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ASSESSMENT OF AIR QUALITY IN AN INDUSTRIAL FACILITY IN RUMUEME, PORT HARCOURT, NIGERIA

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Abstract. Air quality in Port Harcourt, Nigeria is being assessed due to black soot, raising concerns among residents. The survey aims to assess airborne particulates in an industrial area in Rumueme, Port Harcourt, measuring pollutants with air sampling devices at different locations. GPS locates sampling spots, measurements taken at 1.6 m, and noise levels measured. Particulate matter analyzed using GC-FID method. The residential area was found to Unhealthy levels of PM2.5 are present above USEPA and WHO limits, at 38.70 µg/m⁻³. Sensitive individuals are advised to minimize outdoor activities, restrict traffic, and wear masks. Nighttime noise levels exceed the recommended limit at 50.1 dB(A) and noise mapping can identify sources. In the office area, PM2.5 levels for sensitive individuals are above the WHO limit at 28.30 µg/m⁻³, while PM10 levels are within limits at $60.57 \,\mu\text{g/m}^{-3}$. The noise level is below 90 dB(A) and harmful gases are undetectable, with trace metals meeting USEPA and OSHA limits. The helipad area has moderate PM2.5 air pollution exceeding the WHO limit at 25 µg/m⁻³, and PM10 at 65.30 μg/m⁻³. The average noise level is 58.87 dB(A), which is below the limit of 90 dB(A). In the jetty area, PM2.5 levels are higher than WHO guidelines at 30.50 μg/m⁻³, while PM10 levels are at 62.87 µg/m⁻³ causing moderate health concerns. The warehouse has high AQI for PM2.5, suggesting a need to reduce traffic. Noise level averages 66.83 dB(A), recommended.

Keywords: quality of air, PM10, PM2.5, noise level, Port Harcourt.

1. Introduction

Crude oil exploration and refining are major industrial activities in Rivers State, Nigeria, which have led to an increase in airborne particulates, specifically soot, in the air around Port Harcourt city metropolis. These particulates contain toxic components, such as aromatic hydrocarbons condensates, that can have quantifiable health impacts. The scope of toxicity from soot may be greater than other air pollutants due to its mixed toxic components. The soot phenomenon in Rivers State appears to have a regional spread across the city of Port Harcourt, raising concerns about the overall air quality in the area.

Studies have shown that urban residents primarily spend their time indoors, with a significant portion of their day spent in residential buildings. Research by Kornartit et al. (Kornartit et al., 2010) and De Kluizenaar et al. (De Kluizenaar et al., 2017) revealed that over half of the day is spent at home. Survey on Patterns of human activity in the United States indicated that, on average, individuals spend approximately 16.6 hours per day in residential buildings (Klepeis et al., 2001). In New Jersey, observations by Baxter et al. (Baxter et al., 2013) showed a slightly higher range of 16.98 to 18.05 hours spent at home daily. Similarly, the Canadian Survey found that adult Canadians spend around 15.83 to 16.0 hours per day in their residences (Leech et al., 2002; Matz et al., 2015). For children in

Windsor, Ontario, Van Ryswyk et al. (Van Ryswyk et al., 2014) documented a daily duration of 16.1 to 17.35 hours spent at home. Additionally, reports from seven European cities, as cited by Schweizer et al. (Schweizer et al., 2007), indicated an average of 13.95 hours per day spent in residential settings.

Based on research conducted in Germany, Belgium, and Denmark, individuals spend approximately 15.7 hours (Brasche and Bischof, 2005), 15.84 hours (Dons et al., 2011), and 17.3 hours (Bekö et al., 2015) per day at their residences. These findings highlight the significant amount of time spent in domestic settings. Residential environments are greatly influenced by pollution in the, particulate matter being a prominent factor. Extensive research has been dedicated to studying the impact of PM on health, with a focus on PM2.5. This Particulate matter measuring less than 2.5 µm in aerodynamic diameter, poses serious health risks as it can be easily absorbed by the lungs and distributed throughout the body, leading to severe morbidity and mortality (Zhu et al., 2018).

Multiple studies have shown a correlation between PM2.5 levels and health issues, such as respiratory and cardiovascular diseases (Sun et al., 2019). In a study conducted in urban outdoor environments, Cakmak et al. (Cakmak et al., 2018) investigated the relationship in ambient PM2.5 exposure linked to disease-related deaths in Canada. They found that a 10 μg m⁻³ increase in long-term PM2.5 exposure led to a hazard ratio of 1.26 for lung cancer mortality. You et al. (You et al., 2017) studied PM exposure and element deposition in the human respiratory system near a highway in Singapore, while Perrone et al. (Perrone et al., 2013) analyzed the chemical composition of PM in Italian urban areas. Additionally, Zwozdziak et al. (Zwozdziak et al., 2017) estimated the inhaled dose of ambient PM in a southern urban area of Poland. In their 2008 study, Martuzevicius and colleagues estimated the levels of PM2.5 caused by traffic near major highways in Cincinnati, USA. Chen et al. (Chen et al., 2017) conducted research in Guangzhou, China, to identify the chemical components of regional PM2.5 and their sources. Bai et al. (Bai et al., 2020) investigated the health risks of PAHs in PM2.5 in office indoor environments. Additionally, Chen et al. (Chen et al., 2018) studied the connection between PM2.5 and asthmatic or allergic conditions in Chinese preschoolers. In South Asia, Junaid et al. (Junaid et al., 2018) found that exposure to indoor PM emissions from human activities poses significant health risks. Lastly, Zhao et al. (Zhao et al., 2019) assessed the health risks associated with PAHs from cooking emissions in residential settings.

Martuzevicius et al. (Martuzevicius et al., 2008) estimated PM2.5 levels caused by traffic closer to highways in Cincinnati, USA. Chen et al. (Chen et

al., 2017) conducted research in Guangzhou, China, to identify the chemical components of regional PM2.5 and their sources. Bai et al. (Bai et al., (2020) investigated the health risks of PAHs in PM2.5 in office indoor environments. Additionally, Chen et al. (Chen et al., 2018) studied the connection between PM2.5 and asthmatic or allergic conditions in Chinese preschoolers. In South Asia, Junaid et al. (Junaid et al., 2018) found that exposure to indoor PM emissions from human activities poses significant health risks. Lastly, Zhao et al. (Zhao et al., 2019) assessed the health associated risks with PAHs from cooking emissions in residential settings.

Morawska et al. (Morawska et al., 2017) examined how outdoor airborne particles infiltrate indoor spaces like residences, schools, offices, and care facilities. While other researchers have reviewed air pollutants in office settings, they have not offered a comprehensive analysis of PM2.5 levels or the key factors affecting air quality in urban homes. Given that people spend a significant amount of time in residential buildings, especially in their living areas, it is crucial to thoroughly study PM2.5 concentrations in these spaces to effectively manage indoor air quality. Therefore, we present a review focusing on PM2.5 levels in urban residential buildings, with a specific emphasis on research conducted in these settings.

The goal of this study is to measure and characterize airborne particles in an industrial facility located in Rumueme, Port Harcourt. The findings will help assess the potential health risks faced by employees working at the facility, showcasing their dedication to safeguarding the health of nearby urban dwellers.

Study Objective: This study aims to evaluate the concentrations of airborne particles and determine the Air Quality Index within an industrial facility situated in Rumueme, Port Harcourt. These study objectives to: Evaluate the levels of key air quality indicators in the vicinity of the establishment. Compare these indicators with both local and global standards and examine the health implications in relation to the Air Quality Index. Document and categorize climate and meteorological data within the premises. Study the variations in air quality indicators throughout the establishment.

The focus of this research involves the monitoring of air quality and various meteorological factors in a designated area. These factors include wind speed, humidity, toxic gases (NH₃, SO_x, H₂S, NO_x, CO), noise levels, suspended particulates (PM2.5, PM10), hydrocarbons (PAHs), and trace metals. The primary objectives of the study are to determine the Air Quality Index, identify sources of pollution, and examine relationships between air quality metrics and meteorological conditions. The target audience for this research likely in-

cludes environmental scientists, policy makers, and organizations interested in enhancing air quality within the study region.

2. Materials and Methods

2.1. Area of Study

The research was carried out in Port Harcourt, Rivers State, Nigeria, situated between latitudes 4°51'30"N and 4°57'30"N and longitudes 6°50'00"E and 7°00'00"E. It is bounded by the Atlantic Ocean to the south, Bayelsa and Delta States to the west, Imo, Abia, and Anambra States to the north, and Akwa Ibom State to the east. The region falls within a sub-equatorial zone with a tropical climate, experiencing an average temperature

of 30 °C, humidity ranging from 80 % to 100 %, and approximately 2,300 mm of rainfall per year (Mmom & Fred-Nwagwu, 2013). The predominant Air Mass System present is the Tropical Maritime Air Mass (mT), leading to the SW Monsoon Wind and significant precipitation. The Tropical Continental (cT) air mass has a minimal impact, resulting in harmattan conditions from December to February, known as the NE Trade Wind. The tropical rainforest covers the inland areas of Rivers State, with mangrove swamps dominating the coastal regions along the Atlantic Ocean. This vegetation is considered one of the most lush, complex, and diverse terrestrial ecosystems on the planet (Eludoyin et al., 2013). Andoni, Ekpeye, Engenni, Etche, Ibali, and Ikwerre (Figs. 1-4).

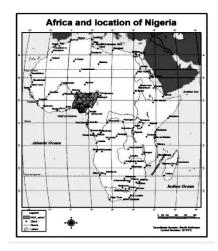


Fig. 1. Map of Africa with location of Nigeria

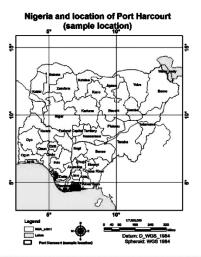


Fig. 2. Map of Nigeria and location of Port Harcourt. Source: ESRI

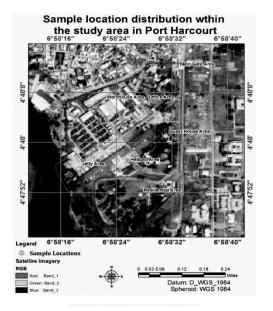


Fig. 3. Map of Rivers State

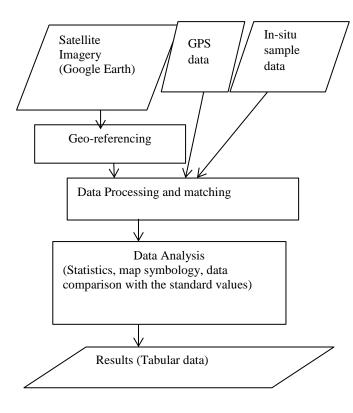


Fig. 4. Methodology Flowchart

2.2. Data collection

Within the study area, eight monitored locations were carefully chosen for the air quality study (Tabls. 1, 2).

Site and description

Table 1

S/N	Latitude	Longitude	Description
1	04°47'51.6'	006°58'27.5"	Residential Area
2	04°48'06.5"	006°58'28.2"	Office Area
3	04°47'56.5"	006°58'25.6"	Helipad Area
4	04°47'55.8"	006°58'18.6"	Jetty Area
5	04°48'06.5"	006°58'22.2"	Warehouse Area
6	04°48'01.0"	006°58'31.1"	Guest House Area
7	04°48'11.8"	006°58'32.7"	Main Gate Area

Table 2

Equipment Used

No.	Tools	Uses
1	Aeroqual Series 500	Insitu measurement for gases
2	Kestrel Weather Tracker	Meteorology measurement
3	Dwyer	Measurement of noise level
4	ToxiRae PID II meter	Measurement of VOC
5	Kanomax Model 3900	Measurement of Suspended Particulate Matter.
6	Membrane Filter	Heavy metals / Hydrocarbon determinations
7	GPS (Garmin 60csx)	Location (Co-ordinates)

Table 3

2.3. Methods

Air samples were collected at different locations using various sampling devices for measurements. Gaseous pollutants were analyzed on-site using handheld meters equipped with electrochemical sensors. The locations' coordinates were acquired through the use of a handheld GPS device (Garmin 60csx).

Air samples were collected at an approximate altitude of 1.6 meters above ground level at each designated monitoring site utilizing an Active Sampling approach for air sampling. Noise levels were measured at all sampling locations using a pre-calibrated Dwyer precision (class 2) sound level meter. The determination of Airborne Suspended Particulate Matter (PM2.5 and PM10) was conducted in accordance with ISO 14644/EPA 10-2 standards using a Kanomax 3900 Portable Counter High Volume Sampler (Andover, USA) and HoldPeak particle counter (Zhuahai, China). Particulate samples captured on air filters were extracted and analyzed using the USEPA 3550C/8015C standard method with the assistance of an Agilent 6890N GC-FID calibrated with 35 components.

The air filter particulate samples were extracted and analyzed following USEPA standards (3550C/8270D) using an Agilent 6890N/5973 GC/MS system

calibrated with 16 components. BTEX analysis was done with USEPA method 8260B. VOA vials (EPA type 3) were used for Headspace-GCMS analysis of the trapped air. Tekmar 7000/Agilent 6890N/5973 Headspace/GCMS system calibrated with 6 analytes was used for analysis. ASTM methods D1971/4691 were utilized for trace metal analysis (Cd, Ni, Cr, Pb, Hg, Fe) using a Shimadzu AA-6650 atomic absorption spectrophotometer. Toxic gases (CO, NO₂, SO₂, H₂S, NH₃, VOCs) were measured with an Aeroqual 500 Series air quality sensor. Results were calculated based on ASTM D1914 - 2005 standards. Wind speed, humidity, and temperature were recorded using a Kestrel Weather Tracker (4250) and ArcGIS 10.3 was used for mapping the study area. Microsoft Excel was used for statistical analysis.

3. Results and Discussion

The Table 3 to 7 below are results and statistics on air quality, noise levels, and meteorological conditions in an industrial base located in Port Harcourt, Rivers State. The results obtained were compared with FMEnv, USEPA and WHO regulatory limits

Air Quality, Noise and Meteorology – Residential Area

Air Quanty, Noise and Meteorology – Residential Area									
D	Tir	ne Of Sampl	ing	Mani	EME	LICEDA	WIIO	USEPA	
Parameters	7:24 am	12:15 pm	9:00 pm	Mean	FMEnv	USEPA	WHO	(AQI)	
Noise level						^a 55	^a 55		
dB (A)	50.1	51.2	50.1	50.47±0.64	90	⁶ 45 ⁶ 90	^b 45	N.A	
1	2	3	4	5	6	7	8	9	
PM2.5, μg/m ⁻³	36.9	20.5	58.7	38.70±15.65	N.A.	^d 35	^d 25	*108	
PM10, μg/m ⁻	76.3	64.1	73.2	71.20±6.34	N.A.	^d 150	^d 70	58	
SO ₂ , ppm	< 0.1	< 0.1	< 0.1	< 0.1	°0.1	°0.075	°0.03	#0	
CO, ppm	<1.0	<1.0	<1.0	<1.0	^d 10	^d 9	^d 9	#4	
NO ₂ , ppm	<0.1	< 0.1	< 0.1	< 0.1	$^{d}0.04 - 0.06$	°0.1	d0.04	#10	
NH ₃ , ppm	<2.0	<2.0	<2.0	<2.0	N.A.	N.A.	N.A.	N.A.	
H ₂ S, ppm	< 0.012	< 0.012	< 0.012	< 0.012	N.A.	N.A.	N.A.	N.A.	
Cd, $\mu g/m^{-3}$	< 0.012	< 0.012	< 0.012	< 0.012	N.A.	°2.500	f0.005	N.A.	
Ni, μg/m ⁻³	0.141	0.188	0.13	0.153±0.025	N.A.	°1000.0	f0.01	N.A.	
Cr, µg/m ⁻³	0.178	0.236	0.153	0.189±0.035	N.A.	°5.000	f0.02	N.A.	
Pb, μg/m ⁻³	< 0.012	< 0.012	< 0.012	< 0.012	N.A.	°50.00	e1.5	N.A.	

Continuation of Table 3

1	2	3	4	5	6	7	8	9
Hg, μg/m ⁻³	< 0.012	< 0.012	< 0.012	< 0.012	N.A.	°100.00	f0.014	N.A.
VOC, μg/m ⁻³	< 0.012	< 0.012	< 0.012	< 0.012	N.A.	N.A.	N.A.	N.A.
Aliphatic Hydrocarbon, µg/m ⁻³	<0.118	<0.118	<0.118	<0.118	N.A.	N.A.	N.A.	N.A.
BTEX, μg/m ⁻³	<0.118	<0.118	<0.118	<0.118	N.A.	N.A.	N.A.	N.A.
Temperature, °C	28.7	32.5	27.1	29.43±2.77	N.A.	N.A.	N.A.	N.A.
Humidity, % RH	83	68.7	80.1	77.27±7.56	N.A.	N.A.	N.A.	N.A.
Wind Speed, m/s	0.6	3.2	0.6	1.47±1.50	N.A.	N.A.	N.A.	N.A.

N.A. = Not Available; a = Daytime residential limit; b = Night time residential limit; c = hourly limit; d = daily limit; e = quarterly limit; f = Annual limit; o = occupational exposure threshold limit.

Table 4
Air quality, noise and meteorology – industrial area

Parameters	Tin	ne of sampli	ing	Mean	FMEnv	USEPA	WHO	USEPA	
Tarameters	8:00 am	3:45 pm	9:45 pm	ivican	TWILITY	USLI A	WIIO	AQI	
Noise level,						^a 55	^a 55		
dB(A)	41.2	60.9	51.9	58.87±3.35	90	⁶ 45 ⁶ 90	^b 45	N.A	
1	2	3	4	5	6	7	8	9	
PM2.5, μg/m ⁻³	36.6	14.2	32.4	27.73±9.72	N.A.	^d 35	^d 25	83	
PM10, μg/m ⁻³	71.6	59.9	64.4	65.30±5.90	N.A.	^d 150	^d 70	55	
SO ₂ , ppm	< 0.1	< 0.1	< 0.1	< 0.1	°0.1	°0.075	°0.03	0	
CO, ppm	<1.0	<1.0	<1.0	<1.0	^d 10	^d 9	^d 9	4	
NO ₂ , ppm	<0.1	<0.1	<0.1	<0.1	^d 0.04 – 0.06	°0.1	d0.04	10	
NH ₃ , ppm	<2.0	<2.0	<2.0	<2.0	N.A.	N.A.	N.A.	N.A.	
H ₂ S, ppm	<0.012	<0.012	<0.012	<0.012	N.A.	N.A.	N.A.	N.A.	
Cd, µg/m ⁻³	0.059	0.153	0.094	0.102±0.039	N.A.	°2.500	f0.005	N.A.	
Ni, μg/m ⁻³	0.165	0.2	0.13	0.165±0.029	N.A.	°1000.0	f0.01	N.A.	
Cr, µg/m ⁻³	0.165	0.236	0.212	0.204±0.029	N.A.	°5.000	f0.02	N.A.	
Pb, μg/m ⁻³	0.188	0.259	0.224	0.224±0.029	N.A.	°50.00	e1.5	N.A.	
Hg, μg/m ⁻³	<0.012	<0.012	<0.012	< 0.012	N.A.	°100.00	f0.014	N.A.	

Continuation of Table 4

1	2	3	4	5	6	7	8	9
VOC, μg/m ⁻³	< 0.012	< 0.012	< 0.012	< 0.012	N.A.	N.A.	N.A.	N.A.
Aliphatic Hydrocarbon, µg/m ⁻³	<0.118	<0.118	<0.118	<0.118	N.A.	N.A.	N.A.	N.A.
BTEX, μg/m ⁻³	<0.118	<0.118	<0.118	<0.118	N.A.	N.A.	N.A.	N.A.
Temperature, °C	29.2	29.5	28.2	28.97±0.68	N.A.	N.A.	N.A.	N.A.
Humidity, % RH	78.1	73	81.9	77.67±4.47	N.A.	N.A.	N.A.	N.A.
Wind Speed, m/s	0.8	6.9	1.3	3.00±3.39	N.A.	N.A.	N.A.	N.A.

N.A. = Not Available; a = Daytime residential limit; b = Night time residential limit; c = hourly limit; d = daily limit; e = quarterly limit; e =

Table 5

Diurnal concentrations of 16 USEPA PAHs for sites

Parameter	Residential Area		Area	Office Area			Helipad Area			Jetty Area		
T drameter	M	A	N	M	A	N	M	A	N	M	A	N
Naphthalene	< 0.177	<0.177	<0.177	<0.177	<0.177	<0.177	<0.177	1.67	< 0.177	1.67	1.67	1.67
Acenaphthalene	<0.177						<0.177		< 0.177	< 0.177	< 0.177	<0.177
Acenaphthene	<0.177	< 0.177	< 0.177	< 0.177	<0.177	< 0.177	< 0.177	< 0.177	< 0.177	< 0.177	< 0.177	< 0.177
Fluorene	<0.177						< 0.177		< 0.177			<0.177
Phenathrene	<0.177						<0.177		< 0.177			<0.177
Anthracene	<0.177		< 0.177				< 0.177		< 0.177			<0.177
Fluoranthene	<0.177		< 0.177				< 0.177		< 0.177			<0.177
Pyrene	<0.177	< 0.177	< 0.177	< 0.177	<0.177	< 0.177	< 0.177	< 0.177			<0.177	<0.177
Benzo(a)anthracene	<0.177	< 0.177	< 0.177	<0.177	<0.177	< 0.177	< 0.177	< 0.177	< 0.177	< 0.177	< 0.177	< 0.177
Chrysene	<0.177	< 0.177	< 0.177	<0.177	<0.177	< 0.177	< 0.177	< 0.177	< 0.177	< 0.177	< 0.177	< 0.177
Benzo(b)fluoranthrene	<0.177						< 0.177		< 0.177	< 0.177	< 0.177	<0.177
Benzo(a)pyrene	<0.177	< 0.177	< 0.177	<0.177	<0.177	< 0.177	< 0.177	< 0.177	< 0.177	< 0.177	<0.177	<0.177
Benzo(k)fluoranthrene	<0.177						< 0.177		< 0.177	< 0.177	< 0.177	< 0.177
Indeno(1,2,3 cd) perylene	<0.177	< 0.177	< 0.177	<0.177	<0.177	< 0.177	< 0.177	< 0.177	< 0.177	< 0.177	< 0.177	< 0.177
Dibenzo(a,h)anthracene	< 0.177	< 0.177	< 0.177	< 0.177	< 0.177	< 0.177	< 0.177	< 0.177	< 0.177	< 0.177	< 0.177	< 0.177
Benzo(g,h,i) perylene	< 0.177	< 0.177	< 0.177	< 0.177	<0.177	< 0.177	< 0.177	< 0.177	< 0.177	< 0.177	< 0.177	< 0.177
Total, ug/m ³	<0.177	< 0.177	< 0.177	< 0.177	3.34	< 0.177	< 0.177	1.67	<0.177	1.67	1.67	1.67

Table 6

Correlation between quantifiable pollutants and site meteorology

		Noise level, dB (A)	$PM_{2.5}$, $\mu g/m^{-3}$	PM_{10} , $\mu g/m^{-3}$	Cd,	Ni, ppm	Cr,	Pb,	Temp., °C	Humidity, % RH	Wind Speed, m/s
Noise level,	Pearson Correlation	1	536 [*]	254	.494	.578**	.179	.308	.207	492*	.232
dB(A)	Sig. (2-tailed)		.012	.266	.102	.006	.437	.284	.369	.023	.312
	N	21	21	21	12	21	21	14	21	21	21
PM2.5,	Pearson Correlation	536*	1	.099	248	172	312	043	385	.758**	417
$\mu g/m^{-3}$	Sig. (2-tailed)	.012		.671	.437	.455	.168	.884	.085	.000	.060
	N	21	21	21	12	21	21	14	21	21	21
PM10,	Pearson Correlation	254	.099	1	158	155	046	115	144	.083	067
$\mu g/m^{-3}$	Sig. (2- tailed)	.266	.671		.623	.503	.842	.694	.532	.722	.773
	N	21	21	21	12	21	21	14	21	21	21
	Pearson Correlation	.494	248	158	1	.799**	.526	.384	284	331	128
Cd, ppm	Sig. (2-tailed)	.102	.437	.623		.002	.079	.218	.371	.293	.692
	N	12	12	12	12	12	12	12	12	12	12
Ni, ppm	Pearson Correlation	.578**	172	155	.799**	1	.249	.243	083	205	.072
тчі, рріп	Sig. (2-tailed)	.006	.455	.503	.002		.277	.403	.721	.374	.755
	N	21	21	21	12	21	21	14	21	21	21
	Pearson Correlation	.179	312	046	.526	.249	1	.596*	.101	312	.265
Cr, ppm	Sig. (2-tailed)	.437	.168	.842	.079	.277		.025	.663	.168	.245
	N	21	21	21	12	21	21	14	21	21	21
	Pearson Correlation	.308	043	115	.384	.243	.596*	1	.297	466	.348
Pb, ppm	Sig. (2-tailed)	.284	.884	.694	.218	.403	.025		.302	.093	.223
	N	14	14	14	12	14	14	14	14	14	14
Temperatu-	Pearson Correlation	.207	385	144	284	083	.101	.297	1	542*	.533*
re, °C	Sig. (2-tailed)	.369	.085	.532	.371	.721	.663	.302		.011	.013
	N	21	21	21	12	21	21	14	21	21	21
Humidity,	Pearson Correlation	492*	.758**	.083	331	205	312	466	542*	1	508 [*]
% RH	Sig. (2-tailed)	.023	.000	.722	.293	.374	.168	.093	.011		.019
	N	21	21	21	12	21	21	14	21	21	21
Wind	Pearson Correlation	.232	417	067	128	.072	.265	.348	.533*	508*	1
Speed, m/s	Sig. (2-tailed)	.312	.060	.773	.692	.755	.245	.223	.013	.019	
	N	21	21	21	12	21	21	14	21	21	21

^{*.} The correlation is statistically significant at p < 0.05 (two-tailed). **. The correlation is statistically significant at the 0.01 level for a two-tailed test.

Table 7

Parameter	F Statistics	Significance
Noise level, dB(A)	1.840	0.163
PM2.5, μg/m ³	2.041	0.127
PM10, μg/m ³	0.412	0.859
Cd, ppm	54.381	0.000
Ni, ppm	7.897	0.001
Cr, ppm	0.878	0.536
Pb, ppm	69.822	0.000
Temperature, °C	0.659	0.684
Humidity, % RH	0.687	0.664
Wind Speed, m/s	1.353	0.299

Analysis of variance of quantifiable pollutants across all evaluated sites

Table 3 shows noise level around residential area was mostly constant at mean of (50.47±0.64) dB(A). It's within FMEnv regulatory limit of 90 dB(A). Night value of 50.1 dB(A) was above WHO AND USEPA limit of 45 dB(A) for residential areas at night. Further indoor noise study in residential area may be needed to check for night violations of WHO and USEPA standards. Noise mapping needed to find source of elevated night noise.

Mean PM2.5 concentration, $(38.70\pm15.65)~\mu g/m^{-3}$, exceeded WHO and USEPA limits of 35 and 25 $\mu g/m^{-3}$, primarily from fossil fuel combustion in engines. Reducing vehicular usage can help cut PM2.5 levels. Continued monitoring can refine mitigation strategies. Mean PM10 concentration, $(71.20\pm6.34)~\mu g/m^{-3}$, complies with the EPA's 150 $\mu g/m^{-3}$ limit, but exceeds the WHO's 70 $\mu g/m^{-3}$ limit due to road dust resuspension. Wetting ground surfaces may aid PM10 control, particularly in dry seasons.

Toxic gases, BTEX, VOCs, Aliphatic hydrocarbons, and PAHs checked were below detection limits in the residential area. Trace metals Cd, Ni, Cr, Pb, Hg, were well below OSHA permissible limits. PM2.5 concerns air quality, especially for those with respiratory issues. They should limit outdoor time and exertion. Measures to reduce PM2.5 can improve AQI.

In the Office Area, noise values were within regulatory limits. Mean noise level: (50.83 ± 6.46) dB(A). The mean PM2.5 concentration was within the USEPA daily limit of 35 μ g/m⁻³ but exceeded the WHO limit of 25 μ g/m⁻³. Continued monitoring is necessary to track trends and suggest better mitigation strategies to enhance air quality. Concentrations of PM10 had a mean concentration of (60.57 ± 10.37) μ g/m⁻³ across the day. This mean value fell within the USEPA and WHO regulatory limits of 150 and 70 μ g/m⁻³ respectively. Toxic

gases, BTEX, VOCs, and Aliphatic hydrocarbons in this study were mostly undetectable. Among 16 USEPA PAHs in the particles, only fluorene and anthracene were detected above limits at $(0.56\pm0.78)~\mu g/m^{-3}$ each. The main regulated PAH is Benzo(a)pyrene, with a $0.005~\mu g/m^{-3}$ daily exposure limit. Toxic gases, BTEX, VOCs, and Aliphatic hydrocarbons in this study were mostly undetectable. Among 16 USEPA PAHs in the particles, only fluorene and anthracene were detected above limits at $(0.56\pm0.78)~\mu g/m^{-3}$ each. The main regulated PAH is Benzo(a)pyrene, with a $0.005~\mu g/m^{-3}$ daily exposure limit.

The noise level at Helipad Area was $(58.87 \pm 3.35) \, dB(A)$. Daytime exposure limit of 55 dB(A) was exceeded with a noise level of 60.9 dB(A) during afternoon sampling. The values are within the occupational exposure limit of 90 dB(A) for work areas.

For airborne particulates, mean PM2.5 and PM10 were respectively (27.73 ± 9.72) and (65.30 ± 5.90) µg/m⁻³. The PM10 concentration fell well within the USEPA and WHO regulatory limit. Toxic gases, BTEX, VOCs, and Aliphatic hydrocarbons were all below detection limits in the study. Naphthalene was the only PAH detected with a mean concentration of (0.56 ± 0.78) µg/m⁻³, below the OSHA limit of 525.2 µg/m⁻³.

Mean concentrations for Cd, Ni, Cr, and Pb: (0.102 ± 0.039) , (0.165 ± 0.029) , (0.204 ± 0.029) , and (0.224 ± 0.029) µg/m⁻³. All values within OSHA limits. Mercury below detection limit. AQI indicates air quality as "Good" and "Moderate" for toxic gases and particulates (PM2.5 and PM10). Mitigation measures can further improve air quality.

In this area, the average noise level falls within regulatory limits set by USEPA and WHO (90 dB(A)). PM2.5 concentration was below USEPA but exceeded WHO limit, while PM10 was within limits. Trace metals were mostly high except Hg, which was undetectable.

