different rates. They bioaccumulate in living organisms and are known to be carcinogenic and mutagenic, posing significant health risks to humans and other organisms [8-10]. Therefore, controlling petroleum hydrocarbon release and mitigating their impact on the environment is crucial for sustainable development and public health.

The current review summarizes the current state of research on the effects of organic pollutants, hydrocarbons especially, on agricultural soil, and development and growth of crops.

Materials and methods

The materials for this paper are represented by the review articles, research manuscripts of scientific journals, conference proceedings, scientific books and other online publications and sources of information. All these collected articles were explored, consulted, studied, analyzed and the most important and relevant information was summarized about the impact of soil organic pollutants on the environment. All materials used are cited in the text and presented in the list of references.

Results and discussion

Soil interaction with petroleum pollutants

The interaction between petroleum hydrocarbons and soil is a critical aspect of environmental chemistry and soil science. The behavior of petroleum hydrocarbons in the soil and the degree to which they are retained within the soil depends on several factors, such as the soil type, soil composition, soil properties (porosity, permeability), the physical and chemical properties of petroleum pollutants (solubility, hydrophobicity, polarity, lipophilicity, molecular structure) and environmental conditions (moisture, temperature) [11]. Petroleum hydrocarbons, including polycyclic aromatic hydrocarbons, tend to accumulate in the surface layers of the soil to the depths of 40 cm [12]. After the petroleum pollutants entering the soil, there are several processes, including migration, adsorption, and degradation [13]. Petroleum pollutants can migrate through soil due to their fluid nature and that can lead to the spread of contamination even to groundwater and water surface. Organic contaminants, including petroleum hydrocarbons, are often adsorbed into soil surfaces through physical mechanisms, due to hydrophobic forces [14]. Absorption can reduce pollutant mobility in the soil limiting their potential to migrate further. Degradation processes can transform petroleum pollutants into simpler compounds, less harmful and non-hazardous substances. Thus, biodegradation is a treatment method used to remove petroleum hydrocarbon contaminants from the soil, improving the microbial diversity and community [15; 16].

The interaction of petroleum pollutants with soil components and microorganisms can significantly alter their properties and transport behavior in the environment [17].

As it was shown in many research papers, the presence of petroleum hydrocarbons in soil can have significant impacts on the soil properties and microbial activity [18], thereby altering the ecological structure and functional soils [19]: affect the soil moisture levels, influence the soil pH (cause alteration of the availability of nutrients in the soil), affect the availability and cycling of nitrogen in soil, exchangeable potassium content in soil and enzyme activity (urease, catalase, dehydrogenase) [20-22]. Increased pollutant concentration leads to aggregation and increased clay content [23], decreased soil porosity and increased impermeability and hydrophobicity [24], inhibiting plant root growth and decreasing the soil bacterial numbers. Soil bacteria play a crucial role in nutrient cycling, decomposition, soil fertility, and soil health. Straight-chain alkanes have the greatest influence on the number of bacterial species [25]. According to studies, the main contaminant that causes soil salinization and acidification is benzopyrene, which is present in petroleum [26]. Petroleum-derived compounds fill the pore spaces in soil, leading to compaction and it causes limitation of the movement of water, air [27] and nutrients (sodium, potassium, sulfates, phosphates, nitrates) within the soil [28; 29]. The increasing of toxic compounds present in agricultural soil contaminated with petroleum hydrocarbons minimizes the development and growth of crops and thus causes decline in crop productivity [7].

Impact of petroleum pollutants on crop growth and development

Pollutants in the soil find their way into plants through various passive transport and uptake processes [30]: absorption with transpiration water – pollutants dissolved in soil water can be taken up by plant roots along with essential nutrients, and they are transported through the plant via the xylem and phloem vessels as part of the transpiration stream; diffusion from soil into roots – pollutants can diffuse into the root tissues; attachment of soil particles, followed by diffusion into plant – pollutants adhere to soil particles, and when these come into contact with plant roots, can diffuse into root tissues (Fig. 1).

