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CONTENTS

ENVIRONMENTAL PROBLEMS

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THE FIRST STEP TO SKETCH THE SPATIO-TEMPORAL EVOLUTION OF BIOCHEMICAL AND PHYSICAL PARAMETERS INVOLVING IN THE HARMFUL ALGAL BLOOMS (HAB) IN MATTATALL LAKE (NOVA SCOTIA, CANADA)

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Abstract. Many watercourses in Nova Scotia (Canada) have recently had algal blooms in a surprisingly increasing way in frequency and diversity without any good understanding or explanation about causes and effects. The blooms triggered in Mattatall Lake (Wentworth, Nova Scotia) have many particular aspects: toxic species domination, nutrients increasing on a monthly basis, and blooms that co-exist with icy conditions. In this paper, we suggest an approach to create a map system with an appropriate interpolation and validation of necessary data in order to deal with this issue in Mattatall Lake and to contribute to the analysis framework and management plan on the entire area. Our long-term objective is aiming to suggest a modeling process for the entire watershed.

Key words: Harmful Algal Bloom (HAB), Mattatall Lake, GIS, Artificial Neural Network (ANN) model.

1. Introduction

There are between 1000 and 2000 species of cyanobacteria (blue-green algae) worldwide that can colonize to form a Harmful Algal Bloom (HAB) (Krogmann 1981). Degraded water quality from increased nutrient pollution promotes the development and persistence of many HABs and is one of the reasons for their expansion and proliferation in aquatic environments. HABs are unfortunately a growing problem in Canada over the last few years. Several cases of blue-green algae blooms have been reported in Manitoba’s Lake Winnipeg over the past few years. Algal blooms in Lake Winnipeg have increased in intensity and frequency with accumulation of Phosphorus and nitrogen nutrients in the lake (SMW 2011). Multiple public health advisories have been issued in Quebec due to Microcystin concentrations exceeding the Canadian drinking water guidelines in Missisquoi Bay. The blooms had been appearing since 2000, so a quantitative approach was developed for the detection of cyanobacteria blooms (Fortin et al. 2010). The first documented HAB in Newfoundland and Labrador was blue-green algae in the late summer and early fall of 2007 and in the spring of 2008 (Government of Newfoundland and Labrador 2008). In 2011, Lake Erie, Ontario, experienced a severe harmful algal bloom consisting of the following toxic cyanobacteria genera: *Microcystis and Anabaena* (Michalak et al. 2013). Nova Scotia has documented incidents of algae blooms in lakes including Porcupine Lake (Digby), Fanning Lake, and Parr Lake (Yarmouth) (Environment and Labour 2007); however, there is little research that has been done and there are no monitoring plans set in Nova Scotia.

During the fall of 2014, massive algal blooms appeared in Mattatall Lake, located near Wentworth, Nova Scotia (NS), and persisted until late December. The duration of this phenomenon was extremely unusual. Algal blooms have not been known as coexisting with icy conditions. The dominant species in this bloom was identified to be *Anabaena planctonica*, which may produce the neurotoxin *Anatoxin-a*.

There are many factors that affect the development of a HAB, all of which can be divided into controllable or uncontrollable parameters. Light intensity, temperature and wind direction are uncontrollable, whereas nutrient availability (especially total Phosphorus) can be restrained. Identifying the nutrient point and non-point sources within the watershed is a key to establish a management plan. Management of nutrient inputs to the watershed can lead to significant reduction of HABs. The more data identified the better and more accurate analysis for a plan of management.

To do so, field experiments are extremely necessary to elucidate various factors that affect microalgae blooms and their proliferation. However, factors that can be determined in field experiments are limited, costly and time consuming. Mathematical models therefore have many advantages for studying fluid dynamic effects coupled with parameters more realistic: nutrients, light and temperature. Acquiring sufficient data is as important in both developing predictive models as well as making accurate predictions. Microalgae dynamics modeling is considered an effective tool for complementing the limitations of field and laboratory experiments, and is an approach that can be used at a minimal cost.

All these arguments allow us to think about the very first step of a long term modeling process for the watershed, including collecting and building a dataset as well as to create a map system with a good interpolation and validation of necessary data, analysis framework and management plan on the entire area. Based on this initiative, mapping and modeling approaches such as Geographical Information System (GIS) and Artificial Neural Network (ANN) will be used.

Multiple scientists have used GIS approaches in their studies on a large variety of problems. We can cite here the work of Biswas et al. (2002) who used remote sensing and GIS techniques to recommend soil and watershed conservation measures for a number of micro-watersheds in eastern India (Biswas et al. 2002). Another example is the work of Mantzafleri et al. (2009) who did a water quality monitoring study to provide information about the geographic distribution of the qualitative parameters to support pollution reduction strategies for Lake Kastoria in the Region of Western Macedonia (Mantzafleri et al. 2009).

Therefore, the GIS approach is not a new approach in the studies related to watersheds. Nevertheless, the novelty of our paper has relied on the fact that we would sketch a ‘standard process’ for data acquisition and mapping for the algal bloom patterns which very recently boomed in the whole province of NS where no physical and chemical data related to this lake have been done systematically. So far, none of the research work is focused on cyanobacteria bloom mapping in Canada. In performing this ‘standard process’, we will use Mattatall Lake as a pilot study to apply to other lakes having the same bloom issues in Nova Scotia and in Canada. Moreover, the mapping results will help us to build our database and to have panoramic viewpoints on the entire watershed, and hence to suggest a correlation between governing parameters of algal bloom pattern as well as to predict possible scenarios for bloom occurrence and proliferation in the future. The objectives of this paper are:

1) To determine the distribution of nutrient levels (especially two important components for algal bloom growths: Total Phosphorus (TP) and Nitrates) within the watershed. This includes: a) nutrients in the lake, brooks and tributaries flowing into the lake and b) the TP in soil samples of the watershed, which might contribute mainly to the high TP level in the lake.

2) To determine the biological consequences of these nutrient levels in the lake and related watershed via two important parameters: *Chlorophyll-a* and *Phycocyanin*.

3) Based on the data determined, interpolated and validated by mapping on the entire study area with the GIS approach, we try to evaluate the spatial temporal evolution of the above-mentioned parameters for the HAB occurrence.

4) The last goal is a trial to predict the future bloom scenarios by using a mathematical modeling approach. As mentioned previously, the pattern of massive blooms was just recently appearing (since 2014) and we just started a systematic sampling process for data since June 2015. With the data for this summer season from June to October, we try to simulate and predict different bloom scenarios for the future based on an Artificial Neural Network (ANN) model.

2. Methodology

2.1. Study area

Mattatall Lake is located on the Cumberland/Colchester County line and is approximately 5-kilometer length (Fig. 1). Mattatall Lake is mainly spring fed with multiple brooks. There is an outlet from the lake draining into the French River, then draining into Northumberland Strait. In 2011 some small blooms were first noticed on the lake by local residents beginning in late June early July; however, they dissipated by September. Over the past 2 years the algal blooms became gradually worse and late September 2014 the bloom totally expanded, covering the entire lake until December 2014.

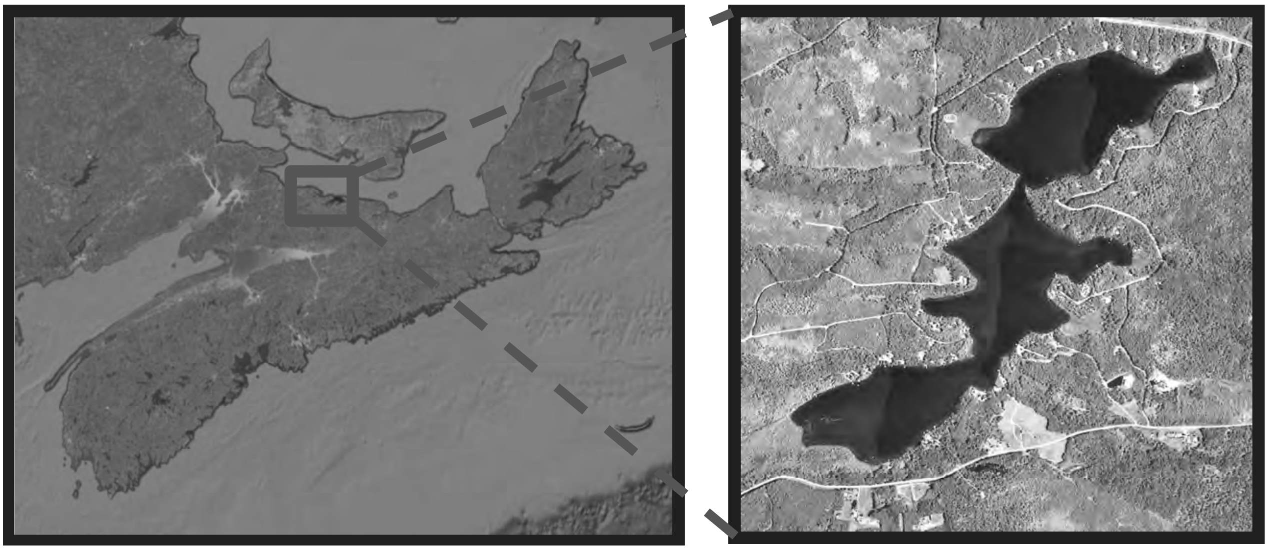

Fig. 1. Google Earth view of Nova Scotia highlighting Mattatall Lake area (left) and Government of Nova Scotia aerial photograph of Mattatall Lake (right)

2.2. Governing parameters involving in our study

2.2.1. Chemical Parameters

Phosphorus is a nutrient that plays a vital role to human, animal, and plant growth. It's one of the most common substances found in nature and indispensable for the low level of ecological food web. Phosphorus occurs unnaturally from various artificial sources such as fertilizers (used in agriculture), cleaners (used in industry) and wastewater (from household sewage). Phosphorus is found in water, solids (detritus), and in the bodies of biological organisms. However, high levels of Phosphorus in nature can create algal blooms causing eutrophication or the premature "aging" of a water body. In other words, HABs may develop in eutrophic water bodies (high Phosphorus and Nitrates) as well as in oligotrophic water (Sorichetti et al. 2014). This eutrophication process decreases sunlight and oxygen levels (hypoxia) thus affecting fish and other aquatic life.

Since Phosphorus loading and phytoplankton production in fresh water bodies are strongly correlated (Anderson et al. 2002), Phosphorus levels in soil within the watershed and in surface water samples will be considered to determine the potential sources of nutrient loading into the lake. Different samples and analyses for TP in brooks and ponds of the Mattatall Lake watershed gave us a panoramic view of nutrient sources streaming to the lake and how they could disperse and redistribute in the lake.

Nitrogen in the lake is detected under the forms of *Ammoniacal Nitrogen, Nitrates,* and *Nitrites*. These three types of Nitrogen formed a parameter named Dissolved Inorganic Nitrogen (DIN). This factor DIN couples with the organic form of Nitrogen to define Total Nitrogen (TN). *Total Nitrogen* and *Total Phosphorus* are two of the most important micronutrient components for algal development and hence very important parameters to be used for predicting scenarios of algal bloom occurrence and proliferation.

Unfortunately, due to many reasons such as the lack of an appropriate equipment, Total Nitrogen cannot be easily defined. We can just evaluate the mineral forms of Nitrogen such as Ammoniacal Nitrogen, Nitrites and Nitrates. The term Nitrates (N) which will be used hereafter comprises of two components: Nitrates and Nitrites, and they are main Nitrogen parameters in our study for the development of algal blooms.

2.2.2. Biological parameters

There are two biological parameters representing for the existence and growth of algae in general and cyanobacteria in particular: *Chlorophyll-a* and *Phycocyanin.*

Chlorophyll-a is usually used as a parameter that determines the quantity of primary photosynthetic pigment in cells of aquatic micro plants. Chlorophyll-a is a specific form of Chlorophyll, used in oxygenic photosynthesis. Measurement and determination of this parameter are the basic analysis to evaluate the characteristics of algae blooms in many research works in the world. Unfortunately, Chlorophyll-a represents just the whole quantity of photosynthesis pigment released from all algae and micro-plants present in water, hence it cannot help to distinguish cyanobacteria existence among all living micro plants and algae in the waterbody. To be able to define and confirm the existence of Cyanobacteria species in the composition of aquatic microalgae, another pigment form, Phycocyanin, is used. Phycocyanin is the pigment, which differs cyanobacteria species from another planktonic species, and could give us a real picture of quantity of cyanobacterial genera in the water. Phycocyanin is actually a pigment-protein complex from the light-harvesting phycobiliprotein family, along with allophycocyanin and phycoerythrin. It is considered as an accessory pigment to Chlorophyll.

In using the index of Chlorophyll-a to evaluate the risk for water quality, WHO suggested the following criteria:

Chlorophyll-a must be < 3.5 (mg/L) (Drinking Water) and <10 (mg/L) (Recreational Water) (1)

Regarding the Phycocyanin criteria for the risk of water quality, research on this parameter were rare. Brient et al. (2008) cited in their paper the following criteria according to WHO (Brient et al. 2008) for Phycocyanin equivalent to the cyanobacterial number of cells in the waterbody.

Phycocyanin < 30 ±2 µg/L, equivalent to the number of cells < 20 000 cells/ml (Alert level 1) (2)

Phycocyanin > 90±2 µg/L, equivalent to the number of cells > 100 000 cells/ml (Alert level 2) (3)

The pigment Chlorophyll-a is largely associated with phytoplankton biomass in the lake, while the pigment Phycocyanin can confirm the presence of Cyanobacterial species. Hence, in this study, Chlorophyll-a and Phycocyanin from all water samples at the surface and bottom levels will be considered as an estimate of microalgal biomass and cyanobacterial bloom occurrence at the sampling locations and in the waterbody. Both Chlorophyll-a and Phycocyanin are main parameters to be used in the map for estimating and predicting algal bloom patterns.

2.3. Data collection

Water samples and soil samples were taken triweekly or around monthly during the summer time of 2015 in order to monitor all parameters closely and evaluate how they evolved with time. Besides, this frequency of sampling will also indicate the effects of some factors that initiate algal scums, which is useful to establish a management plan for prevention, mitigation and prediction of algal blooms in the future at Mattatall Lake.

The duplicate water samples were systematically taken at 13 different locations (Fig. 2) across Mattatall Lake at three different depths: surface, 2 meters and bottom levels. However, due to the shallow depth of the lake, many sampling locations have the bottom level at around 3 or 4m deep and the variation of measured parameters is not very high between 2-meter level and/or surface or bottom level. Hence, to simplify our analysis, we will just present hereafter the results of the surface and bottom levels. A YSI probe was used to measure multiple *in-situ* parameters including Dissolved Oxygen (DO), pH and water temperature for each depth. All water samples were then analyzed for the presence of Nitrates, Phosphates, Total Phosphorus, Chlorophyll-a and Phycocyanin. Besides, several ponds and brooks, which drain directly into Mattatall Lake, were also sampled at the surface level for testing the presence of Chlorophyll-a, Nitrates, Phosphates and TP (Fig. 3).

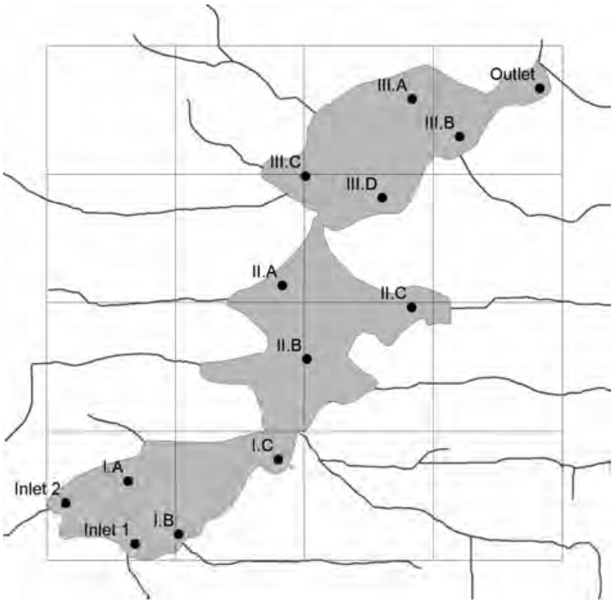

Fig. 2. Water sampling locations in the lake

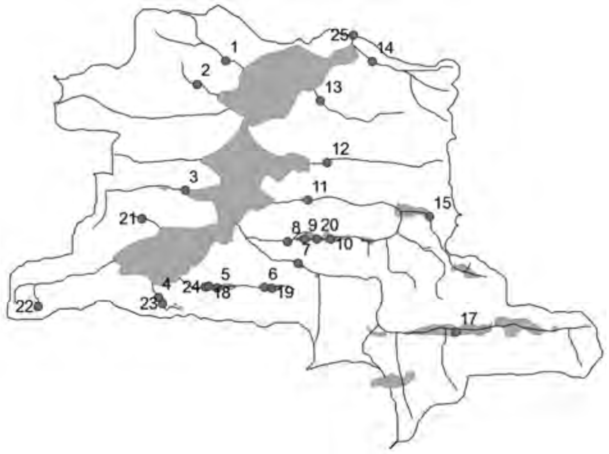

Fig. 3. Water sampling locations at some brooks and ponds

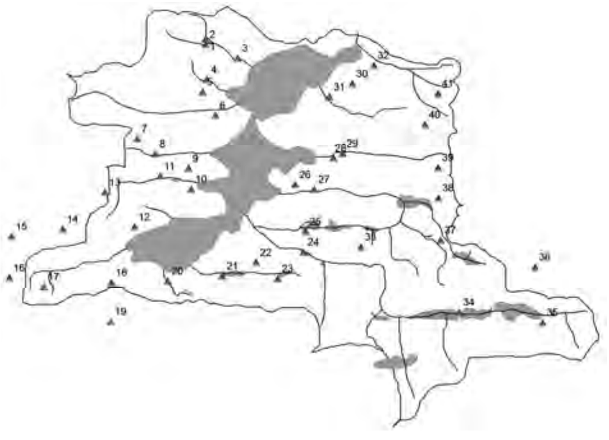

Fig. 4. Soil Sampling locations

The number of soil samples was systematically defined after the watershed boundary had been delineated. Soil samples were also taken double at the depth of 5 inches from the surface at 41 locations within the watershed (Fig. 4). This is to ensure that samples accurately represent the actual soil conditions rather than reflect the effects of other external factors on the ground surface. Those samples were then analyzed for the presence of total Phosphorus.

2.4. Watershed delineation

The crucial data used to delineate watershed boundary is elevation map. A map of 5-meter contour lines was downloaded from Geographic Information Systems Centre (GISC) at Dalhousie University in order to construct a Digital Elevation Model (DEM) by using the "*Topo to Raster*" tool in ArcGIS. The DEM was then used as input data for watershed delineation. The procedure of watershed delineation is presented in Fig. 5. The Nova Scotia Coordinate Referencing System Viewer (NSCRS Viewer) and field observations of brooks locations were used to validate the number of rivers and watershed boundary generated in ArcGIS.

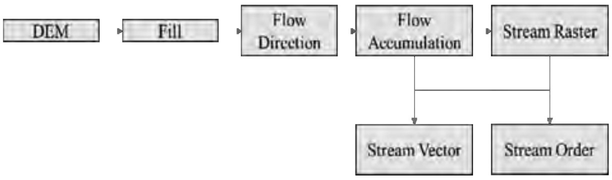

Fig. 5. Flow chart of watershed delineation

2.5. Land-use map

The land use map is indispensable for the natural resource management as well as for the modification of natural environment. Therefore, determining the land use map will help us to identify the sources and causes which might affect most to an increase in nutrients in the lake.

The Landsat 8 imagery produced on June 10th 2015 was used to develop a classification scheme that constructed land use map, and includes 11 bands with 30-meter resolution except for band 8 (15-meter resolution). A composite photograph based on band 5-4-3 was developed and displayed as infrared color, which showed the differences of objectives in practice such as forest, clear-cut, regrowth, buildings, etc. The *Supervised Classification* tool in ArcGIS was used in this process to collect the training samples that distinguished land use types from others. The method is based on the special analysis Maximum Likelihood Classification (ESRI). All three-band values are considered in each pixel during the classification. By creating training samples, a specific range of values is assigned to a single land use type. Therefore, all cells will be classified. The categories used in the classification include blueberry fields, building, grass, regrowth, clear-cut and forest.

The aerial photos downloaded from NSCRS Viewer and field observations were used to validate the land use map generated in ArcGIS. Due to the 30-meter resolution of the Landsat imagery, errors were generated during validation. However, appropriate modifications were made to the land use map to correct those errors.

2.6. Interpolation methods and residuals

The analyzed results from water samples and soil samples were interpolated in Surfer Golden Software to create the distribution maps of the considered parameters such as Chlorophyll-a, Phosphate, Total Phosphorus, and Nitrate which evolve definitely in function of time.

Since only a limited number of samples can be taken over such a large surface area due to the reasons of time and costs, interpolation of each data set is required in order to obtain continuous data over the area of interest. Interpolation is the process where values at locations, with no original data existing, are estimated based on a given data set of some sample points. Therefore, the interrelationship and variability of the examined data across a surface can be determined. Interpolation uses the spatial autocorrelation to determine whether the values are interrelated to find out a spatial pattern (Childs 2004).

From a set of sampling points, the output data is a grid of representation for a surface. It is a continuous surface since for any location with x, y coordinates, a single value of z exists irrespectively on the direction from which that point is approached. A grid consists of rows and columns, which generate an array of equally dimensioned cells. Every cell has a distinct value to express a change in z-value (Childs 2004).

There are two categories of interpolation techniques: *deterministic* and *geostatistical*. Deterministic interpolation techniques create surfaces based on measured points or mathematical formulas and can be divided into two groups, global and local. The global techniques calculate predictions using the entire dataset, whereas the local techniques calculate predictions using measured points within neighborhoods, which are smaller spatial areas within the larger study area. A deterministic interpolation can either force the modeling surface to pass through the data values or not. Geostatistical interpolation techniques utilize the statistical properties of the measured points; quantify the spatial autocorrelation among measured points and account for the spatial configuration of the sample points around the prediction location. Because geostatistical interpolation is based on statistics, these techniques produce not only prediction surfaces but also error or uncertainty, giving an indication of how good the predictions are. An interpolation technique that predicts a value identical to the measured value at a sampled location is known as an exact interpolator. An inexact interpolator predicts a value that is different from the measured value (Childs 2004).

Four methods of interpolation are used in this study including Inverse Distance Weighted (IDW), Kriging, Minimum Curvature and Natural Neighbor. The same set of input data was interpolated in turn with different methods to produce various results, which were mutually compared to choose the best fit with the dataset based on the minimum residual criterion. The latter is defined as the average of the absolute difference between observed data and corresponding predicted values generated from the interpolation method. The average residual should be close to zero to indicate a good prediction model. Hence, the map representing each parameter was finally produced using the best method selected in the validation process. Equation used to calculate the average residual is shown as follows:

$$\overline{R} = \frac{\sum_{i}^{n} |O_i - P_i|}{n}, \qquad (4)$$

where: O_i – Observed value; P_i – Predicted value; $\overline{R}$ – Average residual; n – Number of data used in an interpolation.

Table 1 (a, b, c, d, e) has shown the obtained average residuals for each interpolation method we have calculated. We actually have to choose the method for interpolation with the lowest value of residual and it is clear that the Inverse Distance Weighted (IDW) was our final choice (Table 1 a–e).

Table 1a

Obtained residuals for *Chlorophyll-a* in the lake by each interpolation method (the bold value is the lowest residual)

	Sample ID	Interpolation methods			
		Natural Neighbor	Kriging	IDW	Minimum curvature
Absolute value of residuals	IA	0	6.98E-04	5.83E-06	3.02E-03
	IB	0	1.70E-04	3.80E-07	4.14E-04
	IC	4.70E-04	3.87E-04	7.27E-06	1.84E-06
	IIA	0	3.40E-04	2.53E-06	5.49E-03
	IIB	0	2.75E-03	4.65E-05	6.72E-04
	IIC	8.15E-04	2.59E-05	1.14E-05	1.25E-04
	IIIA	3.55E-03	2.44E-03	4.32E-05	9.02E-04
	IIIB	0	5.29E-04	1.10E-05	1.12E-03
	IIIC	0	6.90E-05	1.82E-06	2.49E-03
	IIID	0	1.01E-04	6.58E-06	1.14E-02
	Outlet	4.50E-03	5.44E-04	4.80E-05	2.40E-03
	Inlet 1	2.77E-04	2.84E-03	8.20E-06	1.34E-06
	Inlet 2	5.50E-04	7.84E-04	2.18E-05	4.49E-03
Average		1.02E-02	1.17E-02	**2.15E-04**	3.25E-02

Table 1b

Obtained residuals for *Phycocyanin* in the lake by each interpolation method (the bold value is the lowest residual)

	Sample ID	Interpolation methods			
		Natural Neighbor	Kriging	IDW	Minimum curvature
Absolute value of residuals	IA	0	6.71E-03	8.44E-04	1.36E-02
	IB	9.75E-03	3.40E-03	2.74E-03	4.54E-03
	IC	0.00E+00	6.06E-03	2.42E-03	1.26E-03
	IIA	1.34E-03	1.50E-03	3.28E-03	3.97E-03
	IIB	3.84E-03	2.31E-03	2.91E-03	2.80E-03
	IIC	1.63E-03	3.66E-03	2.27E-03	2.15E-03
	IIIA	0.00E+00	2.48E-03	3.31E-03	1.73E-03
	IIIB	1.72E-03	1.18E-03	2.27E-03	5.92E-03
	IIIC	4.79E-03	1.83E-03	2.29E-03	3.79E-03
	IIID	9.87E-03	4.05E-03	2.17E-03	7.53E-03
	Outlet	4.55E-03	2.44E-04	4.80E-05	2.04E-03
	Inlet 1	4.77E-04	2.34E-03	2.20E-06	1.34E-06
	Inlet 2	1.50E-04	7.44E-04	1.18E-05	4.05E-03
Average		3.81E-02	3.65E-02	**2.46E-02**	5.34E-02

Table 1c

Obtained residuals for *Nitrates* in the lake

	Sample ID	Interpolation methods			
		Natural Neighbor	Kriging	IDW	Minimum curvature
Absolute value of residuals	IA	0	1.08E-03	4.79E-05	3.32E-04
	IB	2.86E-03	8.03E-04	4.51E-06	1.41E-03
	IC	1.71E-02	1.67E-03	2.43E-05	1.45E-02
	IIA	0	6.61E-03	7.37E-05	1.43E-02
	IIB	0	2.12E-03	1.14E-05	2.54E-04
	IIC	0	1.64E-02	4.87E-04	8.19E-03
	IIIA	0	5.15E-03	1.05E-04	5.39E-03
	IIIB	5.91E-02	9.77E-03	9.99E-03	1.09E-02
	IIIC	1.00E-02	9.29E-03	1.00E-02	3.48E-03
	IIID	8.36E-03	2.08E-06	1.04E-05	1.04E-02
	Outlet	1.55E-03	3.67E-04	7.80E-05	3.04E-03
	Inlet 1	1.77E-04	5.78E-03	2.78E-05	1.57E-06
	Inlet 2	1.90E-04	6.42E-04	1.82E-05	4.78E-03
Average		9.94E-02	5.97E-02	**2.09E-02**	7.70E-02

Table 1d

Obtained residuals for *Total Phosphorus* in the lake by each interpolation method (the bold value is the lowest residual)

	Sample ID	Interpolation methods			
		Natural Neighbor	Kriging	IDW	Minimum curvature
Absolute value of residuals	IA	0	1.46E-04	1.01E-06	6.30E-04
	IB	0	3.40E-04	3.33E-06	3.19E-04
	IC	4.02E-04	3.09E-04	5.35E-06	5.13E-05
	IIA	0	2.24E-06	9.18E-07	9.80E-04
	IIB	0	7.34E-04	1.34E-05	2.35E-04
	IIC	2.76E-04	5.64E-05	4.14E-06	9.98E-05
	IIIA	7.53E-04	4.99E-04	8.18E-06	4.15E-04
	IIIB	0	5.18E-05	2.23E-06	4.14E-04
	IIIC	0	1.57E-04	2.41E-06	3.49E-04
	IIID	0	8.70E-04	1.57E-05	1.37E-02
	Outlet	7.87E-04	4.87E-04	2.45E-06	6.87E-03
	Inlet 1	1.56E-04	1.56E-03	4.88E-05	1.56E-06
	Inlet 2	6.49E-04	1.67E-04	1.35E-05	6.87E-03
Average		3.02E-03	5.38E-03	**1.21E-04**	3.09E-02

Table 1e

Obtained residuals for *Total Phosphorus in watershed soil* by each interpolation method (the bold value is the lowest residual)

Total Phosphorus in soil	Sample ID	Interpolation method			
		Natural Neighbor	Kriging	IDW	Minimum curvature
1	2	3	4	5	6
Absolute value of residuals	1	0.00E+00	7.63E-02	1.43E-02	5.18E-02
	2	3.39E-01	1.69E-01	2.26E-02	2.73E-03
	3	4.52E-01	2.44E-01	1.33E-02	7.77E-03
	4	1.12E+00	5.81E-01	4.30E-02	1.94E-01
	5	1.52E+00	8.50E-01	7.37E-02	1.28E-01
	6	2.81E-01	3.33E-01	1.87E-02	1.01E-01
	7	1.50E-01	2.72E-01	1.51E-02	6.45E-02
	8	7.86E-01	5.33E-01	3.44E-02	2.41E-01

1	2	3	4	5	6
	9	2.36E-01	1.88E-01	2.06E-02	1.54E-01
	10	1.86E-02	1.67E-03	7.50E-03	4.95E-02
	11	1.31E-01	1.23E-01	9.60E-03	8.71E-02
	12	3.20E-01	2.86E-01	1.18E-02	1.17E-01
	13	5.60E-02	6.36E-02	5.73E-04	1.98E-02
	14	2.42E-01	2.11E-01	5.22E-03	9.76E-02
	15	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	16	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	17	2.27E-01	5.26E-02	2.47E-03	4.93E-03
	18	3.58E-01	4.22E-01	1.10E-02	7.53E-02
	19	0.00E+00	5.50E-02	1.06E-02	4.51E-01
	20	8.68E-01	4.97E-01	2.95E-02	4.23E-02
	21	5.98E-01	4.25E-01	4.02E-03	1.94E-02
	22	1.05E-01	8.92E-02	6.90E-03	1.99E-02
	23	2.12E-02	8.70E-02	3.67E-03	5.76E-03
	24	1.61E-01	1.46E-01	9.46E-03	1.17E-01
	25	3.35E-01	2.73E-01	1.72E-02	1.44E-02
	26	8.01E-02	1.12E-01	1.11E-02	4.27E-02
	27	1.21E-01	1.10E-01	5.76E-03	1.65E-01
	28	2.46E-01	1.37E-01	1.66E-02	6.93E-02
	29	7.17E-02	9.03E-02	5.79E-03	1.27E-01
	30	1.80E-03	1.17E-02	7.34E-04	5.19E-03
	31	7.46E-02	3.90E-02	2.87E-03	6.50E-02
	32	0.00E+00	1.04E-02	9.52E-04	8.83E-03
	33	9.80E-02	1.01E-01	7.39E-03	1.32E-01
	34	1.79E-01	2.49E-02	2.16E-03	1.55E-02
	35	0.00E+00	1.44E-02	1.15E-03	3.34E-03
	36	0.00E+00	1.53E-02	9.71E-04	2.84E-02
	37	4.29E-03	1.44E-03	1.14E-03	2.12E-02
	38	7.76E-02	5.29E-02	5.54E-04	1.17E-02
	39	6.50E-02	5.97E-02	3.32E-03	2.98E-03
	40	1.13E-01	7.83E-02	2.21E-03	5.50E-02
	41	0.00E+00	9.73E-03	8.68E-04	7.19E-03
Average		2.31E-01	1.67E-01	**1.09E-02**	6.89E-02

2.7. Prediction of algal development by ANN (Artificial Neural Network) model

The mathematical approach can be a powerful tool to deal with the coupling effects of governing parameters in the bloom occurrence issue. In this part, we simply would like to present some preliminary results of the simulation we obtained to predict the algal bloom in Mattatal Lake. The mathematical model we used is the type of Artificial Neural Network (ANN) model. For a more profound version of algal bloom simulation and prediction by ANN model, we will present in another detailed paper in the near future. Also, for one approach using the statistical approach to estimate the risk of algal blooms, we refer to Ndong et al. (2014).

Inspired by the biological nervous system and artificial intelligence (McCulloch and Pitts 1943), the ANN applied in our project consists of a large number of simple processing elements that are variously called neurons or nodes. Each neuron or node is connected to other nodes by means of direct communication links, each with an associated weight function. The weights represent information being used the net to solve the problem. We suggest the back-propagation multi-layer neural network which is the most common and convenient ANN used in engineering sciences. In this network, nodes are arranged into layers: input layer (data observations), hidden layer(s) (intermediate nodes) and output layer (conclusions). An important step in developing ANN models is to select the input variables that have the most significant impact on the model's performance. A good subset of input variables can substantially improve model performance.

Our study herein is based on a set of five main parameters for the input sets: 1) Total Phosphorus; 2) Nitrate; 3) DO; 4) Water temperature; and 5) pH. The only output in this model (for this preliminary step) is the quantity of Chlorophyll-a, representing for the growth of algal bloom. The design of this experiment used random sampling to cover all equation surfaces. Data collected in the summer months will be summarized in the input table and will be used to design the ANN model. Table 2 as an example shows ten different values among dataset under the form of inputs/output we used for our simulation by ANN. In fact, we did use a data set with one hundred points to train and validate the model (These points were selected from five different field trips done in last summer-fall terms).

Table 2

Example of ten values of data for inputs and output set inserted in the Artificial Neural Network (ANN) model

Inputs X_1 to X_5					Output
Total Phosphorus (mg/L)	Nitrate + + Nitrite (mg/L)	pH	Temperature (C°)	DO (mg/L)	Chlorophyll-a (µg/L)
0.858	0.26	7.18	17.47	10.39	1.60
0.066	0.16	7.18	17.42	10.38	1.56
0.264	0.64	7.17	17.40	10.83	2.32
0.165	0.64	7.17	17.50	10.27	2.10
0.198	0.44	7.15	17.40	10.97	3.11
0.099	0.18	7.06	16.84	10.89	1.28
0.033	0.58	7.18	17.90	10.29	1.88
0.066	0.16	7.17	17.60	10.60	1.92
0.066	0.4	7.13	11.30	17.40	2.49
0.297	0.54	7.15	10.07	17.90	2.07
…	…	…	…	…	…

Precisely for this study, a neural network was designed with five input nodes and one output node. Five input nodes represented by variables $X_i=1$ *to* 5 stand for five main parameters we mentioned above. One output node is represented by *Y* standing for Chlorophyll-a (Fig. 6).

3. Results and Discussions

3.1. Watershed boundary and land use map

The delineation of the Mattatall Lake watershed and sub-watershed boundaries resulted in a total area of about 10.3 km^2, including 14 main sub-watersheds (Fig. 7). There are also 14 main brooks flowing directly into the lake. It is noted that the largest sub-boundary is located in the southeast of Mattatall Lake. We also observed that there were multiple natural beaver dams, located in sub-watersheds 1, 8, 10 and 11 (areas numbered in Fig. 7), and some of them contained visible algae blooms.

The land use map generated from satellite images (Fig. 8) indicates that the majority of land in the Mattatall Lake watershed are forest (very light color) and regrowth (dark color). Agricultural areas are minimal within the watershed. However, there is a proportion of a single wild blueberry fields and domestic gardens. According to responses from the conducted survey sent to all lake residents, there has been a rapid urban development within the last four years along the northern shoreline of the lake.

3.2. Distribution of TP in soil within the watershed

To have a general idea about nutrient source in the watershed, we collected the data from soils and build the first distribution map of TP concentration within the watershed in the summer months of 2015 (Table 3 and Fig. 9a). From this TP map for the whole watershed, we can observe that the highest concentration of TP is at the south part where there is a brook linking the beaver dam to the lake (sub-boundaries 6, 7 and 8 in Fig. 7).

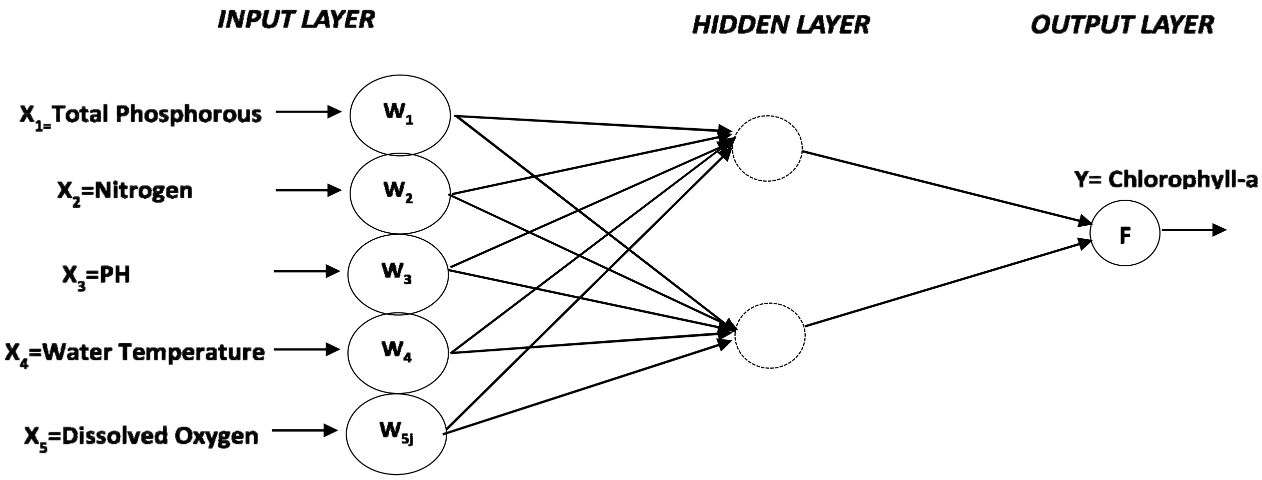

Fig. 6. Multilayer ANN model for Chlorophyll-a development

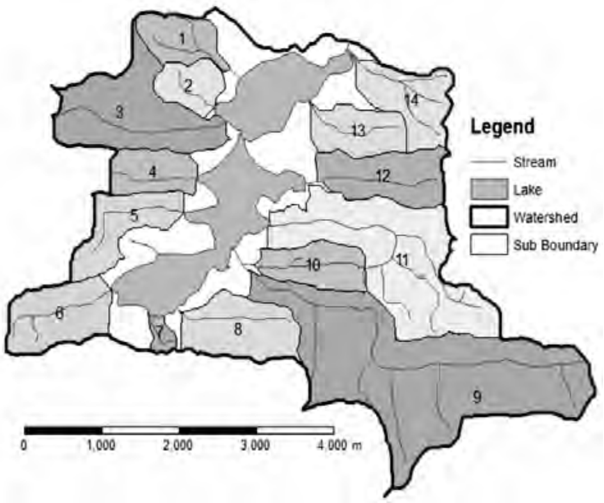

Fig. 7. Resulting map displaying the delineated watershed and sub-boundaries

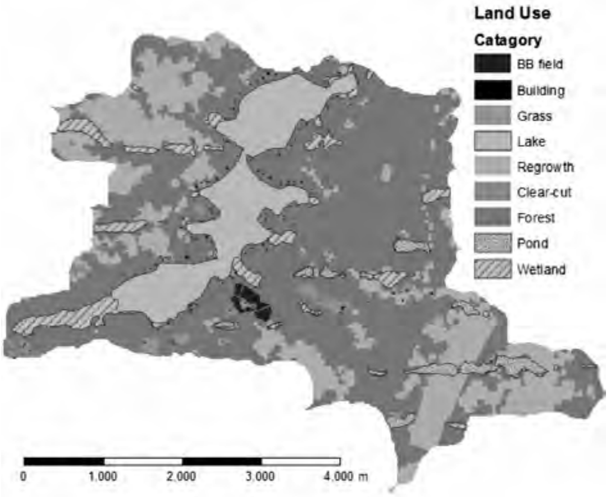

Fig. 8. Land use map of the Mattatall Lake watershed

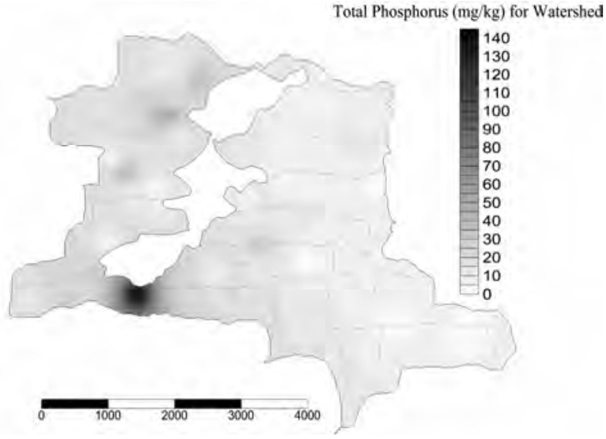

Fig. 9a. Distribution of Total Phosphorus in the entire watershed – Summer 2015

The second section of the high Phosphorus concentration is located in the north-western region, including sub-boundaries one, two and three (Fig. 7).

