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Olena Mitryasova
Chad Staddon

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CONTENTS

ASSESSMENT OF WATER POLLUTION BY BIOINDICATION METHOD

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ABSTRACT

The quality of polluted water was assessed using a bioindication method based on the identification of changes in algal reproduction due to the influence of toxic substances contained in the aquatic medium. This makes it possible to assess the influence not only from the concentration of pollutants, but also by final effect, i.e. their toxic action on living organisms. The investigation was carried out using the example of water pollution by chlorination by-products and batteries. The results show the high reliability of the bioindication method for water pollution assessment. In addition, the method of monitoring water objects was improved. This method is based on the identification of phytoplankton particles, which is achieved by comparing array multispectral images using the Bayesian Classifier based on Mahalanobis distance.

Keywords: water, pollution, bioindication, phytoplankton.

INTRODUCTION

Since water is the main factor supporting human life, then ensuring water quality must be a priority for every country. Increased pollution of natural water bodies and the impossibility of providing high quality of drinking water with outdated sewage treatment technologies make health risks of water consumption very high.

Chlorination by-products and substances contained in batteries are among the most widespread water pollutants.

There are many toxic by-products formed during water disinfection by chlorine (sodium hypochlorite, etc.) [Nikolaou]: trihalomethanes, haloacetic acids, halogenated aldehydes, halogenated ketones, haloacetonitrils, chloropicrin, chlorophenols. They cause a chronic impact on humans if orally ingested, inhaled or absorbed through the skin [Villanueva]. Some of these organochlorine compounds are carcinogenic, mutagenic (break DNA chains, causing birth defects such as interventricular septum defects and obstructive urinary tract defects), or teratogenic, according to [Morris, King, Kasim, Sharma]. However, regulatory limits are established only for a few substances. For example, there are no limits for toxic and carcinogenic haloacetic acids and carcinogenic and mutagenic haloacetonitrils in many countries, although the World Health Organization and the US Environmental Protection Agency (USEPA) have established limits for some substances from these groups.

According to [Recknagel, Moreno-Merino], heavy metal content in many batteries is over limit values. Therefore, batteries pose a serious danger to the environment. Since methods of non-hazardous waste utilization are unsuitable for battery processing, heavy metal release to water is totally uncontrolled [Moreno-Merino].

Due to the potential toxic effects of chlorination by-products and heavy metals, it is necessary to evaluate their impact on living organisms. Phytoplankton is known to be useful test-object. Bioindication is used in environmental research as a method of identifying anthropogenic influences on ecosystems. This method is based on investigation of variable factors which influence different characteristics of biological objects and systems. The biological systems or organisms which are the most sensitive to investigated factors are used as bioindicators [Styskal]. The objective of this study is to investigate how batteries influence living organisms using a bioindication method.

In addition, the theoretical and practical aspects of automated control of water ecosystems are not developed enough due to the relativistic approach and subjectivity of integral indicators used for quality assessing. The main parameter of polydisperse mediums is concentration of phytoplankton particles. The quantitative correlation between the concentrations of these particles is the criteria of water quality assessment, including indices of biodiversity, ecological balance, integrated bioindicators of the human and industrial impact of various pollutants, and others.

METHODOLOGY OF RESEARCH

For well and river water chlorination by different doses of sodium hypochlorite solution (SHS), the mass concentration of active chlorine in SHS was defined. For this purpose, potassium iodide was added to SHS and the solution was titrated by sodium thiosulfate. After chlorination, free residual chlorine in the investigated samples was measured using a method of titrating by methyl orange.

Investigations of the toxic impact of water chlorination by-products and heavy metals of batteries were carried out using a bioindication method. Chlorella and

Scenedesmus were used as bioindicators. Eleven samples were prepared by mixing an equal volume (100 ml) of well and river water disinfected with different SHS doses and a phytoplankton solution. The same was done for a non-disinfected well, river and tap water. The samples were placed in a sunny spot for 90 days. Additionally, water with bioindicators was divided up into 20 samples by adding 10 different types of batteries (2 batteries of each type: damaged and undamaged), and one control sample without batteries. The batteries were prepared so that one battery had undamaged casing and another (of the same type) was damaged. This enabled direct contact between the investigated water medium and the battery's content. These samples were placed in a lit spot for 14 days. Measurements of the samples' pH and visual observation of changes were carried out during the 14 days. Visual investigation of the samples was carried out at the end of experiment using a microscope, DCM-300 (400x zoom).