Metal concentrations met OSHA limits. Toxic gases, BTEX, VOCs, and Aliphatic hydrocarbons were undetectable. Naphthalene was below OSHA limit. The air quality had a moderate AQI.

Mean noise level in Warehouse Area is $(66.83\pm10.96)~dB(A)$, falling within USEPA's 90 dB(A) limit for industrial areas. Personnel can wear ear protective equipment to lower exposure. Conduct noise audit to assess noise pattern and sources for further reduction. PM2.5 in the area has a mean of $(42.20\pm10.19)~\mu g/m^{-3}$, exceeding USEPA and WHO limits of 35 and 25 $~\mu g/m^{-3}$. Reduce automobile use, especially high-emission vehicles, to lower fine particulate levels. Recommend air quality audit to assess PM2.5 sources and emission patterns in the area.

Concentrations of Cd, Ni, Cr, and Pb were below OSHA limits. Metal levels higher in this area than others. AQI: 117 for PM2.5 and 54 for PM10, toxic gases scored well. PM2.5 AQI lowest in study, concerning health impacts. Air audit needed to find sources. Smelting, fuel combustion possible sources. Workers near should wear masks for PM2.5.

Guest house area had mean noise level of (56.20 ± 8.88) dB(A), violating daytime 55 dB(A) limit by USEPA and WHO. Night time value also exceeded 45 dB(A) limit. Noise survey recommended. PM2.5 concentration was low with mean of $(23.10\pm3.96)\,\mu\text{g/m}^{-3}$, below USEPA and WHO limits. PM10 mean concentration was $(70.83\pm20.74)\,\mu\text{g/m}^{-3}$. Toxic gases, BTEX, VOCs, Aliphatic hydrocarbons, and PAHs were below detection limits. Ni, Cr, and Pb were detected with mean concentrations of (0.204 ± 0.062) , (0.212 ± 0.020) , and $(0.106\pm0.079)\,\mu\text{g/m}^{-3}$ respectively, all below limits.

Range of noise: 55.0–70.6 dB(A) with mean of $(60.53\pm8.730~\mu g/m^{-3})$. Values exceed residential limit but within work exposure limit. Workers can use ear protection. PM2.5 and PM10 near gate: (23.43 ± 1.67) and $(63.07\pm10.82)~\mu g/m^{-3}$, within USEPA and WHO limits. Toxic gases, BTEX, VOCs, aliphatic hydrocarbons, and PAHs not detected. Trace metals tested: Cd, Ni, Cr, Pb, Hg, below OSHA limits. AQI: moderate and good for particulates and toxic gases. Data for air quality parameters underwent 1-way Analysis of Variance to assess spatial variation across 7 sites. See Table 6 for results.

The *p*-value at 95 % confidence level shows significant variation for Cd, Ni, and Pb across 7 sites, indicating local metal sources. Cd sources might be near Helipad, Jetty, Warehouse, and Main Gate. Noise, PM2.5, PM10, and Chromium had no

significant variation. Table 14 displays Pearson's correlation between air and meteorology parameters at 7 sites. PM10 had a strong positive correlation with humidity (r=0.758 at 99 % Confidence Level) compared to PM2.5 and humidity (r=0.215 at 99 % Confidence Level), suggesting humid air favors the aggregation of fine particulates into larger ones.

The correlation between airborne PM (PM2.5 and PM10) and wind speed was weak but negative: -0.251 and -0.417 respectively. Stagnant air promotes particulate buildup in the NAOC base troposphere. The Pearson's correlation coefficient for Ni and Cd is 0.800, indicating a strong positive correlation possibly from a common source.

4. Conclusions

This study shows air quality indices in the industrial Base, Port Harcourt, Nigeria. PM2.5 most affected AQI. Mean PM2.5 concentrations were (38.70 ± 15.65) µg/m⁻³ in residential areas and (42.20±10.19) μg/m⁻³ in warehouses, both violating USEPA and WHO limits. PM10 levels met USEPA limits at all 7 locations, but exceeded WHO limits at residential and guesthouse areas. Noise data for work areas met FMEnv, USEPA, and WHO standards of 90 dB(A). Nighttime noise levels surpassed 45 dB(A) limit. Gases were undetectable at all locations. Polycyclic aromatic hydrocarbons (PAHs) found in 3 of 7 sites. Only 3 of 16 USEPA PAHs detected: Naphthalene, Fluorene, Anthracene. Trace metals concentrations below USEPA OSHA limits. More detailed air quality monitoring may be needed to validate study findings. Noise mapping indoors and outdoors in residential and guesthouse areas is advised. Continuous measurement over time is needed to confirm PM2.5 levels. Workers may wear masks filtering PM2.5 dust. A 24-hour sampling survey is necessary to compare particulates with the W.H.O daily limit of 5 ng/m³ for Benzo(a)pyrene.

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LOGISTICS PROCESSES OF DESTRUCTION WASTE

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Abstract. Ukraine currently has an imperfect system for the collection and transportation of municipal solid waste (MSW). This system needs to be improved and constantly adapted to the increasing volumes and types of household waste due to the growth of the urban population, improved welfare and changes in the residential, commercial and industrial sectors. The article identifies the peculiarities of Ukraine's environmental policy in the context of the European integration process. The main purpose of the article is to comprehensively cover the issues related to effective waste management, in particular, the logistical aspects of waste disposal, to develop a conceptual framework for the formation of a strategy for the implementation of environmental waste logistics in the context of sustainable and environmentally balanced development, and to determine the volume of accumulated waste. Practical experience of municipal solid waste management in Ukraine and developed countries are studied. The dependence of solid waste accumulation on the influence of key social, environmental and economic factors is identified, which makes it possible to predict its dynamics as a basis for making effective management decisions. The relevance of forming management decisions in the environmental logistics of solid waste to reduce the negative impact on the environment is demonstrated. The role of logistics in reducing waste and achieving economic, social and environmental goals is shown. The role of environmental information and environmental knowledge as a special resource in the innovation economy is highlighted.

Keywords: environment, ecological crisis, destruction waste, logistics, landfill, sustainable development.

1. Introduction

The adopted National Waste Management Strategy in Ukraine (Waste management, 2008) introduces a systematic approach to waste management at the state

and regional levels and creates conditions for improving the living standards of the population by reducing waste generation and increasing the volume of its recycling and reuse. Local waste management plans have been developed accordingly. The implementation of the measures envisaged by these documents is carried out mainly at the local level by territorial communities (TCs) and at the municipal level by cities of regional or district significance. The market for waste management services is underdeveloped, and information on the potential for recycling solid waste (Kotsiuba et al., 2021) and construction waste is often scattered among different sources or is difficult to access. Waste sorting systems in amalgamated communities are underdeveloped due to insufficient demand for secondary resources and a lack of information on means and methods of waste disposal, especially military waste. The problem is that the amount of waste sorted by the population is small and of poor quality. The costs of collection and disposal are too high and do not bring the expected benefits to business.

A large proportion of resource-intensive components are often disposed of in landfills and dumps; recycling waste and construction waste and reusing them for commercial and industrial purposes will reduce the amount of waste in landfills. However, such measures require community involvement and support (Cosimato & Troisi, 2014), additional funding for waste management, especially for construction waste, and the introduction of systematic environmental education. An important element is the support of national and local authorities.

particular interest to S. Belyaeva, R. Berling, H. Vygovska, T. Halushkina, O. Hubanova, N. Zinovchuk, O. Kashenko, V. Kyslyy, L. Melnyk, O. Oksanych, Y. Stadnytskyi, Y. Stadnytskyi, S. Rybalka, V. Rudnytskyi, V. Rudnytskyi, and other domestic scholars. The works of Y. Stadnytskyi, S. Kharichkov and other national scholars have always been of particular interest. Issues related to the inclusion of environmental elements in logistics management systems were considered in the works of E. Krikavsky, N. Pakhomova, T. Skorobogatova, V. Meshalkin, and M. Nekrasova (Kotsiuba et al., 2018). However, the issues of improving waste management systems are mostly focused on one functional area of logistics, for example, resource conservation.

Waste management in communities is an important component of the economic system, but the current crisis in the provision of public services affects solid waste management (Kotsiuba et al., 2016). Waste management companies are unable to provide quality public services to residents of amalgamated communities. Their equipment is mostly outdated and worn out. Only a small proportion of household solid waste, construction waste, and waste from buildings destroyed as a result of military operations is collected separately and recycled. There are some successful enterprises in Ukraine, but their number is quite small.

Thus, the existing waste management system at the regional level does not ensure the economic and environmental security of the state. Solving this problem requires a new, modern approach to the formation of waste management systems at the community level.

2. Experimental part

An integral part of the logistics system for processing solid waste and construction waste is the process of sorting, processing or delivery to a storage facility, which ensures the organization of collection and transportation of solid waste and construction waste to a processing plant. Waste transportation is one of the most important factors that negatively affect the environment. Therefore, the choice of a business structure for the transportation of solid waste and construction waste is an important step in optimizing the logistics system of waste management.

Certain criteria should be used for a comprehensive assessment of the impact of the system of transportation, disposal and recycling of solid waste and demolition waste (Long et al., 2016). These criteria

Research issues in this area have always been of should include environmental impact criteria, costeffectiveness criteria, and transportation and operational (logistical) criteria. There are several partial criteria for assessing the environmental and economic efficiency of transport and logistics systems as a component of the waste management system. The criteria of durability, availability of new equipment, service life of a new vehicle fleet or fleet of vehicles, and availability of own repair and treatment facilities are very important criteria for the normal functioning of the enterprise.

> An important criterion for choosing a waste carrier is the availability of its own containers for separate collection (at least 30 % of the container fleet). Therefore, the number and availability of such containers is also considered an important indicator. The company's experience demonstrates its capacity and development prospects in this area. Obviously, the one that has been recognized in the market for many years and fully satisfies the users of its services will be chosen from the two companies. Therefore, it is advisable to choose practical experience as another criterion (Chun & Kim, 2012).

3. Results and Discussion

The concept of consumer waste is associated with the life cycle of products, which is a set of processes that are realized from the moment the needs in the product arise to the moment of their satisfaction and the disposal of the product as its consumer properties are exhausted. At the moment, the absolute majority of consumer waste is placed in landfills or incinerated. At the same time, it is known that consumer waste can be a valuable secondary material resource, which in the process of operation mainly do not change their original properties. Thus, recycling of consumer waste should have the character of targeted interaction aimed at solving both environmental and economic problems

In this study, it is advisable to use one that fully reflects the efficiency of the transportation process and its impact on the environment. When selecting criteria, attention should be paid to indicators that take into account the principles of sustainable development, consumption of natural resources (in the transport process, fuel is produced from oil, an exhaustible natural resource), the level of environmental impact of harmful components of exhaust gases emitted by vehicle engines, and minimization of environmental

According to the P_2M program management methodology (Khrutba et al., 2021), the most acceptable and effective way to form a system of program performance indicators is the 5 E's and 2 A's method The 5 E's and 2 A's method includes the following indicators: 5 E's – efficiency, effectiveness, earned value, ethics and environment ethics and environment, and two A's – accountability and acceptability.

Recycling logistics has borrowed many principles from the "traditional" areas of logistics and covers the planning, management, execution and control of all residual material flows as well as their associated information flows. Recycling logistics traces the entire path of waste movement from the place of generation to the place of disposal and recycling. Waste management is a typical example of solving a cross-sectoral system problem, where the following process steps should be developed in an integrated manner:

- forecasting the amount of waste generated;
- collection and accumulation of waste and its preliminary sorting;
- waste transportation;
- sorting of solid waste, sampling, baling and accumulation of waste types for sale and recycling;
- recycling of waste into secondary material resources;
- compacting and transporting "tailings" (residual solid waste after sorting) to a landfill.

This whole multi-stage system is constructed by calculating for each specific situation and each specific case. Predicting the amount of waste is the starting point for calculating the capacity of the entire recycling chain. An error in the prediction will lead to a geometric progression of errors in the calculation of the projected logistics chain, so a fairly wide range of complementary methods are used in predicting the amount of waste generated.

In the sphere of consumption finished products as a result of physical or moral wear and tear after some time become unusable, and due to the impact of physicochemical, mechanical and biological factors products can lose part of the original mass. Then the volume of consumption waste generation is determined by the following formula:

$$R^{o} = \sum_{i=1}^{n} V(t0 - Ts)Ki(1 - qi),$$
 (1)

where i is the type of consumed products (i=1, 2, 3, ..., n); (to is the year for which resources are calculated; T_S is the service life of products; V_i (to-T_S) is the volume of products distributed in the sphere of consumption,

based on consumption in (to -TS)-th year; K_i is the correction factor; q_i is the coefficient characterizing mass losses of the i-th product during operation.

Due to the difficulties in obtaining reliable information on the volume of consumption by the population of the region of a particular type of product as a result of its migration from region to region, the volume of formation of the relevant types of waste can be determined by the formula:

$$R^{\circ} \sum_{i=1}^{n} \sum_{i=1}^{m} pHJ(1-qi), \qquad (2)$$

where - average annual per capita consumption of products from the i-th type of raw materials; Chj is the population of the j-th region (j=1,2,3,...,m).

Due to the fact that of the total volume of consumption waste due to objective factors, some waste is currently unused, the volume of secondary material resources can be determined by the formula:

$$R^{B.C}=R^{0}(1-d),$$
 (3)

where d is the coefficient that takes into account the volume of unused consumption waste.

In essence, secondary raw material resources calculated by this formula represent consumption waste to be collected for further utilization. In order to improve the accuracy of the forecast of generated consumption waste, it is advisable to apply regression analysis. Regression analysis is usually understood as a method of stochastic analysis of the dependence of a random variable Y on variables (i = 1, 2, ..., k), considered as non-random variables, regardless of the true law of distribution. With the help of regression equation used for economic analysis, it is possible to measure the influence of individual factors on t he dependent variable, which makes the analysis specific and significantly increases its cognitive value. This task is quite simply solved with the help of existing computer programs that analyze a variety of possible situations. A big problem in organizing a system for the disposal of consumer waste is the rational organization of its collection and delivery to the place of recycling. Therefore, the correct location of the recycling center is of utmost importance. When determining the capacity of the center, it is necessary to take into account the requirements for the conditions and terms of transportation, storage of materials, finished products, etc. When choosing the location of the waste recycling center from among the possible options, the optimal one is considered to be the one that provides a minimum of total costs for the construction and further operation of the center and transportation costs for delivery and dispatch of cargoes. Transportation costs include initial capital investments for the development of the transportation network (construction and reconstruction of access roads, purchase of rolling stock, construction of garages, repair facilities, etc.) and operational costs of cargo delivery and dispatch (costs associated with cargo transportation, maintenance and repair of vehicles, devices and facilities). Expenses for construction and operation of the center include, first of all, expenses for construction of the building (structure) and purchase of equipment, as well as expenses related to their further operation (maintenance and repair of the building and equipment, wages, electricity, etc.). When increasing the capacity and size of the center, specific capital costs per 1t of cargo turnover and storage reserves decrease, which speaks in favor of the construction of larger centers. However, on the other hand, this most often entails a reduction in the number of centers, and, consequently, an increase in transportation costs when delivering resources to the place of processing.

When using the principle of minimizing the cost of delivery of consumption waste, the approximate coordinates of the location of the center are calculated using the known coordinates of the places from where the deliveries will be made. Let (xi; yi) – coordinates of the places of "formation" of resources, Γi – capacities of the corresponding points (Fig. 1).

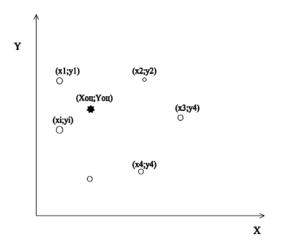


Fig. 1. Determination of the tentative location of the consumer waste recycling center

These coordinates are approximate, as they do not take into account the location of roads in the vicinity of the center. To determine the exact coordinates, the intersections of major roads (nodal points) in close proximity to the found indicative location should be considered (Fig. 2).

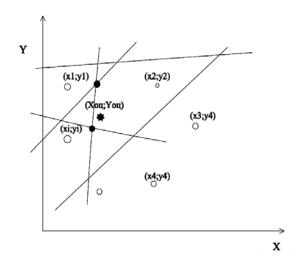


Fig. 2. Determination of the location of the consumer waste recycling center by the method of node point enumeration

The point, which corresponds to the minimum value of K_j , is the point of optimal location of the consumption waste center Difficulties in solving regional problems of consumption waste utilization are associated with both insufficient elaborations of the legislative base and territorial and economic peculiarities of the regions. In this regard, it is necessary to form a full-fledged regulatory system, a range of market and administrative tools that stimulate the collection and recycling of waste. This type of activity should be actively supported by the state and local authorities.

Thus, the solution to the problems of consumer waste utilization should represent a system of intersectoral interaction, starting from the stage of product design and ending with the stage of returning the recycled product to production. The participants of this system should be the state, local authorities, manufacturing companies, investors and ordinary citizens.

Whenever there is a disruption in the material flow, there is a high probability of financial losses. One of the main goals is to strive for a constant flow of materials, which ensures more reliable delivery and greater value for customers. That is why it is very important that internal logistics are clear and properly planned. The easiest way to eliminate supply shortages is to create a smooth flow of materials. Efforts are also made to reduce large production stocks and keep only the necessary amount of materials in stock. We can optimize all this thanks to the already existing systems. A method of managing the flow of materials and information to satisfy the customer by delivering the right product at the right time and in the required quality.

The cost minimization problem considers two variables: the shipment size and the reordering point (to reduce the amount of inventory costs), the ordering

costs, and the storage costs. Transportation costs are assumed to be proportional to demand and therefore irrelevant to the problem as long as expected demand remains constant. However, a closer look at transportation costs reveals that not all of them are charged per unit. The picture is different for the stages at which shipment size can influence the choice of vehicle size (vehicle capacity), i. e., distribution and delivery. If there are upper and lower bounds on vehicle capacity, the cost of using the smallest available vehicle will be the cost per shipment or part of the order cost and is significant for the cost minimization problem. The cost of choosing a larger vehicle size will also be significant, implying that capacity should be included as a choice variable in the cost minimization problem.

Large-scale waste recycling is possible provided that the appropriate infrastructure is created, which includes a logistics scheme as a complete integrated economic system of collection, storage, sorting, certification and identification, sales, disposal and recycling with elements of the corresponding service: information, marketing, transport, comercial.

In accordance with the functional structure of waste logistics, the formation of a logistics scheme occurs in several stages.

The first stage – waste collection and storage – includes rationally built logistics chains of waste search (generation), transportation, collection and storage.

To ensure efficient operation at this stage, it is necessary to carry out procurement work, create specialized collection points, warehouses and a vehicle fleet.

The creation of points for receiving waste from the population and organizations is complicated by the need to stimulate the waste sorting process. The solution to this problem can be the use of organizational, administrative and economic methods (fines for unsorted waste, partial compensation for waste removal fees when sorting it, organization of counter sales of high-demand goods in exchange for high-quality recyclable materials) with the active participation of city authorities, the media, and public organizations. The next stage is the stage of waste sorting, certification and identification. At this stage, the quantitative and qualitative composition of waste is determined, a database of existing waste is formed, and their ecological and economic assessment is carried out.

An integral part of the logistics system is distribution logistics, which is characterized by the features of warehouse management and inventory management.

Evaluation of waste flows is important, the results of which are used to select transport, containers, as well as for the economic assessment of this resource. Economic assessment of waste involves determining the amount of costs for their storage and preparation for processing, assessing the economic result from their use in the production and business cycle, comparing the cost of placement and disposal of waste with the prices of the corresponding natural resources.

At the stage of promotion to the market and sale of secondary raw materials removed from household waste, it is necessary to form a specialized commercial intermediary network.

At the same time, the corresponding logistics functions are carried out: management of transport flows, flows of secondary raw materials, warehouse logistics operations in order to minimize costs. It should be noted that for the effective organization of the logistics scheme for the disposal of household waste, the management of the information flow, including data on the formation of waste, places of its accumulation, the need for certain types of secondary raw materials at enterprises, etc., is of particular importance.

When selecting the criteria, one should rely on the available quantitative and qualitative indicators of the enterprise's performance. The developed criteria make it possible to select enterprises that provide the relevant services. The set of local standards can be used by the enterprises themselves to implement specific measures.

Consider applying criteria to select more environmentally friendly vehicles for MSW and waste transportation.

From the proposed set of criteria, select the criteria that best characterize the environmental and economic efficiency of waste transportation.

Fuel costs affect the cost of waste transportation along with logistics costs, but this is an uncontrollable parameter, as fuel prices depend on the price of oil.

Environmental pollution and economic losses due to harmful pollutants emitted by internal combustion engines of vehicles mainly depend on the Euro class of the vehicle (Kotsiuba et al., 2023). In other words, the fewer pollutants an engine emits into the environment, the less environmental damage it causes, and, accordingly, the more environmentally friendly vehicles can be replaced, thereby minimizing the negative impact on the environment.

The environmental and economic damage cau-sed by environmental pollution by motor vehicles is calculated in accordance with the methodology for determining the level of environmental pollution by References motor vehicles according to European standards set out in the guidelines "Assessment of Motor Vehicles as a Source of Hazardous Substances".

Logistics costs for the transportation of solid waste and construction waste depend on the transport and operational characteristics of trucks. Fuel con-sumption and emissions of harmful substances depend on the Cosimato, S., & Troisi, O. (2014). The Influence of Green vehicle's Euro class and, accordingly, determine the environmental and economic damage caused to the environment. An equally important criterion is the carrying capacity, which determines how many trips a vehicle must make to transport the required weight of cargo to a certain location (Demchuk & Nonik, 2024).

The environmental and economic efficiency of MSW and demolition waste management systems can be defined as the total environmental and economic damage caused to the environment; the less damage, the more efficient the waste management system (Cosimato, Troisi, 2014):

$$\sum EEZ \rightarrow min.$$
 (4)

When determining the effectiveness of the C&D waste management system, the subsequent environmental damage (in the case of landfilling bottles) and the benefits derived from this activity should be taken into account.

4. Conclusions

As a result of the study, a conceptual model of an environmentally friendly innovative logistics syst-em for community waste management has been for med. A schematic model of the logistics system of the regional waste management plan of the ATC is pro-posed, which includes a waste management coor-dinator who manages all logistics flows (monetary, material and information) of solid household and construction waste. A set of criteria is proposed for a comprehensive assessment of the impact of the system of transportation, utilization and recycling of solid waste, including material and technical criteria, criteria of professional requirements, financial and economic criteria, environmental criteria and social criteria. Each group of criteria is characterized by a set of local criteria that allow to choose the business structure of the carrier for the transportation of solid waste and demolition waste, while optimizing the logistics system of waste management.

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COMPARISON BIOFILM CHARACTERISTICS ON DIFFERENT TYPES OF CARRIERS FOR WASTEWATER TREATMENT

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Abstract. Enhancing the operational efficiency of wastewater treatment plant can be achieved by increasing the biomass concentration within the reactor volume. For this purpose, the use of immobilized microorganisms on carriers has become progressively prevalent in wastewater biological treatment technologies, aiming to enhance the quality of treated water. The analysis of the characteristics biofilms on spherical, disc-shaped and wheel-shaped on carriers under the same conditions was carried out. All investigated carriers are classified as dispersed, distributed throughout the volume of the air tank. The following characteristics of four biofilm carrier samples were investigated: the concentration of biomass immobilized on the surface of the carrier and the specific biomass per unit area of surface for different types of loading for the treatment of domestic wastewater. It has been determined that the biomass concentration immobilized on the surfaces of four distinct carriers, varying in shape and size, spans from 5425 mg/dm3 to 138 mg/dm3. The study showed that the carriers with a diameter of Ø 9.95 mm had the highest biomass concentration immobilized on the surface, and such carrier can be effectively used in MMBR systems for wastewater treatment, as well as to improve the performance of aeration tanks by upgrading them. The choice of biofilm carrier is a critical factor as it influences the optimal thickness of the biofilm, biomass growth, and the efficiency of various natures pollutants biodegradation.

Keywords: biological wastewater treatment, biofilm, carriers, immobilization.

1. Introduction

One of the approaches to intensifying the operation of biological wastewater treatment plants is to increase the concentration of biomass, particularly wastewater treatment microorganisms, in the volume of the plant. For this purpose, the use of immobilized microorganisms on carriers is increase in biological wastewater treatment technologies as a means of enhancing the treatment properties of aeration tanks.

Immobilized microorganisms are those affixed to the surface or encapsulated within a carrier to stabilize their activity. These immobilized systems are utilized in wastewater treatment to improve biological processes, particularly in the treatment of complex or heavily polluted waters. The use of immobilized microorganisms enables a more effective degradation of organic pollutants, biogenic substances etc.

The advantages of applying immobilized microorganisms include:

- Higher efficiency: greater degree of decomposition of complex organic and toxic substances;
- Increasing the biomass of treatment microorganisms in the plant;

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- Reduced biomass growth: as immobilized microorganisms are more stable, their biomass growth is less compared to activated sludge;
- Compactness of treatment plant: reactors with immobilized microorganisms require less space:
- Reduced operational costs: Technologies employying immobilized microorganisms can lower operational expenses due to reduced energy and reagent consumption (Sabliy & Zhukova, 2022; Sabliy et al., 2019; An et al., 2018).

Today, there exists a vast array of carriers including plates, spatial grids, meshes with cells in the shapes of squares, rectangles, circles, ovals, triangles, hexagons, and octagons, bristles, cylindrical, cubic and helical polymer elements, fibers, fabrics made from natural and synthetic materials, granules of zeolites (clinoptilolite, mordenite, chabazite, phillipsite), volcanic slags, polyurethane foam, polymer fibers, threads, woven and non-woven materials from nylon – VIA, polyethylene, lavsan, polypropylene, polyamide fibers, fiberglass, cubes of expanded polyether, and others (Widjaya et al., 2023; Blyashyna et al., 2018; Wang et al., 2005).

When the carrier for immobilization of microorganisms is chosen wisely, taking into account the specific conditions of the microbial transformation of organic substances contained in wastewater, the carrier can actively influence the surrounding environment, stimulate microbial metabolism, protect cells from adverse factors, and promote the long-term preservation of their biochemical activity.

The choice of biofilm carrier is a critical factor, as the carrier influences the optimal thickness of the biofilm, biomass growth, and the effectiveness of biodegradation of pollutants of various natures. In IFAS and MBBR systems, two groups of carriers are used: dispersed, which are distributed throughout the volume of the aeration tank, and fixed (immobilized) carriers. Dispersed carriers have advantages in effective mixing and large surface area, they are self-cleaning, do not require backwashing, and systems with such carriers are economically advantageous and simple to operate. Fixed carriers can provide more effective nitrification in cold climates, and the biomass on them is more resistant to changes in hydraulic regime (Al-Amshawee et al., 2020; Zinatizadeh & Ghaytooli, 2015; Al-Zuhairy et al., 2015).

The nature of the microbial cells in activated sludge facilitates their attachment and aggregation on solid surfaces (Cresson et al., 2009). Moreover, the retention (maintenance on carriers) of slowly growing

nitrifying colonies in the form of biofilm in a bioreactor enhances the wastewater treatment efficiency (for carbon, phosphorus compounds, ammonia, and ammonium salts) (Gieseke et al., 2001; Kermani et al., 2008).

A wide range of synthetic solid materials (such as polyurethane, polypropylene, polyethylene) and natural solid materials, such as plant parts and stones, have been investigated for the colonization of microorganisms without biomass processing to increase retention by solids and reduce the required contact area.

A biofilm is a biocenosis of microorganisms consisting of bacteria, protozoa, and fungi living together on a solid surface. These microorganisms produce extracellular polymeric substances (EPS), which stabilize the microbial community and also adsorb and accumulate organic and inorganic substances (such as pesticides, chlorophenols, polycyclic aromatic hydrocarbons, heavy metal ions). The main components of EPS, such as lipids, nucleic acids, proteins, and polysaccharides, determine the metabolic activity, elasticity, strength, diffusional capability, porosity, and density of the biofilm.

The aim of this study was to determine the technical and technological characteristics of different types of carriers for immobilization of microorganisms.

2. Materials and Methods

The study was conducted at the Department of Bioenergetics, Bioinformatics, and Ecobiotechnology of the Igor Sikorsky Kyiv Polytechnic Institute.

For the research, four samples of different types of carriers for the immobilization of microorganisms were used. The immobilization of microorganisms on these carriers was performed using activated sludge collected from the Bortnychi Aeration Station in Kyiv, where municipal wastewater from Kyiv and surrounding settlements is treated.

The analysis of the biofilm from the surface of the carriers and the activated sludge was conducted using standard methods and techniques.

Four bioreactors were used as the experimental setup, in which identical conditions for the process of biomass growth on the surface of the carriers were maintained. In each bioreactor, an aerator was placed at the bottom (center) and an additional flexible aerator around the perimeter of the base. Both provided fine bubble aeration using identical compressors. To maintain viability, 10 ml/day of a nutritive (model) solution was added to each bioreactor to supply the micro-

organisms with biogenic substances. The composition of this solution was based on a BOD: N: F ratio of 100:5:1 to sustain the activated sludge. The composition included glucose as a sugar source, organic matter, sources of biogenic elements, nitrogen (KNO₃), and phosphorus (K₂HPO₄). After hydraulic testing, activated sludge and a specific type of carrier were introduced into each bioreactor. The start-up period lasted 14 days, after which the growth of biofilms on the carriers was studied.

3. Results and Discussion

Biomass growth on the carriers was facilitated using microorganisms from activated sludge, with

provisions for air (aeration system) and biogenic substances (model solution). An analysis of the characteristics of the biofilm on plastic elements of four different shapes and sizes was conducted: spherical with a diameter of 47.09 mm; disc-shaped – 125.93 mm; and wheel-shaped diameters of 9.95 mm and 9.34 mm under identical conditions is shown in the table. All the studied carriers are classified as dispersed, distributed throughout the volume of the aeration tank. They vary in size, structure, surface area, and the material from which they are made. To precisely determine the geometric parameters, 3D models of the four carriers were created and the surface areas calculated using the SolidWorks software environment.

Characteristics of the studied carriers for microorganism immobilization

No. of bioreactor	Carrier diameter, mm	Carrier photo	Surface area of one carrier element, cm ²	3D Models of studied carriers
1	47.09		153	947.09
2	125.93	*	1266	
3	9.95		20.83	
4	9.34		13.15	N. S.

The following characteristics of four biofilm carrier samples were investigated: the concentration of biomass immobilized on the surface of the carrier and the specific biomass per unit area of surface for different types of loading for the treatment of domestic wastewater.