Table 3

TP measured in the watershed during the summer 2015

Location	X coordinate	Y coordinate	TP (ppm)
1	-7063335.5668	5699774.4844	8.1
2	-7064725.4203	5700313.8283	3.2
3	-7064977.3387	5699891.9604	15.2
4	-7064777.5433	5701140.9174	6.0
5	-7064190.1671	5701566.2360	8.5
6	-7063512.8905	5700762.8217	11.5
7	-7066605.0978	5699893.6714	8.6
8	-7067660.4457	5698631.6207	19.8
9	-7066919.3904	5698654.7648	141.1
10	-7067747.1655	5699848.7580	17.9
11	-7067020.6844	5700068.2965	10.5
12	-7067357.2351	5699384.0826	5.8
13	-7068304.3130	5699354.1847	27.4
14	-7069014.4561	5698698.0167	17.9
15	-7068981.9564	5699253.2239	3.6
16	-7067673.0600	5698106.7820	54.9
17	-7068557.4918	5698576.3478	12.6
18	-7065120.4407	5699042.2549	12.2
19	-7066191.5835	5698720.6711	22.9
20	-7065462.9975	5698686.5268	20.8
21	-7065091.8583	5699318.7729	26.0
22	-7065989.0597	5701662.2879	35.0
23	-7066416.7244	5701925.6991	10.4
24	-7066400.5127	5701372.1207	17.7
25	-7066455.9389	5701205.3266	52.2
26	-7067083.3331	5700368.5995	35.9
27	-7066284.8693	5700889.8169	9.5
28	-7067320.6971	5700574.8233	6.8
29	-7065750.3130	5698905.3699	9.2
30	-7064473.9238	5701316.8157	8.5
31	-7064360.4893	5699109.6073	1.4
32	-7063061.6134	5698232.8176	2.4
33	-7066643.9860	5700174.0686	3.8
34	-7066420.0111	5701849.3222	6.8
35	-7061962.3356	5698093.8891	2.7
36	-7062061.6106	5698842.3129	4.6
37	-7063307.1837	5699203.7911	4.8
38	-7065230.5220	5699953.7039	6.1
39	-7064600.3053	5700373.5478	7.4
40	-7063338.4319	5700184.5446	2.5
41	-7063338.4319	5701184.5447	8.4

The southeast part corresponding to the sub-boundaries 9, 10 and 11 consisting mainly of forest, a few residences with lawns and a number of ponds and wetlands contribute also to the nutrient source of the lake. Tables 4a and 4b present the indication of brooks and ponds as well as their related data we obtained in the middle of summer.

Table 4a

Brook and pond water sample results
for the July 20, 2015 field trip
(samples taken during periods of heavy rain)

ID[1]	Sample Name	TP (mg/L)	Chlorophyll-a (µg/L)
1	Brook 1	0.066	0.59
2	Brook 2	0.165	1.11
3	Brook 3	0.099	1.78
4	Brook 4	0.264	2.84
5	Pond 5	0.264	3.96
7	Brook 7	0.231	0.7
8	Brook 8	0.033	7.74
9	Pond 9	0.033	5.38
10	Pond 10	0.132	8.71
11	Brook 11	0.231	2.25
12	Brook 12	0.132	5
14	Brook 14	0.264	3.16

Table 4b

Brook and pond water sample results
for the field trip from July 30 to August 17, 2015

ID[1]	Sample Name	TP (mg/L)	Chlorophyll-a (µg/L)
1	Brook 1	0.033	1.0
2	Brook 2	0.099	0.1525
3	Brook 3	0.033	0.881355932
4	Brook 4	0.099	0.582142857
5	Pond 5	0.033	3.277310924
6	Pond 6	0.033	2.531746032
7	Brook 7	0.066	1.563218391
8	Brook 8	0.066	3.130434783
9	Pond 9	0.066	1.747663551
10	Pond 10	0.033	4.55
11	Brook 11	0.066	13.41463415
12	Brook 12	0.033	0.656
13	Brook 13	0.066	0.222222222
14	Brook 14	0.066	0.092771084
15	Pond 15, brook in the pond	0.033	0.807692308
15	Pond 15 algae	0.033	114.3076923
17	Pond 17	0.033	1.979591837
18	Brook 18	0.033	6.373831776
19	Brook 19	0	5.533898305
20	Brook 20	0.066	7.926829268
21	W1	0.462	0.08
22	W2	0.264	6.25
23	W3	0.099	0.76
24	W4	0.198	0.86
25	W5	0.297	0.64

[1] Identification given in Fig. 3

A single brook located in the sub-boundary 7 (indicated in Fig. 7) also through that region of high Phosphorus concentration and could be a contributing factor to the consequence of the higher nutrient levels in the southern section of Mattatall Lake.

3.3. Evolution of TP in the lake

Fig. 10 shows the evolution of TP in the lake waterbody during the summer time. It is noticed that the concentration of TP was regular from June to July and dramatically increased in August *(beyond 0.4mg/L)*, especially in October. The high concentration of TP detected since September in the south part of the lake where the inlet of the lake receives the water from brooks with very high levels of TP as well. We were also able to notice the occurrence of many blooms everywhere on the south section of the lake with high concentration of TP. That might be explained by the facts that: 1) the area of watershed, which is adjacent to the lake southern part, has also the high concentration of TP (Fig. 9a); 2) nutrient flows by rainfall-runoff and washed out directly into the lake waterbody. This assumption is confirmed by the fact that the TP continued to increase until October 2015, but the main component of TP was mostly under the organic form. This matter strongly confirms that there is an interrelationship between the lake and its watershed, and the unhealthy situation of the watershed affects significantly on the quality of the lake water. Fig.9b has shown a significant effect of TP from watershed on the TP level in the lake waterbody. The values of TP in the lake (Fig. 9b) were measured on September 10th 2015, after three days of heavy rains since August 27. More specifically, from Fig. 10, we can see that, since September 10th, TP spreads all over the surface of the lake and is concentrated mostly in the north due to the direction of flow South-North into outlet (the outlet is indicated in Fig. 2), with a permanent area of high concentration in the south. On October 4th the concentration in the south increased and spread northwards. There is also a section of the middle (east) with a high concentration. At the end of October, the concentration of TP has spread over the lake, and the high point in the south is still persisting. The highest concentration of TP is located in the north (Section III) area of the lake.

It is interesting to note that by the wind data obtained from our weather station, during the period of September-October in Mattatall Lake, there were no strong winds. The average wind speed was less than 2 m/s with maximum values around 5 m/s in some days. For example, on Sept 7, the maximum wind speed was 4.78 m/s South direction with gust speed over 10 m/s South-East direction; Oct. 10 with maximum speed of 4.28 m/s; Oct.17 and 20 with maximum speed of 4.03 m/s South-East direction). So, the fact that TP increasing and spreading all over the lake may not be associated with circulations by strong winds but possibly with other factors such as algae development and detritus as well as with the nutrient provided from the watershed.

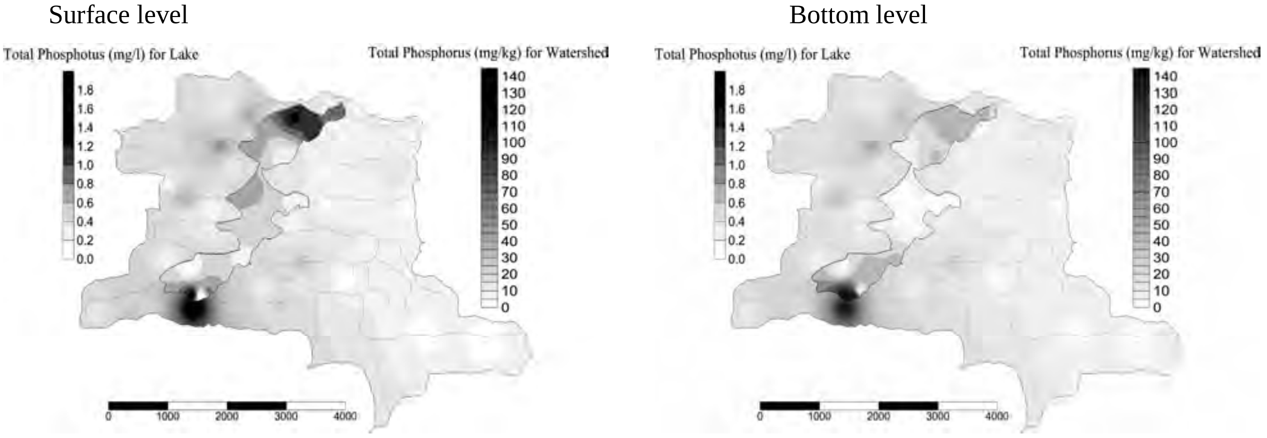

Fig. 9b. Total Phosphorus distribution in the lake waterbody affected by the watershed in September 2015
(Left: TP at the lake surface – Right: TP at the lake bottom)

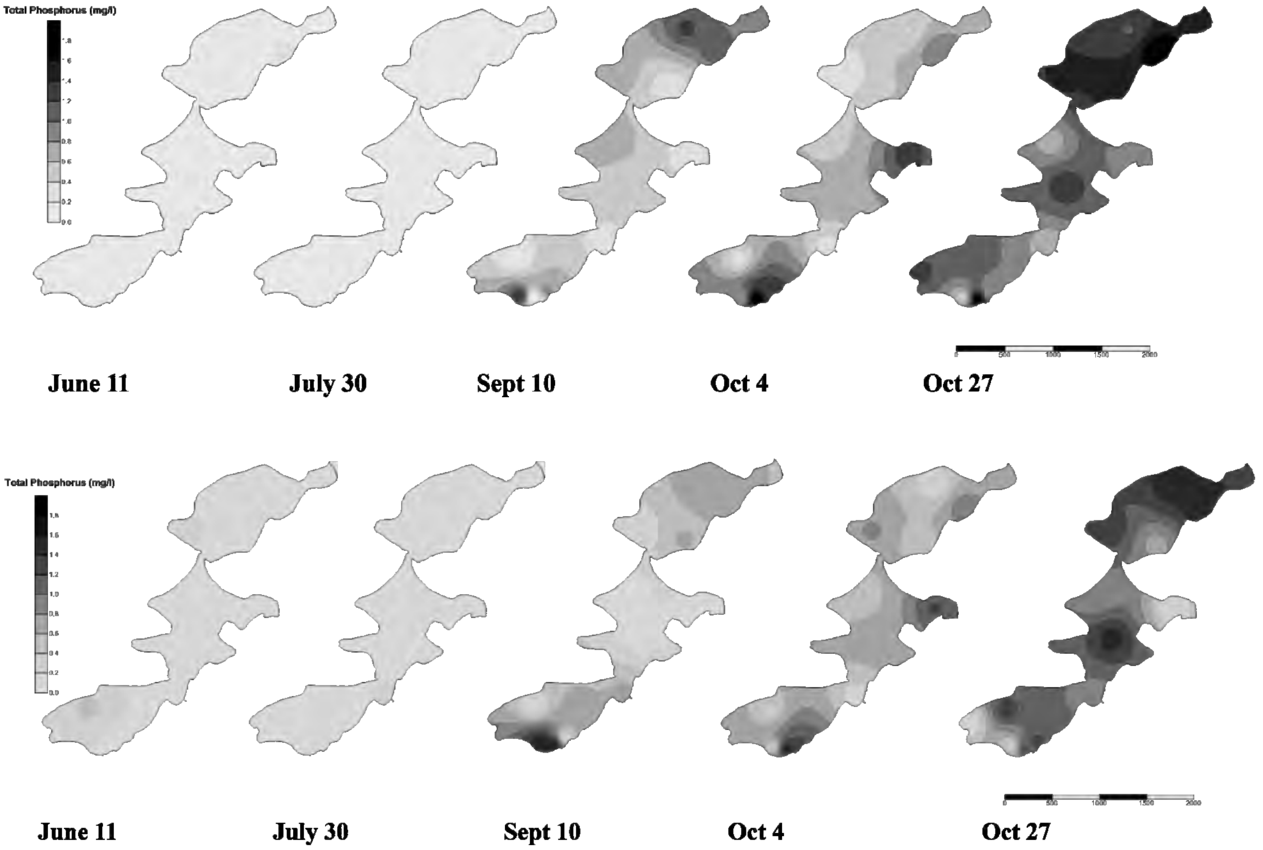

Fig. 10. Spatial and temporal distribution of TP at the lake surface (above) and bottom (below)

At the surface

It is also noted that the point IAI in the South section is very particular because due to the higher values of Phosphates at the surface level comparing to others locations. The values of Phosphates at this point were recorded as 0.3 mg/L (August 17), 0.15 mg/L (Sept 10) and 0.32 mg/L (October 27). That might be explained by the fact that there were some contaminant sources from the watershed side streaming to this location.

At the bottom

Data from June showed small concentrations in the south end of the lake, and in July, those concentrations were gone. In September, the south end of the lake began having a high concentration. There was also a section in the north that had a high concentration. The south concentration appeared to spread north in the month of October, and the middle of the lake had the presence of TP. On October 27th most of the lake had a high concentration of TP, but the highest areas were the north and the middle.

3.4. Evolution of Nitrates in the lake

The evolution of Nitrate distribution is mapped through Fig. 11. The region of higher Nitrates concentration consists mainly of regrowth and has experienced the most developed urban zone in the past four years.

At the surface

The first results from June showed that the concentration of Nitrates was relatively constant throughout the lake. However, there was a point in the north of the lake (section III) where the concentration was very high. In July, the high concentration in the north was gone. The Nitrate levels were still constant, except there were several small areas of Nitrates on the lake (south, middle and north sections). The concentration remained constant into September, however, in the south area of the lake there was a small area with a still high Nitrates concentration (around 1.00 mg/L), and it could be strongly associated with Brook 1 and beaver dam where we obtained a high Nitrate concentration (2.5 mg/L) on August 17. Nitrate levels in October have stayed the same and even decreased comparing to previous months.

At the bottom

The pattern of Nitrate distribution on the bottom of the lake is similar to the surface in June: the high concentration point in the north end. There were also small areas in the middle and south area of the lake with a higher concentration. Nitrate levels in July were with the highest concentrations. It should be noted that the very high concentrations, more than 1 mg/L, started from point IC going to the North direction to point IIIA. After July, Nitrates decreased significantly and were almost identical to the values measured from June, except for the high point near to the outlet of the North section. The concentration of Nitrates lowered throughout September and October. In those two months, Nitrates spread more evenly over the bottom of the lake, with a slight increase on October 27th.

The very high level of Nitrates accidentally happening in June-July might be explained by the clear-cutting of large areas of forest, affecting the concentration of dissolved nutrients in the runoff water, the beaver damps leaking and many other dissolved organic matters after springtime.

3.5. Evolution of Chlorophyll-a

The maps of Chlorophyll-a distribution are successively displayed from Fig. 12. The results show the low level of Chlorophyll-a (*2µg/L)* at all levels in the waterbody until June 2015. This can be explained by the fact that the weather, water temperatures and PAR (Photosynthesis Active Radiation), even high during May and June, but needed the accumulation time to support the biomass growth. That was why the Chlorophyll started higher in July and some blooms also appeared from this month of July. In Fig. 12, the very dark color displays the high concentration of Chlorophyll-a appearing from July to September 2015. It is interesting to notice that those bloom locations correspond to algae bloom places observed by the lake residents in the fall 2014.

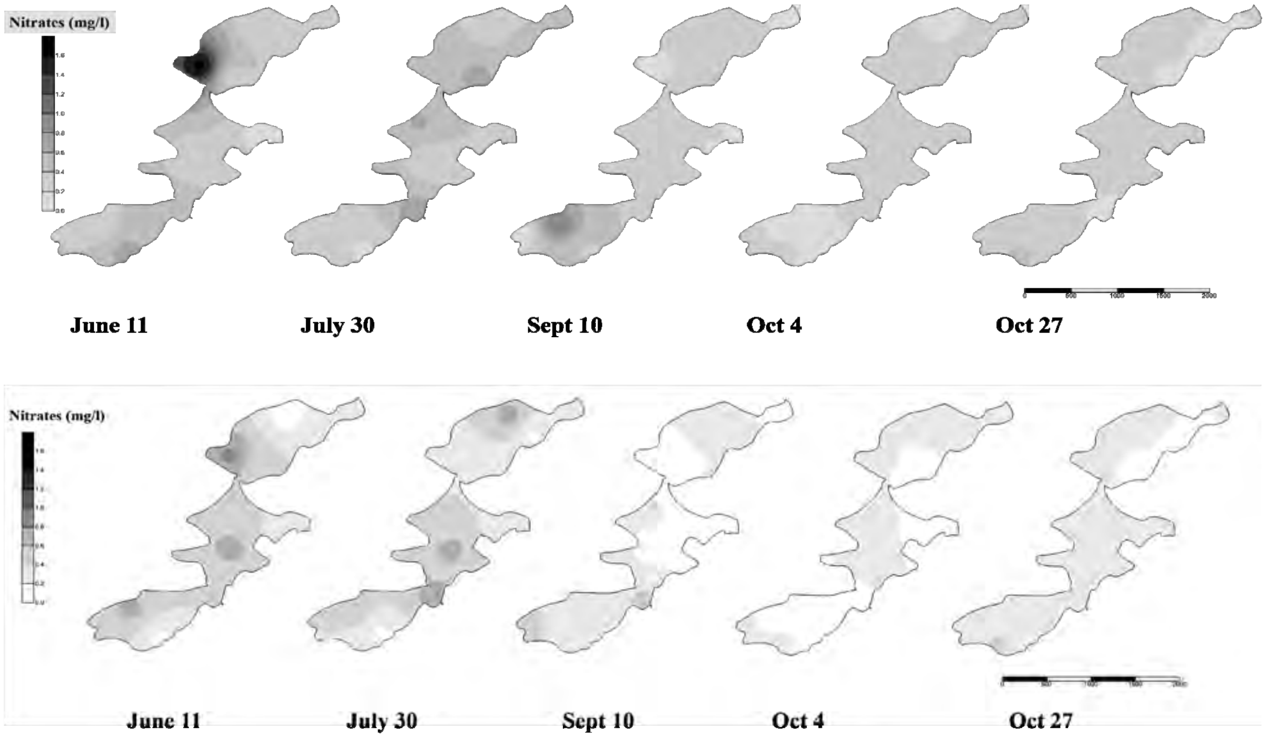

Fig. 11. Spatial and temporal distribution of Nitrates at the lake surface (above) and bottom (below)

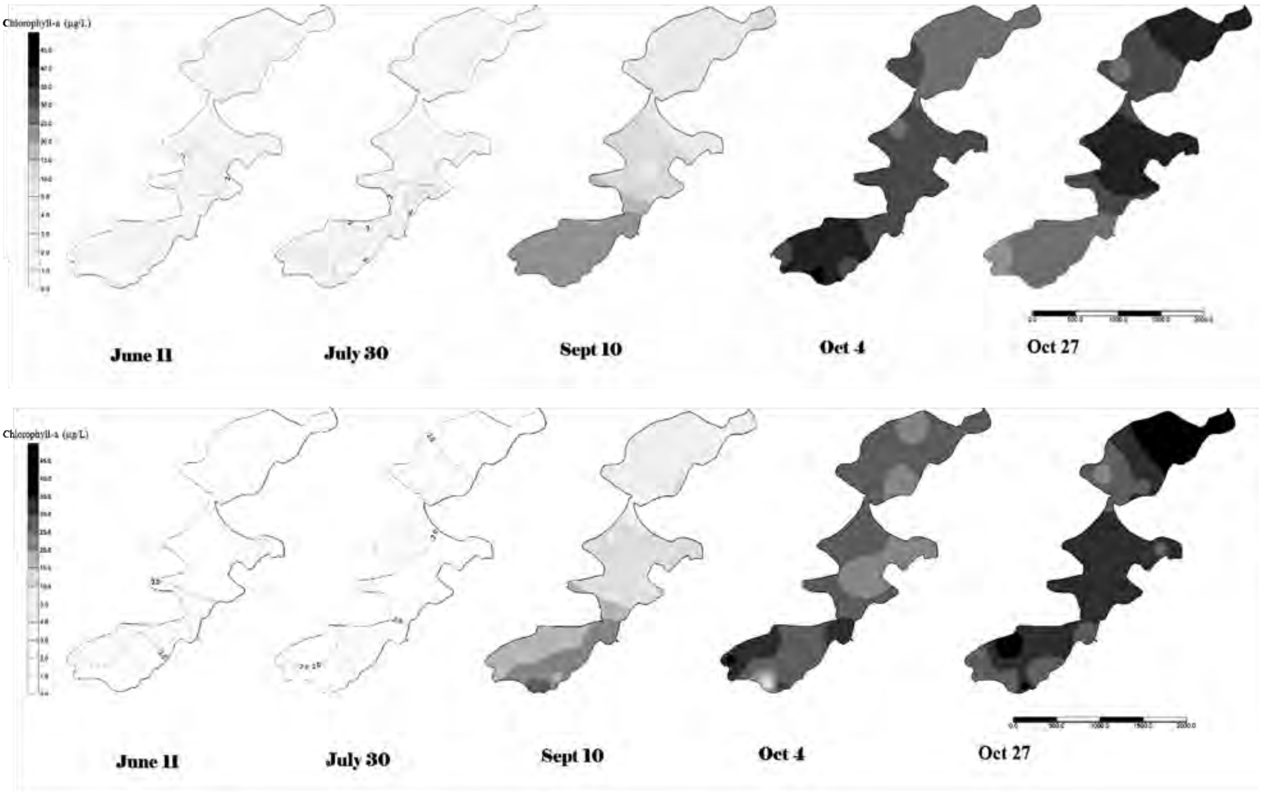

Fig. 12. Spatial and temporal distribution of Chlorophyll-a at the lake surface (above) and bottom (below)

In those areas, a higher supply of nutrients is available for the uptake by algae. The results in September shows that high concentration of Chlorophyll-a everywhere especially the south part of the lake. It was observed that lake water turned in green, and algal blooms were detected over the entire area in this time as well. The high detection of Chlorophyll-a does not suggest the presence of a bloom but rather identifies those locations to have more favorable conditions for the development of an algal bloom. Other tests to identify the biomass species will need to be performed in order to determine the locations of cyanobacteria algal blooms. More specifically from June, we can observe that:

At the surface

The levels of Chlorophyll-a in the lake from June 11th to July 30th were low, less than 2 µg/L. When the lake was tested in September, it was noticed that the Chlorophyll-a concentration increased. The south end (section I) of the lake had the highest concentration on that day. The transition into October showed how the concentration increased and spread northwards due to the domination of South wind. The highest amount of Chlorophyll-a still remained in the south part of the lake. The results from October 27th showed how the Chlorophyll-a concentration continued to travel north, with the highest amount being in the middle and north parts of the lake (Sections II and III).

At the bottom

The bottom of the lake followed the pattern of the surface for the months of June and July: low levels of chlorophyll-a. In September, the concentration was higher in the south section of the lake, similar to the surface, except a smaller area on the bottom. The Chlorophyll-a spread throughout the bottom of the lake in October like other elements (TP and Nitrates) due to strong winds. The concentration of Chlorophyll-a on October 4th is highest in the south part of the lake and from October 27th data the concentration flowed to the north section of the lake. Generally, during the September-October field trips, Chlorophyll-a concentration at the bottom level showed that the development of algae blooms seemed more concentrated from the middle of the lake, the location near inlet parts, and the point IAI. Certainly, wind factors influence on all water column in the lake and due to the shallow depth, strong winds can mix water from the bottom to the surface level and vice-versa.

3.6. Evolution of Phycocyanin

The evolution of Phycocyanin during the summer is presented from Fig. 13. Cyanobacteria occurrence and dominance have increased from June to September. It is found that the southern part of the lake has the highest concentration of Phycocyanin (approximately 50 µg/L), and Phycocyanin presents relatively highly over the lake.

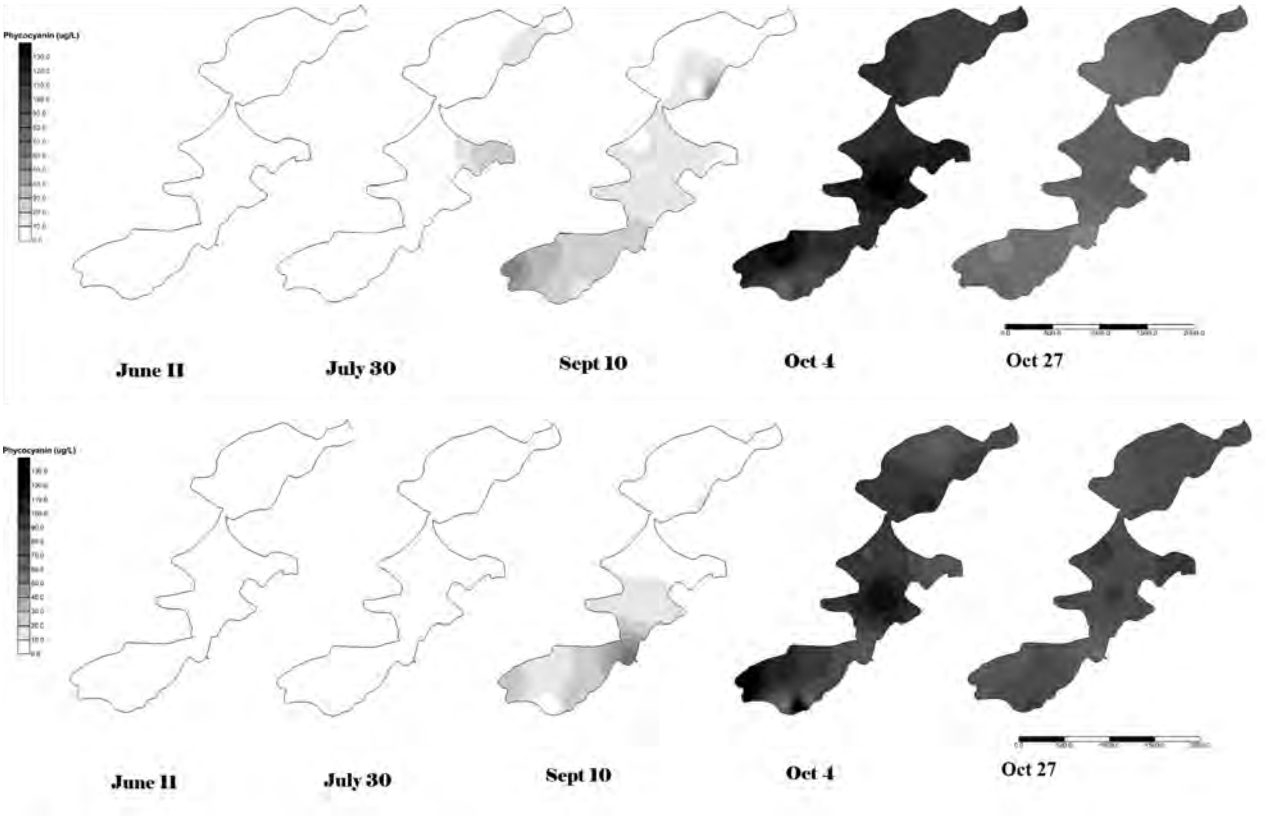

Fig. 13. Spatial and temporal distribution of Phycocyanin at the lake surface (above) and bottom (below)

At the surface

In June, there was little presence of Phycocyanin on the surface of the lake. Phycocyanin was not present until July 30th in the middle-east and north sections of the lake. On September 10th most of the surface was covered with a low concentration except for a small section in the far north. Early October on the lake had the highest concentration of Phycocyanin. The whole lake was covered and the concentration was above 110 µg/L. The south and middle sections of the lake had the highest concentration on October 4th. On the 27th of October the lake was still covered, but the concentration had lowered to approximately 80 µg/L. The highest concentration is in the north of the lake as well as the middle.

At the bottom

There was no presence of Phycocyanin in the lake in June or July. The first appearance was in September. The Phycocyanin was in the south end of the lake and spread into the middle section. The pattern of Phycocyanin on October 4th was very similar to the surface, except the concentration was lower. On the October 27th the concentration was lower than the 4th, and the distribution was still over the bottom of the lake.

The presence of Phycocyanin recorded since the end of July beginning of August has shown an increasing tendency of cyanobacteria in the lake, and the dominant species was identified as *Anabaena planctonia*. The June-July data showed that blooms made the value of Chlorophyll-a increasing, but with no Phycocyanin presence, due to a dominant nontoxic species named *Mougeotia sp*. In other words, algal blooms in Mattatall Lake in the summer time (June to August) were affected by nontoxic species *Mougeotia sp.* while algal blooms in fall and winter time were due to toxic cyanobacteria *Anabaena planctonica*, and hence the *Phycocyanin* increased all over the lake. This scenario, investigated and detected via our field data and shown herein with the mapping process, was well fitting with the results given by our various taxonomic tests. To have a more profound insight of taxonomy in Mattatall Lake, we will present all details in another manuscript which is currently prepared.

3.7. Simulation and prediction of algal development by ANN model

Figure 14 shows the relationship between TP and chlorophyll-a. The simulation has the starting TP value set to 0 mg/L, while the beginning Chlorophyll-a value is approximately 20 µg/L (that was the value of Chlorophyll-a when we started our study in this season). As time passes and TP is increased, the concentration of Chlorophyll-a slowly increases. Once the value of TP surpasses 0.25 mg/L, the concentration of Chlorophyll-a increases fairly sharply. Once the TP value is over 0.7 mg/L, the Chlorophyll-a value plateaus at 90 µg/L.

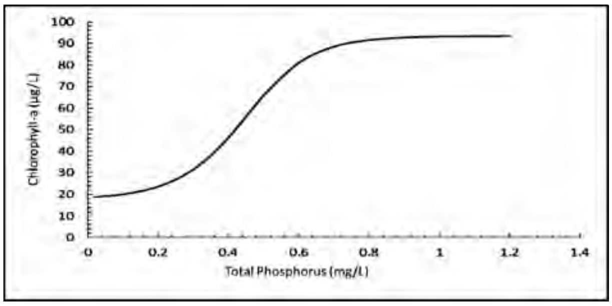

Fig. 14. TP versus Chlorophyll-a development

Fig.15 compares the value of Nitrates to the concentration of Chlorophyll-a. Comparing two figures 14 and 15, it is clear that Nitrates do not have as fast an effect on the Chlorophyll-a as TP does. The level of Nitrate starts at 0 mg/L (again, initial value of the study after winter season), and the predicted value of Chlorophyll-a is 12 µg/L. The concentration of Chlorophyll-a increases slowly until the value of Nitrate is 0.6 mg/L. At this point, the value of Chlorophyll-a increases at a steeper slope until Nitrate reaches 1.6 mg/L.

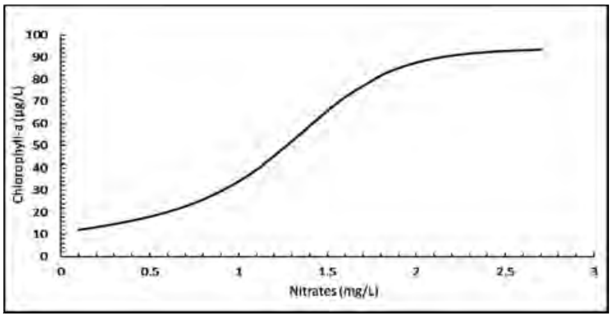

Fig. 15. Nitrates *versus* Chlorophyll-a development

The temperature has a very visible effect on the Chlorophyll-a concentration (Fig. 16). We can see from the simulation if the temperature goes beyond 30 °C, the Chlorophyll-a decreases and tends to zero when temperature reaching 35 °C. It means phytoplankton cannot survive the high temperature above 35 °C. The simulation also shows when the temperature decreases to the low values less than 11 °C, there is a sharp decrease in the value of Chlorophyll-a. The maximum value of Chlorophyll-a in function of temperature obtained by simulation is around 42 µg/L at 11 °C (Fig. 16).

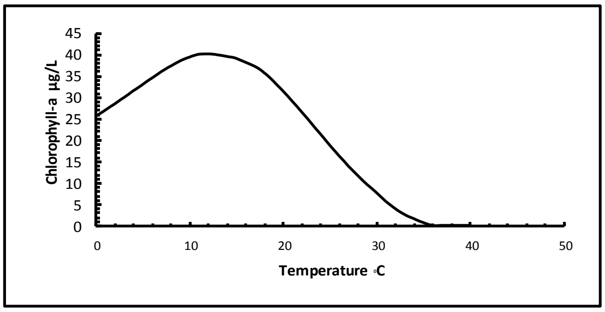

Fig. 16. Water temperature *versus* Chlorophyll-a development

DO is another parameter that effects the levels of Chlorophyll-a. Fig.17 shows the relationship between DO and chlorophyll-a. DO starts at approximately 2 mg/L and Chlorophyll-a at 30 µg/L. As the value of DO is increased, the Chlorophyll-a concentration slowly decreases until DO reaches 8 mg/L. Once the value of DO surpasses 8 mg/L, Chlorophyll-a starts to increase with DO until the maximum predicted value of 37 µg/L is reached when DO is around mg/L. This ‘win-win’ relationship between DO and Chlorophyll-a showed also an inverse effect, that means when DO can increase by the fact that when the algae develop (Chlorophyll-a increasing), the photosynthesis of diverse species of algae release more oxygen to the waterbody.

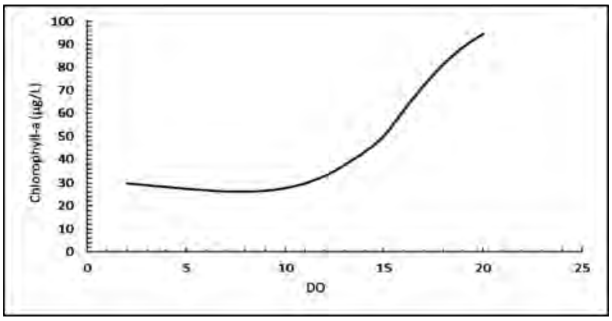

Fig. 17. DO *versus* Chlorophyll-a development

The prediction for pH appears to have an error starting out (Fig. 18). The value of Chlorophyll-a is in the negative numbers until pH reaches the value of 7. Out of all the single effect parameters, pH appears to be one of the top parameters to effect Chlorophyll-a concentration, next to temperature. When the pH value exceeds 7, the Chlorophyll-a concentration sharply increases. This increase stopped once the pH reaches 9, and once that value is exceeded, the Chlorophyll-a concentration slightly decreases to a plateau of 80 µg/L (Fig. 18).

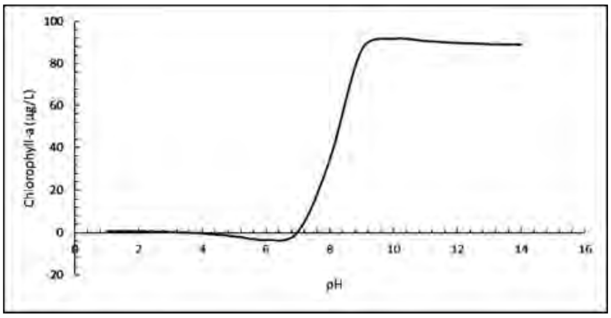

Fig. 18. pH *versus* Chlorophyll-a development

Figs. 19 and 20 show the coupled effects of duo-parameters on Chlorophyll-a concentration. The first figure (Fig. 19) presents the effect of DO and TP on Chlorophyll-a concentration. As both TP and DO are increased, the concentration of Chlorophyll-a increases as well. If the values of TP and DO are set to their maximum (5 mg/L and 13 mg/L respectively) the

Chlorophyll-a concentration will be at its highest: 70 µg/L. From this simulation, we can see that essentially no high levels of Chlorophyll-a until 375 TP and 10.5 DO, that means if just single effect of TP of DO, we cannot have the Chlorophyll-a values, i.e. no algal development. In other words, the single effect of TP or DO cannot trigger the blooms. The same remark can be made when we consider the duo TP and Nitrates (Fig.20), as they appear to have a stronger relationship than TP and DO. As TP and Nitrates are increased, so is Chlorophyll-a. The maximum value of Chlorophyll-a (100 µg/L) is predicted when TP and Nitrates are at their maximum; 6 mg/L and 1.8 mg/L respectively. Again, the single effect of Nitrates or TP even when they are very high cannot be significant for the Chlorophyll-a quantity hence the bloom development.

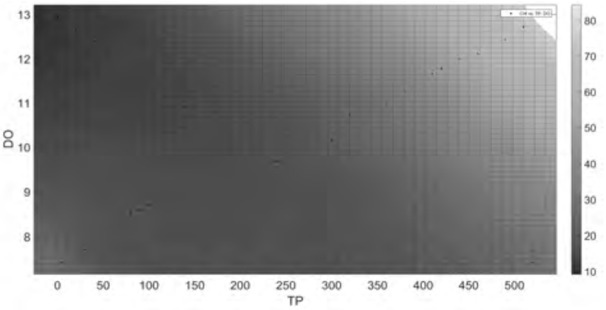

Fig. 19. Duo-effects of TP and DO on Chlorophyll-a development

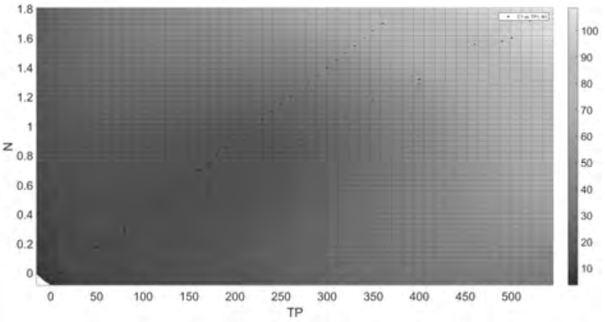

Fig. 20. Duo-effects of TP and N on Chlorophyll-a development

4. Conclusions

Recently toxic massive algal blooms of *Anabaena planctonica* trigged in Mattatall Lake (Canada) in a worrisome way, and persisted until the wintertime. The duration of this phenomenon was extremely unusual: starting from July and coexisting with icy conditions until late December. This issue has caused the lake residents to suffer. This study hence examined the evolution of chemical factors Nitrates and Total Phosphorus and the biological consequences via two parameters Chlorophyll-a and Phycocyanin in water samples collected from the lake and TP in soil samples in its watershed by using a predetermined, regularly spaced, grid sampling design for mapping. With GIS and remote sensing approach, we can gather the useful information regarding land cover change, and compile spatial distribution maps of sampling parameters, which serves as an indicator for algal blooms in the lake. The findings show that there is a strong relationship between Mattatall Lake and its watershed and a mutual effect.

As other lakes, the main supply of Mattatall Lake is from its own watershed including brooks and tributaries. Soils within watershed, which are contaminated by human or natural activities, will certainly affect the water source flowing into the lake. For example, some cottages on the southwestern shore were built at the same level of the lake. Hence, there is a risk of leaching septic tanks into the lake. Other possible reasons making the nutrient level of the lake higher could be the decomposition and defrosting of various organic materials that had been frozen through the winter and spring periods. Multiple brooks flowing into Mattatall Lake pass through the higher Phosphorus concentration areas year round by human activities (clear-cutting, spraying, etc.). Consequently, dissolved nutrients coming from those sources by rainfall-runoff and/or brooks wasting directly into the lake contribute to the growth of nutrient level on the lake waterbody.

It is evident that the south section also was the place where algal blooms were first observed in this season, and hence *Chlorophyll-a and Phycocyanin* are found to be high due to the development of massive algal quantity including cyanobacteria species. However, the reason of the high total Phosphorus concentration in watershed in the south part has not been well determined yet. Changes of the lake and its surrounding environment, especially watershed need to be reliably assessed from further studies to find out the primary causes of algae blooms. One of the future investigations is how to define the *accurate correlation* between nutrients from the watershed streaming into the lake waterbody.

Although the data are just collected consecutively during one summer and fall season (2015), and we need to continue more sampling next several years for a complete database of Mattatall Lake and for a more advanced model of the prediction and prevention. The novelty and innovation of this study rely on a systematic investigation and the suggested methodology for a standard process. This study could certainly serve as a pilot study for many lakes that unfortunately have the same worldwide issue under the global warming and climate change effects. A lake turns green is not good for anyone, not for the residents (they cannot use their own lake for all purposes, and there will be the drop in property values), nor for the visitors (the lake would be closed for their recreational use), and not the municipal councils (loss of tax revenue). The greater the degree of human activity, the greater the risk for the lake water quality. Moreover, we hope that the findings of this study should be a good solid scientific evidence and advice to inform the related administrative authorities at *all levels* for many lakes with the same issue.

Acknowledgements

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PROSPECTS OF USING PET WASTE FOR ENVIRONMENTALLY FRIENDLY MINERAL FERTILIZERS

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Abstract. The article presents the technological possibility of using PET wastes for encapsulation of granulated mineral fertilizers. The schematic flowsheet is proposed to obtain film-forming composition. An encapsulated ammonium nitrate with predictable kinetics of fertilizer components release was obtained.

Key words: polyethylene terephthalate, wastes, encapsulated fertilizers.

1. Introduction

Polyethylene terephthalate (PET) is a strong, firm and light weight material of new generation. PET physical properties make it an ideal one to be used in different fields: production of packaging (bottles, aprons, etc.), films, fibers, structural elements. The used bottles are the main kind of PET waste. Currently, more than 10,000 tones of PET chips per month are imported in Ukraine. The bulk of material in the form of bottles is directed to the markets, so it eventually becomes waste. Only 1,000 tones of PET waste per month are recycled, the rest is stored at landfills and garbage dumps or piled up along roadsides [1, 2]. It is reasonable to study the use of PET waste for encapsulation of granular fertilizers. Encapsulated fertilizers are characterized by a high rate of mineral nutrients assimilation by plants. Hence, the required dose and multiplicity of applied fertilizers, as well as environment pollution by residual agrochemicals are reduced. Despite the advantages of encapsulated fertilizers in comparison with traditional ones, mainly nitrogen fertilizers are produced. The world production of encapsulated fertilizers is only 0.4 ÷ 0.5 % [3] in spite of a significant number of developed film-forming materials [4, 5]. The reason is a high cost compared to usual granular fertilizers. Thus, the investigation of waste use for fertilizers encapsulation is an urgent problem, because the cost of fertilizers production will be reduced and economic attractiveness for agriculture will increase.

2. Investigation Materials

For the investigation we used PET package waste in the form of flakes and granular mineral fertilizer – ammonium nitrate. Polyethylene terephthalate is a polyester obtained via teraphthalic acid polycondensation (Fig. 1).

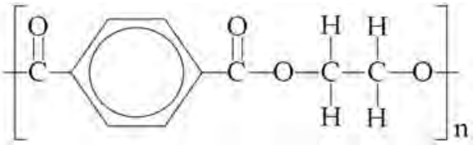

Fig. 1. Schematic drawing of PET molecule fragment

3. Results and Discussion

At the production of encapsulated mineral fertilizers the polymers are used as a basis of film-forming composition. Polymeric materials allow to obtain long-acting fertilizers with predicted properties and minimal thickness of the covering. The use of waste for encapsulated fertilizers production may be represented in the following way:

- collection of used PET products;
- primary processing of waste;
- obtaining of film-forming composition;
- encapsulation of granular fertilizers.

Collection of used PET products. PET waste is already formed during products manufacturing as technological residues or spoilages. This is industrial waste, its processing requires minimal costs, and as a rule, it is usually re-used at the enterprises as a feedstock. The main part of PET waste is formed after use of packaging. The sources of such waste formation cover a wide area. In this case, it is necessary to collect and deliver waste to the plant, where its primary processing takes place. In the city of Lviv separated collection of household waste is provided by means of waste sorting in different containers. The main bulk of material is obtained while collecting used bottles. Identification of the bottles is usually not difficult. All bottles for beverages are made of PET and bottles for other liquids have a special marking – a recycling symbol with “1”.

