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TOXICITY OF PETROLEUM SUBSTANCES TO MICROORGANISMS AND PLANTS

TOKSYCZNOŚĆ SUBSTANCJI ROPOPOCHODNYCH DLA DROBNOUSTROJÓW I ROŚLIN

Abstract: The paper discusses sources of petroleum substances in environment and threats caused by petroleum contamination of water and soil. The physicochemical and biological properties of petroleum substances have been determined along with their toxicity, particularly that of aromatic hydrocarbons, including the so-called *BTEX* group (benzene, toluene, ethyl benzene and xylenes) to microorganisms and plants. Much emphasis has been laid on the properties which shape toxicity. The effect (typically degrading one) on live organisms present in water and soil environment, including biological equilibrium of soil (abundance of microorganisms, enzymatic activity), has been discussed as well as the growth and development of plants growing on soil polluted with these substances. In addition, factors (soil or water properties and condition, C:N ratio, pH reaction, soil moisture, content of organic substance, fertilization, type and species of aquatic or land organisms) which influence the effect produced by petroleum substances on live organisms in environment have been mentioned.

Keywords: toxicity, petroleum substances, sources of contamination, microorganisms, soil, plants

Sources of petroleum substances in environment

Man has long been interfering with and frequently disturbing the natural balance in ecosystems, thus modifying and re-shaping the surrounding nature [1]. The development of civilization, accompanied by industrialization, has caused severe contamination of natural environment over extensive parts of many countries. The whole biosphere is being degraded due to man's destructive activity, and live organisms are poisoned by noxious substances from various sources [2, 3].

Recently, the advancing industrialization of the world economy has led to a large increase in the consumption of petrochemical compounds [4, 5]. Likewise, in Poland the dynamically growing number of motor vehicles leads to increased demand for fuel, which in turn means purchasing and processing more crude oil. It also stimulates fuel transport, storage and distribution. As a result, the risk that petroleum substances will permeate into

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environment has increased [6]. Thus, contamination of natural environment with petroleum substances has become a major issue in ecology. Migration of petroleum substances to open water reservoirs, groundwater and soil can have serious consequences due to the highly toxic and cancerogenic nature of such chemicals [7, 8].

Petroleum substances when introduced to environment affect both its abiotic (non-live) and biotic elements, including microorganisms, plants, animals and people. Thus, soil contamination with these chemicals is a grave problem as the components of petroleum products affect all live organisms [9].

Petroleum products consist of over 1,200 different hydrocarbons [10], of which around 230 contain from 3 to 12 carbon atoms, which means that they include aliphatic, aromatic and cyclic hydrocarbons [11]. Paraffin (aliphatic) hydrocarbons are the basic hydrocarbon group of the oldest types of petrol and dominate in the petrol fraction. They are chemically inert, therefore are of no risk to environment [12]. However, the most abundant in petroleum (over 50% of its mass) are naphthene (cycloparaffin) hydrocarbons, whose amount increases as the boiling point is higher. Within this group, methylcyclopentane and methylcyclohexene are the most numerous, in some cases constituting 2% of petroleum mass [13]. As for aromatic hydrocarbons, petroleum rarely contains more than 15% of these compounds. Noticeable are mono- and polycyclic aromatic hydrocarbons. The former include the so-called BTEX group: benzene, toluene, ethyl benzene and xylenes, which are highly toxic and common pollutants of soil and groundwater due to petrol leaks from leaking tanks [14]. Polycyclic hydrocarbons are not very mobile in soil, hardly soluble in water and resistant to physical, chemical or biological degradation [15].

Products obtained from petroleum have different physical, chemical or toxic properties; they are characterized by different refinement additives and produce various effects to environment [8]. It is unquestionable that use of petroleum and petroleum-based products is very dangerous to nature. Therefore, identification of toxicity of particular petroleum components is extremely important as it will enable people to recognize potential ecological threats connected with exploitation of petroleum products [16].

The actual toxicity of petroleum and petroleum products can vary depending on the chemical composition and structure of hydrocarbons. Large concentrations of such substances in nature are sources of severe contamination and an immediate threat to all live organisms dwelling in a polluted habitat. Petroleum pollution also influences plant production, threatens groundwater and creates a risk of poisoning animals and people, in extreme cases causing death [17]. It needs to be emphasised that petroleum substances can accumulate in food and this is the most common way in which they enter live organisms [16].

