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Andrzej G. CHMIELEWSKI[1]

DREAMS OR REALITY - FOSSIL FUELS, RENEWABLES OR NUCLEAR POWER?

MARZENIA A RZECZYWISTOŚĆ - PALIWA KOPALNE, ODNAWIALNE ŹRÓDŁA ENERGII CZY TEŻ ENERGETYKA JĄDROWA?

Abstract: The recent developments regarding energy production plans and the measures needed to follow to ensure environment conservation including the prevention of climate changes are discussed. The research performed concern development of nuclear fuel based on country indigenous resources and application of hydrometallurgical sol-gel technology, the nuclear energy is the most environmentally friendly technology allowing fossil hydrocarbon resources preservation. Nevertheless, biotechnologically based renewable energy is other important resource for energy production and a new biogas plant is under development. Never less for the next generation the coal will be a main energy source and flue gas treatment technology based on the electron accelerators has been developed.

Keywords: energy, nuclear energy, uranium, biogas, electron beam flue gas treatment

Introduction

The human being is a creature which dreams or believes more than agrees with the laws of the science. Therefore we do believe or we do not believe in global warming, in Hubbert peak, in results of Chernobyl's disaster or in wonderful panacea on our diseases and miracles in the energy savings or productions which broke down the rules of thermodynamics.

Next what we do believe are taxes, we do not like to pay more for health care, for electricity, for waste collection, for nothing. Therefore the next players beside the dreams are money. Some countries which claim that they are implementing sustainable development are using more and more natural gas for electricity production in the big power units, what is in principle a crime, as said an old professor of organic technology who knows as important is the gas as raw material for the all industries. One day the next generation will generate hydrogen from the water which we produced in the gas combustion process. Do we know the Hess's law?

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Despite of environmental limitations the world needs energy; still two billion of the people do not have access to the electricity. The increase in the electricity production is a must. Here from the dreams we come to the reality. We will burn fossil fuels, we will develop renewable energy sources and we will develop nuclear energy. The future and the limitations of these technologies are discussed in the paper.

The present state of art does not guarantee sustainable and economical development of the sector. The activities of the author's research group in the field of development of environment protection processes in fossil fuel power sector (electron beam plasma), renewable high efficiency technologies testing (biogas production and upgrading) and nuclear fuel cycle (uranium resources, fuel reprocessing and radioactive waste storage) are presented to demonstrate that some solutions are possible.

The research follows the international and national programs and is carried out in the frame of several R&D projects; Balticnet - PlasTEP (electron plasma gaseous pollutants treatment c/o TZV, Greifswald), INITECH (high efficiency biogas plant and mobile membrane installation for biogas enrichment, c/o Uniserv, Gliwice), POIG (uranium resources c/o PIG - PIB, Warszawa), EURATOM (uranium/thorium oxides fuel precursors - ACSEPT). Collaboration of the scientists all over the world and support of governments of the research in the field of energy production leads to the positive conclusion, if we will be smart enough we will solve the problem. However, not the money but real sustainable development must be a priority.

Energy production

Energy demand and primary energy sources are listed in Table 1 [1]. The share of transport rose from 24.2% in 1973 to just under 30% in 2001. World energy demand has continued to increase even while the efficiency of many vehicles and energy-using appliances has improved. Both developed and developing countries are responsible for the growth. Improvements in energy efficiency in developed countries over the recent past did not lead to decreases in energy demand, because higher living standards have resulted in higher consumer expectations. In developing countries, rural and urban electrification programmes, together with the development of transport and industrialization, led to a strong increase in energy demand.

Table 1

World primary energy demand (million tones oil equivalent)

	1971	2002	2010	2020	2030
Coal	1 407	2 389	2 763	3 193	3 601
Oil	2 413	3 676	4 308	5 074	5 766
Gas	892	2 190	2 703	3 451	4 130
Nuclear	29	692	778	776	764
Hydro	104	224	276	321	365
Biomass and waste	687	1 119	1 264	1 428	1 605
Other renewables	4	55	101	162	256
Total	5 536	10 345	12 194	14 404	16 487

The increase in demand was often faster than the growth in population. However, still some 2.4 billion people rely on traditional biomass for cooking and heating. That number will increase to 2.6 billion by 2030. In developing countries, biomass use will still represent over half of residential energy consumption in 30 years. Without policy changes, world energy demand is projected to increase steadily at 1.7% per year through 2030, less than the 2.1% annual growth over the past 30 years. In that event, fossil fuels will remain the primary sources of energy and will meet 90% of the increase in demand to 2030.

Special attention should be put on electricity production, since all over the world a big percentage of population lives in the mega - cities and in this case huge electricity generation power plants are required. The second reason is that in some cases power stations are located close to open - cast mines like Belchatow and Turow in Poland. Therefore their impact on the environment is meaningful.

The installed electricity generation capacity by the primary energy source category is presented in Table 2. Some 1.6 billion people - one-quarter of world population - have no access to electricity. About 80% of these people are located in India and sub-Saharan Africa.

Table 2

Electricity generation capacity installed by sources

Fuel	**Power [GW]**		
	Installed in 1995	**Estimated for 2020**	**Net increase**
Coal	870	1836	966
Gas	435	1296	861
Oil	435	648	213
Hydro	667	1026	359
Nuclear	348	378	30
Other	145	216	71
Total	2900	5400	2500

In Poland more than 30% of electricity production is based on coal combustion. However, very soon the taxes on CO_2 emission will be introduced. Therefore the government has decided to develop nuclear power. The recent crises on gas and oil market have shown that the countries have to relay on their own energy sources if possible, the study regarding shale gas resources and search for uranium deposits have started in Poland. Beside the knowledge about the ore localization the chemical methods for its extraction have to be studied to evaluate the economy of the process [2].

Coal combustion

Although nuclear energy will become available in Poland, for decade the coal will be the main energy source. However it is most dirty fuel from all fossils. A big amounts of CO_2, SO_2 and NO_x are emitted, additionally beside the fact that Electrostatic Precipitator (ESP) are applied PM2.5 emission becomes be a problem limited by standards. New concerns in the case of coal combustion are Hg and polyaromatic hydrocarbons (PAH) emission. The new technologies are searched for air pollution control. The plasma technologies are among promising ones. The most successful is Polish solution based on electron beam application. The big industrial installation for deSO$_x$ and deNO$_x$ has been built in EPS Pomorzany, Szczecin [3]. The technology provides simultaneous removal of the both pollutants [4] and additionally laboratory experiments have proven that the technology can be applied for PAH [5, 6] and Hg [7] treatment. Therefore the process has be qualified as one of the most advanced processes for air pollution control [8].

Renewable energy sources

Being realistic in the future of energy production, the coal will be a main primary energy source, however to make it environment friendly air pollution control have to be introduced, what was discussed in the previous chapter. The other developments concerning base load electricity supply should be based on nuclear energy, while dispersed sources should consider usage of renewable energy sources. The big expectations were devoted to the development of the last mentioned type of energy. However, the market penetration of renewables is slower than was hoped and improvements in energy efficiency in general have not offset the increasing demand for energy due to economic development (Table 3). Some aspects of limitations their applications are listed in Table 1. The real role in further development will play hydroenergy and biomass. The combustion of biomass is followed by a big concern regarding environment pollution effects. The most promising in the field of biotechnological means of biomass energetic content into energy seems to be biogas production. The Institute of Nuclear Chemistry and Technology in cooperation of SEP Zamosc and Uniserv Co., Gliwice is developing a new type biogas production plant based on the two stage process in which hydrolysis was separated form methanogenesis providing higher biogas yield and higher concentration of methane in biogas in comparison with conventional single stage processes. Further enrichment of the biogas is based on the membrane system applications [8], after this enrichment biogas can be used as a standard gas for municipal and industrial applications or in compressed form as vehicle fuel.

Table 3

Present status of renewable energy

	Photovoltaic	**Wind power**	**Nuclear energy**
Area	20 m^2/kW 130 km^2/1000 MW	500 m^2 for two 250 kW class unit (height 30 m, diameter of vane 28 m)	0.4 km^2/1000 MW
Operation rate	Annual Capacity Factor ca.12% No generation during night-time	Annual Capacity Factor 20÷25% Wind velocity > 6 m/s	Annual Capacity Factor ca 80%

Conclusions

The energy production for the few next decades will depend on fossil fuel combustion, however these processes require air pollution control technologies application. One of the most advanced processes based on plasma principles is an electron beam flue gas technology, which can be used for simultaneous removal of different pollutants from flue gas.

However other options which have to be developed are nuclear energy and renewable energy sources. First of them has to have ensured fuel supply at reasonable prices, what can be achieved by new resources exploration and development of chemical and process engineering methods of the extraction of fissile elements from depleted uranium or thorium resources.

From the renewable energy acquisition the biogas production and enrichment seems to be most promising and new highly effective processes for biomass conversion and biogas enrichment are searched for.

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MARZENIA A RZECZYWISTOŚĆ - PALIWA KOPALNE, ODNAWIALNE ŹRÓDŁA ENERGII CZY TEŻ ENERGETYKA JĄDROWA?

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Abstrakt: W opracowaniu analizowane są programy dotyczące rozwoju energetyki i związane z jej rozwojem wymagania dotyczące ochrony środowiska, łącznie z zapobieganiem zmianom klimatycznym. Bez wątpienia najbardziej przyjazna środowisku jest energetyka jądrowa, której rozwój pozwala na ochronę zasobów kopalnych węglowodorów. Innymi ważnymi w rozwoju energetyki są źródła odnawialne oparte o biotechnologię, w tym wykorzystujące nowy typ biogazowni. Jednakże jeszcze dla następnego pokolenia węgiel pozostanie głównym paliwem energetycznym i dlatego rozwijane są technologie oczyszczania gazów spalinowych, w tym wykorzystujące akceleratory elektronów.

Słowa kluczowe: energetyka, energetyka jądrowa, biogaz, oczyszczanie gazów spalinowych, wiązka elektronów

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Artur PAWŁOWSKI[1]

THE ROLE OF ENVIRONMENTAL ENGINEERING IN INTRODUCING SUSTAINABLE DEVELOPMENT

ZADANIA INŻYNIERII ŚRODOWISKA WE WDRAŻANIU ROZWOJU ZRÓWNOWAŻONEGO

Abstract: Sustainable development is perhaps the most important idea of our present time. This concept anticipates major civilisational change on the ecological, social and economic level. In this paper the discussion is extended to ethical, technical, legal and political aspects. The tremendous scope of these changes makes it reasonable to expect this new vision of development to achieve the status of a "Revolution" comparable with those known from the past: the agricultural, scientific and industrial revolutions. To make this happen, we need not only the knowledge given by the social sciences, but also technical means. This is the aim of environmental engineering, which is shaping the human environment. The second part of the article is showing the connection between sustainable development and environmental engineering, especially in the field of energy issues, which must include the shift from fossil fuels to other sources of energy.

Keywords: sustainable development, environmental engineering, energy, globalization

Introduction

The Persian king Xerxes lived at the turn of the 6th and 5th centuries B.C. During an expedition through today's Turkey, near the town of Kallatebus, he paid attention to a beautiful plane-tree. In order to preserve the tree, a special sign was hung on it and a guard was left to see that the tree was not cut down [1]. Perhaps it is the first documented human action for the protection of nature in history.

Probably the earliest formal decree on protection of the environment in wider scale was introduced in China, during the reign of Zhou Dynasty around 1122 B.C. It regarded the necessity to preserve the more valuable tree types, forests and green areas and establishing the office of forester. The decree was repeatedly reintroduced and found its place among general rules of forest economy, which even included the financial support for afforestation of private property [2].

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Unfortunately, it can be noticed that not only protection of nature date back far into the past. We must mention that also the problem of destruction of the environment caused by mankind has long history, and actually refers to as far as human appearance on Earth. Still, the earliest changes were purely local and caused no disturbance in the environment. The primitive nomad usually moved elsewhere in the face of an ecological problem. With territorial expansion, increase in the human population and obtaining new skills - the scale of our impact on the environment grew and the situation became much more complicated.