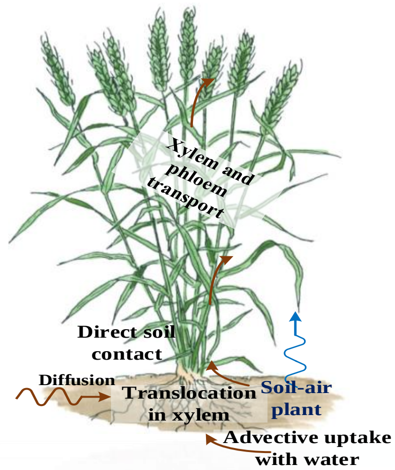

Fig.1. **Transport and uptake process in soil-plant system** (adapted by [30])

Thus, plants absorb petroleum pollutants from soil through their roots (phytoextraction), transport them to leaves and fruits, as well as store pollutants in these plant parts. When hydrocarbons enter the intercellular spaces of plant tissues, they cause damage to cell walls, leading to leakage of plant tissue contents, plasmolysis, cell shriveling, disruption of conducting tissue function, and tissue dehydration. In cereals, deposition of petroleum-derived substances is observed around cell walls and parenchyma preventing water transport [24].

The severity of plant responses to petroleum pollution depends on various factors, including the type and concentration of pollutants, plant species, environmental conditions, soil characteristics, and duration of exposure [31-35].

Plants exhibit responses to petroleum pollution at multiple levels such as physiological, biochemical, and molecular.

The presence of PAHs can trigger biochemical and physiological changes in plants even before anatomical and morphological changes become apparent [40]. This early detection mechanism is crucial for plants to respond effectively to stress factors. Plants are known to respond to stress factors by adjusting their production of phytohormone [41; 42]. This process is influenced by changes in the levels and activities of enzymes involved in phytohormone biosynthesis and degradation [43]. Ethylene (C2H4) is a gaseous phytohormone that plays a significant role in plant growth and stress responses. Increased ethylene production is often one of the initial reactions of plants to stress factors, including exposure to PAHs [44; 45]. Another indicator by which the researchers measure the stress tolerance in plants is proline content. In the case of rye plants exposed to soil pollution with petroleum hydrocarbons, the proline content increased in the shoots of plants [46], suggesting that they are undergoing stress and responding by accumulating this amino acid.

The absorption of PAHs by plants can vary based on the molecular weight of the PAH compound [47]. In paper [47] was shown that three-and four-ring PAHs are typically absorbed more readily by plants compared to higher-molecular-weight (five-and six-ring) PAHs. This is because smaller PAH molecules are more water-soluble and have greater mobility in the soil, making them more available for uptake by plant roots. However, high-molecular-weight PAHs are less soluble in water and tend to be more strongly adsorbed by soil particles. Additionally, plant roots may exude certain compounds, known as root exudates, which can influence the availability and uptake of PAHs. These exudates can include substances that enhance or inhibit the uptake of specific chemicals from the soil into the plant roots. Furthermore, the outer layers of plant roots, including the root exodermis and root peel, can act as barriers that limit the entry of certain substances into the plant vascular system. This natural defense mechanism can help prevent the uptake of larger, less soluble PAHs by plants, particularly those with taproots that penetrate deeply into the soil.

Pollution of soil by hydrocarbons affects the growth and development of plants, inhibition of germination, reduction in the height and weight, reduction of the biomass, the root quantity, the size of the leaves, the chlorophyll content, changes in the cellular structure and even death of the canopy [36].

Root growth is particularly sensitive to the presence of toxic substances like PAHs because root tissues are in direct contact with the contaminated environment [48]. Changes in root growth patterns can serve as early indicators of stress and contamination, providing valuable information about the health and condition of plants. Numerous studies have demonstrated that the presence of hydrocarbons in soil significantly induces severe phytotoxicity, causes inhibition of seed germination and reduced growth and development of plants [48-51]. In the paper [50] it was shown how the presence of fluoranthene polycyclic aromatic hydrocarbons affects the germination, growth, and morphological characteristics of the root system of corn and pea plants. It was observed how the inhibition of the growth of the primary root and the formation of secondary roots, replacing its function, takes place. The total length of primary and lateral roots was significantly reduced at fluoranthene concentrations higher than 1 $mg \cdot l^{-1}$ in maize and 4 and 7 $mg \cdot l^{-1}$ in pea. In both maize and pea plants, the number of lateral roots increased significantly at concentrations lower than 1 $mg \cdot l^{-1}$ and inhibited at concentrations of 4 and 7 $mg \cdot l^{-1}$.