In addition, the method of measuring television multispectral environmental control of water bodies was used for water quality assessment, which was based on identifying the qualitative and quantitative composition of microalgal cells. Data were compared to normalized values, by performing multispectral television flow analysis of phytoplankton particle, where images of particles flowing in the measured cell received at characteristic wavelengths of phytoplankton pigments with a microscope and CCD-TV camera are compared with images from the database of phytoplankton particles in certain specialized processors in real time using the Bayesian optimal Classifier with a solved function based on Mahalanobis distance.

RESULTS OF RESEARCH AND DISCUSSION

Assessment of water pollution

Visual analysis of the investigated samples was conducted (see fig. 1–6).

The results indicate reduced phytoplankton activity with increasing SHS doses for both underwater and river water. In addition, more phytoplankton was found in the samples of good water compared to the samples of river water with the same SHS dose. This confirms the theory that chlorination by-products increase with increasing organic substances in the water (river water contains far more organic compounds than good water). Some samples were of special interest. These were samples of normal well water and good water chlorinated with 0,49 g/l of SHS. They both had a gray-white taint of unknown origin (fig. 1 and 2). One can assume that this is probably due to the development of pathogenic microflora caused by a lack of disinfectant. Such a phenomenon was not observed in other samples with larger SHS doses. Also, there were yellow-white clusters noticed in the sample of tap water with phytoplankton (fig. 3). These could be precipitated salts – carbonates etc.

The residual chlorine content of 0,3 mg/l is considered normal according to Ukrainian standards. Therefore, theoretically well water chlorinated by an SHS dose of 0,49 g/l and river water chlorinated by an SHS dose of 3,7 g/l can be consumed by humans without risk. But according to fig.2 and assumptions mentioned above, the SHS dose of 0,49 g/l does not remove all pathogens and drinking such water can be dangerous to health.

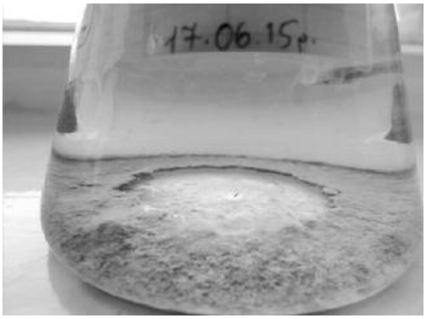

Figure 1. Well water with phytoplankton

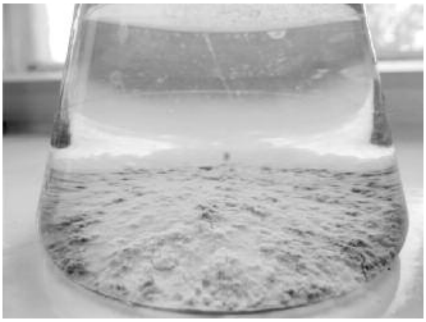

Figure 2. Well water with phytoplankton and SHS dose of 0,49 g/l

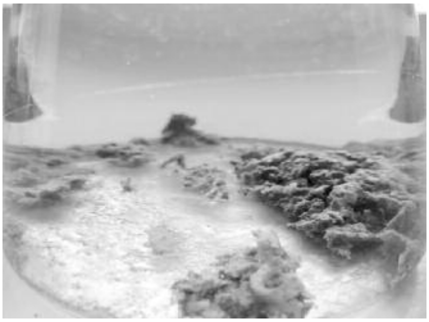

Figure 3. Well water with phytoplankton and SHS dose of 3,7 g/l

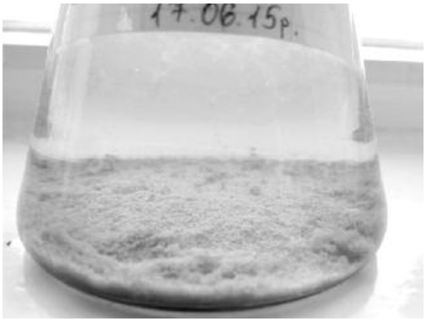

Figure 4. Distilled water with phytoplankton

The largest impact of batteries on the bioindicator was found in the samples with alkaline batteries, while the lowest influence was in the samples with 9V block batteries of the 6F22 type (fig. 5–6). Importantly, all the samples with damaged batteries were characterized by higher levels of mortality to organisms in comparison with the samples with the undamaged batteries of the same type.