Underestimating the environmental conditions lead to the downfall of the first literate and highly advanced civilization in history, the Sumerians [3], stabilized as early as 3000 B.C. The area it occupied, between the rivers of Euphrates and Tigris (Lower Mesopotamia), favored agricultural development. The yields were high due to the highly developed irrigating system. A rapid increase in population was observed, along with the increasing demand for food. The increase in yields slowed down however, and depleted systematically, reaching one-third of the maximal yields about 1800 B.C. The signs of crisis were ignored, however, which led to a complete breakdown of the agriculture as well as the entire civilization. Among many causes of the yields' decrease, two deserve a special mention.

- Widespread irrigation favored the increase of soil's salinity (one of the major causes of soil degradation).
- The growing demand for food, along with the increasing population entailed expanding cultivated area. After utilizing all available farming areas, forests were cut out and the land obtained in this way was cultivated. This resulted in increasing erosion - another important form of soil degradation. Moreover, depletion of plant cover and erosion made way to creating large runoffs and the silting of rivers, which caused floods as a consequence.

Modern technical powers of mankind are much bigger however, than those of the Sumerians. Our pressure on the environment has also increased. Not only can mankind cause its own extinction, but the destruction of the entire biosphere.

Not so long ago it seemed that environmental protection will bring rescue. A breakthrough moment of its development was the U'Thant report in 1969. Media publicity, that accompanied the report helped shape the worldwide society's awareness of the environmental threats.

Alas, classic environmental protection was not able to stop biosphere degradation. Therefore, the discussion was broadened in 1987, with the formulation of sustainable development concept, merging various problematic groups, including technology, ecology, economics, but also politics, philosophy or social backgrounds.

Discussion over the Notion of Sustainable Development

Some studies suggest describing this notion of sustainable development as primary and indefinable. In my opinion, such an approach is incorrect, since the concept of sustainable development is already too ambiguous - hence the inclusion of an ordering definitive aspect has become necessary.

Sustainable development idea refers to a highly popular category of “development” as such. It plays a major role in economics, especially in the context of economic growth. Apart from that, many other features are assigned to growth, such as: intensiveness, dynamism, rapidity, speed, and on the other hand extensiveness, slowness or durability, sustainability, suspense [4]. It can also be referred to pan-civilizational changes as well as more specific issues, such as science, culture, language, economy or society.

Generally speaking, “development” may be connected with “progress”, so is a change of state of a given structure (in a civilizational sense, it would be the whole of a society's activities: aware or unaware) that is thought of as desirable (better, more perfect) in the given conditions, based on a set of criteria [5]. Consequently, “regress” is an undesirable (worse, less perfect) change of state of a given structure, based on the same criteria. At the same time, it needs to have a normative character with a very specific axiological aspect. It should include both materialistic as well as spiritual aspects. In both cases it can be assumed that a change for the better is expected. In terms of materialistic values, usually a more complicated state (eg improved machines) will be recognized as progressive. In terms of spiritual aspect, it need not be such - a turn to simplicity may be presented as more desirable (a commonly known slogan: through simplicity toward perfection, the value of asceticism). Moreover, the interactions between the two fields are of significance, i.e. “to have” or “to be”, or maybe “to have and to be”?

Having this in mind, sustainability may be expressed in structural aspect of a given system and means reaching a state of balance between its components, eg the actions taken within separate fields of sustainable development must not lead to degradation of the bio-social system.

Sustainability also means durability, whose main characteristic is measured in time. If a given system has been functioning in the past, is functioning now and nothing indicates it could be damaged - that means it is durable in time. Time is also an important factor when it comes to the devastation caused by humans to the environment. In some cases, they are visible almost immediately, but often - especially when it comes to health issues - they become observable after a long period of the so-called “hibernation”.

Durability also means self-support of the development process, related to the dynamism of life. This includes securing the reserves (energetic among others), that not only would support the present-day status, but also allow taking up new challenges as well as foster creativity, which creates stimulation of further development.

The commonly accepted definition of sustainable development comes from the UN report *Our Common Future* from 1987. This publication was the result of the research of an independent World Commission on Environment and Development, established in 1983. It was an attempt on a holistic approach to the problems of the modern world. It discouraged from the commonly accepted narrow understanding of the term 'progress' (which only included purely economical development) as well as from an equally narrow term “environment”. In the modern world - as pointed out by Donald J. Johnston in the OECD commentary - the environment is not independent from human actions, ambitions nor needs [6]. Modern crisis situations (in their environmental aspect, as well as developmental, agricultural, social or energetic) are also not independent from each other. It is one global crisis related to man's approach towards the environment, which cannot be resolved within jurisdiction of separate countries.

Sustainable development has been defined in *Our Common Future* report as such, “that meets the needs of the present without compromising the ability of future generations to meet their own needs” [7]. Despite a couple of similar proposals and definitions, it was *Our Common Future* report that proved to be a breakthrough. Its major achievement was to accept the concept of sustainable development in science as well as in politics and among the broad circles of global public opinion. The definition (referred to as the principle of sustainable development) gained a normative character and is connected with all development strategies presently formulated [8-10].

Sustainable Development Problematics

Speaking in detail, three problematic fields of sustainable development are distinguished in UN documents and strategies:

- ✓ Ecological (natural and artificial environment protection, also spatial planning).
- ✓ Social (not only natural environment, but also society may degrade).
- ✓ Economic (taxes, subsidies and other economic instruments).

In 2006 in the journal *Problems of Sustainable Development/Problemy Ekorozwoju* [11], I have introduced an enhancement to the list, with a couple of other problematic groups. Discussing the multidimensionality of sustainable development, I have pointed to the following additional aspects:

- ✓ Ethical layer (human responsibility for nature).
- ✓ Technical layer (new technologies, saving raw materials).
- ✓ Legal layer (environmental law).
- ✓ Political layer (formulating strategies of sustainable development, introduction and control thereof).

Then, in 2008 in the journal *Sustainable Development* [12], and later on in the *Problems of Sustainable Development/Problemy Ekorozwoju* [13], I have proposed a hierarchical order of the layers in question (see Table 1).

Table 1

Hierarchy of the layers of sustainable development. Author's own work

Level I		Ethical layer	
Level II	Ecological layer	Social layer	Economic layer
Level III	Technical layer	Legal layer	Political layer

The first level, which is the foundation to others, is an ethical reflection. It is one matter when a person makes decisions based on their beliefs or their system of values, and entirely different, when those decisions are determined only by the regulations of a legal system in force. It is the ethical justification of important questions like: what values must be accepted, or: why should we act in this way and not otherwise - is the foundation of the whole discussion [14-16].

Level two covers ecological, social and economic issues, all treated as equally important.

The third level is an analysis of technical, legal and political issues. It is equally important as level II, however covering more detailed areas of problems.

The traditional discussion over sustainable development concentrates on the second level. It will be incomplete, however, if not rooted in ethics (level one). On the other hand, without level three, actual practical solutions may escape our mind.

It needs to be pointed out that, despite their hierarchical structure, the layers interpenetrate one with another, which makes it hard to discuss problems characteristic exclusively for any one of them. Even in the case of fulfilling mankind's nonmaterial needs, we cannot avoid associations with the environment. This results from the biological principles of the functioning of the human body, which is in constant need for nourishment and therefore interacts with the environment in this sense at least.

The presented hierarchy proposal offers a new view at the problem of sustainable development. Such a wide range of problems proposed, together with an equally vast variety of changes postulated within individual layers as well as within the actual adopted strategies, allows for making the following assertion: should sustainable development be implemented, it would become a revolution comparable to the breakthroughs in mankind's history, also referred to as revolutions.

In this context, is it not - after the agricultural, scientific and industrial revolutions [17] - the time for a sustainable development revolution (see Table 2)? Or are present environmental problems still part of the industrial revolution? Also, it cannot be ruled out that another stage of human development will go in an entirely different, unsustainable direction [18].

Table 2

Key stages in mankind’s development. Author’s own work

Name of the stage	**Time period referred to**
Hunter-gatherer period	Upper Paleolithic
Agricultural Revolution	Began around 9000 years ago in Asia, and approx. 4000 years later in Europe.
Scientific Revolution	1543 - symbolic beginnings with Copernicus' publication of *On the Revolutions of the Celestial Spheres.* 1687 - development period, with I. Newton's publication of *Principia Mathematica*.
Industrial Revolution	1769 - significant improvement to steam engine by Watt. Further stage (1860-1914): the beginning of oil use (in combustion engines) and electricity.
Sustainable Development Revolution	Three crucial dates: 1969 - U’Thant's report. 1987 - sustainable development definition introduced by the UN. 1992 - UN conference in Rio de Janeiro.

The problem is, that the current phase of development has not been clearly defined so far. Industry certainly still plays an important part in the shaping of our civilization, but a number of new phenomena have also appeared. Do these changes mean another revolution? Some authors support this and suggest that we are now dealing with a modernization revolution, understood as a conversion from the agricultural society living in the countryside, to a typically urban and industrial society. This process would not be possible without prior scientific and industrial revolutions. These entailed ie the development of a new kind of modern urban infrastructure (water supply, waste collection, transportation of people and goods, including food, labor market and health service) that ensures the safe functioning of hundreds of thousands of people living in the same place. Does mankind’s transfer from the countryside to cities deserve the title of a revolution? Certainly, the negative human impact on the planet Earth is associated with urban rather than rural environments; therefore their massive expansion increases human pressure on the environment. However, this does not change the present shape of the relations between man and nature.

Also, there are opinions that we are currently dealing with Informatics Technologies Revolution bound up with the widespread use of the Internet, which is thought of as the next step after the industrial revolution. The Internet is indeed an extraordinary platform that allows accessing and spreading important information, which contributes to the development of an information society. On the other hand, this technology seems to run toward a dead end. In 2008, up to 95% of emails received by the users were the so-called spam messages, namely unwanted material containing brazen advertisement (as recently as 2001 this was only 5% of the mail). Moreover, the authors of these messages are impersonating well-known institutions and websites for the purpose of fraud and swindling personal data. Furthermore, the Internet has not changed people's approach towards nature, whereas even with their ever-improving ability to communicate, the people did not reduce their pressure on the environment. Informatics technologies are but a tool, which may be utilized in a more general revolution (analogically, a significant improvement to steam engine by Watt was but a symbol of the Industrial Revolution).

If so, what can bring about a desirable change?

In my opinion, sustainable development can be one such thing. Although development of this type has not been introduced yet, many contemporary political, as well as legal, economic and technological initiatives move in that direction.

Assessment of sustainable development revolution is difficult because of the relatively limited time horizon available. Moreover, there is not much we can say about the future, since different factors may appear at any moment that could change our previous point of view completely. Just as terrorist attacks of September 11th in New York destroyed the illusion of safety in the modern world, we can experience unexpected ecological catastrophes, resulting from environment pollution caused by humans (such as rapid climate changes). We may as well witness new groundbreaking scientific or technical discoveries that could regard new, efficient energy sources as an alternative to decreasing fossil fuel reserves.

Undoubtedly, current human impact on the biosphere has a global character and calls for a global and sustainable immediate response in all areas of human activity. Therefore, intense work is being made on international forums to clarify the basic paradigms of sustainable development, short-, middle- and long-term objectives as well as to search for the tools necessary to achieve the established goals.

Securing sustainable development is among the most important priorities in the EU politics. It can, therefore, be assumed that securing sustainable development is becoming the most important goal contemporary societies set before them.

Environmental Engineering

Introduction of sustainable development is associated with using the knowledge from the fields of both social and technical sciences. Within the second group, a crucial position is occupied by environmental engineering.

Environmental engineering can be defined as [19] a discipline in the field of technical science, utilizing engineering methods:

- ✓ For preserving, rational shaping and using external natural environment (eg water resources, waste management, air protection, soil protection),

- ✓ For preserving and shaping internal environment of rooms and constructions (devices and installations).

Environmental engineering realizes a wide variety of pro-ecologic activities within the described fields:

- Shapes appropriate conditions and technological methods to uphold proper parameters regarding the human environment,
- Shapes appropriate technical conditions and technological methods to secure the environment's natural biological balance,
- Limits adverse effects of mankind's economic activity,
- Provides technology allowing to reduce the usage of nonrenewable resources (eg cleaner production, recycling raw materials from waste),
- Mitigates the effects of natural disasters (floods, droughts, pollution in water, air and soil).

This definition shows how important environmental engineering is for realization of the sustainable development concept. It shapes the conditions of human life; it touches upon the issue of resources, which in turn determines meeting human material needs, both for the present generation and in the future.

