CZASOPISMO TECHNICZNE Ch
WYDAWNICTWO POLITECHNIKI KRAKOWSKIEJ

z. 2-Ch/2008
ISSN 0011-4561
ISSN 1897-6298

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EFFECT OF PETROL STATIONS ON THE CONTAMINATION OF THE SOIL ENVIRONMENT

WPŁYW STACJI BENZYNOWEJ NA ZANIECZYSZCZENIE ŚRODOWISKA GLEBOWEGO

A b s t r a c t

The study was carried out on soil samples collected in the proximity of a fuel tank at the distances of 5 m, 10 m, 50 m, 100 m and 200 m from it. The samples were analyzed for the content of crude oil derivative substances (Soxlet extraction method) and for the presence of organic carbon (Tiurin method and differential thermal analysis).

Keywords: petrol station, oil derivative substances, organic carbon

S t r e s z c z e n i e

W artykule przedstawiono wyniki badań gleby pobranej bezpośrednio przy zbiorniku, 5 m, 10 m, 50 m, 100 m i 200 m od zbiornika paliwa. Badania obejmowały zawartość substancji ropopochodnych oznaczonych metodą ekstrakcji w aparacie Soxleta oraz węgla organicznego metodą analizy różnicowej.

Słowa kluczowe: stacja benzynowa, substancje ropopochodne, węgiel organiczny

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1. Introduction

Today, approximately 6700 petrol stations, 56 fuel bases and 27,000 fuel tanks are operated in Poland. Petrol stations are classified as objects of a potentially high environmental impact, and that is why very strict environmental regulations together with relevant recommendations of the Office of Technical Inspection and The Energy Regulatory Office regulate their construction and operation. The Decree of the Minister of Economy (issued on 21 November 2005) specifies the technical conditions that must be met by liquid fuel bases, liquid fuel tanks and oil pipelines (providing long-distance transport of crude oil and petroleum products), and defines the requirements for their location [1]. Wastewater and precipitation water discharged by petrol stations must be treated before being sent to the sewer system [2]. The Water Act regulates the operation of petrol stations in the context of attaining relevant permissions [3].

A petrol station can be operated only upon obtaining the so-called administrative decision. Such decision is issued after submission of appropriate ecological permits and expires after 10 years. The ecological permits required for the administrative decision on the operation of a petrol station include: the permission to discharge wastewater into water bodies or soil and into sewer systems [2, 3], the permission to emit gases or particulates into the atmosphere [4], and the permission to generate solid wastes [5, 6].

By virtue of the Decree of the Minister of Economy issued on 21 November 2005, every liquid fuel base and station has to be equipped not only with installations, devices and systems preventing penetration of petroleum products into soil, surface water and groundwater, but also with measuring systems that permit monitoring and adequate warning of potential hazards. The deadline for executing this task was 31 December 2007.

Particular groups of petroleum products have been assigned detailed regulations pertaining to environmental issues, industrial safety and fire protection. According to their flash points, petroleum products (except liquefied petroleum gas) can be grouped into three classes [1]:

1. Class I: crude oil and petroleum products of flash point up to 294.15K (21°C).
2. Class II: petroleum products of flash point ranging between 294.15K and 328.15K (55°C).
3. Class III: petroleum products of flash point varying from 328.15K to 373.15K (100°C).

Crude oil and petroleum products storing tanks, as well as pipelines, are made subject to leak proof tests according to the following pattern: up to 30 years of service, ground tanks and pipelines should be tested every 10 years; after 30 years of service every 6 years [1]. Underground tanks and pipelines are to be tested every 10 years up to 20 years of service and thereafter every 5 years. Crude oil and petroleum products storing tanks in which the tightness of the interwall space is monitored continuously need not be subjected to leak proof tests [1].