Comparison of pH dynamics of the samples with undamaged batteries showed that the sample with the most similar dynamics to control sample was the sample containing Li-Ion battery of the CR2032 type. This was probably either due to the lowest weight of this type battery among all investigated batteries or due to a less aggressive chemical composition. Similar pH dynamics were also noticed for the sample containing the Ni-Cd rechargeable battery. Therefore, one can assume that the result of this sample was similar to the result of the control sample due to absence of contact between the sample's water medium and battery content during the experiment.

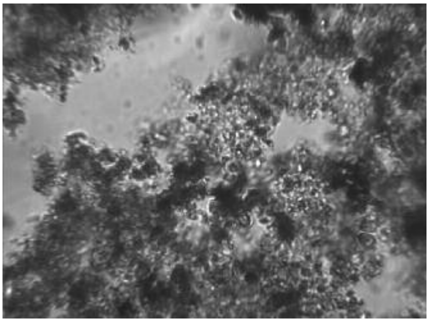

Figure 5. Sample with a zinc-carbon battery of a 6F22 type at 400x zoom

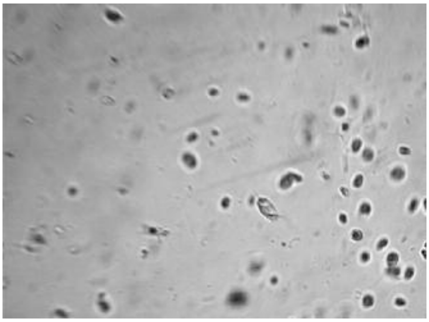

Figure 6. Sample with a alkaline battery of a LR20 type at 400x zoom

The most significant pH changes occurred in the samples containing zinc-carbon batteries. Additionally, one of these samples was the single one where an acid environment was noticed at the end of experiment despite its pH increasing due to the presence of algae. It is most likely that this result was caused by the much greater weight of the battery in this sample (zinc-carbon battery of R20 type) in comparison to the majority of the other investigated batteries. Therefore, more hazardous substances could potentially come to the sample's water medium. The last assumption can indirectly prove the instability of zinc-carbon batteries' casing.

High pH values for some samples with undamaged batteries could be the consequence of the influence of a few factors: the instability of zinc-carbon battery casing that, in turn, could cause the release of electrolytes with ammonium ions into the water medium, potentially leading to their binding by ions of Fe and Zn (for example, to insoluble forms).

The analysis of the pH dynamics of the samples with damaged batteries has shown a larger dispersion of pH values in comparison to the samples with undamaged batteries. The samples can be divided into several groups by pH dynamics. The changes in pH that were most similar to the control sample were noticed in the samples containing damaged batteries. The samples with undamaged batteries demonstrated pH values similar to those in control sample.

The smallest pH deviation from values in control sample were in the sample with Li-Ion battery of the CR2032 type. It should be noted that other above-mentioned samples (which correspond to the majority of alkaline batteries and to one type of rechargeable batteries) were characterized by dramatic increases in pH (to over 12) at the beginning of experiment followed by reduction to control values. This can be explained by alkaline electrolyte release from damaged batteries to the water medium as previously described.

The sample with damaged alkaline battery of the LR20 type had the highest pH value (almost 13) from the first day of the experiment due to its large electrolyte volume (a battery of such type has larger dimensions compared with majority of other batteries). The sample with a damaged zinc-carbon battery of the 6F22 type had the lowest pH value (below 5 at the end of the experiment) as it was also in the case of undamaged batteries. But there was no temporary pH increase observed in the samples with damaged batteries.

The same dynamics were noticed for other samples where pH gradually fell to neutral or acid values. These were the samples containing zinc-carbon batteries and the rechargeable phone battery. Therefore, potential pH increases due to electrolyte influence in abovementioned samples could be neutralized by the act of other substances from a given type of battery. For example, chloride in the electrolytes of zinc-carbon batteries can cause pH reduction due to hydrochloric acid formation.

Similar pH values were observed in some samples with the same batteries types, one of which was damaged and another one was undamaged. They include a zinc-carbon battery of a R20 type, an alkaline battery of a LR03 type, a Li-Ion battery of a CR2032 type and a rechargeable battery of a KR6 type. These could have be influenced by several factors: the low content of substances able to change pH or their instability, the neutralization of such substances by the bioindicator (algae), the low hermeticity of the metal casing of the battery or its self-damage during the experiment.