Also environmental engineering is connected with new technical approaches to the environment known as:

- ✓ industrial ecology - which aim is to adapt an understanding of the natural system and apply it to the design of the manmade system [20],
- ✓ and green chemistry, known also as green engineering [21] - which is about the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances [22],

Among detailed problems, energy issues must be pointed out: energy supply, preserving energy carriers and, especially, the usage of fossil fuels.

Energy issues

Much has been said in recent years about energy security. Within the EU, situation is very diversified (see Table 3). Denmark is in the best position, since it has a surplus of energy reaching almost 40%.

All countries are grappling with the problem, that producing energy out of conventional fuels means an irrevocable loss of those resources.

Estimates say [24] that the world's reserves contain enough coal for about 150-200 years, enough oil for about 40 years and enough natural gas for about 60 years.

These periods may actually be slightly longer. Data published in various sources vary from one to another, moreover, some authors point at the possibility of exploiting deposits that are uneconomic today, and therefore, prolonging the time of resources availability (eg of crude oil by another 20 years). This does not change the main problem, however: world's resources will run out and the time of that disaster is very near. That is not all - it needs to be remembered that natural gas and oil deposits are distributed unevenly on our planet.

Table 3

The characteristic of energy consumption and import dependence of individual EU countries; data from the end of 2008 [23]

No.	**Country**	**Total energy consumption in millions of tons of fuel**	**[%] of imported energy**
1.	Cyprus	2.6	100
2.	Malta	0.9	100
3.	Luxemburg	4.7	98.9
4.	Ireland	15.5	90.9
5.	Italy	186.1	86.8
6.	Portugal	25.3	83.1
7.	Spain	143.9	81.4
8.	Belgium	60.4	77.9
9.	Austria	34.1	72.9
10.	Greece	31.5	71.9
11.	Latvia	4.6	65.7
12.	Lithuania	8.4	64
13.	Slovakia	18.8	64
14.	Hungary	27.8	62.5
15.	Germany	349	61.3
16.	Finland	37.8	54.6
17.	EU 27	1825.2	53.8
18.	Slovenia	7.3	52.1
19.	France	273.1	51.4
20.	Bulgaria	20.5	46.2
21.	Netherlands	80.5	38
22.	Sweden	50.8	37.4
23.	Estonia	5.4	33.5
24.	Romania	40.9	29.1
25.	Czech Republic	46.2	28
26.	United Kingdom	229.5	21.3
27.	Poland	98.3	19.9
28.	Denmark	20.9	-36.8

Table 4 characterizes the available gas reserves, and Table 5 crude oil deposits.

Table 4

Countries in possession of the world's largest natural gas deposits, data from the end of 2008 [23]

No.	**Country**	**Quantity [trillions of m^3]**	**Graphic presentation**
1.	Russian Federation	43.30	
2.	Iran	29.61	
3.	Qatar	25.46	
4.	Turkmenistan	7.94	
5.	Saudi Arabia	7.57	
6.	USA	6.73	
7.	United Arab Emirates	6.43	
8.	Nigeria	5.22	
9.	Venezuela	4.84	
10.	Algeria	4.50	

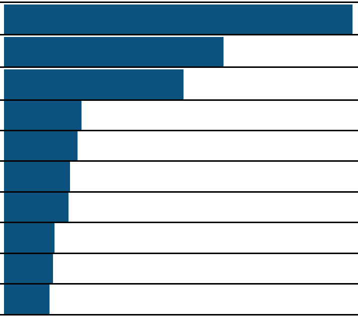
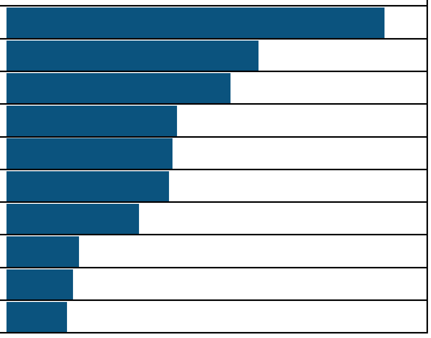


Table 5

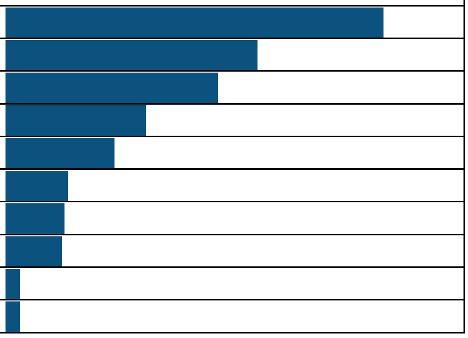
Countries in possession of the world's largest crude oil deposits, data from the end of 2008 [23]

No.	**Country**	**Quantity [billion barrels]**	**Graphic presentation**
1.	Saudi Arabia	264.1	
2.	Iran	137.6	
3.	Iraq	115.0	
4.	Kuwait	101.5	
5.	Venezuela	99.4	
6.	Un. Arab Emirates	97.8	
7.	Russian Federation	79.0	
8.	Libya	43.7	
9.	Kazakhstan	39.8	
10.	Nigeria	36.2	

Unquestionable position of the Russian Federation is noteworthy. Beside it, Iran and Qatar have large gas reserves - although half that size. The Russian Federation also has significant coal reserves (2nd to the US, see Table 6).

Table 6

Countries in possession of the world's largest coal deposits, data from the end of 2008 [23]

No.	**Country**	**Quantity [million tons]**	**Graphic presentation**
1.	USA	238308	
2.	Russian Federation	157010	
3.	China	114500	
4.	Australia	76200	
5.	India	58600	
6.	Ukraine	33873	
7.	Kazakhstan	31300	
8.	South Africa	30408	
9.	Poland	7502	
10.	Brazil	7059	

Another significant issue is that, along with the depletion of natural resources, a demand for energy, required for the processing of the poor resources, rises, eg smelting 1 Mg of iron from a 5% iron ore requires much higher energy input than in the case of a 20% iron ore.

Moreover, the growing consumption of fossil fuels is associated with an increasing emission of dust and gases to the atmosphere. The one gas that has drawn scientists' special attention is carbon dioxide, considered to be the main cause of global warming.

Taking into account that CO_2 concentration in the atmosphere was 0.0280% at the beginning of the industrial era, 0.0315% in 1960 and 0.0385% at present day, is it possible that an increase in carbon dioxide concentration in the atmosphere by 0.0105% had such a long-term impact?

Or do other issues play a more significant role here? Cutting out forests - especially tropical forests - can be pointed out. It is no mystery that during the 20th century alone as much as half of them have been cut out [25] about 12 million ha is being cut out every year and about 50 ha every minute [5]. Since forests are known to serve as climate stabilizers, cutting out such a large part of the world's forests must have a significant impact on Earth's climate destabilization.

In fact, the issues of the diminishing forest cover and the growing carbon dioxide emission are linked to each other. It is estimated that forests - tropical and subtropical forests in particular - can bind around 25% of CO_2 released to the atmosphere! Moreover, with a proper economy the plant-based binding can be increased before 2050 by another 10÷20% [26].

Table 7

Characteristic of the changes in CO_2 emission in the chosen countries in the years 2003-2007. Emissions shown in millions of tons of CO_2 per year [23]

Country	**2003**	**2004**	**2005**	**2006**	**2007**	**Kyoto limit 2012**	**% below the Kyoto limit**
Latvia	10.7	10.7	10.9	11.7	**12.1**	23.3	+48.07
Estonia	21.2	21.2	20.7	19.2	**22.0**	40	+45.00
Lithuania	16.7	21.1	22.6	22.8	**24.7**	44.1	+43.99
Romania	-	60.1	153.7	53.9	**52.3**	259.9	+41.40
Bulgaria	-	68.9	69.8	71.5	**75.7**	127.3	+40.53
Hungary	83.3	79.5	80.5	78.8	**75.9**	114.9	+33.94
Slovakia	51.1	49.5	48.7	49.0	**47.0**	67.2	+30.06
Poland	382.5	96.7	399	99.3	**98.9**	551.7	+27.70
Czech Rep.	147.5	147.1	145.6	49.1	**150.8**	180.6	+16.50
Sweden	70.9	69.7	67	66.9	**65.4**	75.2	+13.03
Un. Kingdom	658	60.4	657.4	647.9	**636.7**	678.3	+6.13
France	560.9	556.1	553.4	541.7	**531.1**	564	+5.83
Greece	137.2	137.6	139.2	128.1	**131.9**	139.6	+5.52
Belgium	147.6	147.6	143.8	36.6	**131.3**	135.9	+3.38
Germany	1024.4	1025	1001.5	980.0	**56.1**	972.9	+1.73
Country	**2003**	**2004**	**2005**	**2006**	**2007**	**Kyoto limit 2012**	**% above the Kyoto limit**
Netherlands	215.4	218.4	212.1	208.5	**207.5**	200.4	–3.54
Portugal	83.7	84.6	85.5	84.7	**81.8**	77.4	–5.68
Ireland	68.4	68.6	69.9	69.7	**69.2**	63	–9.84
Finland	85.4	81.2	69.3	79.9	**78.3**	71.1	–10.13
Slovenia	19.7	19.9	20.3	20.5	**20.7**	18.6	–11.29
Italy	577.3	580.5	582.2	563.0	**552.8**	485.7	–13.82
Denmark	73.6	68.2	63.9	71.0	**66.6**	54.8	–21.53
Austria	92.5	91.2	93.3	91.6	**88.0**	68.7	–28.09
Spain	407.4	425.2	440.6	433.0	**442.3**	331.6	–33.38
Luxemburg	11.3	12.8	12.7	13.3	**12.9**	9.1	– 41.76
Malta	3.1	3.2	3.4	2.9	**3.0**	-	-
Cyprus	9.2	9.9	9.9	9.9	**10.1**	-	-

Admittedly, the question of connecting climate changes to anthropogenic CO_2 emission is being challenged [27, 28], but we should utilize the attitude of humility. The large emission of various pollutants from our scientific-technical civilization to the environment certainly does no good to the nature. Should our concerns over CO_2 turn out to be false, we will bear the costs, but the environment will not deteriorate. And what if our concerns are confirmed? We must remember that drastic climate changes and anomalies may lead to the downfall of our civilization - in this context the example of the Sumerians is a notable warning. Taking remedial action is fully justified.

Table 7 shows CO_2 emission in the years 2003-2007 as well as the degree of individual countries closeness to the limit specified in *The Kyoto Protocol*. The data indicate that 15 of the EU countries (including Poland) have already reached CO_2 emission below the limit set by the Kyoto agreement for the year 2012.

Limiting CO_2 and other pollutants' emissions does not change the primary challenge, namely the depletion of the resources. The principle of sustainable development calls for preserving our planet's ability to meet the needs of future generations, and since their access to energy carriers is threatened that means alternative solutions are required.

The progress of nuclear power is one of the possible ways we may choose. Contrary to the popular belief, uranium deposits are limited as well. If only the most popular reactor types are exploited - that is Pressurized Water Reactors (PWR, 60% of the market) and Boiling Water Reactors (BWR, 24% of the market) - there should be enough fuel for some 140 years. There are, however, alternative technological solutions. Introducing fast-neutron reactors for exploitation would prolong the time of uranium availability for power production by hundreds of years. The problem is, using fast reactors in civilian technology is associated with facilitated access to materials that might be used for the manufacture of nuclear weapon. Also, the risk of meltdowns and nuclear disasters is being disputed. Even with the use of the most advanced technology, accidents cannot be ruled out. In September 1999, there has been a major breakdown at a Japanese nuclear power plant Takamura, which could have ended up in disaster. The cause was disregard for safety procedures - as much as 7 times more enriched uranium was added to the container than the technological standard allowed. A chain reaction broke out, but was luckily suppressed. Still, the radiation level jumped to such value that two employees were killed and several hundred people have been heavily radiated [29]. This incident entailed a series of publications critical towards safety in the supposedly highly advanced Japanese nuclear power plants. Therefore, since erecting new nuclear power plants is probably inevitable, the scientific community must pay special attention to safety issues - there can be no savings here.

Or should we rely on renewable energy sources [30]?

In economic policies of the EU action can be observed, leading to combining sustainable development with a well-balanced energy management, including renewables.