An important task of studying different carrier options is to determine and compare the biomass growth on carriers under experimental conditions created in bioreactors. Studies aimed at determining the amount of biomass growth on carriers placed in bioreactors were conducted in three replicates (3 series).

Fig. 1 presents photographs of clean carriers and carriers with dried with biofilm. All carriers differ externally in color, which may indicate variations in biomass quantity and biofilm layer thickness. The most significant color difference was observed for the carrier with a diameter of \emptyset 9.95 mm, position 3. Comparing it with the carrier of \emptyset 9.34 mm in diameter, a cl ear difference in the biofilm layer is evident, despite the external similarity of these carriers. In contrast, the smallest color difference is seen for the carrier with a diameter of \emptyset 125.93 mm.

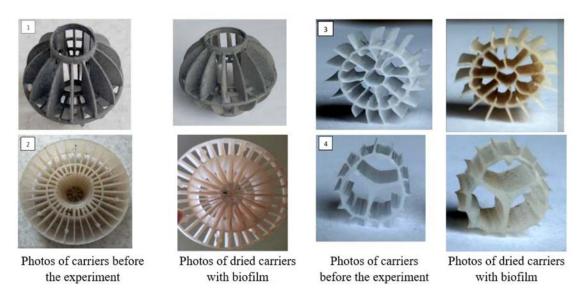


Fig. 1. Photos of carrier samples before the experiment (1-4) and dried with biofilm, respectively

According to the averaged results of three experimental series, the most biomass is immobilized on the carrier with a diameter of Ø 9.95 mm (Fig. 2). For the carrier Ø 9.95 mm, the average biomass concentration immobilized on the surface in setup 1 was 5425 mg/dm³. For other types of carriers, lower average biomass concentrations were observed (in decreasing order): for

carriers Ø 9.34 mm, Ø 47.09 mm, and Ø 125.93 mm, respectively, 2015, 869, and 138 mg/dm³. The biomass concentration per unit surface area of the carrier was also highest for the Ø 9.95 mm carrier - 0.83 mg/cm², with carriers Ø 9.34 mm and Ø 47.09 mm showing close results of 0.48 a nd 0.28 mg/cm², while the carrier Ø 125.93 mm had the lowest value - 0.11 mg/cm².

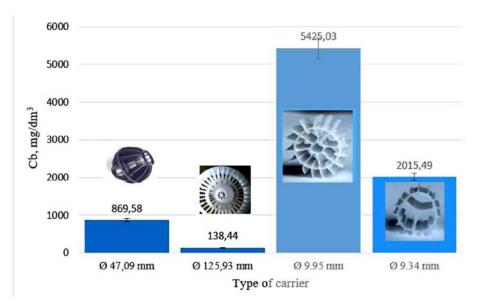


Fig. 2. Comparison of averaged biomass concentrations on different types of carriers across three experimental series

The highest biomass concentration on the plastic carrier can be explained by its highly developed external surface (the wheel-shaped carrier Ø 9.95 mm

has the largest area -20.83 cm²), complex configuration of the carrier element (multiple partitions, ribbed surfaces), small dimensions, and a large number

of elements in the volume of the bioreactor (350 pcs.). The advantage of the wheel-shaped carrier is also due to the intensive movement of individual carrier elements in the water column "from top to bottom" and vice versa under the action of air bubbles, which facilitates good washing by the activated sludge, promoting more intensive contact of the microorganisms in the activated sludge with the carrier surface and rapid formation and growth of the biofilm layer on the carrier.

The behavior of the carrier in the bioreactor plays an important role. Under the action of fine-dispersed air bubbles from the aeration system, individual elements of the carrier Ø 9.95 mm move in the water column "from top to bottom" and vice versa, are well washed by the activated sludge, which promotes more intensive contact of the microorganisms in the activated sludge with the carrier surface and rapid formation and growth of the biofilm layer on the carrier, as shown in Fig. 2.

Meanwhile, other carriers remained in a stationary position in the reactor. Carriers \emptyset 9.34 mm and \emptyset 47.09 mm, due to the dispersion of air bubbles and the low density of the material, floated and constantly remained in the upper layer of the bioreactor. The carrier \emptyset 125.93 mm, due to its own size and weight, lay in the thickness of the water, resting against the walls and bottom of the reactor vessel. The mobility of the carrier \emptyset 9.95 mm can be explained by several factors – a higher density of the polymer material compared to the carrier \emptyset 9.34 mm; greater surface area and configuration.

4. Conclusions

The analysis of research results conducted by the department's scientists and contemporary publications in the field of wastewater treatment highlights the potential of using methods and technologies of biological purification involving microorganisms immobilized on carriers. The advantages of such technologies are: high efficiency of removal of complex organic and toxic substances, nitrification and denitrification processes; increase in biomass of treatment microorganisms in the plant; reduction of biomass growth; compactness of treatment plants; reduction of operating costs due to lower energy and reagent consumption.

The method of biological wastewater treatment using immobilized microorganisms is innovative and highly effective, currently being researched and widely implemented in Ukraine and European countries in both traditional technologies (in existing aeration tanks at treatment plants) and in new technologies (in special bioreactors).

The choice of biofilm carrier is a critical factor as it in fluences the optimal thickness of the biofilm, biomass growth, and the efficiency of various natures pollutants biodegradation.

The study found that the carrier with a diameter of \varnothing 9.95 mm had the highest average biomass concentration immobilized on the surface -5425 mg/dm³, compared to others: \varnothing 9.34 mm, \varnothing 47.09 mm, and \varnothing 125.93 mm, which showed 2015, 869, and 138 mg/dm³, respectively.

Thus, wheel-shaped carriers with a diameter of 9.95 mm can be effectively used in MMBR systems for wastewater treatment, and also for enhancing the operation of aeration tanks through their modernization—creating zones with carriers to increase the efficiency of wastewater purification from organic substances, nitrogen compounds, especially at the stage of nitrification, phosphorus compounds, and other pollutants.

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HYDROCHEMICAL ANALYSIS OF SURFACE WATER PARAMETERS DYNAMICS IN THE RIKA AND TEREBLIA RIVER (UKRAINE)

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Abstract. This study assesses the hydrochemical dynamics of the Rika and Tereblia Rivers in Ukraine to evaluate water quality trends. Key water quality parameters, including biological oxygen demand, dissolved oxygen, total suspended solids, ammonium, nitrate, nitrite, phosphate, and sulphate, were analysed over a 1 0-year monitoring period. Statistical tools, such as Pearson correlation and regression analysis, were applied to determine relationships among these parameters and identify pollution sources. Results show that nutrient loading from agricultural activities, natural processes, erosion, and occasional industrial discharge contribute to water quality variability, impacting dissolved oxygen levels and increasing the risk of eutrophication. The results underscore the need for integrated water management practices to mitigate nutrient and organic matter influx and maintain the ecological health of these river systems.

Keywords: water quality, ecological monitoring, ecological safety, hydrochemical analysis, correlation analysis, regression analysis.

1. Introduction

Hydrochemical analysis of surface water parameters dynamics is essential for understanding the ecological state of rivers and addressing pressing environmental challenges (Behmel et al., 2016; Durkowski & Jarnuszewski, 2015; Kieu & Quoc, 2024; Matovelle et al., 2024; Nayak et al., 2024; Nguyen & Huynh, 2022).

According to the Cabinet of Ministers of Ukraine's Resolution No. 1100, dated September 11, 1996, "On approval of the Procedure for the development of standards for the maximum permissible discharge of pollutants into water bodies and the list of pollutants whose discharge into water bodies is regulated", a set of regulated pollutants has been established, including: ammonium nitrogen, organic substances (measured by biological oxygen demand (BOD₅) and chemical oxygen demand (COD)), total suspended solids, petroleum products, nitrates, nitrites, sulphates, phosphates, chlorides.

Monitoring the hydrochemical dynamics of water bodies allows researchers to track fluctuations in key water quality indicators, such as nutrient levels, dissolved oxygen (Sánchez et al., 2007), and concentrations of pollutants, which are critical for maintaining healthy aquatic ecosystems (Fisher et al., 2009; Kale et al., 2021; Pandey & Umamahesh, 2024). Such analysis is particularly important for mountain rivers of Ukraine, which are known for their relatively clean water but are increasingly threatened by anthropogenic factors.

The pollution of rivers, including mountain rivers, poses significant environmental concerns. Industrial discharges, agricultural runoff, and deforestation contribute to the degradation of water quality. In mountain regions, the steep terrain and rapid water flow can exacerbate these issues, as pollutants are quickly transported downstream, affecting broader ecosystems. Mountain rivers (Chen et al., 2024; Lenart-Boroń et al.,

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2022; Yu et al., 2022; Zhang et al., 2023; Zhao et al., 2024; Zhou et al., 2019) are also sensitive to changes in hydrological regimes, particularly due to the construction of reservoirs and hydropower plants, which can alter natural water flow and impact the surrounding environment.

Effective hydrochemical monitoring is important for early detection of pollution and for the development of strategies to mitigate its impact. However, the challenges in conducting consistent and widespread monitoring, especially in remote mountainous areas, often hinder timely responses. Addressing these issues requires improved monitoring systems, stricter regulations, and sustainable practices to protect the vital water resources that mountain rivers provide.

Statistical methods, such as descriptive statistics, the Shapiro-Wilk test, the Kruskal-Wallis test (Phan et al., 2024), correlation and regression analysis (Kothari et al., 2021; Phan et al., 2023), as well as principal component analysis, play a crucial role in assessing water quality parameters by revealing patterns and evaluating relationships among various hydrochemical indicators (Dzhumelia & Spodaryk, 2022; Gopchak et al., 2020; Kale et al., 2021; Olatinwo & Joubert, 2024; Phan et al., 2024). The application of these methods provides objective conclusions that aid in decisionmaking for ecological management and the preservation of water resources.

Regression analysis is an important tool for predicting water parameters, as it helps identify and assess relationships between various environmental variables. This aids in developing effective water resource management strategies, particularly in the context of water quality preservation and wastewater management. The use of regression models enhances the accuracy of predictions, which is critical for planning in agriculture and ecology (Pandey & Umamahesh, 2024).

Correlation analysis is a crucial tool in studying water quality, as it helps identify and assess the relationships between various hydrochemical parameters. This analysis enhances our understanding of how changes in one parameter can affect others, which is key to developing effective water resource management strategies. It enables the detection of statistically significant links between parameters such as dissolved oxygen, nitrates, ammonium, and phosphates. For instance, a strong correlation between nitrate and phosphate concentrations may indicate a common origin related to agricultural runoff. Additionally, correlation analysis allows for evaluating the impact of anthropogenic factors, such as wastewater discharge and fertilizer use, on water quality. Recognizing these relationships aids in the development of pollution control measures. Furthermore, it is essential for monitoring the ecological status of rivers and water bodies, enabling the identification of quality changes due to seasonal fluctuations, climatic conditions, or human influences.

For instance, study (Phan et al., 2023) have identified strong correlations between the hydrochemical compositions of surface and groundwater, highlighting the importance of an integrated approach to water quality analysis. Ultimately, correlation analysis provides valuable insights for making informed decisions in ecological management, contributing to sustainable water resource management and ecosystem preservation.

The aim of this work is to assess long-term water quality trends in the Rika and Tereblia rivers (Ukraine), identifying key natural processes and anthropogenic influences and pollutant interactions to support effective water management and ecosystem preservation.

2. Experimental Part

2.1. Study Area

The study was conducted in the Rika and Tereblia rivers in the Zakarpattia region (Ukraine), focusing on the surface waters in this area (Table, Fig. 1). The Rika and Tereblia rivers are important watercourses in the Zakarpattia region, playing a significant role in both the natural environment and the economic development of the area. The Rika River, approximately 92 km in length, originates in the northern part of the Carpathians, flows through the Khust district, and discharges into the Tysa (Tisza) River near the town of Khust. It exhibits the fast-flowing characteristics typical of mountain rivers, making it a critical source of water supply for local communities and industrial facilities. A key feature of the Rika River is its use in electricity generation. The most notable hydroelectric power plant in the region is the Tereblia-Rika Hydro Power Plant (HPP), which utilises the waters of both the Tereblia and Rika rivers for power generation.

No	Observation post
P1	Repynka River, 1 km, village Repynne, 1 km, village Repynne, Mizhhiria district, road bridge
P2	Rika river, 1 km, Khust city, mouth, bridge
P3	Tereblia river, 1 km, village Bushtyno, 1 km, village Bushtyno, Tyachiv district, road bridge
P4	Tereblia river, 1 km, village Bushtyno, mouth
P5	Tereblia River, 54 km, village Meryshor, Khust district, road bridge
P6	Umnozhanskyi stream, 0 km, 2 km above Mizhhiria, drinking water intake
P7	Tereblia-Rika HPP, 52 km, village Vilshany, Khust district, dam

Water observation posts

The Tereblia-Rika HPP is a vital energy facility in the region. Its uniqueness lies in the fact that water from the Tereblia River is transported through a 3.7 km tunnel to a reservoir, from where it is directed into the Rika River for electricity production. This hydroelectric power plant supplies a significant portion of Zakarpattia's energy demands, and the interconnection of the two rivers ensures high efficiency in the energy system.

The Tereblia River, 91 km in length, is also a mountain river that originates on the southern slopes of the Vododil Range. Flowing through the Tiachiv district, it traverses picturesque forests and mountains, providing water to local communities and industrial enterprises. In addition to its role in energy production, the river serves as a valuable natural resource, supporting the region's ecosystems.

The ecological condition of the Rika and Tereblia rivers warrants special attention. These rivers are known for their relatively clean water, owing to their mountainous origin and natural filtration through forest ecosystems. However, anthropogenic factors, including industrial pollution, intensive agriculture, and deforestation, can pose significant threats to the ecological balance of these water bodies. For instance, alterations to the natural hydrological regime due to reservoirs and hydroelectric infrastructure can negatively affect local flora and fauna, particularly fish populations that rely on the natural water cycle. The ecological status of these rivers necessitates continuous monitoring, as anthropogenic pressures, such as industrial discharges and modifications to the hydrological regime caused by hydroelectric power stations, present serious challenges to the maintenance of their natural balance.

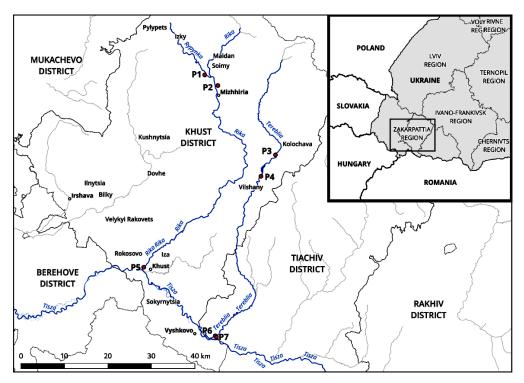


Fig. 1. The study area and observation posts

2.2. Research Methods

The initial phase of this research involved collecting, organizing, and processing available hydrochemical baseline data on water quality. Specialists of the State Agency of Water Resources of Ukraine conducted water quality monitoring to evaluate pollution levels in surface waters at various monitoring points along the Rika and Tereblia rivers as part of the national water quality control program.

The study was conducted based on those hydrochemical parameters from 2014 to 2023. The results of hydroecological observations on the river water quality were performed by the analytical control and monitoring services of the State Agency of Water Resources of Ukraine.

The monitoring stations used in the study were distributed along several key points in the Rika and Tereblia rivers. Data collection involved regular sampling and analysis of hydrochemical indicators, which provided valuable insights into the long-term dynamics of water quality in the region. The primary focus was on assessing levels of pollutants such as nitrates, phosphates, suspended solids, and heavy metals, which are indicative of both natural processes and human activities.

Using statistical analysis methods to assess the state of surface waters, the distribution of sulphates, phosphates, biochemical oxygen demand, dissolved oxygen, and total suspended solids was analysed based on results over a period of 10 years.

To analyse the data, statistical methods were applied, including the calculation of descriptive statistics (mean, range, standard deviation) and the generation of box plots to visualize the distribution of each parameter.

To identify the most significant parameter of water quality and its correlation with other parameters correlation matrix studies were done. The correlation method in the Pandas library in Python was used for the computation the Pearson correlation between water parameters. This allowed for the identification of significant correlations between pollutants. The use of Plotly Express for regression analysis, combined with descriptive statistics and correlation studies, provided a comprehensive approach to understanding the hydrochemical dynamics of the Rika and Tereblia rivers.

3. Results and Discussion

For waters designated for fishery purposes in Ukraine, the maximum permissible concentration (MPC) of chlorides is set at 300 m g/dm³. Elevated chloride levels in such waters can negatively affect fish and other aquatic organisms by altering osmotic balance and reducing habitat suitability.

In the Rika and Tereblia rivers, chloride concentrations were generally within permissible limits, indicating minimal anthropogenic pollution. Natural processes, such as soil leaching and mineral dissolution, are likely the primary sources of chloride in these waters. The absence of exceedances suggests that industrial discharges or other human sources have a limited impact on chloride levels in this region.

The dissolved oxygen (DO) concentration is regulated by sanitary standards, with MPCs set at a minimum of 6 mg O₂/dm³ for fishery waters and 4 mg O₂/dm³ for domestic water use.

Biochemical oxygen demand over five days (BOD₅) represents the oxygen microorganisms need to decompose organic matter at 20 °C, providing insight into organic pollution levels. High BOD5 levels indicate significant organic presence, potentially reducing DO and harming aquatic ecosystems. For freshwater bodies, the BOD₅ limit is 3 mg O₂/dm³, while for wastewater it typically should not exceed 25-30 mg/dm³.

Total suspended solids (TSS) reflect the mass of solid particles suspended in water, impacting clarity and plant photosynthesis. In Ukraine, the MPC for TSS is 15 mg/dm³. These solids stem from both natural sources (e.g., erosion) and human activities (e.g., sewage, construction). Elevated TSS levels can hinder fish gill function and reduce DO, affecting aquatic life and transporting pollutants such as heavy metals.

Sulphates occur naturally in water from gypsum and mineral leaching; however, industrial and domestic waste can increase their concentration significantly. According to Ukraine's environmental standards, as specified in the 2021 O rder of the Ministry of Environmental Protection and Natural Resources, the maximum permissible sulphate concentration for fishing water is 100 mg/dm³, while for household use it is 500 mg/dm³.

The data presented in Figs. 2-8 in our study provides an in-depth examination of water quality parameters in the Rika and Tereblia Rivers, focusing on critical hydrochemical indicators and their interactions. Fig. 2's boxplot, displaying biological oxygen demand, dissolved oxygen, ammonium, chloride, nitrate, nitrite, and sulphate concentrations, reveals that BOD levels generally fall within acceptable

limits for aquatic ecosystems designated for fishery purposes. However, occasional elevations in BOD suggest localized organic pollution, potentially linked to agricultural runoff or urban wastewater. Dissolved Oxygen levels, while largely compliant with standards necessary to support aquatic life, show notable reductions at sites with elevated BOD, underscoring an inverse relationship where organic material

decomposition intensifies oxygen demand, thereby lowering DO availability. Ammonium concentrations exhibit spatial variability, with heightened levels at particular monitoring sites, indicative of inputs potentially associated with agricultural or municipal wastewater sources, which, through nitrification, contribute to decreased oxygen levels.

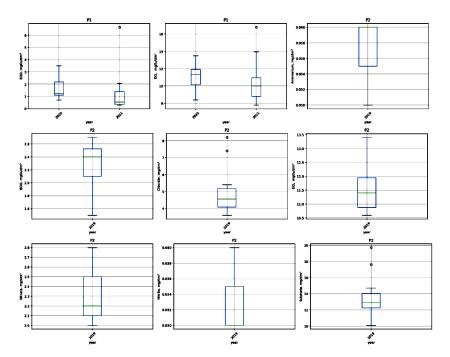


Fig. 2. The boxplot showing the distribution of BOD, DO, ammonium, chloride, nitrate, nitrite, sulphate in the observed points

Fig. 3 further emphasizes the inverse relationship between BOD and DO, highlighting the impact of organic pollution on ox ygen consumption. As organic matter decomposes, microbial activity elevates oxygen demand, consequently reducing DO levels, especially in areas of concentrated organic contamination.

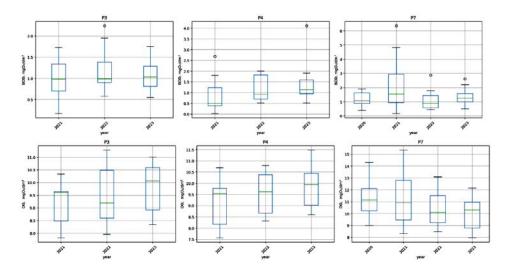


Fig. 3. The boxplot showing the distribution of BOD, DO in the observed points

Figs. 4 and 5 extend the analysis by including total suspended solids and phosphate along with the previously examined indicators, providing a more comprehensive perspective on pollution sources. Elevated TSS levels at some observation points suggest erosion, construction activities, or wastewater discharge as contributors to suspended particle concentrations, which impair water transparency and potentially disrupt photosynthetic processes, imposing stress on a quatic organisms. Elevated phosphate levels further suggest nutrient enrichment likely stemming from agricultural fertilizer use, a phenomenon often observed in tandem with higher ammonium and TSS levels, signifying the impact of agricultural practices on nutrient loading and subsequent eutrophication risks.

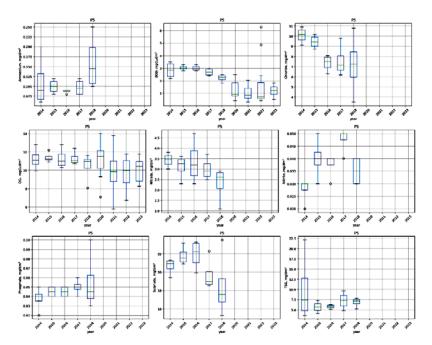


Fig. 4. The boxplot showing the distribution of BOD, DO, TSS, phosphate, ammonium, chloride, nitrate, nitrite, sulphate in the observed points

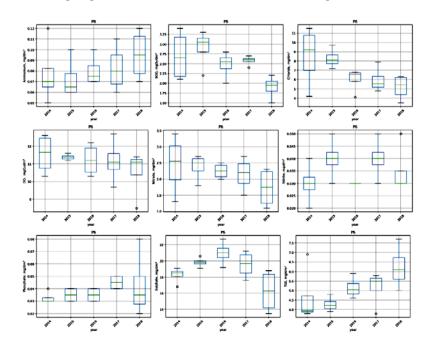


Fig. 5. The boxplot showing the distribution of BOD, DO, TSS, ammonium, chloride, nitrate, nitrite, sulphate, phosphate in the observed points

Pearson's correlation analysis is a preliminary descriptive technique to estimate the degree of association among multiple variables involved in the study. Therefore, a correlation matrix was computed which shows the degree of a linear association between any two of the parameters, and measured by the degree of correlation as a coefficient (R). R-value is used to identify the highly correlated and interrelated water quality parameter and that may influence the water quality of the area. The value of R ranges from -1 to +1; R = +1, or near to one indicates a strongest positive linear correlation between two parameters

compared and R = -1 or near to -1 reveals strongest negative linear correlation (Kothari et al., 2021).

The correlation analysis (Fig. 6) of water quality parameters in the Rika and Tereblia rivers provides insight into the interrelationships between various indicators of water health:

1. There is a moderate positive correlation (r = 0.568) between BOD and nitrate levels, suggesting that higher levels of organic pollution are associated with elevated nitrate concentrations. This may be due to the decomposition of organic matter, which releases nitrogen compounds into the water.

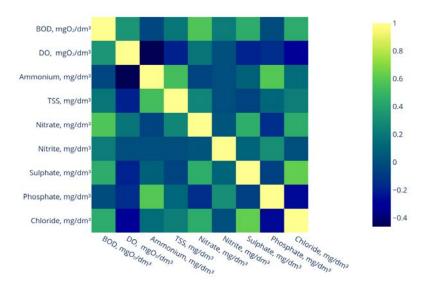


Fig. 6. The Pearson correlation matrix of the hydrochemical properties at the observed points the Rika and Tereblia rivers

- 2. A moderate negative correlation (r = -0.463) exists between DO and ammonium, indicating that as ammonium levels increase, DO tends to decrease. This relationship could be due to oxygen consumption during nitrification processes, where ammonium is converted to nitrate, a process that requires oxygen.
- 3. Ammonium and phosphate show a moderate positive correlation (r = 0.589), implying that they may originate from similar sources, such as agricultural runoff. The presence of both nutrients in elevated concentrations suggests potential nutrient loading from fertilizers or wastewater discharges.
- 4. The high positive correlation (r = 0.624) between sulphate and chloride indicates that these ions may have common sources, possibly geological (natural mineral dissolution) or anthropogenic, such as industrial discharges. Elevated levels of both ions could be a sign of industrial or urban influences on water quality.

- 5. The moderate positive correlation (r = 0.537) between TSS and ammonium suggests that suspended particles in the water may contribute to ammonium levels, possibly due to organic matter attached to these particles that releases ammonium upon decomposition.
- 6. There is also a moderate positive correlation (r = 0.305) between phosphate and nitrite, suggesting common sources of nutrient enrichment, such as wastewater or agricultural runoff. Elevated levels of these nutrients can lead to eutrophication, negatively impacting water quality and aquatic life.

Figs 7 and 8, which employ linear regression analyses, illustrate temporal trends in BOD and DO concentrations. The observed upward trend in BOD levels suggests a gradual increase in organic pollution, possibly attributable to intensified agricultural and urban activities, which augments the demand for oxygen and places additional stress on aquatic ecosystems. In contrast, the downward trend in DO levels

corresponds with the rising BOD, reflecting how escalating organic pollutants progressively reduce available oxygen. This trend is of ecological concern,

as declining DO levels are associated with adverse impacts on biodiversity and the stability of aquatic ecosystems.

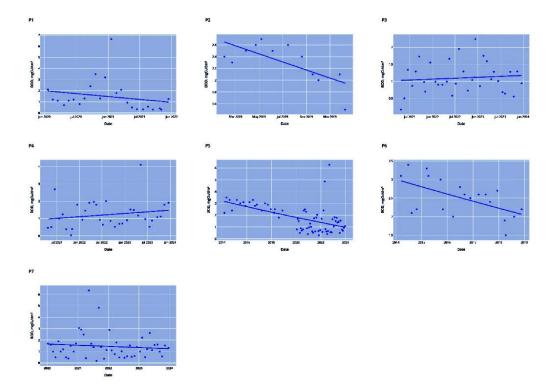


Fig. 7. Linear regression of BOD₅

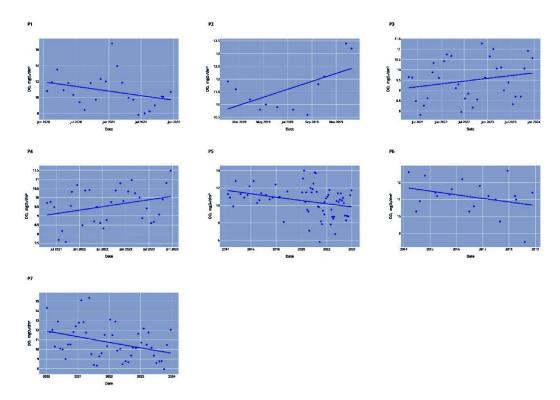


Fig. 8. Linear regression of DO

This analysis highlights the need for integrated water management strategies that target nutrient and organic pollution control. By addressing these key pollutants, such strategies would help maintain the ecological balance of the Rika and Tereblia Rivers, preserving their health and resilience in the face of ongoing anthropogenic pressures. Hydrochemical analysis of water quality is crucial for understanding the ecological health of river systems and informing water management strategies. However, the main issue lies in the unsystematic and irregular approach to data collection, reflecting broader challenges within the state system for ecological monitoring of water bodies. This lack of consistency in monitoring hinders both accurate assessments and timely responses to water quality issues, limiting the effecttiveness of management efforts aimed at preserving the ecological integrity of rivers such as the Rika and Tereblia. Addressing these challenges requires a more standardized and continuous data collection framework to support reliable long-term analysis.

4. Conclusions

This study demonstrates that the Rika and Tereblia Rivers are subject to natural processes and anthropogenic influences, particularly from agricultural runoff and localized industrial discharge, which affect their hydrochemical profiles.

Elevated BOD values in certain areas indicate organic pollution, likely due to agricultural and urban inputs, which correlates with reduced DO levels and increased oxygen demand.

Ammonium, nitrate, and phosphate levels show a pattern consistent with agricultural runoff, while elevated TSS concentrations suggest additional inputs from erosion and construction activities. These factors contribute to nutrient loading, increasing eutrophication risks.

Pearson correlation analysis highlights significant relationships, such as the inverse association between DO and ammonium, and positive correlations among BOD, nitrate, and sulphate, indicating shared pollution sources.

The data emphasize the need for enhanced water quality monitoring and management strategies to control nutrient and organic pollution to ensure sustainable ecological balance in these rivers. Addressing these challenges is essential to preserving water quality due to increasing anthropogenic pressures.

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HYDROCHEMICAL REGIME AND ECOLOGICAL STATE OF SURFACE WATERS IN THE SYNIUKHA RIVER BASIN

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Abstract. Preserving and restoring the ecological status of rivers in the southern regions of Ukraine is long-standing and pressing issue. These territories have a significant permanent water shortage. The problem of water supply has been exacerbated not only by military operations, but also by climatic factors, including the record-breaking hot summer of 2024. The Syniukha River is one of the largest tributaries of the lower part of the Southern Bug, whose water is actively used in various areas of economic activity. The results of the analysis of the dynamics of the hydrochemical regime and the assessment of the quality of surface waters of the Syniukha River for the period from 1993 to 2023 show that the degree of pollution of the river's waters varies according to different indicators. The water quality in the river corresponded to Class II and was described as good. Over the many years, the highest pollution was observed for nitrogen and phosphorus compounds, and the deterioration of dissolved oxygen. The state of the Syniukha River in its upper reaches is not environmentally stable due to the high level of anthropogenic pressure on the river, which exceeds the capacity of the river's aquatic ecosystem to regenerate itself. Deterioration of the ecological state of the Syniukha River requires constant monitoring by environmental institutions and the implementation of water protection measures.

Keywords: hydrochemical regime, water quality assessment, water management activities, anthropogenic impact, ecological status, risk assessment.

1. Introduction

As a result of anthropogenic impact, natural waters are polluted, their composition and properties change, which leads to a deterioration in water quality for water use. Contaminated water may become

unusable for a number of water users. Accordingly, when assessing the impact of economic activity on water resources, it is necessary to take into account not only their quantitative but also qualitative changes (Peleshenko & Khilchevskyi, 1997; Osadchyi & Blazhko, 2017). Such an assessment is especially relevant for water bodies that are sources of drinking water supply.

