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Assessment of pollutants emissions into the atmosphere due to the fire at the Kalynivka oil depot caused by a missile strike in March 2022

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The study assessed the scale of atmospheric pollution as a result of the fire at the Kalynivka oil depot in March 2022 due to missile shelling, which led to the burning of 6124.6 tons of gasoline and diesel fuel. Using an approved method, the volumes of pollutants emitted into the atmosphere due to the fire were calculated, namely: CO_2 (14.3 tons), particulate matter $PM_{2.5}$, PM_{10} and soot (27.4 tons), NO_x (5.8 tons), SO_2 (0.05 ton) and also H_2O (6.5 tons), etc. Burning truck tires additionally caused emissions of polycyclic aromatic hydrocarbons, metalcompounds, and other toxic substances. Extinguishing the fire using fluorinated foam (AFFF, AFFF AR) caused additional emissions of fluorinated surfactants. The fire extinguishing area was about 1.4 hectares, and the volume of foam used was 12—15 thousand liters. The discharged substances pose serious risks to ecosystems, including toxicity, climate impacts, and threats to human health.

Key words: oil depot fire, atmospheric pollution, emission assessment.

Introduction. On March 24, 2022, a massive fire broke out at the AC-Investment Ltd Kalynivka oil depot (Kyiv region, Ukraine) due to missile fire from the aggressor country, resulting in massive environmental pollution [Karamushka et al., 2024]. Diesel and gasoline combustion produces a wide range of pollutants that enter the atmosphere. These are carbon dioxide (CO_2), nitrogen dioxide (NO_x), carbon monoxide (CO), particulate matter of mean aerodynamic diameter 10 μm (PM_{10}) and 2.5 μm ($PM_{2.5}$), soot, dioxins, benzo(a)pyrene (B[a]P), polycyclic aromatic hydrocarbon (PAHnon-methane

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volatile organic compounds (NMVOC), metals and their oxides, sulfur oxides (SO_x), etc. [Bernodusson et al., 2018].

According to [Bernodusson et al., 2018], burning 1 kg of gasoline (C_7H_{16}, normal gasoline) involves, on average, 3.5 kg of oxygen. The emissions contain, on average, 3.1 kg of CO_2 and 1.4 kg of H_2O.When 1 kg of diesel fuel is burned, about 3.5 kg of oxygen is involved, releasing about 3.18 kg of CO_2 and 1.25 kg of H_2O. The estimates are for ideal engine conditions, but in an emergency resulting from a fire, these values can be different.

The purpose of the study is to estimate the volumes of pollutant emissions from the fire caused by a missile strike at the Kalynivka oil depot.

Methods and materials. To assess the atmospheric emissions and the extent of damage caused, we used the methodology approved by the Ministry of Environmental Protection and Natural Resources of Ukraine [Order…, 2022]. For each substance or mixture of substances, the released mass $M_{\text{emis}(i)}$ was calculated using the formula:

$$M_{\text{emis}} = E_{f(i)}\rho_o M_{bs(i)}, \text{ton} \qquad (1)$$

where (i) is the pollutant or mixture (CO, NO_x, SO_2, etc.); $E_{f(i)}$ is emission factor for a given fuel, c_o is coefficient of the average density of the fuel substance; $M_{\text{bs}(i)}$ is mass of the burned substance, ton. If the volume of the burned substance is known, its mass is calculated using the density c_o ($c_{o(\text{Gasoline})}$ is 0.68 and $c_{o(\text{Diesel})}$ is 0.78).

The cost of damage (CD) caused by the emissions during martial law was calculated using the formula:

$$\text{AD} = M_{\text{emis(T)}} \times$$
$$\times \text{TR} \cdot C_{\text{PH}} \cdot C_{\text{EI}} \cdot C_{\text{SE}} \cdot C_{\text{TE}} \text{ in UAH}, \qquad (2)$$

where $M_{\text{emis(T)}}$ is the mass of a pollutant released into the atmosphere; TR is the tax rate for emissions of pollutants into the atmosphere (in accordance with Article 243 of the Tax Code of Ukraine), UAH/ton; CPH is the coefficient of pollutant hazard class; C_{EI} is the coefficient of environmental impact depending on event duration (for events lasting less than12 hours it is 4, 12 to 24 hours, 5, over 24 hours, 6); C_{SE} is the coefficient depending on the scale of the event (till 50 is 1.2; from 50 to 149 is 2; from 150 to 449 is 3; from 500 to 999 is 4; 1000 tons and more is 5); C_{TE} is the coefficient of event type (for martial law it is 10, for the state of emergency without the possibility of living on the territory, 5, for the state of emergency, 3).

Research results. ***Emissions of pollution into the atmosphere during the combustion of petroleum products.*** According to the administration of the oil depot, at the time of the missile strike, 4515.5 tons of diesel fuel and 1603.2 tons of gasoline were stored there. Also, 9 DAF FT and MAN TGA tractors and trucks were located on the territory of the oil depot with about 3.2 tons of fuel in the tanks and 2.7 tons of diesel fuel remaining. The estimated amount of fuel lost was 6124.6 tons. Emissions were estimated taking into account the amount of fuel burned, and the emission factor of pollutants used for «open burning» according to the methodology of [Order…, 2022].