Primary processing of waste. The company “Halpet” is the main enterprise in the West region which collects and preprocesses PET waste. The primary processing includes the following. Originally pressed bales are broken into separate bottles and external heavy impurities are removed. Next, the bottles are sorted, crushed, they undergo air separation, after this they are washed in special bath using alkaline solutions and new detergents, floated, etc. Then the material is ground to obtain the commodity fraction, it undergoes secondary air separation and packed. Pure flakes are granulated, i.e. a high quality secondary crystal granule is obtained via complete melting of raw material, its filtration and granulation [1].

Obtaining of film-forming composition. The shell of encapsulated fertilizer granule contains various functional additives apart from polymer. The shell components mixing, as well as its applying over granule surface should be done in liquid state. This task may be solved in two ways:

1) by dissolving of desired components using solvents;
2) by components mixing in PET melt.

The use of melts as the film-forming shell requires corresponding equipment, where necessary temperature is provided. Since PET melting point is 280 °C, the use of melt leads to additional heat consumption. At the same time, it is not recommended to heat the nitrogen granulated fertilizers above 70 °C, due to their thermal decomposition [6]. The method using aqueous solutions has not mentioned shortcomings, though the expenditures for materials, evaporation and purification of air from solvent vapors increase. From the standpoint of ecology and material costs the application of aqueous solutions would be more preferable. However, PET is insoluble in water and many organic solvents. Within the temperature range of 40–150 °C it is dissolved in phenols and their alkyl- and chlorine-substituted compounds, aniline, benzyl alcohol, chloroform, pyridine, di-chloroacetic and chlorosulfonic acid, cyclohexanone, etc. To determine the molecular weight by viscosimetry PET solutions with cresols, o-chlorophenols, phenol-tetrachloromethane are used [7]. To our mind, it is inexpediently to use acids or aromatic solvents to dissolve PET because they are aggressive and high toxic substances. This will lead to excessive material and energy costs while obtaining capsulated fertilizers and consequently reduce their availability for mass agricultural production.

To increase the PET waste solubility, its chemical modification by diethyleneglycol has been developed [8]. The essence of the process is alcoholysis of ground PET-packing at 493 K and vacuum distillation of ethylene glycol under the residual pressure of 20 kPa. The modification time is 3.5 hours. The obtained product is soluble in ethylacetate, carbon tetrachloride, etc. at the room temperature. This simplifies the obtaining of film-forming compositions and its cost as a result. We propose the principal flowsheet to prepare film-forming composition for encapsulation of granulated mineral fertilizers (Fig. 2).

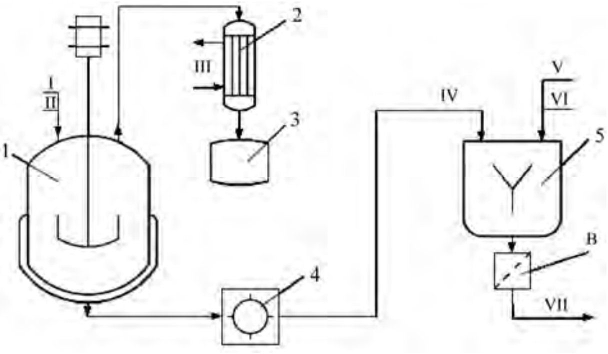

Fig. 2. Principal flowsheet for preparation of film-forming composition:
1 – reactor; 2 – ethylene glycol condenser; 3 – ethylene glycol collector; 4 – chipper; 5 – mixer; 6 – screen filter; I – PET; II – diethylene glycol; III – refrigerant; IV – modified PET; V – solvent; VI – composite additives; VII – film-forming composition

PET waste in the form of flakes and diethylene glycol is loaded into a reactor 1, where alcoholysis is carried out. Ethylene glycol formed during the reaction is taken off the reactor, condensed in the condenser 2 and directed to the collector 3. After the reaction end the product is reloaded into the chipper 4, where it is ground to the size of < 0.5 mm. The ground modified PET, solvent and composite additives are directed to the mixer 5. In our case we added hydrolytic lignin which provides the biological decomposition of the shell. Hydrolytic lignin is an artificial substance, waste of wood-pulp industry, residue of wood hydrolysis. Carbon tetrachloride was used as the solvent, because ethyl acetate decomposes while heated and forms ethyl alcohol and acetic acid. The solvent is fire-safe, inflammable and low-toxic one. The solution of film-forming composition obtained according to the mentioned scheme was used for encapsulation of granulated ammonium nitrate.

Encapsulation of granulated mineral fertilizers. Granulated fertilizers should be encapsulated via shell sputtering over surface of particles being in fluidized state. This method is realized in the fluidized-bed apparatus. Such equipment is characterized by high intensity of heat-and-mass transfer during encapsulation and provides high quality of covering. The encapsulation of ammonium nitrate is carried out in the cylindrical fluidized-bed batch reactor under following conditions [9]:

- Air rate – 6.10 m/s;
- Flow rate of film-forming composition – 0.032 kg/s;
- Encapsulation time for 1 wt % of covering per fertilizer weight – 75 s;
- Temperature of fluidizing air at the reactor inlet – 70 °C.

The important quality coefficient of applied covering is uniformity of shell thickness. It allows to predict the intensity of components release into the soil and produce encapsulated fertilizers with necessary term of action. According to above-mentioned conditions, we encapsulated ammonium nitrate by modified PET: lignin mixture (ratio 8:2). The covering value was 10, 20 and 30 wt% relative to the fertilize weight. The encapsulation quality was controlled by the nature of release curve [10]. The kinetics of components release from the encapsulated particles was studied by conductimetric method. The experimental results are represented in Fig. 3.

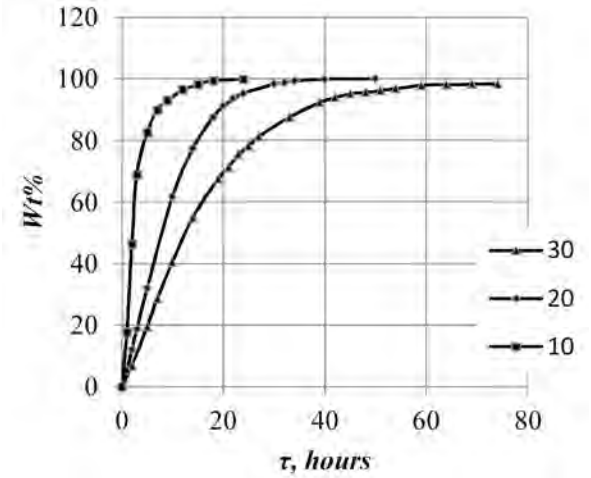

Fig. 3. Kinetics of ammonium nitrate release from the capsulated particles with different covering values, wt %

One can see from Fig.3 that the kinetic curves of the release process are smooth. It is the proof of uniform high-quality covering which allows to produce fertilizers of prolonged action with controlled time of release.

4. Conclusions

The technological possibility of using PET wastes for the encapsulation of granulated mineral fertilizers is examined on the basis of theoretical and experimental investigations. The modified PET/hydrolytic lignin film-forming composition has been obtained. The granulated ammonium nitrate has been encapsulated in the fluidized-bed reactor. The covering uniformity has been confirmed by the experiments which allows to produce encapsulated fertilizers with preset properties.

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Vol. 1, No. 1, 2016

TRITIUM AND ITS PLACE IN THE OVERALL RADIATION UKRAINE TECHNOGENESIS

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Abstract. The problem of migration accumulation of tritium, as one of the radionuclides with low radiation doses, is of great value for Ukraine in our time. The current state analysis of the tritium migration accumulation in the components of eco – and bio-systems taking into account its biological effect on living organisms is the aim of the study. The paper presents a general model of ecological system state changes under the influence of tritium migration flows.

Key words: tritium, pollution sources, biological aspects, model

1. Inroduction

The study of environmental aspects of migration accumulation of radionuclides with low radiation doses is of special value for Ukraine, as for the territory with tense radiation technogenesis. One of the most biologically hazardous radionuclides in its effect on the living organisms is tritium. Tritium is a radioactive isotope of hydrogen (heavy hydrogen), denoted by the symbols T and ^{3}H, with a half-life (12,32 ± 0,02) years. Rapidly oxidized, forming tritium water HTO that tastes and smells like ordinary water, but is a very chemically active substance. Tritium is a very dangerous radionuclide in terms of its impact on environmental and biological systems and, ultimately, on humans.

2. Problem formulation

During the 1960s – the 1990s scientific literature [1–6] fairly paid much attention to the results of the research on the action of technogenic tritium on the components of the environment and biological systems. Nowadays the study of migration accumulation of technogenic tritium in the environment has become topical again because of the energy needs of mankind, leading to the expansion of nuclear power. This necessitates the analysis of the current state of radioactive contamination and the place of technogenic tritium in it.

Technogenic tritium that enters the environment comes in the links of ecological system in several ways. The amount of tritium, which enters the environment, is the main factor determining the activity of radionuclide in the ecological system links. The concentration of tritium in any link of the ecological system as a whole meets its concentration in water.

Tritium is effectively included in the biological tissue and is a mutagenic disorders potential source due to radiation of the average energy (5,8 keV) and due to molecular bonds expense, caused by a change of hydrogen (H) isotope by a neutral body (He) which was formed as a result of T β-decay.

As shown by the experiments on different animal species [1], even after a single submission of oxide tritium, the normal functioning of the body is disrupted, early significant violation of immune reactivity is caused, diffuse circulation disorders such as hemorrhage, disorders of normal tone of vessels, perivascular outflows with degeneration of cellular elements of the body and other violations develop.

Tritium can enter the living organisms in several ways. The first way is orally administered, with food and water. The process of water suction occurs in the intestine where this process takes place at high speed. Tritium is determined in venous blood after 2–9 minutes after swallowing HTO. After that the contents of tritium in venous blood increases linearly in time. The second way of tritium flow to the body is breathing. The experiments on animals showed that during the inhalation of the air, containing tritium oxide, from 85 to 100 % of HTO is sucked in the lungs. When calculating the maximum permissible levels of HTO in the air, it is accepted, that during a regular respiratory cycle, 100 % of tritium oxide is absorbed in the lungs [1].

Over the past decades, the most powerful incident technogenic tritium pollution occurred due to the accidents at nuclear power plants.

The abundance of tritium has escaped into the atmosphere in 1986 during the Chornobyl nuclear power plant (CNPP) disaster. The nature of the radionuclides scattering was determined by lots of factors: weather conditions, time of emission, temperature of radioactive cloud and others. Tritium contamination occurred both locally and globally. For example, to illustrate the globality of environmental pollution by technogenic tritium process, we can cite the observations, which were held in 1986 in Austria, where the concentration of tritium in precipitation relative to level 20–30 TE observed during winter and early spring of 1986, came to the level of more than 100 TE in the late April of that year [5, 6].

The areas adjacent to the Chornobyl NPP were subjected to tritium contamination most of all. Unfortunately assessment of the total amount of tritium, which got into the biosphere during the Chornobyl disaster, as well as calculation of radiation doses of this isotope, are unknown, but a significant increase of tritium in surface and ground waters, both in the areas surrounding Chornobyl, where its concentration was 400 Bq per liter, and at a considerable distance from the CNPP, show significant contamination of environment component by this isotope.

The concentrations of tritium in natural waters within the boundaries of the 30 km zone after the Chornobyl accident can be regarded as a superposition of global nature factors, native activity of Chornobyl in pre accident period and the release during the accident with the dominance of the role of the latter factor. In the hydrogeological cycle, a major source of global tritium pollution is the atmosphere. Precipitation forms isotope composition of rivers, lakes, groundwater and interstratal waters, seas and oceans. Deep groundwater and perennial glaciers serve as a global reservoir for runoff, where the radioactive tritium decays. The concentration of tritium in surface waters is close to its concentration in precipitation (in the absence of other sources of pollution) [7, 8].

In 2011 there was a strong accident at Japanese nuclear power plant “Fukushima-1”, provoked by the earthquake and tsunami. This caused a meltdown of the reactor core at blocks 1,2 and 3. As a result there was contamination of surrounding areas by radionuclides and transboundary migration of tritium, both by air and by water, almost around the globe. In the summer of 2013 the level of tritium in the waters adjacent to the NPP (within 25 m) increased almost 10 times, and 17 times in groundwater. In September 2015 the work on ocean dumping of 850 tons of liquid, free from radioactive substances was performed. But the level of tritium was 600 Bq/l. Permanent discharges of tritium water to the ocean resulted in its getting into biological objects (ocean fish, marine animals and plants). This caused the transition of tritium by food chain to human body [9, 10].

Nuclear power engineering, even in its regular work, is traditionally considered to be one of the constant sources of technogenic tritium that enters the environment. The content of tritium in liquid discharges during the regular operation of nuclear power plant far exceeds the absolute value of the contents of all other radionuclides, and in gaseous emissions to the environment it is the second after the amount of inert radioactive gases. Due to the chemical equivalence to ordinary hydrogen tritium in the form of HTO accumulates in NPP technological waters and enters the reservoir-cooler and then the nearby ponds, groundwater, surface layer of the atmosphere. In Ukraine there are four nuclear power plants, which have 15 blocks with VVER-type reactors that are the most powerful sources of technogenic tritium, compared with other types of reactors. VVER-type reactors emit tritium into the atmosphere and hydrosphere to 33 GBq / MW (e) / a year. [11–13].

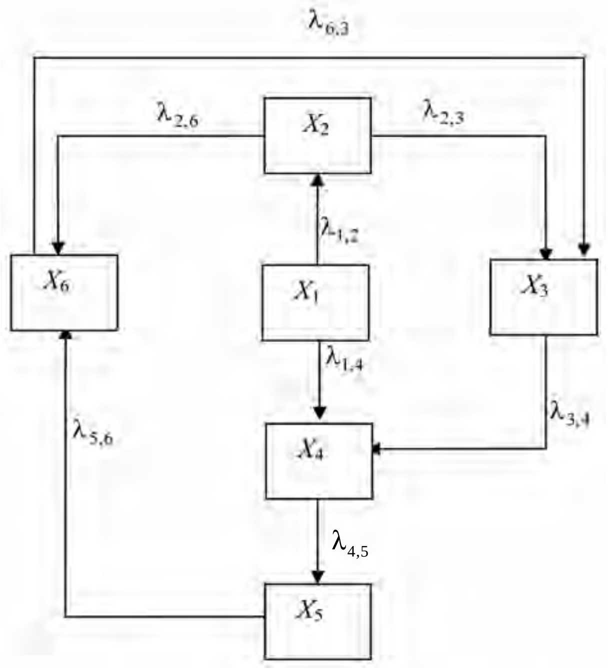
The most powerful technogenic pollution sources are the plants for processing spent nuclear fuel. Until recently, Ukraine had no such plants, but if, as planned, the following sources of technogenesis are built, it will have bad influence on the general state of environmental situation and genetics of the future generations of Ukrainian population.

For many years the study of migration of tritium in the environment did not take into account the impact of radioactive waste disposal points (RWDP) including tritium solid waste (TSW). As tritium pollution sources, they were considered only in recent decades, due to emergency incidents at RWDP in Kharkiv and Pirogovo near Kyiv.

The experience of operation of tritium-containing waste disposal points shows that it is impossible to completely locate the waste in conventional ground vaults. Every year RWDPs become a constant source of tritium supply in the environment components. Thus, depending on the geological structure of the underground system of species, watersheds and specific water horizons, tritium can contaminate even deeper aquifers [14–16].

Since there is no relevant technical solution for the localization of tritium-containing wastes and the existing surface storages are not able to completely prevent the release of hazardous radionuclides into the environment, they become permanent sources of technogenic tritium, which determines not only local, but global pollution of the biosphere. In addition, considering the significant contribution of NPP into the nuclear energy of Ukraine and that the increase of a number of VVER-type reactors at existing nuclear power plants is planned, it can be argued that the amount of technogenic tritium in water resources and soil of Ukraine will grow.

For the study, analysis and forecast of migration processes in ecosystems it is proposed to apply the following approach. Let's consider migration scheme of tritium movement, which corresponds to the iconographic model (see. Figure). A generalized model of appropriate changes in ecosystem conditions is built on its basis. The process of changing conditions of ecological systems under the influence of technogenic load of the migration flows of tritium in the environment links is a stochastic process that can be represented as a Markov's process. Stochasticity in considering this process arises due to the presence of uncertainties caused by the lack of information about the process in real natural conditions and its insufficient study.



Migration of tritium in the components of the environment

Where $\lambda_{i,j}$ – density of the flow of events that transform the system from state i into state j; X_i – those states which can be (in our case, these states are characterized by the relevant components of the environment, in which tritium was, respectively: X_1 – tritium pollution source; X_2 – tritium in the air; X_3 – tritium in soil; X_4 – tritium in the area aeration; X_5 – tritium in groundwater; X_6 – tritium in surface waters).

Migration flows can be considered as some stationary flows of events, whose impact on corresponding environment component transforms the entire system into another state. Then a generalized model of ecological system state changes under the influence of migration flows of tritium can be represented as a system of Kolmogorov-Chapman equations (1) corresponding to the ecosystem graph of states (topological model) (Figure).

$$\begin{cases} \frac{dp_1(t)}{dt} = -\left(\lambda_{1,2}+\lambda_{1,4}\right)p_1(t); \\ \frac{dp_2(t)}{dt} = \lambda_{1,2}p_1(t)-\left(\lambda_{2,3}+\lambda_{2,6}\right)p_2(t); \\ \frac{dp_3(t)}{dt} = \lambda_{2,3}p_2(t)+\lambda_{6,3}p_6(t)-\lambda_{3,4}p_3(t); \\ \frac{dp_4(t)}{dt} = \lambda_{1,4}p_1(t)+\lambda_{3,4}p_3(t)-\lambda_{4,5}p_4(t); \\ \frac{dp_5(t)}{dt} = \lambda_{4,5}p_4(t)-\lambda_{5,6}p_5(t); \\ \frac{dp_6(t)}{dt} = \lambda_{5,6}p_5(t)+\lambda_{2,6}p_2(t)-\lambda_{6,3}p_6(t); \end{cases} \quad (1)$$

$$\sum_{i=1}^{6} p_i = 1,$$

where $p_i(t)$ – the probability that at time t the system is in a state X_i.

The initial conditions for differential equations system (1) integration reflect the state of the system at the time before tritium contamination.

In our case the event is defined by tritium activity in migration flow at some point of time. The density (intensity) of events flow is the average number of events that occur one after another at random times.

If, for example, the system at $t = 0$ was in some state X_k, we suggest that $p_k(0) = 1$,, $p_i(0) = 0$, with $i \neq k$. Note that the limit mode for the system is a random process that is installed in the system at $t \to \infty$. If we assume that the number of states of the system includes at least one critical state of the ecosystem (state without output), then at $t \to \infty$ system with practical reliability certainty will be in it.

If all the streams of events that transform the system from state to state are stationary (λ_{ij} = const), and the total number of states is finite, and no states without output, then there is a limit mode characterized by limiting state probabilities $p_1, p_2, ..., p_N$, and $(\sum_{j=1}^{N} p_j = 1)$.

The resulting model allows an approximate estimation of the ecological system states changes, according to the observations of the monitoring system on the migration routes of tritium in the components of the environment.

3. Conclusions

1. The basic sources of technogenic tritium in the environment were analyzed.
2. The data on migration accumulation of tritium in biological systems, described in the literature, were researched and analyzed.
3. A generalized model of ecological system state changes under the influence of migration flows of tritium was synthesized.

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HAZARDOUS HOUSEHOLD WASTE MANAGEMENT IN VINNYTSIA REGION

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Abstract. The article analyzes hazardous household waste, including detergents, paints, adhesives, expired medicines, luminescent lamps, pesticides, fertilizers, batteries and accumulators, electrical and electronic waste, mercury-containing materials. Research shows that they contain a large quantity of dangerous and toxic substances (compounds of heavy metals, chlorinated polymers, aromatic hydrocarbons, surfactants, etc.), which pose a significant risk to the environment and human. The analysis of hazardous household waste management in the Vinnytsia region has showed absence of the appropriate management system. Hazardous household waste is collected separately only fragmentary and is released into environment together with other household waste, creating an environmental hazard in the region. The article also contains recommendations for the hazardous household waste management.

Key words: hazardous household waste, toxic substances, waste management, batteries, luminescent lamps, mercury-containing materials, detergents.

1. Introduction

It is known [1] that municipal solid waste (MSW) includes approximately 0,1 % of hazardous household waste. This is the waste which has been generated due to human activity in the residential and non-residential buildings, and which has physical, chemical, biological or other hazardous properties that create or could create a significant risk to the environment or human health, and which requires special methods and means of handling. Such hazardous household waste includes detergents, paints, adhesives, expired medicines, luminescent lamps, pesticides, fertilizers, batteries and accumulators, electrical and electronic equipment waste, mercury-containing materials (e.g. thermometers). Nowadays, this type of waste is collected together with other municipal or household waste. It accumulates at landfills (waste dump sites), where it poses a serious risk to the environment and human health, because the toxic compounds it contains have free contact with the environment. At the same time, in Ukraine there is no effective mechanism for managing this type of waste. The purpose of this article is to analyze hazardous household waste in the Vinnytsia region and ways of managing them, and providing appropriate recommendations as well.

2. Materials and methods

According to the data [2], MSW contain about 0,25 % (by weight) batteries, which in turn create 50 % of hazardous household waste. They contain hazardous substances such as compounds of heavy metals (zinc, manganese, mercury, copper, lead, cadmium, nickel), acids and so on. The metal covering of used and taken out together with other MSW batteries is destroyed, hazardous substances get into the environment, contaminating it.

Rapid technological development of society causes a sharp increase in electrical and electronic equipment waste. This includes, in particular, used household techniques, telecommunications equipment, computer equipment and its components, office equipment, telephones, cameras, radios, lighting equipment, electrical tools, toys with electrical or electronic components, other automatic device. The authors of the research [3] have found in such kind of waste polymeric materials consisting of polystyrene (42 %), acrylonitrile-butadiene-styrene (38 %) and polypropylene (10 %). The remaining 10 % are polyethylene, polyvinyl chloride and other polymers. Polymeric ingredients of electronic waste consist of synthetic high-molecular compounds. During their manufacture a lot of binders, plasticizers and fillers are used. These binders do not react with organic basis and may be released from the composition and pollute the environment. Under certain conditions in the environment (effects of ultraviolet radiation, temperature, humidity), not only products of their own decomposition can be released from such polymer materials, but also trace amounts of low-molecular chemicals (monomers, plasticizers, hardeners, solvents, dyes, stabilizers, destruction products, etc.) can be found there. They typically have a strong biological action. However, the main environment polluters as a part of electrical and electronic equipment waste are heavy metals (mainly lead, mercury, cadmium and hexavalent chromium) and flame retardants – polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDEs).

There are also widely used paints, varnishes, adhesives, glues. Their main components are binders (polymers, rubbers, cellulose derivatives, etc.) and pigments. The latter contain oxides and salts of metals that are potentially hazardous for the environment. These are, for example, lead carbonate, zinc sulfide, zinc chromate, chromate and lead sulphate, manganese and chromium oxides. Paint and varnish products are dangerous due to evaporation of volatile solvents. In some cases products of such substances decomposition are even more dangerous. This, for example, refers to such substance as styrene [4].

Very often, particularly in the residential houses, in the total MSW volume the remains of pesticides, which are highly toxic, can appear. In many pesticides generally nonionic surfactants are used (emulsifiers, dispersants), for example, acrylic esters of polyoxyethylene, or mixtures of ionic surfactants, such as alkyl benzene sulphonate. Anionic polyelectrolytes are used as stabilizers (alkylsulphonates of Na or Ca) [4]. In addition, the base of the entire group of pesticides is dangerous sulfur- and phosphorus-containing organic compounds. The environmental risk of pesticides is connected to their persistence, i.e. the ability to exist in the environment for some time without losing biological activity. As a result of pesticides degradation, other very dangerous compounds are produced – dioxins that are strong carcinogens.

Most washing powders and detergents are made from phosphates, chlorine, anionic surfactants, oil products. Besides, household chemicals contain hydrochloride sodium (causes the cardiovascular system damage), oil distillates (negatively affect the vision and nervous system), phenol and cresol (may cause disruption of liver and kidneys), nitrobenzene, formaldehyde (strong carcinogen) [5]. Thus, releasing the traces of these substances into the environment along with other household waste also poses a risk. If there is no treatment of domestic waste water (typical situation for majority of municipalities) these substances can move free to the environment and contaminate sources of drinking water.

Medical waste periodically appears in household waste. It can consist, for example, of expired medicines, bandages, used syringes. In medical facilities such waste is subject to mandatory incineration, but in households it is a part of total MSW volume. Thus, there is a serious risk of biological pollution.

Mercury-containing waste materials are among the most dangerous MSW components. The most common ones are thermometers and luminescent lamps. If they are damaged or handled improperly, including taking out with other household waste, mercury is released to the environment. For example, one luminescent lamp contains 80 to 120 mg of mercury, which relates to substances of 1st class of hazard and together with the general toxic effect has embryotoxic, teratogenic and mutagenic effects. The danger of mercury and its vapor is increased by high rate of evaporation. The concentration of mercury vapor in the room depends on the area of evaporation, air velocity over the mercury surface, the state of its surface, temperature and other factors. It is known [6] that the rate of evaporation of metallic mercury in still air at 20 °C is 0,002 mg/(cm^2·hour), and at 35–40 °C if it is exposed to the sunlight, it increases 15–18 times and can reach 0,036 mg/(cm^2·h). In the case of breaking a luminescent lamp that contains 80 mg of metallic mercury, more than 11000 mercury balls with diameter of 0,01 cm and overall total surface of 3,454 cm^2 are formed. After one hour at 20 °C in a room with the volume of 60 m^3, mercury concentration will reach 0,4 of the average daily limit value [6].

Summarized information about dangerous chemicals in the above mentioned hazardous household waste is given in the Table.

Dangerous chemicals in hazardous household waste

Hazardous household waste	Substances
Detergents and household chemicals	Phosphates, sulphates, chlorine, acids, amines, phenols, anionic surfactants
Varnishes, paints, adhesives, glues	Compounds of lead, zinc and chromium, volatile solvents (styrene, benzene, acetone, butyl acetate, xylene, butanol), phenol
Luminescent lamps and other mercury containing materials	mercury
Pesticides, fertilizers	Heavy metals and their compounds, chlorine compounds, dangerous sulfur- and phosphorus-containing organic compounds
Accumulators, batteries	Nickel, cadmium, lead, manganese, mercury, sulfuric acid
Electrical and electronic equipment waste	Mercury, cadmium, lead, tin, nickel, zinc and their compounds, organic compounds containing bromine

3. Results and discussions

3.1. Analysis of ways of hazardous household waste handling in the Vinnytsia region

The situation with hazardous household waste in the Vinnytsia region remains very difficult. Companies and organizations are obliged to collect such waste separately and enter into contracts with licensed companies for their removal or disposal. Therefore, hazardous waste management in the commercial sector is generally carried out in a proper way, except for some cases of absence of such contracts with appropriate sanctions for companies-violators. In addition, all organizations that deal with hazardous waste have to get a special permit under the Regulations on the procedure for issuing permission to operate with hazardous waste.

The situation with the hazardous household waste handling by people is much worse. According to the "Rules of providing the waste management services" hazardous household waste is transferred by consumers and by providers of waste management services in accordance with the sanitary requirements to specialized companies which have received licenses for operations with hazardous waste. Despite the existing legislation, programs and commitment not to take out hazardous household waste together with other MSW there are no mechanisms of realization of the state policy in this sphere.

Only recently in some areas (Vinnytsia, Ladyzhyn, Stryzhavka of Vinnytsia region) the collection points for the most common hazardous household waste were organized (luminescent lamps, batteries, thermometers). This initiative has been implemented by private companies and the public. Some points have information materials (see Fig.).

Collection point for hazardous household waste
in Ladyzhyn

A campaign of organized collection and recycling of used batteries started in Vinnytsia in cooperation with Poland in 2013. The project involves collaboration with educational institutions (participation of most schools and universities), public organizations and shops, which were provided special containers to collect used batteries free of charge. Transportation and processing is also provided by the project organizers. During the first two months over 1 ton of used batteries was collected. Besides this, seminars where participants were acquainted with the Polish experience and methods of effective education campaigns were held and they encouraged people to collect hazardous household waste.

Efficient and environment-friendly system of MSW management in the Vinnytsia region is only being formed. Thus, such projects are of particular importance for the development of the infrastructure of MSW management and for increasing the environmental awareness and culture of citizens.

In all other cases, hazardous household waste is taken out together with other waste, coming further to landfills (waste dump sites). Unfortunately, companies specializing in hazardous waste management in the Vinnytsia region operate only in Vinnytsia and the surrounding area. They collect following hazardous waste for further handling : luminescent lamps and other waste containing mercury; oil; lead-acid batteries; solutions of acids or alkalis; waste and scrap of electrical and electronic products; medical waste; waste of production, preparation and usage of pharmaceutical products; waste of production and usage of inks, dyes, pigments, paints, lacquers, varnishes; waste of production and usage of rubbers, latex, plasticizers, glues, binders; waste containing chemicals that do not meet specifications or which are expired; waste of mixtures oil/water, carbohydrates/water, emulsions; galvanic mud; solutions after metals etching. Even if collection points of hazardous household waste exist, there is a problem of its further transportation. Such geographical location actually makes it impossible to operate in most areas of the Vinnytsia region. In addition, specialized companies working in the Vinnytsia region do not recycle or disarm hazardous waste, but only collect it and transfer to other companies. It should be noted that capacity of companies that can recycle or disarm the hazardous household waste is very small in Ukraine.

3.2. Recommendations for hazardous household waste management

The most relevant recommendations in the sphere of hazardous household waste management are as follows:

- harmonization of European [7–9] and Ukrainian legislation [10] in the sphere of hazardous household waste management. The legal basis for the establishment of an effective and unified system of hazardous household waste management should be prepared.
- improvement and legislative strengthening of the list of hazardous household waste, applying to it the requirements that now exist for other dangerous (industrial) waste.

- obligation of producers of goods, which become hazardous household waste after usage, to keep records of the quantities, properties and origin of this waste and the provision of information availability to all stakeholders.
- preventing hazardous household waste from being released into the environment due to its separate collection.
- creating collection points for hazardous household waste and identifying the requirements for them.
- creating an effective system of monitoring of hazardous household waste and companies involved in handling it.
- establishing the rules of packaging and labelling of hazardous household waste in accordance with international and EU standards.
- development of guidelines for the identification of hazardous household waste, its separation and basic rules of its handling.
- establishing the coordinated activities of local and regional authorities, public and other stakeholders in the sphere of hazardous household waste management.
- creating an effective system of informing the public about safe hazardous household waste handling.
- development a stimulation system for correct hazardous household waste management.
- establishing the responsibility for violations of hazardous household waste management.

4. Conclusion

The authors have identified a large quantity of hazardous and toxic substances (compounds of heavy metals, chlorinated polymers, aromatic hydrocarbons, surfactants and others) in the hazardous household waste. The situation in the sphere of hazardous household waste management in the Vinnytsia region is quite complicated. Only recently the collection points for the most common hazardous household waste (batteries and, sometimes, mercury-containing lamps) were organized in some localities. Unfortunately, one more reason why the situation does not improve is insufficient quantity and capacity of specialized companies in the sphere of hazardous waste management. Thus, even if collection points for hazardous household waste exist, there is a problem of their further transportation and processing. Nowadays, in the Vinnytsia region there are no real mechanisms to reduce the environmental impact of hazardous household waste except for some public initiatives. The main recommendations for the effective handling of hazardous household waste are preparing an appropriate legislative framework, taking into account international experience and creating the real mechanisms for environment-friendly management of this type of waste.

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Vol. 1, No. 1, 2016

POLLUTION OF SOIL ENVIRONMENT WITH MINERAL FERTILIZERS AND WAYS OF THEIR MIGRATION DEEP INTO THE SOIL

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Abstract. One of the major problems of pollution of soil environment, namely by components of mineral fertilizers due to their massive and continuous use in agriculture was analysed in the article. Possible ways of penetration of not absorbed mineral fertilizers deep into the soil as the main reason for getting fertilizers in the lower layers of the soil environment were investigated. A comparison of the impact of soil and climatic conditions on the rate of penetration of fertilizers deep into the soil was done.

Key words: mineral fertilizers, penetration, soil environment, adsorption, pollution.

1. Introduction

Mineral and organic fertilizers are widely used in agricultural practice, as basic substances that increase soil fertility and increase crop resistance to the variability of climatic conditions, thus allowing to obtain high harvest. Considering the fact that assimilation of components of mineral fertilizers occurs gradually, and the period of their bringing in is at the beginning of the plants growing season, there is a real danger that a lot of fertilizers, and according to the literature [1–4] this number is within 40 to 60 %, will penetrate into the deep layers of the soil and contaminate them. In this case, nitrogen and potash fertilizers that are soluble in water and can easily migrate in vertical soil profile occupy the main place among all types of fertilizers.

The rate of penetration of fertilizers deep into the soil is determined by various factors. This process affects both soil-adsorption capacity of the soil and the soil and climatic conditions (temperature, humidity balance, content of clay and sand fractions, etc.) [5]. One of the most important properties that characterize the soil is its adsorption capacity, because it affects both the soil formation processes, and the processes of establishment of its fertility. The adsorption capacity regulates the nutrient regime of soil and causes the accumulation and maintenance of nutrients in it. This property of the soil also affects the distribution and penetration of mineral fertilizers in the soil environment. This makes it possible to reduce the frequency of bringing in doses of fertilizers and increase the amount of fertilizers at a time.

Moreover the process of penetration of fertilizers deeper into soil is affected by the processes of molecular and convective diffusion that are constantly present in the soil environment. It can be proved by the fact that fertilizers penetration is different on sandy soils and humus or dark grey ashed soils. On the one hand, this is due to different penetrating ability, that is water permeability of the soil, which affects mostly the convective transfer of fertilizers deep into the soil, on the other hand, this depends on how humidified soil environment where molecular diffusion process is possible is.

Considering the current ecological status of most soils, a lot of research has been conducted to establish the ways of penetration of pollutants in vertical and horizontal soil profile [6-9], but not enough attention has been paid to study the migration of components of fertilizers, which can also become pollutants. Taking into consideration the fact that migration of various components of fertilizers occurs in the soil environment in different ways, as some components, for example, NH_4^+, K^+, Ca^{2+} are adsorbed by the soil adsorbing complex, and NO_3^- is not adsorbed, the study of the basic processes of penetration of fertilizers in vertical profile of soil is an urgent and important task for predicting possible ways of penetration of fertilizer components deep into soil.

2. Experimental part

The main fertilizers that are widely used in agriculture are nitrate fertilizers, which include anion NO_3^- and cation or NH_4^+, or K^+, or Ca^{2+} etc. These fertilizers are well soluble in water and are made mainly in the spring season. According to the literature [1, 2], the loss of these fertilizers is within 40 % of the introduced amount, thereby leading to constant accumulation, including nitrates, in the deep layers of soil and subsoil waters. That is why we have chosen to study the following fertilizers: potassium nitrate, calcium nitrate and ammonium nitrate.

Research of the adsorption properties of soil was carried out on the example of potassium nitrate and calcium nitrate, where there are ions K^+ and Ca^{2+} that are well adsorbed by the soil and kept in its pores, and studies of convective diffusion were performed on the example of ammonium nitrate where there is an ion NO_3^- that is not adsorbed by the soil-adsorbing complex and easily penetrates deep into the soil, especially during precipitation. Potassium and calcium are essential nutrients, full plant nutrition is impossible without them, but abundance of these elements in the soil leads to its pollution and getting into surface and underground aquifers.

2.1. Research of adsorption capacity of the soil

Research of adsorption properties of soil was carried out on the example of potassium and calcium ions. Podzolic humus, that is widespread in the Lviv region was used as soil. During experimental studies dried to constant mass soil was used.

Samples of dried to constant mass soil (≈1 g.) were put in measuring tanks and the tanks were then filled up with 100 ml of calcium nitrate or potassium nitrate with known concentrations. The solutions were mixed thoroughly and left for two days in the thermostat. Determination of the concentration of calcium ions in the solution was conducted by titrimetric analysis. The mass of adsorbed calcium was determined by the difference of concentrations of the primary and final solutions. Analysis of solutions on ionomer was performed to determine the concentration of potassium ions and the mass of adsorbed ions was determined by the difference of concentrations in the primary and final solutions. The results of experimental studies are presented in Fig. 1, 2.

2.2. Research of convective migration of fertilizers

Investigation of convective transfer of fertilizers deep into the soil environment and the possibility of contamination of the lower layers of soil was carried out on the example of ammonium nitrate, which is most widely used in agricultural practice. Here there is an ion NO_3^-, that is easily adsorbed by the root system of plants, but at the same time it easily penetrates deep into the soil environment with precipitation, as it is not kept in the pores of the soil. Two types of soil, such as sandy and clay loam were chosen for the research. These soils have varying water permeability, thereby affecting the penetration of fertilizer components in the deeper layers of soil. Measurements of quantity of filtrate which has passed through the soil were conducted during the study, the rate of filtration and content of nitrates in the filtrate and quantity of fertilizers washed out from the soil were determined. Soil layer with the thickness of 20 cm was chosen for the research since, according to the previous studies, the main part of the root system of plants is in the layer with the depth of 30 cm [5]. Ammonium nitrate was applied on the surface layer of the soil and regular watering of the soil depending on the amount of rainfall in the Lviv region in April was carried out [10]. The results of experimental studies are presented in Fig. 3, a, b, 4, a, b.

3. The results of research

The results of experimental studies of soil adsorption properties (Fig. 1, 2) indicate that the adsorption capacity of soil affects on the rate of penetration of fertilizers deep into the soil.

The results indicate that soil adsorption of ions as calcium or potassium in different concentrations is different. So, at low concentrations adsorption and ion exchange filling of the pores is possible, which leads to lower adsorption capacity of the soil. In this case, impact of adsorption capacity of the environment has less impact on the penetration of fertilizer components deep into the soil and is manifested by smaller quantities. In the case of increasing of the concentration of the substance in the solution the adsorption capacity of the soil environment increases. This is because it is possible to form a bimolecular layer of the soil that increases the static activity and increases adsorption properties of soil.

Considering the fact that the impact of adsorption properties is greater at high concentrations of the substance, the newly applied high concentrations of soluble fertilizers (fertilizer doses are calculated for the entire vegetation season) will be adsorbed by the soil-adsorbing complex of soil and kept in its pores. Besides, such a property of the soil significantly reduces amount of fertilizers that will penetrate deep into the soil immediately after their rapid dissolution in moist soil and they will be available for adsorption by the root system of plants for a long time.

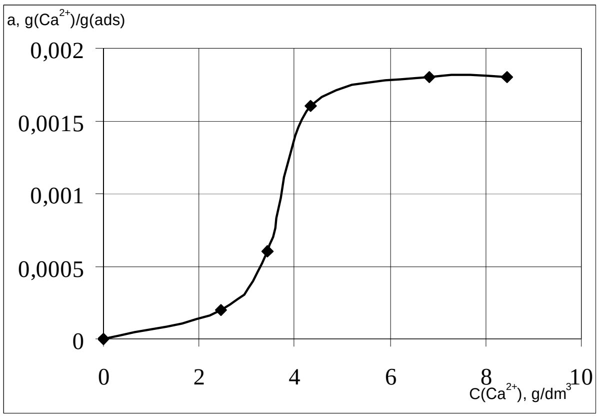


Fig. 1. Determination of adsorptivity of podzolic humus *a* to the concentration of calcium ion C in a liquid

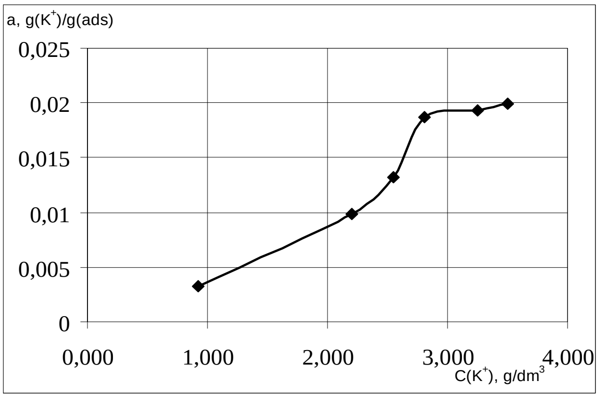


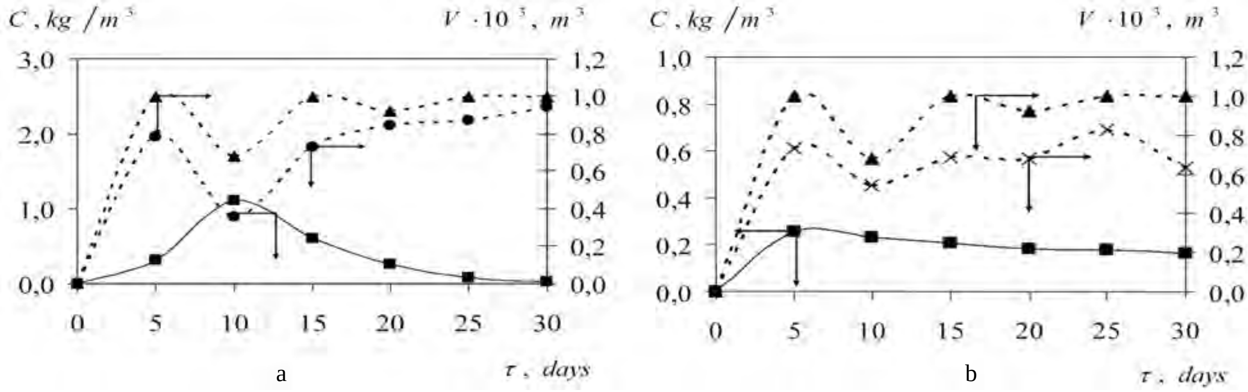
Fig. 2. Determination of adsorptivity of podzolic humus *a* to the concentration of potassium ion C in a liquid

The results of experimental studies of washing out of fertilizers during precipitation are presented in Fig. 3, a, b and 4, a, b.