Even now one of these sources - water energy - comprises to as much as 20% of power installed in various power plants around the world (see Figure 1). In Europe's scale Norway and Brazil are among water tycoons.

Still, the largest potential source of energy is the solar radiation. During one year 7500 times more solar energy (86000 TW) hit the Earth than the energy consumed by the whole human civilization. Perhaps that is why the EU conducted research over building a 400-billion-Euro solar power plant on the Sahara, which could cover about 20% of the whole EU's energy demand. This is in accordance to the general policy of the Commonwealth, which postulates that the member countries will gain 20% of their energy from renewables before 2020.

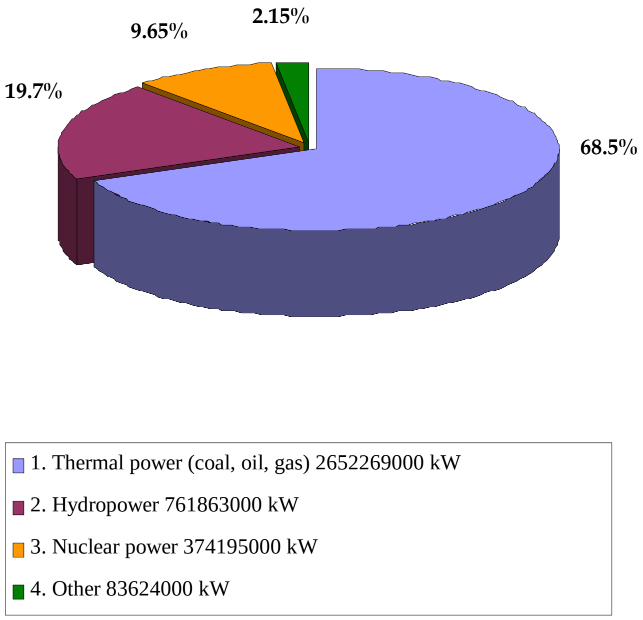


Fig. 1. Total installed electricity capacity by type. Source: International Energy Annual 2006 [31]

Table 8 shows the characteristic of renewable energy coverage of individual member countries of the EU.

Developing technologies related to the usage of various energy sources is an important engineering task. The development of energy-saving technologies is just as significant. This is not only the issue of industrial facilities, but also of internal environment. It is a key problem field in environmental engineering, related to heating, ventilation and air conditionings. Its needs consume 17÷32% of the world's total energy consumption. In the EU countries, it came at 26.5%.

This means that there are huge prospects both for energy saving and decreasing fossil fuel consumption in this sector. It is a crucial challenge for environmental engineering!

Speaking in detail, the main directions of engineers' work for the coming years should include searching energy-saving solutions and new ways to use renewable energy sources also in the communal sector - the usage of biomass to heat rooms in particular.

In some countries, eg in Poland, biomass is already the most popular renewable energy source.

Dry biomass burning for heating purposes in properly fixed ovens (another key design task for environmental engineering) is not the whole thing, however. The ash left over from the process should be used for fertilizing energy plants in plantations (like *Salix*), so that the soils occupied by them would not deteriorate. This is one of the most important directions consistent with the principle of sustainable development, since not only it helps to reduce the consumption of nonrenewable energy sources (replaced with the biomass), but also prevents the soil from exhaustion of elements necessary for cultivation.

Table 8

A percentage characteristic of the renewable energy share in the energy balance in the EU countries [23]

No.	Country	Share of energy from renewables in 2006	2020 objective	Amount missing
	EU	9.25%	20%	10.8%
1.	United Kingdom	1.5 %	15%	13.5%
2.	Ireland	2.9%	16%	13.1%
3.	Denmark	17.2%	30%	12.8%
4.	France	10.5%	23%	12.5%
5.	Netherlands	2.7%	14%	11.3%
6.	Spain	8.7%	20%	11.3%
7.	Greece	7.15%	18%	10.9%
8.	Italy	6.3%	17%	10.7%
9.	Latvia	31.4%	42%	10.6%
10.	Belgium	2.6%	13%	10.4%
11.	Cyprus	2.7%	13%	10.3%
12.	Germany	7.8%	18%	10.2%
13.	Luxemburg	1%	11%	10%
14.	Malta	0%	10%	10%
15.	Portugal	21.5%	31%	9.5%
16.	Slovenia	15.5%	25%	9.5%
17.	Finland	28.9%	38%	9.1%
18.	Austria	25.1%	34%	8.9%
19.	Lithuania	14.6%	23%	8.4%
20.	Estonia	16.6%	25%	8.4%
21.	Hungary	5.1%	13%	7.9%
22.	Sweden	41.3%	49%	7.7%
23.	Poland	7.5%	15%	7.5%
24.	Slovakia	6.8%	14%	7.2%
25.	Bulgaria	8.9%	16%	7.1%
26.	Romania	17%	24%	7%
27.	Czech Republic	6.5%	13%	6.5%

These positive conditions of 'green' energy do not exhaust the topic, however. The point is that the energy gained from renewable energy sources still is more expensive than that derived from fossil fuels. Adopting appropriate legal and economic mechanisms is the key. There is plenty of possible solutions; let’s mention few examples regarding biomass burning. In countries like Finland, wider use of biomass as an energy source was achieved by introducing an appropriate tax on fossil fuels. In Austria a similar effect was reached by subsidies for investments making use of biomass. In the case of Netherlands, three separate fiscal instruments were applied: green funds, an energy tax and tax credits [32]. Also, we may expect that EU limits on CO_2 emissions will favor the development of renewable energy, including biomass burning.

Moreover, it is noteworthy that the development of new technologies regarding renewable energy sources contributes to a growth of employment level. When it comes to biomass, according to Hillring [33], each PJ of energy produced with the use of biomass gives from 1.5 (where wood waste is used) to even 113 jobs (in the case of weakly mechanized, rapidly-growing plantations).

Conclusion

When, at the end of the 19th century, gas lamps used so far were replaced by electric lights, the quality of air in the cities improved immediately. Unfortunately, the progress in coal energetics lead to much greater pollution levels in the second half of the 20th century, growing over the urban environment and becoming a global problem. It is a peculiar paradox. A solution, which brought good results at first, turned out to be a threat in the long run [10, 34].

Research conducted in the field of sustainable development is interdisciplinary, which makes it ideally adapted to coping with the complex challenges of the modern world. There is, however, one phenomenon that escapes control - globalization.

Nowadays globalization is defined as an integrated, global socio-economic system, linked with large corporations, characterized by its transnational diffusion of capital and adopting the principle of free trade in the field of economy - so economic globalization - as well as assimilation of cultural models - so cultural globalization [35].

Large corporations are an obstacle in the implementation of sustainable development, because they are profit-oriented and because of their transnational, post-national or somewhat anti-national character [36], thus weakening the role, played so far by the authorities of individual countries. If the solutions or strategies adopted by a country or a group of countries (even one like the EU) are seen as adverse, they simply move that part of their activities to other countries, where such actions are acceptable. Moreover, as many economists point out, corporations are able to destroy nearly any company that does not belong to them [37, 38].

In this context it is worth asking: is sustainable development an alternative to globalization? Suggestions are formulated, that globalization and sustainable development are both two sides of one coin. Just as Duncan French convinces us, globalization organizes the world anew, whereas sustainable development points to the threats brought by this new order, which result from previous mankind's history [39].

Note that globalization needs not to rely on the currently dominant egoistic axiology - there also is an eco-humanistic (inclusive) globalization - one that refers to the common good. As John Paul II said in 2001 “globalization is not *a priori* good or evil. It will by such, as we make it” (the address at the 7th Plenary Session of the Pontifical Academy of Social Sciences, held in Vatican City on 25th-27th April 2001). This line of thought is carried on by Benedict XVI. In his address in 2008 he said that egoistic globalization “is not the synonym of the world order - on the contrary. The conflicts generated by the pursuit of economic primacy and providing for oneself access to energy, water and resource reserves impede the efforts of those who struggle for a world more just. It became clear that only through adopting a balanced way of life accompanied by serious efforts for equal distribution of goods, a fair and sustainable development is achievable. This requires people who have great hope and great courage” (the address from 1st June 2008, made during Epiphany mass). This line of thought has been expanded in the encyclical *Caritas in Veritate* [40].

Such is the outline of the road towards eco-humanistic globalization, as well as an outline of the road towards sustainable development. It is also the road, which environmental engineers take, providing us with necessary technical tools that would show us how to preserve the environment and use it rationally. It is a challenge, but also a great responsibility in the struggle for our planet's future.

Be it assumed that we are on the threshold of a new revolution - the sustainable development revolution - then our conversion from fossil fuels to new energy sources is one of the most important tasks. Environmental engineering is the one discipline that can achieve this.

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ZADANIA INŻYNIERII ŚRODOWISKA WE WDRAŻANIU ROZWOJU ZRÓWNOWAŻONEGO

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Abstrakt: Rozwój zrównoważony to jedna z najważniejszych idei naszych czasów, która postuluje istotne zmiany cywilizacyjne na poziomach ekologicznym, społecznym i ekonomicznym. W artykule dyskusja ulega poszerzeniu o kwestie etyczne, techniczne, prawne i polityczne. Ogromny zakres tematyczny prowadzonej dyskusji uprawnia do sformułowania postulatu głoszącego, że ta nowa wizja rozwoju może osiągnąć status „rewolucji” porównywalnej ze znanymi z dziejów ludzkości rewolucjami rolniczą, naukową i przemysłową. Aby tak się stało, potrzebujemy nie tylko wiedzy z zakresu nauk społecznych, ale także technicznych. Taki jest także cel inżynierii środowiska, odnoszącej się do kształtowania środowiska, w którym bytuje człowiek. Druga część artykułu ukazuje powiązania pomiędzy rozwojem zrównoważonym a inżynierią środowiska. Szczególną uwagę poświęcono kwestiom energetycznym, odnoszącym się do konieczności poszukiwania alternatywnych źródeł energii, dzięki którym zmaleje presja na pozyskiwanie wyczerpywanych kopalnych nośników energii.

Słowa kluczowe: rozwój zrównoważony, inżynieria środowiska, energia, globalizacja

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RESPONSE OF *Hypericum perforatum* PLANTS TO SUPPLY OF CADMIUM COMPOUNDS CONTAINING DIFFERENT FORMS OF SELENIUM

WPŁYW RÓŻNYCH FORM SELENU NA AKUMULACJĘ ZWIĄZKÓW KADMU PRZEZ ROŚLINY *Hypericum perforatum*

Abstract: The effect of cadmium compounds containing selenium in different oxidation states such as Se(IV), Se(VI), and Se(–II) on production characteristics, shoot water content and chlorophyll content in the leaves as well as Cd and Se accumulation in plant organs of *Hypericum perforatum* plants was investigated. Complexes with nicotinamide (nia) of the type $Cd(NCX)_2(nia)_2$ where X = Se or S as well as $CdSO_4$ were used to compare the effect of Se and S on the above-mentioned parameters. The studied compounds applied at concentrations 12, 24 and 60 $\mu mol \cdot dm^{-3}$ reduced dry mass of plant organs. In general, water content of shoots as well as chlorophyll content in the leaves decreased with increasing the compound concentrations. Se speciation significantly affected accumulated amount of Cd and Se [$mg \cdot g^{-1}$ d.m.] in plant organs of *H. perforatum* plans what was reflected in the values of bioaccumulation factors (BAF), translocation factors (TF) as well as portion from the total metal amount accumulated by the plant occurring in the shoots. The comparison of the effect of $CdSO_4$ and $CdSeO_4$ as well as $Cd(NCS)_2(nia)_2$ and $Cd(NCSe)_2(nia)$ showed that exchange of S for Se in the NCX^- ligand led to decreased translocation of Cd into the shoots. The application of $CdSeO_4$ resulted in intensive translocation of Cd as well as Se into the shoots. Portion of Cd allocated in shoots related to the total Cd amount accumulated by the plant was about 20% for treatment with $CdSO_4$ and $Cd(NCS)_2(nia)_2$, about 12.8, 10 and 6% for treatment with $Cd(NCSe)_2(nia)_2$, $CdSeO_4$ and $CdSeO_3$. On the other hand, portion of Se allocated in shoots related to the total Se amount accumulated by *H. perforatum* plants achieved approx. 86, 48.6 and 45.9% after addition of $CdSeO_4$, $Cd(NCSe)_2(nia)_2$ and $CdSeO_3$.