Besides, hydrocarbons and their derivatives are the most numerous and widespread group of organic compounds which occur in surface and groundwaters. It is so because they can penetrate the hydrosphere as a result of transport accidents or industrial failures, in surface effluents or with sewage [18]. Contamination of water reservoirs with petroleum substances is extremely dangerous as such pollutants create on the surface of a water body a membrane, which cuts off oxygen supply and hinders the self-cleaning of water [19]. Moreover, decomposition of petrol in water causes oxygen consumption from water and is determined by the water temperature, salinity, chemical composition and reaction [20].

Seas are mainly polluted by crude petroleum, which can be spilt due to accidents involving tankers, faulty operations on oil rigs and leaking tanks stored in port warehouses.

Such spills are typically single events, but volumes of spilt oil are usually large enough to cause enormous ecological disasters. Much smaller amounts of petroleum enter seawaters with waste discharged from ships and as natural leaks from oil deposits under seabed [21]. However, the amounts of petroleum reaching seas and oceans due to tectonic motions of the earth's crust are almost negligible when compared with the oil spills occurring as a result of man's activity [22]. Evidently, the highest proportion of the pollutants found in seawater, over 1/3 of crude oil permeating into sea, is made up by petroleum and paraffin derivatives released during regular exploitation of ships. One of the major sources is ballast water discharged from cargo holds of tankers, which contains about $0.3 \div 1.0\%$ of petroleum [18].

A small amount of petrol spilt on sea makes a spill which spreads with waves and wind at a speed of about $3\div4\%$ of the wind speed. The spill is obviously the thickest at the source of spill and thinner at the edges, and typically equals 0.01 to 1 µm. An oil spill disappears in 12-24 hours owing to evaporation, photolysis and absorption by sea plants and animals [6]. Nevertheless, petroleum and its products are very harmful to water bodies as they can float on water surface for a long time [20], thus limiting oxygen and sunlight access to deep water. Besides, under the influence of gravitational forces and surface tension, a petroleum spill spreads and stratifies itself over the sea surface. In between one to three weeks, some petroleum (about 1/3) evaporates and, airborne, travels over large distances. With rainwater, it can re-enter sea or reach land [18].

Effect of petroleum substances on microorganisms

Both small and large oil spills affect organisms inhabiting aquatic habitats, causing their diseases and death [23]. Petroleum compounds often accumulate in organisms of animals dwelling at seabed, thus entering a food chain in which man is the final link. Aromatic hydrocarbons of a low boiling point are highly toxic to nearly all water organisms, unlike paraffin hydrocarbons, which do not reveal toxic properties. Furthermore, petroleum lying on feeding grounds of birds may accelerate their extinction [22].

Among the components of petroleum and petroleum products, the most toxic are aromatic compounds, particularly polycyclic aromatic hydrocarbons, which are highly mutagenic and cancerogenic. It has been found out that presence of petroleum pollutants in water facilitates solubility of PAHs and increases contamination of water with toxic combinations of these compounds. According to the Ordinance of the Minister for the Environment of 20th August 2008 [24], the permissible quantity of petroleum derived compounds, the oil index for inland waters, should not exceed 0.2 mg dm⁻³, including 0.1 μ g dm⁻³ of benzo[a]pyrene, 0.03 μ g dm⁻³ of total benzo[b]fluoranthene and benzo[k]fluoranthene, and 0.002 μ g dm⁻³ of total benzo[g,h,i]perylene and indeno[1,2,3-c,d]pyrene.

Petroleum compounds can enter soil environment with falling dust, after which they strongly absorb to soil surface [22]. Benzene, toluene and other aromatic hydrocarbons make up 82% of the total hydrocarbon pollutants which permeate from the aeration sphere into groundwater [25]. Moreover, the uptake of these hydrocarbons by edible and fodder plants can have serious ecological consequences, both sanitary and health-related ones [15].

Due to their very slow migration, which is associated with the persistence and insolubility of their particles, PAHs accumulate in soil and can persist in it for a very long time. It is important to add that these compounds are hardly biodegradable. They can

undergo biotransformation via adduction to other organic compounds and entering biochemical cycles. Benzo[a]pyrene is considered to be the strongest cancerogenic polycyclic hydrocarbon [22]. The list of mutagenic and cancerogenic substances includes a large number of indirect products obtained while processing petroleum [26]. The Ordinance of the Minister for the Environment of 9th September 2007 [27] states that the permissible amount of benzo[a]pyrene in soil, depending on soil usage, ranges from 0.02 to 5 mg kg⁻¹ d.m., that of the total PAHs is from 1 to 2 mg kg⁻¹ d.m. and for benzene from 0.05 to 3 mg kg⁻¹ d.m. of soil.