The study of washing out of components of fertilizers from the soil environment was based on the filtration rate of fertilizers through the soil environment. Considering the fact that soil has the ability to retain water and to become saturated the penetration of fertilizers will continue even after the rain. This type of filtration is called filtration under the forces of gravity. We have experimentally investigated filtration rate during rainfall, which is on selected soils 15,8 and 0,8 m/day (on sandy soil and clay loam soil respectively) and filtration rate under the forces of gravity, which is 0,06 and 0,03 m/day respectively.

From the submitted graphic dependencies it can be seen that the main part of fertilizers is washed out from sandy soil in up to 10 days after application, while fertilizers are washed out from clay loam soil much more slowly, which reduces harmful effect on the environment. According to the results of research, in 30 days of the experiment the degree of washing out of fertilizers from the sandy soil is 97 %, and from the clay loam is 58 %. Considering the fact that the washing out process is constant, the fertilizer residues that remain in the soil layer in autumn and winter will be completely washed out to the lower layers of soil and will become the pollutants of subsoil waters.

The accumulation of fertilizers in the lower layers of the soil is constant with each rainfall, because there is a constant penetration of fertilizers in vertical soil profile (Fig .4, a, b). So, application of excessive doses of nitrate fertilizers leads to a constant flow of nitrates in the deeper layers of soil.

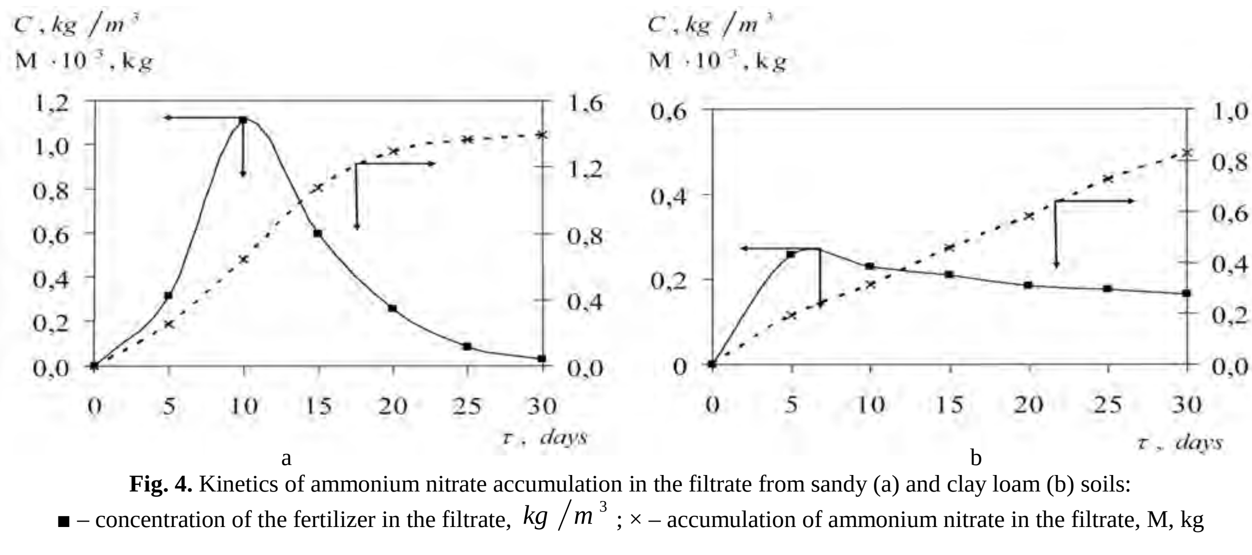


a b

Fig. 3. Kinetics of washing out of ammonium nitrate from sandy (a) and clay loam (b) soil layer:

■ – the concentration of ammonium nitrate in the filtrate, kg/m^3; ▲ – precipitation volume, V, m^3;

• – the volume of filtrate from the sandy soil, V, m^3; × – the volume of filtrate from clay loam soil, V, m^3



a b

Fig. 4. Kinetics of ammonium nitrate accumulation in the filtrate from sandy (a) and clay loam (b) soils:

■ – concentration of the fertilizer in the filtrate, kg/m^3; × – accumulation of ammonium nitrate in the filtrate, M, kg

4. Conclusions

Contamination of soil and groundwater aquifers is perhaps one of the major problems of environmental pollution. One of the most widespread pollutants that are spread throughout Ukraine are fertilizers, particularly nitrogen, which cause accumulation of a number of pollutants in soil and groundwater. This applies to nitrates and other nutrients that are a part of fertilizers because abundance of all these substances causes negative processes in the environment.

Experimental studies have shown that soil adsorption properties have significant impact on penetration and distribution of components of fertilizers in the vertical soil layer. This impact is particularly significant at high concentrations of substances, which creates favourable conditions for the gradual assimilation of the components of fertilizer by plants for a long period of time. The results of experimental studies makes it possible to assess and predict the possible losses of fertilizer from the soil, and thus adjust the doses of mineral fertilizers.

At the same time experimental studies of the process of washing out of fertilizer components and particularly nitrates from the soil, shows that there is a real danger of pollution of the lower layers of soil and groundwater, especially while application of high concentrations of fertilizers. This process is affected by many factors, but the main one is the type of soil with its water permeability, since the higher the water permeability of the soil is, the faster nitrates are washed out from it and the bigger their amount is. So, it is more appropriate to use encapsulated fertilizers on sandy soils, which will reduce the amount of losses to the environment due to the gradual flow of components to the soil.

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ECOLOGICAL SAFETY OF VISUAL ENVIRONMENT AND VIDEOECOLOGICAL PERCEPTION (VEP) OF VINNITSIA

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Abstract. The object of the research is landscapes of the urban ecosystem of the town of Vinnytsia.

The purpose of the work is to investigate and evaluate the level of videoecological perception and geopotential sustainability of Vinnytsia and set the main risks to natural and artificial visual environment of the city.

The paper deals with the method of calculation for the evaluation of videcoecological favourableness of the urban environment and methods of visual pollution control in the urban environment.

During the research videoecological perception of the town of Vinnytsia was analyzed, the main environmental risks of the technosphere were identified and an evaluation of the sustainability of the urban environment of the city was made; the ways to optimize visual sensitivity of natural and artificial environment in the city were reviewed. A map-scheme based on experimental data and patterns of the range of videoecologiacal perception was made and its distribution among the territory of Vinnytsia was shown.

Key words: videoecology, saccade automaticity, visual pollution, visual environment, homogeneous fields, landscape design

1. Introduction

Today the problem of environmental safety acquires paramount importance. Along with the main environmental problems (air quality, water pollution, increased noise and radiation level) not less important environmental factor – permanent visible environment and its condition, remains aloof.

The processes of urbanization, industrialization and rationalization distanced us from the visual ideal: an artificial environment no longer bring aesthetic pleasure. Architecture of the last 50 years has a negative impact on the psycho-emotional state of a person. Nowadays visual environment is dramatically altered in cities: dominated by dark gray, straight lines and angles, city buildings are static and have a lot of planes which negatively affects visual processes.

Research relevance: environmental safety of visual perception of the environment and environmental risks of technosphere management, is conditioned by spreading monotonous aggressive environment for human visual perception; low architectural-planning construction level and lack of construction colour saturation that leads to the deterioration of emotional well-being of the population.

The aim is to improve the efficiency of the research of videoecological aspects of urban ecosystems contamination on the example of Vinnitsia by calculating real videoecological perception scoring (coefficients) and data processing optimization with results visualization to provide the environmental safety of the visual perception of the urban area in general. The object of the research is the process of urban landscapes ecosystem structure changing on the example of Vinnitsia. The subject of the study is videoecological features of urban landscapes and existing influence factors of technosphere on the environmental safety of visual perception.

2. Evaluation of territorial videoecological perception (TVEP) of Vinnitsia

Urban landscapes define the main features of the city and the level of urban environment videoecological perception. They consist of zones: parks, ponds, objects of contact green zone (CGZ), city home construction, the city center, industrial warehouse zone, etc. [1].

During the research for VEP valuation the TVEP coefficient (K_{TVEP}) calculation was done according to appropriate methodology [2], the essence of which is reduced to the calculation formula 1

$$K_{TVEP} = \frac{\sum_{1}^{m} k_a \left(\frac{S_1}{S}\right)_{st} + \sum_{1}^{l} k_a \left(\frac{S_1}{S}\right)_{arch} + \sum_{1}^{n} k_a \left(\frac{S_1}{S}\right)_{CGZ}}{3}, \quad (1)$$

where $(S_1/S)_{CGZ}$ – the ratio of the area occupied by the appropriate *CGZ* gradations to the area of territorial estimated squares of Vinnitsia; $(S_1/S)_{storey}$ – the ratio of the area occupied by the relevant of storeys building types to the area of territorial estimated squares of

Vinnitsia; $(S_1/S)_{architect}$ – the ratio of the area occupied by the relevant architectural gradations to the area of territorial estimated squares of Vinnitsia; k_a – additive factors listed in table 1 [2].

Using the map of Vinnitsia on map service "Google Maps" [3], we find the abovementioned types of zonal distribution of the city, structurally presenting them in the basic three administrative districts, which allocate ten main micro-districts: Leninskyi district (S = 2,900 hectares): Vishenka, Sverdlovskyi massive, Slavyanka, Piatnychany, Center; Starogorodskyi district (S = 1,830 hectares): Stare misto, Mali Khutory; Zamostianskyi district (S = 2,200 hectares): Zamostia, Tiazhyliv, Shevchenko Khutir.

The city's zonal distribution types and experimental data of the objects measured areas for each of the ten Vinnitsia's micro districts were listed into the table. Components arrangement of the city contact zones was made on the basis of videoecological principles, and their boundaries were defined by walking distance to landscape objects, their recreational attractiveness and visual perception.

Carry out the necessary calculations for each city district of Vinnitsia.

a) Vishenka:

1) Calculate the ratio of the area occupied by the relevant types of storeys building (S1) to the estimated area (S) for the residential micro-district zone, taking into account appropriate additive factors from Table 1, as a result we obtain the videoecological perception factor of the researched zone $K_{VEP(st)}$:

$$K_{VEP(st)}=\sum_{1}^{m}k_a\left(\frac{S_1}{S}\right)_{st.}=1\cdot\frac{70\ ha}{700\ ha}+0,5\cdot\frac{175\ ha}{700\ ha}+$$
$$+0,125\cdot\frac{420\ ha}{700\ ha}+0,0625\cdot\frac{35\,ha}{700\ ha}=$$
$$=0,1+0,125+0,075+0,003=0,3.$$

2) Coefficient of videoecological perception of administrative and cultural zone $K_{VEP(arch)}$ is :

$$K_{VEP(arch)}=\sum_{1}^{l}k_a\left(\frac{S_1}{S}\right)_{arch}=0,5\cdot\frac{170,4\ ha}{341,3\ ha}+$$
$$+0,125\cdot\frac{133,3\ ha}{341,3\ ha}+0,6\cdot\frac{8,5\ ha}{341,3\ ha}+1\cdot\frac{4\ ha}{341,3\ ha}+$$
$$+1\cdot\frac{19,31ha}{341,3ha}+1\cdot\frac{0,5\ ha}{341,3\ ha}=0,25+0,05+0,015+$$
$$+0,012+0,06+0,001=0,4.$$

3) Coefficient of videoecological perception of green zone $K_{VEP(CGZ)}$:

$$K_{VEP(CGZ)}=\sum_{1}^{n}k_a\left(\frac{S_1}{S}\right)_{CGZ}=1\cdot\frac{90\ ha}{234,4\ ha}+$$
$$+1\cdot\frac{67,53\ ha}{234,4\ ha}+1\cdot\frac{72,01\ ha}{234,4\ ha}+0,5\cdot\frac{4,86\ ha}{234,4\ ha}=$$
$$=0,38+0,29+0,31+0,01=0,9.$$

Thus, overall coefficient of videoecological perception (KVE) for the territory of the district Cherry is:

$$K_{TVEP}=\frac{\sum_{1}^{m}k_a\left(\frac{S_1}{S}\right)_{st}+\sum_{1}^{l}k_a\left(\frac{S_1}{S}\right)_{arch}+\sum_{1}^{n}k_a\left(\frac{S_1}{S}\right)_{CGZ}}{3}=$$
$$=\frac{0,3+0,4+0,9}{3}=0,5.$$

The results of similar calculations performed for other micro-districts are presented in Table 2.

The results of TVEP factor calculation are visually represented in Figure 1.

Table 1

Numerical values of additive factors for K_{TVEP} calculation

k_a	Gradation (1; n)	k_a	Gradation (1; m)	k_a	Gradation (1; l)
1	recreational spaces	1	no buildings	1	historical town
0,5	green corridors	0,5	low-rise (1 – 3 storeys)	0,5	single architectural monuments
0,125	walking distance zone of CGZ objects	0,125	medium-rise (5 – 9 storeys)	0,125	areas of new buildings
0,0625	visual orientation area	0,0625	high-rise (9 – 16 storeys)		

Table 2

Results of calculations for ten micro-districts of Vinnitsia

K_{VE} Micro district	District	$K_{VEP(st.)}$	$K_{VEP(arch)}$	$K_{VEP(CGZ)}$	K_{TVEP}
Vishenka	Leninskyi district	0,3	0,4	0,9	0,5
Sverdlovskyi massive		0,4	0,5	0,8	0,6
Slavianka		0,4	0,3	0,9	0,5
Piatnychany		0,5	0,6	0,7	0,6
Center		0,7	0,9	0,92	0,9
Stare misto	Starogorodskyi district	0,6	0,4	0,7	0,6
Mali Khutory		0,3	0,4	0,6	0,4
Zamostia	Zamostianskyi district	0,4	0,1	0,5	0,3
Tiazhyliv		0,1	0,1	0,5	0,2
		0,4	0,1	0,5	0,3

The heterogeneity in the distribution of TVEP levels, based on the calculated factors, are visually represented in the diagrams (Fig. 2–5), which makes it possible to talk about the relative inferiority of comfortable visible environment, a significant need for optimization the ways of solution to these shortcomings and analyze it as a factor of technosphere environmental risk concerning the impact on visual perception in each of the studied zones of the micro-districts (residential (storey), administrative, cultural (architectural), green (contact green zone)) and the city in general.

As seen from the map and the diagrams, overall TVEP factor of Vinnstsa ranges from 0,1 to 0,9. Higher values of the coefficient are observed in the central parts of the city. These parts make up a historical center of the city, and it is the largest area of recreational facilities of citywide importance.

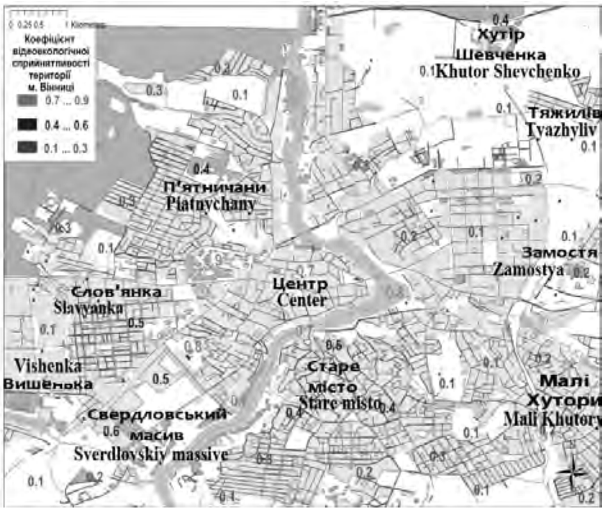

Fig. 1. Map of Vinnitsia's videoecological perception

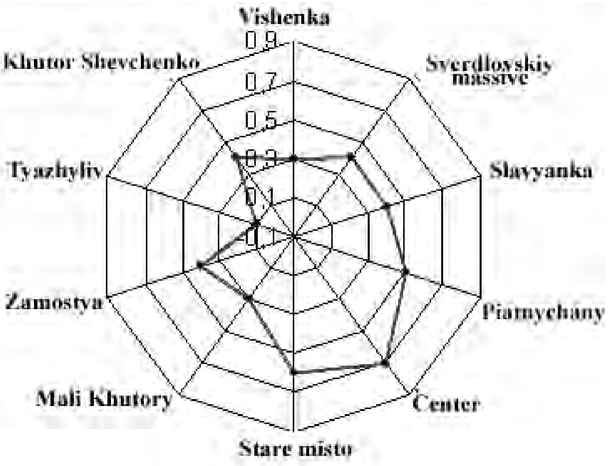

Fig. 2. Average levels of VEP residential zones of Vinnitsia's micro-districts

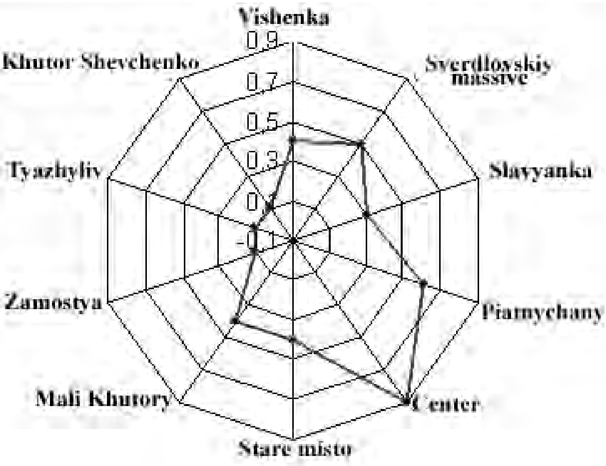

Fig. 3. Average levels of VEP of Vinnitsia's administrative and cultural zones

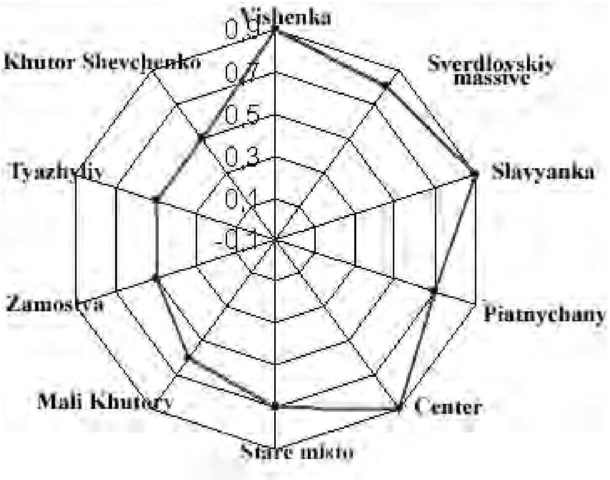

Fig. 4. Average levels of VEP of Vinnitsia's green zones

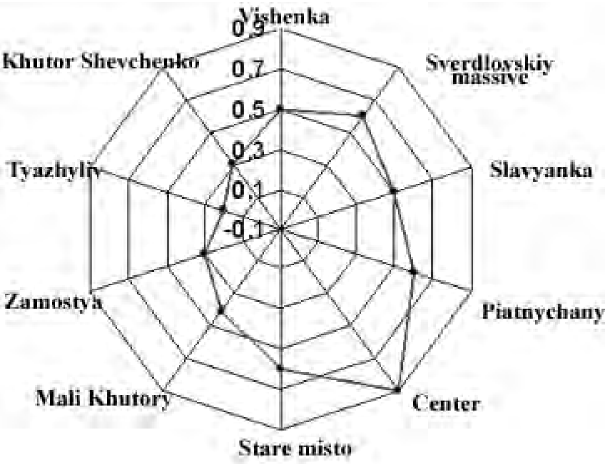

Fig. 5. Average levels of VEP of Vinnitsia's urban environment

3. Conclusions

1. During the videoecological analysis of urban environment the architecture and environment interaction was studied and a typology of contact zones for the city of Vinnitsia developed. The components of the city contact zones were systematized.

2. Areas of the analyzed components were experimentally measured (areas of objects CZ, CGZ, functional areas, the calculated squares, etc.). Scoring of the territorial video-ecological perception of Vinnitsia was provided on the basis of the appropriate methodology. According to the results of calculation, a map- scheme of video-ecological perception of Vinnstsa was established; a distribution diagram of video-ecological sensitivity levels was built for each of the functional areas of the city (residential, administrative, cultural, green) and the urban area as a whole

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Vol. 1, No. 1, 2016

THE CONCEPT OF ENVIRONMENTAL SAFETY OF VINNYTSIA REGION IN THE WASTE MANAGEMENT SPHERE

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Abstract. The aim of the research is to collect the information and analyze integrated systems of municipal solid waste (MSW) management and treatment in Vinnytsia region for its further optimization.

The state of landfills and waste dump sites in Vinnytsia region, existing MSW collection system (container availability) and waste transportation system (availability and frequency of transportation) in all districts of Vinnytsia region, legal framework in the field of solid waste management, the state of public awareness and public opinion on MSW management in Vinnytsia region are analyzed; recommendations for environmental safety of Vinnytsia region in the waste management sphere are given.

Key words: municipal solid waste (MSW), waste management, waste separation, landfill, concept of environmental safety.

1. Introduction

Active movement and integration to the Europe Community have been recently declared in Ukraine. But one of the requirements to achieve this is to create an operating system for waste sorting. Currently such system does not exist.

Within the actual law on waste [1] in Ukraine, the storage of unsorted waste and toxic or harmful waste will be prohibited since January 1, 2018. The consequence of this law is a ban on usual landfill operation and its closure, which will increase the relevance of waste problem. Some local authorities prepare themselves in advance to these changes and do the preparatory work, creating the basis for waste sorting, plan budget funds and involve experts and scientists in the work, but others neglect due to the lack of funds and experience.

It is well known that one of the factors slowing down the introduction of advanced technologies of recycling and waste management is a low level of understanding of waste issues relevance by people. Also, the inertia of this process is increased by insufficient funding, unwillingness to change, incorrect tariff policy, inadequate legislation.

However, there are examples of progressive implementation of urban development programs in the field of waste management in Ukraine.

One of the important stages of the development of waste management concept is to collect detailed information on the current state of the problem [2]. For this purpose the analytical and exploratory research are conducted within Vinnytsia region about the quantity and characteristics of landfills, waste volume, lifetime, waste composition, tariffs on waste collection, quantity of available staff, availability of containers and other equipment, tariffs on secondary resources, and so on [3]. Figure 1 shows the areas of information collection for further development of the mechanisms of the existing system improvement and designing the effective concept of MSW management.

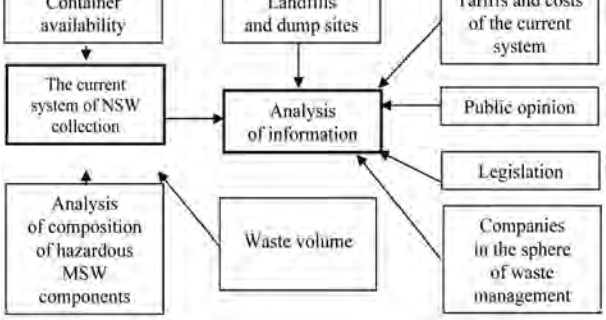

Fig. 1. Scheme of objective data collecting on the problem state

2. Experiment

There are 27 districts in Vinnytsia region, each populated by 25–55 thousand residents, about half of them live in district centers and the rest people live in villages. Also these districts have about 30–50 waste dump sites, in fact, in every village or village council (see fig. 2). Overall, Vinnytsia region has only 5–7 landfills built on relevant modern technologies. That is, 1 landfill in 3–4 districts [4, 5].

During the research we have found that the periodic waste collection is provided in about 20 % of Vinnytsia region. Other territories are not covered with systematical waste collection. This causes a large number of waste dump sites in unsettled areas.

Overall, the system of MSW management in Vinnytsia region is actually presented only by waste transportation to landfills or dump sites. Sometimes even such management is not provided.

Some municipalities in Vinnytsia region have waste sorting stations. They are in Vinnytsia, Kalynivka, Murovani-Kurylivtsi, Kryzhopil and Bar (see Fig. 3) [6]. However, almost all of them do not work due to the lack of funds for their startup or due to financial inefficiency. The real state of most of them (which cost a few million hryvnias each) is very poor, since the stations degrade when stopped. An example of the right use of waste sorting station is one in Stadnytsia village near Vinnytsia.

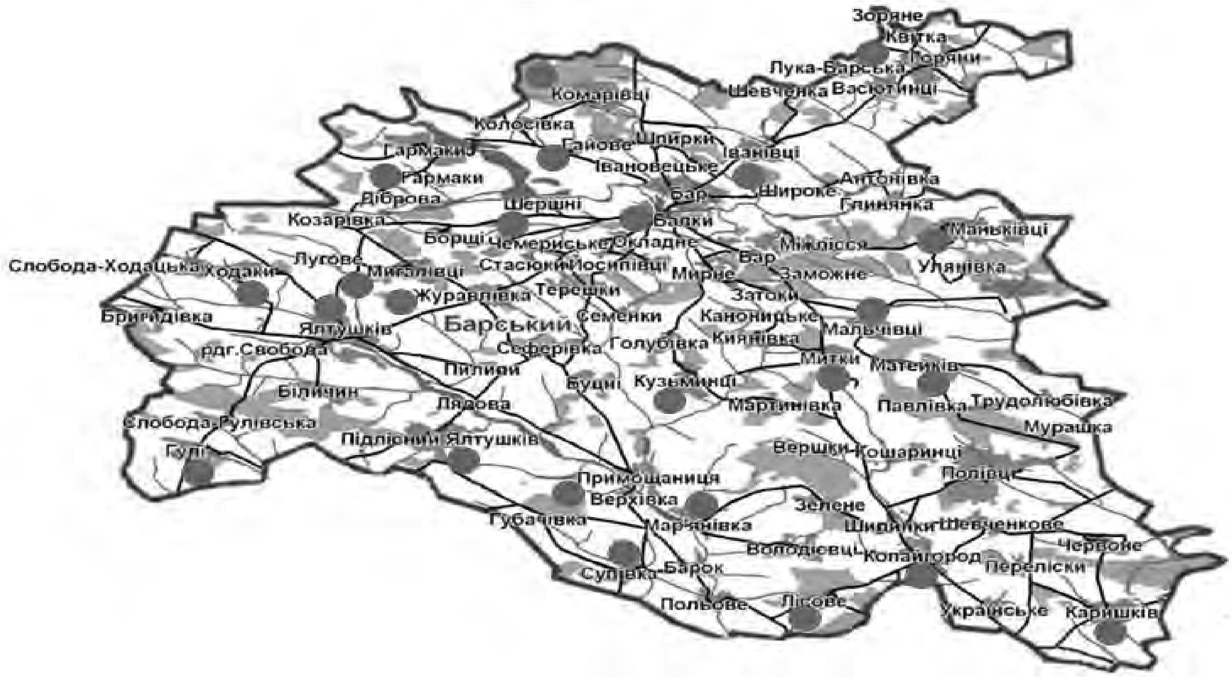

Fig. 2. Map of landfills and waste dump sites in Bar district

Fig. 3. Project of placing of inter-district waste sorting stations

To start a waste sorting station one needs about two million hryvnias. European countries' experience shows that more effective is the use of small waste sorting stations with the capacity of 20–30 cubic meters of waste per day for several towns and villages.

Ukraine plans to implement administrative reform, by which combining and amalgamation of local councils and the reducing of the power of district and regional authorities will be done. It can give an impulse to the realization and real implementation of widespread waste collection and environment friendly MSW management [7–9].

The investigation of chemical compounds content in soils near landfills and waste dump sites is also an important part of landfills analysis. We have analyzed the soils for the presence of metal cations (nickel, lead, copper, cadmium, manganese and zinc) near the next town landfills: Koziatyn, Yampil, Gnivan, Bar, Kalynivka, Haisyn, Zhmerynka, Tomashpil, Tyvriv, Voronovytsia, Vinnytsia, Mazurivka village and others. After analyzing the data it is clear that the excess of maximum permissible concentration is observed in 4 out of 13 investigated landfills and waste dump sites. Near Bar landfill zinc concentration in soil is 10,35 mg/kg higher than the limit value, and lead concentration is 13.6 mg/kg higher (see Fig. 4). There is a slight excess of nickel content near Haisyn landfill (see Fig. 5). Zinc content in the soil near Gnivan landfill is almost 5 times higher than permissible standards, and 1.5 times higher in the soil near Yampil landfill [10].

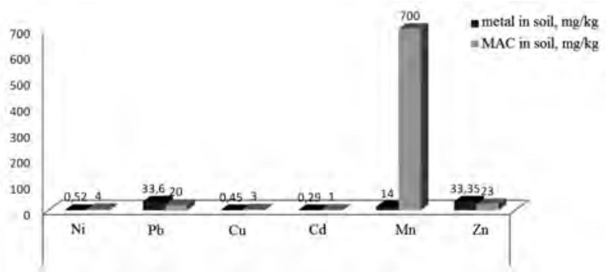

Fig. 4. Content of heavy metals in soils near Bar landfill

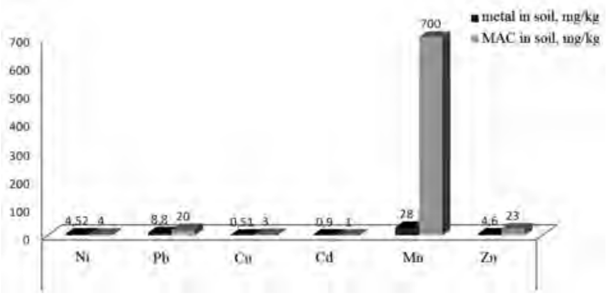

Fig. 5. Content of heavy metals in soils near Haisyn landfill

3. Results and Discussion

1. Analysis of the landfills in Vinnytsia region shows:

- the state of most landfills is unsatisfactory, a lot of them do not meet the specified requirements and need to develop measures to improve their conditions and meet the requirements;
- average percentage of landfills filling is about 25 %, that allows to use them for a long time, but usually the biggest landfills and waste dump sites in district centers are filled much more – near 80 %. This fact requires immediate actions against them. Particularly noteworthy are landfills near the following settlements: Bar, Bershad, Haisyn, Illintsi, Kryzhopil, Lypovets, Lityn, Vendychany (Mohyliv-Podilskyi district), Murovani Kurylivtsi, Bratslav (Nemyriv district), Kudlai (Nemyriv district), Ulaniv (Khmilnyk district), Sharhorod, Galzgbiivka (Yampil district) [11];
- an average term of landfills use is about 20 years and according to landfill passports they can be used for another 20-30 years. However, some landfills have already been used for 40–60 years, which exceeds projected term of use and requires their immediate closure or intervention. Particularly noteworthy are landfills near the following settlements: Nosivtsi (Haisyn district), Uladivka (Lityn district), Teplyk, Ulaniv (Khmilnyk district), Sharhorod;
- the majority of landfills have an area of about 0.5–1 hectares, but some have an area of 3–5 hectares, that shows the high rate of their filling or a long term of use, and therefore they require increased controlling;
- the limit exceeding of pollutants concentration in soils near some observed landfills is observed.

2. Analysis of the waste management system in Vinnytsia region shows the following key shortcomings:

- insufficient quantity of containers for waste collection (very often there are no containers even in the localities where waste is collected);
- a lot of communities are not covered with MSW management system;
- the lack of specialized vehicles for waste transportation in many communities (available only in larger districts centers), very high (more than 80 %) vehicles depreciation;
- very limited resources for the development of MSW management infrastructure;
- focusing of producers on their own economic interests associated with increased profits, and insufficient attention to the waste problem;
- very slow implementation of economic instruments to attract MSW to recycling, lack of elaborated mechanisms for their application;
- inconsistency of main directions of MSW management policy at different levels of government;
- uncertainty and merger of functions of appropriate organizations at regional, district or local level in MSW management;
- limited interaction between municipalities, small scale of the problems solved by them, which does not help to solve the waste problem as a whole;
- insufficient, incomplete, no real time information about qualitative and quantitative parameters of MSW management.

It should be noted that separate collection of MSW is introduced only fragmentally (the best examples are in the towns of Tulchyn,. Mohyliv-Podilskyi, Vinnytsia) and a general system does not exist.

The problem of hazardous waste as a part of MSW is solved very slowly and its separate collection occurs only in a few places.

3. Legislation in MSW management at the national and regional levels as a whole is sufficient. There are accepted and valid national and regional programs of MSW management. However, the main problem is the lack of effective mechanisms of implementing the thesis of these programs at a local level.

Currently there are several bills under consideration in the Parliament, regarding public commitment to sign contracts for waste management. Their adoption would give a significant impulse to solve the waste problem.

4. Contact with people during waste management has a very small scale. Mostly people do not have any information about the problems, which can occur in case of improper waste management, and the possible solutions. Solving this issue could be the key to the future introduction of effective waste management system.

The responsibilities and powers in waste management sphere are currently transferred to the local level by legislation. At the same time, local authorities have very limited financial possibilities for the implementation of these powers. Most of the rural areas are not covered with any system of MSW management and a lot of rural communities have no possibility to create their own system. Thus we have a very difficult situation for local communities and local authorities in rural areas. It requires immediate actions by communities and local authorities to develop join local plans of MSW management, the involvement and the effective use of all possible resources to create sustainable models of MSW management. This is only possible by combining the resources of communities, including inter-municipal cooperation.

General recommendations for the concept of environmental safety in Vinnytsia region in the waste management sphere are the following:

1. The current system of MSW management in Vinnytsia region is presented only by its disposal at landfills and waste dump sites and needs radical change and improvement.

2. All state institutions, involved in waste management, as well as the media have to conduct explanatory and educational activities regarding waste management, in particular: release promotional and educational leaflets, books, brochures; significantly increase the quantity and quality of broadcasts on environmental issues, including those dedicated to the problem of waste; conduct explanatory work in kindergartens, schools and neighbourhood to inform people and fundamentally change people’s conscience from the post-Soviet to eco-civilizational.

3. Public environmental organizations, students-environmentalists and others in their work with population should focus on the ideas of sustainable development: the necessity of self-limiting, ecologisation of life, transition from harmful and dangerous technologies to modern and resource-saving eco-technologies, proper waste management.

4. It is recommended to sort the waste at the first stage of its appearance at home or at the container places, and increase the responsibility for the waste disposal in unauthorized places and non-compliance with other requirements of legislation in waste management.

5. During the development and implementation of new landfills all necessary environmental, construction and sanitary norms and state standards should be carefully considered.

6. For appropriate state organizations and local authorities it is recommended to work out a clear scheme of the most effective use of the existing waste sorting stations, which have been purchased by several regional centers, taking into account the interests of local communities throughout Vinnitsa region.

7. State and local authorities should consider possible options of attracting investments to solve the waste problem.

8. It is necessary to revise the tariffs on waste management because their low level does not allow to solve the waste problem.

9. It is recommended to increase the number of places of the recycled materials collecting and solve the problem of separate collecting of hazardous household waste.

10. It is recommended to create ecological coordination center for waste management based on a working group and relevant experts, representatives of utility companies, local authorities and the public.

4. Conclusion

One of the main problems of the existing waste management system is the lack of financing and low tariffs on waste management. This, in turn, is caused by low incomes of the people and public misunderstanding of the problem urgency and its consequences.

To create an effective system of transportation, collection and recycling of MSW laws of Ukraine should be changed to encourage private entrepreneurs to invest money into this sphere, as well as to incinerate MSW or landfill gas and sell the electricity to the network at a favorable rate. Thus, it is possible to achieve effective waste collecting and recycling, and, most importantly, partly solve the problems of waste and overflow of landfills and waste dump sites.

The concept of waste management designed for Vinnytsia region is relevant for most regions of Ukraine as well.

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DECONTAMINATION OF RADIOACTIVE LIQUID SYSTEMS BY MODIFIED CLAY MINERALS

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Abstract. The process mechanism for sorption of strontium and cesium from liquid radioactive waste using modified bentonites from Yaziv sulfur deposit was investigated. The technique for predicting the intensity of the sorption process based on the comparison of experimental and calculated values of mass transfer coefficients was proposed. It was detected that the process of sorption extraction of strontium and cesium from liquid medium using modified clay minerals may be best described by a three-parameter model of the adsorption isotherms.

Key words: modified bentonite, adsorbent, liquid radioactive waste (LRW), diffusion.

1. Introduction

Steady growth in human economic activity leads to a considerable increase in polluted water volumes. Although a large number of sewage treatment plants have been put into operation at the enterprises of this country in recent decades, the technologies used today mostly are outdated and ineffective. As a result the insufficiently treated waste water, its falling into the hydrosphere creates a significant environmental hazard. Therefore, researchers have faced an urgent need to develop modern highly effective technologies for integrated wastewater treatment from hazardous environmental contaminants with minimum cost and with maximum purification degree. In full, it concerns wastewater contaminated with dyes, radionuclides and organic solvents, which belong to the most dangerous ones for the hydrosphere.

Radioactive materials and ionizing radiation sources are widely used in nuclear power engineering, in medicine, in many industries and in scientific research. The emergence of liquid radioactive waste (LRW) is possible in any of these areas. The LRW can be formed as a result of rules violation while handling radioactive materials, as a result of depressurization of containers with ionizing radiation sources during decontamination or decommissioning of nuclear installations.

An effective method for the LRW decontamination is the flotation and coagulation process. In water decontamination it is difficult to separate flotation and coagulation, because the scheme implements the consequent application of the both methods – coagulation followed by flotation of sludge with foaming [1].

In case of applying iron hydroxide paired with flotation reagent at pH=7 the degree of extraction of Sr-90 was 35–40 %, whereas at pH = 11 it increased to 98 % [2], this can be explained by chemical deposition of Sr-90 in the form of hydroxide. Removal of Sr-90 with the use of iron and manganese hydroxides does not exceed 50 % in acidic medium, while 70 % – in neutral and 98 % – in alkaline medium. In contrast, the removal of Cs-134 with manganese hydroxide does not occur throughout the pH range. Overall, the removal of Sr-90 and Cs-137 by coagulation cannot achieve the high levels of exclusion.

Swedish scientists [3] found that coagulation and flotation methods may remove virtually all radionuclides, except Sr and Cs, in the case of aluminum and iron salts application with subsequent filtering through sand filters. The disadvantage of this method is formation of large amounts of radioactive sludge.

At present considerable attention of leading domestic and foreign scientists is paid to adsorption methods, including obtaining the effective adsorbents based on natural minerals. Besides, the mineral resources of Ukraine are represented by many minerals (natural zeolites, glauconites, bentonites, palygorskites) which have a developed porous structure and possess the adsorption and ion exchange properties, they can be successfully used in environment protection technologies for the sorption treatment of wastewater.

2. Research goals

The aim of the work is to explore kinetic characteristics of the process of adsorption of Sr-90 and

Cs-134 by modified clay minerals from liquid radioactive waste, and to develop a technique for predicting the intensity of sorption processes on the basis of comparative analysis of experimental and calculated data as well as their compliance with the adsorption isotherm.

3. Results and theoretical interpretation

The form of the adsorption isotherm curve allows characterizing the intensity of sorption processes. For most of the adsorption systems, this curve has a peculiar form of the Langmuir isotherm. A specific feature of this type of adsorption isotherms is that the value of a particular component concentration in solution is such that in the solid phase the equilibrium concentration reaches the value which can be considered almost constant.

In order to increase the sorption capacity of bentonite minerals we performed their modification using ferrocyanides of iron (III) and copper (II), hydroxide of titanium (IV), a solution of titanium (IV), chloride of stannum (IV) in an organic solvent and hydroxide of antimony (V).

The infrared spectra of the samples of modified bentonite clay in the area of 2800-3800 cm^{-1} are shown in Figure 1, a. The presence of identical bands in the spectra of all samples at 3697 cm^{-1} and 3620 cm^{-1} (curves 1 – 6) indicates the equivalence of surface and internal hydroxyl groups associated with structural silicon and aluminum both in natural clay and in its modifications.

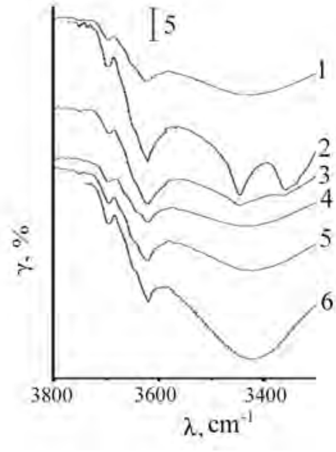
For the samples of the clay matrix with ferrocyanide of iron, with hydroxides of titanium, stannum and antimony (curves 1, 4, 5, 6) the band in 3430 cm^{-1} is identical, while for the samples with ferrocyanide of copper and ferrocyanide of copper and potassium (curves 2, 3) a split of peak is observed which forms two absorption bands in 3440 cm^{-1} and 3356 cm^{-1}. Such character of peaks is observed in the infrared spectra of Cu-form montmorillonite belonging to the vibrations of hydroxyl groups associated with dimerized copper molecules. It should be noted that the partial replacement of copper ions for potassium ions (ferrocyanide of copper-potassium on clay matrix sample) decreases the number of hydroxyl groups involved in the formation of hydrogen bonds with water molecules, which is manifested by the reduction of peak intensity after 3356 cm^{-1} (Fig. 1, *a* – curve 3).

Figure 1, *b* shows the absorption spectra of samples in the area 700–1800 cm^{-1}. All spectra (curves 1–6) are present a band in 1630 cm^{-1}, that is characteristic of the deformation vibrations of water adsorbed on the surface of the mineral. It should be noted that its position for the sample modified with ferrocyanide of iron (curve 1) remains unchanged as compared to the natural mineral, whereas for the samples with hydroxides of antimony, titanium, and stannum (curves 4, 5, 6) the band bias is observed in the region of higher frequencies (1636 cm^{-1}). This indicates the formation of additional hydrogen bonds between the adsorbed water and coordinating metal centres present in the modified clay mineral. The band shift into the area of lower frequencies (1616 cm^{-1}) for the samples with ferrocyanides of copper and copper-potassium (curves 4, 5) is associated with structural changes in clay mineral that occur due to formation of these ferrocyanides.

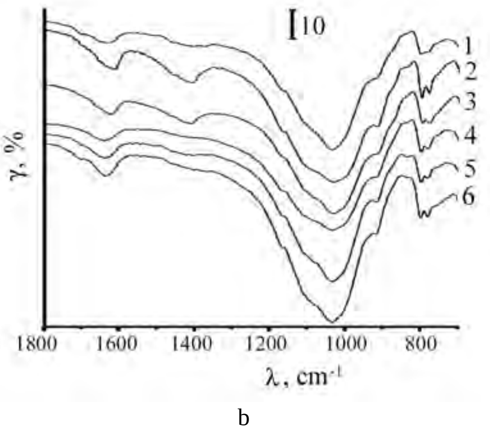
In the process of modification the destruction of calcium and magnesium carbonates takes place. This is confirmed by the disappearance of the characteristic peaks of carbonate component after 874 cm^{-1} and 710 cm^{-1} (Fig. 1, *b*, curves 1–6).