The aim of this study is to investigate the hydrochemical regime and ecological status of surface waters in the Syniukha River basin.

The results of the study of the hydroecology of the Syniukha River are relatively few and are mostly presented in review publication sand specialised reference books. Significant amounts of material devoted to this river are available in the review works of V. M. Timchenko, V. K. Khilchevsky (Khilchevskyi, 2021; Khilchevskyi et al., 2006) and reference books of different periods (Yatsyk et al., 1991; Vyshnevskyi, 2000). The hydrochemical characteristics of the Syniukha waters are given in the works of O. O. Ukhan et al. (Ukhan, 2016; Ukhan et al., 2015). The latest data on the current hydrological characteristics of the rivers and the hydrochemical composition of the water in the Syniukha hydrosystem are available on the websites of the Regional Office of Water Resources in Mykolaiv region, Kirovohrad and Cherkasy regions and the website of the Basin Administration of Water Resources of the Southern Bug River. However, against the background of a significant volume of publications on the Dniester and Southern Bug, the list of publications on the Syniukha River is clearly limited, which directly indicates an insufficient level of research on this water body, especially in recent decades.

2. Materials and Methods

The study was based on official monitoring data on hydrochemical water quality indicators of the Water and soil quality monitoring laboratory of the Regional Office of Water Resources in Mykolaiv region, which were collected at the Pervomaisk post (in the area of drinking water intake) for the period from 1993 to 2023.

The water quality assessment of the Syniukha River in the control stations was performed using the methodology for environmental assessment of surface water quality by relevant categories (Hrytsenko et el., 2012). This methodology makes it possible to assess trends in the quality of surface waters of land and estuaries of Ukraine in time and space, to determine the impact of anthropogenic pressure on water body ecosystems, and to assess changes in the state of water resources. The level of water suitability of the Syniukha River for various types of water use was determined by the value of the combinatorial water pollution index (Snizhko, 2001).

According to the EU Water Framework Directive (WFD) (EU WFD 2000/60/EC, 2006; Directive 2000/60/EC, 2000) (Directive 2000/60/EC, 2000), a management plan should be developed for each of the main river basins of Ukraine, the purpose of which is to achieve environmental objectives within the established

timeframe - "good" ecological status of surface bodies, as well as "good" ecological potential of artificial or significantly modified surface water. In order to implement the objectives of EU-Ukraine cooperation in the field of environmental protection and in accordance with paragraph 2 of part two of Article 132 of the Water Code of Ukraine (Vodnyi kodeks Ukrainy, 1995), paragraph 6 of Resolution No. 336 of the Cabinet of Ministers of Ukraine of 18 May 2017, Methodological Recommendations for Determining the Main Anthropogenic Pressures and Their Impacts on the State of Surface Waters were developed (Pro zatverdzhennia Metodyky vyznachennia masyviv poverkhnevykh ta pidzemnykh vod, 2019; Vykhryst et el., 2018). The criterion for assessing the main anthropogenic pressures on the state of surface waters or surface water bodies is to determine the risk of failure to achieve environmental objectives. Depending on the qualitative or quantitative indicators of anthropogenic pressures, 3 c ategories of anthropogenic impacts are identified: 'no risk'; "possibly at risk"; "at risk". The results of the assessment of the main anthropogenic pressures and their impacts are the basis for the development and implementation of a programme of measures to achieve environmental goals.

3. Results and Discussion

The Syniukha River basin is located in the Novoarkhangelskyi and Vilshanskyi districts of Kirovohrad region and Pervomaiskyi district of Mykolaiv region, a left tributary of the Southern Bug (Vyshnevskyi, 2000) (Fig. 1).

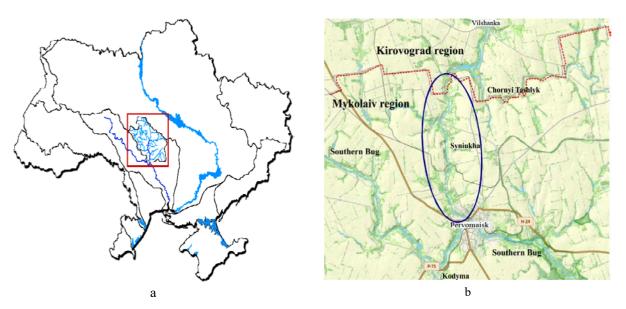


Fig. 1. The basin of the Syniukha River (a) and the study area (b)

The river is 111 km long and drains an area of 16700 km². It is formed by the confluence of the Velyka Bys and Tikych rivers and flows through the Prydniprovska Upland mainly in a south-westerly direction. The Syniukha flows into the Pivdennyi Buh on the territory of Pervomaisk and at their confluence, the water comes from about 60 % of the entire basin. The valley is trapezoidal, often asymmetrical, the slopes are dissected by ravines, and rock outcrops are typical. The valley is up to 2.5 km wide and up to 60 m deep. The floodplain in the upper and middle reaches is dry, covered with meadow vegetation. The riverbed is meandering, in some areas rapids; width 40-50 m (in the lower reaches up to 90-120 m). The river slope is 0.46 m/km. Average water discharge at a distance of 12 km from the mouth is 29.4 m³/s. Main tributaries: Tikich, Yatran (right), Velyka Vysya, Kagarlyk, Sukhyi Tashlyk, Chornyi Tashlyk (left). It is fed mainly by snow. It freezes in December and thaws in March. Ice cover is unstable. There are small hydropower plants; three reservoirs have been created. River water is used for domestic, industrial and agricultural water supply.

At the confluence of the Syniukha with the Southern Bug – Pervomaisk, the river's shore zone is reforested and alkaline Steppe soils are common in this part of the river basin. The climatic conditions upstream in the Syniukha basin are quite different from those of the Steppe zone and have more pronounced signs of a temperate continental climate with precipitation levels of up to 500 mm/year. The lower part of the basin, which is partly located within the Steppe, is characterised by a pronounced similarities to the South Steppe climate, with relatively short winters and hot summers. The negative water balance in this area is caused not so much by a lack of precipitation (480 mm) as by high evaporation (800 mm or more). This is further associated with the extremely low local runoff, which is practically not taken in to account in hydrological calculations of the water budget of Syniukha, which is perennial due to the inflow of water from the upper parts of the collecting basin.

Since 1992, the temperature regime of the Syniukha basin has shown an upward trend, especially in winter. Very hot summer periods accompanied by prolonged dry spells have become more common (Mahas, 2024 a). The average annual temperature in 1961–2023 increased by almost +2.5 °C to 10.2 °C, reaching more than +11 °C in some years.

In the context of climatic instability in recent years, against the background of rising ambient temperatures and a powerful agrogenic transformation of the catchment, there has been a significant, more than 69 %, in water discharge (Q), which has caused a number of negative reactions of the river hydrosystem and related natural objects. At present, water discharge is in a prolonged low-water phase, which significantly affects the hydrochemical indicators of river water quality (Mahas, 2024 b).

The negative anthropogenic impact on the water balance of the Syniukha River is also evident, resulting from surface water abstraction, flow regulation by hydraulic structures and an increase in the water surface area with corresponding evaporation losses. The main sources of pollution in the Syniukha River basin include surface runoff from agricultural and urbanised areas, municipal waste water from inoperative or inefficient sewage treatment plants, fish farms, and sugar, fat and sunflower oil industries factories, and mines (Ekolohichnyi pasport Mykolaivskoi Kirovohradskoi oblasti, 2023).

Since chernozems are common in the upper part of the Syniukha River basin, infiltration water entering the channel network during the period of maximum soil moisture during the recession of spring floods introduces relatively only small amounts of salts, mainly calcium and magnesium bicarbonates (Mahas & Tuz, 2024).

In summer and winter, the river is fed exclusively by groundwater, which also contributes to an increase in the content of hydrocarbonate compounds.

The hydrochemical regime of the Syniukha River is characterised by monitoring data at the Pervomaisk station for the period from 1993 to 2023 (Table 1).

The data averaged over 30 years (Table 1) on the hydrochemical regime of the Syniukha River within the study area indicate the natural presence of quite significant seasonal fluctuations in the content of its components and a certain dependence of the chemical structure of river water on the volume of surface runoff, which is the main source of migratory components of agrogenic origin (nitrates, ammonium compounds, potassium, detritus, etc.). In addition, groundwater has a certain influence on the hydrochemical structure of river water, which is discharged in the erosion cuts of the Syniukha and tributary rivers.

Table 1

Hydrochemical parameters of the Syniukha River
at Pervomaisk during the period 1993–2023

In disease	Values of indicators				
Indicator	Average	Maximum	Minimum		
Temperature, °C	12.32	29	0		
Smell, points	1	1	1		
Transparency, cm	37.43	41	3		
Mass concentration of suspended solids, mg/dm ³	10.87	486	0		
Color, hail. PCS	35	101	0.37		
Hydrogen index (pH), pH units	8.19	8.83	1.6		
Dissolved oxygen, mgO ₂ /dm ³	10.98	34.2	3.44		
Measure of oxygen saturation, %	99.28	254	41.3		
Calcium, mg/dm³	63.98	108	36		
Magnesium, mg/dm ³	13	58	13		
Sodium, mg/dm ³	86.56	170.3	5.04		
Potassium, mg/dm ³	5.31	21.27	1.63		
Total calcium and magnesium content (water	6.33	8.3	4.1		
hardness), mg-eq/dm ³					
Hydrogen carbonate ions, mg/dm ³	383.79	539.9	40.26		
Sulfate ions, mg/dm ³	86.58	297.6	33.28		
Chloride ions, mg/dm ³	52.01	82	19.85		
Mineralization, mg/dm ³	498.04	561.8	432.7		
Dry residue (dissolved solids), mg/dm³	564.73	755	340		
Phosphate ions(polyphosphates), mg/dm³	0.34	1.068	0		
Total phosphorus, mg/dm³	0.25	0.796	0.016		
Nitrite ions, mg/dm ³	0.09	13.5	0		
Nitrate ions, mg/dm ³	5.18	45	0		
Mass concentration of ammonium ions, mg/dm ³	0.09	0.86	0		
Silicon (silicon), mg/dm ³	4.38	7.769	0.393		
Total iron, mg/dm ³	0.28	21.6	0		
Permanganate oxidizability, mgO/dm³	8.65	14.6	3.64		
Biochemical oxygen demand (BOD5), mgO ₂ /dm ³	2.29	15.7	0.2		
Biochemical oxygen demand (BOD20), mg/dm ³	2.89	14	0.3		
Chemical oxygen consumption, mgO/dm³	26.82	49.51	11.76		
Total alkalinity, mg-eq/dm ³	6.3	8.2	4		
Aluminium, mg/dm³	0.02	0.445	0		
Manganese, mg/dm ³	0.06	1.156	0		
Copper, mg/dm ³	0.01	0.119	0		
Nickel, mg/dm ³	0.02	0.67	0		
Total chromium, mg/dm ³	0	0.015	0		
Zinc, mg/dm ³	0.04	0.47	0		
Mass concentration of anionic surfactants, mg/dm ³	0.03	0.6	0		
Oil products, mg/dm³	0.14	2.25	0		

The chemical composition of the basin's groundwater is characterized by elevated levels of mineralization (4–5 thousand mg/l) with a high content of sulfates and magnesium compounds. Since the groundwater horizons within the river hydraulic system are drained by the Syniukha Valley and its tributaries, they have a direct hydraulic connection

with surface water, showing increased sensitivity to pollution. Thus, it is the combination of geological, structural, climatic, and meteorological conditions of the catchment that determine the hydrochemical regime of river waters and, accordingly, the associated groundwater. The latter, in the absence of powerful water-bearing rock horizons, are formed in

cracks in Lower Proterozoic crystalline rocks and porous layers of Mesozoic-Cenozoic sediments, which are typical for the entire southern slope of the Ukrainian Crystal Shield (Stan pidzemnykh vod Ukrainy, 2021; Liuta, 2023).

The ionic structure of water is a key hydrochemical parameter by which surface and groundwater are classified and the compliance of the latter with existing standards for different types of water use is assessed. According to the above characteristics (Table 1), the waters of the Syniukha River in its lower reaches are clearly identified within the hydrocarbonate class with a slightly increased content of sulfates and sodium. The most characteristic is the hydrocarbonate complex. According to the monitoring data, the content of hydrocarbonate ions in the water of the Syniukha River ranged from 40.26 to 539.9 mg/dm³ in the period 1993–2023.

Sulphate ions are present in almost all natural waters and usually rank second in content after hydrocarbonates. They enter the water mainly as a result of chemical weathering with sedimentary rocks, during the oxidation of sulphides, and the dissolution of minerals containing sulphur (usually gypsum). There are also sulphates of anthropogenic origin, the content of which is usually related to the decomposition of industrial and domestic wastewater. The sulphate regime is determined by redox processes, the biological situation in the water body, and human activity. According to the observations, the sulphate content at the Syniukha River station – m. Pervomaisk varied between 33.2 and 297 mg/dm³.

Chloride ions are characterised by high migration capacity due to their good solubility, low sorption on suspended solids and limited consumption by aquatic organisms. Chlorides enter natural waters through the dissolution of chlorine-containing minerals and saline deposits (Khilchevskyi et al., 2019; Khilchevskyi et al., 2013). In recent years, the role of industrial and domestic wastewater in increasing the content of chlorides in water bodies has been identified. Chlorides are found in the waters of the Syniukha River near Pervomaisk in concentrations ranging from 19.8 to 82 mg/dm³.

Calcium ion is the dominant cation in low-mineralized waters. The main sources of calcium in surface waters are chemical weathering and mineral dissolution. Significant amounts of Ca are introduced with industrial wastewater and from agricultural land. According to observations in the Syniukha River, the calcium content ranged from 36 to 108 mg/dm³.

Magnesium ions enter surface waters through chemical weathering and dissolution of rocks (dolomites, marls) and wastewater. According to long-term observations (1993–2023), the content of magnesium ions in the water of the Syniukha River ranged from 13 to 58 mg/dm³.

The total content of calcium and magnesium ions in water forms its total hardness (hardness). According to the monitoring data, the total hardness of the Syniukha River water was 4.1–8.3 mg-eq/dm³.

Sodium and potassium ions enter surface waters with domestic and industrial wastewater and irrigation water from agricultural land. The sodium content in the mouth of the Syniukha River ranged from 5.04 to 170.3 mg/dm³, and the potassium content – from 1.63 to 21.27 mg/dm³.

Water mineralisation (or the sum of ions) is the total content of all minerals detected during chemical analysis of water (Khilchevskyi et al., 2006; Shakirzanova & Kichuk, 2019). Fluctuations in surface water salinity are seasonal. The lowest values are usually observed during spring floods and high waters. The highest values – during the period of low water. During the study period, water salinity ranged from 340 to 755 mg/dm³.

The hydrogen index (pH) is determined by the presence of free hydrogen ions. Although seasonal fluctuations occur, caused primarily by hydrobiological processes, the pH value is a fairly stable indicator. A sharp change in the pH of water indicates that the water body is polluted by acidic or alkaline wastewater from industrial enterprises. In natural waters, the concentration of hydrogen ions is mainly determined by the ratio of free carbon dioxide and hydrogen carbonate ions, and is also influenced by the high content of humus substances, basic carbonates and metal hydroxides formed as a result of CO₂ absorption during photosynthesis, as well as the presence of hydrolysable salts in the water. In addition, contaminated surface water may contain strong acids or bases that affect the acidity of the water. The concentration of hydrogen ions is of great importance for chemical and biological processes in natural waters (Khilchevskyi, 2021; Khilchevskyi & Chunarov, 2009). The development and vital activity of aquatic plants and the stability of various forms of element migration depend on pH. According to longterm observation data, the pH of the Syniukha River waters ranged from 1.6 to 8.83.

According to the monitoring data, the water of the Syniukha River near Pervomaisk has a significant content of suspended solids (up to 486 mg/dm³), which is a r esult of excessive agricultural deve-

lopment of its basin, high degree of ploughing, insufficient forest cover and deterioration of the river's self-purification capacity due to the general deterioration of its condition. Water transparency ranged from 3 to 41 cm.

The content of a large amount of organic and humus compounds in the water of the Syniukha River, especially during periods of increased water content, determines the high dynamics of water colour, which ranges from 0.37 to 101 degrees.

Dissolved oxygen in water is one of the most important physicochemical indicators. At the same time, it is the most significant natural oxidant, determining the quality of water and the ability to maintain the ontogeny of aquatic organisms. The main consumers of dissolved oxygen are the processes of respiration of aquatic organisms and oxidation of organic substances. Low dissolved oxygen content affects the entire range of biochemical and ecological processes in a water body. In surface waters, the oxygen content varies widely and is subject to seasonal and daily fluctuations. Oxygen deficiency is more common in water bodies with high concentrations of polluting organic substances and in eutrophic water bodies containing large amounts of nutrients and humus substances. The dissolved oxygen content in the water of the Syniukha River -Pervomaisk ranged from 3.44 to 34.2 mgO₂/dm³ or 41.3-254 % saturation.

Chemical oxygen demand COD is an indicative indicator of water pollution. In the water of the Syniukha River, this indicator varied from 11.7 to 49.5 mg/dm³. The content of organic substances in the water according to the permanganate oxidation index is quite significant and ranged from 3.64 to 14.6 mg O/dm³.

Biochemical oxygen consumption (BOD₅) provides indirect information about the amount of organic matter in water and allows to assess the degree of pollution of a water body and the content of organic matter that is easily oxidised. This indicator ranged from 0.2 to 15.7 mgO/dm³ over the entire study period.

Nutrients are among the most important indicators of water quality and the state of the aquatic ecosystem. They determine the level of development of aquatic organisms, the trophic level of water bodies, and the degree of their pollution (Mahas & Trokhymenko, 2009).

Nutrients in natural waters include nitrogen, phosphorus and silicon compounds. Nitrogen and phosphorus are most actively involved in the vital activity of aquatic organisms. The most important in biological and biochemical terms are compounds of orthophosphoric and nitric acids, the amount of which in certain periods of the year determines the intensity of organic life in a water body (Mahas & Trokhymenko, 2009). Biogenic substances are catalysts for the process of anthropogenic eutrophication of surface waters. In addition, a significant concentration of nutrients in water can be quite dangerous for humans. The main sources of nutrients (nitrogen and phosphorus compounds) in river waters include residential and urban runoff and wastewaters, industry, agriculture, livestock, agriculture, and precipitation. Internal processes in the water body also play a significant role.

Mineral nitrogen compounds in river waters occur mainly in the form of nitrates, nitrites and ammonium salts dissolved in water. Organic nitrogen compounds are also present in surface waters as a result of the breakdown of protein substances. The main source of nitrogen compounds in river waters is protein degradation processes that occur both in water bodies and in the surrounding soils. One of the indicators of the degree of eutrophication of water bodies is the content of inorganic nitrogen compounds in them.

The main sources of ammonium ions in water bodies are domestic wastewater, surface runoff from agricultural land when ammonium fertilisers are used, and wastewater from various industries. Seasonal fluctuations in ammonium concentration are typically characterised by a decrease in spring and during periods of intensive phytoplankton photosynthetic activity and an increase in summer, when bacterial decomposition of organic matter intensifies. A significant amount of it is a sign of recent water pollution or the result of intensive reduction processes that are common for humic compounds in marsh waters. The concentration of ammonium nitrogen in the water of the Syniukha River – Pervomaisk ranged from 0 to 0.86 mg/dm³.

Nitrites are intermediate products in the nitrogen cycle (organic ammonium – nitrite – nitrate), so their concentrations in water are usually low compared to ammonium and nitrate nitrogen. The presence of nitrite in uncontaminated water bodies is mainly due to the decomposition of organic matter and nitrification (Mahas & Trokhymenko, 2009). Nitrite is detected in significant concentrations when there is a shortage of oxygen in the water body, and high levels can also be found in areas where

wastewater is discharged from enterprises that use nitrite and salt in their production processes. In addition, changes in nitrite content also reflect the self-purification processes of natural waters. The nitrite concentration in the water of the Syniukha River – Pervomaisk ranged from 0 to 13.5 mg/dm³.

Nitrate nitrogen is formed in natural waters as a result of aqueous nitrification of ammonium ions in the presence of acid under the influence of nitrifying bacteria, which is why nitrate concentrations increase in summer during the massive die-off of phytoplankton (Mahas & Trokhymenko, 2009). Another source of nitrates in surface waters is precipitation. The concentration of nitrate nitrogen in the water of the Syniukha River varied from 0 to 45 mg/dm³.

Phosphates enter river waters as a result of water erosion of rocks. In natural waters, phosphorus is found in the form of both mineral and organic compounds. Some of it is soluble, while others are found in the form of colloids and suspended solids. Phosphates largely determine the productivity of a water body, as they are a nutrient for aquatic organisms. In river waters, the natural concentration of phosphate is usually low during the growing season due to consumption by biological processes, and is maximised in winter due to the decomposition of organic residues. Elevated phosphorus concentrations in waters sometimes indicate pollution. The content of phosphate ions in the water of the Syniukha River ranged from 0.01 to 1.07 mg/dm³.

Iron is almost always present in natural waters, as it is ubiquitous in rocks. The concentration of total iron in natural waters is low due to its low migration capacity. The main factors that determine the volume and intensity of Fe inputs to surface waters include the processes of chemical weathering of rocks. A significant amount of soluble iron compounds enters surface water bodies with underground flow, as a result of underground recharge, with wastewater from various industries and agriculture, storm water runoff, surface-slope runoff from urbanised areas and agricultural land. Iron content in the waters of the Syniukha River ranged from 0 to 21.6 mg/dm³.

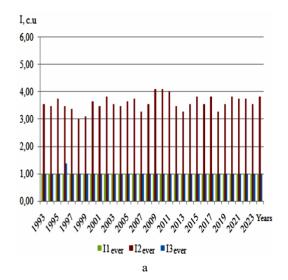
The silicon concentration in the water of the Syniukha River at the Pervomaisk control point ranged from 0.39 to 7.76 mg/dm³ in 1993–2023.

The content of heavy metals (copper, zinc, nickel, chromium, manganese) in the waters of the Syniukha River is limited by high pH, water turbidity, and intensive biological processes. Sources of heavy metals include industrial wastewater, quarry water, various reagents containing copper, and runoff from

agricultural land. In many cases, the content of heavy metals in the water of the Syniukha River is highest during floods and high water, which is explained by their washing away from the catchment surface. That is why, over the entire period of observation, the content of copper in the river water ranged from 0 to 0.12 mg/dm³, zinc from 0 to 0.47 mg/dm³, nickel from 0 to 0.67 mg/dm³, chromium from 0 to 0.015 mg/dm³, and manganese from 0 to 1.16 mg/dm³.

The content of pollutants, such as oil products, synthetic surfactants and phenols, in natural waters mainly depends on the anthropogenic load on water bodies. Large quantities of oil products enter surface waters with wastewater from oil refineries, chemical and other industries, and with domestic wastewater. The main source of synthetic surfactants in natural water bodies is domestic and industrial wastewater. When these compounds enter water bodies they can affect their physicochemical state, worsening the oxygen regime and organoleptic properties. At the same time, these compounds remain in river water for a long time and slowly decompose. The content of synthetic surfactants in the Syniukha River near Pervomaisk ranges from 0 to 0.6 mg/dm³.

Water quality was assessed by three sets of indicators: components of the salt composition (total ions, chlorides, sulfates), tropho-saprobiological criteria (suspended solids, transparency, pH, ammonium nitrogen, nitrite nitrogen, nitrate nitrogen, phosphorus phosphate, dissolved oxygen measure of oxygen saturation, permanganate oxidizability, bichromate oxidizability, BOD₅), the content of specific substances of toxic effect (copper, zinc, chromium, manganese, total iron, nickel, oil products and synthetic surfactants). The analysis of water quality monitoring and assessment data showed that the degree of water pollution in the Syniukha River is not the same according to different indicators. The results of the generalized ecological assessment of the water quality of the Syniukha River for the period 1993-2023 show that, according to the average and worst values of mineralization indicators, the river water belonged to fresh water, and its ionic composition was of the hydrocarbonate class, calcium group, type III. In both cases, among the block indices, the index of the ecological and sanitary block worsens water quality the most (Fig. 2). That is, the water of the Syniukha River has excessive concentrations of nitrogen and phosphorus compounds, and a rather unstable oxygen regime and pH.



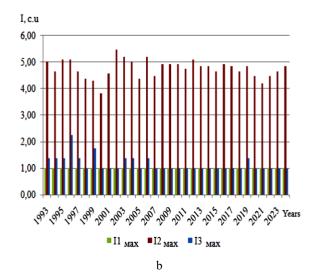


Fig. 2. Temporal changes in water quality in the Syniukha River according to the environmental block indices: a - for annual average values; b - for the worst values

During the entire study period, there was significant water pollution with organic substances, characterizedby an increase in the BOD₅. In terms of maximum values, the 4-5th class of water quality is predominant ("poor-very poor" in terms of condition, "dirtyvery dirty" in terms of purity). The deterioration of water quality to Class 3 is observed in terms of oxidation (PO, COD). The oxygen regime of the Syniukha River corresponds to Class 3 ("mediocre", "moderately polluted") using average values of the indicator, but using the worst values it is much worse - Classes 4-5. That is, in most samples, the oxygen regime of the river is mostly at an acceptable level, but there are still frequent cases of a critical decrease in dissolved oxygen content, up to and including frostbite. This can be explained by the fact that the river and its tributaries are regulated by numerous reservoirs that have limited water exchange at depth in them. The deterioration of the oxygen regime occurs as a result of seasonal hydrobiological processes, as well as pollution by domestic and industrial wastewater and surface runoff from agricultural land. It is also worth noting the very high level of biogenic pollution of the Syniukha River waters in terms of nitrogen and phosphorus compounds, where the water quality varied from class 4 to 5 (in terms of condition "bad, very bad" and in terms of purity "dirty-very dirty"). It is the high content of such compounds caused by anthropogenic factors that leads to "blooming" of water in the created reservoirs and deterioration of the oxygen regime.

According to the integrated assessment, during the study period, the waters of the Syniukha River in the Pervomaisk city reach correspond to Class II, Category 2 and are assessed as "very good-clear" in terms of their average values of indicators. According to the worst values of indicators, the water corresponds to Class II, Category 3 and the water quality of the Syniukha River is assessed as "good – quite clean".

If we look at the results for individual years (Fig. 3), we can see that the situation has not changed significantly over the entire observation period. The water quality in terms of average and worst indicators fluctuated within the second class, with only the quality categories changing. Among the block indices, the highest values are for the block of environmental and sanitary indicators.

The indice variations at their maximum values indicate limited fluctuations in pollution levels and a tendency to stabilize the hydrochemical state of the water in the Syniukha River. Such changes can be explained by a decrease in uncontrolled wastewater discharges and surface runoff in the river basin. However, against the backdrop of a decline in economic activity in the river basin and the volume of its pollution, there is a tendency for water quality to deteriorate in terms of average indicators, which is explained by a significant decrease in water flow in the river and the accumulation of pollutants near the river mouth.

Thus, in general, the ecological condition of the river is not good due to high anthropogenic pressure and limited capacity for self-purification of water. This requires attention from environmental institutions and the need to develop and implement an effective environmental program aimed at both improving the condition of the watershed and limiting further pollution of the water body.

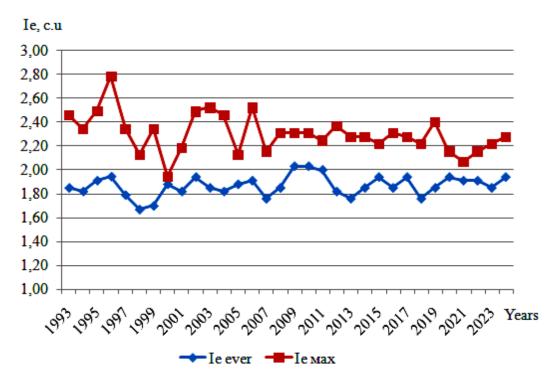


Fig. 3. Changes in the environmental indices of water quality in the Syniukha River

The level of water suitability of the Syniukha River for various types of water use was determined by the value of the combinatorial water pollution index (CWPI) using the values of maximum permissible concentrations for water bodies of fishery significance (MPC) (Table 2).

 $Table\ 2$ Results of water quality assessment of the Syniukha River according to fishery MPC standards

Water quality indicator	s of the Syniukha Ri	ver – Pervomaisk	city according to	fishery MPC standa	rds
	<i>n</i> =24; <i>n</i> ′=17; <i>K</i> =71	1 %; CWPI=77; q	uality class III b -	- "dirty"	
1	2	3	4	5	6
Indicator	[O ₂]	[Ca] ²⁺	$[\mathbf{Mg}]^{2+}$	[Na] ⁺	[K] ⁺
MPC, mg/dm ³	6	180	40	120	50
N	378	378	378	278	278
N'	359	0	140	14	0
No	95.0	0.0	37.0	5.0	0.0
Evaluation indices	4	1	3	1	1
Ki	1.83	0.36	0.95	0.72	0.11
Valuation indices	1	1	1	1	1
Evaluation points Si	4	1	3	1	1
Indicator	[Cl] ⁻	[SO ₄] ²⁻	[Pmin]	[NO ₂]	[NO ₃]
MPC, mg/dm ³	300	100	1	0.02	9.1
N	378	378	51	378	378
N'	0	93	0	307	52
No	0.0	24.6	0.0	81.2	13.8
Evaluation indices	1	2	1	4	2
Ki	0.17	0.87	0.25	4.61	0.57
Valuation indices	1	1	1	2	1

Continuation of Table 2

1	2	3	4	5	6
Evaluation points Si	1	2	1	8	2
Indicator	[NH ₄] ⁺	[Fe _{sum}]	[COD]	[BOD ₅]	Suspended matter
MPC, mg/dm ³	0.39	0.1	20	2.25	15
N	378	378	266	378	378
N'	6	323	232	148	79
No	1.6	85.4	87.2	39.2	20.9
Evaluation indices	1	4	4	3	2
Ki	0.24	2.77	1.34	1.02	0.72
Valuation indices	1	2	1	1	1
Evaluation points Si	1	8	4	3	2
Indicator	pН	Mineralization	[Cu] ²⁺	[Zn] ²⁺	[Cr] ⁶⁺
MPC, mg/dm ³	6.5-8.5	1000	0.001	0.01	0.001
N	378	378	375	375	378
N'	9	0	307	310	18
No	2.4	0.0	81.9	82.7	4.8
Evaluation indices	1	1	4	4	1
Ki	0.96	0.56	7.14	3.57	0.20
Valuation indices	1	1	2	2	1

In general, for the period from 1993 to 2023, out of 24 indicators 17 exceeded the MPC with varied extent, so the pollution complexity index was 71 %. Referring to individual indicators, the level of water pollution was distributed as follows:

- The content of chlorides, mineralization, phosphates, nickel, chromium, and surfactants was recorded as "single low-level contamination" and the water was "slightly contaminated";
- The content of suspended solids, sulfates, and nitrates was recorded as "unstable low-level pollution" and the water was "polluted";
- The BOD content was recorded as "persistent low-level pollution" and the water was "dirty";
- Dissolved oxygen and COD indicators showed "characteristic low-level contamination" and the water was "dirty";
- The content of petroleum products was recorded as "stable medium-level pollution" and the water as "very dirty";
- In terms of iron, copper, and chromium, "characteristic medium-level contamination" was recorded, and the water was "very dirty";
- In terms of nitrite, iron, manganese, copper, and zinc, the water was found to be "characteristically medium polluted" and "very dirty".