The most significant pH change took place on the first day which demonstrates the intensity of the batteries' impact. Generally, pH changes correspond to the type of substances contained in batteries regardless of whether they were damaged or undamaged. Comparing the samples with damaged and undamaged batteries of the same type showed nearly identical pH dynamics. In the case of zinc-carbon and rechargeable phone batteries, the samples with damaged batteries had constantly lower pH values and, conversely, in the case of other batteries types they had higher pH values. Naturally, this is explained by the chemical composition of batteries, including the electrolyte type.

The level of bioindicator death was the highest in the samples which had pH values similar to the control (almost all alkaline batteries, the Li-Ion button and rechargeable batteries), as well as in the sample with a highly alkaline environment (an alkaline battery of an LR20 type). These are the battery types containing the largest quantity of mercury. Alternatively, the samples with pH values different from the control sample (all zinc-carbon batteries and the damaged Li-Ion rechargeable phone battery) had the lowest level of algal death, except for the samples with zinc-carbon batteries of the R20 type.

Therefore, one can assume that pH change during contact between sample medium and battery content is not a reliable indicator for defining the degree of batteries' impact on the environment. In turn, the metals contained in batteries affect ecosystems without any pH change. For example, the level of algal death is considerable in the samples with batteries containing nickel and cadmium, especially in the sample with the damaged battery, although its pH was similar to values in the control sample.

Method of controlling the phytoplankton concentration

The proposed method for controlling the concentration of phytoplankton particles uses comparable array spectral polarimetric images of particles obtained in vitro using the CCD camera developed in the controls (fig. 7). The volume concentration and quantitative correlation between certain types of particles are determined from characteristic wavelengths of pigments in the specified positions and angles of a polarizer analyzer, which allows their identification more reliably [Petruk].

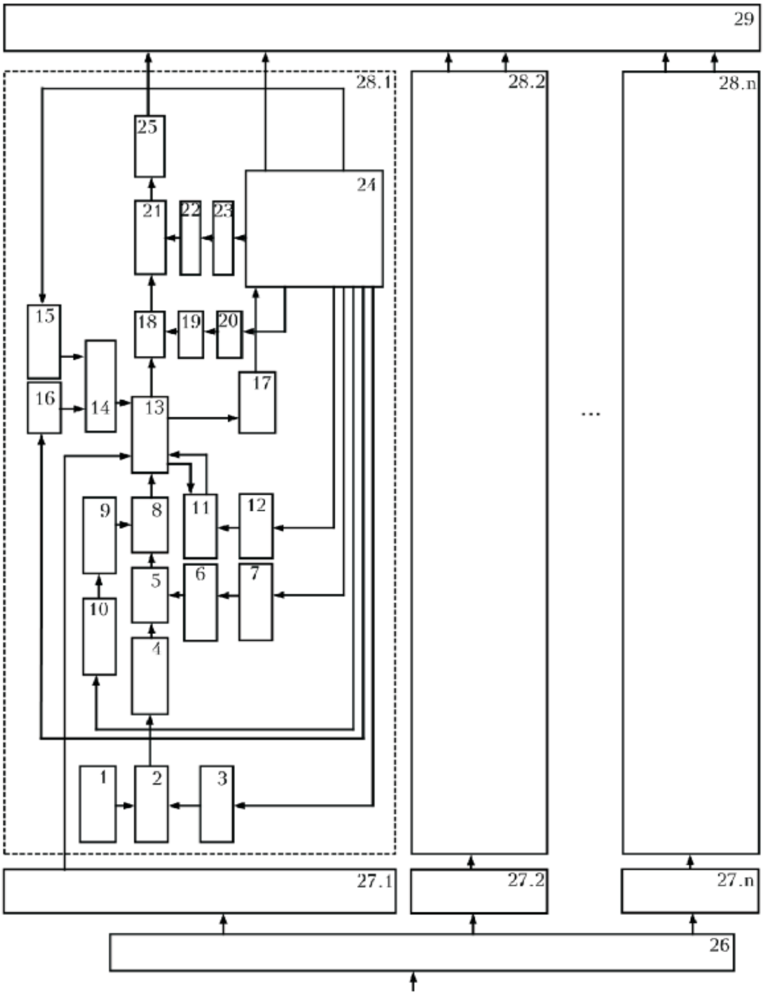

Figure 7. Block diagram of the automated means of phytoplankton concentration control