The undertaken investigations of chemical modification prove that the destruction of carbonate component occurs on the surface of montmorillonite and the phases of ferrocyanides of iron (III), copper (II), copper-potassium, as well as hydroxides of titanium (IV), stannum (IV) and antimony (V) are formed. The modified samples have a well-developed surface that allows to predict the external-diffusion mechanism of sorption.

Taking into account the character and properties of pollutants we can choose the optimal method of modifying natural sorbents for intensification of sorption processes during the treatment of contaminated liquid media.



a



b

Fig. 1. Infrared spectra of the samples of modified bentonite clay (where λ- wavelength, γ – bandwidth)

The isotherm of strontium sorption by the natural clay (taken from Yaziv sulfur deposit and modified by ferrocyanide of iron at the temperature of 20 °C) is presented in Figure 2. The process kinetics for Langmuir isotherms in the area of component high concentrations in the solution has internal-diffusive character. In the area of low concentrations corresponding with the linear part of adsorption isotherms the limiting stage of the process is external-diffusive kinetics ($C = 5 \cdot 10^{-4}$ mol/dm^3). In the transient interval of concentrations the kinetics is mixed.

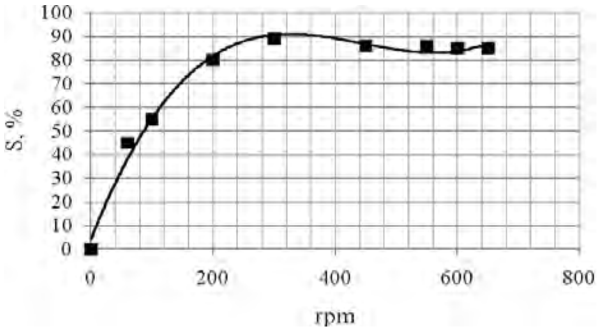


Fig. 2. The isotherm of strontium sorption by bentonite clay (taken from Yaziv sulfur deposit and modified by ferrocyanide of iron). The ratio "liquid: solid phase" equals 100 cm^3/mg, pH=7

We investigated the process of absorption of strontium at the concentration of $C = 1 \cdot 10^{-4} - 5 \cdot 10^{-4}$ mol / dm^3, corresponding to pollution of real water bodies and lies in the intermediate area.

Natural clay of Yaziv sulfur deposit has a capacity of 0,14 mEq Sr per 1 g of clay. Relatively high sorption capacity in respect to Sr is explained by the content of carbonates [4]. The increase of sorption capacity is determined by the ion-exchange character of sorption when Ca^{2+} ions being present in the structure of the clay matrix are replaced by Sr^{2+} ions.

Modifying natural clay by ferrocyanides of transition metals significantly increases the sorption capacity regarding Sr to 0,19; 0,20 and 0,25 mEq Sr per 1 g of ferrocyanide of iron, ferrocyanide of copper, and ferrocyanide of copper-potassium, respectively. However, for such modified sorbents as hydroxide of titanium, hydroxide of stannum, and hydroxide of antimony the sorption capacity increases to the values of 0,35; 0,25 and 0, 23 mEq Sr per 1 g of sorbent respectively [6].

Therefore, we investigated the mechanism of external diffusion on the example of sorbent modified by titanium oxide, which has the highest ability to absorb strontium from a solution. For this purpose, we have studied the process of Sr^{2+} sorption by modified sorbent (hydroxide of titanium on clay matrix) in dynamic conditions. To examine the sorption of Sr using the method of weighed portions, we prepared the working solutions with 0,01 mol / dm^3 concentration, which were diluted with distilled water to the required concentration. Thus, the model solutions that simulate active water were created.

To carry out the sorption experiments in static conditions, a weighted portion of clay sorbent was placed in a container, then the appropriate volume of Sr solution was added, observing optimum ratio of "solid phase: liquid" = 1:100 [5, 6]. Constant process temperature of 20 °C in a water bath was maintained. After the experiments a suspension was separated by centrifugation (400 rpm, time of separation – 15 min) then the aliquot of solution was collected and the content of Sr^{2+} was analyzed.

The study was conducted on a device with paddle stirrer, the frequency of revolutions of which was varied in the range of 50–650 rpm. Samples were taken at the certain time intervals and were analyzed regarding the content of Sr^{2+} in solution.

The data shown in Figure 3 indicate that the increase in the number of revolutions over 300 rpm does not enlarge the rate of sorption process that allows to assert that adsorption process goes into internal diffusion area in which the external parameters do not affect the kinetics of sorption.

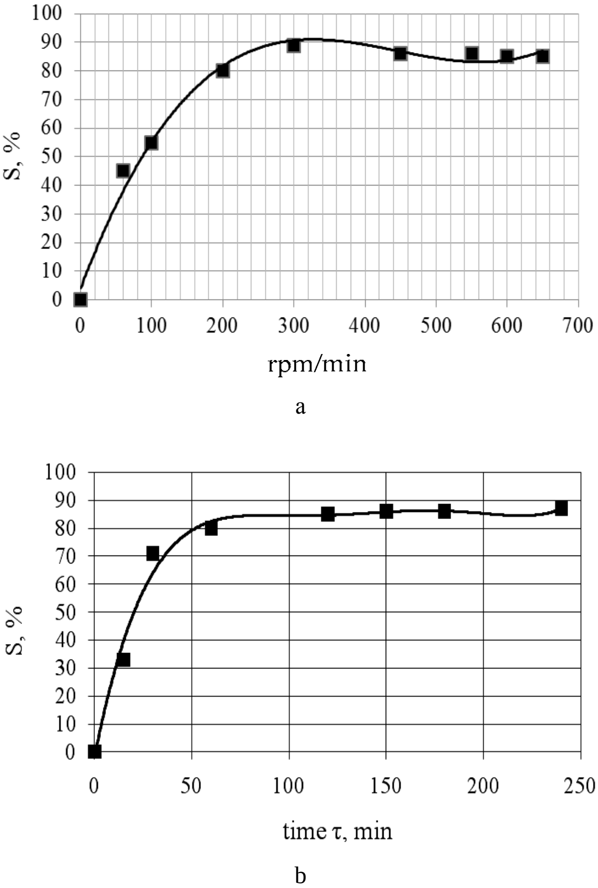


Fig. 3. The dependence of degree of strontium sorption by bentonite clays on:
a – the number of revolutions per minute n (rpm);
b – time τ (min).
The bentonite clays were taken from Yaziv sulfur deposit and were modified by titanium oxide.
The ratio "liquid: solid phase" equals 100 cm^3/mg, initial concentration of strontium is $5 \cdot 10^{-4}$ mol/dm^3, pH=7

The duration of stirring at the maximum level of sorption is within 40-50 minutes. Efficiency of sorption of cesium by ferrocyanide of iron on clay matrix correlates straightly to the amount of the added sorbent. The increase in the ratio of “liquid: solid phase” from 500 to 100 dm^3 / kg sorption enlarges the sorption by 40 %, while a further increase up to 50 dm^3 / kg leads only to 9 % growth. The dependence of the sorption of cesium on the amount of another added sorbent – ferrocyanide of copper-potassium on clay matrix – is similar as for the removal of strontium.

Thus, the most effective ratio of “liquid: solid phase” which provides a maximum area of contact of sorbent with the liquid and maximum degree of purification, should be considered as 100 dm^3 / kg.

To confirm the sorption kinetics we performed mathematical calculations of internally-diffusive process of sorption. The results of calculations are presented in Table 1.

Assessing the process kinetics on the whole it should be noted that the effective time to achieve the highest possible degree of strontium sorption for all sorbents investigated does not exceed 1 hour.

The primary source of information on the progress of the adsorption process is the adsorption isotherm. In order to determine optimal parameters and type of adsorption isotherm we conducted the interpretation of experimental data within the known theoretical models.

The established types of isotherms which best describe the sorption process of removal by modified clay minerals (on the example of Cs) are given in the Table 2.

The sorption process of Cs removal on natural clay is described best of all using three-parametric models and Langmuir isotherm. In other cases, the process of sorption removal of Cs is best described by isotherms of Redlich – Peterson (for clay materials modified with ferrocyanide of iron, with ferrocyanide of copper, with hydroxide of titanium), Langmuir ((for clay materials modified with ferrocyanide of copper-potassium), Tosh (for clay materials modified with hydroxide of stannum), and Langmuir – Freundlich (for clay materials modified with hydroxide of stibium). In all cases, the three-parametric isotherms give high values of the determination coefficient indicating the chemical heterogeneity of sorbents surface and the presence of sorption groups of different chemical nature, which differ in chemical activity. During the sorption process the filling of the most active centers of sorption is observed primarily. The surface is continuously filled until all the centers with the lowest energy are be occupied. Data compliance with three-parametric isotherms shows that the sorption proceeds with formation of a monomolecular layer. This is especially true for the removal of cesium in clay materials modified with ferrocyanide of iron and modified with ferrocyanide of copper-potassium for which a constant value is approaching 1, thus the sorption proceeds according to Langmuir mechanism.

Introduction into the structure of the clay mineral hydroxides of transition metals (clay minerals modified by hydroxides of titanium, stannum, stibium) slightly increases sorption capacity. Minor differences in sorption capacity as compared to the natural clay mineral, are probably caused by acid activation of clay mineral surface, that occurs in the process of modification under the influence of free hydrochloric acid.

The process of sorption removal of Sr can be described by Redlich-Peterson isotherms (for natural clay, for clay materials modified with ferrocyanides of iron and copper-potassium), Langmuir isotherms (for clay materials modified with ferrocyanides of copper), Freundlich isotherms (clay minerals modified by hydroxides of titanium, stannum, stibium) (see Figure 4). The three-parameter isotherms in the case of sorbents of the ferrocyanides and natural clay group give high values of determination coefficient whereas in the case of hydroxides on clay matrix $K_{LF} \rightarrow 0$, that is why the Langmuir-Freundlich isotherm cannot describe the process correctly, and the data are interpreted according Freundlich model.

Table 1

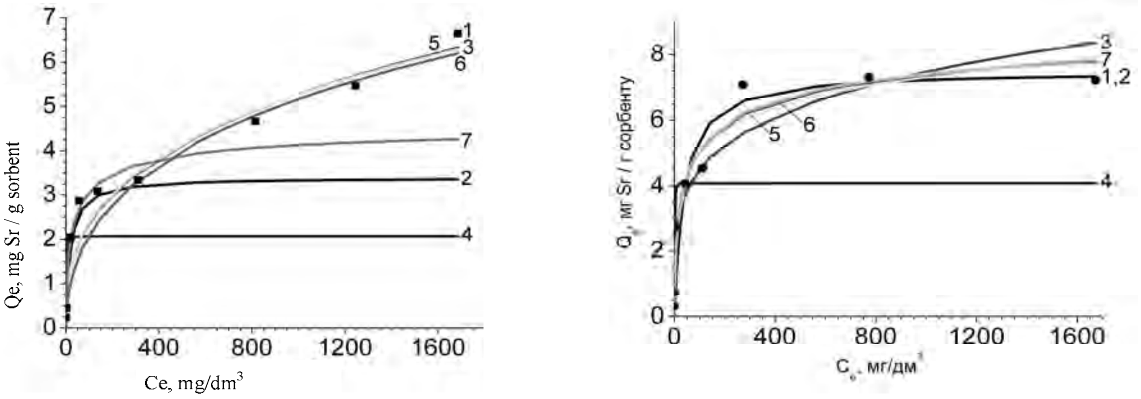
Calculation results of internally-diffusive process of sorption

Modified sorbent based on the clay matrix	μ_n	tgα	Coefficient of internal diffusion D_{in}, m^2/s	Mass transfer coefficient at internal diffusion, *m/s*
Ferrocyanide of copper-potassium on clay matrix	4,471	$2,23 \cdot 10^{-4}$	$7,748 \cdot 10^{-12}$	$1,068 \cdot 10^{-2}$
Ferrocyanide of copper on clay matrix	10,791	$4,92 \cdot 10^{-4}$	$6,445 \cdot 10^{-12}$	$0,921 \cdot 10^{-2}$
Hydroxide of titanium on clay matrix	7,693	$2,72 \cdot 10^{-4}$	$3,892 \cdot 10^{-12}$	$0,556 \cdot 10^{-2}$
Hydroxide of antimony (stibium) on clay matrix	10,795	$5,15 \cdot 10^{-4}$	$3,748 \cdot 10^{-12}$	$0,535 \cdot 10^{-2}$
Hydroxide of tin (stannum) on clay matrix	11,991	$5,83 \cdot 10^{-4}$	$3,485 \cdot 10^{-12}$	$0,497 \cdot 10^{-2}$
Ferrocyanide of iron on clay matrix	17,091	$4,10 \cdot 10^{-4}$	$1,784 \cdot 10^{-12}$	$0,254 \cdot 10^{-2}$
Natural clay	6,993	$7,69 \cdot 10^{-4}$	$0,877 \cdot 10^{-12}$	$0,125 \cdot 10^{-2}$

Table 2

Parameters of adsorption isotherms and criteria for statistical evaluation of the process of sorption removal of cesium on the modified clay minerals

	Natural clay	Ferrocyanide of iron on clay matrix	Ferrocyanide of copper on clay matrix	Ferrocyanide of copper-potassium on clay matrix	Hydroxide of titanium on clay matrix	Hydroxide of tin (stannum) on clay matrix	Hydroxide of antimony (stibium) on clay matrix
1	2	3	4	5	6	7	8
Langmuir isotherm							
q_m	6,59	14,53	24,14	**43,82**	10,26	6,52	6,41
K_L	0,03	0,76	0,20	**0,11**	0,01	0,02	0,02
R^2	0,9937	0,8838	0,7724	**0,9404**	0,9548	0,9658	0,9700
SNE	3,91	3,57	3,99	**3,32**	3,74	4,07	4,01
Freundlich isotherm							
K_f	1,22	1,06	1,30	2,14	0,25	0,24	0,22
n	0,15	2,26	1,98	1,99	1,48	1,52	1,66
R^2	0,8474	0,8086	0,8804	0,8668	0,9740	0,9869	0,9556
SNE	3,81	3,66	3,51	3,99	3,53	3,84	3,82
Dubinin-Radushkevych isotherm							
q_m	0,21	14,27	24,88	41,31	3,54	3,08	2,18
E	0,22	1,29	1,86	0,26	9,70	0,22	0,21
R^2	0,3738	0,8685	0,7545	0,9087	0,7448	0,7800	0,6632
SNE	3,90	3,62	3,76	3,80	3,93	3,86	3,84
Redlich-Peterson isotherm							
K_{RP}	1,75	**3,04**	**5,91**	5,39	**1,01**	0,67	0,65
a_{RP}	0,00	**0,17**	**1,04**	0,17	**13,95**	1,85	1,85
в	0,14	**0,97**	**0,73**	0,95	**0,001**	0,45	0,51
R^2	0,9996	**0,9115**	**0,8907**	0,9430	**0,9885**	0,9347	0,9232
SNE	3,80	**3,27**	**3,31**	3,44	**3,36**	3,65	3,67
Tosh isotherm							
q_m	**2,73**	27,65	25,67	46,41	3,88	3,10	**3,73**
b_T	**0,01**	1,50	0,60	0,06	0,10	0,40	**0,54**
n_T	**1,50**	0,49	0,22	1,01	0,07	0,21	**0,21**
R^2	**0,9956**	0,9524	0,8955	0,9387	0,9904	0,9010	**0,8762**
SNE	**3,67**	3,63	3,33	3,81	3,96	3,61	**3,54**
Langmuir-Freundlich isotherm							
q_m	4,76	18,22	24,56	44,32	–	**6,43**	8,19
K_{LF}	0,06	0,35	0,74	0,07	–	**0,01**	0,01
n_{LF}	1,48	0,62	1,08	1,04	–	**0,75**	0,90
R^2	0,9993	0,9547	0,8917	0,9383	–	**0,8408**	0,9789
SNE	3,92	3,36	4,10	3,53	–	**3,53**	3,78



a b

Fig. 4. Strontium sorption isotherms:
a – ferrocyanide of iron on clay matrix; b – ferrocyanide of copper on clay matrix
(1 – experimental data, 2 – Langmuir isotherm; 3 – Freundlich isotherm; 4 – Dubinin-Radushkevych isotherm;
5 – Redlich-Peterson isotherm; 6 – Tosh isotherm; 7 – Langmuir-Freundlich isotherm).
The ratio “liquid: solid phase” equals 100 cm^3/mg, pH=7

Describing the affinity of strontium to sorption materials based on modified minerals, it should be mentioned that it is rational to build a kinship series only for the materials where sorption is satisfactorily described by Freundlich equation (all the materials except sorbents modified by ferrocyanides of copper and copper-potassium). By affinity the sorbents are placed as follows: natural clay > sorbent modified by hydroxide of antimony > sorbent modified by hydroxide of titanium > sorbent modified by hydroxide of stannum. Characteristically, the materials based on hydroxides have better absorption characteristics than natural minerals (see Figure 4).

The obtained data and its interpretation for different types of adsorption isotherms allows to describe and to predict the process of LRW sorption cleaning on modified clay minerals as well as to choose the materials with the best sorption properties regarding Cs and Sr (clay sorbents modified by ferrocyanides of iron, copper and copper-potassium for Cs sorption, and bentonite clay sorbents modified by ferrocyanide of copper-potassium, by hydroxides of titanium and antimony for Sr sorption).

4. Conclusion

It was revealed that the process of sorption removal of Cs and Sr with the modified clay minerals is best described by the three-parameter models of Redlich – Peterson and Langmuir – Freundlich. This testifies the presence of active centers of different chemical nature in the sorbents. It was shown that surface modification of bentonite clay with ferrocyanides of iron and copper significantly increases mineral sorption capacity regarding cesium, as well as modification with hydroxides of titanium, tin and antimony – regarding strontium.

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ADAPTATION OF IUCN CLASSIFICATION SCHEMES FOR ENVIRONMENTAL SAFETY PASSPORTS OF SPECIES

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Abstract. This study aimed to improve the ways of risk assessment for environmental safety. The implementation of “Environmental safety passports of species” is of practical importance for effective risk assessment of individual species impact to the environment, humans and other living organisms. The classification schemes of International Union for Conservation of Nature for evaluating habitats, threats & stresses, use and trade, livelihoods of species were analyzed and adapted to the requirements of environmental safety. Some sections such as general information about species, their distribution, ecological classification, metabolism features, risks evaluation and beneficial use were itemized to be included into the structure of ESPS.

Keywords: environmental safety, risk assessment, evaluating schemes, certification.

1. Introduction

Problems of environmental safety and nature protection are closely related. However behooves of particular species can be in confrontation with interests of humans, other living organisms and ecosystems [1]. “Environmental safety passports of species” (ESPS) appear to be a universal platform for impersonal evaluating of risk taking into account the interests and tasks of environmental safety and nature protection [2]. ESPS accumulate veracious scientific information about individual species and evaluation of risk probability of real and potential threats from this organism to the environment, humans and other bio-objects [3]. This system will enhance control level of particular species activity and improve the effectiveness of environmental protection [4].

The implementation of ESPS will promote nature conservation, because it will help to discover some risks from individual species for the environment on the one hand, and ground their environmental protection on the other hand. The leader of scientific developments in species protection is International Union for Conservation of Nature (IUCN). This organization was founded in 1948 as the world’s first global environmental structure for conserving biodiversity and helps to find pragmatic solutions to most pressing environment and development challenges. It has an official observer status at the United Nations General Assembly and influences international environmental conventions, policies and laws. IUCN is the world’s largest global environmental organization with more than 1,200 government and NGO members and almost 11,000 volunteer experts grouped in six commissions in some 160 countries.

IUCN’s work focuses on valuing and conserving nature, ensuring effective and equitable governance of its use, and deploying nature-based solutions to global challenges in climate, sustainable development and food security. The central mission of IUCN is to demonstrate that biodiversity is fundamental for solving some of the world’s greatest problems. Scientific experts set definite international global standards of species extinction risk assessment for the IUCN Red List of Threatened Species [5]. A set of standard terms has been developed for documenting taxa on the IUCN Red List [6]. These classification schemes ensure global uniformity when describing the habitat in which a taxon occurs, the threats to the species, the conservation actions needed and practical ways of using taxon [7]. The **objective** of this study is adaptation of IUCN classification schemes to ESPS to find the optimum way of risk assessment from biological objects to environmental safety.

2. Analysis of IUCN Classification Schemes for applying in environmental safety

IUCN classification schemes are used and constantly improved by a lot of scientists around the world during a long period. It is a very appropriate platform for applying in environmental safety. The analysis of these schemes is needed for adaptation to the requirements of species certification. The classification schemes used in the Red List IUCN assessments include: habitats, threats, stresses, conservation actions in place, conservation actions needed, research needed, use and trade, plant growth forms, ecosystem services, livelihoods [8]. All data are accumulated in the Species Information Service (SIS), which is the central database used by IUCN to store and manage species accounts and assessments for publication on the IUCN Red List. SIS allows the user to enter biological, population, range, and habitat information about the species and have the system of automatic calculation of the categories and criteria of the current Red List. It provides a standardized data format for conducting assessments thereby ensuring assessments using the same classification systems (for threats, habitats, etc) as well as ensuring taxonomic integrity. As an online web application, it allows experts to collaborate remotely on assessments and provides safe, secure storage of assessment information. SIS can also be downloaded and used offline when no reliable internet connection is available. The SIS code source is open and free – anyone can take the SIS system and adapt it to their needs. This service even supports entering uncertain information and calculates a range of possible categories based on uncertain information. Some of the main parts of IUCN classification schemes are analyzed below and grouped by environmental safety precedence.

2.1. Habitat

IUCN habitats classification schemes contain 18 main levels: forest & woodland, savanna, shrubland, native grassland, wetlands, inland rocky areas, caves & subterranean habitats, desert, marine – neritic, marine – oceanic, marine – deep ocean floor (benthic and demersal), marine – intertidal, marine – coastal / supratidal, artificial – terrestrial, artificial – aquatic, introduced vegetation, other, unknown [9]. These levels are divided into sublevels with definitions and examples of alternative habitat terms especially those used in different parts of the world. The habitat types are standard terms used to describe the major habitats in which taxa occur. The importance of each habitat recorded is indicated by coding its suitable – the species occurs in the habitat regularly or frequently, marginal – the species occurs in the habitat irregularly or rarely, or only a small proportion of individuals are found in the habitat, and seasonality – resident, breeding, non-breeding, passage, unknown.

2.2. Threats & stresses

Any analysis of the threats should preferably take into account the timing – past, ongoing or future, scope – the proportion of the total population affected, and severity – the overall declines caused by the threat to calculate an impact score. The analysis also shows the threats impact on taxa concerned as recorded by the stresses. Threats are presented by 12 levels of classification: residential & commercial development, agriculture & aquaculture, energy production & mining, transportation & service corridors, biological resource use, human intrusions & disturbance, natural system modifications, invasive & other problematic species (or genes), diseases, pollution, geological events (volcanoes, earthquakes, avalanches), climate change & severe weather, other options. Stresses are those attributes of a taxon that are impaired directly or indirectly by human activities or processes, e.g., reduced population or fragmentation of forest habitat. Stress is not a threat in and of itself, but rather a degraded condition or "symptom" of the taxon that results from a direct threat. Stresses classification scheme is divided into ecosystem or community and species stresses [10].

2.3. Livelihoods, use and trade

This part shows practical use of living organisms: livelihood, economic & other incentives linked with enterprises & livelihood alternatives, substitution, market forces, conservation payments, non-monetary values. In livelihoods classification scheme a separate record should be created for each type of the product. General consumtion details include the scale of use (local, national, regional, global) and description of the product (e.g. skin, meat, horn, fibre, etc.). Annual consumption of the product can be estimated in volume (m^3), weight (kg), number of individuals. Primary the level of human reliance on this product can be evaluated as emergency resource, optional alternative and essential staple, geographically variable. The question should be asked, who the primary consumers of this resource are: men, women, children, multiple, poorer households, all households, richer households, or another groups. To value the livelihoods it is necessary to calculate the proportion (as %) of total population benefiting from this product, the proportion of household consumption of dietary (as a %) protein/carbohydrate and the proportion of household income for this product. An annual cash income from this product is counted [11].

2.4. Conservation activity

This paragraph combines conservation actions in place, conservation actions needed, research needed and ecosystem services. Conservation activity includes habitat & resource management and protection, species management and recovery, education & awareness, law & policy regulations, research, monitoring, planning and other actions. For ecosystem services IUCN proposes to care about water quality & supplies, flood control, climate regulation, landscape, air quality, nutrient cycling, habitat maintenance, provision of critical habitat, pollination, erosion control, bio-control, shoreline protection [12].

3. Results

After the analysis of IUCN classification schemes it was necessary to modify the structure of ESPS using a lot of experience of species evaluation during many years. The main difference between Red List IUCN evaluation and assessment of species for ESPS is in estimation target: in the first case it is necessary to find the reason for protection of species, in the second one – to discover potential or real risks from this species to humans, other living organisms or nature. But in both cases it is necessary to accumulate information about the evaluated species, therefore some elements of IUCN classification schemes can be included to plan the structure of ESPS. As a result the next plan for the main part of species passport scheme is proposed below.

3.1. General information about species includes taxonomical position, morphology, life cycle, etc. ESPS summarize the data of scientific researchers from different fields of science in any accessible way. It will provide the most comprehensive information about different aspects of the species from the reliable sources of information. All available data about each species of living organisms will be conveniently structured in the passport. ESPS will have an open structure for addition of new data obtained by the experts. In this way scientific information becomes available to a wide range of stakeholders which will help to avoid wrong interpretations and enhance the systematization of environmental safety.

3.2. Habitat & geographical distribution

A habitat is the ecological or environmental area where an organism lives, finds food, shelter, protection and mates for reproduction. A habitat is made up of physical factors such as soil, moisture, range of temperature, and availability of light as well as biotic factors. A habitat classification scheme can be defined as a structured system of habitat types, arranged in a hierarchy, where the types are clearly defined and recur in different geographical places. Worldwide, there are many habitat classification schemes and whilst many have a hierarchical structure, others are not hierarchical, providing a structured list of habitat attributes instead. In a hierarchical system habitat classes are described at various levels of detail and are nested so that numerous detailed habitats lay within a smaller number of more broadly-defined habitat classes. It is a guiding principle that classes should recur under similar environmental conditions in other geographical areas to justify their inclusion into a classification system. Habitat description was developed in IUCN classification schemes in a very rational and detailed way, so it is expedient to use this structure with related links [9].

3.3. Ecological classification of species shows the adaptation way of organisms to the environment, their place in nature and types of relationships with other living organisms and human. Functional groups of organisms are based on morphological, physiological, behavioral, biochemical, environmental responses or on trophic criteria. Classification considers ecological role, degree of specialization, trophic level, adaptations and behavior of organisms. There are six main ecological relationships between organisms two of which are oppositional and four are symbiotic. The oppositional relationships are predation and competition. The symbiotic relationships are mutualism, commensalism, amensalism and parasitism. The ecological relationship an organism depends on is the way the organism adapted to its environmental pressures on evolutionary bases. Ecological niche shows the role the organisms play in the ecosystem: producers, consumers, herbivores, carnivores, omnivores, scavengers, decomposers, etc. Interspecific relations are numerous interactions between different species, which are usually described according to their beneficial, detrimental, or neutral effect: for example, mutualism is relation (++), or competition is relation (--). Other interspecific relations include parasitism, infectious disease and competition for limited resources, which can occur when two species share the same ecological niche. Ecological classification also depends on physical and mechanical fields, based on such abiotic factors, as light, temperature, electromagnetic field, radionuclides, noise, etc. The analysis of the impacts of abiotic factors from habitat to species vital activity shows the range of tolerance, optimum, minimum and maximum value of each factor. Geological, geographical, hydrological, atmosphere and climatological parameters are also taken into account.

3.4. Metabolism features discover the role of the species in nutrient cycle; absorbed, released and accumulated substances of this species; bioactive and toxic molecules produced by this organism. Metabolism is a set of life-sustaining chemical transformations within living organisms. The chemical reactions of metabolism are organized into metabolic pathways, in which one chemical is transformed through a series of steps. The metabolic system of a particular organism determines which substances it will find nutritious and which poisonous. Three basic classes of molecules (amino acids, carbohydrates and lipids) are vital for life; metabolic reactions either focus on making these molecules during the construction of cells and tissues, or by breaking them down and using them as a source of energy, by their digestion. Some organisms produce secondary metabolites, which influence the growth, survival, and reproduction of other organisms. These biochemicals are known as allelochemicals and can have beneficial (positive allelopathy) or detrimental (negative allelopathy) effects on the target organisms. A striking feature of metabolism is the similarity of the basic metabolic pathways and components between even vastly different species. The main metabolic reactions comprise transformation of carbon-containing compounds, transfer of energy from one substrate to another molecular, and oxidation-reduction reactions. If organisms use sunlight as energy source, they are called phototrophic, if organisms preform molecules for energy, they are named chemotrophic. Depending on electron donor there are organotrophic (organic compound) and lithotrophic (inorganic compound). According to carbon source used for the synthesis of organic substances all organisms are divided into heterotrophic (organic compound) and autotrophs (inorganic compound). These three criteria of classification with two variants forming 8 possible combinations exist in nature.

3.5. Risks evaluation

The main purpose of the introduction of passports is to systematize scientific information for determination of effect of the evaluated species on the environment, humans and other living organisms. As a result of the analysis of the information about the evaluated organisms it is be possible to draw a conclusion about the risks and danger impact on this species. The passport calculates statistical probability of negative effects that this species can cause on other organisms, humans and the environment, with specified possible conditions. In Bayesian methods of environmental safety the methodology for risk assessment is perspective for the probability analysis.

3.5.1. Threats for species

Direct threats of proximate human activities or processes that have affected, are affecting, or may affect the status of the species have been assessed. Direct threats are synonymous to the sources of stress and proximate pressures. Threats can be past (historical, unlikely to return or historical, likely to return), ongoing, and/or likely to occur in the future. For each threat additional information may be recorded, some elements of which are required as a part of the minimum documentation standards: timing of the threat (past, ongoing, future, unknown); scope (how much of the species is impacted by the threat) and severity (what is the impact of the threat). The timing, scope and severity are used to calculate an impact score which is useful for the analysis and for distinguishing between major and minor threats. These are threats connected with the area of human intrusion, disturbance and commercial development. It can be urban, industrial, transportation, recreational, agriculture, aquaculture and other activity. This category includes different types of pollution: waste water, effluents, oil spills, seepage from mining, nutrient loads, pesticides, air-borne pollutants (acid rain, smog, ozone) and excess energy pollution (light, thermal, noise). Species can be affected by war, civil unrest, storms, flooding, droughts, volcanoes, earthquakes, tsunamis, avalanches, landslides, climate change and severe weather. Habitat of species can be shifting alteration as a result of natural system modifications. Ecosystem conversion can be realized by degradation and indirect ecosystem effect because of fire, dams, soil erosion, etc. Threats from consumptive use of "wild" biological resources including both deliberate and unintentional harvesting effects: hunting, fishing, gathering, collecting, logging, harvesting. Threats in the class can affect both target species as well as “collateral damage” to non-target species and habitats. Persecution involves harming or killing species because they are considered undesirable [10].

3.5.1. Danger from species

The analysis of species habitats, ecology, distribution and metabolism to find out that these organisms can be really dangerous for the environment, humans and other living organisms has been made. Species can directly affect other organisms’ mortality and disturbance. Also it can be indirect species effect, such as hybridization, competition, inbreeding, loss of mutualism. Species can reduce reproductive success and cause skewed sex ratios, loss of pollinator or other factors which may prevent reproduction of other species. Threats from non-native species or genetic materials have or are predicted to have harmful effects on biodiversity after their occurrence, spread and increase in abundance. Native species can be problematic, when they become superabundant or otherwise cause problems. Harmful organisms not originally found within the ecosystem in question are directly or indirectly introduced and spread into it by human activities. For diseases, it is the infective agent which is considered to be the threat, with the disease being its manifestation in individuals. A number of them are important pathogens which can result in diseases which significantly reduce reproduction or increase mortality. Harmful species originally found within the ecosystem in question, have become “out-of-balance” or “released” directly or indirectly due to human activities. It is a bit of a judgment call as to when a species becomes “problematic”, also referred to as species being "outside its natural range of variation". For diseases it is the infective agent which is considered to be the threat, with the disease being its manifestation in individuals [10].

3.6. Beneficial use

This section applies the paradigm of payments for environmental services (PES), which is a highly promising conservation approach that can improve the resource base over traditional conservation approaches [13]. PES, also known as payments for ecosystem services have been defined as a transparent system for the additional provision of environmental services through conditional payments to voluntary providers. Twenty-four specific ecosystem services were identified and assessed by the Millennium Ecosystem Assessment report in 2005 designed to assess the state of the world's ecosystems. The report defined broad categories of ecosystem services such as food production (in the form of crops, livestock, fisheries, aquaculture, and wild food), fiber (in the form of timber, cotton, hemp, and silk), genetic resources (biochemicals, natural medicines, and pharmaceuticals), fresh water, air quality regulation, climate regulation, water regulation, erosion regulation, water purification & waste treatment, disease regulation, pest regulation, pollination, natural hazard regulation, and cultural services (including spiritual, religious, and aesthetic values, recreation and ecotourism). Notably, there is a “big three” among these 24 services which are currently receiving most interest worldwide: these are climate change mitigation, watershed services and biodiversity conservation [13]. In analogy (reciprocally) the system of evaluation for species services will be developed for ESPS. It can be useful for assessment of beneficial use of any living organisms for human and their significance for nature.

4. Discussion

IUCN classification schemes contain many utility specifications which can be used for the developing structure of ESPS. Adaptation of these schemes is itemized in ESPS structure in such sections as general information about species, habitat & geographical distribution, ecological classification, metabolism features, risks evaluation and beneficial use. Passport systematizes scientific information for determination of the effect of this species on the environment, humans and other living organisms. On the other hand, threats for this species from other species, people and different ecological factors could be evaluated with this passport. ESPS are necessary for effective monitoring and management of environmental safety. Implementation of species certification will increase the level of control in the system of ecological safety and effectiveness of protection actions for environment and humans. It is a comprehensive document which is necessary for all species of living organisms. This minimizes the possibility of incorrect interpretation of scientific data and creates the conditions for constructive interaction between scientists and managers. Work in this direction can help to carry out “The Strategic Plan for Biodiversity 2011–2020”, which includes the values of biodiversity and further develops or enhances the systems for integrating biodiversity values into decision making processes [14]. Global-extent, high-resolution analyses using broad biodiversity and anthropogenic data are needed in order to inform about decision making within the Convention on Biological Diversity resolutions [12]. Some basic methodologies do exist which can serve as a starting point for further monitoring or provide baseline information. The resulting information should be integrated into development plans to ensure that some species receive necessary protection and investments. Such system could help to plan preventive measures for protection from dangerous species. It is important that the results of such analysis are made publicly available and easy to access, so that they can be further utilized, evaluated, and improved. ESPS are necessary for effective monitoring and management of environmental safety. Implementation of species certification will increase the level of control in the system of ecological safety and effectiveness of protection actions for the environment and the humans.

5. Conclusions

1. The bases platform of ESPS structure was improved as a result of IUCN classification schemes analysis for evaluating features and abilities of certain species for the relevant requirements of environmental safety.
2. The adapted ESPS content includes two main parts: the fist section accumulates general information about species, its taxonomy, morphology, life cycle, ecological classification, habitats, distribution, metabolism features, nutrient cycle, bioactive and toxic molecules, etc.; the second part provides evaluation of impact risks to this species and danger effects of this species, considering the beneficial human and environmental use.
3. ESPS contributes to nature protection by discovering some risks from individual species to environment, and at the same time this passport provides the background for conservation of the estimated species by assessment of threats to them.
4. The analyzed methodologies of payments for environmental services can be transformed into the system of evaluation for human use of certain species and environmental services by any living organisms and assess of their significance for nature and people.
5. The implementation of Environmental safety passports of species can forward “The Strategic Plan for Biodiversity 2011–2020”, to develop and enhances systems for integrating biodiversity values into decision making processes.

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Vol. 1, No. 1, 2016

PREPARATION OF QUALITY DRINKING WATER AS A BASIS OF THE ENVIRONMETAL SAFETY AND HUMAN HEALTH

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Abstract. The problem of drinking water preparation with specified quantitative and qualitative composition is very acute today in various countries including Ukraine. The consequences of using the method of reverse osmosis at tap water purification using the equipment with the membrane element Filmtec XLE 440 (8"), produced by DOW Chemical (USA), have been reviewed. Positive characteristics as well as economical and technological shortcomings of reverse osmosis equipment have been proved.

Key words: drinking water; reverse osmosis; preparation of potable water.

1. Introduction

The uneven distribution of fresh water in different regions of the world, including separate countries, the growing consumption of fresh water by industrial and agricultural production, as well as residential areas against the background of continuous decline in the quality of water sources (natural water, mineral water, underground water), as a result of anthropogenic pollution, place the provision of the world's population with quality drinking water among the most important social and economic world’s problems [1].

“The lack of clean water causes more deaths worldwide than war. In some countries, half of the population has no access to safe drinking water and as a result, has poor health” [2].

Unimproved technologies of purification of polluted water that have not been significantly changed over the centuries, contribute to the problem of environmental safety and human health. Therefore, it is relevant today to search for new approaches and development of new effective technologies for drinking water, which are baromembrane methods.

2. Problem formulation

Today, centralized water supply stations in Ukraine use water purification system in three stages: coagulation, filtration and chlorination. These technologies are outdated and do not meet the DSanPiN 2.2.4-171-10 standards [3], adopted in Ukraine, not to mention the standards in force in European countries.

However, about 40 years ago a fundamentally different water treatment technology – baromembrane technology, started to develop. It is based on passing the water under pressure through a semi-permeable membrane and separating water into two streams, the filtrate (purified water) and concentrate (concentrated solution impurities) [4].

First baromembranes technologies were used only in the research areas, which is typical for the process of innovation. The volume of consumption was small, the cost was high and the range of consumers was narrow. Then, membrane technology was applied in space research and defense industries. The consumption increased, production became technological, the cost of the membranes decreased and it became possible to use the membranes in such industries as medicine, pharmacology and others. Reduced prices for membrane materials led to the increase in the production volume of these products and start of the use of its application in industries with significant production capacity, for example, food industry. Worsening of environmental problems and rising energy prices made it possible to use baromembrane technology in water preparation for power plants, water supply, and purification of industrial and household polluted water [5].

First of all, the advantages of baromembrane processes include the implementation of all these processes without changing the aggregation state of water which determines their economic attractiveness and technological efficiency, eliminating the competitors among the classical methods of water treatment [6–8].

Such features of the baromembrane processes are associated with the use of membranes whose properties are set during the design and synthesis of new polymers. For example, the selectivity of the membrane is set by creating new polymers with specified molecular weight, viscosity, concentration, mechanical properties, the structure of the polymer material that makes possible to use baromembrane methods for solution of a wide range of tasks in drinking water preparation.

Baromembrane processes, depending on the composition of the aqueous solution that is necessary to separate, are conventionally classified as follows: microfiltration, ultrafiltration, nanofiltration and reverse osmosis, which is the most popular today, particularly in drinking water preparation.

Reverse osmosis systems as water preparation equipment, since its inception, were developed not for centralized or autonomous (artesian well, well) water supply, but for desalination of salt and brackish water (salinity > 1000 mg / dm^3), wastewater purification, preparation of high purity water for industrial operations.

Over time, however, a number of large companies that are engaged in the development and delivery of water purification equipment began to produce both industrial reverse osmosis systems and household ones.

The positive characteristics of the household reverse osmosis systems include the following [9]:

- The possibility to purify water with various salt contents from different water sources including purification of the water that has been prepared at centralized treatment plants.
- Caring for a semi-permeable membrane, which is a key element of a reverse osmosis set, does not need the use of chemical reagents. Therefore, reverse osmosis equipment is considered to be environmentally safe for using.
- Duration of the membrane cartridge using (up to one year), that is profitable.
- Ability to accumulate about 12 liters of purified water in the set reservoir that is effective when cold water is disconnected.
- Simultaneous removal from water not only salts and other substances in the ionized state, but also organic substances, colloids, bacteria, viruses (particle size 0,001–0,0001 microns; operating pressure from 0,5 MPa).

The efficiency of reverse osmosis plants for a wide range of issues, including preparation of potable water, is determined by the quality of their basic element – membranes, represented at the world market in a wide range, which work at low (up to 1,5 MPa), medium (2,5–3,0 MPa) and high (more than 3,0 MPa) pressure and have different physicochemical and technical characteristics.

For reverse osmosis systems that are available today at the commercial market, the membrane elements (cartridges) are the basic elements, that are made from multilayer polymeric composite membranes, mainly produced by the USA (Hydranautics, Filmtec), Germany (Koch Membrane Systems), Korea (Saehan), Japan (Nitto Denko and Toray Inc.).

So the quality of the water, which passed through the preparation process by reverse osmosis, and the productivity of reverse osmosis set are determined directly by such physicochemical properties of the membrane as the structure of its pore size, selectivity and permeability.

The disadvantages of reverse osmosis domestic systems include [9]:

- The supplied to the reverse osmosis set water must be free from chlorine that needs an additional stage of water purification, for example, by carbon adsorption filter.
- The value of permanganate oxidation of water supplied to the reverse osmosis set must not exceed 3. 0 mgO$_2$ / dm³, which needs an additional step to reduce the concentration of organic substances (ion exchange filters, filters based on the activated carbon).
- On average, the reverse osmosis system spends 3 liters of water to prepare 1 liter of purified water (permeate) that is technologically not profitable. Furthermore, the technology of concentrate recycling from the reverse osmosis set must be provided.
- As a result of contamination of the membrane surface by slightly soluble salts, suspended solids, microorganisms, that reduces the productivity of the plant, there is a need for periodic regeneration of membranes, which requires additional economic and technological costs.
- The level of water purification, which was prepared in the reverse osmosis set, reaches 99,8 %, which is the main drawback of reverse osmosis household equipment.

Reverse osmosis in the demineralization process divides tap water into two streams: demineralized water (permeate), which flows into the storage tank and water with high salt content (concentrate) which is discharged into the sewer.