Keywords: bioaccumulation, cadmium, chlorophyll, selenate(VI), selenate(IV), St. John's wort, water content

Introduction

Hypericum perforatum L. is a plant which has been traditionally used for many ethnopharmacological purposes, including treatment of mental disorders. Preclinical studies on the central nervous system activities of the plant extracts have exhibited that the extracts showed antidepressant, anxiolytic, sedative, nootropic, antischizophrenic, anticonvulsant

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and analgesic activities. Several clinical data have confirmed the extracts or commercial preparations as effective as some standard antidepressants used for mild or moderate depression [1].

Metals have been investigated in different medicinal plant materials in order to establish their normal concentration range and consider their role in plants as part of human medicinal treatment. Metal monitoring as a pattern recognition method is a promising tool in the characterization and/or standardization of phytomedicines [2]. Since common St. John's wort (*Hypericum perforatum*) is particularly responsive to changes in climate, it could serve as indicator of biological responses to climate change [3].

Metal treatment can significantly change the chemical composition of secondary metabolites in *H. perforatum* plants and thereby seriously influence the quality, safety and efficacy of natural plant products produced by medicinal species. A treatment with 0.01 mmol $\cdot$ dm^{-3} Cr(VI) for seven days resulted in an increased production of protopseudohypericin (+ 135%), hypericin (+38%) and pseudohypericin (+ 5%). Treatment with 0.1 mmol $\cdot$ dm^{-3} Cr(VI) for two days also caused an increase of protopseudohypericin (+ 167%), hypericin (25%) and pseudohypericin (+5%) whereas after 7 d treatment massive increase of protopseudohypericin (+404%) and pseudohypericin (+379%) was observed but hypericin content was not be changed [4]. Murch et al [5] observed that *H. perforatum* seedlings grown in a sterile, controlled environment supplemented with 25 or 50 mmol $\cdot$ dm^{-3} nickel lost completely the capacity to produce or accumulate hyperforin and demonstrated a 15-20-fold decrease in the concentration of pseudohypericin and hypericin.

Masarovicova et al [6] found that stress-induced higher root respiration rate of the Cd-treated *H. perforatum* plants correlated with root growth inhibition accompanied with the lower value of root dry mass. Relatively high Cd uptake into the root required increased energy costs coming from root respiration. Previously it was confirmed that cadmium accumulation in plant organs of medicinal plant *Matricaria recutita* L. could be strongly affected by the presence of Se in different oxidation states [7, 8].

This paper is aimed to investigate the study of the effect of cadmium compounds containing Se in different oxidation states such as Se(IV), Se(VI), and Se(–II) on production characteristics, shoot water content and chlorophyll content in leaves as well as Cd and Se accumulation in plant organs of *Hypericum perforatum* plants. Complexes with nicotinamide (nia) of the type $Cd(NCX)_2(nia)_2$ where X = Se or S as well as $CdSO_4$ were used to compare the effect of Se and S on the above-mentioned parameters.

Material and methods

For experiments the following cadmium compounds were used: $(CdSO_4)_3(H_2O)_8$, $CdSeO_4$, $CdSeO_3$, $Cd(NCSe)_2(nia)_2$ and $Cd(NCS)_2(nia)_2$. $(CdSO_4)_3(H_2O)_8$ of analytical purity was purchased from Lachema (Brno, Czech Republic), the further compounds were prepared according to procedures described by Kralova et al [8, 9].

For cultivation of experimental plants seeds of *Hypericum perforatum* L. (Research Institute of Agroecology in Michalovce, Slovakia) were used. Six weeks old plants were cultivated in hydroponic solution at controlled conditions (photoperiod 16 h light/8 h dark; irradiation: 80 μmol $\cdot$ m^{-2} $\cdot$ s^{-1} PAR; mean air temperature: 28°C): control variant in Hoagland solution and metal variants containing studied compounds (12, 24 and 60 μmol $\cdot$ dm^{-3}, respectively) and the response of plants to metal treatment was evaluated 7 d after Cd application. Then dry mass of roots and shoots as well as shoot water content and chlorophyll concentration in the leaves were determined. Fresh and dry shoot mass (dried at 80°C to constant dry mass) was estimated in order to determine the shoot water content [100 - (dry mass x100/fresh mass)]. Chlorophyll concentration was estimated spectrophotometrically (Genesys 6, Thermo Scientific, U.S.A) after extraction into 80% acetone and calculated according to Lichtenthaler [10]. The results were evaluated by the multifactorial ANOVA algorithm ($p \leq 0.05$) after verification of normality and homogeneity of the variance. The multiple comparisons of means were based on the method of Tukey contrast.

Cadmium and selenium concentrations in shoot dry mass were determined using the flame atomic absorption spectrometry (AAS) (Perkin Elmer 110, USA). Cadmium concentration was determined according to method described by Kralova et al [8]. Selenium concentrations were determined using hydride generation AAS. Prereduction of Se(VI) to Se(IV) was achieved by heating of 5 cm^3 aliquot of the digest in 6 $mol \cdot dm^{-3}$ HCl for 15 min at 90°C. Hydride generation was performed from the media of 6 $mol \cdot dm^{-3}$ HCl using solution of 10 $g \cdot dm^{-3}$ $NaBH_4$ in 10 $g \cdot dm^{-3}$ NaOH as the reductant.

Results and discussion

Production characteristics of *H. perforatum* plants treated with the studied compounds are presented in Table 1. The phytotoxicity of the highest concentration of studied compounds (60 $\mu mol \cdot dm^{-3}$) was manifested by desiccated leaves and leaf fall what was reflected in reduced shoot dry mass. The leaves of these experimental plants were yellow or brownish.

Table 1

Root and shoot length and dry mass of *Hypericum perforatum plants* treated with the studied compounds. Mean ± S.E., n = 6. Data followed by different letters are significantly different at the 0.05 probability level.
I - $CdSO_4$, *II* - $CdSeO_4$, *III* - $CdSeO_3$, *IV* - $Cd(NCS)_2(nia)_2$, *V* - $Cd(NCSe)_2(nia)_2$

Compound	Concn. [$\mu mol\ dm^{-3}$]	Root length [cm]	Shoot length [cm]	Root d.m. [mg]	Shoot d.m. [mg]
Control	0	18.7 ± 1.7^{ab}	19.7 ± 1.1^{abc}	65.3 ± 8.7^{a}	245.4 ± 52.7^{bcde}
I	12	17.5 ± 1.7^{ab}	22.0 ± 1.0^{abcd}	70.6 ± 13.5^{a}	259.5 ± 45.2^{cde}
	24	17.7 ± 0.9^{ab}	22.9 ± 1.6^{cd}	70.1 ± 8.9^{a}	218.3 ± 14.3^{bcde}
	60	19.7 ± 1.4^{ab}	21.2 ± 1.7^{abcd}	47.4 ± 3.0^{a}	158.5 ± 22.0^{abc}
II	12	17.2 ± 1.4^{a}	18.5 ± 2.1^{ab}	74.7 ± 11.0^{a}	234.4 ± 47.6^{bcde}
	24	19.1 ± 1.8^{ab}	21.8 ± 1.8^{abcd}	72.5 ± 14.7^{a}	174.8 ± 33.3^{abcd}
	60	19.2 ± 2.5^{ab}	17.9 ± 1.7^{abcd}	50.9 ± 6.2^{a}	100.7 ± 16.2^{a}
III	12	18.1 ± 0.8^{ab}	24.9 ± 1.4^{d}	79.2 ± 18.3^{a}	293.6 ± 49.5^{e}
	24	18.5 ± 1.5^{ab}	22.3 ± 2.0^{abcd}	72.1 ± 14.9^{a}	272.8 ± 59.8^{de}
	60	18.9 ± 2.0^{ab}	19.4 ± 1.3^{abc}	61.3 ± 11.9^{a}	187.4 ± 24.9^{abcde}
IV	12	21.8 ± 1.3^{b}	22.5 ± 1.1^{bcd}	77.9 ± 16.7^{a}	284.1 ± 41.1^{e}
	24	16.7 ± 1.0^{ab}	20.0 ± 1.1^{abc}	57.4 ± 9.9^{a}	228.9 ± 20.3^{bcde}
	60	19.2 ± 1.5^{ab}	20.6 ± 1.4^{abcd}	55.6 ± 6.9^{a}	234.4 ± 18.1^{bcde}
V	12	19.6 ± 2.2^{ab}	19.6 ± 2.1^{abc}	54.1 ± 6.0^{a}	199.3 ± 41.1^{abcde}
	24	17.1 ± 1.6^{a}	22.0 ± 1.2^{abcd}	52.8 ± 7.9^{a}	163.2 ± 20.3^{abc}
	60	18.5 ± 1.8^{ab}	21.6 ± 1.5^{abcd}	67.0 ± 17.0^{a}	150.3 ± 18.1^{ab}

Figure 1 presents results concerning dependence of total chlorophyll (Ch) content of leaves on the applied compound concentrations. Reduction of Chl content by $CdSO_4$ and $Cd(NCS)_2(nia)_2$ (compounds without Se) application was found to be lower than the effect of selenium containing compounds. The most toxic compound was found $Cd(NCSe)_2(nia)_2$. Cadmium was reported to affect chlorophyll biosynthesis and inhibit protochlorophyll reductase and aminolevulinic acid (ALA) synthesis [11]. According to Padmaja et al [12] the inhibitory effect of Se on Chl synthesis is not only by acting on constituent biosynthetic enzymes but also through lipoxygenase-mediated lipid peroxide levels and inhibition of antioxidant defence component. Moreover, cadmium also affects degradation of assimilation pigments [13]. Reduction of chlorophyll concentration in lettuce (*Lactuca sativa*) treated with H_2SeO_4 was observed by Xue et al [14] and also adult coffee plants leaves infiltrated with selenate(IV) showed significant decrease of photosynthetic pigments (chlorophylls, carotenoids and xanthophylls) [15]. Reduction of chlorophyll concentration after application of studied compounds was also confirmed previously in *M. recutita* plants [7].

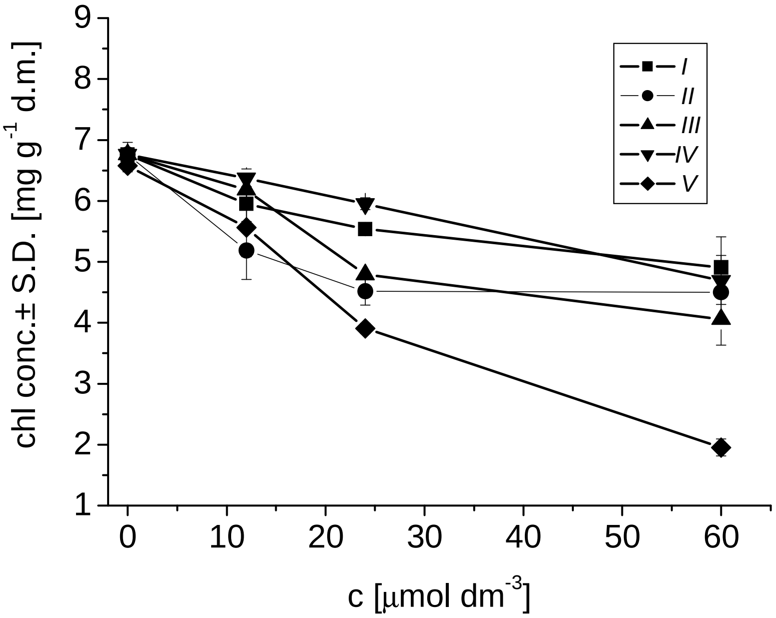

Fig. 1. Dependence of chlorophyll concentration in leaves of *H. perforatum* plants treated with the studied compounds. I - $CdSO_4$, II - $CdSeO_4$, III - $CdSeO_3$, IV - $Cd(NCS)_2(nia)_2$, V - $Cd(NCSe)_2(nia)_2$

Stronger loss of water (water stress induction) in shoots of *H. perforatum* plants was observed only for treatment with 60 μmol · dm^{-3} $Cd(NCSe)_2(nia)_2$, $CdSeO_4$ and $CdSO_4$ (Fig. 2). Toxic metals such as cadmium affect plasma membrane permeability what results in reduction of water content [16, 17].