It is also important that aromatic hydrocarbons are capable to join DNA and RNA, thus revealing mutagenic activity by disturbing the proper structure of genetic material of multiplying cells in a living organism, typically in a way that is not seen in a given individual but in its progeny, resulting in physical or mental retardation or in genetic diseases. Aromatic hydrocarbons act as initiators of mutation and cancer processes, which cause transformation of healthy cells, which means that they do not always directly cause mutation in DNA but are the so-called premutagenes, ie having entered an organism they undergo metabolic activation, stimulated by appropriate enzymes, and this activated form of PAHs has a degenerative influence on the cell DNA [28].

Oils, like other petroleum products entering soil, can produce varied effects on soil microorganisms [29, 30], including saprophytic fungi [31, 32], causing changes in quantitative and qualitative composition of soil microorganisms. Moreover, petroleum products can affect other soil properties. In a study conducted by Wyszkowski and Ziolkowska [33], soil pollution with diesel oil raised the acidity of soil, expressed as lowered soil pH, total exchangeable cations, total exchangeable capacity and degree of alkaline cation saturation as well as tendency towards increasing hydrolytic acidity. The influence of petrol on physicochemical properties of soil was evidently weaker than that of diesel oil. Petroleum substances can also influence the content of organic carbon and available forms of micronutrients in soil [34]. Such modifications of the physicochemical soil properties cause changes in the biological composition of soil habitats, particularly mass mortality among animals inhabiting topmost layers of soil and rapidly increasing content of organic matter [18]; resultant is the disruption of the biological equilibrium of soil [35]. This is due to the decreasing number of aerobic microorganisms [30]. Small amounts of petroleum substances can stimulate abundance of soil microbes. With this respect, diesel oil produces better effects than petrol, which is more toxic [36]. Many studies [37-43, 45, 46] confirm that petroleum substances can considerably modify the natural biological activity of soils. In most cases, they are highly toxic, strongly inhibiting the development of microorganisms and, consequently, depressing the enzymatic activity of soils. Oleic components derived from petroleum coat soil particles and crops with thin film which retards proper course of live processes and disturb microbiological processes in soil [19].

Moderate soil pollution with petroleum substances can stimulate the enzymatic activity of soil [41], including the activities of dehydrogenases, urease, alkaline phosphatase and nitrification activity of soil [35]. Galas et al [47] as well as Xu and Johnson [48] found out that the level of the activity of dehydrogenases is largely a function of the concentration of hydrocarbons in soil. Higher biological activity of most of the examined parameters of soil contaminated with diesel oil is most likely caused by enhanced multiplication of microorganisms and their raised activity, as diesel oil is a good potential nutrient substrate to some microorganisms [45, 49-51]. Soil contamination with petroleum substances for the first few weeks caused increased activity of amylases [9], proteases [9], dehydrogenases [9, 35], urease [35], alkaline phosphatase [35] and soil nitrifying activity [35], whereas later it typically depressed the activity of these enzymes [9, 35].

However, the enzymatic activity of soil depends on many other factors, such as soil pH reaction or presence of organic matter. Amending soil with organic substance, for example compost, or modifying the soil reaction by liming can stimulate the activity of urease, alkaline phosphatase and soil nitrifying activity [35]. Raised activity of dehydrogenases, urease, alkaline phosphatase and soil nitrifying activity in a limed series can most probably be attributed to the increased pH value, as in the soil of a reaction close to neutral the growth of bacteria and *Actinomyces* is more intensive whereas that of fungi slows down [47]. Moreover, amounts of plant available nutrients increase, which stimulates the growth and development of plants [5, 52]. Activities of particular soil enzymes are mutually correlated. In the study of Wyszkowska and Wyszkowski [35], the activity of dehydrogenases, urease, alkaline phosphatase in soil contaminated with diesel oil was positively correlated while that of acidic phosphatase - negatively correlated with soil nitrifying activity.