At the same time, there are a number of uncertainties associated with emission estimates regarding the values of emission factors of a pollutant for a certain fuel, the volume of fuel stored, and the part that burned. Some fuel could have seeped into the soil and groundwater, and some remaining spilled on the territory of the oil depot after the fire was extinguished. Therefore, for further assessment of pollutant emissions into the atmosphere, we assume that 90 % of the available mass of fuel was completely burned.

According to our calculations using the methodology of [Order…, 2022] given the emission factors and fuel type, the emissions included: CO_2 — 14326.9 tons, H_2O — 6470.2 tons, particulate matters (PM_{10}, $PM_{2.5}$) and soot — 27.6 tons and NO_x — 5.8 tons, and SO_2 — 0.05 tons (Table 1). As we can see, the largest share of emissions is carbon dioxide (CO_2), followed by significant but noticeably smaller emissions of carbon monoxide (CO), suspended particles (PM), and soot.

Emissions of pollutants into the atmosphere from burning car tires. At the time of

the missile attack, nine tractors and gas trucks with trailers were on the territory of the oil depot. They burned down, polluting the environment. Each vehicle had ten wheels with tires, with a total weight of approximately 6.3 tons.

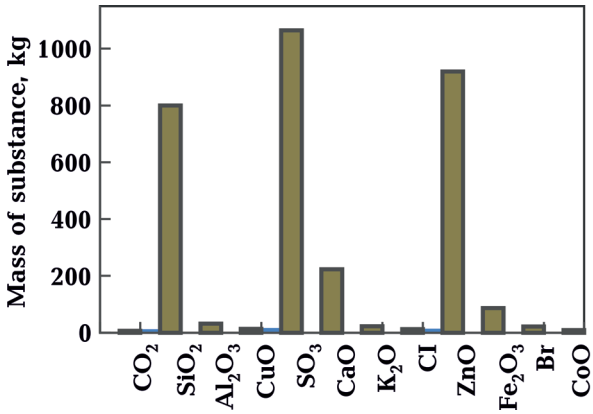
Chemicals in car tires include polycyclic aromatic hydrocarbons, metals, and other toxic and carcinogenic compounds [Mohamad et al., 2016]. On average, a truck tire consists of natural and synthetic rubber (40—45 %), carbon black (20—30 %), acid clays and metal oxides (10—27 %), cord metal and textile threads (2—10 %), silicon dioxide (5—15 %), various additives (7—10 %), and oils, resins, and adhesive mixtures (7—10 %) [Klockner et al., 2020] (figure).

As shown in [Mohamad et al., 2016], the solid residue after burning tires is about 51 % of the initial mass. Table 2 shows the percentage of chemicals remaining in the tire ash according to [Mohamad et al., 2016] and the calculated masses of pollutants thathypothetically could have remained in the ash (i.e., 3.213 tons, or 51 % of the total mass). The residue of the substance in the ash from tires burned at the Kalynivka oil depot on March 24, 2022, is shown on Fig. 1.

Emissions of pollutants into the atmosphere from the use of fluorinated foam for fire extinguishing. Fluorinated foams (fluor synthetic film-forming agent type AFFF, AFFF AR) are used to extinguish light petroleum products. The standard coverage of the fire area with a foam layer is 5 l/m^2, but the amount of foam used can be greater. Fluorinated foams consist of an average of water (80 %), solvents (propylene glycol, 10 %), fluorinated surfactants (CFCs, 3 %), hydrocarbon surfactants (2 %), foaming agents (4 %), and stabilizers (1 %). These components are resistant to biodegradation and can be accumulated in living organisms, provoking oncological diseases and endocrine disruption [Sunderland et al., 2019].

Table 1. Calculated emissions of pollutants due to the combustion of petroleum products (gasoline and diesel fuel)

Substance	$E_{f(i)}$	Diesel, ton $M_{\text{emis(D)}}$	Gasoline, ton $M_{\text{emis(G)}}$	Total, ton $M_{\text{emis(T)}}$
Nitrogen oxides (NO_x)	0.0014	4.441	1.374	5.814
Ammonia (NH_3)	0.000003	0.010	0.003	0.012
Benzo(a)pyrene (C_2OH_{15})	3.02E–11	9.58E–08	2.96E–08	1.25E–07
Carbon dioxide (CO_2)	3.4498184	10942.142	3384.740	14326.882
Carbon monoxide (CO)	0.0063	19.982	6.181	26.164
Cadmium (Cd)	0.00002	0.063	0.020	0.083
Copper (Cu)	0.0000016	0.005	0.002	0.007
Arsenic, inorganic compounds (AsIII, AsV)	0.0000038	0.012	0.004	0.016
NMVOC	0.0018	5.709	1.766	7.475
Nickel (Ni)	0.000038	0.121	0.037	0.158
Mercury (Hg)	0.0000047	0.015	0.005	0.020
Lead (Pb)	0.0000049	0.016	0.005	0.020
Sulfur dioxide (SO_2)	0.000013	0.041	0.013	0.054
$PM_{2.5}$	0.0026	8.247	2.551	10.798
PM_{10}	0.0026	8.247	2.551	10.798
Soot (56 % from $PM_{2.5}$)	0.001456	4.618	1.429	6.047
Selenium (Se, mg/m^3)	0.0000004	0.001	3.92E–04	0.002
Chromium (Cr VI)	0.0000013	0.004	0.001	0.005
Zinc (Zn)	0.00052	1.649	0.510	2.160



The residues of the substance in the ash from tires burned at the Kalynivka oil depoton March 24, 2022.