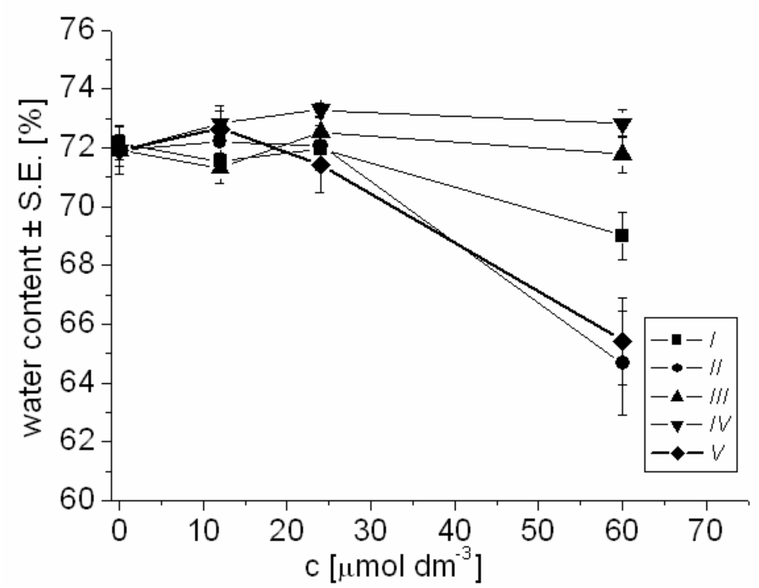

Fig. 2. Dependence of water content in shoots of *H. perforatum* plants treated with the studied

Cadmium and selenium concentration in roots and shoots *Hypericum perforatum* plants treated with the studied compounds and corresponding values of bioaccumulation (BAF) and translocations factors (TF) are summarized in Table 2. Bioaccumulation factors (BAF) express the ratio of the metal concentration in the biological material [μmol or μg · g^{-1} dry mass] to the metal concentration in external solution in [μmol or μg · dm^{-3}]. This parameter is important from the aspect that for phytotherapeutical use the aboveground parts of chamomile plants are of the interest.

The higher BAF values estimated for shoots reflect more effective mobility of the corresponding elements (Cd or Se) in the plants. The translocation factor TF corresponds to the ratio of accumulated Cd (or Se) amount in shoots and roots and thus it depends also on the actual dry mass of these plant organs (similarly as the portion from the total accumulated metal amount by the plant occurring in the shoots).

The dependence of accumulated Cd concentration in roots on the applied concentration of $CdSeO_4$, $CdSO_4$ and $Cd(NCS)_2(nia)_2$ showed linear increase, whereas for the treatment with $CdSO_4$ and $Cd(NCSe)_2(nia)_2$ at 60 μmol · dm^{-3} consecutive saturation of the roots with Cd was observed. The concentration of Se in roots and shoots of experimental plants increased linearly with the applied compound concentration. However, due to the treatment with the highest $Cd(NCSe)_2(nia)_2$ concentration saturation of the roots with Se was observed. The highest accumulated Cd concentration in both plant organs was obtained with $CdSO_4$ treatment. Substitution of sulphur with Se led to strong decrease of Cd concentration, mainly in shoots, indicating Cd-Se interference. It is necessary to stress that selenium and sulphur in plants share common metabolic pathways and these elements compete in biochemical processes affecting uptake, translocation, and assimilation pathways in plants [18].

Table 2

Cadmium and selenium concentration in roots and shoots of *Hypericum perforatum* plants treated with the studied compounds. *I* - $CdSO_4$, *II* - $CdSeO_4$, *III* - $CdSeO_3$, *IV* - $Cd(NCS)_2(nia)_2$, *V* - $Cd(NCSe)_2(nia)_2$ and corresponding values of bioaccumulation (BAF) and translocations factors (TF)

Comp.	c [µmol dm^{-3}]	Cd (Se) concn. [mg kg^{-1} d.m.] **BAF**				TF **% Cd (Se) in shoot**	
		Root		Shoot			
		Cd	Se	Cd	Se	Cd	Se
Control	0	31.8	7.0	2.5	4.6	-	-
I	12	2197 **1628.6**	-	126.5 **93.8**	-	0.212 **17.5**	-
	24	3811 **1412.5**	-	270.7 **100.3**	-	0.221 **18.1**	-
	60	6081 **901.6**	-	531.0 **78.7**	-	0.292 **22.6**	-
II	12	595 **441**	28.2 **29.8**	23.0 **17.1**	78.3 **82.6**	0.121 **10.8**	8.713 **89.7**
	24	1021 **378.4**	63.9 **33.7**	47.1 **17.5**	149.6 **78.9**	0.111 **10.0**	5.645 **85.0**
	60	2578 **382.2**	140.3 **29.6**	135.9 **20.2**	370.2 **78.1**	0.104 **9.4**	5.220 **83.9**
III	12	251 **185.7**	99.5 **105.0**	4.72 **3.5**	18.2 **19.2**	0.070 **6.5**	0.678 **40.4**
	24	491 **182.1**	178.2 **94.4**	7.5 **2.8**	37.8 **19.9**	0.058 **5.4**	0.803 **44.5**
	60	1337 **198.2**	319.0 **67.3**	27.8 **4.1**	116.8 **24.7**	0.064 **6.0**	1.119 **52.8**
IV	12	571 **423.3**	-	25.7 **19.1**	-	0.164 **14.1**	-
	24	997 **369.5**	-	65.1 **24.1**	-	0.260 **20.7**	-
	60	2010 **298.0**	-	172.8 **25.6**	-	0.362 **26.6**	-
V	12	723 **536.0**	192.4 **101.5**	31.1 **23.1**	109.6 **57.8**	0.158 **13.7**	0.558 **35.8**
	24	1263 **468.1**	262.9 **69.4**	62.8 **23.3**	212 **55.9**	0.154 **13.3**	0.519 **34.2**
	60	2400 **355.8**	329.3 **34.6**	138.5 **20.5**	398.2 **42.0**	0.129 **11.5**	0.372 **27.1**

Chizzola and Lukas [19] collected *Hypericum perforatum* plants and soil samples from many regions in Eastern Austria to study the variability in the Cd content. The higher Cd levels often with bioaccumulation factor > 1 were determined in plants growing in regions with somewhat lower soil pH and carbonate content than in other regions. High Cd concentrations have been found in the *H. perforatum* shoots in mining valley in NW Madrid (Spain) where soils affected by mining activities presented total Cd, Cu and Zn concentrations above toxic thresholds [20]. Germ et al [21] applied foliar spraying with selenium (10 mg · dm^{-3} Se in the form of sodium selenate(VI)) to *H. perforatum* plants. The concentration of Se in the organs of plants foliarly sprayed with Se ranged from 1000 ng · g^{-1} to 12 000 ng · g^{-1} whereas Se concentration in unsprayed plants was achieved only 20 ng · g^{-1} - 120 ng · g^{-1} what indicate that foliar application of Se fertiliser is feasible and effective in St. John's wort and results in Se-enriched nutritional supplements.

It is evident that accumulation of Cd in plant organs was strongly affected by Se oxidation state (Table 2). After selenate(VI) treatment Cd root concentration drops to a half in comparison with that obtained in the presence of selenate(VI), however this decrease was even significantly higher for Cd shoot concentration (approx by 80%). Cd root concentration after $Cd(NCSe)_2(nia)_2$ treatment was lower than that obtained after selenate(VI) addition (nevertheless higher than after selenate(IV) treatment) but shoot Cd concentration slightly exceeded that determined for selenate(VI) addition (Table 2). Substitution of Se with sulphur in $Cd(NCX)_2(nia)_2$ increased root Cd concentration approx by 24%, shoot Cd concentration was comparable (consequently, similar increase of Cd shoot concentration as in case of $CdSO_4$ in comparison to $CdSeO_4$ was not observed). With regards to application of individual studied compounds root Se content decreased in the following order: $CdSeO_3$ > $Cd(NCSe)_2(nia)_2$ > $CdSeO_4$, whereas for shoot Se concentration this sequence was opposite: $CdSeO_4$ > $Cd(NCSe)_2(nia)_2$ > $CdSeO_3$. This is in accordance with previous findings confirming higher mobility of selenate(VI) in the plants [7, 22]. However, the presence of selenium reduces the availability of metal ions (such as cadmium), blocking them in insoluble compounds. According to Shanker et al [22] the less mobile selenate(IV) after being reduced to selenide tends to form Cd–Se complex, which appears to be unavailable for the plants. On the other hand, the more mobile anion selenate(VI) is available for Cd–Se formation only after following a more complicated redox processes involving Se(VI) in SeO_4^{2-}, Se(IV) in SeO_3^{2-}, and Se(0) species.

In general it can be concluded that root to shoot translocation of Cd in *H. perforatum* plants was relatively low. Portion of Cd allocated in shoots related to the total Cd amount accumulated by the plant was about 20% for treatment with $CdSO_4$ and $Cd(NCS)_2(nia)_2$, about 12.8%, 10% and 6% for treatment with $Cd(NCSe)_2(nia)_2$, $CdSeO_4$ and $CdSeO_3$. On the other hand, portion of Se allocated in shoots related to the total Se amount accumulated by *H. perforatum* plants achieved approx 86%, 48.6% and 45.9% after addition of $CdSeO_4$, $Cd(NCSe)_2(nia)_2$ and $CdSeO_3$. For comparison portion of Cd allocated in shoots was 53.9% ($CdSeO_4$), 33.2% ($CdSeO_3$), 23.4% ($Cd(NCSe)_2(nia)_2$) and 42.5% ($Cd(NCS)_2(nia)_2$) for *Matricaria recutita*, cv. Goral [7], 61.8% ($CdSeO_4$), 42.9% ($CdSeO_3$), 36.2% ($Cd(NCSe)_2(nia)_2$) and 53.9% ($Cd(NCS)_2(nia)_2$) for *Brassica juncea* [23] as well as 38% ($CdSeO_4$) and 18% ($CdSeO_3$ and $Cd(NCSe)_2(nia)_2$) for *Pisum sativ*um plants [24]; portion of Se allocated in shoots reached 91.5% ($CdSeO_4$), 25.8% ($CdSeO_3$), 27.8% ($Cd(NCSe)_2(nia)_2$) for *M. recutita* [7], cv. Goral, 90.3% ($CdSeO_4$), 26.4% ($CdSeO_3$), 51.5% ($Cd(NCSe)_2(nia)_2$) for *B. juncea* [23] as well as 89% ($CdSeO_4$) and 18% ($CdSeO_3$ and $Cd(NCSe)_2(nia)_2$) for *Pisum sativum* plants [24].

The differences in the toxicity of both studied complexes could be also connected with diverse values of the corresponding stability constants related to NCS^- and $NCSe^-$ ligands. The overall stability constant (β_2) of the complex compound $Cd(NCS)_2$ is 602.56 ($\beta_2 = 10^{2.78}$), whereas β_2 estimated for $Cd(NCSe)_2$ is only 199.53 ($\beta_2 = 10^{2.3}$) indicating three times lower stability of the compound comprising $NCSe^-$ ligands [25]. Due to the release of NCS^- or $NCSe^-$ anions from the complex, not only cadmium but also these toxic anions could interact with suitable target groups of biomolecules.