The overall volume of storing tanks and the volume of a single tank at liquid fuel stations must not be larger than 500 m^3 and 100 m^3, respectively; the volume of a single tank at a container station must not exceed 30 m^3. Liquid fuel stations have to be sewered and equipped with the following items: specialized devices that prevent penetration of petroleum products into soil, surface water and groundwater; systems for measuring and monitoring the level of crude oil products being stored, and devices preventing the emission of vapours of class I petroleum products into the atmosphere. Annual losses in class I petroleum products that result from loading of fuel tanks should not exceed 0.01% of their capacity [1].

The distance of the liquid fuel dispenser (with the exception of the petrol station pavilion) must not be less than 10 m from buildings of a non-flammable construction, 20 m from other buildings, 20 m from the forest boundary, and 5 m from the boundary of the neighbouring undeveloped lot [1].

2. Ecological aspects of soil contamination with crude oil products

Owing to the character of services they offer, fuel bases and stations create a risk of soil contamination as a result of fuel tank leakage, and petrol or diesel oil spillage. The migration of the contaminants in the soil depends on a variety of factors which include, *inter alia*, the concentration of petroleum products, climate, and the following parameters of the soil: type, sorptive capacity, pH, and content of solid, liquid and air phase. In the case of wet soils, when high temperatures dominate, this will give rise to the occurrence of fast biodegradation of petroleum-related pollutants, evaporation, soaking deep into soil, mineralization and humification. At low temperatures, the biodegradation process will run at a slower rate, and the reduction in the concentration of pollutants will be primarily due to the processes of diffusion and soaking. In Poland, the temperatures of the summer season support evaporation and diffusion in surface and groundwater. The humus horizon is a major contributory factor in the soil retention of petroleum-related pollutants, which is attributable to its high water and air capacity, and its notable sorptive properties. Sandy soils are characterized by high permeability, which favours separation of particular phases of petroleum products and migration of gases to the surface [7].

The Polish standards (developed by the National Inspection of Environmental Protection) which specify the admissible soil concentrations for crude oil derivative substances relate these values to the soil profile. Thus, some asphalts, tars, waxes and oils accumulate on the soil surface. Poorly water-soluble aliphatic hydrocarbons move to the depth of the soil profile and form a layer which encloses the grains of the sand. Aromatic hydrocarbons, characterized by comparatively higher water-solubility, migrate towards precipitation and groundwaters. Of the aromatic hydrocarbons that are present in the petroleum products, benzene, toluene and xylene are classified as the most toxic petrol components. The admissible concentrations of crude oil derivative substances in clean soil vary from 20 mg/kg soil for groundwater to 10 μg/kg soil for water [8, 9].

Both crude oil and its derivative products are composed of a variety of chemical compounds. These include aliphatic hydrocarbons (practically water-insoluble, but low--molecular-weight species have comparatively high vapor pressure), aromatic hydrocarbons (characterized by high water-solubility), naphthenes (exhibiting low water-solubility but their saturated vapour pressure is high), and polycyclic aromatic hydrocarbons (whose water-solubility is poor). Besides the organic substances mentioned, both crude oil and its products contain oxygen, sulphur, nitrogen, metals, and a number of other species. The composition of petrol depends on the source of origin of crude oil and the processing method applied. The typical petrol composition includes from 57 to 63 vol.% of aliphatic hydrocarbons, from 3.5 to 7.5 vol.% of naphthenes, and from 30 to 38 vol.% of aromatic hydrocarbons. Owing to their high water-solubility, aromatic hydrocarbons dissolve in precipitation water and in this way penetrate into the groundwater. Because of the presence of benzene, toluene and xylene (which, as already mentioned, fall into the category of the most toxic petrol components), aromatic hydrocarbons represent a health hazard to population. Polycyclic aromatic hydrocarbons have been classified as hazardous carcinogenic toxins. They penetrate into water, soil and atmosphere, and accumulate in the adipose tissues of living organisms. Aromatic hydrocarbons account for approximately 80% of the total volume of the pollutants that migrate from fuel spills to groundwater and underground water. Aliphatic hydrocarbons undergo evaporation, primarily to the atmosphere. While they evaporize, aliphatic hydrocarbons (and to a certain extent naphthenes) show a propensity to explode if their limit concentrations are exceeded; they may also accumulate, together with soil air, in the intergranular space, thus creating explosive conditions and producing fire hazard. Owing to their low water-solubility, naphthenes can contaminate both soils and groundwater; they evaporize mainly to the soil air [10].