In general, the water quality of the Syniukha River corresponded to the CWPI index of 77 points, which indicates that the investigated water body belongs to the

III b class of water quality. The state of pollution of the water body can be characterized as "dirty", which indicates that its waters are unsuitable for safe fish farming.

According to hydrochemical monitoring data, the Syniukha River is polluted and is under the influence of a high anthropogenic load (the river's waters are heavily polluted by domestic and industrial wastewater). The presence of significant volumes of discharges causes an unacceptably high content of organic and, in many cases, toxic substances in the river waters. The main pollutants are biogenic substances (nitrogen and phosphorus compounds). The high and persistent level of pollution over time indicates the poor efficiency of the waste water treatment plants that discharge water in to the Syniukha River basin.

The analysis of long-term data on hydrochemical water quality indicators" (Tabl "3) showed that the risk" of not achieving environmental objectives arises from the high content of ammonium nitrogen and phosphates in the water of the Syniukha River, for which the corresponding actual values exceed the critical ones. Water pollution with these substances indicates the presence of point sources of untreated municipal wastewater, which may be caused by the absence and improper operation of treatment facilities in the studied surface water massif. There are no risks in terms of oxygen, BOD_5 and pH.

Risk assessment of anthropogenic load for chemical and physical-chemical indicators based on monitoring data of the Syniukha River inPervomaisk for 1993–2023

Indicator	Actual values	Critical values	Risk assessment
Oxygen*, % saturation	99.28	70	without risk
BOD ₅ **, mg/dm ³	2.29	6	without risk
NH ₄ **, mg/dm ³	0.76	0.6	at risk
NH ₄ ***, mg/dm ³	0.47	0.2	at risk
PO ₄ ***, mg/dm ³	0.34	0.3	at risk
рН	8.19	6.5-8.5	without risk

- * 10 th percentile.
- ** 90 th percentile.

The results of the assessment can serve as a basis for developing ways to address economic and social issues related to river protection, planning and implementing water protection measures to achieve good ecological status of the river, and evaluating the effectiveness of such measures.

4. Conclusions

This paper investigates the ecological state and water quality of the Syniukha River, a large tributary of the Southern Bug River, based on long-term observations in its estuary, the area of drinking water intake at the Pervomaisk post (1993–2023, 24 indicators).

An indicative ecological assessment of the water quality of the Syniukha River showed that the degree of pollution of the river's waters varies according to differrent indicators. In general, for the period 1993–2023, the value of the ecological index of water quality of the Syniukha River in terms of average concentrations of indicators corresponded to the 2nd Class of Category 2 (very good water quality, clean water quality). Using the worst values of indicators, the environmental index corresponded to Class II, Category 3 (water condition "good", water clarity "fairly clean"). Therefore, the water quality class is relatively consistent over the entire study period.

Comparison of the block indices of the environmental assessment shows that the water of the Syniu-kha River in its estuary has been most polluted over the years by substances of the environmental and sanitary block, namely nitrogen and phosphorus compounds, poor dissolved oxygen conditions, and high organic matter content.

In terms of chronological trends, the average values of the indicators show an increase in the environmental index, which indicates a certain deterioration in the water quality and ecological status of the Syniukha River. The main reasons for such changes include a decrease in water flow in the river over the past 100 years, a high level of anthropogenic pressure and limited capacity for water self-purification.

The assessment results of water quality in the mouth of the Syniukha River, according to fishery MPC standards, correspond to Class III (b) and characterize as the water as "dirty" and unsuitable for safe fish farming. The deterioration in water quality is caused by elevated concentrations of nitrite and COD, which can be explainned by the significant development of agriculture in the river catchment, including the use of fertilizer sand plant protection products that are periodically washed into the river with surface and groundwater runoff. The high concentrations of iron, manganese, copper, zinc, and oil products are caused by the discharge of polluted industrial wastewater.

The results of the study indicate that for the period 1993-2023, the state of the Syniukha River in the estuary cannot be considered ecologically stable and optimal due to the high level of anthropogenic pressure on the river, which clearly exceeds the capacity of the river's aquatic ecosystem to regenerate itself. This situation indicates an increased level of environmental hazard in the river basin. Given the importance of the Syniukha River as the largest tributary of the Southern Bug in its lower reaches and a source of drinking water supply in Mykolaiv region, the problem of deterioration ecological state of the Syniukha River requires attention from environmental protection agencies and the need to develop comprehensive water quality management based on the identification and assessment of the impact of major sources of pollution, and regulation of water management activities in the river basin.

^{***} Average annual value.

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DIRECTIONS OF SUSTAINABLE DEVELOPMENT OF A MACHINE-BUILDING ENTERPRISE ON THE EXAMPLE OF SE "SILPROEKT"

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Abstract. The paper presents the results of analysing the activities of a machine-building enterprise, taking into account the influence of factors of the political and socioeconomic crisis. Based on the results of the PEST- and SWOT-analysis, the most promising directions of sustainnable development of an engineering enterprise are identified, namely, implementation of energy-efficient solutions, use of circular economy principles, application of environmentally friendly technologies, digitalisation, and personnel training. The introduction of an environmental management system will significantly contribute to expanding the development opportunities of machine-building enterprises, increasing their competitiveness and ensuring sustainable development.

Keywords: sustainable development, machine-building enterprise, PEST-analysis, SWOT-analysis, energy efficiency.

1. Introduction

In the modern world, sustainability is becoming a key issue for businesses in all industries, and the machine building industry is no exception. In the context of global climate change, depletion of natural resources and increasing competitiveness in international markets, machine-building companies must adapt to new challenges. For this purpose, it is important to implement the principles of sustainable development aimed at minimising the negative impact

on the environment, optimising the use of resources and ensuring long-term socio-economic growth and environmental safety.

The issues of defining the essence of the mechanism of sustainable development of an enterprise and the directions of its formation have become relevant and are covered in a number of works by foreign researchers (Hall et al., 2010; Kates et al., 2005; Dyllick & Muff, 2015; Baumgartner, 2013). In Ukraine, scientists from various fields, including economics, ecology, engineering and management, are engaged in the problems of sustainable development of enterprises. The works of Ukrainian scientists explore various economic and environmental aspects of sustainable development to optimise production processes (Kvyatkovska, 2013; Hrechko, & Ocheretiana, 2020; Mishchenko, 2011; Kuzmina, 2015), areas of implementation of energyefficient and resource-saving technologies at enterprises (Veremeenko, 2018; Dzhedzhula, 2014; Denysiuk & Vasylenko, 2016), methods of forming social responsibility of entrepreneurial structures and their motivation (Kyrych et al., 2015; Melnyk et al., 2018), effectiveness of implementation of the environmental management system (Dekaliuk & Stasiuk, 2010; Vasylenko et al., 2017).

The sustainable development of industrial enterprises is a continuous dynamic process of innovative development based on technological modernisation, which ensures the scientific and technological security

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of the country and improves the quality of life of the population (Rahmana & Bawono, 2021). Therefore, there is a need for further research aimed at studying the activities of machine-building enterprises in the difficult conditions of war and socio-economic crisis in Ukraine, which significantly affects their development. However, despite these challenges, it is the crises that stimulate enterprises to find new solutions, modernise production facilities, introduce innovations and energy-efficient technologies, and switch to more sustainable business models. In particular, machine-building enterprises that produce equipment for processing agricultural raw materials may gain additional opportunities for sustainnable development by increasing demand for products that are essential for food security in Ukraine and other countries.

The purpose of the study is to analyse the activities of an engineering enterprise, taking into account the factors of the political and socio-economic crisis, and to substantiate its further development in the context of sustainable solutions to ensure economic, food and environmental security.

2. Materials and Methods

Today, the Ukrainian economy is facing unprecedented challenges in its history. Russia's full-scale military invasion has dealt a powerful blow to all parts of our country's economic system (The economy of war and post-war economic development of Ukraine, 2022). Due to the hostilities and disrupted supply chains, many businesses are losing access to raw materials, components or markets. This leads to production shutdowns or significant slowdowns. In Ukraine, the destruction of transport infrastructure, power supply and other critical facilities seriously hinder the efficient operation of industrial structures. The lack of stable communications complicates both production and logistics processes. Rising costs of energy, materials and logistics lead to higher production costs, which reduces the competitiveness of enterprises in the domestic and foreign markets. There is a shortage of capital due to economic difficulties. The war leads to the mobilization of labour, loss of specialists, and migration of skilled personnel to other countries. Businesses face a shortage of skilled workers. At the same time, consumers may reconsider their priorities and demand for goods and services, preferring more sustainable and affordable options. Such a crisis situation can pose a serious threat to an industrial enterprise, forcing it to adapt to new realities.

The machine building industry is one of the leading sectors of the Ukrainian economy. To operate successfully, the industry needs to provide its facilities with fuel and energy resources, metals, various raw materials, water resources, labour and transport networks. Developed infrastructure in cities and the presence of other related industries allow engineering companies to obtain all the resources they need for production. The processing of raw materials and the production of finished products in the machine building industry involve the generation of a large amount of various wastes that can have a negative impact on the environment.

Given the significant material and energy intensity of production processes at machine-building enterprises, the implementation of sustainable development principles in the crisis is crucial for the long-term competitiveness and survival of the business (Lepeiko, & Mazorenko, 2017). Enterprises that implement sustainable development strategies can improve the efficiency of energy and material resources. This helps to reduce costs, which is especially important during the economic crisis. Sustainable development encourages businesses to innovate and create new products or services that can meet market needs in times of crisis, such as environmentally friendly products or new business models related to the circular economy. Companies that demonstrate sustainability and responsibility to society and the environment can strengthen their reputation and consumer confidence, which is an important factor for survival during a crisis (Demyanenko, 2020). At the same time, investors increasingly prefer companies that adhere to the principles of sustainable development and environmentally friendly production. This can be an additionnal source of funding during a crisis (Kravchenko & Prudkyi, 2020). All of the above involves analysing and managing environmental and social risks, which allows businesses to be more flexible and prepared for changing market conditions.

Taking into account all the above, we can identify the main directions of sustainable development of an engineering enterprise, which will contribute to increasing its resilience to socio-economic and environmental risks.

- 1. Energy efficiency and carbon footprint reduction. Implementing technologies that reduce energy consumption is of paramount importance. This includes:
- optimisation of production processes, using highly efficient equipment;
- switching to renewable energy sources such as solar or wind power;

- energy recovery systems that allow for the reuse of excess heat and other resources;
- reducing the carbon footprint also requires the development and implementation of methods to minimise CO₂ and other harmful emissions.
- 2. Rational use of resources at all stages of the production cycle with minimal losses. Key steps in this direction include:
- use of secondary materials and recycling of production waste;
- designing products with a view to recycling and reusing components;
- optimisation of supply chains to minimise losses in transportation and storage of resources.

These measures not only reduce the environmental impact but also increase economic efficiency by reducing the cost of raw materials.

- 3. Implementation of environmentally friendly production technologies, including:
- application of green technologies in production processes that minimise environmental pollution;
- development and use of environmentally friendly materials that are easily recycled and do not harm ecosystems;
- continuous monitoring and reduction of harmful emissions and production waste, which is especially important in the context of tightening environmental regulations and standards.

The use of such technologies allows companies not only to meet regulatory requirements but also to strengthen their image as a responsible producer.

- 4. Implementation of digital technologies and automation, which contributes to
- optimisation of production processes to increase efficiency
- improving control over resource consumption and minimising losses;
- improving the accuracy of forecasting and planning to reduce the risks of overproduction and related losses;
- reducing the number of errors and defective products associated with the human factor.
- 5. Social responsibility, staff development and environmental awareness:
- ensuring safe and comfortable working conditions for employees;
- implementation of professional training and development programmes to improve staff qualifycations and raise environmental awareness;

development of corporate social responsibility aimed at supporting local communities and solving social problems.

Improving the social environment at an enterprise helps to increase employee loyalty and reduce staff turnover, which has a positive impact on business sustainability.

Thus, sustainable development is not only a tool for improving efficiency, but also a strategic advantage that allows companies to adapt to crisis conditions while maintaining their competitiveness in the market.

To analyze the activities of a machine-building enterprise in the context of sustainable development, PEST-analysis and SWOT-analysis methods were used. These methods complement each other as they cover different but interconnected aspects of strategic analysis. PEST-analysis (Political, Economic, Social, Technological) helps assess the external environment of the company by identifying macroeconomic factors that may affect its operations. SWOT-analysis (Strengths, Weaknesses, Opportunities, Threats) combines an analysis of internal factors (strengths and weaknesses) with an analysis of external factors (opportunities and threats). Thus, the combined use of these methods provides a more comprehensive understanding of the company's position and helps develop an effective strategy for its further development.

The primary data for the study were the company's annual reports, equipment quality certificates, technological documentation, and a series of interviews with the company's administration and employees.

3. Results and Discussion

The international TransLearn project analysed the sustainability of the machine-building enterprise "Silproekt", located in Mykolaiv. "Silproekt" has been operating in the Ukrainian market of equipment for the food and grain processing industry as a manufacturer since 1994. Since 1998, it has also been operating on the foreign market. The main activity of the company is the development and production of a universal, energy-saving cereal complex UKR-2 for processing cereals into groats and flakes, as well as related units. The company manufactures UKR-2 cereal lines: equipment for the production of cereals and flakes from wheat, buckwheat, millet, barley, corn, peas, oats, rice, spelt, and lentils.

The cereal market, like any other market, is an area of interaction between supply and demand. The food traditions established in Ukraine determine a significant demand from the population for various cereals made from buckwheat, millet, rice, oats, barley, wheat, corn and peas. External demand for domestic cereal products has a significant potential for growth, given the worsening global food crisis. At the same time, the expansion of its supply by Ukrainian producers is constrained by

significant fluctuations in profitability and periodic interventions of cheap cereals at reduced prices from neighbouring countries in cases of overproduction.

To identify the main external factors affecting the activities of the machine-building enterprise, a PEST analysis was conducted, which is a strategic analysis tool that allows identifying and taking into account potential risks and opportunities arising from changes in the current external environment (Table 1).

Table 1 PEST-analysis of factors influencing the activities of SE "Silproekt"

Political	Economical
Military actions	Increased cost of raw materials
Liberalisation of legislation and easier access to EU markets	Devaluation of the national currency
Frequent changes in the legislative system	Decrease in real incomes of potential consumers
Market restrictions	Change of suppliers due to military operations
Social	Technological
Social tensions, first due to the COVID-19 pandemic, then	Increased speed of technology transfer
due to military actions Increased consumer demands for quality of service,	The need to upgrade the equipment manufacturing base
equipment repair, and equipment design	Access to modern technologies
Changing consumer tastes and needs due to the development of healthy food systems	Weak state support for innovation

Having examined the generalised PEST-analysis matrix, it can be concluded that the most influential factors for the enterprise are economic factors, namely changes in the level of prices for raw materials and opportunities for obtaining them, as well as political factors, which are manifested in political instability and changes in legislation.

Another useful tool for assessing the current state and development prospects of an engineering company, especially in the context of sustainable development, is a SWOT-analysis. It is necessary due to several important factors:

- assessment of internal potential. Strengths help to identify the key competitive advantages of the company: the availability of advanced technologies, qualified personnel, high efficiency of production processes and stable relationships with suppliers and customers. Weaknesses reveal internal shortcomings: low energy efficiency, outdated equipment, lack of investment in research and development, which can limit the potential for sustainable development.
- Identification of opportunities and threats. Opportunities are related to external factors, such as new technologies, government or market support for environmental initiatives, and new markets for environmentally friendly products that can contribute to the company's growth. Threats include factors that may hinder the realisation of sustainable development goals: increased

environmental standards, competition from more environmentally friendly businesses, changes in legislation, and resource shortages.

- Sustainable development planning. A SWOTanalysis helps to strategically plan how to maximise your strengths and external opportunities for sustainable growth. For example, if a company has strengths in innovation, it can be directed towards the development of green technologies. The analysis also reveals which weaknesses should be addressed to meet the requirements of sustainable development.
- Risk mitigation. An assessment of threats and weaknesses allows a company to prepare in advance for potential risks, such as rising energy costs or the introduction of new environmental regulations. This allows the company to be more flexible and ready for external changes.
- Decision-making support. SWOT-analysis serves as a basis for strategic decision-making. In the context of sustainable development, it helps to understand what steps need to be taken to reduce the environmental footprint, improve energy efficiency and comply with the principles of the circular economy.

The SWOT-analysis helps machine-building companies to effectively integrate sustainable practices into their operations, reducing risks and opening up new opportunities for growth and innovation (Table 2).

In the context of martial law and the dangerous location of the enterprise, it would seem inappropriate to talk about sustainable development. However, the company has been awarded many awards, diplomas and certificates at agricultural and industrial exhibittions for technological products, for the best development for agriculture, for the active implementation of energy-saving technologies, and for the best project to restore agricultural production from 1994 to 2020.

For example, one original energy-saving feature is that buckwheat husks are used as fuel for steaming, and energy consumption is 1 kW per 100 kg of processed grain. For comparison, hydrothermal grain processing of cereals of similar capacity, using standard technology, consumes 65 kW per 100 kg of buckwheat processed. The payback period for cereal processing plants, including all costs, is 5 to 9 months when operating in two shifts.

 $Table\ 2$ SWOT-analysis of SE "Silproekt" activities in the context of sustainable development

Strength	Weakness
Competitiveness Extensive experience in various economic conditions	Decrease in sales volumes
Already a well-known brand	Changes in marketing and advertising support
Energy efficiency of the equipment Own production plant and processing workshop Possibility to train personnel who will work on the manu-	Lack of innovative technologies and equipment for manufacturing parts
factured products	High production costs
High share of the domestic market Loyal pricing policy	Low foreign economic activity
Profitable operations.	
Ability to supply spare parts to customers Availability of space for scientific research and its	
implementation in production	Threats
Opportunity	War
Lower barriers to entry to the EU market	Growing political and economic crisis. Increased
Growing demand for cereal products	competition in the production market
Introduction of innovative technologies	Increased cost of raw materials Devaluation of the national currency
Opportunity to participate in grant support programmes	Decreased solvency of potential consumers
	Increase in energy prices
	Decrease in the number of people
	Saturation of the market with products
	Mobilisation of employees

To improve its operations in line with sustainable development goals, SE "Silproekt" participated in the Solar Energy programme to install solar panels and equipment that switches from transformer to inverter operation. The company switched from a common heating system with high heat losses to its own pellet heating; re-equipped the entire technological process to use and recycle production waste; reduced the installed capacity of equipment through the introduction of the latest technologies in production, re-equipment of production and reduction of energy intensity of equipment.

In addition, as a stakeholder, "Silproekt" has established long-term relations with the Admiral Makarov National University of Shipbuilding. This cooperation is mutually beneficial and has a significant impact on the innovative development of both parties. The university has a strong research base and experts in various fields who can help the company develop new technologies and products and provide advice on specialised technical issues, helping the company to optimise production or solve technical problems. A university can be a source of innovation through its students and researchers. Collaboration with university-based start-ups can give a business access to new solutions and technologies.

SE "Silproekt" works closely with the University to train specialists that meet their needs. For this purpose, internships and training at the company's production sites are provided, which allows students to gain real production experience. In its

turn, "Silproekt" actively participates in the discussion and development of educational programmes in the fields of Ecology and Environmental Protection Technologies.

Such synergy contributes to both the technological progress of the enterprise and the improvement of students' training and research at the university, which generally improves the competitiveness of both parties in the market.

Thus, even in times of war and being close to the front line, the machine-building enterprise is implementing energy-efficient measures and fruitfully cooperating with the university to further achieve its sustainable development goals.

4. Conclusions

Sustainable development of machine-building enterprises is a multifaceted process that includes both technological and social aspects. Implementation of energyefficient solutions, use of circular economy principles, application of environmentally friendly technologies, digitalisation and attention to personnel development all play a key role in creating a competitive and sustainable enterprise. In the face of global challenges and market changes, only those companies that actively apply these principles and integrate them into their daily operations will succeed.

Given the achievements already made by "Silproekt" in the context of energy efficiency and resource conservation, it would be advisable to implement an environmental management system that would help expand the capabilities of the machinebuilding enterprise and provide certain benefits:

- reduction of the enterprise's production costs, in particular, by reducing energy consumption, waste and recycling of materials;
- improvement of production processes leads to an increase in the overall efficiency of the enterprise and product quality;
- development of new technologies that are more energy efficient and less harmful to the environment, which also stimulates the search for new, environmentally friendly materials and production processes:
- compliance with environmental standards and regulations opens up a ccess to environmentally orientated markets and tenders, and reduces the risk of fines and sanctions:
- an environmentally conscious company creates a positive image in society, which can help increase customer loyalty and attract new partners. It also helps

improve relations with local communities and government agencies;

- more motivated employees who feel that they are working for the benefit of society and the environment. This helps to increase employee loyalty and productivity;
- the ability to anticipate and minimise environmental risks that may arise in the course of operations. This includes preventing accidents that could lead to environmental disasters and reducing the risk of reputational damage.

Thus, the implementation of environmental management at an engineering enterprise is a strategy that not only helps to protect the environment, but also contributes to the efficiency in crisis situations, competitiveness and long-term success of the enterprise to ensure sustainable development.

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LICHEN-INDICATIVE ASSESSMENT OF THE ECOLOGICAL STATE OF ATMOSPHERIC AIR IN URBANISED AREAS OF EASTERN UKRAINE

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Abstract. The article presents the results of a comprehensive study of the state of atmospheric air in urbanized areas of Poltava and Kharkiv regions using the lichen indication method. The dynamics of changes in the main pollutants in the period 2020–2023 is analyzed, and correlations between lichen indication data and instrumental measurements are established. The species composition and distribution features of indicator lichens in different functional zones of the studied territories are determined. The high efficiency of the lichen-indication method for assessing the quality of atmospheric air in an urban environment has been revealed. The peculiarities of the martial law impact on the ecological situation in the region and its reflection in the changes of lichen flora are established.

Keywords: lichen indication, urbanized areas, air pollution, environmental monitoring, indicator species.

1. Introduction

The problem of air pollution in urbanized areas is becoming particularly relevant in the context of modern environmental challenges. According to the World Health Organization, air pollution causes about 7 million premature deaths annually worldwide (Air Quality and Health Statistics, 2023). According to the latest research by the European Environment Agency (Air quality in Europe – 2023 report, 2023), air quality in urban areas continues to be a critical factor affecting public health, especially in the context of increasing industrial pressure and climate change.

In the eastern regions of Ukraine, in particular, in Poltava and Kharkiv regions, this problem is exacerbated by the combined impact of industrial emissions, transport, and the effects of military operations. According to the State Ecological Inspectorate of Ukraine (Zvit pro stan dovkillia v umovakh viiny, 2023), significant changes in the structure and intensity of air pollution are observed under martial law, which requires the development of new approaches to environmental monitoring.

Today, lichen indication is a promising and most developed environmental monitoring method. This method allows to determine the degree of air pollution and assess the impact of industrial emissions and other pollution on the environment reliably and at low cost. The expediency of using lichens for biomonitoring purposes is based on the fact that they are one of the most sensitive groups of living organisms to environmental stress. The peculiarities of these organisms' structure and nutrition make it possible to use them widely as environmental indicators.

Epiphytic forms are used to indicate the state of the air, as they are the most sensitive to the chemical composition of the air. The response of lichens and higher plants to chemical pollution is somewhat different, as damage to the lichen thallus remains until it dies, while plant tissues are capable of regeneration. That is why the special value of the lichen indication method lies in the possibility of an integrated assessment of pollution over a long period, which is extremely important in conditions of limited access to the territories and the complexity of regular instrumental measurements (Ristić et al., 2021).

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Modern studies (Ristić et al., 2021; Takano et al., 2024) demonstrate the high efficiency of lichens as bioindicators of air pollution. For example, lichens are adversely affected by substances that increase the environment's acidity, such as sulphur dioxide and nitrogen oxides. In particular, Ristić S. et al. note the sensitivity of lichens to sulphur and nitrogen compounds, making them indispensable indicators of industrial pollution. They are most susceptible to sulphur dioxide (SO₂), one of the most common pollutants, a product of the combustion of any sulphur-containing fuel. Research by British scientists (Niepsch et al., 2024) demonstrates the effectiveness of using an integrated approach to lichen identification, which includes analysis of not only species diversity but also biochemical indicators of lichens. Applying this methodology in eastern Ukraine could provide a more detailed picture of pollution.

A. P. C. Takano et al. (Takano et al., 2024) emphasizes the cost-effectiveness of bioindication methods compared to traditional instrumental measurements.

According to S. Y. Kondratiuk (Kondratiuk, 2008), in Ukraine, the most informative methodology is the well-known lichen indication methodology, which has as its first stage the mapping of lichens, which means determining their species composition, assessing the projective coverage and establishing the frequency of species occurrence. Based on the assessment of population vitality, the determination of the field tolerance index and the analysis of morphological changes in the melt, the air purity index (IAP) is calculated. Correlation, factor, and regression analyses are used for statistical data processing.

Biocenotic monitoring takes into account various indicators of species diversity. Bioindication methods are divided into two types: recording bioindication and accumulative bioindication. Recording bioindication allows us to conclude the impact of environmental factors based on the condition of individuals of a species or population. In contrast, accumulative bioindication uses the property of lichens to accumulate certain chemicals. According to these methods. recording accumulating indicators are distinguished. Registering indicators respond to changes in the environment by changing their numbers, tissue damage, somatic manifestations (including disfigurement), changes in growth rate, and other clearly visible signs. Accumulative indicators concentrate pollutants in their tissues, which are further used to determine the degree of environmental pollution by means of chemical analysis (Kondratiuk, 2008).

The analysis of modern research (Windisch, 2017; Heiner et al., 2023; Niepsch et al., 2024) shows that the effectiveness of lichen indication is significantly increased with the integrated use of various methods and taking into account the regional characteristics of the studied areas.

2. Materials and Methods

The paper uses a comprehensive scientific analysis of literary sources, research and observation, statistical processing, and synthesis of the obtained research and scientific and theoretical data.

The research was conducted in large cities (Kharkiv and Poltava) in 2020–2023. According to regional environmental reports (Ekolohichnyi pasport Kharkivskoi oblasti, 2023; Ekolohichnyi pasport Poltavskoi oblasti, 2023), the study areas are characterized by a diversity of industrial load and transport infrastructure. The study area was divided into functional zones in accordance with the recommendations of the European Environment Agency (Air quality in Europe – 2023 report, 2023):

- 1) the central part of cities;
- 2) industrial areas;
- 3) sleeping areas;
- 4) park areas and green spaces.

In Kharkiv, 10 monitoring sites were surveyed (expanded from the original 8). In Poltava, the monitoring network covered 8 key sites covering areas with varying degrees of urbanization.

The methodological basis of the study was expanded to take into account modern European protocols and adapted to the specifics of the studied territories. Field studies were carried out according to the modified Braun-Blanquet methodology (Braun-Blanquet, 1964) using European standards for air quality assessment (Directive 2008/50/EC of the European Parliament and of the Council, 2008). Taking into account that lichens can inhabit different species of trees in different ways, we chose the most common trees in both cities: sharp-leaved maple (Acer platanoides L.), heart-leaved linden (Tilia cordata Mill.) and common ash (Fraxinus excelsior L.). According to the methodology, 10 trees were selected in each of the experimental plots, the number of lichens of each type was counted, and the degree of coverage of the pallet area by lichen in the most overgrown part of the tree was measured. Lichens were described at the base of the forophyte (up to 0.5 m) and in the middle part of the trunk (up to 2.0 m from the soil surface). Observations were made twice a year, in April and September, during 2020-2023.

For each type of lichen (crustose, leafy, and fruticose), the average frequency of occurrence and degree of coverage were calculated, and then a conditional score of relative air purity was determined. This indicator was used to conclude the degree of air pollution according to the scale shown in Table 1.

Table 1 Scale for assessing air pollution based on the results of lichen indication

Frequency of occurrence and degree	Conditional score for the	Pollution assessment
of coverage	relative air purity	Tonution assessment
0.0–0.20	1	strong ("lichen desert")
0.21–0.40	2	quite strong
0.41-0.60	3	middle
0.61-0.80	4	insignificant
0.81–1.0	5	no pollution is present

Pearson's correlation coefficient was calculated using Google Sheets, Version 2024, Google LLC (Google Sheets [Online Software], 2024).

3. Results and Discussion

In the study area, 35 species of lichens were found in Kharkiv and 49 species in Poltava, which corresponds to the European indicators for urban areas (Air quality in Europe – 2023 report, 2023). It is known that lichens are more demanding on air purity in the order "crustose → foliose→ fruticose". In other words, the hardiest and most tolerant lichens are the crustose lichens. The foliose lichens show medium sensitivity to air pollution, and the fruticose lichens disappear at the first symptoms of pollution (Sujetovienė, 2017). Among the identified genera, Lecanora, Khanthoria, Physcia, and Phaeophyscia were the most resistant to air pollution. The foliose lichens of the genera Parmelia and Hypogymnia are mediumsensitive indicators. The most sensitive indicators are fruticose lichens of the genera Ramalina, Evernia, and Usnea.

The dynamics of changes in lichen indication indicators, namely the average frequency of lichen occurrence and the degree of coverage of sites Q and the conditional score of relative atmospheric purity P during the observation period, are shown in Tables 2, 3.