Water that was cleaned by reverse osmosis becomes brackish. Its total mineralization is 3–100 mg/dm^3, depending on the physical and chemical characteristics of the membrane that is used in the set. For example, a mineralization of distilled water is up to 10 mg/dm^3, and water with salinity 1000 mg / dm^3 is recommended for permanent use [3].

3. An experimental part

Table 1 shows the experimental results of changes in the concentration of basic components of water, that was additionally cleaned in the reverse osmosis set with a capacity of 2,0–3,0 m^3 / h and Filmtec XLE membrane element 440 (8"), produced by DOW Chemical (USA) , with a working pressure of 18 atm [10, 11].

As it can be seen from these results, the value of the original color and turbidity of water changed after the reverse osmosis system to a zero value.

Table 1

Changing the fundamentals of water over time (τ) after the reverse osmosis on the membrane of Filmtec type XLE 440 (8") at a pressure of P = 18 atm

Quality of water	Unit of measurement	Output water	Water after reverse osmosis P = 18 atm, the membrane Filmtec (USA)	Selectivity membrane φ, %
Turbidity	mg / dm^3	0,58	0	100
Chromaticity	hail	18,0	0	100
Hydrogen pH		7,75	6,43	-
Alkalinity (HCO_3^-)	mg / dm^3 (mg-eq / dm^3)	244,0 (4,0)	48,8 (0,8)	80,0
Sulfates (SO_4^{2-})	mg / dm^3	18,47	13,85	25,0
Chlorides (Cl^-)	mg / dm^3	20,0	10,2	50,0
Hardness total	(mg-eq / dm^3)	4,8	0,53	90,0
Magnesium (Mg^{2+})	mg / dm^3	13,38	3,3	75,0
Calcium (Ca^{2+})	mg / dm^3	74,15	4,0	94,5
Iron (Fe^{3+})	mg / dm^3	0,109	0,03	70,0
Nitrate (NO_3^-)	mg / dm^3	11,07	8,85	20,0
Nitrite (NO_2^-)	mg / dm^3	0,39	0,29	25,0
Nitrogen ammonium (NH_4^+)	mg / dm^3	0,15	0,08	46,0
Permanganate oxidation ($KMnO_4$)	mg / dm^3	5,04	6,24	–
Sodium (Na^+)	mg / dm^3	12,7	0,13	99,0
Potassium (K^+)	mg / dm^3	4,0	0,04	99,0
Total mineralization	mg / dm^3	290,0	65,4	77,5

The pH water value after reverse osmosis has changed from 7,75 to the average 6,3, which describes the received water as acidic environment (pH < 7,0). This is also confirmed by the decrease in the total alkalinity (HCO^{3-}) from 4,0 mg-eq / dm^3 to the value received after reverse osmosis – 0,8 mg-eq / dm^3.

The organism balances the pH of the internal fluid, maintaining the value at some level. The acid-alkaline balance in the body is a certain ratio of acids and alkalis in it that supports its normal functioning. Acid-base balance depends on maintaining relatively constant proportions between the intracellular and intercellular water in body tissues. If the acid-alkaline balance of fluids in the body is not maintained constantly, the normal functioning and preservation of human life will be impossible [12].

The fundamental indicators such as Ca^{2+} and Mg^{2+} are important for human health. For the full physiological functioning of the human body Ca^{2+} concentration in the water should be within the range of 25,0–75,0 mg/dm^3, Mg^{2+} – within the range of 10,0–50,0 mg/dm^3 [3].

Considering the values obtained for the concentrations of these important parameters after the reverse osmosis, an important conclusion can be made that the selectivity of the membrane in reference to Ca^{2+} is 94,5 %, and in reference to Mg^{2+} it is 75 %.

The constant use of water with the lack of Ca^{2+} and Mg^{2+} has a negative effect on the bone strength, muscles work, especially the heart, causing blood pressure, seizures and risk of cancer, skin diseases, brain diseases, cardiovascular system and leukemia. Magnesium deficiency in children leads to serious diseases such as rickets, retardation [12].

The selectivity of the membrane relative to sulfates is 25 %. The selectivity of iron is 70 % [11].

The selectivity of the membrane towards chlorides is 50 %. This means that the membrane partially transmits molecules of Cl^-, because of approximately equal values of water molecules size (0,3 nm) and the molecules of chlorine Cl^- (0.37 nm) (pore size is not larger than a water molecule (0,3 nm), that leads to the detention of approximately equal size molecules and screening of larger size molecules).

An important result of this research is to increase the post-treatment values of permanganate oxidation of water at the set output. This phenomenon is a consequence of leaching of organics from the membrane layers included in the basis of its components (a membrane consists of layers of organic solvents such as aromatic polyamide (PA) and polysulfone (PS)). Also, the main disadvantage of polyamides is their sensitivity to free chlorine, which causes destruction of the amide groups. Thus, such membranes have a sufficiently large thickness (up to 150 micron), and thick membranes lead to a rapid decrease of mass transfer, i.e. to the reduction of reverse osmosis sets productivity [11].

Organic substances that contribute to the increased value of permanganate oxidation negatively affect liver, kidneys, reproductive function, as well as the central nervous and immune system of a person [12].

The membrane has a low selectivity for monovalent ions such as NO_3^-, NO_2^-, NH_4^+, as the size of a nitrogen molecule is 0,32 nm, which is close to the size of a water molecule.

The selectivity of the membrane relative to such water parameters as NO_3^-, NO_2^-, NH_4^+ is low and equals to 20,0; 25.0 and 46,0 %, respectively (Table 1).

Large amounts of nitrates (NO^{3-}) that get into a body can cause pulmonary edema, chronic nephritis and hepatitis. Long-term consumption of drinking water that contains nitrates causes the increase of methemoglobin, worsening of the blood function, especially concerning children. A direct relationship between the occurrence of malignant tumors and the intensity of the inflow of nitrates has been found out.

Nitrites (NO_2^-) in the human body are converted into nitroso-compounds – carcinogens that lead to the progress of liver cancer and lung cancer.

The constant water consumption with a high level of ammonia nitrogen (NH_4^+) causes changes in the tissues [12].

Such water components as sodium and potassium are important to maintain an appropriate level of environmental safety and human health. The recommended value of their concentration varies from 2,0 to 20,0 mg / dm^3 for the maintenance of the body physiological completeness. It is very important for these components to be in the ratio of 1:1 that makes a sodium-potassium pump in the human body, which provides transport of glucose and amino acids through biological cell membranes. It is necessary for normal functioning of nerve endings, nerve impulse transmission and muscle activity, as well as for the assimilation of the relevant nutrients by the human body [12].

The reverse osmosis membranes selectivity relative to Na^+ and K^+ is significantly high and amounts approximately 99 % that confirms almost complete removal of these important for human body components.

4. Conclusions

1. After purification of tap water with salt content of 300.0 mg / dm^3 by a reverse osmosis set, water has a total mineralization value up to 70 mg / dm^3, but all the vital for human health components (calcium, magnesium, sodium, potassium) are almost removed. Therefore, the phases of water enrichment by the minerals (e.g. phase of the energy fields and minerals impact to the quality of drinking water, as well as the phase of biological adaptation of water) must be provided, that makes additional economic and technological costs.

2. During the process of tap water reverse osmosis treatment the pH value and total water alkalinity are reduced, that characterizes the environment of water as an acid.

3. It was confirmed that during the process of reverse osmosis the organic substances, which are formed from organic polymers (polyamide, polysulfone), are vanished from the membrane layers and then these organic substances get directly into the drinking water which is consumed.

4. Reverse osmosis membrane has low selectivity to the singly charged ions, such as nitrates, nitrites, ammonia nitrogen and chlorine (which is typical for tap water), which badly influence the vital activity and human health.

Having considered the disadvantages of the reverse osmosis, it can be concluded that the method of reverse osmosis has no competitors in the area of water treatment at the demineralization of marine or brackish water or preparation of service water.

As for the post-treatment of tap water in the household reverse osmosis sets, this leads to a range of negative and important consequences, that must be considered both in terms of environmental safety and human health and technological and economic aspects.

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Vol. 1, No. 1, 2016

REDUCTION OF THE ENVIRONMENTAL THREAT FROM UNCONTROLLED DEVELOPMENT OF CYANOBACTERIA IN THE WATERS OF THE DNIEPER RESERVOIRS

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Abstract. We have analyzed the ecological hazard that has emerged as a result of the construction of hydropower plants on the Dnieper, which became the cause of uncontrolled development of cyanobacteria. The environmental risks that are caused by the uncontrolled development of cyanobacteria and their biodegradability were studied. The efficiency of application of the known methods of suppression of mass development of the blue-green algae was analyzed. The amount of biogas that can be synthesized from cyanobacteria biomass of Kremenchug reservoir was estimated. The strategy of avoiding the ecological disaster from the uncontrolled development of cyanobacteria and its negative impact on the environment was suggested.

Key words: ecological hazard, cyanobacteria, blue-green algae, biogas, biodegrading..

1. Introduction

In addition to the expected result – the production of cheap electricity, the construction of the hydroelectric complex on the Dnieper river has caused a threat to the ecological safety of Ukraine – a significant deterioration of the ecological state of the Dnieper river.

Such negative environmental effects were caused by two main reasons:

1. Flooding by the waters of newly created reservoirs the territories with settlements, agricultural lands, livestock farms, living space of the population.
2. Significant decrease in the speed of the Dnieper flow.

In general, the total area of the hydroelectric reservoirs of the Dnieper cascade is about 7000 km^2, and there is about 45 km3 of water in these reservoirs. If we consider that the annual flow of the Dnieper river is about 50 km^3 of water, it becomes clear that the amount of water that fills the artificial reservoir of the Dnieper river, close to its annual flow. Thanks to the advent of artificial reservoirs, the section of the river channel, which determines the rate of continuous flow, became much larger, so in the reservoirs (in particular, in Kremenchuk, which is the largest) the velocity of water is so small that it can be considered stagnant. On this basis it is fair to accept the current state of the Dnieper in the middle and lower channel not as a river but as a cascade of flowing ponds with large area and volume of water.

Based on the information above, it will be most methodologically correct to use the limnological approach to the study of the Dnieper river ecosystems. Huge areas of the farmland that are located under the waters of the newly created reservoirs caused saturation of the water with organic compounds. The amount of these compounds is increasing continuously and huge masses of municipal and industrial wastewater, contaminated rainwater and melted snow water run into the Dnieper. Coastal zone unlike reed beds of the Dnieper river historically was included into intense field technology, whereby the surface water (which later falls into the Dnieper) saturated with mineral and organic fertilizers. Such a radical change (a significant decrease of the Dnieper in large reservoirs up to an almost standing state, and the enrichment of organic contaminants) ultimately led to radical changes in the biota of the river. Creating a new interaction in a new biota as well as the creation of a new biotic hierarchy have resulted in a rapid uncontrolled development of blue-green algae that have invaded the newly created reservoirs of the Dnieper [1, 2]. Depending on hydrodynamic conditions, shape of the coastline, the strength and direction of the wind, blue-green algae concentrated in different parts of the Dnieper reservoirs. This led to a loss of the Dnieper river's ability to cleanse itself, which caused a progressive uncontrolled development of blue-green algae (Fig. 1).

Fig. 1. The Accumulation of blue-green algae near Kremenchug hydroelectric station

The nature of the biological cycle of life and death of blue-green algae causes a dominant role in the ecosystem of the Dnieper. Since blue-green algae do not need the soil environment, their quantities are not affected by the depth of the reservoir. Therefore, under the influence of the wind blue-green algae (Fig. 2), migrate along the reservoir, which creates conditions for their progressive reproduction.

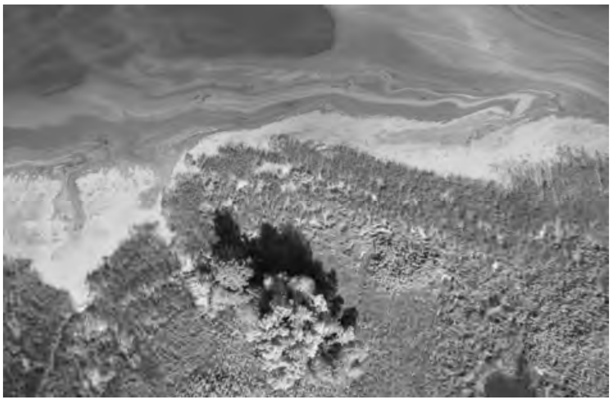

Fig. 2. Aerophotography of water "blooming", caused by the massive development of cyanobacteria

Density of cyanobacteria is somewhat less than the density of water, so even after a heavy storm they float to the surface quickly and keep developing rapidly, consuming solar energy. The dense surface layer of blue – green algae is formed in a short time, which reduces the reflectance of sunlight. This, in its turn, contributes to additional heating of the surface layer (where cyanobacteria is concentrated), and thus accelerates the development of algae – the process becomes autocatalytic .This contributes to the uncontrolled development of cyanobacteria as well as to the absence of species for which it would appear as food.

The result of the impact of uncontrolled development of cyanobacteria in artificial reservoirs of the Dnieper is the transformation of the river water during the period of decomposition of blue-green algae (from the second half of July to late September) into a dirty liquid with a strong unpleasant odor. This makes it impossible to purify the river water up to the requirements of the standards for drinking water at the stations of primary water purification intakes of coastal cities. The air is filled with a sickening smell of decay that causes numerous diseases of the respiratory tract. The decay of cyanobacteria in the Dnieper waters reduces oxygen, which causes suffocation of valuable fish species (perch, bream, chub, saber fish, etc.), causing considerable damage to fisheries of the country. The evidence of suffocation is a mass floating of dead fish on the surface and its decomposition, which creates an additional environmental threat to the ecosystem. Catastrophic reduction of oxygen content in the water is also confirmed by the analyses of the air above the waters of Rybinsk reservoir in the period of its algal bloom. Among the components the authors [3] have detected methane, which is formed during anaerobic fermentation. Thus, during the decomposition of blue-green algae the oxygen concentration reduction in the river water is so significant that in the surface layer oxygen-free fermentation takes place.

Due to fluctuations in the level of water in artificial reservoirs the coastal strips of the Dnieper are often flooded (marshes, lakes, sleeves and oxbows of the Dnieper) and cyanobacteria is getting spread. As a result of siltation many famous sandy Dnieper beaches, the places that used to be a pride and beauty of the Dnieper as well as well-known recreational areas, are disappearing. An unpleasant odor of decomposing algae significantly reduced the popularity and the quantity of boating tourism and in the summer the water becomes a dangerous source of microbiological contamination.

2. Analysis of recent researches and publications

There is a positive experience of the restoration of lake waters of Canada [4] – a significant reduction of estratest of Great lakes (lake Erie – 25,8 thousand km^2, 458 km^3, lake Ontario – 190 thousand km^2, 1638 km^3), which emerged in the 1960s and 1970s due to the growth of population and the consequent water pollution by nutrients, that led to the development of an undesirable flora, in particular cyanobacteria. During four decades (1930–1970) the pollution of Great lakes was increasing, which led to the formation of zones, poor in oxygen. Two important things should be noted: huge amounts of recovered, at least partially, drinking water – the object of restoration have been the reservoirs transformed by anthropogenic pollution of natural origin, i.e. the reservoirs, which have sufficiently powerful mechanisms of self-purification; the improvement of basins of Great lakes has been achieved through blocking the contamination sources, in particular, the elimination of phosphorus from the content of widely used detergents.

According to the results of our observations and analysis it can be stated that the cascade of the Dnieper reservoirs differ from the lakes of Canada as well as from powerful artificial wastewater treatment plants, and, therefore, it is not possible to directly use the experience to restore the quality of water accumulated in these projects [1, 5].

Statement of the problem. The aim of the research was to establish the degree of ecological danger from uncontrolled development of cyanobacteria, the extent of their negative impact on the environment and assessment of the prospects of using cyanobacteria collected for energy production.

3. Results and Discussion

To suppress mass development of blue-green algae, the following methods should be considered: mechanical, physical, chemical, ecological and biological methods (Fig. 3).

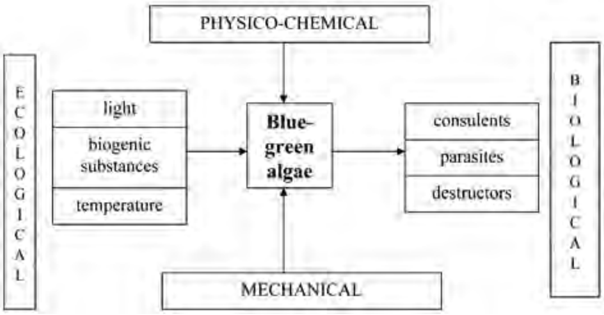

Fig. 3. Methods of suppression of mass development of the blue-green algae

The most effective physico-chemical methods include aeration of water and application of algaecides. Even though the application of these methods leads to a dramatic reduction in a number of cyanobacteria, but they have significant drawbacks. Aeration of large amounts of water air is uneconomical (65–90 kopecks/m^3), and the use of algaecides is possible only in bodies of water that is not intended for drinking or fishing as well as in the reverse water supply systems.

Another method that can give some good results is the collection of cyanobacteria and its subsequent disposal (production of biogas, lipids and fertilizers). Among the existing technologies of cyanobacteria processing we would like to concentrate on the option of building a biological station for the production of biogas, fertilizer and other valuable for industry and agriculture products.

The basis for the biogas production is the method of purification surface waters from blue-green algae owing to collection and use of its concentrated biomass as a substrate for the biogas production through biotechnology methane “fermentation” and ensuring the desired level of water quality in reservoirs cascade under the condition of energy savings. The outcome of the biogas mixture at +28°C per 1 day was 200 ml of 1 dm^3 of the substrate. Analysis of the biogas flame spectrum makes it possible to conclude that the percentage of methane in the studied gas mixture was dominating [6]. Economical and ecological efficiency in the use of cyanobacteria for the production of biogas (on the example of the Kremenchug reservoir with water surface area of 2250 km^2) is estimated as follows: assuming the collection of seston in the amount up to 50 kg/m3 [1] from 828 million m^3 of water from shallow waters its biomass will be 4,14.107t during the growing season. While fermenting this biomass in the process of methane “fermentation” one can receive up to 30 million m^3 of biogas (18,8 million m^3 of methane), which is equivalent to 20 tons of oil or 17 thousand tons of diesel fuel.

Without the use of pretreatment only a small portion of the energy contained in biomass can be taken out. Cavitation, which yet has not found a wide application in industrial technologies, is an effective method of hydro-mechanical intensification of chemical-engineering, food, pharmaceutical, biological and other processes. The effectiveness of cavitation process is stipulated by cavitation crashing of the solid phase, turbulance of the boundary diffusion layer of the liquid by cavitation bubbles, emergence of mass transfer aspects, which are characterized by high values of mass transfer coefficients.

Processing of biological objects in a cavitation field can be used as an independent process and ensure an inactivation and extinction of microorganisms or as cyanobacteria pre-treatment stage with the aim of increasing the mass transfer surface for the following extraction or biochemical processes. The results of microscopic analysis showed that for certain modes of processing liquid substances in the cavitation field, the decrease of contrast cells is observed as well as damage to the cell membrane, reducing the clarity of contours, cell shape change, aggregation and mechanical damage. Experimental studies [8] have established that in case of hydrodynamic cavitation to increase the effectiveness of the process of obtaining energy from cyanobacterial biomass, a degree of lipid extraction increases by 54,3 % and the amount of synthesized biogas increases by 28,3 %. In the cyanobacterial biomass treated in a hydrodynamic cavitation field.

The use of cyanobacteria has the below environmental effects:

- The use of ecologically safe, without significant energy costs, method of seston collection.
- The fulfillment of conditions of the Kyoto Protocol to the UN Framework Convention on Climate Change (Rio de Janeiro, 1992).

- Accession to the Directive 2000/60 / EC of the European Parliament and of the Council “establishing a framework for Community action in the field of water policy" from October 23, 2000.
- Recovery of the broken structural-functional organization of the littoral ecosystems of the Dnieper cascade reservoirs (gas balance, hydrochemical regime, reducing the toxicity of water and spawning fish fauna etc.).
- Rehabilitation of the environment and the population by improving the quality of natural as well as drinking water.
- The use of manufactured products as organic mineral fertilizers in agriculture and forestry;
- The use of social and financial effect for sustainable ecological and economic development of the Dnieper regions.

Utilization of cyanobacteria has the below energy resources and energy-saving effects:

- Free use of raw materials as substrate for fermentation;
- Introduction of low-cost production of biogas and its transformation into electricity;

Based on the analysis of the research data [8] there was developed a strategy of avoiding ecological hazard from uncontrolled development of cyanobacteria and their negative impact on the environment, which includes the consistent implementation of the following stages: collection of cyanobacteria and transporting them to biological stations ⇒ processing of biomass into a hydrodynamic cavitation field ⇒ concentration of biomass ⇒ extraction of lipids from biomass ⇒ biomass biodegradation with biogas extraction ⇒ use of waste biomass as a fertilizer.

4. Conclusions

Based on the analysis of the sources of ecological hazard in the waters of the Dnieper reservoirs of Kremenchug territorial-production complex it was concluded that one of its determining factors is the uncontrolled development of blue-green algae and their negative impact on the environment. The feasibility of producing biogas from the biomass of blue-green algae was scientifically proved. The efficiency of pretreatment of the biomass of cyanobacteria in the field of hydrodynamic cavitation in order to increase the completeness of the biomass decomposition was established.

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Vol. 1, No. 1, 2016

INTEGRATED ADSORPTION AND ULTRASONIC TECHNOLOGY FOR WATER TREATMENT PROCESSES

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Abstract. The aim of this work is to study the process of water purification from mechanical and chemical pollution and pathogenic microflora by adsorption and ultrasonic methods. Proposed technology reduces bacterial contamination and purifies water from organic pollutants, improving its quality.

Key words: natural sorbents, ultrasound, adsorption.

1. Introduction

Any water reservoir or water source is an integral part of the surrounding environment. It is influenced by formation conditions of surface or underground water runoff, various natural phenomena, industry, construction engineering, transport, human economic and domestic activity. The emergence of new unusual substances or pollutants which deteriorate the water quality in the water environment is the result of such influences.

Types of pollution affecting the water environment are classified depending on approaches, criteria and tasks. As a rule chemical, physical and biological types of pollution are differentiated.

The main sources of natural waters pollution are:

- atmospheric waters carrying a significant amount of pollutants that are washed out of the air and mainly have industrial origin. When flowing down the slopes, atmospheric and melt-waters grasp additionally a significant amount of substances. Runoff from city streets and industrial sites is especially dangerous, as it carries a significant amount of oil products, phenols, various acids;
- city waste waters which include mainly sanitary waste waters containing excrements, detergents, and microorganisms among which are pathogenic ones;
- industrial waste waters formed in various manufacturing fields; among them ferrous metallurgy, chemical, timber-chemical, and oil refining industries which consume water most extensively.

Often the level of water pollution is so high, that without implementation of new technologies it will not be possible to receive water that meets sanitary and hygienic requirements for economic and domestic needs.

Therefore, nowadays in water treatment processes special attention is paid to the application of physical methods for natural waters disinfection:

- ultrasonic cavitation which provides the fast inactivation of microorganisms,
- natural sorbents reducing the concentration of organic pollutants [1].

2. Methodology

Ultrasonic action is used for water treatment due to the high efficiency of water purification from chemical pollution, biological objects: saprophytic and pathogenic microorganisms, viruses, animalculines etc. Ultrasonic is an effective reagentless highly ecological method of water purification from organic and microbiological components [2].

During the cavities collapse the emitted energy causes the processes of microorganism destruction. The pathogenic microflora is destructed and active radicals are formed around the collapse points. Cavities develop in the ultrasonic emitter chamber with the frequency of several tens of kilohertz mainly on inhomogeneities that are represented by spores of mushrooms and bacteria [5].

At the first stage of research synthetic solution of Bacillus bacteria was used. It was put into the ultrasonic reactor (Drawing 1). The ultrasonic oscillations (frequency 22 kHz, power 35W, intensity 1,65 W/cm^3 per volume unit) from the UZDN-2T generator were transmitted with the help of magnetostrictive emitter immersed into the test water (V 150 cm^3) [3, 4].

During the whole process CO_2, O_2, He, and Ar were bubbled through the test water. The reactor was cooled constantly by the current water. The experiments conditions are the following: T = 298 K, P = $1\cdot10^5$ Pa, ν_{us} = 22 kHz, process time – 2 hours.

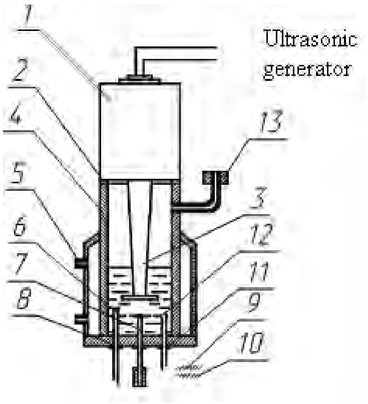

Fig. 1. The reactor scheme for water treatment process: 1 – magnetostrictor; 2, 8, 9 – thickening; 3 – waveguide; 4 – reactor; 5 – heat carrier nozzles; 6 – thermocouple; 7 – gas input nozzles; 10, 11 – cap nuts; 12 – sampler; 13 – gas output nozzles

In the second part of work water from natural pond polluted with different microorganisms was used. Stage I was ultrasonic treatment using oxygen gas. Parameters of the processes were the same as during the first part. Stage II was sorption on natural sorbents. In our study three types of sorbents – bentonites, zeolites, glauconites were used [6, 7]. They are the most common natural sorbents that can be used for water treatment.

The application method of natural dispersed sorbents is also very perspective and has the following advantages [8, 9]:

- the natural sorbents are widely distributed all over the Ukrainian territory;
- they are available and inexpensive materials;
- adsorption technologies using natural dispersed sorbents provide the high quality level of water treatment process;
- using natural adsorbent does not require regeneration.

The experiment conditions are the following:

- sorbent type – bentonite, zeolite, glauconite;
- sorbent concentration – 7 g/l, 20 g/l, 35 g/l respectively;
- water used – natural water from pond
- sorption time – 1 hour;
- constant mixing.

Sampling was carried out before the experiment, after the ultrasonic reactor stage and after natural sorbent was used.

Samples were analyzed for Chemical Oxygen Demand (COD) [10] and Microbial Number (MN) [11].

3. Results and discussions

The data of water purification of the model substance by ultrasonic is provided below (MN_0 – number of microorganisms, cfu/cm^3)(Tables 1–2, Fig. 2).

Table 1

Water disinfection levels (D_d) and effective constants of destruction frequency of Bacillus type bacteria (k_d) ($MN_0 = 8{\cdot}10^2$ n /cm^3)

Process conditions	D_d, %	$k_d \cdot 10^4$, c^{-1}
Ar/ultrasound	95,9	4,29±0,06
He/ ultrasound	93,6	3,68±0,07
O_2/ultrasound	90,5	3,6±0,07
CO_2/ultrasound	91,1	1,67±0,13

Table 2

Effective constants of frequency of Bacillus type bacteria dying and their destruction levels ($MN_0 = 7 \cdot 10^5$ cfu/cm^3)

Ar/ultrasound		O_2/ultrasound	
$k_d \cdot 10^4$, c^{-1}	D_d, %	$k_d \cdot 10^4$, c^{-1}	D_d, %
10,1±0,01	99,9	9,76±0,01	99,8

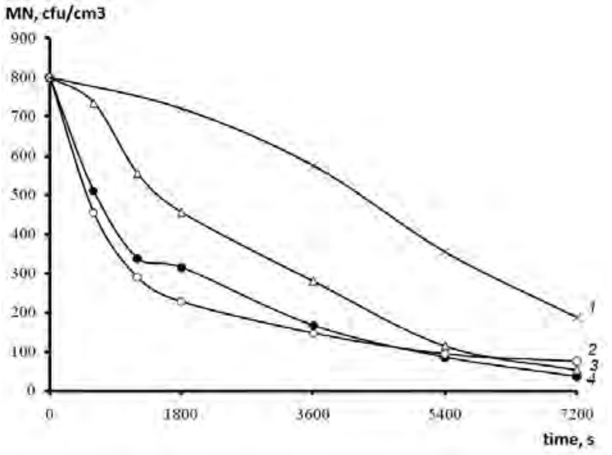

Fig. 2. Dependence of changes in number of microorganisms (Bacillus type bacteria) from duration of gas/ultrasound action by bubbling different types of gases: CO_2 (1), O_2 (2), He (3) та Ar (4)

Samples were analyzed for chemical oxygen demand (COD) and microbial number (MN) (Tables 3–5, Fig. 3–4).

As it can be seen from Fig. 3, all three types of sorbent can purify water, but the best results were obtained by water purification by bentonite (C = 35 g/L).

Table 3

Changes in COD and MN when C = 7 g/l

	COD_0 mg/dm^3	COD after ultrasound mg/dm^3	COD after sorption mg/dm^3	MN_0 cfu/cm^3	MN_0 after ultrasound cfu/cm^3	MN after sorption cfu/cm^3
Bentonite	256	192	224	22 000	45 000	10 700
Zeolite	320	224	192	25 000	33 000	9 000
Glauconite	288	192	176	76 500	55 000	25 000

Table 4

Changes in COD and MN when C = 20 g/l

	COD_0 mg/dm^3	COD after ultrasound mg/dm^3	COD after sorption mg/dm^3	MN_0 cfu/cm^3	MN_0 after ultrasound cfu/cm^3	MN after sorption cfu/cm^3
Bentonite	256	240	128	22 000	41 200	3 000
Zeolite	320	224	160	25 000	30 800	2 000
Glauconite	288	192	160	76 500	60 000	5 000

Table 5

Changes in COD and MN when C = 35 g/l

	COD_0 mg/dm^3	COD after ultrasound mg/dm^3 COD after sorption mg/dm^3	MN_0 cfu/cm^3	MN_0 after ultrasound cfu/cm^3	MN after sorption cfu/cm^3	
Bentonite	128	96	64	22 000	39 000	2 000
Zeolite	320	160	96	15 000	23 000	7 000
Glauconite	288	192	96	61 000	53 000	4 000

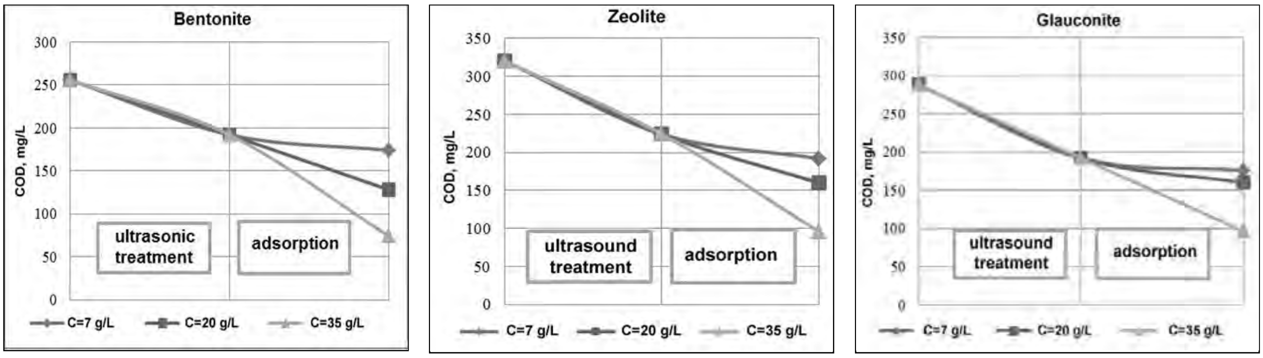

Fig. 3. Changes in COD

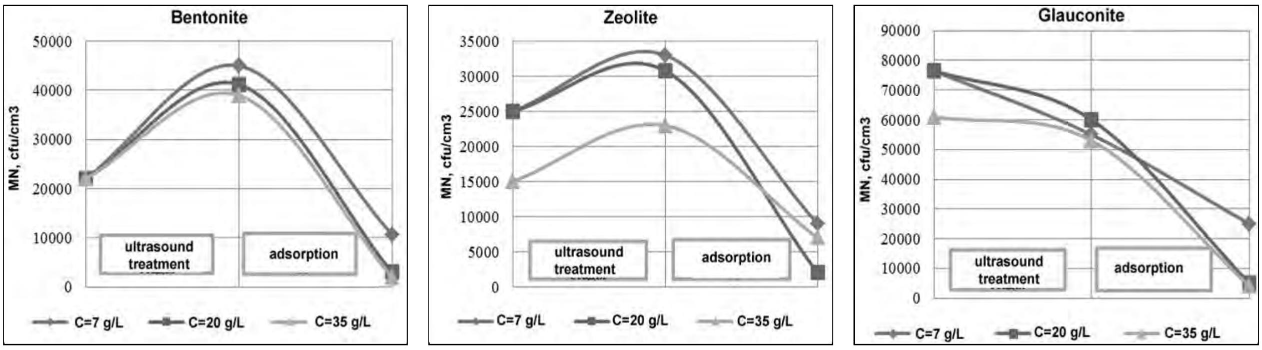

Fig. 4. Changes in MN

At the first stage of purification MN increases due to cavitation during insonation. At the second stage, when we added sorbent, best results in purification of water were obtained by ceolite (C = 20 g/L). The research results showed that the combination of ultrasound and absorption methods can significantly increase the quality level of water purification.

4. Conclusions

The use of ultrasonic cavitation energy allows intensifying water treatment and is an effective method of water sanitization.

The application of dispersed sorbents in water treatment allows further decreasing of both COD and microbial number after ultrasonic cavitation step.

The main advantages of the use of natural minerals are: large geological reserves, low-cost exploitation of minerals, easy preparation for transportation and usage, possibility to reuse sorbents in other technologies, thus eliminating the need of expensive regeneration.

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Vol. 1, No. 1, 2016

METHODOLOGICAL PRINCIPLES OF ELECTROMAGNETIC SCREENS APPLICATION FOR PUBLIC PROTECTION FROM ELECTROMAGNETIC FIELDS AND RADIATION

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Abstract. The growing levels of electromagnetic fields require the improvement of protective shielding methods. Frequency and amplitude parameters of fields have been analyzed according to national and international standards of electromagnetic safety and guidelines on shielding application have been given. The methodological principles of choosing and applying electromagnetic screens depending on radiation parameters and the required protection efficiency have been developed.

Key words: shielding; electromagnetic field; reflection coefficient.

1. Introduction

The increasing electromagnetic impact on the environment, growing number of electric and electronic facilities applied in industry and households raise the question of protection people from negative impact of electromagnetic fields and radiation. The complexity of solving this task is caused by a wide permanent frequency range of electromagnetic impact: from quasi-stationary electromagnetic fields of power line frequency to microwave frequency radiation of communication equipment. As a result, different technical approaches must be applied to electromagnetic protection. Traditional protection approaches (protection with distance and time) are depleted or not efficient enough.

Nowadays electromagnetic shielding is under detailed investigation, but technique and conditions of various shielding materials application, as well as providing optimal efficiency of shielding are not sufficiently determined.

These tasks are also urgent because of gradual implementation of the European Council Directive on electromagnetic safety and enactment according to the Decree of the Cabinet of Ministers of Ukraine (№ 1483 КМ 29.12.2014) of a range of common European standards on electromagnetic safety and compatibility of technical facilities, that in many cases are stricter than Ukrainian national standards.

2. Problem formulation

Electromagnetic screens application for public protection from electromagnetic fields and radiation impact is regulated by both international [1, 2] and national standard acts [3, 4]. At the same time, none of them characterize the application conditions and screen parameters depending on shielded field frequency and amplitude values. For example, sanitary norms [3] recommend application of bars and solid surfaces made of aluminum and copper alloys, electro-technical steels and permalloys as protective screens without setting efficiency criteria under various conditions.

In the recent years a great number of studies on electromagnetic screens efficiency have been conducted [5–7]. Most of them are experimental because theoretical studies in this area are a bit abstractive and they are not suitable for application [8, 9]. Study and development of modern protective materials [10, 11] proved the possibility of protective properties management, i.e. production of screens with required shielding factor, in particular, protective electromagnetic screens with regulated protective properties [12]. Studies of shielding efficiency have been conducted mainly in lab conditions and their results are not completely matched with the measured results at real objects, which is conditioned, in our opinion, by both final dimensions of screens and external sources and over-radiation impact. Our previous studies [13] have shown that shielding efficiency depends not only on the chosen material properties, but also on the screen dimensions, its allocation relatively to the source of field and radiation, diffraction phenomenon etc. These aspects have not been studied enough yet.

The aim of the study is to determine the electromagnetic screens application depending on frequency and amplitude of shielded field or radiation, their sources allocation and provision of practical guidelines on regulation of protective materials selection.

Electromagnetic shielding is the most urgent for the provision of standard electromagnetic environment in buildings and constructions (except certain objects, for example, civil aviation enterprises), i.e. for electromagnetic ecology of premises. It is also necessary to take into account the presence of both internal and external sources of fields and radiation. External sources are generally radio-technical objects of communication facilities with extremely low radiation wavelength (to 1 centimeter) and power supply objects – transmission facilities, transforming station and open switching centers with extremely wide wavelength (6000 kilometers). It’s obvious that protective methods for different types of radiation must be different. The internal sources are power supply systems with power line frequency electromagnetic fields and electromagnetic fields of industrial or household equipment, which have various and unpredictable frequency spectrum in many cases.

Technical approaches to the protection from the impact of these two categories of sources differ substantially. In many cases efficient protection from the impact of external sources can worsen electromagnetic environment as a result of internal sources impact. The cause of it is that internal source radiation reflection from electromagnetic screen into the room increases electromagnetic background level. This also partially refers to external sources. Our measurements have shown that reflection of base station electromagnetic radiation from well-shielded construction surfaces (metal decorative coats) significantly worsens electromagnetic environment in adjacent areas. Sometimes this worsening makes up 70–80 %. Partial reflection is observed even from concrete construction. It is important to note that this parameter depends substantially on weather conditions, for example, the electromagnetic fields reflection index on the surfaces of roofs and buildings changes significantly in the presence of precipitation. Neighboring buildings orientation in relation to the incident and reflected waves is also important.

In any case, reflection phenomenon has unfavorable character in terms of human safety. Therefore, it is necessary to determine the maximum permissible reflection coefficient while selecting the material for electromagnetic screen production, if the required general screening coefficient is known. As for separate premises their full shielding, even at minimum reflection coefficient, can cause certain inconveniences, for example, blocking of communication with base stations, experienced by citizens. It can block the activity of wireless computer net within a certain building.

Another problem is magnetization of ferromagnetic screen in an external magnetic field, which may cause the increase of field level while approaching it. Our study has proved that ferromagnetic electromagnetic screens have to be applied as entirely closed screens around high-power electro-technical facilities or as the screens developed on the basis of the specular reflection phenomenon, which is a fundamental physical principle. Such screen is located at the back of the source, instead of being placed between the source and the public zone. Depending on relative distances in the public area, the decrease of power line frequency and other low-frequency magnetic fields level by 16–17 % is achieved which is confirmed by the results of the conducted experiments.

The benefit of such shielding is that its efficiency can be accurately calculated [14]. The exception is ferromagnetic and magnetic screens made of soft magnetic amorphous alloys, but their application is limited by the high cost of these materials due to complex production technology. The most efficient screens for protection from both external and internal sources impact are flexible metal-polymeric materials with managed protective properties. Determination of frequency and amplitude characteristics of radiation, to be shielded, must precede screen production, and required screen parameters are determined from the developed dependencies (Fig. 1).

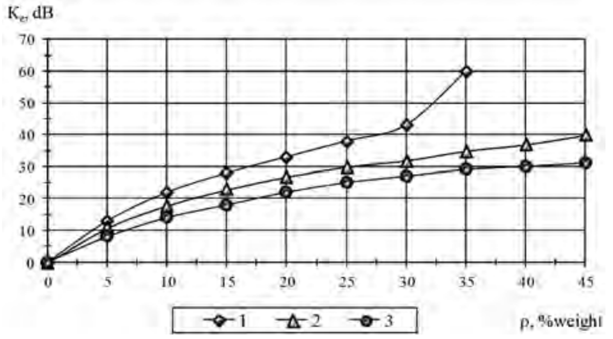

Fig. 1. Dependence of shielding coefficient of flexible protective material on conductive component content: thickness 1 – 5,0 mm; 2 – 3,0 mm; 3 – 1,0 mm

Reflection coefficients can be determined according to ratios in Fig. 2.

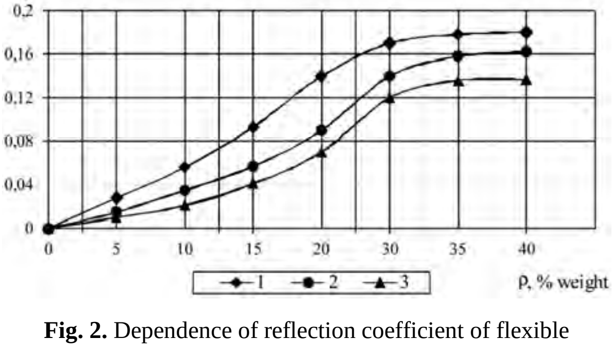

Fig. 2. Dependence of reflection coefficient of flexible protective material on conductive component content: thickness 1 – 5,0 mm; 2 – 3,0 mm; 3 – 1,0 mm

To determine the efficiency of electromagnetic screens for the provision of required parameters it is necessary to take into account a range of factors: reflection level, attenuation, caused by energy penetration through the screen material, and diffraction phenomena. The last issue is applied to perforated and latticed surfaces and screens with limited dimensions (length and width). Additionally it is important to take into account separately located big radio-reflective surfaces and certain emitters, which sometimes increase the level of the field in the radio shadow zone. The solution of these tasks will be efficient with application of both theoretical and experimental methods. Application of mathematic models with acceptable accuracy for the selection of protection methods provides significant reduction of time and costs used for the provision of required protection levels. To fulfill such work it is necessary to apply fundamentals of geometry [14]. The scheme to calculate the impact of the screen geometric configuration, taking into account the diffraction phenomena, is given in Fig. 3.