Seed germination and plant growth of wild oat, sweet corn, wheat, and lettuce in soil contaminated with methyl tert-butyl ether (MTBE – an organic, water-insoluble, ethanol-soluble, ether compound used as a gasoline additive worldwide to reduce emissions of carbon monoxide, ozone, and unburned hydrocarbons) are significantly reduced [52]. The main source of soil contamination with MTBE is the accidental spillage of fuel during storage or transport [53]. Due to its high solubility in water, MTBE can be readily absorbed by plants and transported within the plant from roots to stems. [52]. Seed germination in diesel-contaminated soil (diesel is a complex mixture of hydrocarbons having an average carbon number of C8-C26; there are many aromatic compounds and long hydrocarbon chains) varies greatly between plant species, but also within species [12] and, as shown in [32], where 25 plant species were studied, inhibition of germination increases with increasing the diesel concentration. Plants grown in diesel-contaminated soil show changes in the root system through root structures appearing in unusual positions or lateral roots, which do not appear in the case of plants grown on uncontaminated soil. The level of contamination determines the degree of damage and inhibition. At high levels of contamination, although there is germination, in some crop plants, there is a reduction in seed germination, affecting radicle and plumule length [54]. In [55] reduced germination of maize, perennial ryegrass, alfalfa, pea, and soybean seeds is described as the level of diesel contamination increased. Germination rates were higher in corn than in the case of the other studied plants, which were much more sensitive to diesel contamination. The authors of the papers [54; 55] concluded that maize can be used for phytoremediation of oil-contaminated soils, being able to withstand all levels of contamination. Maize, mung bean, millet and sorghum crops tolerated diesel contamination at levels of 2.5 - 5% [37] with a total seed germination percentage between 43.7% and 86.7%. Level of contamination of 7.5% diesel significantly reduces maize germination of 74% reduction, followed by millet with a 67% reduction [37]. In addition, in the paper [37] was reported that diesel contamination also caused a reduction in the radicle length of the four cultivated plants studied. At 5% contamination level, the longest radicle (1.92 cm) was recorded in bean followed by maize (1.36 cm). Also, at a level of 10% diesel contamination, these two plant species showed greater root growth than sorghum and millet. There was a reduction in radicle growth in all plant species in the later contamination levels. Phytotoxicity bioassay results showed that maize and bean plants showed better growth and germination even at high concentrations of diesel compared to sorghum and millet. Therefore, these two species have a greater potential for phytoremediation in diesel-contaminated soils. On the other hand, biological testing of sensitive plants such as sorghum and millet can assess soil pollution and remediation, as the plant reactions can reflect the level of pollution in its environment [37]. Similar results were shown in [38], where diesel contamination at 5% causes reduction in seed germination of maize by 40%, and reduction of the root and shoot length. The significant reduction in germination and seedling growth of wheat cultivated in soil contaminated with phenanthrene (polycyclic aromatic hydrocarbon) by 68.0% and 89.1% respectively [39], indicates the toxic effects of this compound on the plant.

Exposure of plant seeds to diesel impacts viability and germination rate depending on the contaminant concentration and/or duration of exposure [37; 56]. The mechanisms by which diesel oil impacts seed viability and germination rate can be classified into: biological damage (toxicity) and physical constraints (oxygen and water repellent). Diesel fuel contains both volatile and non-volatile components [32]. It is the volatile fraction, rather than the non-volatile components, that is primarily responsible for the inhibition of seed germination and plant growth [32]. At temperatures lower than 20^{o} C, this effect is minimal, due to the reduced volatility of hydrocarbons [57]. In the paper [56] it was shown that alfalfa seeds soaked in vitro in diesel tend to have a delay phase before germination, and this delay increases with exposure to higher and higher concentrations of diesel. This can be attributed to the ability of hydrophobic diesel to create a water-repellent coating around the seeds.