Soils contaminated with crude oil products are reclaimed using physical, chemical and biological methods both *in situ* and *ex situ*. Those most frequently used can be itemized as follows: 1. Ex-situ methods: Remediation: thermal, extraction (soil rinsing, flotation), electroreclamation; Bioremediation: landfarming, composting, bioreactors. 2. In-situ methods: Remediation: active ventilation (vapour extraction, air injection), hydraulic–soil rinsing, heating, electroreclamation; Bioremediation: landfarming, bioextraction (water--stimulated bioremediation; air-stimulated bioremediation).

According to literature, when soil is contaminated with petrol, it is recommendable to use the ventilation method; soil contamination due to diesel oil, fuel oil or aircraft fuel requires the use of bioremediation methods [9, 11–16].

3. Experimental

The aim of the study was to determine the impact of a petrol station on the soil environment in the immediate vicinity. The object under study is a medium-size petrol station of a surface area approaching 1.5 ha, located a long way from dwelling houses, at the exit from a town in Lower Silesia. The station is a holder of the administrative decision and follows relevant regulations and legal articles. The object sells a monthly fuel volume approaching 400,000 litres and has been in service for over twenty years. The petrol station under study sells four types of fuel: petrols Eurosuper 95, Super Plus 98 and U-95, and diesel oil Ekodiesel Plus.

Lead-free **Eurosuper 95** petrol is used in spark-ignition combustion engines (with the exception of aircraft engines). Owing to a low sulphur content (0.01 wt.%), Eurosuper 95 does not exert an adverse effect on the stability and performance of the catalyst. The fuel is also used in engines working under high load at low temperatures. Eurosuper 95 does not contain alkaline-metal-based lubricating additives, phosphorus or colorants. It has a natural colour and smell (typical of petroleum products) and fulfils the cleanliness requirements for the inlet system. Eurosuper 95 is a blend of hydrocarbons obtained from crude oil refining and contains approximately 10 wt.% of methyl tertbutyl ether. Owing to the presence of ether, alkylate and isomerizate, the fuel has a moderate content of aromatic hydrocarbons and olefins. Eurosuper 95 contains an additive which acts as an antioxidant, as well as a number of high-quality improvers, such as detergents, deemulgators and corrosion inhibitors.

Super Plus 98 is a high-quality environment-friendly petrol with the highest octane number. It has been enriched with improvers which guarantee the cleanliness of the outlet system of the engine. Super Plus 98 does not contain lead, phosphorus or colorants. Owing to a low sulphur content, the fuel does not exert an adverse effect on the stability and performance of the catalyst. Super Plus 98 is a blend of hydrocarbons obtained from crude oil refining and contains approximately 15 wt.% of methyl tertbutyl ether. The presence of high-octane components (ether, alkylate and isomerizate) accounts for the low content of aromatic hydrocarbons (approx. 35 to 40 vol.%) and olefins.

The intended use of **U-95 (Universal Petrol)** is in motor-car engines where wear--resistant valve-seats are lacking, and it can be used in motor-car engines equipped with catalytic fuel converters. U-95 has all the properties of lead-free Eurosuper 95 petrol, contains lead-substituting additives, and has been enriched with improvers and corrosion inhibitors. U-95 can be blended in arbitrary proportions and can be used interchangeably with Etylina 94 (a leaded petrol) and the lead-free petrol Eurosuper 95. U-95 contains a blend of hydrocarbons obtained from both conservative and recovery processes, and from crude oil refining, but it also includes high-octane components: ether, alkalies, and isomerizate. The fuel is characterized by a colour and smell typical of petroleum products.