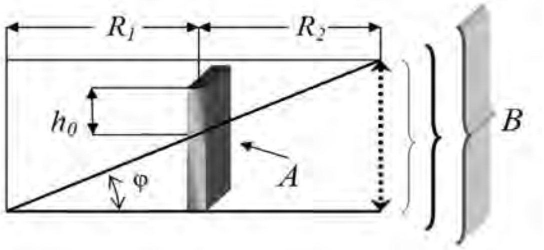

Fig. 3. Scheme of relative placement of electromagnetic screen *A* and field source. h_0 – distance between the screen edge and the source axis; R_1 – distance from the source to the screen; R_2 – distance from the screen to the protected zone *B*

To account the diffraction numerically it is useful to introduce the dimensionless parameter – screen efficiency factor η:

$$\eta = h_0 \cdot \cos\ \varphi = \sqrt{\frac{2}{\lambda}\cdot\left(\frac{1}{R_1}+\frac{1}{R_2}\right)},$$

where h_0 – distance between the screen edge and the source axis, λ – wavelength, R_1 – distance from the source to the screen, R_2 – distance from the screen to the protected zone.

Experimental dependencies of diffraction attenuation depending on integral parameter η, which is determined by the distances from the screen to the source and the protected zone (R_1 R_2) and the length of the electromagnetic wave λ and the distances h_0 between the screen edge and the source axis – the border of the protected zone (Fig. 4).

Analysis of Fig. 4 proves that solid conductive screens give relatively high attenuation of electromagnetic radiation that is not always necessary for low amplitude and high frequency fields. Therefore, perforated surfaces and metal lattice which sufficiently reduce the levels of the field but have low weight and cost, can be applied for protection.

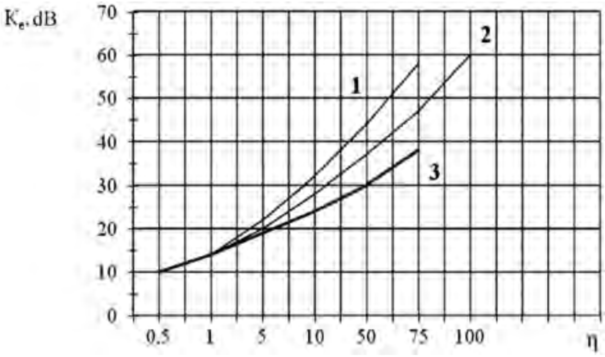

Fig. 4. Dependence of shielding coefficient on field source location and screen dimensions:
1– for field component, which is parallel to the screen;
2 – integral shielding; 3 – for field component, which is perpendicular to the screen

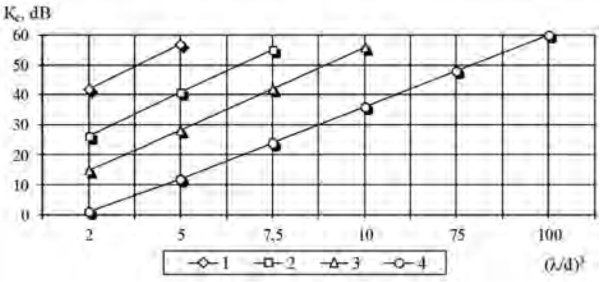

Fig. 5. Dependence of shielding properties of electromagnetic screen on perforation parameters ℓ:
1 – 50 mm, 2 – 20 mm, 3 – 10 mm, 4 – 5 mm

Perforated screens constructions have to meet the requirements of shielding minimum. Efficiency of such screens depends mainly on the diameter of holes *d* and distances between them *ℓ*. Experimental data on correlation between perforated surfaces shielding coefficient, the length of the electromagnetic wave λ and perforation parameters are given in Fig. 5.

Shielding coefficients for latticed and linear periodical structures (alternation of metal wires with a determined step) depend on wires diameters, distances between their axes and the length of a shielded wave.

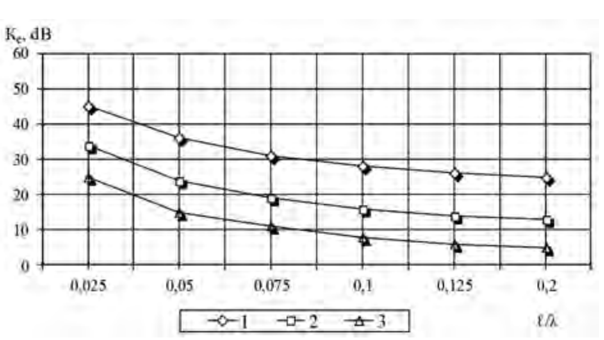

Fig. 6. Dependence of shielding coefficient of electromagnetic field on latticed structure parameters: *ℓ*– distance between wire axes, *d* – diameter of wires, λ – wavelength; 1, 2 and 3 – represent the following rations of *ℓ*/*d*=2; 5; 10

Dependences of protective properties of such screens on the mentioned parameters are given in Fig. 6.

Material of wires doesn't have noticeable influence on shielding coefficients in a high-frequency range; therefore, wires conductivity can be neglected in practice. Therefore, material selection is conditioned by economic reasons. Copper and aluminum structures are more efficient than steel constructions due to higher specific conductivity for low and super-low frequencies.

In all cases, electromagnetic screen functioning efficiency is provided with reliable galvanic contact in the places of certain lattice element connections.

3. Conclusions

1. Assessment of electromagnetic environment has to be conducted prior to screen material and structure selection; it includes determination of frequency and amplitude parameters of electromagnetic fields and external and internal sources of radiation.
2. It is necessary to choose reasonable correlation of attenuation and reflection screen parameters for maximum reduction of this physical factor impact on the human. It is efficient to apply graphic dependencies given in this paper.
3. Ferromagnetic electromagnetic screens application is most acceptable under the condition of full blocking of field source or taking into account reflection effect that enables preliminary calculation of shielding efficiency based on geometric issues exclusively.
4. Variability of shielding coefficients has to be taken into account at electromagnetic shielding application because of diffraction phenomena at the screen edges.
5. Perforation parameters and screen lattices have to be taken into account at high frequencies of electromagnetic radiation, it is reasonable to apply given graphic dependencies for this aim.
6. In all cases it is necessary to take into account the feasibility of screen production and installation, as well as its cost, which is provided by rationalization of shielding and reflection coefficients selection (i.e. according to the principle of reasonable adequacy).

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Vol. 1, No. 1, 2016

SPATIAL AND TEMPORAL VARIABILITY OF POLLUTANTS IN THE BOTTOM SEDIMENTS IN THE NORTHWEST PART OF THE BLACK SEA

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Abstract. The level of pollution of the bottom sediments in the Northwest shelf of the Black Sea is examined. Modern data are compared with those of the late 20th century and their variability over 30 years. Substantial increase (by two orders) of copper, lead and nickel concentration has been marked.

Key words: Black Sea, Northwest shelf, pollutant, bottom sediments.

1. Introduction

The Northwestern part of the Black sea (NWBS) is a unique marine ecosystem. Characteristic features of the NWBS are fresh water input from the Danube, the Dniper and the Dniester rivers and nutrients that provide one of the biggest productivity levels in the World Ocean. However, since the 1970s, the process of anthropogenic water euthrophication and the near bottom hypoxia linked with it, have caused widespread benthos fauna mortality. A lot of scientific publications were dedicated to the process of the anthropogenic euthrophication of the Black Sea shelf and its consequences (Berlinsky *et al*., 2006; Gomoiu, 2004; Zaitsev, 1977).

In addition to this negative phenomenon a lot of contaminations and pollutants are washed out from the coastal urban agglomerations by the river flow. In the process of sedimentation the suspended matter is accumulated in the bottom sediments. It reinforces negative changes in benthic habitat conditions. For this reason, the attempt is made to examine the matter using the available literature and retrospective data base to analyze the intensity, accumulation and distribution of pollutants including heavy metals and oil in NWBS shelf.

2. Relevance and methodology

The influence of pollutants on the biotic organisms and the environment is widely reflected in scientific literature. Therefore assessment of the level of pollutants accumulated in the bottom sediments in the NWBS shelf should be considered as a rather actual problem.

The average value of the studied parameters were processed by linear interpolation and given to the centers of squares, ranked by hydrological features (Berlinsky *et al*., 2000). The total volume of data base includes 5417 parameters (Hydrological and hydrochemical status, 1998).

3. Discussion

The aggregate values averaging of pollutants concentration in the bottom sediments of the NWBS was done taking into consideration the spatial and temporal data discreteness which allowed to obtain some interannual dynamics of the investigated parameters, characterized by trends and tendencies (Table 1, 2).

Heavy metals (lead, cadmium, chromium) are present in wastewater of many industrial enterprises and as impurities in a great number of technical reagents used in drilling fluids [8, 10]

The content of heavy metals in the bottom sediments in the NWBS shelf is mainly within the natural geochemical background. For the period of the 1980s the natural geochemical values for mercury, copper, lead, cadmium, nickel and chromium were, 0,06; 3,4; 0,4; 0,17; 5,9 and 2,2 mg/kg accordingly (Geology of the shelf, 1985). The original data base (Hydrological and hydrochemical status, 1998) as well as the data from literature sources (Berlinsky *et al*., 2006; Berlinskyi, 2012) was used for the analyses.

Mercury and its compounds are most dangerous for the living organisms. There is permanent accumulation of mercury in the bottom sediments over the past two decades. The natural geochemical value of mercury concentration was 0,06 mg/kg in the 1980s, but 30 years later it rose up to 0,08 mg/kg which created an additional threat to benthic organisms in the process of desorption, when secondary contamination of the bottom water layer occurred (Table 2).

For the period of the 1980s the natural geochemical value of copper concentration was 3, 4 mg/kg, three decades later it increased by an order

For the same period lead concentration increased by two orders from the values of 0,4 mg/kg in the 1980s up to 22 mg/kg in 2013. This sharp rise in average values is correlated with modern data obtained for the Caucasian coast waters (http://esimo.oceanography). It characterizes the process of the overall growth of the concentration almost in the entire coastal zone located under the huge technogenic press from industrial agglomerations.

Table 1

The average concentration of pollutants in the NWBS shelf in the summer period (1991–2013)

Pollutant, (mg/kg)	Number of the region		
	Danube	Dniester	Open area
Oil	197,5	330,0	152,5
Hg	0,11	0,08	0,12
Cu	26,82	22,10	19,43
Pb	17,1	19,6	11,6
Cd	0,22	0,27	0,13
Ni	32,6	24,6	27,8
Zn	78,95	60,62	41,07
As	8,91	8,47	7,55
Phenols	0,82	0,34	0,50

Table 2

Variability of the natural geochemical background of pollutants in the NWBS

Pollutant, (mg/kg)	1985 [4]	1991–2013 [6]
Oil	200	200
Hg	0.06	0,08
Cu	3,4	25,4
Pb	0,4	19,2
Cd	0,17	0,22
Ni	5,9	33,3
Zn	–	63,98
As	–	9,48
Cr	2,2	–
Phenols	–	0,56

The average meaning of lead concentration in the Caucasian coast is 73,2 mg/kg with fluctuation range from 0,91 up to 1189 mg/g. For the NWBS area the average meaning of lead concentration in the bottom sediments during the period of 1991 – 2013 is 19,75 mg/g with fluctuation range from 15 up to 34 mg/g. The probable reason for this significant increase in the concentration of lead is the intensification of petroleum hydrocarbons mining of Stormy, Arhangelsk and Galitsin deposits located in the NWBS shelf. Thus, the concentration of lead in drilling fluid reaches 505 mg/g [5] (Pankratova, Sebah, 1994). According to Table 1, maximum concentration of lead is marked in the central region near the Crimean Peninsula.

As for cadmium concentration in bottom sediments on the shelf, its max value was 0,39 mg/kg since the 1990s. Since 2013 the concentration decreased to the natural geochemical value for the period of the 1980s, that is 0,17 mg/kg with average value 0,22 mg/kg in the modern period.

The natural geochemical value for nickel was 5,9 mg/g in the 1980s, its concentration in the bottom sediments increased by an order at present. New geochemical value for nickel is more than 40 mg/g .

Thus, it is necessary to mark a significant increase in concentration of such heavy metals as mercury, copper, lead and nickel in the bottom sediments of the NWBS shelf. At the same time the average geochemical values for copper, lead, and nickel have extremely increased. On the other hand cadmium concentration got down to the average geochemical values of the 1980s but the variability was rather high - from 0,35 to 17 mg/g. The reasons for this high variability are not clear and can be linked with local and temporal anthropogenic and technogenic influence.

One of the most important negative ingredients of the aquatic systems is the level of oil concentration in water and bottom sediments. At present there is an intensive process of increasing oil concentration in the bottom sediments in the NWBS shelf.

According to (Pankratova *et al.*, 1994; Sebakh and Pankratova, 1995) the average typical value of oil concentration in the uncontaminated areas of the Black and Azov Seas for the 1980s was 200 mg/kg. The cleanest area of the NWBS shelf was its central part. The maximum level of oil concentration was 1,000 mg/kg. In the period from 1992 to 2013 the average value didn't exceed 200 mg/kg (Table 2), but there is a sustainable tendency to oil accumulation in bottom sediments and in perspective the encrease in the natural geochemical value will be expected. (Rajsintseva *et al.*, 1998).

In the modern period the highest values of oil concentration were marked in the Dniester estuary (more than 300 mg/kg). The second is the Danube estuary area with the values a little less than 200 mg/kg. The Dnieper – Bug and Odessa Bay regions have the lowest values – up to 140 mg/kg. The Central part of the NWBS is characterized by the values of 150 – 180 mg/kg (Table 1).

The Danube estuary has a high level of pollutants that is due to their removal with the flow of the Danube, the process of sedimentation of suspended matters and accumulation in bottom sediments. (Rajsintseva *et al.*, 1998).

In the shallow water of the Danube estuary the comparison of Ukrainian's and Romanian's average pollutants concentration in the bottom sediments has been made (Hydrological and hydrochemical status, 1998; Oaie, *et al.*, 1999; Rajsintseva *et al.*, 1998; Ungureanu *et al.*, 2004). The average data were used for the whole area of the Romanian region of the Denube shown in Oaie, *et al.*, 1999, for the separate parts between the Sulina and St. George estuaries. The common results are shown in Table 3.

So, it is possible to mark, that in the Denube estuary the temporal dynamics of oil concentration in the bottom sediments reflects the technogenic presss during the long period (30 years,) at least in the Ukrainian part. So, oil concentration during the period of 1993–1997 was linked with the effect of active navigation and the values were rather high – 1800 mg/kg. Later in the period of 1994–2005 oil concentration decreased sharply to 142,9 mg/kg that was linked with the lack of navigation in this region.

At present oil concentration increased slightly up to 285 mg/kg, probably due to the influence of the active process of navigation via Bystryi arm. Mercury concentration both in Ukrainian and Romanian parts of the Danube region exceeds the natural geochemical condition for the whole NWBS shelf 2 and 7 times respectively (Table 2, 3).

Copper background values in the NWBS at this time make up 25.4 (26.82 mg / kg – for the Danube region over the period of 1991 – 2013), and in estuarine area of the Danube – from 29.52 (Ukrainian part) to 86, 74 mg / kg (Romanian part), i.e. 3 times exceed.

A drastic reduction of cadmium concentration in the Danube region should be marked as a positive factor. In the period of the 1990s its concentration in the Ukrainian part was very high – up to 6,2 mg/kg and at present the values make up from 0,19 mg/kg (Ukrainian part) to 1,71 mg/kg (Romanian part). In the period of 1993–2013 nickel concentration in the Danube region was even less than in the whole NWBS shelf (Table 1, 2). However, in comparison with the period of the 1980s its concentration increased by an order from 5,9 to 33,3 mg/kg. Zink concentration in the period of the 1990s in the Ukrainian part exceeded the concentrations in the Romanian part, but at the beginning of the 2000s this ratio changed in the opposite direction (Table 3). The concentrations of arsenic, phenols, chromium and cobalt are roughly the same in the Romanian and the Ukrainian parts of the Danube.

According to the state of the environment and ecological safety norms, it is recommended to determine 16 priority polycyclic aromatic hydrocarbons (PAHs) as well as six esters of phthalate acid to be included in the list of the controlled chemicals.

PAHs are volatile persistent organic pollutants, characterized by carcinogenic, mutagenic, teratogenic and hepatotoxic effects. They are able to be accumulated in lipid tissues of living organisms and to provoke various serious diseases. PAH is the sum of the 16 determined PAHs indexes – from low molecular weight PAHs (2-3 rings) to high-molecular weight PAHs. Different international agreements included around 60 chemicals in the lists limiting their distribution and requiring the mandatory control of their content in the environment. A group of persistent organic pollutants (POPs) was nicknamed the "dirty dozen", in particular: aldrin, endrin, dieldrin, mirex, DDT, hexachlorobenzene, hep-tachlor, toxaphene, chlordane, polychlorinated biphenyls, dibenzo-p-dioxins and dibenzofuranes.

Table 3

The average concentrations of pollutants in the bottom sediments of the Danube region (mg/kg)

Pollutant, (mg/kg)	1993–1997 (Ukrainian part) [9]	1995–2000 (Ukrainian part) [6]	1995–2000 (Romanian part) [7]	2001–2002 (Romanian part) [11]	2011–2013 (Ukrainian part) [6]
Oil	1800	142,9	–	–	285
Hg	–	0,12	–	0,53	0,15
Cu	48,9	28,31	54,75	86,74	29,52
Pb		24,36	40,95	45,46	21,6
Cd	6,2	0,27	2,16	1,71	0,19
Ni	50,8	–	65,15	71,31	34,86
Zn	138,5	75,64	90,3	161,71	79,74
As	–	10,35	–	13,19	7,6
Phenols	–	0,44	–	–	0,60
Cr	–	74,87	79,76	65,07	79,53
Co	–	–	–	16,77	17,59

The largest percentage of carcinogenic PAHs was in the bottom sediments in the area under the direct influence in the Ukrainian part of the Danube delta and in the Bystryi and Starostambulskyi arms (6.15 and 8.58 correspondently). The reason is a direct impact of anthropogenic pollution on these regions. The minor value of the PAH index (4.72 – 6.28) was recorded for the open area of the sea (Tsymbalyuk *et all.*, 2011).

4. Conclusion

A significant increase of copper, lead and nickel concentrations in the bottom sediments in the NWBS shelf by two orders in a period of 1991–2013 compared with the 1980s has been marked.

Concentrations of mercury and zinc in the bottom sediments of the Danube region exceed the corresponding values in the NWBS shelf.

The analysis of Ukrainian and Romanian data, obtained in different periods, has been made, that showed their close correlation, common order of values and variability of temporal dynamics reflecting causal regularities of natural fluctuations and anthropogenic impacts on the aquatic ecosystem.

The results of the research can be indicators of anthropogenic impact exerted by industrial and municipal waste emissions and economic activity of the ports and dumping on the shallow waters in the Danube area.

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DEVELOPMENT OF MATHEMATIC MODEL OF GAS-TURBINE UNIT COMBUSTION CHAMBER FUNCTIONING

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Abstract. The article presents the basic issues of ecological safety improvement of present-day steady-state gas turbine units. A mathematic model of diagnostics of combustion chamber considering the basic parameters of gas-turbine unit (GTU) operation under different technological modes was developed. These modes include the intake air temperature of the axial-flow compressor, the intake temperature of the actuating medium of the directing set of the high pressure turbine as well as the temperature of the environment.

Key words: combustion chamber, mathematic model, gas turbine engine, ecological characteristics, actuating medium.

1. Introduction

The problem of lowering the toxicity of combustion products of gas dispensing units (GDU) being operated at the compressor stations of the main gas pipelines is the constituent of the scientific and technical progress of the natural gas industry [1]. The key standards, that the low emissive combustion chambers are up to, have already been settled, based on the main ways of the working process arrangement and the tendencies of the improvement of the fuel scorching devices efficiency [2–7]. For their manufacturing application, it is indispensable to increase the design efficiency and improvement of the low emissive combustion chambers.

2. Analysis of present-day foreign and domestic studies and published works

The main ways to lower the toxicity of combustion products in the burning systems of various purposes are: the application of increased air surpluses (V. A. Khrystych, G. N. Liubchyk, N. K. Risk, D. Wels); the application of phasic combustion (I. Ya. Sigal, F. G. Tumanovskii, A. Lefer); the homogenization of the combustion area (G. Leonard, S. M. Korea); the application of micro torch combustion (S. D. Serdiuk, N. P. Danylenko, G. B. Varlamov, A. M. Markushin, A. M. Postnenkov, V. P. Savchenko); the application of catalytic combustion technologies (G. N. Liubchyk, G. S. Marchenko, B. I. Shelkovskii, C. Wilkes, S. V. Santanam).

The testing results of the Solar company device (in the combustion chamber GDU GTC – 10I) [8] demonstrated that when the air surplus increases over the above-mentioned level the CO emission increases roughly. Considering the air surplus ratio $\alpha \to 2{,}0$ the CO in the combustion products leads to $O_2 = 15$ %, and results in 100 мg/м^3, that can cause increased chemical deficiency of fuel combustion. Consequently, when decreasing the air surplus below the above-mentioned level not only the NO_x and CO are essentially increased but also there is a high-frequency combustion, breakdown and a sudden flame [8]. The companies that use the given technology (such as: Solar, Rolls-Royce, Siemens etc.) eliminate such a failure using complex systems of regulating the mix proportion in the combustion area, and variable geometry of the combustion chambers and flow-type part of a compressor. The simulation of the working processes in the combustion chambers is considered to be one of the perspective methods that enables to reduce the cost of the research. In particular, the mathematic model of three-dimensional chemically reacted flows, engineered by G. B. Mostipanenko, enables to predict the output temperature and ecological features of the combustion chambers that use the gaseous fuel.

3. Emphasizing unresolved issues of the general problem

Neither the air consumption nor the actuating medium is measured at any section of gas route of the gas-turbine unit. Moreover, the records done by the existing methods are impossible, as it leads to the hydraulic losses that reduce the capacity and the economic efficiency of the cycle. The only kind of consumption that can be measured practically is the consumption of fuel gas. Evidentially, its component analysis can be considered to be known.

The objective of the research is to develop the mathematic model of diagnostics of combustion chamber considering the basic parameters of a gas-turbine unit operation under different technological modes including the intake air temperature of the axial-flow compressor, the intake temperature of the actuating medium of the directing set of the high pressure turbine as well as the temperature of the environment.

4. Reporting the principal subject matter

The combustion chamber of gas-turbine unit is specified for the actuating medium preparation that will perform the useful work when expanding at the turbine trowel. For this purpose, the gas fuel burning takes place in the primary air medium with the creation of pure combustion products in the combustion chamber. Then, the process of mixing with the reiterative air for obtaining the admissible temperature of the actuating medium follows. Hence, the composition of the actuating medium can be given like the mixture of the pure combustion products with the reiterative air. To describe the actuating medium the concept of the air surplus coefficient α is given. This is the ratio of total air consumption (primary L and reiterative L_0) to the primary air consumption, theoretically necessary for combustion of 1kg of fuel gas [1].

$$\alpha = \frac{L + L_0}{L_0}. \tag{1}$$

The required quantity of air for combustion of 1 kg of fuel gas of the known component composition with the density ρ' can theoretically be computed in the following way:

$$L_o = \frac{1,293}{21\rho}\left[0,5(\mathrm{CO}) + 0,5(\mathrm{H_2}) + 2(\mathrm{CH_4}) + \right. \\ \left. + \sum (m + n/4)(C_m H_n) + 1,5(\mathrm{H_2S}) - (\mathrm{O_2})\right]. \tag{2}$$

Here the symbols in the brackets mean the volumetric bits of every component in the mixture of gases. The air surplus in the combustion chamber in comparison with its theoretically indispensable quantity leads to the cooling of the actuating liquid. The air surplus coefficient is related to the maximum temperature of the ratio cycle:

$$\alpha = \frac{Q_H^P \eta_k + C_\Pi t_\Pi + C_P^{"} t_3}{L_0\left(C_P^{"} t_3 - C_P^{"} t_2\right)}, \tag{3}$$

where C_Π, t_n – is the heat capacity and temperature of the fuel gas.

Without determining the heat value of the fuel Q_H^p and its heat capacity C_m it is pointed out that the air surplus coefficient can be found from the equation (3) on the basis of the fuel gas temperature dimension $t_т$ the air after the axial-flow compressor t_2 and the actuating liquid before the gas turbine t_3. Then the mass consumption of the actuating liquid and air can be shown through the mass consumption of the fuel gas.

$$M'' = \alpha\left(L_0 + 1\right) M_n, \tag{4}$$

$$M' = \alpha\left(L_0 - 1\right) M_n, \tag{5}$$

The volumetric air consumption is set to the input conditions of the first grade of the axial-flow compressor:

$$Q_1 = \frac{L_o(\alpha - 1) M_\Pi}{P_1} 287 T_1 \tag{6}$$

Thus, using the equations (3) and (6) the productivity of the axial-flow compressor can be determined which will enable us to define the diagnostic features for every mode of the gas turbine unit. However, for the application of the equation (3) it is indispensable to determine the mean specific volume of the air heat capacity $C'_{m'}$ in the temperature span (t_1, t_2) and the actuating medium $C''_{p'm'}$ in the temperature span (t_4, t_3). If there is no difficulty in determining the air heat capacity that is mean in the known temperature span there is some difficulty in determining the mean mass heat capacity of the actuating medium $C''_{p'm'}$ as the composition of the actuating medium is unknown. Consequently for the computation of the air surplus coefficient the method of successive approximation is worth applying. The following computation algorithm is applied:

1. In the first approximation the values of actuating medium heat capacity $C''_{p'm'}$ are specified. This value is equal to the air heat capacity with the same data:

$$C''_{pm} = C'_{pm}. \tag{7}$$

2. When using equation (3) the first approximation of the air surplus coefficient is computed.

3. The mass consumption of the actuating medium on the assumption that of 1kg of fuel gas consumption is computed.

$$M^{''} = M_{\mathrm{CO_2}} + M_{\mathrm{H_2O}} + M_{\mathrm{N_2}} + M_{\mathrm{O_2}}, \tag{8}$$

where

$$\begin{aligned} M_{\mathrm{CO_2}} &= \frac{0,44}{22,4}\left[(\mathrm{CO_2}) + (\mathrm{CO}) + \sum m(C_m H_n)\right], \\ M_{\mathrm{H_2O}} &= \frac{0,18}{22,4}\left[(\mathrm{H_2}) + 2(\mathrm{CH_4}) + \sum \frac{n}{2}(C_m H_n)\right], \\ M_{\mathrm{N_2}} &= 0,769 L_0 \alpha^{(1)}, \\ M_{\mathrm{O_2}} &= 0,231 L_0\left(\alpha^{(1)} - 1\right). \end{aligned} \tag{9}$$

4. The mass bits of every given component in the actuating medium are computed:

$$\begin{aligned} m_{\mathrm{CO_2}} &= M_{\mathrm{CO_2}} / M''; \quad m_{\mathrm{H_2O}} = M_{\mathrm{H_2O}} / M''; \\ m_{\mathrm{O_2}} &= M_{\mathrm{O_2}} / M''; \quad m_{\mathrm{N_2}} = M_{\mathrm{N_2}} / M''. \end{aligned} \tag{10}$$

5. The heat capacity of the actuating liquid is computed:

$$C''_{pm} = m_{\mathrm{CO_2}} C_{pm}^{\mathrm{CO_2}} + m_{\mathrm{H_2O}} C_{pm}^{\mathrm{H_2O}} + m_{\mathrm{O_2}} C_{pm}^{\mathrm{O_2}} + m_{\mathrm{N_2}} C_{pm}^{\mathrm{N_2}}. \quad (11)$$

6. When using equation (3) the air surplus coefficient is defined more accurately and the calculations for achieving the given accuracy are computed:

$$\left| \alpha^{i-1} - \alpha^{i} \right| < \varepsilon_0 . \quad (12)$$

The complex processes happening in the combustion chamber demand the hypothesis admission while formalizing. Thus, for the narrow range of the air surplus coefficient change in the burning part of the combustion chamber, it can be admitted that the combustion temperature does not depend on the air surplus and is constant.

If to admit that the pressure and temperature after the axial-flow compressor as well as air and fuel gas consumption are known, then for the motion in the combustion chamber the following system of differential equations can be given:

$$\begin{cases} \dfrac{dP}{dt} + \dfrac{c^2}{F}\left(\dfrac{dM'}{dx} + ML_0(\alpha+1)\delta(x-x_0) \right) = 0, \\ \dfrac{dP}{dx} + \left(\xi_k / 2pF^2 \right) M^2 + \dfrac{1}{F}\dfrac{dM}{dt} = 0, \\ \dfrac{dM}{dt} + \dfrac{M'}{\rho' F}\dfrac{dT}{dx} + \dfrac{ML_0(\alpha+1)C'_p}{p'' C''_p F} T_2 \delta(x-x_0) - \\ -\alpha \dfrac{d^2T}{dx^2} - \dfrac{\pi D(T_0 - T)}{p'' C''_p F} = 0. \end{cases} \quad (13)$$

The link between the basic parameters of the actuating medium (pressure *P*, temperature *T* and mass consumption *M*) for different periods of time and various parts of the combustion chamber that are characterized with the linear coordinate *x* can be given with the above-mentioned equations. At the point of combustion and mixing ($x = x_0$) the step consumption increase can be observed. It is caused by the reiterative air supply with the consumption M_1. Thus, the actuating medium consumption as a function of the linear coordinate can be given in the following equation:

$$M = M_r (L_0 + 1) + M' L_0 (\alpha - 1) \sigma(x - x_0), \quad (14)$$

where L_0 – is theoretically indispensable air for combustion of 1kg of fuel; α – air surplus coefficient; $\sigma(x - x_0)$ – Heaviside's unit function;

$$\sigma(x - x_0) = \begin{cases} 1, & if \quad x > x_0 \\ 0, & if \quad x < x_0 \end{cases}. \quad (15)$$

For simulating the step change of temperature consumption in the point of supply of the reiterative air ($x = x_0$) the Dirac's function of source in the equations $\delta(x = x_0)$ is given. It is worth considering that for some combustion chambers the diameter *D* and the sectional area *F* can be changed on the linear coordinate *x*. The air density ρ', actuating medium ρ'', and pure combustion products ρ (when there are the specified conditions in the combustion chamber) can be shown through pressure and temperature:

$$\rho' = \frac{P}{R'T}, \quad \rho'' = \frac{P}{R''T}, \quad \rho = \frac{P}{RT}. \quad (16)$$

Thus, the system (13) is a closed system of the differential equations that combine the parameters of the combustion chamber functioning with its typical dimensions and physical properties of the actuating medium. The system includes also the coefficient of the hydraulic resistance of the combustion chamber ξ_k and the coefficient of the heat exchange with the environment *K*. The gas-turbine units operation proved that exactly these coefficients demonstrate the real condition of the combustion chamber. So, the coefficient of the hydraulic resistance of the combustion chamber and the absolute coefficient of the heat exchange with the environment *K* can be used as the diagnostic features. The simplification of the mathematic model given in the equation (13) for the standard mode has been performed due to the division of the gas dynamic and thermodynamic processes. For the permanent gas dynamic process in the combustion chamber the equation of motion can be presented in the following way:

$$\frac{dP}{dx} = -\frac{\varepsilon_\kappa M''^2}{2D\rho F^2}. \quad (17)$$

The actuating medium consumption can be determined through the measured consumption of the fuel gas $\mathrm{M}_{\text{Г}}$ and the coefficient of the air surplus in the combustion chamber computed by the approach given above:

$$M'' = \alpha(L_0 + 1) M_{\Pi} . \quad (18)$$

Through the computed composition of the actuating medium its gas constant from the equation can be determined:

$$\frac{1}{R''} = \sum_{i=1}^{4} \frac{m_i}{R_i}, \quad (19)$$

where m_i, R_i – are mass fractions of the *i* component in the actuating medium and its gas constant. The mean pressure and temperature in the mixing zone are computed as the arithmetic mean:

$$P_c = \frac{1}{2}(P_2 + P_3), \quad (20)$$

where P_2, P_3 – are the input and output pressures of the combustion chamber, that are determined via measurements; T_{2L} – is the intake air temperature of the mixing zone of the combustion chamber, the approach of determining it will be given later; T_3 – the measured temperature at the output of the combustion chamber.

Then the density of the actuating medium under the average conditions in the combustion chamber can be determined from the equation of the state:

$$P_c = (P_2 + P_3)/2; \; T_c = (T_{2L} + T_3)/2,$$

$$\rho = \frac{P_c}{R''T_c}. \tag{21}$$

The answer from the equation (17) can be given in the following way:

$$\frac{P_2 - P_3}{L} = \frac{\xi_k M''^2}{2\rho F^2}, \tag{22}$$

where L, F – are the length and the area of the section of the combustion chamber correspondingly.

From equation (22) the coefficient of the resistance of the combustion chamber as the following can be computed:

$$\xi_k = 2\rho F^2 \left(P_2 - P_3\right) / LM^2. \tag{23}$$

The permanent heat exchange of the actuating medium that moves in the flue tube after the mixing zone with the flow of the reiterative air in the conditions of counterflow can be given as:

$$K_1 \pi D(T_3(x) - T_2(x))dx = M''c''_p dT_3(x), \tag{24}$$

where K_1 – is the coefficient of the heat exchange from the actuating medium to the air; D – is the diameter of the flue tube (given); $M'' = M_{\varPi}\left(L_0 + 1\right)\alpha$ – is the mass consumption of the actuating medium; C'' – heat capacity of the actuating medium under the temperature T_3 .

The permanent heat exchange of the reiterative air with the actuating medium and environment can be presented with the following equation:

$$\begin{gathered} K_1 \pi D\left(T_3(x) - T_2(x)\right)dx - \\ -K_2 \pi D_0 T_2(x) - T_0(x)dx = M'C'_p dT_2, \end{gathered} \tag{25}$$

where K_2 – is the coefficient of heat transmission from the reiterative air into environment through the casing with the given diameter D_0 under the temperature of the environment T_0; C_p – is the air heat capacity under the temperature T_2.

The equation for the heat balance of the combustion area is the following:

$$T_{30} C''_p \left(\alpha L_0 + 1\right) = \alpha L_0 C'_p T_{2L} + \left(\alpha_1 L_0 + 1\right) C_p T_{03}, \tag{26}$$

where T_{30} – is the intake temperature of the actuating medium into the mixing zone; T_{03} – is the torch temperature in the combustion area; T_{2L} – is the intake temperature of the primary air that comes into the combustion area with the surplus coefficient α_1; C_p – is the heat capacity of the combustion products under the temperature T_{03}.

The joint answer to the equations (23)–(25) under the specified intake temperature in the combustion chamber T_2 and the temperature of the actuating medium in the blade of the directing set of the high pressure turbine T_3 can be given as the following:

$$\begin{gathered} (((T_{2i} - T_{0i})/(1 - W_T(K_T/W_m + K_0/W_{\varPi} - \\ -\sqrt{(K_T/W_m + K_0/W_m) - 4K_0K_T/W_TW_{\varPi}}/2K_T + T_{0i})\times \\ \times C''_p(\alpha L_0 + 1) - (\alpha L_0 + 1)C_pT_{03}/\alpha L_0 - T_{0i} = \\ = 1 - W_T(K_T/W_m + K_0/W_{\varPi}) - \\ -\sqrt{(K_T/W_m + K_0/W_m) - 4K_0K_T/WW_{\varPi}}/2K_T)\times \\ \times(T_{3i} - T_{0i} - (\alpha_1 L_0 + 1)C_PT_{03}/\alpha L_0 - \\ -T_{0i}(\exp(-((K_T/W_m + K_0/W_{\varPi}) + \\ +\sqrt{(K_T/W_m + K_0/W_m) - 4K_0K_T/W_TW_{\varPi}}))\frac{L}{2} - \\ -(\exp(-((K_T/W_m + K_0/W_{\varPi}) - \\ -\sqrt{(K_T/W_m + K_0/W_m) - 4K_0K_T/W_TW_{\varPi}}))\frac{L}{2})), \end{gathered} \tag{27}$$

where $W_{\varPi}$,W_m – are the water equivalents of the air and actuating medium correspondingly;

$$W_{\varPi} = C'_p M' \cdot W_m = C''_p M'', \tag{28}$$

W_m – is the mixed water equivalent;

$$W_m = W''_n \cdot W_m / (W_n + W_m), \tag{29}$$

K, K_0 – are the given coefficients of heat transmission from the actuating medium to the reiterative air and from the reiterative air into the environment.

5. Conclusions

The present mathematic model enables to determine the given heat transmission coefficients K_n and K_0 as well as the intake of reiterative air in the mixing zone of the combustion chamber temperature T_{2L}, if the operation parameters of GTU in three modes are known. Whereupon, the technological modes due to which the combustion chamber is diagnosed differ by the intake air temperature of the axial-flow compressor, by the output actuating medium temperature into the directing set of the high pressure turbine as well as by the temperature of the environment. Besides, the steady-state conditions of GTU operation are adhered to in every mode.

Thus, the given mathematic model of the burning processes in the combustion chamber will enable not only to determine the key features of the combustion chamber but also to study the basic technological modes to decrease the emission of the polluted substances of the adjacent territories of compressor stations.

Such an approach will enable to carry out various computations and research as well as determine the indicated indices of exhaust combustion products and develop the ecological characteristics under the different operative modes of the GTU.

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INFLUENCE OF DOBROTVIR THERMAL POWER PLANT ON ENVIRONMENTAL SPECIFICATIONS

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Abstract. The influence of the emissions of Dobrotvir TPP on the state of environmental pollution was evaluated: the state of air and soils and the state of waste management. The necessity to perform combined researches and ecological measures to reduce the negative impact of waste dumps on the environment was justified. It was established that the state of soils of ash and slag dumps was in crisis, the content of total forms of heavy metals in the soil is 2–10 times higher than TLV or a background concentration, large excesses of heavy metals of the I class of danger, namely Copper, Zinc and Lead were detected.

Key words: thermal power plant, ash and slag dumps, environmental pollution, heavy metals.

1. Introduction

Energetics is a branch of the economy, which covers energy resources, extraction, transformation, transmission and use of different types of energy. Electricity production in the world ranks an advanced place among all branches of production. There are three basic types of power plants that produce electricity. They are nuclear power plants (NPP), thermal power plants (TPP) and hydropower plants (HPP).

Thermal power plants (TPP) convert chemical energy of fuel (coal, oil, gas, etc.) sequentially to thermal, mechanical and electrical energy. By power equipment TPP are divided into steam, diesel and gas turbine power plants. Thermal power plants are the basis of power. The fuel which is used in thermal power plants is coal, natural gas, fuel oil, shale, wood. The increase of a single power of TPP determines the increase of absolute consumption of fuel consumption by individual power plants.

In different countries of the world the ratio of one or other particular type of power depends on the geographic location and scientific and technological potential of the country. Worldwide the thermal power plants produce 63 % of electricity, hydropower plants – 19 %; nuclear power plants – 17 % [1–4]. At the same time the structure of electricity production varies between regions. The share of nuclear power plants is much higher in Europe (27 %) and in Latin America there is a very high share of hydropower plants (75 %). Even more essential are the differences in structure between countries. The share of electricity production in Ukraine between the stations of different types is the following: TPP – 65,57; NPP – 25,83; GPP – 2,37; other power plants – 0,03.

Depending on the structural particularities of the world country, electricity producers can be divided into several groups. The first and fundamental group is consisted of countries where the princiapl part of the electricity produced is by the thermal power stations. Among those countries there are South Africa, the Netherlands, Poland, Russia, Ukraine, China, UK, USA and others. Overall, the share of thermal power plants in electricity production is growing, because their construction is cheaper, the terms of the construction are shorter, the power is great.

The presence of a large number of thermal power plants in Ukraine is due to huge reserves of coal during the Soviet times, which are mainly concentrated in Donetsk, Luhansk and Dnipropetrovsk regions even in Soviet times. When burning the solid types of fuel in the furnaces of thermal power plants the ash is generated in the form of residues similar to dust and lump slag as well as ash and slag mixtures. They are products of high-temperature treatment at temperatures of 1200... 1700 °C of the mineral part of the fuel. The chemical composition of ash and slag waste depends on the type of solid fuel (coal), which is subjected to burning, but the average of the waste includes the following oxides: SiO_2 – 55,3 %, Al_2O_3 – 17,3 %, Fe_2O_3 – 3,2 %, CaO – 3,59 %, MgO – 1,86 %, TiO_2 – 1,44 %, K_2O – 1,86, Na_2O – 0,72 %, and the oxides of vanadium, gallium and others. [5]. Ash slags which are formed as a result of the coal combustion in thermal power plants are large-tonnage waste. For their transportation the systems of hydraulic ash removal are used. Thus most of ash slags is transported in a form of the slurry of low concentration slurry to place it the hydraulic ash dumps, which are one of the major sources of environmental pollution in the production of electric energy [5].

Modern industrial society is impossible without such not renewable energy sources as gas, oil and coal. Highly developed countries get 80 % of energy from them. Over the past 30 years at TPP, which are the largest producer of electricity, 76 billion tons of coal, 3 billion tons of oil fuel, 3 trillion m^3 of gas. Despite of the large amount of produced electricity, a huge lack of TPP is environmental pollution in both a local and planetary scale [6–8].

The largest TPP are located in Donbass (Vuhlehirska, Starobeshevska, Myronivska, Kurahivska etc.), Prydniprovye (Prydniprovska, Krivorozhska), Kharkiv (Zmiyivska), Kyiv (Tripilska), Ivano-Frankivsk (Burshtynska), Lviv (Dobrotvirska) regions, in Zaporizhya, Odessa and others. Most of these power plants produce heat too (TPC). TPP are the major stations that provide electricity in half-peak and together with HPP and HNPP during peak hours.

In Lviv region five companies are included in the “List of 100 objects that are the major environmental polluters in Ukraine”: “Dobrotvirsk TPP”, OAO “Lviv Coal Company” Novorozdilsk State Mining and Chemical Enterprise (SMCE) “Sirka (Sulfur)”, Lviv communal enterprise “Zbyranka” Novoiavorivsk SE “Ecotransenergo”.

Dobrotvir TPP was launched in 1956 when the first phase of production capacities was put into operation. It had three boilers PK-19 of the plant № 1-3 with the release of flue gases station into the high-level smokestack № 1 (H = 101 m). Currently these boilers worked out and were removed, the smokestack № 1 is inactive. In 1961, the second phase of the station was put into operation, it had six boilers TP-10. These boilers run on two steam turbines K100-90-6 LMZ. The gas passages from six boilers № 5-10 are connected to a high-level smokestack № 2 (H = 105 m). In 1963 in the STPP the third phase of the station started to function, it was based on two power units of the station of 150 MWt. The release of flue gases from the boilers TP-92 is performing through the smokestack № 3 (H = 120 m). In the late 80's the construction of the fourth phase of Dobrotvir TPP (DTPP-2) began, it would consist of three power units of 225 MWt each. The high-level smokestack and partly an industrial building were constructed. In the early 90's, after the collapse of the USSR, in connection with the termination of financing the construction was stopped. In the strategic directions of the development of generating capacities of open JSC “Zahidenergo” for the period up to 2030 the completion of the construction of the shunting power unit № 9 of the capacity of 225 MWt and the construction of new power units № 10 and № 11 were planned for Dobrotvir TPP-2.