Table 2 Dynamics of changes in lichen indication indicators in Kharkiv during the observation period

	Year of observation									
Area of the city	20	20	2021		2021		2022		2023	
	Q	P	Q	P	Q	P	Q	P		
central part	0.43	3	0.44	3	0.38	2	0.32	2		
industrial areas	0.39	2	0.37	2	0.30	2	0.28	2		
sleeping areas	0.48	3	0.46	3	0.39	2	0.36	2		
park areas and green spaces	0.64	4	0.63	4	0.59	3	0.56	3		

As can be seen from the results of the lichen biomonitoring of the air, the industrial areas of both cities were characterized by quite severe pollution, the central and residential areas by medium pollution, and the green areas by minor pollution. At the same time, the environmental situation in Kharkiv deteriorated significantly during the war (2022–2023), which can be explained by the proximity to the war zone and frequent shelling of all districts of the city without exception.

 $Table\ 3$ Dynamics of changes in lichen indication indicators in Poltava during the observation period

	Year of observation								
Area of the city	2020		20	2021		2022		23	
	Q	P	Q	P	Q	P	Q	P	
central part	0.39	2	0.44	3	0.43	3	0.37	2	
industrial areas	0.35	2	0.37	2	0.34	2	0.33	2	
sleeping areas	0.42	3	0.46	3	0.42	3	0.41	3	
park areas and green	0.62	4	0.63	4	0.61	4	0.56	4	
spaces									

The data obtained were compared with the air quality indicators provided in the regional reports of the Department of Environmental Protection and Nature Management of the Kharkiv Regional State Administration (since 2022 – Kharkiv Regional Military (State) Administration) (Dopovid pro stan navkolyshnoho pryrodnoho seredovyshcha v K harkivskii oblasti, 2020, 2021, 2022, 2023) and Department of Ecology and Natu-

ral Resources of the Poltava Regional State Administration (since 2022 – Poltava Regional Military (State) Administration) (Rehionalna dopovid pro stan navkolyshnoho pryrodnoho seredovyshcha v Poltavskii oblasti, 2020, 2021, 2022, 2023). According to the provided reports, there is a negative trend in the most significant indicators of air pollution in populated cities, namely sulfur dioxide, nitrogen dioxide, and dust (Tables 4, 5).

 $Table\ 4$ Dynamics of changes in key indicators of air pollution in Kharkiv over the monitoring period

Pollutant	Annu	MAC ma/m³			
Pollutant	2020	2021	2022	2023	MAC, mg/m ³
Sulfur Dioxide	0.007	0.007	0.011	0.014	0.05
Nitrogen Dioxide	0.03	0.03	0.03	0.028	0.04
Dust	0.09	0.07	0.43	0.43	0.15
Carbon monoxide	1.31	1.4	1.3	1.18	3.0

 $Table\ 5$ Dynamics of changes in key indicators of air pollution in Poltava over the monitoring period

Pollutant	Annu	MAC, mg/m ³			
1 Officialit	2020	2021	2022	2023	WAC, mg/m
Sulfur Dioxide	0.027	0.003	0.003	0.003	0.05
Nitrogen Dioxide	0.0275	0.037	0.038	0.04	0.04
Dust	0.109	0.141	1.166	1.156	0.15
Carbon monoxide	0.193	1.95	1.975	1.95	3.0

This trend can be explained by the direct correlation between the intensity of military actions and the deterioration of air quality. According to satellite monitoring data (Status report of air quality in Europe for year 2023,

2024), in zones of active combat operations, there is an increase in particulate matter concentration by 200–300 %, increase in SO_2 content by 150–400 %, and increase in NO_x concentration by 180–250 %.

Table 6

In particular, the current state of atmospheric air pollution in the Kharkiv region is affected by emissions of pollutants from mobile and stationary sources of pollution, as well as daily emissions of pollutants due to explosions and fires resulting from active combat operations in the region. Simultaneously, the forced use of alternative energy sources (solid fuel, diesel

generators, etc.) during planned and emergency power outages also deteriorates the quality of atmospheric air (Zvit pro stan dovkillia v umovakh viiny, 2023).

Comparing the results of lichen indication mapping and air pollution observation data in cities, the territories were zoned according to pollution levels (Tables 6, 7).

Species composition of lichens in the studied areas of Kharkiv

Number of Area of the city Dominant species Air Purity Index (IAP) species central part 5–7 Phaeophyscia orbicularis, Xanthoria parietina 0-20 3–5 industrial areas Lecanora conizaeoides 0 - 158-12 Parmelia sulcata, Hypogymnia physodes 20-35 sleeping areas park areas and 15 - 20Evernia prunastri, Ramalina farinacea 35-50 green spaces

Table 7
Species composition of lichens in the studied areas of Poltava

Area of the city	Number of species	Dominant species	Air Purity Index (IAP)
central part	7–9	Xanthoria parietina, Physcia adscendens	15–25
industrial areas	4–6	Lecanora conizaeoides, Scoliciosporum chlorococcum	10–20
sleeping areas	10–14	Parmelia sulcata, Hypogymnia physodes	25–40
park areas and	18–22	Evernia prunastri, Ramalina farinacea, Usnea hirta	40–55
green spaces			

The study revealed variations in lichen species composition. Overall, the epiphytic complex of cities consists of species resistant to moisture deficiency and air pollution. In industrial zones with the most polluted air, toxicotolerant crustose lichens of the species Lecanora conizaeoides predominate. Medium-sensitive to atmospheric pollution, foliose lichens (Parmelia sulcata, Hypogymnia physodes) dominate in residential areas of both cities.

The lichen complexes in the central districts of both cities are primarily composed of crustose species such as Xanthoria parietina, with Phaeophyscia orbicularis also common in Kharkiv and Physcia adscendens in Poltava. The distribution of these epiphytic lichen species of the genus Physcia indicates the prevalence of species classified as synanthropic, whose distribution is associated with significant dust pollution and reduced competition from other species, which is a characteristic feature of urbanized territories. In the cleanest zones of both cities, fruticose lichens of the genera Evernia and Ramalina are found, and in Poltava's park zones, Usnea as well, which are highly

sensitive indicators of acid air pollution and completely disappear in areas with elevated content of pollutants such as sulfur and nitrogen oxides. It should be noted that both in terms of species diversity and coverage degree in the studied areas of Poltava, a better situation is observed, which is confirmed by relatively higher values of the air purity index.

Furthermore, comparative analysis of lichen species composition revealed a 50–70 % decrease in fruticose lichen species in military impact zones and a corresponding 30–50 % increase in "lichen desert" areas, as well as the dominance of pollution-resistant species (predominantly crustose forms).

Comparing the results of lichen species composition analysis, the frequency of occurrence of individual species, and the degree of area coverage with air pollution indicators, a high degree of correlation was established between lichen indication data and instrumental measurement results. According to our data, lichens of the genera Xanthoria and Physcia are appropriate to use as indicator species for sulphur dioxide air pollution (correlation coefficients 0.87 and 0.85, respectively).

4. Conclusions

- 1. It was found that lichen identification is an effective method for evaluating air quality in urban areas, as shown by a strong correlation ($r_{xy} = 0.85$ – between lichen monitoring instrumental pollution measurements. The most quality informative indicator species for air monitoring in urban environments have identified, specifically Xanthoria parietina and Physcia adscendens.
- 2. A significant deterioration in atmospheric air quality has been established in the studied regions during 2020–2023, correlating with the intensity of military actions. A critical reduction in lichen biodiversity (by 40–90 %) has been recorded in areas with increased military impact. The formation of new "lichen deserts" has been identified in areas of industrial facility destruction and intensive military equipment use
- 3. Based on the conducted research results and the experience of domestic and foreign developments, a series of recommendations have been developed regarding the expansion and effective application of lichen monitoring across various levels of environmental supervision. For local government authorities, it is proposed to implement a system of continuous atmospheric air quality monitoring using lichen indication methods, develop and implement urban greening programs considering lichen indication zoning results, and create interactive air pollution maps based on lichen indication data. For industrial enterprises, we consider it necessary to implement a biomonitoring system as a component of environmental management and develop emission reduction programs considering lichen indication data.
- 4. For environmental scientific institutions, we consider the expansion of monitoring site networks, implementation of modern lichen indication data analysis methods, and development of regional sensitivity scales for indicator species as promising directions. Considering the ongoing reformation of the state environmental monitoring system under martial law conditions, which provides for systematic observations at all levels - from national to facilityspecific, we also propose the implementation of biomonitoring as part of systematic monitoring of territories affected by combat operations, continuation of research on developing methods for assessing the impact of military actions on atmospheric air quality, and creation of a database for post-war environmental monitoring restoration

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DETERMINATION OF THE REMOVAL EFFICIENCY OF CHLORAMPHENICOL FROM WASTEWATER DEPENDING ON LEMNA MINOR BIOMASS

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Abstract. The article is dedicated to studying the effectiveness of wastewater treatment contaminated with chloramphenicol using Lemna minor with a specific biomass of 36 and 50 g/L. Purification of model solutions with an antibiotic concentration of 2-20 mg/L continued for 1-72 hours. The conducted research showed that the degree of chloramphenicol removal depends on the specific biomass of plants and the time of the process. The greatest decrease in the content of the antibiotic was observed during 24-48 hours of the purification process, then the efficiency of its removal decreased and after 72 hours it practically did not change. For concentrations of 2 and 5 mg/L with a specific biomass of L. minor of 36 g/L, the purification efficiency in 72 hours reached 23.2 % and 26.8 %, respectively. When the biomass increased to 50 g/L, the efficiency was 17 % and 19 %, respectively. The removal efficiency of chloramphenicol at a concentration of 10 mg/L reached 33 % when the specific biomass of L. minor was 36 g/L, and at a concentration of 20 mg/L - 29.5 %. For a specific biomass of 50 g/L, this indicator was 23.6 % with an antibiotic content of 10 mg/L and 21% with a content of 20 mg/L. According to the obtained results, the rational parameters of the cleaning process were established: time 48 hours and specific biomass 36 g/L allowed to achieve 29.4 % efficiency of chloramphenicol removal from wastewater at its initial concentration of 10 mg/L. Further increase in treatment time has a negligible effect on the increase in purification efficiency. An increase in duckweed biomass leads to a decrease in the efficiency of antibiotic adsorption. To process duckweed after its use in wastewater treatment to remove antibiotics fermentation technology in a methane tank can be employed along with other station waste.

Keywords: wastewater, treatment, biological method, duckweed, antibiotics.

1. Introduction

Environmental pollution by pharmaceuticals, particularly antibiotics, has become a significant ecological and societal problem with growing scale and impact. Antibiotic resistance driven by the accumulation of pharmaceutical substances in natural water bodies has already been recognized as a global threat requiring urgent action. Chloramphenicol, a broadspectrum antibiotic found in wastewater due to medical and veterinary use, can enhance pathogen resistance adversely affect aquatic flora and fauna and penetrate food chains (Ahammad et al., 2021; Ahmed et al., 2017; Ahmed et al., 2017).

The insufficient efficacy of traditional waste-water treatment methods for removing pharmaceutical residues like chloramphenicol necessitates innovative approaches. One such method is biological purification using aquatic plants such as *Lemna minor* (duckweed) which demonstrates high pollutant removal efficiency due to its rapid biomass growth and ability to absorb toxic substances (Ambekar et al., 2000; Balarak et al., 2020).

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Chloramphenicol is an antibiotic capable of inhibiting bacterial infections in animals and humans. However, due to its toxicity and severe side effects its use is strictly controlled or prohibited in veterinary medicine in many countries. Despite such restrictions, chloramphenicol concentrations are still detected in wastewater within a range of 0.1 to 2 µg/L attributed to discharges from medical and veterinary facilities (Ahammad et al., 2021; Busch et al., 2020; Carrales-Alvarado D. H. et al., 2020; Chaturvedi et al., 2021; Chen et al., 2021). Once in water bodies the antibiotic can contribute to pathogen resistance and pose a threat to human health creating a global problem (Busch et al., 2020; Chen et al., 2020).

Modern wastewater treatment technologies often struggle to remove contaminants like chloramphenicol driving the search for environmentally friendly and cost-effective alternatives. Biological purification using aquatic plants is a promising method as plants can absorb, transform and accumulate toxins (Carrales-Alvarado D. H. et al., 2020; Cheng et al., 2020; Choi et al., 2008; Bhargava et al., 2023). The use of *Lemna minor* for chloramphenicol removal from wastewater relies on its ability to reduce pollutant concentrations through photosynthesis, rapid growth and metabolism (Chaturvedi et al., 2021; Chen et al., 2021; Lai et al., 2009).

Research indicates that the effectiveness of pollutant removal is directly related to the biomass of duckweed in treatment systems. Increasing the biomass of *Lemna minor* enhances its pollutant absorption capacity as a greater contact surface with water results in improved uptake capabilities (Chen et al., 2021; Lai et al., 2009; Leston et al., 2013). Additionally, duckweed produces enzymes that contribute to the breakdown of pollutant molecules. Understanding the relationship between biomass and pollutant removal efficiency is crucial for designing biological purification systems capable of handling high contaminant loads (Chen et al., 2020; Li A. et al., 2020; Li P. et al., 2020).

Aquatic plants and activated sludge are used to remove heavy metals such as chromium, lead and also pharmaceuticals. For example, *Pistia stratiotes* (water lettuce) is successfully applied to reduce heavy metal concentrations in polluted waters; the removal efficiency of 1 mg/L and 3 mg/L of lead and 1 mg/L of chromium is 99.13 %, 79.86 % and 76.25 %, respectively (Zahari et al., 2021). *Eichhornia crassipes* (water hyacinth) helps in the purification of water from phenols and cyanide showing absorption

efficiencies of 96.42 % for phenol (300 mg/L) and 92.66 % for cyanide (30 mg/L) (Singh and Balomajumder, 2021). Activated sludge is capable of metabolizing organic compounds, pharmaceuticals and heavy metals due to the activity of microorganisms (Libing & Jianlong, 2023).

The relevance of research on the biological treatment of chloramphenical with the help of *Lemna minor* is growing in the context of the global problem of antibiotic resistance and water pollution. The relationship between plant biomass and antibiotic removal efficiency forms the basis for developing new wastewater treatment technologies.

The aim of this work is to determine the efficiency of wastewater purification from the antibiotic chloramphenical using *Lemna minor*, depending on the initial antibiotic concentration, the time of the process and the specific biomass of duckweed.

2. Materials and Methods

The purification process was studied in laboratory conditions on model solutions that simulated wastewater containing chloramphenicol at concentrations of 2, 5, 10 and 20 mg/L. The process was investigated in a static mode in bioreactors with *Lemna minor* biomass at specific concentrations of 36 and 50 g/L with sampling of the purified solutions after 1, 2, 4, 6, 21, 24, 48 and 72 hours.

To determine the chloramphenicol content in the purified solutions liquid chromatography and a calibration curve were used. To confirm the hypothesis that the reduction in antibiotic content occurs specifically due to the action of duckweed control studies were conducted on model solutions without *Lemna minor*.

Chromatographic analysis of the samples was performed using a liquid chromatograph Agilent 1260 Infinity II and results were processed with Agilent OpenLab software.

For the quantitative determination of the content of chloramphenical the areas of the peaks on the graph were used, the value of which is proportional to the antibiotic concentration in the sample.

To calculate the removal efficiency of chloramphenicol (E, %) from the pharmaceutical wastewater, the following formula was used:

$$E = \frac{C_0 - C_t}{C_0} \cdot 100,$$

where C_0 is the initial concentration of chloramphenicol, mg/L; C_t is the concentration of chloram-

phenicol in the treated model solutions for t hours, mg/L; 100 is for converting the result into percentage.

3. Results and Discussion

In the control bioreactors (without *L. minor*) all values of chloramphenicol concentrations (2–20 mg/L) remained almost unchanged for 72 hours. This suggests that without the addition of duckweed no reduction in antibiotic concentration occurs (Figs. 1, 2).

The change in the content of chloramphenicol in model solutions depending on the time of purification in bioreactors with *L. minor* biomass of 36 g/L is shown in Fig. 1.

Increasing the purification time in bioreactors with *L. minor* biomass at 36 g/L leads to a reduction in the content of chloramphenicol in solutions for all initial concentrations of the antibiotic. For instance, at

an initial concentration of 20 m g/L the antibiotic content decreases to 14.34 mg/L after 72 hours of purification. Extending the time over 48 hours almost does not change the content of the antibiotic in the purified solutions.

It was established that the dependences of the content of chloramphenicol in solutions purified for 72 hours using *Lemna minor* with a biomass of 36 and 50 g/L at initial values of 2–20 mg/L are almost the same.

A decrease in the content of chloramphenicol was observed in solutions using *L. minor* with a biomass of 50 g/L for all studied concentrations. At an initial concentration of 20 m g/L after 72 hours of purification the content of the antibiotic decreases to 15.97 mg/L After 48 hours of the cleaning process the content of the antibiotic in the solutions becomes practically unchanged.

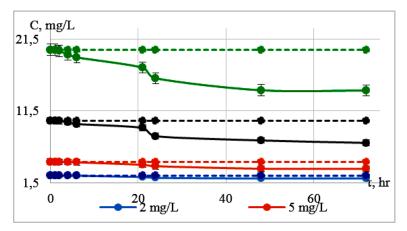


Fig. 1. Dependence of the chloramphenical content on the time of purification of model solutions using L. *minor* with a biomass of 36 g/L and in control solutions

The change in the content of chloramphenicol in model solutions depending on the time of puri-

fication in bioreactors with *L. minor* biomass of 50 g/L is shown in Fig. 2.

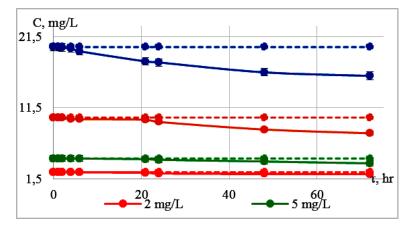


Fig. 2. Dependence of the chloramphenical content on the time of purification of model solutions using L. *minor* with a biomass of 50 g/L and in control solutions

From Fig. 1 and 2 it is evident that the dependencies of chloramphenicol content on the time of model solution purification using *Lemna minor* biomass at concentrations of 36 and 50 g/L are similar.

At lower antibiotic concentrations of 2 and 5 mg/L the cleaning efficiency at a specific biomass of *L. minor* of 36 g/L reached a maximum of 23.2 and 26.8 %, respectively, after 72 hour s. For higher antibiotic concentrations of 10 and 20 mg/L a gradual increase in efficiency was also observed which after 72 hours reached a maximum of 33 % at 10 mg/L chloramphenicol and 29.5 % – at 20 mg/L.

Clearly, reducing the antibiotic content leads to the oxidation of the chloramphenicol molecule through enzymes like cytochrome P450 or other oxidoreductases. These enzymes can alter the structure of chloramphenicol, facilitating its degradation (Bhandari et al., 2021).

At antibiotic concentrations of 2 and 5 mg/L the purification efficiency with a *L. minor* biomass of 50 g/L reached 17 % and 19 % after 72 hours, respectively. For antibiotic concentrations of 10 and 20 mg/L the removal rates were 23.6 % for 10 mg/L and 21 % – for 20 mg/L.

It was found that the antibiotic removal efficiency depends on the time of purification, the initial antibiotic concentration, and the biomass of *L. minor*. The greatest reduction in antibiotic content was observed within the first 24–48 hours after which the process slows and the content remains almost unchanged during the final 72 hours of purification. Thus, using *L. minor* at a specific biomass of 36 g/L contributes to a more effective purification process. Increasing the duckweed biomass to 50 g/L appears to reduce antibiotic adsorption due to the limited contact area between the roots of the upper layers of duckweed and the solution surface. Additionally, the increased duckweed density suppresses photosynthetic activity in the lower layers.

During the purification of model solutions, the leaves of *Lemna minor* turned yellow. This suggests that photosynthesis was disrupted and chloroplasts were damaged due to the antibiotic's effects.

Based on the observed results, an optimal *Lemna minor* biomass of 36 g/L and a purification time of 48 hours were determined.

4. Conclusions

The obtained results showed a decrease in the content of chloramphenical over time from the start of the process at a specific mass of *Lemna minor* of 36 and 50 g/L.

It was established that the efficiency of antibiotic removal depends on the time of purification of the solutions the initial content of the antibiotic and the biomass of L. minor. The greatest decrease in the content of the antibiotic was observed within 24-48 hours after which the process slows down and the content becomes practically unchanged during the 72 hours of cleaning. At lower concentrations (2 and 5 mg/L) the cleaning efficiency using Lemna minor with a specific biomass of 36 g/L gradually increases during the first 24 hours and reaches a maximum of 23.2 and 26.8 %, respectively, after 72 hours for a specific biomass of 50~g/L - in 17~a nd 19~%. At higher concentrations (10 and 20 m g/L) a gradual increase in efficiency was also observed reaching a maximum of 33.0 % at 10 mg/L chloramphenicol and 29.5 % - at 20 mg/L after 72 hours using Lemna minor specific biomass of 36 g/ L. For a specific biomass of 50 g/L these values are 23.6 and 21 %.

It has been proven that in control studies the content of chloramphenicol remains unchanged during the time of cleaning (72 hours) which indicates that there is no decrease in the content of the antibiotic without *L. minor*.

As a result, rational purification parameters were established that can be used for the design of engineering facilities: a time of 48 hours and a specific biomass of *Lemna minor* 36 g/L which make it possible to achieve the removal efficiency of chloramphenicol from wastewater of 29.4 % at its initial concentration of 10 mg/L.

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RESEARCH ON ATMOSPHERIC AIR QUALITY IN THE PRYKARPATTIA REGION

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Abstract. The goal of this study was to assess and analyze the air quality on the territory of the Ivano-Frankivsk National Technical University of Oil and Gas, evaluate pollution levels, and identify the main sources of harmful emissions. The study was conducted on the territory of the university, where measurements of the main atmospheric air parameters were carried out using the multifunctional device FLUS 5-in-1, the gas detector Walcom W-K-600, and the CEM GD-3803 instrument. Parameters such as wind speed, air temperature and humidity, light intensity, and concentrations of formaldehyde, nitrogen oxide, carbon dioxide, carbon monoxide, and oxygen were measured. A systematic approach was applied with an even distribution of measurement points across the university territory, including areas with high traffic, academic buildings, and green zones. As a result of the study, no excess gases concentrations were recorded. The practical value of the study lies in the development of recommendations to improve air quality, including optimizing traffic flows, increasing green zones, and implementing modern air purification technologies. Further research should focus on a detailed analysis of the impact of different pollution sources and the development of innovative technologies to reduce harmful emissions. The results of this study confirm the relevance of the issue and the need for systematic monitoring of atmospheric air quality, as well as the implementation of effective measures to reduce pollution, which is crucial for improving living conditions and public health.

Keywords: air pollution, harmful emissions, environmental situation, anthropogenic pollution, environmental quality monitoring.

1. Introduction

The issue of air quality is extremely relevant in today's world, especially in the context of rapid urban development and industrialization (Giannico et al., 2021). Air pollution affects human health, ecosystems, and the climate, as confirmed by numerous studies (Azimi & Rahman, 2024).

The study of air quality on the territory of the Ivano-Frankivsk National Technical University of Oil and Gas is necessary to ensure a healthy environment and to take measures to reduce the negative impact on the environment.

The goal of this study is to assess and analyze the air quality on the territory of IFNTUOG, evaluate the level of pollution, and identify the main sources of harmful emissions. The task of this work is to conduct systematic measurements of air quality indicators, analyze the obtained data in the context of modern environmental standards, and develop recommendations for reducing the negative impact of pollution.

The scientific novelty of the work lies in a comprehensive approach to studying air quality on the university's territory, which will allow for more accurate identification of specific pollution sources and the development of effective measures for its improvement. This study is significant both for theoretical understanding of the issue and for the practical implementation of the obtained results into real environmental programs (Pershehuba & Lytvychenko, 2009).

2. Materials and Methods

The study was conducted on the territory of the Ivano-Frankivsk National Technical University of Oil and Gas, Ivano-Frankivsk, Ukraine. The sampling strategy involved the even distribution of mea-

surement points across the university's territory to obtain representative data. The criteria for selecting the locations were based on the various functional zones of the university, including areas with high traffic, academic buildings, green zones, and zones with increased human activity. This approach provided a comprehensive picture of the air quality under different conditions across the university's grounds.

Key atmospheric air parameters, such as wind speed, air temperature, relative humidity, and light intensity, were measured using the multifunctional FLUS 5-in-1 device. To assess air quality, the Walcom W-K-600 gas detector was used to measure formaldehyde and nitrogen oxide concentrations. Additionally, carbon dioxide, carbon monoxide, and oxygen levels were measured at five locations on the university grounds using the CEM GD-3803 device.

The research procedure consisted of several stages. Initially, all devices were calibrated according to the manufacturer's instructions. Then, simultaneous measurements were taken at each selected location using the respective instruments to obtain a comprehensive assessment of the conditions and air quality.

3. Results

In our modern world, air pollution is a very common problem (World Health Organization, 2003). With the development of technologies, more pollutants are entering the atmosphere, harming not only the environment but also humans (Tryhub & Domuschy, 2023).

Carbon dioxide is naturally present in the air, but its concentration increases due to human activities such as burning fossil fuels, industrial processes, and vehicle emissions (Dzyba & Kyriienko, 2024). In the state building codes DBN V.2.5-67:2013 "Heating, Ventilation, Air Conditioning", the permissible concentrations of CO₂ in the air are specified, taking into account the amount of carbon dioxide in the air outside the buildings. 350-400 ppm is the level for outdoor air, representing conditions for being outdoors in fresh air (Shpak et al., 2022.

Carbon monoxide enters the atmosphere in the greatest quantity from vehicle exhaust gases, as well as from emissions from oil, petroleum refining industries, ferrous metallurgy, and thermal power plants. It is classified as an inert gas, does not

participate in chemical reactions with other impurities, and is hardly removed by precipitation (Buckland & Pojani, 2023). Its content is mainly regulated by the conditions of transport and dispersion (Van Dingenen et al., 2009). The permissible concentration of carbon monoxide (CO) in fresh air is less than 10 ppm. A concentration above 520 ppm for two hours causes headaches, dizziness, nausea, while a concentration at the level of 1000 ppm leads to loss of consciousness. At a CO concentration of 1500 ppm, a fatal outcome is possible (Bashtannik et al., 2014).

Formaldehyde in the air is formed due to both human activity and natural processes. The main sources of anthropogenic origin are emissions from industrial enterprises, motor vehicles, the burning of fossil fuels, and construction materials. Inhalation of formaldehyde vapors leads to allergies, coughing, irritation of the eyes, nose, throat, and skin, sleep disorders, headaches, and chronic fatigue (Chuhai et al., 2019). The maximum allowable concentration (MAC) of formaldehyde is 0.5 mg/m³ (Nesterenko et al., 2021).

Oxygen is a vital gas necessary for the respiration of most living organisms. Its concentration in the atmosphere is consistently maintained at around 20.9 %. For humans, an oxygen level in the air below 17 % can be dangerous (Kozlowski et al., 2023).

The main sources of nitrogen oxides (NO, NO₂) entering the atmosphere are emissions of high-temperature combustion products and incomplete fuel combustion (Azimi et al., 2024). Natural sources include microbiological processes occurring in the surface layer, photochemical oxidation of ammonia and nitrous oxide in the air, as well as thunderstorms (Kutia et al., 2023). The relative influence of anthropogenic and natural sources on the level of ground-level nitrogen oxide pollution (lower troposphere) varies significantly and depends on many factors (degree of urbanization, amount and quality of fuel, surface characteristics, and season) (Oleshko & Petrovska, 2020). The maximum allowable concentration of nitrogen dioxide is 400 µg/m³ (Dyvak, 2023).

Air quality was assessed on the territory of Ivano-Frankivsk National Technical University of Oil and Gas, with measurements taken at five sites (Fig. 1). The research results are presented in Table.

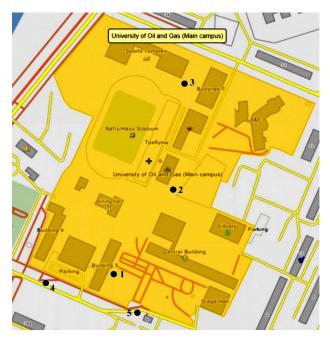


Fig. 1. Study sites on the territory of IFNTUOG

Source: created by the author.

Measurement results

Measurement indicator	No. study area				
	1	2	3	4	5
v, m/s	0.2	0.1	5.1	5.1	1.3
t, °C	15.1	16.7	18.4	18.4	21.1
RH, %	41.7	40	46.4	39	35
E, kLux	3.8	3.73	3.78	3.78	3.81
CO, ppm	0	0	0	0	0
CO ₂ , ppm	362	355	378	395	400
CH ₂ O, mg/m ³	0	0.3	0.4	0.5	0.5
O ₂ , %	20.5	20.5	20.4	20.3	20.3
NO ₂ , mg/m ³	0	0	0	0.4	0.4

Source: created by the author

The study results indicate that there were no recorded exceedances of gas concentration levels in the examined areas. This suggests that the overall air pollution levels within the study area meet established environmental standards and do not pose a threat to public health.

However, the study found elevated levels of pollutants in areas located near roads and construction sites. Although these concentrations remain within permissible limits and do not exceed established norms, they do reflect a local increase in pollution. This increase is likely related to vehicle emissions and ongoing construction activities.

A comparison with data from other studies (Belova et al., 2023) indicates similar trends in air pollution levels in other urban agglomerations. In particular, the study by Savenets (Savenets, 2023) also highlights the high concentration of pollutants in the air of large cities.

These results emphasize the importance of regular monitoring and the implementation of measures toreduce harmful emissions into the atmosphere, particularly in urban environments (Dmytriieva et al., 2016).

4. Discussion

Recent studies by scientists show a significant impact of anthropogenic factors on air quality in urban agglomerations.

Belova et al., (Belova et al., 2023) analyzed the impact of environmental factors on the health of the population in the Ivano-Frankivsk region, pointing to the serious effects of air pollution on human health. Kalenska (Kalenska, 2012) studied the economic consequences of environmental pollution on public health, emphasizing that pollution not only harms health but also negatively affects household incomes.

Rybalova et al. (Rybalova et al., 2015) presented integral and comprehensive assessments of the state of the natural environment, allowing for an overall picture of pollution and its impact on various components of the ecosystem.

Savenets (Savenets, 2023), in his study, focused on the current state of air pollution in Ukraine, highlighting the significant influence of vehicular emissions on overall pollution. Dotsenko and Demidenko (Dotsenko & Demidenko, 2014) compared various methods of determining air pollution levels, which helps in selecting the most effective techniques for monitoring and analysis.

Hryhorieva et al (Hryhorieva et al., 2023) considered environmental monitoring of air quality using indicative measurements, which is important for timely detection and assessment of pollution levels.