Almost 1.4 hectares of the oil depot area were subject to fire extinguishing. This means that at least up to 15 thousand liters of fluorinated foam were used. Fluorinated surfactants enter the atmosphere through evaporation and, due to their stability, can remain there for a long time [Krafft, Riess, 2015]. In the troposphere, they have the properties of greenhouse gases due to their spectral characteristics, but within a few weeks, they can be washed out of the atmosphere by dry or wet sedimentation and then accumulated in water bodies, soils, and living organisms in the process of biomagnification [Saxena, 2019]. However, CFCs can remain in the stratosphere for several years [IPCC, 2021]. Under the influence of UV radiation, they are destroyed. The fluorine residues catalyze the destruction of stratospheric ozone (one fluorine molecule can destroy from 10^3 to 10^5 ozone molecules). Thus, using special mixtures to extinguish fires has an additional negative impact on the environment.

The costof damage caused by emissions of pollutants or mixtures of substances into the atmosphere. The destruction of the Kalynivska oil depot caused significant material losses for businesses and environmental losses. To assess environmental losses, we used the same methodology approved by the Ministry of Environment [Order …, 2022], namely formula (2). According to our estimates, the total of losses from atmospheric pollution as a result of the combustion of only diesel and gasoline is about 184 million UAH or 4.5 million USD. If we take into account emissions from the combustion of other objects and materials and the pollution of the ground and groundwater, the losses will be significantly higher.

Conclusions. The fire at the Kalynivka oil depot burned about 6124.6 tons of fuel, which resulted in significant emissions of carbon

Table 2. The amountof chemicals remaining in the tire ash and residues after the fire at the Kalynivka oil depot

Substance	Ratio of substances, %	Mass of substance, kg
Carbon Dioxide (CO_2)	0.1	6.3
Silicon Dioxide (SiO_2)	12.7	800.1
Aluminium Oxide (Al_2O_3)	0.51	32.13
Copper (II) Oxide (CuO)	0.21	13.23
Sulfur Trioxide (SO_3)	16.9	1064.7
Calcium Oxide (CaO)	3.54	223.02
Potassium Oxide (K_2O)	0.36	22.68
Chlorine (CI)	0.19	11.97
Zinc Oxide (ZnO)	14.6	919.8
Iron(III) Oxide (Fe_2O_3)	1.38	86.94
Bromine (Br)	0.34	21.42
Cobalt (II)Oxide (CoO)	0.14	8.82

dioxide (14.3 tons), water vapor (6.5 tons), particulate matter (27.6 tons), and other toxic substances, including NO_x (5.8 tons) and SO_2 (0.05 ton). Burning truck tires additionally released polycyclic aromatic hydrocarbons, heavy metals, and other toxic compounds. When extinguishing the fire at the oil depot with fluorinated foams, fluorinated surfactants (FSPs) were also released into the atmosphere. The released substances pose serious risks to human health and ecosystems, including toxicity and climate impact.

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Оцінка обсягів викидів забруднюючих речовин в атмосферу внаслідок пожежі на нафтобазі в Калинівці через ракетний обстріл у березні 2022

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У дослідженні оцінюються масштаби забруднення атмосфери внаслідок пожежі на нафтобазі «Калинівка»у березні 2022 р. через ракетний обстріл, що призвело до

спалювання 6124,6 т бензину та дизельного палива. З використанням затвердженої методики було обраховано обсяги забруднень,викинутих атмосферу через пожежу. Вони становили: CO_2 — 14,3 т, H_2O — 6,5 т, твердих частинок розмірами $PM_{2,5}$, PM_{10} — 27,4 т, NO_x — 5,8 т, SO_2 — 0,05 т. Горіння шин вантажних автомобілів додатково спричинило викиди полі циклічних ароматичних вуглеводнів, сполук металів та інших токсичних речовин. При гасінні пожежі з використанням фторованої піни (AFFF, AFFF AR) відбулися додаткові викидів фторованих поверхнево-активних речовин. Площа гасіння пожежі становила близько 1,4 га, а обсяг використаної піни становив 12—15 тис. літрів. Викинуті речовини створюють серйозні ризики для екосистем, включаючи токсичність, вплив на клімат та загрозу здоров'ю людей.

Ключові слова: пожежа на нафтобазі, забруднення атмосфери, оцінка обсягів викидів.