The average age of domestic TPP is 45... 50 years, because their main construction took place in 60's... 70's of the last century, that's why during this time the accumulation of solid waste (slag and ash) reached enormous sizes, 359 million tons, that in turn, takes a lot of land space for their storage. This leads to the disruption of the ecological situation both in the regions and in the country as a whole.

The emissions of thermal power plants in Ukraine in 5–30 times higher than European Union standards [9, 10], and they are the main gross air pollutant in the state.

Currently, there is no complex processing of ash and slag wastes, only their small number (10... 15 %) is used in the construction industry as a component in the production of bricks and a pavement. But the potential of slag wastes is much higher, it is due to the presence of large number of valuable components containing in the slags from TPP (vanadium, gallium, iron, silicon, etc.). Therefore, to improve the ecological situation in the country and to receive new sources of raw materials it is necessary to develop and implement a combined recycling of ash and slag wastes of TPP. The negative side of the function of TPP is an environmental pollution both by gaseous impurities and solid wastes in the form of ash and slag.

The aim of the work is to evaluate the influence of Dobrotvir TPP on the characteristics of the environment.

2. The presentation of the main material

Energy production in TPP is accompanied by a large amount of heat generation, that's why these plants are usually built near cities and industrial centers to use (utilize) this heat. Considering the limited world reserves of fossil fuel, scientists and engineers continue to work on improving the parameters of power units, increasing their coefficient of performance (COP), which provides economical fuel consumption. Further growth of the capacities of the power units is possible in the event of the introduction of so-called cryogenic generators that are refrigerated by liquefied helium. Burning fossil fuel is accompanied by strong environmental pollutions. Consider the main ones.

Air pollution by Dobrotvir TPP. Some issues of air pollution by Dobrotvir TPP were considered in the work [11]. The main air pollution by Dobrotvir TPP is performed by harmful substances that are emitted from the high-level smokestacks in the process of producing electricity and heat. The capacity of the reductions differ depending on the technological equipment of the station and it is constantly changing during the day, week, month and year, according to the controller load schedule.

In recent years, due to the significant rise in prices for natural gas and fuel oil and to the shortage of these types of fuel, the main fuel for STPP is coal of Lviv-Volyn, Donetsk coalfields. The increase in volume of used coal, in turn, leads to increased emissions of products of its combustion in the air such as dioxide, carbon monoxide, sulfur dioxide, methane, vapors of sulfuric and hydrochloric acids, ammonia, carbon tetrachloride, carbon monoxide, vapors of mineral oil, solid particulates, heavy metals such as arsenic, chromium, copper, mercury, nickel, lead, zinc and greenhouse gases.

To reduce the emissions of pollutants from stationary sources into the atmosphere at Dobrotvir TPP the cleaning equipment from dust and gas is exploited. It means ash catching installations of station boilers, cyclones, dust sediment cameras.

“Wet” ash catchers with Venturi smokestacks were used for cleaning flue gases taken out from the furnace of the boilers in the boiler and turbine workshop; cyclones are used to reduce dust emissions of coal concentrate in the fuel and transport workshop and abrasive metal dust emissions in the repair and construction workshop; to reduce abrasive metal dust emissions in the repair and construction workshop dust sediment cameras are used.

Today “wet” ash catchers are replaced on ash catching installations (ACI) with emulsifiers of the second generation. The energy conversion efficiency of the previous ACI (“wet” ash catchers) was 94–95 %, the efficiency of the ash catching installation after installing the battery emulsifiers of the II generation according to the design data is $\geq$ 99 %, respectively, air emissions will be reduced by 85,7–86,7 % (from 1, 4 – 1,96 g/Nm^3 to 0,2 – 0,26 g/Nm^3), herewith possible is cleaning of flue gases from sulfur oxides by 5–15 % without introducing special reagents.

Due to the combustion of hydrocarbon fuel in the furnaces of TPP carbon dioxide is emitted into the atmosphere, its concentration increases by about 0,25 % per year. This is dangerous because in the future it can cause warming of the atmosphere due to the greenhouse effect. From the smokestacks of TPP sulfur and nitrogen oxides are emitted into the atmosphere, which are the cause of acid rains. The case is complicated by the fact that the smokestacks of TPP began to grow up, their height reaches 250–300 and even 400 m, the amount of emissions are not reduced, but now they are scattered on vast areas (the emissions of TPP pollute the air with dust within a radius of 10–15 km). And during the rainy season, combining with water, gaseous toxic substances are converted into acid. These acid rains influence extremely harmfully on the environment: crop productivity is reduced due to damaging the leaves by acids; forests die; calcium, potassium, magnesium are washed out from the soil, causing degradation of flora and fauna;lakes and ponds water is poisoned, fish die, insects, waterfowl birds and animals which nourished by insects disappear (it is known in chemistry that the acidity is measured by the indicator pH. The change of pH by a unit means that the concentration of acid has changed in 10 times. For example, when pH of water system is 6,0–6,5 curls and shellfish die, and when pH is 5,0–6,0 most susceptible planktonic organisms, some types of fish die; air polluted with an acid mist causes respiratory and eye illnesses; the atmosphere is polluted as well with small solid particles of ash, slag incompletely burned fuel (soot).

To minimize the damage from these pollutions it is needed to clean coal from sulfur compounds before its combustion in TPP; to improve the quality of the coal blending it with the coal of ash content of 20–24 % coming from Poland; to capture sulfur and nitrogen oxides from the smoke of TPP using filters, to install electrostatic precipitators and desulphurization on the power unit №8 of Dobrotvir TPP according to order by the Ministry of Fuel and Energy № 300 from 22.08.06; to replace coal and fuel oil for TPP by environmentally friendly fuel, by gas (though at this stage it is not economically profitable). Due to the combustion of natural gas the single most significant air pollutant is nitrogen oxide, but it is produced 20 % less than due to burning coal.

Radioactive contamination. As into the furnaces of TPP with the coal get a lot of empty rocks (shales) containing impurities of natural radioactive elements – uranium-238 and thorium-232, ash particles emitted from the smokestacks of TPP, they are radioactive and cause additional exposure of the population at the territory close to the station, radioactive contamination of the atmosphere and the earth's surface. According to experts' data, the year of functioning TPP leads not only to a significant suppression of the immune system of humans and animals and anomalies of plants, but also to the shortening of life by 3200 person-years.

For electricity production they use fossil fuel, mostly coal, which like many other fossil materials contains a number of naturally occurring radionuclides, among which the most important is 40K, components of natural uranium and thorium radioactive series. During combustion in thermal power plants minerals melt and form glassy residue in a form of a slag, and volatile ash is taken out by hot gases and some part of it, depending on the effectiveness of the cleaning system of TPP gets into the atmosphere. With solid particles of volatile ash into the atmosphere get some natural radionuclides of uranium and thorium series, and 40 K, which are concentrated in it during coal combustion. As a result, thermal power plants are the source of getting natural radioactive isotopes in the environment, leading to its radioactive contamination and additional exposure of people.

To evaluate the influence of emissions of burning coal products by Dobrotvir thermal power station (STPP, Lviv region.) on radiological environmental state by gamma spectrometric method, the radionuclide composition and specific activity of coal that is burned on STPP as well as slags and volatile ash, which is produced due to coal burning were studied. The study was conducted at the accredited gamma spectrometer on the basis of spectrometric complex SU-01. The results of measurements are shown in the table.

Table

The specific activity of radionuclides in coal, burned at Dobrotvir TPP, in ash and slag

Radionuclide	Specific activity of radionuclides, Bq/kg		
	in coal	in ash	in slag
40K	338±35	558±53	625±55
214Bi	58±8	103±13	123±13
226Ra	105±15	192±18	247±22
208Tl	16±4	31±7	35±7
232Th	49±7	68±9	97±10
212Pb	57±8	100±11	122±12
214Pb	65±10	85±12	120±14
212Bi	45±7	71±10	116±13
228Ac	51±7	66±10	92±14

The obtained results showed that both in coal that is burned at STPP and in ash and slag which remain after the incineration, there are 40 K and radionuclides of uranium and thorium series, a range of values of specific activity of which in coal is in the range of 16±4 to 338 ±35 Bq/kg, in ash from 31±7 to 558±53 Bq/kg, and in slag from 35±7 to 625±55 Bq/kg. The concentration of radionuclides in the products of combustion was observed, in ash the specific activities of radionuclides are increasing in 1,6±0,3 times, and in slag in 2,1±0,3 times in comparison with coal.

For calculations such data on the activities of Dobrotvir TPP were used: the amount of coal that is burned at TPP is ~ 750 ths. tons per year; the emission of volatile ash into the atmosphere is ~ 768 tons per year; the amount of ash that remains after burning coal is ~ 80 ths. tons per year; the amount of slag that remains after burning coal is ~ 116 ths. tons per year; the project cleaning efficiency of solid particles at TPP is 98,5 %, and the actual one is 90 %.

The contributions of radionuclides activity in the total activity of coal, ash and slag were defined (Fig. 1–3).

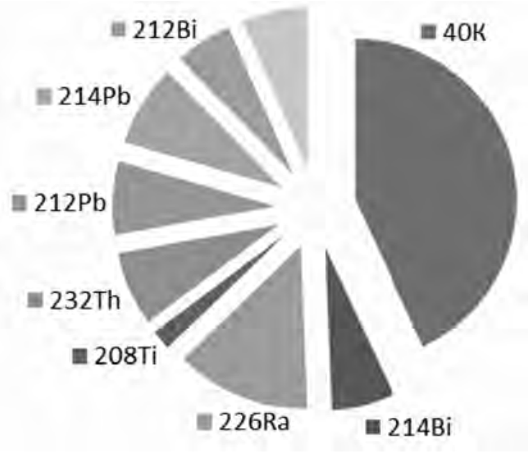

Fig. 1. The contributions of radionuclides activity in the total activity of coal

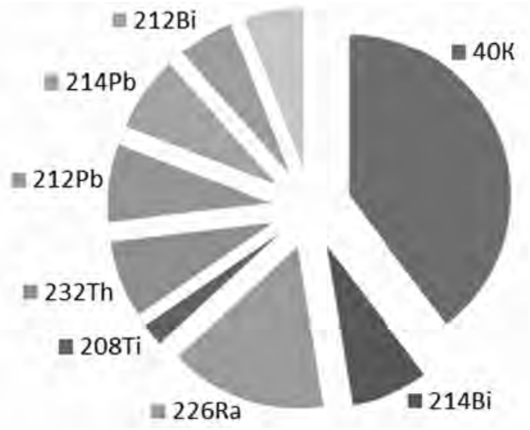

Fig. 2. The contributions of radionuclides activity in the total activity of ash

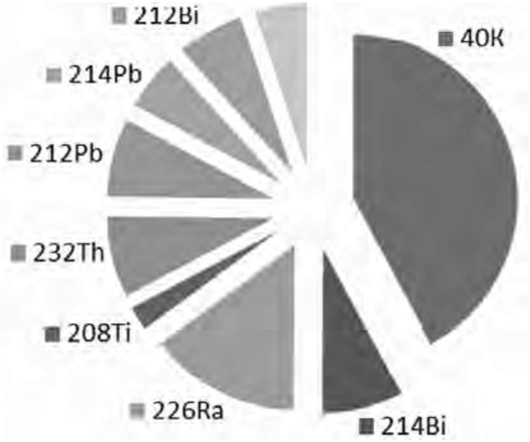

Fig. 3. The contributions of radionuclides activity in the total activity of slag at Dobrotvir TPP

Generally the configuration of this field depends on many factors such as the mass of ejected material and the size of ejected particles, the velocity of the emission of flue gases, the height of the smokestack, the total volume of flue gasese of moving direction and wind speed, the changes of air temperature at different altitudes and some other parameters.

The management with the wastes of Dobrotvir TPP. In order to develop the cost-effective organizational and technical solutions the experience of developed countries on the issue of using ashes of TPP was studied.

The basic ideological difference: in developed countries ash and slag wastes are called an incident product of TPP and the power plants perform product presale preparation, improving its characteristics to the requirements of the official building regulations.

In Ukraine and Russia ash and slag wastes are officially called wastes and power plants offer exactly the waste to consumers but not a technologically refined product with characteristics corresponding to the requirements of building regulations.

In Western Europe and Japan ash dumps at TPP are almost eliminated. Dry ash enters the silos, built next to the main buildings of TPP. For example, in Germany at many plants the capacity of the silos is 40-60 ths. tons and small silos are always built with a daily and two days capacity from which samples for a laboratory analysis of ash are taken, and in which it brings to the accordance to regulatory requirements by technological methods of mising and volumetric dosage in accordance with the fractional composition, then ash is reloaded in ash-storage silos.

In Germany, the largest company on the European continent on the use of ashes of TPP functions, Bau Mineral (BM) which is a subsidiary company of power system. This company is a link between TPP and the construction industry.

The production of BM meet the standards and guidelines of DIN, which are subject to external control by the institutions of testing building materials. The basis of quality assurance is continuous monitoring of products in its own well-equipped laboratories of testing building materials. From 4.3 mln. tons of volatile ash 3,5 mln. tons meet European standard of volatile ash for the materials of volatile ash. Combustion sand and granulated slag are utilized completely. Granulated slag is a substitute of sand in the sandblasting process. The main requirement is the homogeneity of ash properties. The areas of use are additives in concrete, mortar, cement, silicate products, the production of bricks, the underground and road construction. The main direction is the replacement of cement.

In Germany, there are no TPP without silos for ash. For example, at TPP “Molka” the total volume of silos is 60 ths. tons, the output of ash is 600 ths. tons/year. At TPP there are not any ash dumps. The incident products of TPP are exported to neighboring countries. For volatile ash a certificate is required if it comes to building and construction industry.

In Germany 3.1 mln. tons of cement are replaced by ash. Ash is recycled by an environmentally friendly method. The resources, the energy required for cement production are saved; the emissions of CO_2 are reduced by 3,1 mln. tons (during the production of 1 ton of cement the emissions of 1 ton of CO_2 are occuring), which is important according the requirements of the Kyoto Protocol on reducing the emissions of CO_2. The cost of silos, transport and wages are repaid. The power plant (TPP) is a producer of products but not waste. Uniformity is important for ash.

In the US, the builders are legally obliged to apply ash of TPP in concrete and mortars production. The violators are subjected to economic sanctions from the state. TPP often remunerate a consumer for the selection of ash. In China, ash and slag wastes of TPP are sold to consumers for free. In Poland, powerful economic levers, that stimulate the use of ash and slag wastes are used.

Conducting economic activities at Dobrotvir TPP, they create, temporarily store and remove such wastes as waste fluorescent lamps (I class of hazard); they are stored in the central workshop, in the separately designated place; waste car oil which belong to the II-nd class of hazard are formed in motor workshop. Waste car oils are partially used for their own needs, for lubricating machinery; waste turbine oils (III class of hazard) are in the boiler and turbine workshop, they are stored in a tank of volume of 40 m^3. The residue from washing vehicles (IV class of hazard), construction waste, solid household waste are removed to the city dump of the city Dobrotvir; oil sludge of mechanical purification of waste waters (III class of hazard) is transferred to the carriage depot of the city Drohobych; sludge of treatment plants (WTP) is removed to the sludge grounds of treatment plants of Dobrotvir TPP. Waste tires are passed to “Ivano-Frankivsk tire-repairing plant”.

For softening and desalination of water at Dobrotvir TPP they use sulfuric acid, caustic soda and hydrazine-hydrate (levoksin) as an anticorrosive means for processing feed water in boilers and the conservation (the passivation)of the nourishing tract of inner surfaces of boilers. The average annual cost of these substances are respectively 160, 100, 2.5 tons. Contact mechanical sulfuric acid of the 1 grade is stored in three pressurized tanks of the type BNT-16 in a separate closed room, there is water to pour upon spilled acid and alkali and solutions to neutralize them.

Hydrazine hydrate, and its aqueous solutions are powerful reducing agents, containing up to 64 % of hydrazine and they are used as a corrosion inhibitor. Hydrazine-hydrate is stored in stainless steel tanks (2 m^3, 0,5 m^3, 0,3 m^3) in the open acid workshop. Around the containers the territory is heaped round. Hydrazine hydrate is poured from the barrels into the receiver tank, half filled with water. The installation to preparing solutions of hydrazine-hydrate is located in the area of the power unit № 7 in an isolated room, which is equipped with ventilation and has a collector for collection and neutralization of drainage waters. In the room there is a required reserve of chlorinated lime to neutralize an accidentally spilled solution of hydrazine-hydrate.

The main wastes generated in production is ash and slag from coal combustion, primarily from the Lviv-Volyn basin with the content of ash of 24,85 %. During 2013 196,704.490 tons of ash and slag wastes were formed that belong to the waste of IV class of hazard. To build dams 23,733.600 tons were used, 20,354.000 tons were released for use to other owners, 152 616.890 tons were placed. Ash and slag waste is warehoused on two ash and slag dumps by the area of 56 hectares and 75 hectares of the volume of 4,5 mln. m^3 and 8,057 mln. m^3.

The determination of the coefficient of soil pollution by heavy metals in ash and slag dumps. Heavy metals get into the soils with the emissions of enterprises and transport, sewage, industrial waste, household waste, chemical fertilizers and pesticides. Typically, a significant soil pollution occurs within industrial sites, household waste, roads.

To evaluate the degree of soil pollution according to the classification heavy metals of three classes of hazard were taken: the I class – very hazardous – Cd, Pb, Zn; the II class – moderately hazardous – Cr, Co, Cu, Ni; the III class – low-hazardous – Mn, Fe.

To control the technogenic pollution of soils they determine the gross amount of heavy metals in the soils, since the latter has the ability to bind metal compounds.

To evaluate the degree of pollution of heavy metals on the one hand, it is necessary to use the initial point of reference, which is the value of element background content, and on the other hand it is necessary to know the MAC of the element in the soil. Since the MPC of investigated heavy metals is approved only for gross contents of Mn (1500 mg/kg) and Pb (32 mg/kg), so for the evaluation of the level of pollution by gross contents of heavy metals their background concentrations should be taken.

Ecological condition of soils is determined by the following criteria:

- favorable – the content of gross forms of heavy metals in the soil is on the level of percent abundance;
- satisfactory – the content of gross forms of heavy metals in the soil is slightly higher than percent abundance; but does not reach the MPC or the background concentration;
- of a pre-crisis – the content of gross forms of heavy metals in the soil is on the level of MAC or of the background concentration;
- of a crisis – the content of gross forms of heavy metals in the soil is in 2–10 times higher than MAC or the background concentration;
- catastrophic — the content of heavy metals is in hundreds times higher than MAC or the background concentration.

Qualitative and quantitative composition of metals in the soil samples is determined using roentgen analyzer EXPERT 3L. In the Fig. 4–7 the graphs of pollution coefficient in ash and slag dumps are presented.

Was determined that the ecological state of soil pollution at Dobrotvir TPP is satisfactory. The soil state of ash and slag dumps is of a crisis (the content of gross forms of heavy metals in the soil is in 2-10 times higher than MAC or the background concentration), large excesses of heavy metal of the I class of hazard were found out, namely Cu – 4,00, Zn – 2,53 and Pb – 2,16. The soil state at a distance of 10 m and 100 m is satisfactory (the content of gross forms of heavy metals in the soil is slightly higher than percent abundance, but does not reach MAC or the background concentration). At a distance of 30 m from the dumps the significant excesses of the following elements were found out: Mn – 4,7 times, Cu – 3,11 times, Zn – 2,67 times, Pb – 2,24 times. Cadmium was not found in the samples. A significant deviation of the content of heavy metals at a distance of 30 m from th ash and slag dump can be explained by the difference of the relief on the area of Dobrotvir TPP.

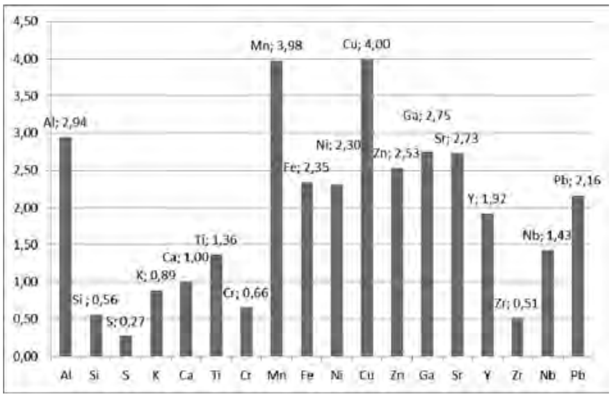

Fig. 4. Coefficient of pollution, ash and slag dump

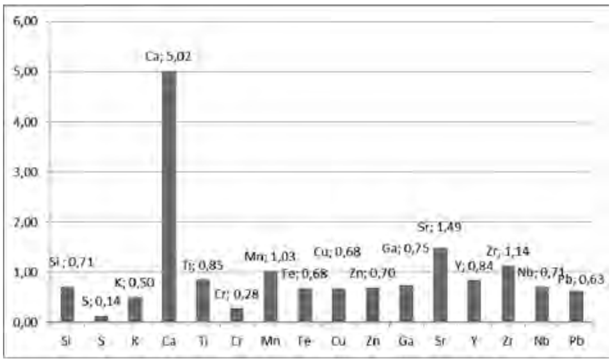

Fig. 5. Coefficient of pollution, distance of 10 m

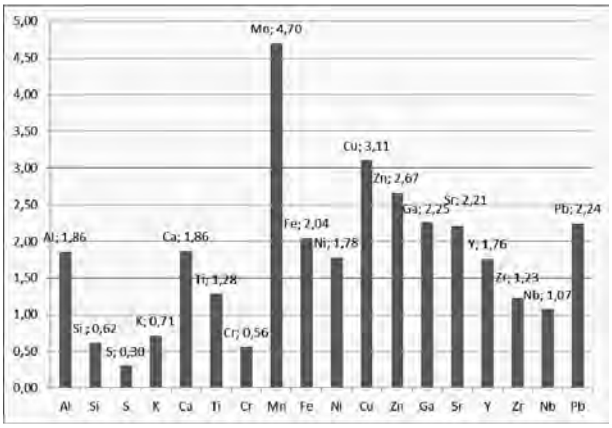

Fig. 6. Coefficient of pollution, distance of 30 m

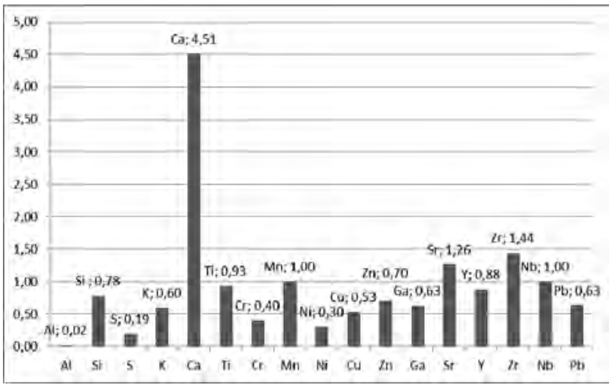

Fig. 7. Coefficient of pollution, distance of 100 m

3. Conclusions

The influence of emissions of Dobrotvir TPP Dobrotvir on the environment and the value of specific activity of radionuclides in coal that burned at Dobrotvir TPP, ash and slag. The installation of gas-cleaning equipment will reduce radioactive contamination of TPP in 100–200 times, ie to almost the background level.

The experience of developed countries on the issue of using ashes of TPP was studied. The state of management with wastes of Dobrotvir TPP was evaluated. The necessity to perform a combined research and environmental measures to reduce the negative influence of waste dumps on the environment was justified.

Ecological condition of soil pollution at Dobrotvir TPP is satisfactory, except ash and slag dumps themselves. The state of soils of ash and slag dumps is of a crisis (the content of gross forms of heavy metals in the soil is in 2-10 times higher than MAC or the background concentration), large excesses of heavy metal of the I class of hazard were found out, namely Cu – 4.00, Zn – 2.53 and Pb – 2.16. At a distance of 30 m from the dumps the significant excesses of the following elements were found out: Mn – 4.7 times, Cu – 3.11 times, Zn – 2.67 times, Pb – 2.24 times.

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MUTATION OF THE *DROSOPHILA MELANOGASTER* L. UNDER THE INFLUENCE OF THE ELECTROMAGNETIC RADIATION

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Abstract. Brief results of the previous studies of the effect of electromagnetic radiation on the fruit flies are quoted. The influence of electromagnetic radiation of industrial frequency on the living organisms has been investigated. Correlative dependence between phenotype *Drosophila melanogaster* L., duration and intensity of harmful factors has been established. Phenotypic manifestations have been fixed and *Drosophila melanogaster* L. mutation under the constant influence of the magnetic field induction from 2,25 to 20 μT in three generations of test objects have been characterized. The dependence of the increased frequency of mutations occurrence and the increase of their diversity caused by the increase of magnetic field induction has been revealed.

Key words: electromagnetic radiation, electromagnetic pollution, test objects, mutation.

1. Introduction

Drosophila melanogaster L. was among the first organisms used for genetic analysis, and today it is one of the most widely used and genetically best-known of all eukaryotic organisms. All organisms use common genetic systems; therefore, decoding such processes as transcription and replication in fruit flies helps to understand these processes in other eukaryotes, including humans. Charles W. Woodworth is considered to be the first to breed *Drosophila* in great quantity and suggest using them for genetic research during his time at Harvard University. Thomas Hunt Morgan began using fruit flies in experimental studies of heredity at Columbia University in 1910.

About 75 % of the known human disease genes have a recognizable match in the genome of fruit flies, and 50 % of fly protein sequences have mammalian homologs. An online database called Homophila is available to search for human disease gene homologues in flies and vice versa. *Drosophila melanogaster* L. is used as a genetic model for several human diseases including the neurodegenerative Parkinson's and Huntington's disorders, spinocerebellar ataxia and Alzheimer's disease. The fly is also used to study mechanisms underlying aging and oxidative stress, immunity, diabetes, and cancer, as well as drug abuse [1].

(Drosophila melanogaster L. is one of the most studied organisms in biological research, in particular in genetics and developmental biology. There are several reasons:

- This culture requires little equipment and little space is needed even for large cultures and, in general, the overall cost is low.
- It is small and easy to grow in the laboratory and its morphology is easy to identify once it is anesthetized (usually with ether, carbon dioxide gas, by cooling them, or with products like FlyNap).
- It has a short generation time (about 10 days at room temperature) so several generations can be studied within a few weeks.
- It has high fecundity (females lay up to 100 eggs per day, and about 2000 in a lifetime) [2].
- Males and females could be readily distinguished and virgin females could be easily isolated, therefore, facilitating genetic crossing.
- The mature larvae show giant chromosomes in the salivary glands called polytene chromosomes – «puffs» indicate regions of transcription and hence gene activity.
- It has only four pairs of chromosomes: three autosomes, and one sex chromosome.
- Males do not show meiotic recombination, consequently, facilitating genetic studies.
- Its recessive lethal «balancer chromosomes» carrying visible genetic markers can be used to keep stocks of lethal alleles in a heterozygous state without recombination due to multiple inversions in the balancer.
- Genetic transformation techniques have been available since 1987.
- Its complete genome was sequenced and first published in 2000 [3].

2. Material and methods

At the beginning of the XX century Carpentero used *Drosophila melanogaster* L. for certain biological problems solution. Medvedev studied the influence of family crossing on the objects [4]. Stervant started the first research on the behavior genetics of *Drosophila melanogaster* L. He compared sexual activity and mating selectivity of normal and mutant animals. He took recessive mutations that change eye pigmentation (white), the body pigmentation (yellow) and influence the shape of the wings (curved) and females with yellow colour of the body. Ginter had found out that interspecies hybridization of *Drosophila melanogaster* L. and *Drosophila* simulans were more successful providing that yellow females were taken for it [5].

In 1971, Ron Konopka and Seymour Benzer published «Clock mutants of *Drosophila melanogaster*», a paper describing the first mutations that affected the animal's behaviour. Wild-type flies show an activity rhythm with a frequency of about a day (24 hours). Researchers found mutants with faster and slower rhythms as well as broken rhythms – flies that move and rest in random spurts. Work over the next 30 years has shown that these mutations (and others like them) affect a group of genes and their products that comprise a biochemical or biological clock. This clock is found in a wide range of fly cells, but the clock-bearing cells that control activity are several dozen neurons in the fly's central brain [6].

The definition of "mutagen sensitivity" of Drosophila after its processing with methyl-methane sulphonate (MMC) or ultraviolet rays at a larval stage, made it possible to conclude that the studied mutation determines experimentally high sensitivity of early and late larvae of fruit flies to lethal action, and 4-5 fold reduction of enzyme activity was recorded in the mutant cells.

In 1985 scientists studied fertility and frequency of dominant lethal mutations of the radiosensitive line of *Drosophila* rad (2) 201G1 after irradiation of females by γ-rays. It has been determined that the doses of γ-rays, which frequency is more than 10 Hz, have strong sterilizing effect on mutant females and contribute to increased mortality of the flies after the irradiation [7]. Scientists Moss I. B. and Savchenko V. K studied the impact of the x-ray radiation and melanin pigment on fertility and vitality of experimental *Drosophila melanogaster* L. populations for 55 generations [8]. The results of this research showed that the viability of the individuals in irradiated populations, on average, is lower than that in the reference population. The fertility at the irradiation first decreases and then increases exceeding the reference level. Addition of melanin in nutrient medium is beneficial for both indicators in irradiated and reference populations.

Genotoxic impact of carcinogenic aromatic compounds on mus-mutants of *Drosophila melanogaster* L. was studied in 1991 by Shpigelman and others [9]. Larvae of homozygotes of all studied mus-lines were sensitive to the carcinogenic aromatic compounds, in comparison with the reference line. In the period from 1993 to 1995 the research group (Ratner V. A., Bubenshikova E. V., Vasileva L. A., and others) determined the doses of γ-radiation that will cause a number of mutations in isogenic strain of *Drosophila melanogaster* L [10].

On the basis of the biotesting method Kniazeva I. R. examined the impact of electromagnetic radiation with 460 MHz frequency and powerful electromagnetic pulses (EMP) on the organism of the maturating fruit fly [11]. In 2002 Chernova G. V. and Vorsobina N. V. studied the effect of low-intensity pulsed laser radiation (LPLR) on life-span of *Drosophila melanogaster* L. [12]. Assessment of the LPLR effectiveness was conducted on the basis of the analysis of the main parameters of aging. The effects of increasing and shortening of the life-span were discovered. In fact, recent studies show that there are over 7000 scientists studying this bug worldwide as a fulltime job.

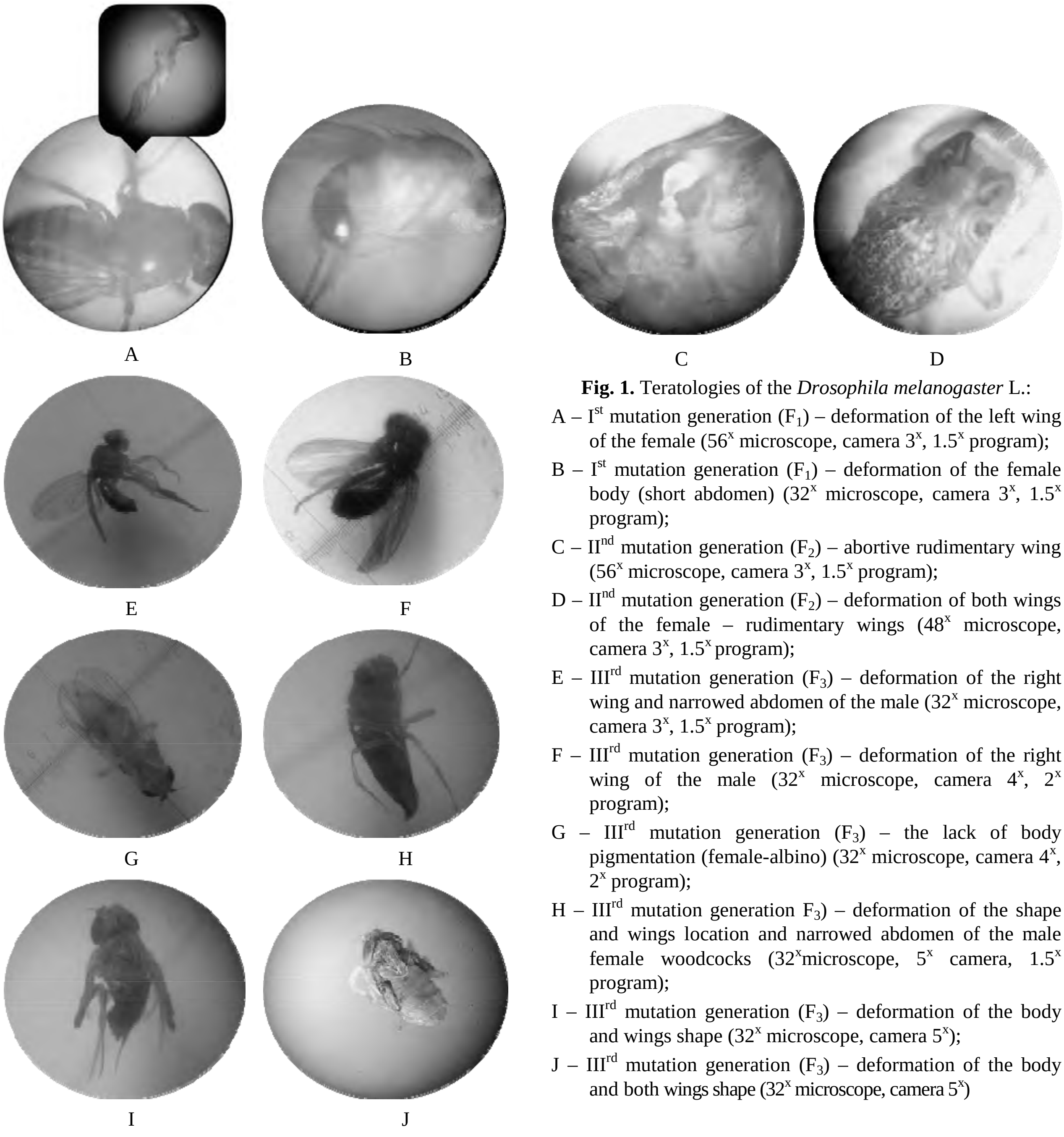
Regular *Drosophila melanogaster* L. have red eyes and their bodies are generally a mixture between brown and yellow [13]. Their general length is about 0.3 cm. The male fruit flies usually have a slightly darker body than the females. Another characteristic of the male *Drosophila* is a larger black spot on the abdomen. The male fruit flies are also slightly smaller than the females which is rather unusual in nature. While mating, the male fruit fly attaches himself to the female with very small hair like bristles before inseminating his target [14].

The development period for *Drosophila melanogaster* L., as many ectothermic species, varies with temperature. The shortest development time (from egg to adult) is 7 days and it is achieved at 28 ^{o}C. Development time is increasing at higher temperatures (11 days at 30 ^{o}C) due to heat stress. Under ideal conditions, the development time at 25 ^{o}C is 8.5 days, at 18 ^{o}C it takes 19 days and at 12 ^{o}C over 50 days. Females lay some 400 eggs (embryos), about five at a time, into rotting fruit or other suitable material such as decaying mushrooms and sap fluxes. The eggs, which are about 0.5 millimeters long, hatch after 12–15 h (at 25 ^{o}C) [15]. The resulting larvae grow for about 4 days (at 25 ^{o}C) while molting twice (into 2nd- and 3rd-instar larvae), at about 24 and 48 h after enclosion. During this time, they feed on the microorganisms that decompose the fruit, as well as on the sugar of the fruit itself. Then the larvae encapsulate in the puparium and undergo a four-day-long metamorphosis (at 25 ^{o}C), after which the adults enclose (emerge) [16].

3. Results

The determination of the negative impact of magnetic field on the test objects is based on the system including the following elements: the activity level, mortality, fertility, occurrence of teratology. The influence of the electromagnetic pollution on the organisms was studied on the basis of changing reaction of the test-objects in the result of different levels of magnetic field induction [17]. During the experiments the normal conditions were maintained, and the effect of noise excess was excluded. The first mutations appearance was recorded during the constant effect of electromagnetic field of industrial frequency with induction 2,25 µT and more. In the first generation of *Drosophila melanogaster* L. the following mutations were found in females: deformation of the left wing (fig. 1 A) and deformation of the female's body (fig. 1 B). None of the females did give the posterity F_2 during the breeding.

The teratologies discovered in the second generation (the abortive rudimentary wing (fig. 1 C) and deformation of female wings (fig. 1 D)) – had the genetic nature and recessive pattern of the inheritance, which caused mortality. Flies with rudimentary wings cannot fly: they have a defect in their "vestigial gene", on the second chromosome. These flies have a recessive mutation. Due to this both vestigial genes carried by each fly (one from each parent) have to be altered to produce the abnormal wing shape. If only one is mutated, the healthy version can override the defect. The largest number and variety of the mutations were recorded in F_3. In the third generation of Drosophila the abnormalities of the proportions and body sizes were revealed (figs 1 D–F), which proves that the electromagnetic field impact can cause the atypical structures.



A B C D

E F

G H

I J

Fig. 1. Teratologies of the *Drosophila melanogaster* L.:

A – Ist mutation generation (F_1) – deformation of the left wing of the female (56^x microscope, camera 3^x, 1.5^x program);

B – Ist mutation generation (F_1) – deformation of the female body (short abdomen) (32^x microscope, camera 3^x, 1.5^x program);

C – IInd mutation generation (F_2) – abortive rudimentary wing (56^x microscope, camera 3^x, 1.5^x program);

D – IInd mutation generation (F_2) – deformation of both wings of the female – rudimentary wings (48^x microscope, camera 3^x, 1.5^x program);

E – IIIrd mutation generation (F_3) – deformation of the right wing and narrowed abdomen of the male (32^x microscope, camera 3^x, 1.5^x program);

F – IIIrd mutation generation (F_3) – deformation of the right wing of the male (32^x microscope, camera 4^x, 2^x program);

G – IIIrd mutation generation (F_3) – the lack of body pigmentation (female-albino) (32^x microscope, camera 4^x, 2^x program);

H – IIIrd mutation generation F_3) – deformation of the shape and wings location and narrowed abdomen of the male female woodcocks (32^{x}microscope, 5^x camera, 1.5^x program);

I – IIIrd mutation generation (F_3) – deformation of the body and wings shape (32^x microscope, camera 5^x);

J – IIIrd mutation generation (F_3) – deformation of the body and both wings shape (32^x microscope, camera 5^x)

The range of the mutant signs or features that are affected by mutations is very wide. There are no signs and features that could not mutate in different levels. All the morphological, physiological, biochemical, behavioral characteristics and properties are affected by genetic variation. These variations are expressed by qualitative and quantitative differences, or in other words, by average values of varying features. Mutations can occur in both directions: towards increasing and decreasing of the intensity of a particular feature or property. Mutations can be either very sharply expressed (up to mortality), or presented as non-significant deviations from the original form (the so-called “small” mutations).

At magnetic field induction about 2,25–5 μT frequency of mutations in *Drosophila melanogaster* L. within three generations varies in the range of 0,2–1 %, and the most prominent are the deformation of the abdomen and the modification of the wings (fig. 2). When the EMP induction is from 5 to 20 μT the frequency of mutations is increasing (up to 3 %) and the mortality is high (>15 %). New forms of mutations occur (fig. 1 G), or deformation of body parts increases (figs 1 H, I, J). It is established that the higher magnetic field induction is, the bigger the number of the mutated animals and a variety of mutations are (from slight distortion of body parts to the albinism and lethal gene mutations).

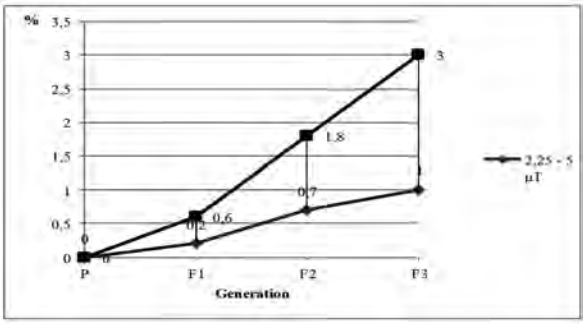


Fig. 2. Frequency of mutations in *Drosophila melanogaster* L. induced by electromagnetic radiation

4. Conclusions

Constant impact of the electromagnetic radiation with the induction over 2,25 μT predetermines the following phenotype subsequent mutations in three generations of *Drosophila melanogaster* L.:

- the deformation of body parts;
- the change in body pigmentation;
- the change of the size of the whole body or components;
- the replacement of one physiological organ by another one.

The level of the mutation changes in the phenotype does not depend on the intensity and duration of the mutagenic factors. So, a weak mutagen, which acts for a short time, sometimes is able to cause more considerable changes in the phenotype than the stronger one. However, with the increasing intensity of the mutagenic factor the frequency of mutations occurrence increases only up to a certain limit.

All of the mutagenic factors do not have the lowest limit of their action, it means that there is no such a limit of their intensity, under which they cannot cause mutations. This property of the mutagens has important theoretical and practical significance, as it proves that the genotype must be protected from all mutagenic factors, whatever low the intensity of their action is. Though, in the early stages of the body development the sensitivity to the mutagenic factors is higher than in adults.

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A compendium with participants papers' abstracts will be printed before the beginning of the Congress.

IMPORTANT DATES

Application, paper submission	**before 01.08.2016**
Registration	**21.09.2016 at 8:30**
Congress opening	**21.09.2016 at 10:00**

Participants meeting

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Fees

Fee for one participant is 60 USD.

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- Text of the report should be supplied in Microsoft Word 97/2000/XP/2003 format. Font: Times New Roman Cyr.
- Formulas: 11 (Σ – 12, tabl. – 9 pt), subscript/superscript – 8 pt (Σ – 11, tabl. – 7 pt), sub-subscript/superscript – 6 pt (Σ – 8, tabl. – 5 pt), symbol – 10 pt.
- Figures: caption in center size 9 pt.

Paper arrangements:

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Title of the report: Omitting one line, print paper title in the middle of the next line in bold capital letters, 12 pt.

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