Eko Diesel Plus was introduced into the market by PKN Orlen SA in 1999. The quality of the diesel oil complies with the standard PN-EN 590. Eko Diesel Plus contains improvers and provides good clearing, anticorrosive, antioxidant and lubricating properties. The cetane number is higher than 49. Eko Diesel Plus meets the requirements of Peugeot tests for the patency of injection systems. The diesel has excellent parameters describing the content of aromatic hydrocarbons and sulphur, and the emission of toxic exhaust gases.

3.1. Methods of analysis

The soil for analysis was collected at 21 sampling sites at various distances from the petrol station:

– sampling site 0: immediate proximity of the fuel tank,
– sampling site 1: 5 m from fuel tank; 4 representative samples collected in circumference,
– sampling site 2: 10 m from fuel tank; 4 representative samples collected in circumference,
– sampling site 3: 50 m from fuel tank; 4 representative samples collected in circumference,
– sampling site 4: 100 m from fuel tank; 4 representative samples collected in circumference,
– sampling site 5: 200 m from fuel tank; 4 representative samples collected in circumference.

Figure 1 shows the scheme for soil sampling. Specimens of approximately 1 kg were collected with a soil sampler, all at the same time. Fresh, averaged samples were made subject to carbon determination by the Tiurin method, by extraction in the Soxlet apparatus, and by differential thermal analysis (DTA). Prior to moisture content determination, the samples were dried at room temperature for two weeks until the air-dry state was achieved. The values obtained were converted into those of the air-dry mass.

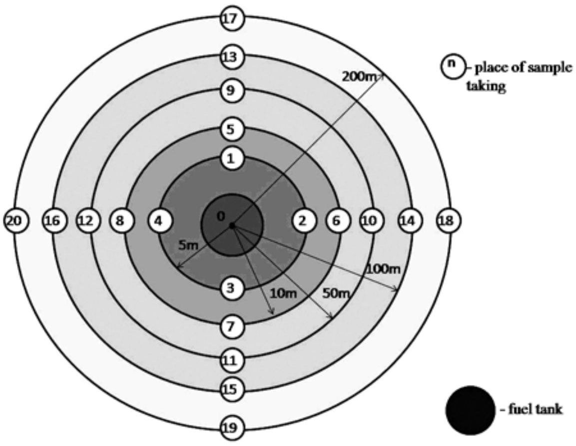

Fig. 1. Soil sampling scheme

Rys. 1. Schemat pobierania próbek gleby

Table 1

Carbon content [wt.%] determined by Tiurin method, by petroleum ether extraction and by differential thermal analysis in soil samples collected at various distances from the fuel tank

Distance from the fuel tank	Sampling site	Number of sample	Carbon content [wt.%] (convert into air-dry mass)		
			Tiurin method	Petroleum ether extraction	Differential thermal analysis
0	0	1	1.08	2.73	3.96
5 m	1	2	0.92	1.67	2.75
		3	1.06	1.75	2.90
		4	0.94	1.58	2.75
		5	0.89	1.71	2.80
10 m	2	6	0.96	1.43	2.59
		7	1.01	1.49	2.65
		8	1.05	1.38	2.61
		9	0.91	1.41	2.55
50 m	3	10	0.82	1.12	2.35
		11	0.80	1.01	2.23
		12	0.86	1.06	2.10
		13	0.93	1.21	2.28
100 m	4	14	0.88	0.74	1.73
		15	0.82	0.70	1.65
		16	0.85	0.78	1.70
		17	0.90	0.65	1.69
200 m	5	18	0.85	0.64	1.57
		19	0.82	0.67	1.60
		20	0.85	0.60	1.59
		21	0.80	0.62	1.61