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WPŁYW RÓŻNYCH FORM SELENU NA AKUMULACJĘ ZWIĄZKÓW KADMU PRZEZ ROŚLINY *Hypericum perforatum*

Abstrakt: Badano wpływ związków kadmu zawierających selen na różnym stopniu utlenienia m.in. Se(IV), Se(VI) i Se(-II) na charakterystyki produkcji, zawartość wody w pędach i zawartość chlorofilu w liściach, a także akumulację Cd i Se w organach roślin *Hypericum perforatum*. Do porównania wpływu Se i S na wyżej wymienione parametry wykorzystano kompleksy amidu kwasu nikotynowego (nia) $Cd(NCX)_2(nia)_2$, gdzie X = S lub Se, a także $CdSO_4$. Zastosowanie badanych związków o stężeniach 12, 24 i 60 μmol · dm^{-3} zmniejszało suchą masą organów roślin. Zazwyczaj zarówno zawartości wody w pędach, jak i zawartości chlorofilu w liściach malała wraz ze wzrostem stężenia związku. Specjacja Se miała znaczny wpływ na stężenie zaakumulowanych Cd i Se [mg · g^{-1} s.m.] w organach roślin *H. perforatum,* co znalazło swoje odzwierciedlenie w wartościach współczynników bioakumulacji (BAF), współczynników transferu (TF), a także w stężeniach zaakumulowanych przez roślinę metali. Porównanie wpływu $CdSO_4$ i $CdSeO_4$ oraz $Cd(NCS)_2(nia)_2$ i $Cd(NCSe)_2(nia)$ wykazało, że wymiana S na Se w ligandzie NCX^- prowadziła do zmniejszenia przenoszenia Cd do pędów. Zastosowanie $CdSeO_4$ spowodowało intensywne przenoszenie Cd oraz Se do pędów. Stężenie Cd w pędach w odniesieniu do całkowitego stężenia Cd zaakumulowanego w roślinie wynosiło ok. 20% w przypadku stosowania $CdSO_4$ i $Cd(NCS)_2(nia)_2$ oraz około 12,8, 10 i 6% w przypadku stosowania $Cd(NCSe)_2(nia)_2$, $CdSeO_4$ i $CdSeO_3$. Z drugiej strony, po dodaniu $CdSeO_4$, $Cd(NCSe)_2(nia)_2$ i $CdSeO_3$ stosunek stężeń Se w pędach do całkowitego stężenia Se zaakumulowanego przez rośliny *H. perforatum* osiągnął ok. 86, 48,6 i 45,9%.

Słowa kluczowe: bioakumulacja, kadm, chlorofil, selenian(IV), selenian(VI), ziele dziurawca, zawartość wody

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ANALYSIS OF LESS BIOACTIVE ELEMENTS IN GREEN PLANTS, FOOD AND FEED SAMPLES (Sc-Y-La-Ce-Rb-Cs-Ti)

ANALIZA PIERWIASTKÓW O NISKIEJ AKTYWNOŚCI BIOLOGICZNEJ W ROŚLINACH ZIELONYCH, PRÓBKACH ŻYWNOŚCI I PASZ (Sc-Y-La-Ce-Rb-Cs-Ti)

Abstract: Standard digestion and multielement methods were tested for routine application to analyze selected elements of low bioactivity (Sc, Y, La, Ce, Rb, Cs and Ti) in food and plant samples by ICP-OES and ICP-MS methods. For ICP-OES, medium power input resulted in better detection limits than high power. Sc and Ti seemed more reliable from the ICP-OES, but it was not sensitive enough to detect Y, La, Ce and Cs in a biomatrix at ambient levels. Small Rb concentrations were occasionally swallowed by a U-shaped background. The ICP-MS as the more sensitive method was preferable for the analysis of Y, La, Ce, Rb and Cs, using In-115 as an internal standard. Digests of green plants, feed and cheese samples were tested for recoveries of 2 µg and 4 µg each. The classical HNO_3-$HClO_4$ digestion in glass cannot be recommended for these elements. Quantitative recoveries of Y, La, Sc, Ce and Ti were obtained from microwave assisted digestions with HNO_3-HF in pressure bombs; whereas green plants needed some hydrofluoric acid, this was not the case for the cheese samples. Storing the fluoride containing digests in glass yielded significant blanks. The microwave assisted digest with $KClO_3$-HNO_3 yielded good recoveries of all these elements from green plants and cheese, but suffered from Rb-blanks. Recently obtained data for green plants, cheese and chocolates are given, and compared with older unpublished data from Austrian coals.

Keywords: rare earth elements, green plants, cheese, chocolates, digests

Introduction

The levels of many elements in the living organisms are governed by metabolic processes, like active transport or excretion. Pattern recognition of metabolically governed element levels of known food might reveal deficiencies or contaminations till respective diseases. For elements of low biological significance, however, there is no need for active transport, and their transfer into the food web should reflect the overall availability from the feed without further enrichment or excretion steps. Their pattern should match the geochemical availability from where feed and potable water are taken, indicating a certain

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assignment to the geographical origin of the sample. Their occurrence in coals is usually at or below mean crust levels [1], thus no enrichment into the biosphere has taken place.

Elemental analysis of green plants, food and feed samples is mainly aimed to investigate nutritional quality or contamination. With respect to the origin of these samples, there is much belief in the labels; thus a database should be created to get a scientific background of this problem. In order to test the hypothesis of a connection between geographical origin and fingerprint elements on a large scale, methods to obtain larger datasets by multielement methods, are needed.

Trace element patterns, in particular rare earths, have been used to assign the origin of wines to certain soils and locations [2-4], and of fruits also [5].

In cow milk, geogenic elements (Al-Au-Ce-Co-Dy-Er-Eu-Gd-La-Lu-Nd-Pr-Sm-Sr-Tb-Th-Y) were considerably higher when fresh grass or clover grass was major part of the diet, than soybased feeding. During a sampling period of about one year, the concentrations of most elements varied significantly according to the week of sampling. Approximately one third of the trace elements showed a considerably increased concentration in the milk in the early summer period [6]. Cow milk from Eastern and Upper Styria purchased in a local supermarket contained more Rb, Cs, Mo, but less Cu, Mn, Zn, La, Tl per litre than soybased baby formulas, which were prepared as 13÷15% suspensions in local tap water [7]. Trace element pattern of Li-K-Rb-Cs-Mn-Se contents could discriminate the region of origin in Italian cheese [8].

Thus, pattern recognition of elemental data might result in a profound assignment of the geographical origin of fruits (wine) and vegetables, the origin of milk and dairy products in a global market, and possibly, if vegetables were grown in soil or in hydroponic cultures; the latter do not get rare earth elements or the like. Milk and dairy products from cows fed on local grass (organically grown, or “bio”-products) might be an argument for higher price levels than products from cows fed on soy from eg Brazil.

Elements of low bioactivity suffer from a low number of available data in the food web, as well as from the lack of certified reference materials. Therefore, this work is primarily aimed to test the suitability of our routinely done digestion and determination methods for the analysis of green plant, food and feed samples, in addition to other routine work. Scandium, yttrium, lanthanum and cerium were chosen as examples for all rare earth and related elements. Rubidium and cesium, as well as the potassium/rubidium relationship, are well known in geochemistry, but data from the biosphere are scarce. Mean crust levels of titanium are rather high, but data from the biosphere are very scattering, possibly because of digestion problems (see below).

These effects may be counteracted by the introduction of rare earth elements to our soils via mineral phosphates. Superphosphate from the Kola peninsula contained 0.26% of total rare earth elements within the final product, which means that at an annual fertilization rate of 300 kg P/ha, significant amounts of rare earths get introduced into the ecosystem [9].

In China, mixtures of rare earth nitrates or citrates in the range of 200÷600 mg/kg have been used to increase weight, egg or milk production [10]. Currently, such experiments have been started with pigs in Vienna also, at a level of 15 and 30 mg/kg of La and Ce.

Within our laboratory, among low bioactive elements, screening by ICP-multielement spectroscopy includes also Li, Sr and Ba, and the results have been confirmed by ring test utilizing the IPE (*International Plant Exchange*) samples of Wageningen University (the Netherlands). Current series of cheese, chocolates, as well as green plant reference samples (from International Plant Exchange, Wageningen, NL) were analyzed for Sc-Y-La-Ce-Rb-Cs-Ti, in addition to the selection of other trace elements routinely done, to get some idea about reproducibility, blanks, and if detection limits are sufficient.

Material and methods

Equipment

Microwave digestion unit: mls 1200 mega high performance microwave digestion unit, MLS GmbH, D-88299 Leutkirch.

ICP-OES: Perkin Elmer Optima 3000XL with axial plasma.

ICP-MS: Perkin Elmer Sciex ICP mass spectrometer ELAN DRC II.

Digestions

In general, 2 blanks were run with each batch.

a) Digestion with nitric(V)/chloric(VII) acid: 1 g of dried green plant, feed, or manure sample was weighed into a 50 cm^3 glass Erlenmeyer flask, 15 cm^3 nitric(V) acid and 4 cm^3 chloric(VII) acid were added, and the sample was gradually fumed at a heating block to almost dryness. 25 cm^3 water was added, the sample was filtered into a capped plastic vessel.

b) Microwave assisted digestion with nitric(V) acid: 0.3 g of dried green plant, feed, or manure sample was weighed into a PTFE vessel, 3.5 cm^3 nitric(V) acid + variable amounts of hydrofluoric acids were added, the vessel was closed and heated by microwaves. The digest was made up to 25 cm^3 in a plastic volumetric flask (one experiment was done using 20 cm^3 glass flasks). The subsequent program time/power program was run: 2 min 250 W/1 min 0/8 min 250 W/1 min 0/6 min 450 W/ 4 min 600 W/1 min 500 W.

c) Microwave assisted digestion with nitric(V) acid: 0.6 g of cheese was weighed into a PTFE vessel, 5 cm^3 nitric acid + 1.5 cm^3 H_2O_2 were added, the vessel was closed and heated by microwaves. The digest was made up to 20 g in a capped plastic vessel at a balance. Similarly, 2 cm^3 of milk were digested with 3 cm^3 HNO_3 and made up to 10 g in a capped plastic vessel at a balance.

d) Microwave assisted digestion with potassium chlorate(V) - nitric(V) acid: 1 g of dried green plant or feed, resp. 0.5 g of cheese or chocolate sample were weighed into a PTFE vessel, 8 cm^3 of a solution containing 20 g $KClO_3$ + 200 cm^3 H_2O + 80 cm^3 HNO_3 were added, the vessel was closed and heated by microwaves. After reopening, 1 cm^3 of digestion solution was added, and the digest made up to 25 cm^3 in a plastic volumetric flask. The subsequent program time/power program was run: 1 min 250 W/2 min 0/5 min 250 W/5 min 400 W/5 min 500 W.

Determinations

For ICP-OES determinations, the digests were run undiluted and 1+1 diluted with water. The ICP-power was varied between 1300 W (default) and 1400 W. Calibration was done with 2-4-10 mg/dm^3 calibrants each.

For ICP-MS determinations, samples were diluted 1+9, and indium added as an internal standard. Calibration was done with 1-2-4-10 µg/dm^3 calibrants each.

Results

Determination conditions and detection limits

Detection limits were calculated at first from the standard deviations of the blanks of the entire procedure. For real series of data close to zero (Y, La, Ce in cheese), a Gaussian distribution with the mean at zero was formed, and the significant values defined as outliers thereof.

In the optical system, lower power did not decrease the signal, but reduced the blank noise, thus resulting in lower detection limits. Detection limits for the lines Ce-413, Ce-418, La-379, La-408, Rb-780, and Sc-361 were 2 times better when the forward power was reduced from 1400 W to 1300 W, whereas they were about equal for Ti-334, T-336 and Y-371. The Rb-signal was placed in a U-shaped background, and recoveries of additions revealed that small amounts might be swallowed. No spectral interferences were noted.

In ICP-MS, the isotopes Rb-85, Rb-87, Y-89, Cs-133, and La-139 were found reliable, when 1+9 diluted digests versus In-115 as an internal standard were measured. Scandium blanks due to dissolved CO_2 appeared; the zero and calibrants have to be sufficiently acid. According to the manual, scandium is positively interfered by Ca-H, BO_2, Si-O and Al-O, which led to incorrect values for some green plants, but chocolates and cheeses seemed to be OK. The signal for titanium was low and software-corrected for Ca, and not quite reliable (too high) in many real samples; for green plants, the OES was sufficiently sensitive. Though Ti-47 and Ti-49 are recommended versus Ti-46 and Ti-48, the Ti-47-ICPMS data for the cheese samples were discarded (mass C-Cl?), because they were much higher than from the OES, and just the data for the chocolates seemed reliable (low S, Si, Al and F).

For the analysis of feed samples (for pigs), detection limits of the ICP-OES were sufficient to obtain data for Y, La, Ce, Ti and Rb, but not for Sc and Cs. The Rb should be checked by standard addition, however. The ICP-MS was about 1000-fold more sensitive towards Ce, and 100-fold more sensitive towards Y, La and Rb, but not applicable for Sc. Due to the low salt tolerance of the ICP-MS, however, a 1 + 9 dilution of the digests is essential, thus one order of magnitude of sensitivity is lost. In the screening of digests of cheese samples (about 0.6 g wet weight in 20 g = about 18 cm^3), contents of Y, La, and Ce remained at or below detection limits in many cases, but a dataset for Rb, Cs, Sc and Ti could be got. As Cs is used in a neighbouring laboratory as a matrix modifier for the K-determination, however, some flyers appeared, and at least double determinations are needed for confirmation.