Table 1

Impact of petroleum pollutant on crops

Plant species	Pollutant type	Pollutant concentration	Impact on plants	Ref.
Rye	Crude oil	30 g·kg^{-1}	Inhibition of rye growth; a decrease in content of chlorophyll and total chlorophylls.	[46]
Sorghum	Diesel oil	15 g·kg^{-1}	Inhibition of seed germination, length of root and shoot.	[58]
Willow and maize	Crude oil	50 g·kg^{-1}	Reduce the chlorophyll content, the growth of the plants, the biomass, the height, the root quantity, and the size of the leaves.	[36]
Maize and millet	Diesel	7.5 g·kg^{-1}	Significantly reduce maize germination of 74% reduction, followed by millet with 67% reduction	[37]
Maize	Diesel fuel	5 g·kg^{-1}	Reduction in seed germination by 40%, and reduction of root and shoot length.	[38]
Wheat	PAHs	0.2 mg·mL^{-1}	Inhibition of seed germination, and reduction of growth and chlorophyll content. Induce oxidative damages in the early development stage of wheat.	[39]
Wheat, barley, alfalfa, and clover	Mixture diesel oil-petrol	20 ml·kg^{-1}	Toxic effect on seed germination and growth.	[59]
Maize and pea plants	PAHs - fluoranthene	1-7 mg·l^{-1}	Affects the germination, growth and morphological characteristics of the root system; inhibition of the growth of the primary root and formation of secondary roots, replacing its function.	[50]
Winter common wheat	Petroleum products: petrol, engine oil, diesel oil	6000 mg·kg^{-1}	Adverse effect on the morphological characteristics of winter wheat; significantly affected the activity of antioxidant enzymes and the levels of antioxidants in the plants; significantly modified the levels of nutrient and heavy metals in the plants.	[60]

Table 1 (continued)

Plant species	Pollutant type	Pollutant concentration	Impact on plants	Ref.
Maize	Crude oil	50 ml·kg^{-1}, 100 ml·kg^{-1} and 150 ml·kg^{-1}	Reduction in the growth, yield and leaf chlorophyll of maize plant. Heavy metal (Cr, Ni, Cd, Cu) concentration significantly increased in leaves, stem, and root, with increase in the volume of crude oil pollution .	[61]
Rye, rape, mustard, peas	Petroleum	1000 - 8000 mg·kg^{-1}	At the maximum concentration of soil pollutant (8000 mg·kg^{-1}), the highest germination rate was obtained for rye (70%) and rape and peas were sigillary affected (60%). In the next stage, of root elongation, the most affected were rye seeds followed by mustard, peas, and rape.	[62]
Sorghum	PAHs - phenanthre ne	10 and 100 mg·kg^{-1}	Affected morphological, physiological, and biochemical characteristics of sorghum plants; decrease in germination capacity, seedling survival, and biomass accumulation; reduced content of photosynthetic pigments.	[63]

Conclusions

1. Contamination by hydrocarbons has severe negative impacts on the plant growth, development, and productivity, as it disrupts essential physiological processes and compromises the structural integrity of plant tissues.
2. The biochemical and physiological responses of plants to PAH exposure involve complex regulatory mechanisms aimed at adapting to and mitigating the effects of environmental stressors.
3. The absorption of PAHs by plants is influenced by various factors including the chemical properties of the PAH compounds, soil characteristics, root exudates, and the structure of the plant root system. Understanding these factors is crucial for assessing the potential risks of PAH contamination to affect the plant health and the environment.

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Author contributions

Conceptualization, E.M.Ș.; methodology, E.M.Ș. and I.I.; formal analysis, M.F., investigation E.M.Ș. M.F. and M.M.; data curation, E.M.Ș. M.F. and M.M; writing - original draft preparation, E.M.Ș.; validation, A.G., I.I. and G.V.; writing - review and editing, E.M.Ș. and M.M., visualization, A.G. and G.V.; project administration, I.I.; funding acquisition, I.I. All authors have read and agreed to the published version of the manuscript.

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