Theautomated tool works as follows. Water particles with different sizes of phytoplankton enter the mixer 26 and share a set of filters with pores of different diameters 27_1 ... 27_n on the flow of particles of a certain size, which are received in the flow measuring cell 13 corresponding to measuring channel 28_1... 28_n. Radiation from a light source enters the monochromator 2, the wavelength is fixed by stepper motor 3 according to the values of the characteristic wavelength pigments in phytoplankton particles. Then radiation passes through the fiber-optic waveguide 4, 5, and polarizer compensator 8, the rotation angles for rotary device (6, 9) are set, which rotate by stepper motors (7; 10). After that, radiation runs through measuring cuvette 13 with a thin layer of phytoplankton. Before the experiment, flow measuring cuvette 13 standard solution is washed by flushing pump 11.

Flow measuring cuvette 13 is placed on the stage of the microscope 14 and can be moved by stepper motors (15; 16) in the directions X and Y. To ensure stability and repeatability of test flow measuring, cuvette 13 is placed in thermostat 17. Radiation then passes through the analyzer 18, the rotation angle is set for rotary device 19 by stepper motor 20. Increases to the size of spectral-polarimetric images of phytoplankton particles are achieved by using an optical microscope system 21. Autofocus microscope is achieved by means of AF 22 and stepper motor 23. Control unit 24 of stepping motor provides the necessary control signals for stepper motors. A magnified image of particles is fixed by photodetector (CCD-camera) 25 and transferred to computer 29. Computer 29, using means of specialized software, compares the received image with a spectral-polarimetric sample and determines the correlation between particles of different species. The obtained correlation between particles of different species of phytoplankton allows assessment of its condition. The number of measuring channels 28_1 ... 28_n and filters 27_1 ... 27_n is defined by the condition of accordance of the sharpness depth of images with particle size and with liquid thickness in the measuring cuvette. Thus, if the concentration of particles with the size d_{min}.... d_{max} needs to be controlled in polydisperse aqueous medium, one should use a certain number of measuring channels where the conditions by sharpness depth of particle images and their resolution has to be provided in each.

CONCLUSIONS

Investigation of the impact of chlorination by-products and heavy metals from batteries on water quality using phytoplankton has resulted in new assumptions. Chlorinated water, in particular by-products of chlorination, indeed affect the phytoplankton activity according to following trends. Increasing SHS doses causes a reduction in the amount of phytoplankton at the end of experiment. In addition, the fact that more phytoplankton were found in the samples of well water compared to the samples of river water with the same SHS dose confirms the theory that chlorination by-products increase with increasing organic substances in the water. It was also experimentally studied that an SHS dose of 0,49 g/l providing free residual chlorine content in the normal range does not remove all pathogens. Therefore, the main objective of water disinfection cannot be achieved in this case.

The research results have also shown that all batteries, including undamaged batteries, affect living organisms when they enter the environment. They change environmental characteristics very quickly. The most significant pH change took place on the first day of the experiment which demonstrates the intensity of the batteries' impact. Batteries with undamaged casing also cause destruction to living organisms, possibly due to gradual damage of the casing in an aggressive environment.

Different types of batteries can provide alkaline or acidic environments. This partly depends on the electrolytes used. But this research has shown the ambiguity of this parameter's influence on living organisms. A much larger impact is caused by hazardous heavy metals (mercury, nickel, cadmium and others) contained in the batteries. When analyzing the impact of the potentially most hazardous batteries containing mercury, nickel and cadmium, the authors noticed the most negative reaction of bioindicator in such samples. These batteries include nickel-cadmium rechargeable batteries and all alkaline batteries. Therefore, one can assume that pH change during contact between the sample medium and battery content is not a reliable indicator for defining the degree of batteries' impact on the environment. In turn, the metals contained in batteries affect ecosystems without pH change. Consequently, the additional research into the impact of heavy metals on living organisms is needed.

The proposed method of using multispectral images and an appropriate device can efficiently control the concentration of phytoplankton in photo-bioreactor wastewater treatment plants, and can be used to assess the state of water and complex human impacts on aquatic ecosystems using bioindication by phytoplankton.

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The book is written for scientists, lecturers, postgraduate students, engineers and students who specialize in the field of environmental researches, where the object of study is water.

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