Ananieva (Ananieva, 2017) researched the hygienic assessment of air pollution from vehicle emissions, which is relevant in the context of the increasing number of cars in cities and the rise in harmful emissions. Turos et al. (Turos et al., 2014) proposed improved approaches to the quantitative assessment of air pollution from motor vehicles, which is important for developing effective pollution reduction measures. Serdiuk et al. (Serdiuk et al., 2021) emphasized the importance of assessing air pollution levels and its safety for the population, which is necessary for taking appropriate health protection measures.

These studies highlight the importance of monitoring and analyzing air quality to develop effective strategies for reducing the negative impact on the environment and public health.

5. Conclusions

The study of air quality on the territory of the Ivano-Frankivsk National Technical University of Oil and Gas found that, in some areas, concentrations of carbon dioxide, formaldehyde, and nitrogen dioxide were elevated but remained within permissible limits. The primary sources of these pollutants are vehicle traffic and construction activities, confirming the significant impact of human activities on air quality.

Elevated concentrations of carbon dioxide, formaldehyde, and nitrogen dioxide were detected in areas with heavy traffic and near construction sites. However, all these levels remain within permissible limits, indicating the presence of local pollution sources without exceeding maximum allowable values.

Future research directions include a more detailed analysis of the impact of various pollution sources on air quality, the development of advanced technologies for emission reduction, and the establishment of comprehensive environmental monitoring programs to enhance living conditions and public health.

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HEAT TRANSFER PROCESS DURING FILTRATION DRYING OF MATCH SPLINTS

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Abstract. The study proposes filtration drying for drying match splints. Experimental methods for investigating heat exchange between the heat agent and the material are presented. Theoretical aspects of heat transfer during filtration drying are analyzed. The effect of the heat agent's velocity on heat exchange efficiency is determined within the Reynolds number range of $200 \le Re \le 500$. The experimentally obtained data are generalized using a dimensionless complex. A dependency for determining the heat transfer coefficient is proposed. A co rrelation between theoretical and experimental values of the heat transfer coefficient is provided.

Keywords: filtration drying, match splints, external heat transfer, heat transfer coefficient, stationary layer.

1. Introduction

Matches are widely used in all countries around the world, both in daily life and in various economic activities. Their popularity is attributed to their ease of use, cost-effectiveness, compactness, versatility, and environmental friendliness.

In Ukraine, matches are manufactured at LLC "UKRAINIAN MATCH FACTORY". One of the key stages of production is drying match splints before impregnation with paraffin. Match splints are produced by cutting steamed wood into veneer and then shredding it into blanks measuring $2\times2\times40$ mm. The moisture content of match splints before drying is approximately 70 % by mass. Wet match splints are dried in tunnel dryers in a stationary layer with a height of 15 centimeters. This drying method requires significant energy consumption since the heat agent

moves only above the material, while moisture diffuses from the lower layers toward the heat agent. As a result, the heat agent is only partially saturated with moisture, and its temperature at the dryer outlet ranges from 50 to 70 °C. Therefore, the equipment is not energy-efficient, making energy-saving solutions a relevant issue.

After all, one of the key goals of sustainable development is rational energy use. Over the years, energy demand has been increasing, significantly impacting the climate. Moreover, energy costs continue to rise. Therefore, improving the energy efficiency of equipment is one of the key concerns for manufacturing industries (Lawrence et al., 2019). As stated by the authors (Cavallaro et al., 2013), energy efficiency can be improved by 10–30 % using existing technologies in production. An important step in implementing lean manufacturing is finding ways to enhance equipment or seeking alternative methods to minimize energy consumption (Salah et al., 2021).

For drying crushed wood, the following types of dryers are used: fluidized bed dryers (Holubets et al., 2003), infrared radiation dryers (Bandura et al., 2019), vacuum dryers, and microwave (MW) dryers (Obleshchenko et al., 2021), whose efficiency is also relatively low. One of the promising methods for wood drying is filtration drying, which is a low-temperature process characterized by high heat and mass transfer coefficients (Mosiuk et al., 2015). Therefore, filtration drying has been proposed as one of the highly efficient and low-temperature methods for drying match splints.

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Considering the above, it can be stated that improving the energy efficiency of match splint drying is a relevant task. This will help reduce the production cost of matches and enhance the competitiveness of their manufacturing.

The filtration drying method is based on the filtration of the heat agent through a porous stationary layer of wet material. As a result, the heat and mass transfer surface includes the surface of all particles in the stationary layer. During drying in a tunnel dryer, the heat agent interacts only with the upper layer of wet match splints, while heat is transferred to the lower layers of splints through thermal conductivity, and moisture evaporation occurs through molecular diffusion.

Therefore, the advantage of the filtration drying method is the large phase contact area and the maximum utilization of the drying potential of the heat agent. Throughout the drying process, the temperature of the heat agent at the material outlet remains close to the wet-bulb temperature and increases only at the final stage, approaching the inlet temperature. This indicates that the heat agent becomes saturated with moisture throughout the entire drying process. Moreover, filtration drying allows the use of a low-temperature heat agent, promoting the rational utilization of secondary heat, which is often used inefficiently in industrial settings (Gnativ et al., 2020; Ivashchuk et al., 2024).

To determine the optimal parameters of the filtration drying process for match splints, it is important to establish the heat transfer coefficients and their dependence on the velocity of the heat agent through the stationary layer of material. Since the intensity of heat transfer directly affects the drying duration and energy costs.

The moisture in match splints is primarily internal and is contained within the pores of the wood. Therefore, during drying, heat is spent on de taching moisture molecules from the cellulose fibers and on moving the moisture to the phase interface through molecular diffusion (Sokolovskyi, 2019).

A significant number of scientific studies are dedicated to heat transfer during drying. In particular, the authors (Pazyuk et al., 2018) analyzed the heat and mass transfer processes during the drying of capillary-porous bodies of spherical shape and proposed equations for determining heat transfer coefficients under various drying conditions. However, since match splints have a parallelepiped shape, the obtained dependencies cannot accurately describe the drying of match splints.

The authors (Kumar et al., 2022; Koukouch et al., 2020) have proposed using thin-layer drying models to describe heat and mass transfer during the convective drying of plant raw materials. According to the authors, these models provide a high level of drying prediction accuracy and demonstrate agreement with experimental data. However, applying the thin-layer model requires obtaining semi-empirical dependencies based on experimental data that consider the influence of the material's structure, shape, and physical properties. Additionally, in industrial drying processes, thin-layer drying is not considered efficient.

In the study by (Messai et al., 2014), heat transfer during the convective drying of spherical aluminum particles in a packed bed was investigated. The authors proposed calculating the heat transfer coefficient from gas to material using the logarithmic mean temperature difference method. The experiments were conducted at temperatures ranging from 120 to 158 °C and air velocities of 1.7 to 3 m/s. However, such drying conditions are unacceptable for match splints, as they would lead to the cracking of wood particles and, consequently, a deterioration in their quality.

In the study by (Mykychak et al. 2013), external heat and mass transfer during the filtration drying of peeled birch veneer was investigated. The obtained dependencies allow for the determination of heat transfer coefficients. However, the study examined a specially formed package of birch veneer with dimensions of $100 \times 100 \times 30$ mm, whereas match splints are dried in a randomly formed layer.

The study (Kindzera et al., 2021) presents the results of heat transfer research during the filtration drying process, with the findings generalized in the form of dimensionless dependencies. However, the obtained equations are of a specific nature and describe crushed sunflower biomass. Therefore, they cannot be applied to determine the heat transfer coefficients during the filtration drying of match splints. Since the shape, physical properties, sizes, and surface roughness differ significantly from the materials studied, this leads to substantial errors between experimental and theoretically calculated results.

Filtration drying of wet materials in a stationary layer has a zonal nature. The mass transfer zone during filtration drying moves in the direction of the heat agent, and in the stationary layer, both dry and wet material layers exist simultaneously. The height of the dry material layer increases during

drying, while the wet material layer decreases. As the heat agent filters through the dry material layer, it transfers part of its heat to the match splints. Therefore, it is important to determine how much heat remains in the dry material layer and how much is used for drying the wet material.

Thus, the purpose of this work is to determine the heat transfer coefficients from the heat agent to the dried match splints during the filtration drying process, to assess the impact of the heat agent's velocity on the efficiency of heat exchange, and to obtain semi-empirical dependencies to describe the process.

2. Experimental part

The experimental studies were conducted using a filtration drying setup, the operating principle of which is described in (Kuzminchuk et al., 2023). To determine the heat transfer coefficients of match splints, a cylindrical container (1) (Fig. 1) made of insulating material with a diameter of 190 mm was used. The studies were carried out in a "thin" layer of match splints (2), previously dried to a constant

weight. The material sample was placed on a perforated bottom (3). The heating agent was heated to the required temperature using a calorifier and filtered through a layer of match splints. The study was conducted at different flow velocities of the heating agent: 0.18, 0.21, 0.23, 0.26, and 0.29 m/s. The inlet air temperature was maintained at a constant level (t in = 60 °C) with an accuracy of ± 0.5 °C using an electronic temperature controller SESTOS DIS 10 (4). To measure and monitor the temperature of the heating agent, thermocouples were installed 20 mm above the match splint layer and 20 mm below the perforated partition. The temperature values were recorded on a personal computer using an eight-channel intelligent measuring transducer PT8-1000 (5) connected to the thermocouples. At the outlet, the temperature was measured at three points every 1.8 seconds: at the center of the flow and at distances of 35 mm and 60 mm from the wall. The average of the three values was used for calculations. The experimental study was conducted until the drying agent's temperature approached the inlet temperature of the cylinder.

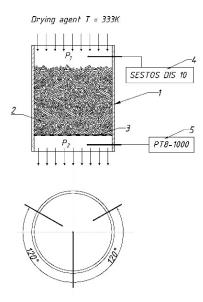


Fig. 1. Schematic representation of the container for investigating heat and mass transfer processes: 1 – cylindrical container; 2 – layer of match splints; 3 – perforated bottom; 4 – electronic temperature controller; 5 – measuring transducer

The experimentally obtained average temperature values allow for the determination of heat transfer coefficients (α) according to the following equation:

$$\alpha = \frac{\Delta Q}{F \cdot (\bar{t} - \overline{T_n}) \cdot \Delta \tau},\tag{1}$$

where ΔQ is the amount of heat transferred from the heating agent to the match splints, \bar{t} is the average temperature at the inlet and outlet of the container, $\overline{T_n}$ is the average temperature on the surface of the match splints, F is the surface area of the material particles, and $\Delta \tau$ is the time interval between measurements.

The amount of heat was determined using the material balance equation for the heating agent:

$$\Delta Q = G \cdot c_a \cdot (t - \overline{T_n}) \cdot \Delta \tau, \tag{2}$$

where G is the mass flow rate of the heating agent in the range of 0.005 to 0.01 kg/s, c_a is the heat capacity of the heating agent at a temperature of 60 °C, which is 1005 J/(kg·K), and t is the temperature of the heating agent at the inlet of the container.

The surface temperature of the particle is practically impossible to determine experimentally, so the temperature was taken based on analytical dependencies (Atamanyuk, Humnytskyi, 2013).

Based on the determined heat transfer coefficients (α) for different flow velocities of the heating agent through the material layer, a dependence $\alpha = f(v)$ was constructed. The obtained data were approximated by a linear function.

To generalize the results of the heat transfer study, a criterion equation was used (Atamanyuk, Humnytskyi, 2013):

$$Nu = A \cdot Re_e^n \cdot Pr^m, \tag{3}$$

where the Nusselt number was determined from the equation:

$$Nu = \frac{\alpha \cdot d_e}{\lambda},\tag{4}$$

where d_e is the equivalent diameter of the channels between match splints through which the heat agent

flows, which is 0.021 m, λ is the thermal conductivity coefficient of the heat agent, which is 0.03 W/(m·K).

The Reynolds number was determined using the dependency:

$$Re_{\rm e} = \frac{v \cdot d_e}{v},\tag{5}$$

where v is the actual velocity of the heat agent, and v is the kinematic viscosity coefficient, which is 1.89×10^{-5} m²/s for temperature 60 °C.

The Prandtl number was determined using the dependency:

$$Pr = \frac{v}{a},\tag{6}$$

where a is the thermal diffusivity coefficient, which is 2.81×10^{-5} m²/s for temperature 60 °C.

To determine the unknown coefficient A and the exponent n, dependency (3) is expressed in a logarithmic coordinate system:

$$\frac{Nu}{Pr^{0.33}} = f(Re_e). \tag{7}$$

Based on dependencies (3) the heat transfer coefficient α was determined:

$$\alpha_t = A \cdot \left(\frac{v \cdot d_e}{v}\right)^n \cdot \left(\frac{v}{a}\right)^m \cdot \frac{\lambda}{d_e}.$$
 (8)

3. Results and Discussion

The values of the heat agent temperature at the outlet of the match splint layer at different velocities are shown in Fig. 2.

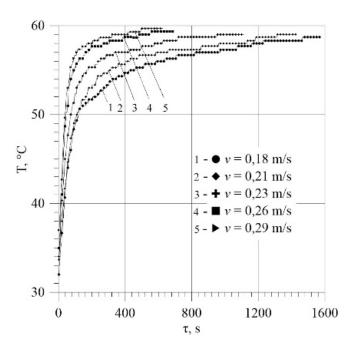


Fig. 2. Heat agent temperature at the outlet of the material at different superficial velocity

The analysis of the figure shows that as the velocity of the heat agent through the match splint layer increases, the temperature at the outlet of the cylinder rises more rapidly. At a heat agent velocity of 0.18 m/s, a temperature of 58.7 °C is reached in 1463 s, whereas at 0.29 m/s, it is achieved in just 243 s. Thus, with a 1.6-fold increase in the heat agent velocity, the temperature of 58.7 °C is established six times faster. A temperature of 59.7 °C is

reached in 495 s at a velocity of 0.29 m/s, whereas at 0.18 m/s, this temperature was not attained during the experimental studies.

The reduction in the time required to reach the outlet temperature of the container is due to the increased velocity, as a greater amount of heat is transferred to the material per unit of time, leading to an increase in heat transfer coefficients.

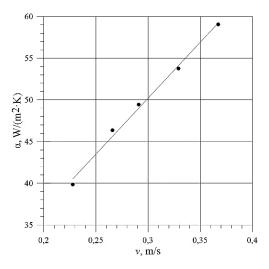


Fig. 3. Dependence of the heat transfer coefficient α on the actual velocity of the heat agent through the layer of match splints

Based on the determined heat transfer coefficients α for different velocities of the heat agent through the material layer, the dependency $\alpha = f(v)$. was constructed.

The obtained heat transfer coefficients represent average values for the entire layer, as the heat agent flows through the curved channels formed by the particles. Due to the uneven arrangement of the match splints, the cross-sectional area of the material layer changes with height. This causes multiple variations in the velocity of the heat agent near the surface of the particles. As a result, the local heat transfer coefficient also changes continuously.

Based on the obtained values, the Reynolds, Nusselt, and Prandtl numbers were determined, and the dependency $Nu/Pr^{0.33} = f(Re_e)$ was constructed in a logarithmic coordinate system (Fig. 4).

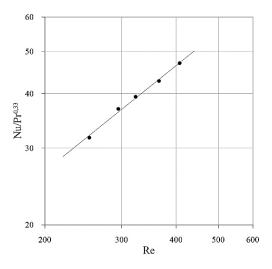


Fig. 4. Generalization of the experimental determination of heat transfer coefficients α

By approximating the obtained dependency with a power function, it was determined that the coefficient A is 0.385, and the exponent n = 0.8. Therefore, equation (3) takes the following form:

$$Nu = 0.385 \cdot Re_e^{0.8} \cdot Pr^{0.33}. \tag{9}$$

The equation for the theoretical determination of the heat transfer coefficient can be written as:

$$\alpha_t = 0.385 \cdot \left(\frac{v \cdot d_e}{v}\right)^{0.8} \cdot \left(\frac{v}{a}\right)^{0.33} \cdot \frac{\lambda}{d_e}.$$
 (10)

The obtained equation allows for the theoretical determination of the heat transfer coefficient during the filtration drying of match splints with sufficient accuracy within the Reynolds number range of $200 \le Re \le 500$. This is essential for further calculation of heat energy consumption.

Fig. 5 presents the correlation between theoretical and experimental values of the heat transfer coefficient.

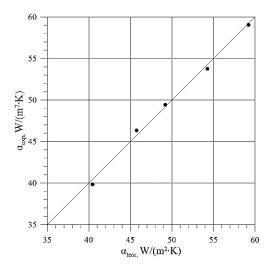


Fig. 5. Correlation dependence between theoretical and experimental values of the heat transfer coefficient

The maximum value of the relative error does not exceed 7 %, which is acceptable for design calculations.

4. Conclusions

For drying match splints, the filtration method has been proposed as a highly efficient and low-temperature. This method enables maximum utilization of the drying potential of the heat agent. The study investigates heat transfer during filtration drying. Based on experimental data, heat transfer coefficients were determined within the Reynolds number range of $200 \le Re \le 500$, ranging from 39 to $60 \text{ W/(m}^2 \cdot \text{K})$. The determined coefficients are expressed through a dimensionless equation: $Nu = 0.385 \times Re_e^{0.8} \times Pr^{0.33}$

For the theoretical determination of the heat transfer coefficient, the following dependence is proposed: $\alpha_t = 0.385 \times (v \times d_e/v)^{0.8} \times (v/a)^{0.33} \times \lambda/d_e$. The maximum value of the relative error between the experimentally and theoretically determined heat transfer coefficients does not exceed 7 %, which is acceptable for design calculations. The obtained dependencies

allow for the determination of heat transfer coefficients with sufficient accuracy, enabling the prediction of energy consumption during drying and the identification of optimal process parameters.

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HYDRODYNAMICS OF FILTRATION DRYING OF WILD CARROT POMACE

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Abstract. The paper presents the results of a study on the hydrodynamics of the stationary layer of wild carrot pomace during filtration drying, as a raw material for the production of ecological alternative solid fuel. The main geometric parameters of individual wild carrot pomace particles and the physicomechanical properties of the stationary layer were determined experimentally. A diagram of the experimental setup is provided. The results of the experimental studies are presented in the form of functional dependencies of pressure loss $\Delta P = f(v_0)$ and Euler's criterion as a function of Reynolds number and the geometric simplex Eu = f(Re, G). The feasibility of pretreatment of wild carrot pomace for alternative biofuel production is justified. The obtained results allow for predicting energy consumption when developing equipment for the filtration drying of this material.

Keywords: wild carrot pomace, stationary layer, hydrodynamics, filtration drying, sustainable development.

1. Introduction

Wild carrot (Daucus carota) contains a significant number of phenolic compounds, terpenes, and flavonoids (Ismail et al., 2024). This plant also has antipyretic, anti-inflammatory, anticancer, and antibacterial properties (Boadi et al., 2021). For this reason, wild carrot extract is widely used in the pharmaceutical industry (Stanojević et al., 2023).

However, as a result of extracting useful substances from wild carrot, a large amount of waste

is produced – wild carrot pomace. Currently, plant waste in the pharmaceutical industry is used inefficiently and, in many cases, is disposed of by being sent to landfills. As plant waste continues to accumulate, it occupies significant areas of landfill sites. Decomposition of this waste occurs in landfills, contaminating groundwater. Chemical leachate is released during the decomposition process, penetrating the soil and leading to toxic contamination. Therefore, there is a problem of ecological disposal of this waste.

One way to dispose of wild carrot pomace is to recycle it as secondary raw material. This will reduce the negative impact of harmful substances on the soil and decrease greenhouse gas emissions (Kumar Sarangi et al., 2023). Processing wild carrot pomace waste also has economic significance, as it contributes to the development of new technologies in the field of pharmaceutical waste disposal (Ivashchuk et al., 2024, a). In Ukraine, the system for managing plant waste is unsatisfactory, so processing and reusing wild carrot pomace contributes to the development of a sustainable system.

Wild carrot pomace, as an organic raw material of plant origin, can be used for the production of biofuel – an alternative, environmentally friendly source of energy (Srivastava et al., 2021). The process of recycling wild carrot pomace is complicated by its high moisture content (approximately 60 % by mass). This directly affects the storage time of this

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raw material for biofuel production. Therefore, one of the key stages in processing plant waste, particularly wild carrot pomace, is drying (Zhou et al., 2019). For the production of fuel briquettes, the moisture content of the plant material must be between 7 and 14 % by mass (Guibunda et al., 2024).

After analyzing the literature (Atamanyuk et al., 2018), it was determined that the most efficient method for drying solid dispersed materials is filtration drying. Filtration drying (Ivashchuk et al., 2024, b) is carried out by filtering the gas flow through a stationary layer of porous material under the influence of pressure difference. The key indicator of the efficiency of this method is the level of specific energy consumption required to maintain the pressure difference (Kobeyeva et al., 2022). The analysis of the hydrodynamics of filtration drying allows for predicting these energy costs and optimizing the drying process (Ivashchuk et al., 2022).

2. Experimental part

The object of the study was wild carrot pomace obtained from a local pharmaceutical production facility. The hydrodynamics of the stationary layer of wild carrot pomace were studied using an experimental setup described in (Atamanyuk et al., 2020). The methodologies used to determine the main physicomechanical characteristics of particles and investigate the hydrodynamics of gas flow filtration through the stationary layer of wild carrot pomace are provided in (Atamaniuk, Humnytskyi, 2013).

The hydrodynamic characteristics of the stationary layer directly affect the efficiency of filtration drying. The filtration speed of the gas flow through the layer of wild carrot pomace determines the intensity and economic feasibility of filtration drying for this material.

The hydrodynamics of the stationary layer of wild carrot pomace were studied at various material heights in the container, specifically: 30 mm, 60 mm, 90 mm, 120 mm, and 150 mm. The initial bulk density for all the studied heights was the same. Each experiment was conducted at least 7 times with new portions of wild carrot pomace.

The pressure losses in the stationary layer of wild carrot pomace were determined using the Darcy – Weisbach equation:

$$\Delta P = \lambda \cdot \frac{H_e}{d_e} \cdot \frac{\rho \cdot v^2}{2}, \qquad (1)$$

where λ is the resistance coefficient of the layer; H_e is the equivalent length of the channels through which the

gas flow moves, defined as $H_e = 1.5 \cdot H$, m; d_e is the equivalent diameter of the wild carrot pomace particles, m; ρ is the density of the gas flow, kg/m³; v is the actual velocity of the gas flow through the stationary layer of wild carrot pomace, m/s.

Considering that the hydraulic resistance coefficient λ depends on the Reynolds number, equation (1) is presented in the form of a two-term expression that takes into account both the losses due to friction and the losses associated with local resistances:

$$\Delta P = A \cdot \frac{\mu \cdot a^2}{32 \cdot \varepsilon^3} \cdot H_e \cdot v_0 + B \cdot \frac{\rho \cdot a}{8 \cdot \varepsilon^3} \cdot H_e \cdot v_0^2, \quad (2)$$

where A and B are unknown coefficients, the values of which were determined through experimental studies; μ is the dynamic viscosity of the gas flow, Pa·s; a is the effective specific surface area of all particles in the stationary layer of wild carrot pomace, m²/m³; ε is the porosity of the stationary layer of wild carrot pomace, m³/m³; v $_{o}$ is the fictitious filtration velocity of the gas flow through the stationary layer of material, m/s.

To determine the unknown coefficients "A" and "B" in equation (2), linearization was performed with respect to the fictitious filtration velocity of the gas flow, after which it was presented in the following form:

$$\frac{\Delta P}{H \cdot v_0} = A^* + B^* \cdot v_0, \tag{3}$$

where
$$A^* = A \cdot \frac{\mu \cdot a^2}{32 \cdot \epsilon^3}$$
 and $B^* = B \cdot \frac{\rho \cdot a}{8 \cdot \epsilon^3}$

The first part of this equation remains a constant for the given experimental conditions, while in the second part, the variable parameter is solely the fictitious velocity.

By empirically determining the unknown coefficients of equation (3) for a specific dispersed material and the defined experimental conditions, it can be used for practical calculations of drying equipment. This allows for the prediction of pressure losses during filtration drying, but only within the range of investigated gas flow velocities.

In practice, it is more convenient to use the dimensionless form of the calculation dependencies, as they account for the specifics of the gas flow movement and the influence of the geometric characteristics of the drying equipment on pressure losses in the stationary layer of the dispersed material. In this approach, pressure losses are described by a functional dependence of the Euler criterion on the Reynolds criterion and the geometric simplex.

Filtering the gas flow through a stationary layer of wild carrot pomace represents a mixed hydrodynamics goal. Since the gas flow during filtration through the stationary layer of wild carrot pomace washes each particle individually (external goal) and moves through the channels between the particles (internal goal). There is no theory for the mixed hydrodynamics goal, so the external and internal goals were studied separately.

The value of Euler's number for the external goal of hydrodynamics was determined based on the dependency:

$$Eu = A \cdot Re^{x} \cdot \left(\frac{H}{d_{p}}\right)^{y}, \tag{4}$$

where Eu – Euler criterion $Eu = \Delta P/(\rho \cdot v^2)$; Re – Reynolds criterion $Re = v \cdot d_p \cdot \rho/\mu$; H – height of the stationary layer of wild carrot pomace, m; d_p – average diameter of particles of wild carrot pomace, m.

For the study of the internal problem of hydrodynamics, the following equation was used:

$$Eu = A \cdot Re_e^x \cdot \left(\frac{H_e}{d_e}\right)^y, \tag{5}$$

where Re is the equivalent value of the Reynolds criterion $Re_e^x = v \cdot d_e \cdot \rho/\mu$.

3. Results and Discussion

The results of the granulometric composition of wild carrot pomace are presented in Table 1 and Fig. 1.

The granulometric composition of wild carrot pomace

Table 1

Fraction $d \cdot 10^3$, m	0.1-0.14	0.14-0.315	0.315-0.63	0.63–1.25	1.25–2.5	2.5–5	Total
Weight of the fraction G, kg	0.00024	0.01013	0.315-0.63	0.1506	0.02674	0.00101	0.2
Percentage content, % mass	0.12	5.06	5.64	75.30	13.37	0.51	100

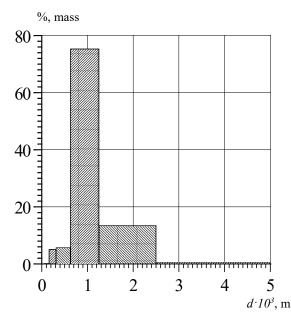


Fig. 1. Granulometric composition of the stationary layer of wild carrot pomace

The geometric particle sizes of wild carrot pomace were determined using an MBB-1A electron

microscope (Fig. 2). More than 100 samples of ground wild carrot pomace particles were analyzed.



Fig. 2. Measurement of the geometric size of wild carrot pomace particles using an MBB-1A microscope

The averaged geometric particle sizes are provided in Table 2.

Geometric characteristics of wild carrot pomace

Table 2

	Ave	Average particle		
Fraction d·10 ³ , m	Length,	Width,	Thickness,	diameter $d_p \cdot 10^3$, m
	$a\cdot 10^3$, m	$b\cdot 10^3$, m	$c \cdot 10^3$, m	
2.5–5	2.8	2.1	0.655	
1.25–2.5	2.15	1.45	0.5	
0.63-1.25	1.15	0.95	0.355	0.832
0.315-0.63	0.57	0.44	0.215	0.832
0.14-0.315	0.31	0.17	0.07	
0.1-0.14	0.13	0.1	0.045	

The following characteristics of the stationary layer of wild carrot pomace were determined using the aforementioned methods:

- bulk density $\rho_b = 407 \text{ kg/m}^3$;
- true density $\rho_t = 512 \text{ kg/m}^3$;

- porosity of the layer $\varepsilon = 0.34 \text{ m}^3/\text{m}^3$.

The results of experimental studies on pressure losses from the fictitious gas flow velocity at different heights of the stationary layer are shown in Fig. 3.

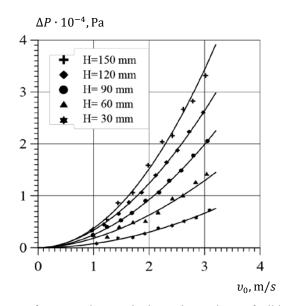


Fig. 3. Dependence of pressure drop ΔP in the stationary layer of wild carrot pomace on the height H at different filtration gas flow velocity values v_0

As seen in Fig. 2, pressure losses increase with the height of the stationary layer. It should also be noted that the curves have a parabolic shape. This indicates that the hydraulic resistance of the investigated material is formed under the influence of both inertial and viscous components.

To generalize the obtained experimental results shown in Fig. 3, we will use the Darcy – Weisbach equation, presented in the form of a two-term equation (3). To this end, we will present the results of the conducted research shown in Fig. 1 as a functional dependence $\frac{\Delta P}{(H \cdot \nu_0)}$. After approximating the experimentally obtained data with a linear relationship for the

segment cutting the ordinate axis, the value of $A^* = A \cdot \frac{\mu \cdot a^2}{32 \cdot \varepsilon^3}$ was obtained, and by taking the tangent of the slope angle of the line, the value of $B^* = B \cdot \frac{\rho \cdot a}{8 \cdot \varepsilon^3}$ was derived. Thus, equation (3) takes the following form:

$$\frac{\Delta P}{H \cdot v_0} = 5000 + 22000 \cdot v_0. \tag{6}$$

The equation (5) within the investigated speed range can be used for predicting pressure loss values and selecting equipment during the filtration drying of wild carrot pomace.

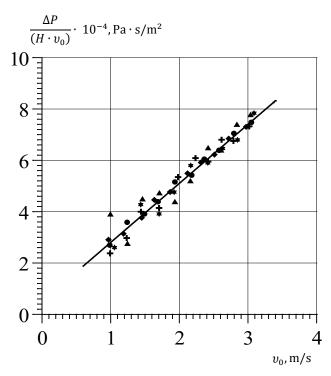


Fig. 4. Dependence $\frac{\Delta P}{H \cdot v_0} = f(v_0)$ for the stationary layer of wild carrot pomace (symbols correspond to those in Fig. 3)

3.1. External goal of hydrodynamics

To obtain the calculated dependencies in the form of dimensionless complexes, the experimental results presented in Fig. 3 were expressed as the relationship between the Euler number and the Reynolds number (Fig. 5). The analysis of Fig. 5 demonstrates that the Euler number depends on the height of the stationary layer of material, and the experimental data are

well described by a power-law dependence. The curves for different heights are nearly parallel, and the distance between them is proportional to the height of the stationary layer.

Fitting the experimental data from Fig. 5 with a power function allowed for the determination of the exponent in the Reynolds number, which was -0.08 for all heights, while the coefficient A varied depending on the height. The obtained results are presented in Table 3.