Effect of petroleum substances on plants

Small amounts of petroleum or petroleum-derived substances are not harmful to soil. However, more than 1 kg petroleum per m^2 of soil surface can lead to necrosis of plants. This effect is due to the anaerobic, hydrophobic conditions created by the pollutants, which cause disorder in the soil-plant-water relationships [53]. Strong contamination of soil with petroleum substances can lead to extensive degradation of plant cover up to its complete disappearance [54-56]. Surface contamination of soil not only limits or deteriorates the conditions for plant growth, but also depresses the value as well as the technological and nutritional usability of plant yields [57]. Wlodkowic and Tomaszewska [4] prove that plants respond variously to soil contamination with petroleum substances. It has been demonstrated that spring oilseed rape is highly sensitive to hydrocarbons leached from soil. Wyszkowski and Ziolkowska [58, 59], who completed experiments with spring barley, spring oilseed rape and yellow lupine as main crop, and maize and oat as aftercrop, demonstrated that depressed growth of crops attributable to soil contamination with petroleum substances depended on plant species and their sensitivity to contamination. Petroleum substances retarded the growth of plants proportionately to the contamination rate. They affected main crops more strongly than aftercrops. Rates of pollutants even as small as 2.5 cm³ kg⁻¹ of soil depressed the growth and development of crops. In general, diesel oil produced stronger effect than petrol. Regarding spring barley, the highest rates $(10 \text{ cm}^3 \text{ kg}^{-1} \text{ soil})$ of petrol completely stopped plant germination whereas identical rates of diesel oil strongly inhibited the process. Toxic effect of diesel oil on growth and development of spring barley has also been evidenced in a study by Przybulewska [60], in which soil contamination with diesel oil at a rate equal 10% w/w soil caused complete inhibition of germination of spring barley kernels. Also Wyszkowska and Kucharski [61] confirmed toxic influence of diesel oil on plants, as they demonstrated that it was highly toxic to yellow lupine on light soil (plant mass decreased by half) when it was introduced to soil in an amount as low as 0.5% of the maximum water capacity. In heavy soil, its negative

effect was much weaker. Toxicity of petroleum substances towards yellow lupine has also been verified in a study by Wyszkowski et al [5], in which the extent of the effect produced by soil contamination with diesel oil on the test crop depended on the type of soil, fertilization and plant organ.

The sanitary and nutritional quality of yields can also be questionable when contamination of soil with petroleum substances does not weaken the vegetative development of crops but can cause accumulation of hydrocarbons in plants [57]. Hydrocarbons, derived from petroleum products, apart from producing an indirect effect on plants via soil [62, 63], can have a direct influence by producing oily film on aerial parts of plants, thus reducing plant transpiration and respiration, decreasing permeability of plant membranes, causing disorders in metabolic processes which result in modifications in the chemical composition of plants and, finally, due to the toxic effect of some hydrocarbons in plants [5, 64].

According to Siuta [57], soil can be degraded to the following degrees:

- small degree, when contamination does not produce adverse effect on plant vegetation but the occurrence of hydrocarbons in the soil topmost layer is high;
- moderate, when point necrosis of grass plants is observable and the growth of arable crops is strongly weakened;
- large, when patches of grass plants die out and yields of crops decline by about 50%;
- very large, when grass plants disappear or completely die out and crop cultivation is impossible without soil rehabilitation treatments.

The actual effect of such pollutants on plants depends on many factors, including the concentration of petroleum substances in soil, soil properties and condition, the C:N ratio, pH reaction, moisture and oxygen content, content of organic substance, fertilization and plant species [65]. Plants which are grown on soils polluted with petroleum substances are often characterized by delayed germination; in some, the meristemal and root hair zones can be damaged. Furthermore, such plants have thin leaves of small assimilation surface and thin, short and poorly branched stems [18, 66]. The growth and development of plants is affected not only by the toxic influence of petroleum substances but also due to the lack of conditions needful for existence of plants [15] caused by the negative influence of petroleum substances, and in particular deficiency of phosphorus and potassium [67] as well as that of nitrogen, oxygen and water [68]. Because of their indirect toxicity, petroleum leaks are harmful to plants, whose resistance or tolerance to contamination with petroleum substances is connected with the depth of root systems, efficiency of replacing leaves that have been shed due to the contamination and whether or not the plants are equipped with storage organs and underground stalks, particularly rhizomes. Biodegradation of hydrocarbons in soil leads to the appearance of anaerobic conditions in the plant rhizosphere. Lack of oxygen and consequent production of hydrogen sulphide destroy roots of most plants, including large trees, which have a well-developed root system [53]. Petroleum contaminants, apart from increasing the amount of hydrocarbons in soil [56, 69], considerably raise the predominance of organic carbon over the content of nitrogen in the humus horizon, and when its availability is very high with a consequent large supply of energy and proportionately depressed availability of nitrogen, strong competition for nitrogen beings between microorganisms decomposing hydrocarbons versus plant root systems. This competition results in an acute shortage of nitrogen for plants, minimizing and sometimes completely inhibiting their growth [48].