The Tiurin method for determination of organic carbon entails oxidation of the carbon in organic compounds with the aid of a strong oxidizer, $K_2Cr_2O_7$, in an acidic medium, using Ag_2SO_4 as a catalyst. The non-reduced oxidizer is subject to back titration with Mohr's salt ($FeSO_4(NH_4)_2 \cdot 6H_2O$) in the presence of orthophenanthroline [17]. Carbon determination by extraction in the Soxlet apparatus consists in extracting an organic substance from the soil into a solvent, distilling off the solvent and weighing the extracted organic carbon [18]. Relevant analyses were performed in a standard Soxlet apparatus, using a powdered soil and $MgSO_4 \cdot H_2O$ mixture, in 20 petroleum ether cycles. The DTA method is not widely used for determination of carbon content. Thermogravimetry (TG) entails examination of mass variations in the sample during linear increase or decrease in temperature [17]. The use of the DTA method makes it possible to take into account the thermal effects that are concomitant with physical or chemical transformations. Analyses were carried out with the aid of the STA 409C apparatus (made by Netzsach Thermal Analysis and enabling simultaneous TG and DTA examinations), in compliance with the manufacturer's specification. The results are shown in Table 1.

Figure 2 relates the averaged organic carbon content to the distance from the fuel tank.

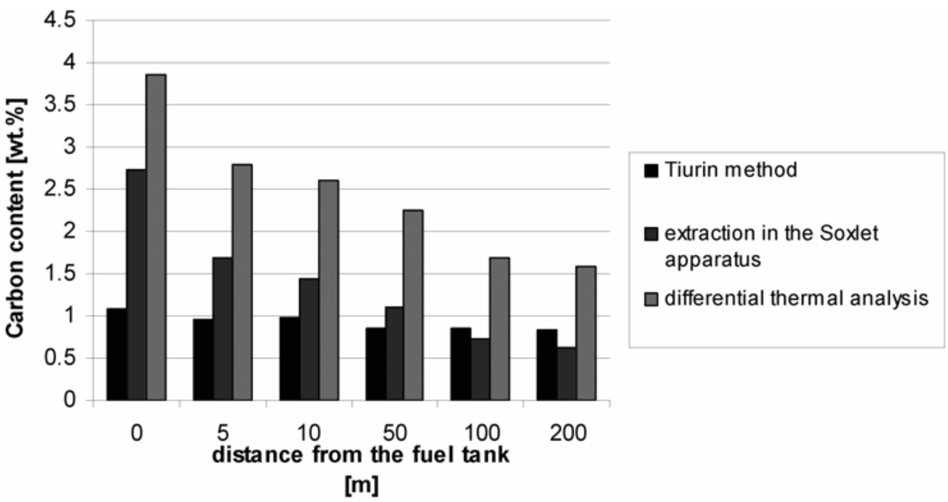

Fig. 2. Averaged organic carbon content [wt.%] in soil vs. distance from fuel tank

Rys. 2. Uśredniona zawartość węgla organicznego [% mas.] w glebie w zależności od odległości od zbiornika paliwa

4. Summary

Fuel spills and their penetration into deep soil layers are the main contributors to soil contamination in the vicinity of a petrol station. In the immediate proximity of the fuel tank the content of crude oil derivative substances determined by extraction with petroleum benzine in the Soxlet apparatus amounted to 2.73 wt.% C, the total organic carbon determined by differential thermal analysis was 3.86 wt.% C, and the content of organic carbon forming complexes with humic substances in the soil totalled 1.08 wt.% C. Additional analyses have revealed the following: in the course of drying the soil samples to the air-dry state, the quantity of organic carbon decreased by 70 wt.% when determined by the extraction method in the Soxlet apparatus; it did not change at all when established by the Tiurin method, and decreased according to the sum of the two values when use was made of differential thermal analysis. In the course of study, wet samples were used, and the values obtained were converted into those of the air-dry mass. The impact of the increased quantity of crude oil products has been observed up to the distance of 10 m from the fuel tank. At a farther distance this impact is insignificant, which seems to be attributable to the migration of petrol with precipitation water. The amount of organic matter which forms complexes with humic substances is slightly higher in the proximity of the tank due to the biodegradation and humification of the petroleum products.

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