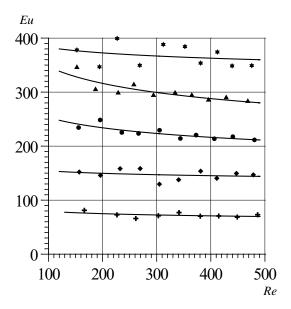


Fig. 5. Dependence of the Euler number on the Reynolds number for different heights of the stationary layer of wild carrot pomace (notations correspond to Fig. 3)

Table 3 The dependence of the unknown coefficients and the exponent on the height of the stationary layer of wild carrot pomace $\frac{1}{2}$

Н, т	0.15	0,12	0.09	0.06	0.03
H/d_p	182.34	145.87	109.40	72.93	36.47
A	580	480	360	230	115
n	-0.08				

To generalize the dependence for all investigated heights, a graph $A^* = f(H/d_p)$ is presented in Fig. 6. It was found that the determined coefficients A for each height lie on a straight line.

Approximating these values with a power function allows for determining the coefficient A^* and the exponent for the geometric simplex (H/d_p) , which is equal to one.

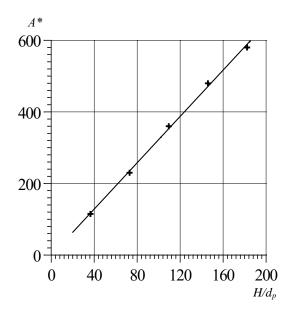


Fig. 6. Dependence of the coefficient A^* on the geometric simplex H/d_p

After summarizing the obtained data, equation (4) took the following form:

$$Eu_{\rm ext} = 3.2 \cdot Re^{-0.08} \cdot \frac{H}{d_{\rm p}} \tag{7}$$

This dependence holds true for Reynolds numbers ranging from 60 to 200. The absolute value of the relative error between the experimental and theoretically calculated values does not exceed 10 %.

3.2. Internal goal of hydrodynamics

The results of the experimental studies are presented as a functional dependence $Eu = f\left(\frac{H_e}{d_e}\right)$ for different values of the Reynolds number (Fig. 7). As can be seen from Fig. 7, the value of the Euler number increases with the increase in the geometric simplex, which leads to an increase in the slope angle of the line relative to the y-axis.

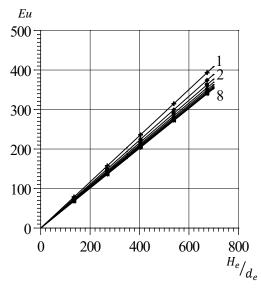


Fig. 7. Dependence of the Reynolds number on the geometric simplex $\frac{H_e}{d_e}$ 1 - Re = 60; 2 - Re = 80; 3 - Re = 100; 4 - Re = 120; 5 - Re = 140; 6 - Re = 160; 7 - Re = 180; 8 - Re = 200

Therefore, to find the unknown coefficient "A", the dependence of the tangent of the slope angle of the line on the Reynolds number was constructed.

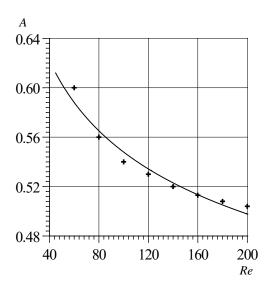


Fig. 8. Dependence of the coefficient A on the Reynolds number

For the internal goal of hydrodynamics, the following form of the equation (3) was obtained:

$$Eu = 1.04 \cdot Re^{-0.14} \cdot \frac{H_e}{d_e} \ . \tag{8}$$

The absolute value of the maximum relative error between the values of the Euler number calculated from the experimental data and those obtained using the equation (7) does not exceed 9 %.

4. Conclusions

The study first investigates the internal and external hydrodynamics of the stationary layer of wild carrot pomace. Unknown coefficients of the Darcy – Weisbach equation, A^* and B^* , are determined for predicting pressure losses in the stationary layer of wild carrot pomace. Experimental data are generalized in the form of a dimensionless equation $Eu = A \cdot Re^x \cdot \left(\frac{H_e}{d_e}\right)^y$ for studying the internal hydrodynamics problem, and in the form of the equation $Eu = A \cdot Re^x \cdot \left(\frac{H}{d_p}\right)^y$ for the external hydrodynamics problem.

For the external hydrodynamics problem, the unknown coefficients are: A = 3.2, x = -0.08, and for the internal problem: A = 1.04, x = -0.14.

A comparison is made between the theoretically calculated data, obtained from equations (6), (7), and (8), and the data obtained experimentally.

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DEVELOPMENT OF COAL FLUE GASES DENITRIFICATION TECHNOLOGIES IN CHINA

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Abstract. In the process of coal burning, a large amount of smoke will be produced, and there is a large amount of NO_X in the flue gas, only by removing these substances can the pollution degree of the flue gas be reduced. This paper analyzes the coal consumption and NO_X emission in China in recent years, and summarizes the industrial emission sources of NO_X. The principle, process flow, research status and development prospect of selective catalytic reduction (SCR), selective non-catalytic reduction (SNCR), ozone oxidation and absorption in traditional flue gas denitrification technology and complex absorption and photocatalytic oxidation in new flue gas denitrification technology are discussed in detail. The denitration rate, advantages and disadvantages of the traditional flue gas denitration technology in the denitration market are summarized. The technological characteristics and economy of the above five flue gas denitration technologies were compared, and the development direction of flue gas denitration technology in China was pointed out.

Keywords: coal-fired boilers, nitrogen oxides, emissions, denitration technology, catalyst.

1. Introduction

Environmental pollution and energy shortage are two major problems facing the world (He et al., 2021). Air pollution problems such as compound acid rain, photochemical smog and haze caused by NO_X

emission seriously endanger human health, destroy the ecological environmental balance, and restrict the rapid economic and social development in our country. In the past 30 years, coal consumption has accounted for about 70 % of China's primary energy consumption (National Bureau of Statistics, 2023). NO_X emissions from coal burning account for about 90 % of national emissions (Jianqiang et al., 2017).

Flue gas denitration technology is the most effective control method in the current flue gas denitration market (Ministry of Ecology and Environment of the People's Republic of China, 2023). Based on the background of ultra-low emission transformation in the coal power industry with the largest NO_X emission, this paper summarizes the traditional industrialized flue gas denitrification technologies in China's current flue gas denitrification market from the perspectives of NO_X emission reduction principle, application status and future prospects, and explores some new flue gas denitrification technologies in laboratory research stage. In order to provide reference for the future research and development of flue gas denitration technology.

Atmospheric pollutants NO_X mainly refer to NO and NO₂, among which about 95 % of NO_X emitted from coal burning is NO, and the rest is NO₂ (Jianhua, 2019). According to the annual report of

Environmental Statistics in 2022 (Ministry of Ecology and Environment of the People's Republic of China, 2023), China's NOx emissions were 8.957 million tons, down 10.34 % from 2021, of which industrial sources, domestic sources and motor

vehicle emissions accounted for 37.21 %, 3.78 % and 58.80 %, respectively, and the rest were emissions from centralized pollution control facilities. The proportion of NO_X emissions from various industries in industrial sources is shown in Fig. 1.

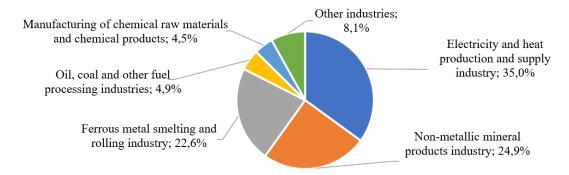


Fig. 1. The proportion of NO_X emissions in various industries in 2022

It can be seen from Fig. 1 that the three industries with large emissions in industrial sources are power, heat production and supply industry, non-metallic mineral products industry, ferrous metal smelting and rolling industry, accounting for 82.5 % of industrial source emissions. For the power industry with the largest NO_X emission, the Action Plan for Energy Conservation and Emission Reduction Upgrading and Transformation of Coal Power Generation (2024–2027) requires that by 2027, all coal power units with the conditions for transformation in China should achieve ultra-low emissions, that is, the NO_X emission concentration should not be higher than 50 mg/m³ (when the benchmark oxygen content is 6 %) (National Development and Reform Commission of the People's Republic of China, 2024). The implementation of the ultra-low emission policy in the coal power industry has accelerated the development of flue gas denitrification technology in China, and promoted the ultra-low emission transformation of cement, chemical and other industries to a certain extent.

2. Materials and Methods

In this study, we used literature analysis and other methods to study and explore the flue gas denitrification technology of coal-fired boilers. By reviewing the research status of traditional flue gas denitrification technology and new flue gas denitrification technology, the denitrification rate, principle, advantages and disadvantages and application status of SCR, SNCR, ozone oxidation absorption

denitrification method, complex absorption method and photocatalytic oxidation method were discussed, and the development direction of flue gas denitrification technology was prospected.

3. Traditional flue gas denitrification technology

The technology of flue gas denitration can be divided into dry method and wet method according to whether water is added in denitration process and the dry and wet state of the product. Traditional dry denitration methods mainly include selective catalytic reduction (SCR), selective non-catalytic reduction (SNCR), activated carbon, electron beam irradiation and pulse corona method. Traditional wet denitration mainly includes liquid phase absorption method and oxidation absorption method. In the following, SCR, SNCR and ozone oxidation absorption method, which are the three flue gas denitrification technologies with high application rate, are discussed in detail and some characteristics of the above technologies are compared and analyzed.

3.1. Selective Catalytic reduction Denitration Technology (SCR)

SCR technology is based on ammonia, liquid ammonia, urea and other reducing agents, supported by metal oxides as catalysts, NH_3 selectively catalyzed the reduction of NO_X to N_2 and $H_2O(g)$ on the catalyst surface without O_2 oxidation in the flue gas. The SCR technology process flow is shown in Fig. 2.

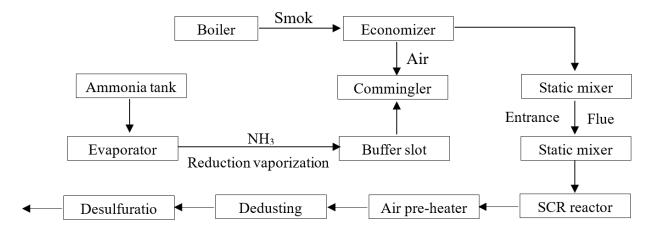


Fig. 2. The technological flow chart of SCR

In this process, the coal flue gas is discharged from the boiler into the economizer and mixed with NH₃ in the inlet flue of the SCR reactor. NH₃ comes from the liquid ammonia storage tank, and the liquid ammonia is evaporated into NH₃ by steam decompression into the buffer tank. Air is injected into the mixer to dilute pure ammonia and increase the oxygen content of the system. After NH₃ is fully mixed with air, it is sprayed into the reactor inlet flue through the jet grating. NH₃ and flue gas are evenly mixed by a static mixer and enter the main body of the reactor. At this time, NO_X is subjected to catalytic reduction under the action of catalysts and reducing agents, and the purified flue gas enters the air preheater for preheating, followed by dust removal and desulfurization. The reaction involved in this process is shown in formula (1)–(3).

$$4NH_3+4NO+O_2 \rightarrow 4N_2+6H_2O$$
 (1)

$$2NH_3+NO+NO_2 \rightarrow 2N_2+3H_2O$$
 (2)

$$8NH_3+6NO_2 \rightarrow 7N_2+12H_2O.$$
 (3)

The main catalysts used in SCR denitration technology are V₂O₅, Fe₂O₃, CuO, Cr₂O₃, etc., among which V₂O₅ has the highest catalytic activity. At present, the catalyst used is a vanadium titanium system dispersed on T iO₂ with V₂O₅ as the main active component and WO₃ or MoO₃ as the cocatalyst, namely V₂O₅–WO₃/TiO₂ or V₂O₅–MoO₃/TiO₂. The principle of catalytic reaction is that NH₃ is quickly adsorbed on the surface of V₂O₅, reacts with NO, forms an intermediate product, decomposing into N₂ and H₂O, and the active point of the catalyst is

quickly recovered in the presence of O2, and continues the next cycle to carry out the chemisorption and reaction process. The reaction steps can be decomposed into: (1) NH₃ diffuses to the catalyst surface; (2) Chemical adsorption of NH₃ on V₂O₅; (3) NO diffuses to the catalyst surface; (4) NO reacts with NH₃ in adsorbed state to generate intermediate products; (5) The intermediate products decompose into the final products N2 and H₂O; (6) Outward diffusion away from the catalyst surface. According to the structure and external shape of the catalyst, there are three types: corrugated type, plate type and honeycomb type. The characteristics of the three catalysts are shown in Table1. Because the reaction is sufficient, the honeycomb catalyst is the most used. SCR occupies an important position in flue gas denitrification technology because of its advantages of high denitrification efficiency and the most mature technology, but the problems such as high investment cost of vanadium-titanium catalysts and solid waste pollution can not be ignored. The waste vanadium and titanium catalysts can be recycled by washing with water, thermal reduction, acid solution and other methods (Wu et al., 2002), which can effectively slow down solid waste pollution and reduce investment costs, and achieve a win-win situation for both environment and economic benefits. The development of SCR catalysts in the future is still mainly based on the wide application of vanadium-titanium catalysts and deepening the research on their regeneration methods, and vigorously develop green and low-cost vanadium-free catalysts.

Table 1

Characteristics comparing three kinds of catalyst

Туре	Base material	Picture	Technical characteristics
Cellular	Bulk extrusion		The overall medium is uniform, the specific surface area is large, the volume is small, the weight is light, the use is wide, the market share is high (about 70 %)
Plate-type	Stainless steel mesh		The specific surface area is small, the volume is large, the production cycle is short, and the ash is easy to accumulate between the upper and lower two catalysts
Ripple type	Fiber		Medium specific surface area, poor wear resistance, between the upper and lower two catalysts, easy to accumulate ash, low market share (not more than 5 %)

3.2. Selective Non-catalytic Reduction Denitration Technology (SNCR)

SNCR is a method of reducing NO_X to N₂ by injecting an amino reducing agent such as ammonia or urea into the boiler furnace or the circulating fluidized bed boiler separator at high temperature under the condition of no catalyst, and rapidly pyrolyzing or evaporating the reducing agent into NH₃. The process is in the boiler outlet smoke temperature 850~1100 °C, urea or ammonia and other reducing agents directly injected, in the case of high temperature, ammonia and the flue gas in the reaction of nitrogen oxides, nitrogen oxides reduction, reduce the concentration of nitrogen oxides. The main reactions involved in this technique are shown in (4)–(7).

$$NH_2CONH_2 \rightarrow 2NH_3 + HNCO$$
 (4)

$$4NH_3+4NO+O_2 \rightarrow 4N_2+6H_2O$$
 (5)

$$4NH_3+2NO_2+O_2 \rightarrow 3N_2+6H_2O$$
 (6)

$$2NO+2HNCO+1/2O_2 \rightarrow 2N_2+2CO_2+H_2O.$$
 (7)

SNCR technology has short construction period, simple construction, no ne ed to replace the induced draft fan, less investment, insensitive to changes in coal, medium denitrification efficiency, and is suitable for the transformation of old boilers in China. The disadvantage of this technology is that the denitrification efficiency is low, and ammonia escape is easy to occur. Therefore, in terms of flue gas

denitrification, the use of SNCR technology alone is subject to some limitations.

In the denitration process, no catalyst is used, and NH₃ escapes at 10~15 ppm. When spraying reducing agent into the furnace, because the reduction reaction of NO_X only occurs between 850 °C and 1100 °C, the reaction temperature of reducing agent is one of the key factors for the reduction efficiency. The optimum reaction temperature is 950 °C. The key to the successful implementation of SNCR technology is that the reducing agent must be sprayed into the most effective temperature range in the furnace, and the total time of the reactants staying in the reactor should be controlled as much as possible, so that the reducing agent can be dispersed and mixed evenly with the flue gas at the most appropriate temperature, so as to maximize the utilization efficiency of the reducing agent and control the minimum ammonia escape.

SNCR process structure is relatively simple, no additional denitrification equipment is required, and is mostly used as a supplementary means of low nitrogen combustion or SCR. SNCR and SCR combined technology is a denitrification technology that integrates the advantages of high denitrification rate of SCR, low ammonia escape and low cost of SNCR. The escaped ammonia in SNCR can be further used as a reducing agent of SCR, effectively saving the consumption of reducing agent and catalyst, and thus reducing the operating cost.

3.3. Ozone oxidation absorption denitrification method

Ozone oxidation absorption and denitrification is a method of oxidizing the water-soluble NO in the flue gas into NO_2 , N_2O_5 and other water-soluble substances, and then spray absorption with water, acid or alkali solution.

After dust removal, the flue gas oxidizes NO into high-priced NO_X with O₃ in the NO_X generator. The flue gas containing high-priced NOx enters the absorption tower and contacts with NaOH solution to generate NaNO₃. After the reaction, the flue gas is purified by the demister and discharged into the atmosphere. Part of the reaction mixture is driven into the tower by the circulating pump for recycling, and part of the reaction mixture is discharged by the pump after filtration, separation and drying to obtain NaNO₃ crystals. The principle involved in this process is shown in equations (8)–(12).

$$O_3+NO \rightarrow NO_2+O_2$$
 (8)

$$O_3 + 2NO_2 \rightarrow N_2O_5 + O_2 \tag{9}$$

$$NO_2+H_2O\rightarrow HNO_3+NO$$
 (10)

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \tag{11}$$

$$HNO_3+NaOH\rightarrow NaNO_3+H_2O.$$
 (12)

The main factors affecting oxidation are the ratio of molar number between O₃ and NO and the oxidation time. Practice shows that the oxidation rate of NO increases with the increase of O₃/NO. Ozone denitrification rate is relatively high, the highest can reach more than 85 %. The main factors affecting ozone denitrification are: ozone amount, reaction time, mixing adequacy of ozone and flue gas, etc. Practice shows that the oxidation residence time of ozone in flue gas is a more important factor.

At present, domestic and foreign research on this method focuses on the study of oxidation and denitrification of O₃ based on wet flue gas desulfurization technologies such as calcium, magnesium and sodium. Sun et al. (Sun et al., 2015) used the combination of O₃ and MgO for denitrification, and the experiment showed that when the pH of solution was 6.5 a nd the concentration of MgO was 0.02 mol/L, the optimal removal rate of NO₂ was 75 %. Shaopeng et al., 2015 conducted desulphurization and denitrification experiments with O₃ and ammonia solution. The research shows that when pH is 10, the molar ratio of O₃/NO is 1, and the ammonia concentration is 0.3 %, the removal rates of SO₂ and NO_X can reach 99 % and 90 % respectively. Chunhu et al., 2014 used O₃ oxidation combined with Na₂S₂O₃ - NaOH solution wet spray to achieve NO removal. When the molar ratio of O_3/NO is $1.1\sim1.2$, the concentration of Na₂S₂O₃ is 2 %, and the pH is 9, the denitrification rate can reach 75 %. Ozone oxidation absorption method has no secondary pollution, the process is simple, only need to install the ozone generator and other devices before the existing desulfurization equipment can achieve simultaneous desulfurization and denitrification, especially suitable for SCR and SNCR can not carry out low-temperature denitrification field (< 200 °C); However, the prepa ration cost of the required ozone is high, and the future should focus on the study of energy-saving and efficient ozone generators to reduce the investment and operating costs of the system.

3.4. Comparison of characteristics of traditional flue gas denitration technology

Table 2 shows the comparison of characteristics of traditional flue gas denitrification technologies.

Table 2
Comparison of characteristics of traditional flue gas denitrification technology

Technology	Denitration rate	Principle	Merits and demerits	Application status
1	2	3	4	5
SCR	80~90 %, up to 95 %	NO _X was reduced to non-toxic N ₂ and H ₂ O by amino reducing agent under catalyst	High desulfurization rate, the most mature technology; However, the investment and operation costs are high, the catalyst is expensive and prone to poisoning, and accompanied by ammonia escape	Widely used; It is mostly used in the coal-fired power industry with large emissions

Continuation of Table 2

1	2	3	4	5
SNCR	> 60 %, up to about 75 %	NO_X is directly reduced to N_2 and H_2O by amino reducing agents	Mature technology, low investment and operating costs; Ammonia escape is serious	Widely used; It is mostly used in the coal-fired power industry with large emissions
Oxidation absorption method	> 85 %, up to 90 % (O ₃ method)	NO is oxidized to NO ₂ by gaseous phase (O ₃ , Cl ₂ , etc.) or liquid phase (NaClO ₂ , HClO ₃ , H ₂ O ₂ , etc.) oxidants, and then removed by re- absorption	O ₃ method is simple to operate, but the investment and operation cost are high; NaClO ₂ , HClO ₃ expensive, easy to corrode equipment; H ₂ O ₂ is easy to decompose and consumes a lot of light	Only O ₃ oxidation method is widely used, mostly used in petrochemical, carbon and other industries; The rest are not widely used in industry
Adsorption method	80~90 % (Activated carbon method)	The adsorbent (activated carbon/coke, molecular sieve, etc.) catalyzes and adsorbs NO _X and then reduces it with amino, and the adsorbent is regenerated by heating or steam	The equipment is simple, can cooperate desulfurization; But the adsorption amount is small, the amount of adsorbent is large, and the regeneration is frequent	Activated carbon/coke method is widely used. Suitable for industries with small emissions
Plasma method (electron beam, pulse corona)	>70 %	The free radical produced by high-energy electrons is used to oxidize NO to NO ₂ , and then into NH ₃ and H ₂ O (g) to produce ammonium nitrate	Simple operation, can cooperate with desulfurization and dust removal, no waste waste water; But high energy consumption	Not widely used
Liquid phase absorption method	>90 %	Use common water, lye (caustic soda, lime milk, ammonia, etc.) or acid (nitric acid, sulfuric acid, etc.) to absorb and remove NO _X	The by-product with high concentration of nitric acid / (nitrite) nitrate can be recycled. However, a high NO ₂ /NO is required	Widely used; It is mostly used in high-concentration NO ₂ exhaust industries, such as nitric acid plants

4. New flue gas denitrification technology

According to the wet method, the new flue gas denitrification technology can be divided into complex absorption method, liquid film method, microbial method, etc. Dry methods are mainly photocatalytic oxidation method, electroassisted catalysis method, etc., such technologies are mostly in the experimental research stage, and the following will be

specifically discussed for complex absorption method and photocatalytic oxidation method.

4.1. Complex absorption method

The complexation absorption method is to use the coordination between the liquid phase complexation agent and NO to absorb NO, and then use microorganisms, electrolysis or adding reducing agents to reduce the complexation agent that absorbed NO, so as to regenerate and recycle the method. At present, the most widely studied process at home and abroad is the removal of NO by the Fe^{II}EDTA chelating agent composed of the ligand ethylenediamine tetraacetic acid (EDTA) combined with biological reduction method (He et al., 2018).

In the process of denitrification, Fe^{II}EDTA and NO are complexed to form ferrous nitrosyl complex, which makes NO enter the liquid phase. Secondly, the denitrifying bacteria reduced Fe^{II}EDTA-NO to N₂ under the organic carbon source such as glucose and then multiplied themselves, while Fe^{II}EDTA was regenerated. In addition, there is a side reaction of Fe²⁺ being oxidized to Fe³⁺ by O₂ in the flue gas. The process reaction is shown in equation (13)–(16).

$$Fe^{II}EDTA+NO \rightarrow Fe^{II}(EDTA)-NO$$
 (13)

$$2Fe^{II}EDTA+1/2O_2+2H^+ \rightarrow 2Fe^{III}EDTA+H_2O$$
 (14)

 $12\text{Fe}^{\text{II}}(\text{EDTA})\text{-NO+C}_6\text{H}_{12}\text{O}_6 \rightarrow$

$$12\text{Fe}^{\,\mathrm{II}}\text{EDTA} + 6\text{N}_2 + 6\text{CO}_2 + 6\text{H}_2\text{O}$$
 (15)

$$24\text{Fe}^{\text{II}}\text{EDTA} + \text{C}_6\text{H}_{12}\text{O}_6 + 24\text{OH}^- \rightarrow$$

$$24 \text{Fe}^{\text{II}} \text{EDTA} + 6 \text{CO}_2 + 18 \text{H}_2 \text{O}.$$
 (16)

In view of the problems of complex agent consumption and low denitrification rate caused by NO complexation absorption capacity of Fe³⁺ generated in the denitrification process, relevant scholars have conducted a lot of research on how to effectively prevent Fe²⁺ oxidation and efficiently regenerate absorptive liquid. Wang Fei et al. (Wang, 2015) carried out nitrogen removal experiments of Fe^{II}EDTA in a rotating packed bed by using super-gravity technology. The study showed that when the super-gravity factor β was 82, the decrease of NO removal rate was only 12.9 %, much lower than 74.2 % ($\beta = 10$), which verified that the rotating packed bed could effectively avoid Fe²⁺ oxidation. Zhang Yu et al. (Yu et al., 2017) studied the simultaneous removal of Fe^{II}EDTA-NO and Fe^{III}EDTA by denitrifying bacteria in an anaerobic reactor with sodium lactic acid carbon source. The results showed that when the hydraulic retention time was 16h and pH was 7, the average removal rate of Fe^{II}EDTA-NO could reach 96.61 %. Jun et al. (Jun et al., 2018) proposed a nitrogen removal reaction of Fe^{II}EDTA in a biological rotary drum filter and studied the NO mass transfer model. Long-term operation results showed that the denitrification rate of the reactor could be stabilized at about 95 %, and the average relative deviation between the model and the experimental data was only 2.27 %. The complex absorption combined with biological reduction method has the advantages of fast reaction rate, recyclable absorption solution, no secondary pollution and simultaneous desulfurization and denitrification. However, due to the oxidation of complex agents and the anaerobic nature of microorganisms, the industrial application of this method is hindered. In the future, the method should focus on cultivating high-efficient aerobic microorganisms and optimizing microbial regeneration equipment to improve the denitrification rate and regeneration rate of the absorption solution.

4.2. Photocatalytic oxidation method

Photocatalytic oxidation is a method of denitrification in which the photocatalyst is stimulated by energy to produce electron-hole pairs under certain light conditions, and the electrons and holes form superoxide and hydroxyl radicals with O_2 and $H_2O(g)$ in the flue gas respectively, and then the NO_X adsorbed on the surface of the catalyst is oxidized to nitric acid. The reaction mechanism involved in this method is shown in equations (17)–(22).

$$TiO_2(h^+)+h\lambda \rightarrow TiO_2(e^-+h^+)$$
 (17)

$$O_2+e^- \rightarrow \cdot O_2^-$$
 (18)

$$OH^-+h^+ \rightarrow OH$$
 (19)

$$NO+2\cdot OH \rightarrow NO_2+H_2O$$
 (20)

$$NO_2 + \cdot OH \rightarrow NO_3 + H^+$$
 (21)

$$NO_X + \cdot O_2 \rightarrow NO_3$$
. (22)

At present, the commonly used photocatalysts at home and abroad are TiO2, ZnO and CdS semiconductors, among which nano TiO2 has been widely studied for its advantages of green environmental protection, high catalytic activity, and good chemical and thermal stability. However, it also has the disadvantages of only absorbing ultraviolet rays in sunlight ($\lambda < 387$ nm) and low utilization of visible light (380 nm $< \lambda < 780$ nm), and easy rapid recombination of electron-hole pairs. In this regard, relevant scholars proposed that the visible light absorption spectrum can be broadened by means of precious metal modification, metal or non-metal doping, semiconductor composite, etc., and the holeelectron pair recombination can be suppressed to improve the nitrogen removal rate (Ye et al., 2016, Xiaoming et al., 2018). Yang Wei (Chunhu et al., 2014) prepared rGO – TiO₂ / ASC catalyst using active semi-coke (ASC) as the carrier, and the results showed that the addition of rGO could effectively inhibit the electron-hole recombination, and the denitrification performance of the photocatalyst remained basically unchanged after three times of water vapor regeneration. Hu Jing (Jing et al., 2017) obtained blackTiO₂ with the function of widening absorption spectrum through TiO₂ self-doping and prepared Bi / BiOI / blackTiO₂. The denitrification rate of the catalyst could reach 70 % under simulated illumination, and the activity of the catalyst could still reach 68 % in 5 regeneration experiments.

Photocatalytic oxidation for denitrification has the advantages of mild reaction conditions, co-desulfurization and no secondary pollution (Shuai et al., 2018), but the problems of high cost and low efficiency caused by the narrow absorption spectrum of visible light caused by the photocatalyst limit the industrial application of this method. In the future, it is still necessary to broaden the research on visible light absorption spectrum and develop new photocatalysts.

Table 3 compares and summarizes the characteristics and economy of the above three traditional flue gas denitrification technologies, SCR, SNCR and O₃ oxidation absorption method, and two new flue gas denitrification technologies, complex absorption method and photocatalytic oxidetion method. The specific contents are shown in Table 3.

 ${\it Table~3}$ Comparison of characteristics of traditional flue gas denitrification technology

Index	SCR	SNCR	O ₃ oxidation absorption method (1 million m ³ /h smoke volume)	Complex absorption method	Photocatalytic oxidation
Sort	Dry method	Dry method	Wet process	Wet process	Dry method
Investment cost /(RMB yuan ·kW-1)	100~150	30~40	50 million yuan	_	-
Running cost /(RMB fen·kWh ⁻¹)	0.7~1.2	< 0.0035	16 yuan/kg(NO _X)	-	-
Secondary pollution	NH ₃ , Waste catalyst	NH ₃	none	none	none
Ammonia escape rate /(mg·L ⁻¹)	3~5	10~15	none	none	none
Simultaneous desulfurization	no	no	yes	yes	yes
Denitration product	N_2	N ₂	NO ₃	N ₂	NO ₃

5. Conclusion

The transformation and upgrading of traditional flue gas denitrification technologies such as SCR and SNCR have made coal-fired power, cement and chemical industries achieve ultra-low emissions. Although such technologies are mature in industrial application and have high removal efficiency, there are serious problems such as nitrogen resource waste and gas-solid secondary pollution, especially waste catalysts in SCR. The complex absorption method developed to solve these problems has the characteristics of no secondary pollution and can cooperate with desulfurization. The photocatalytic oxidation method can recover and apply the nitrogen resources in flue gas, which meets the dual needs of environmental and economic benefits.

In the future, the existing efficient SCR, SNCR and ozone oxidation absorption technologies will be widely used in flue gas denitrification technology, and the integration of desulfurization and denitrification technologies such as adsorption method and plasma method will be vigorously developed. New flue gas denitrification technologies such as complex absorption method and photocatalytic oxidation method will be deeply studied, and flue gas denitrification technologies suitable for local characteristics will be explored.

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