The influence of petroleum substances on the growth and development of plants depends on their type and degree of contamination. Negative impact of small pollution with diesel oil on plants can be stronger than that produced by petrol. The effect produced by these pollutants on aftercrops is typically small, although it can be negative as well [58]. At the same time, petroleum substances affect the uptake of many macro- and micronutrients. Their influence on the content of macronutrients in plants depends on the type and rate of a petroleum substance involved on the species of plants. In an experiment reported by Wyszkowski and Wyszkowska [52], small rates of diesel oil (up to 3 g kg⁻¹ soil) raised the content of nitrogen, potassium and sodium in oat, whereas higher ones depressed these values. The negative influence of diesel oil on nitrogen concentration in plants has also been confirmed by Wyszkowski et al [5] testing yellow lupine. In other experiments, carried out by Wyszkowski and Ziolkowska [58, 70], it has been found out that evidently negative correlations occur between the degree of soil contamination with petrol or diesel oil and the content of N-total and N-protein in yellow lupine and, partly, in maize (only when polluted with diesel oil) [58]. They also depressed the content of most macronutrients in spring oilseed rape and, to a smaller extent, in oat [70] except calcium and magnesium in spring oilseed rape and potassium in oat, whose concentrations in plants increased under the influence of petroleum substances. Smaller modifications were observed in treatments polluted with petrol and larger ones when diesel oil was introduced to soil [70]. Diesel oil favoured accumulation of most macronutrients in aerial parts of maize, particularly the content of sodium, potassium and calcium [52]. Dimitrov and Mitova [71] found out that three out of the seven species they tested contained elevated amounts of macronutrients whereas the content of phosphorus and calcium did not change significantly under the influence of diesel oil. Petrol and diesel oil contamination favoured accumulation of potassium in grain and phosphorus in straw (only petrol) and roots of spring barley, but depressed the concentration of other macronutrients [59].

Thus, petroleum products polluting environment are an increasingly more serious ecological problem as contamination of water and soil with these chemicals has adverse effect on the microbiological and biochemical properties of soil and on plant production. They also have negative impact on animal and human health due to the fact that most of them are toxic to live organisms.

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TOKSYCZNOŚĆ SUBSTANCJI ROPOPOCHODNYCH DLA DROBNOUSTROJÓW I ROŚLIN

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Abstrakt: Przedstawiono źródła obecności substancji ropopochodnych w środowisku i zagrożenia związane z zanieczyszczeniem nimi wód i gruntów. Określono ich właściwości fizykochemiczne i biologiczne z uwzględnieniem toksyczności (zwłaszcza węglowodorów aromatycznych, w tym tzw. grupy BTEX - benzenu, toluenu, etylobenzenu i ksylenów) dla mikroorganizmów i roślin. Szczególny nacisk położono na właściwości decydujące o ich toksyczności. Opisano oddziaływanie (najczęściej degradujące) na organizmy żywe występujące w środowisku wodnym i glebowym, w tym na biologiczną równowagę gleby (liczebność drobnoustrojów, aktywność enzymatyczną) oraz wzrost i rozwój roślin rosnących na terenach zanieczyszczonych tymi substancjami. Przedstawiono także czynniki (właściwości i stan wód lub gleby, stosunek C:N, odczyn pH, uwilgotnienie gruntów, natlenienie, zawartość substancji organicznej, nawożenie, rodzaj lub gatunek organizmów wodnych i lądowych), które wpływają na oddziaływanie substancji ropopochodnych na organizmy żywe występujące w środowisku.

Słowa kluczowe: toksyczność, substancje ropopochodne, źródła zanieczyszczenia, drobnoustroje, gleba, rośliny