Recovery from digests

Recovery was tested with 2 µg and 4 µg added to the samples, for all procedures.

Recovery from milk digested with HNO_3 was o.k. throughout. From our traditional digest of 1 g feed or plant sample with $HNO_3/HClO_4$ in glass, recovery was suitable just for Rb and Cs, others had slight losses. Recovery of Sc was 26÷69%, Y 70÷95% La 69÷93%, Ce 70÷100% and Ti 78%. This matches the results from former experiments, where interactions of the glass with low levels of Ba and Al were noted.

Improvements were seen in the microwave-assisted digest in the pressure bomb with HNO_3, but a slight addition of hydrofluoric acid was needed in order to keep added Sc and

Ti in solution. Addition of 100 mm^3 HF was sufficient for complete recovery of Y and La, whereas Sc and Ce needed 200 mm^3 HF, and recovery of Ti was matrix dependent: zero for lucerne, 83% for rice, and 120 % for cherries. Storing of fluoride-containing digests in glass volumetric flasks led to high and variable blanks for all elements investigated here, except Rb. In addition, Al, Ba, Be, Bi, Cr, Mo, Ni, Li, Pb and V were significantly released from the glass, rendering the digests unsuitable for determinations of these elements.

To the contrary, recovery from cheese samples digested with HNO_3 was complete, without additional fluoride. Maybe there is sufficient fluoride, phosphate, oxalate, chloride or aromatic acids in the sample to keep them in stable complexes. Even titanium was recovered at 82÷84%.

The digests obtained with $KClO_3$-HNO_3 proved surprisingly suitable and yielded correct recovery; just titanium scattered from 63÷126 %, and high blanks from rubidium (but not cesium) had to be considered.

Data from analyzed samples

Table 1

Data for scandium, yttrium, lanthanum and cerium

[mg/kg]	**Sc**		**Y**		**La**		**Ce**	
	median	range	median	range	median	range	median	range
mean crust	5.0		26		18		46	
brown coal	6.24	0.19÷13.6	10.2	1.6÷46.9	17.7	2.1÷40.8	27.9	3.9÷65.3
hard coal	4.16	1.17÷16.8	9.6	5.3÷19.5	16.7	5.0÷40.7	25.8	8.4÷99
green plants	0.035	<0.012÷0.261	0.122	0.004÷ 0.805	0.057	<0.0006÷ 1.15	0.45	<0.0001÷ 2.13
chocolate	0.0055	<0.0026÷ 0.020	0.0040	0.0020÷ 0.0056	0.014	0.0055÷ 0.0153	0.035	0.014÷ 0.037
cheese	0.026	<0.0015÷ 0.094	<0.00033	<0.00033÷ 0.0039	< 0.0004	<0.0004÷ 0.040	<0.0006	<0.0006÷ 0.0026

Table 2

Data for rubidium, cesium and titanium

[mg/kg]	**Rb**		**Cs**		**Ti**	
	median	range	median	range	median	range
mean crust	310		7.0		5600	
brown coal	38.7	2.0÷144	3.84	0.09÷11.3	1400	100-5200
hard coal	15.5	7.4÷59.2	2.33	0.37÷18.0	1000	200÷4000
green plants	4.96	1.67÷48.8	0.016	< - 0.138	15.8	1.76÷134
chocolate	6.35	4.51÷7.55	0.015	0.0086÷0.0215	5.62	3.74÷7.77
cheese	1.19	0.56÷2.12	0.0045	-*	0.087	-*

*for cheese, just a few samples were read for Ti and Cs

Discussion and outlook

In general, the concentrations levels of rare earth elements in green plants are very low, particularly in the grain crops and vegetables. The rare earth element concentration patterns of leaf, stem and root are generally very similar to each other and to their host soil, including the negative Ce and Eu anomaly, because their uptake is governed by the geochemistry of the host soil [11]. In green plants, rare earth element concentrations generally decrease in the order root > leaf > stem > grain (fruit). This was demonstrated for maize, wheat, rice, paprika, and citrus. Like silicon, several rare earth elements increase almost linearly with the age of the tissue [9]. Data from this work (Table 1) show in general that the rare earth elements plus scandium are generally depleted versus coal on an ash basis, which can be assumed at about 2%. The coal data have been taken from an Austrian government report, based on 84 brown coal and 26 hard coal samples, which were analyzed by ICP-OES and XRF (X-ray-fluorescence) methods [1]. Ferns are known to accumulate rare earth elements [11], and their proportion among coal forming plants might have been more significant than today. Another simple explanation is the presence of inorganic clay between the coal macerals.

As the ash content, about 2% can be assumed for chocolates and 3% for cheese, which was obtained via the sum of all elements determined. In chocolates, many trace elements, like Cu, Fe, B etc., and also Rb, Cs and Ti (Table 2) are within the same concentration range than the green plants, because their composition is dominated by the composition of the cocoa beans. The level of rare earth elements + scandium was found to be lower, however. The levels of the investigated elements in this work were lower in cheese than in green plants and chocolates, except for scandium.

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ANALIZA PIERWIASTKÓW O NISKIEJ AKTYWNOŚCI BIOLOGICZNEJ W ROŚLINACH ZIELONYCH, PRÓBKACH ŻYWNOŚCI I PASZ (Sc-Y-La-Ce-Rb-Cs-Ti)

Abstrakt: Omówiono wyniki testów standardowych metod mineralizacji i analizy wielopierwiastkowej pierwiastków o małej aktywności biologicznej (Sc, Y, La, Ce, Rb, Cs i Ti) z próbek żywności i roślin, z wykorzystaniem ICP-OES i ICP-MS. Za pomocą analizy metodą ICP-OES wykazano, że zastosowanie średniej mocy wejściowej daje lepszą wykrywalność niż przy stosowaniu dużej mocy. ICP-OES jest odpowiednią metodą analityczną do wykrywania Sc i Ti, jednak nie była wystarczająco czuła, by wykryć Y, La, Ce i Cs w biomatrycy. Stężenie Rb było czasami maskowane przez U-kształtne tło. ICP-MS, jako metoda bardziej czuła, była odpowiednia do analizy Y, La, Ce, Rb i Cs z wykorzystaniem In-115 jako standardu wewnętrznego. Z próbek roślin zielonych, pasz i sera odzyskiwano jednorazowo 2 i 4 µg z nich. Mineralizacja w mieszaninie HNO_3-$HClO_4$ nie jest zalecana do oznaczaniu tych pierwiastków. Ilościowe odzyskiwanie Y, La, Sc, Ce i Ti z próbek sera prowadzono w mieszaninie HNO_3-HF (dla próbek roślin stosowano kwas fluorowodorowy) z wykorzystaniem pieca mikrofalowego i hermetycznie zamkniętych pojemników. Przechowywanie płynów zawierających fluorki w pojemnikach szklanych powodowało ich znaczne ubytki. Zastosowanie mineralizacji mikrofalowej i roztworu $KClO_3$-HNO_3 umożliwiało odzyskiwanie wszystkich tych pierwiastków z roślin zielonych i sera z wyjątkiem Rb. Otrzymane wyniki badań roślin zielonych, sera i czekolady są porównywalne z wynikami wcześniejszych badań oraz z niepublikowanymi danymi dotyczącymi węgli austriackich.

Słowa kluczowe: pierwiastki ziem rzadkich, rośliny zielone, ser, czekoladki, płyny

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ENVIRONMENT FRIENDLY COAL PROCESSING TECHNOLOGIES FOR SUSTAINABLE DEVELOPMENT OF POLISH ENERGY SECTOR

PRZYJAZNE ŚRODOWISKU TECHNOLOGIE PRZETWÓRSTWA WĘGLA DLA ZRÓWNOWAŻONEGO ROZWOJU POLSKIEGO SEKTORA ENERGETYCZNEGO

Abstract: According to the projections, world net electricity production is predicted to increase from 18.0 trillion kWh in 2006 to 31.8 trillion kWh in 2030. Coal contribution to world electricity supply remains the highest and is said to even slightly increase to 43% in 2030. Being the most abundant and competitive, coal recoverable reserves could satisfy the world's energy needs in the perspective of about 120 years at the current consumption levels. There is, however, a need for further improvement of coal-fired power generation in terms of its economics and environmental impact. The so-called Clean Coal Technologies (CCT) enabling energy efficient and environmentally friendly use of coal include: coal upgrading, improvements in efficiency of existing power plants, advanced power generation technologies, near zero-emission technologies and technologies for CO_2 transport and storage. In the paper the future role of coal in energy systems with a special focus on Polish energy policy, and the main trends in coal processing in the aspect of Clean Coal Technologies are presented.

Keywords: coal, processing, energy

Introduction

A continuous increase in the demand as well as in the share of coal in the energy consumption and electricity production is declared in the reports and forecasts for energy sector. In 2006 the respective values equaled 11,800 Mt_{oe}, 27% and 42% [1]. The energy demand is expected to reach 16,950 Mt_{oe} in 2030 and the share of coal in the energy consumption and power generation are said to be on the similar significant levels of 28% and 42% for it is regarded as a safe and reliable fuel, available from large reserves and worldwide market free of geopolitical constraints, when compared with other fossil fuels as crude oil or natural gas.

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The estimates of coal R/P ratio (*proved reserves to production*) in 2009 support the forecast for its future major role in energy mix as its reserves are said to be sufficient for 122 years, while those of crude oil and natural gas for 42 and 60 years, respectively.

The prices of coal are generally lower and more predictable than prices of crude oil fluctuating in the last decade from about 14 to above 70 USD/bbl[*] (with a peak in 2008 of 100 USD/bbl) and prices of natural gas dependent on the latter ones [2]. Coal price levels in the relevant period in Northwest Europe have risen from about 30 to 80 USD/ton (with a peak in 2008 of about 150 USD/ton). Storage and transport of coal is also economically competitive, eg it does not require high pressure pipelines.

Nevertheless, coal is considered the most carbon-intensive fuel. Global dependence on all fossil fuels since the mid-19th century led to the release of over 1100 $GtCO_2$ into the atmosphere [3]. World CO_2 emissions from fuel combustion account for about 70% of total *greenhouse gas* (GHG) emissions and 80% of total CO_2 emission [4]. The emission of CO_2 from energy sector is expected to grow from 29.0 billion metric tons in 2006 to 40.4 billion metric tons in 2030. Coal share in world CO_2 emissions is also expected to grow from 42% in 2006 to 45% in 2030 [1].

In the light of the above, the technologies aiming at more sustainable coal processing, the so-called *Clean Coal Technologies* (CCT) are of special importance in regard to economies with energy sectors heavily dependent on coal. The paper presents the up-to-date trends in coal utilization technologies for energy needs in the aspect of CCT and characteristics of Polish energy system, with a special emphasis put on coal gasification with CO_2 capture.

Clean Coal Technologies

Coal processing technologies are regarded as one of the most CO_2 intensive with present-day 42% share in fossil fuels-based CO_2 emission [5]. But with an increasing deployment of energy efficient and low carbon technologies coal could be considered addressing its environmental challenges.

The term Clean Coal Technologies refers to technologies developed and implemented in order to mitigate the negative environmental impact of coal utilization. During about 40 years of CCT development the focus in CCT moved from SO_2, NO_x, Hg and dust emissions reduction to GHG emission reduction, with a special emphasis put on *carbon capture and storage* (CCS) technologies. At present there are five groups of technologies with a high potential for CO_2 reduction from coal processing specified by the International Energy Agency (IEA). These include coal upgrading, improvements in efficiency of existing power plants, advanced power generation technologies (eg *Integrated Gasification Combined Cycle*, IGCC), near zero-emission technologies and technologies for CO_2 transport and storage. It is estimated that wider deployment of coal upgrading technologies, well-established in developed countries, such as coal washing, drying and briquetting, could contribute to 5% CO_2 emission reduction, while increasing thermal efficiency of existing coal-fired power plants to 40% by equipment upgrading and monitoring would reduce it by 22% [6].

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[*] bbl - barrel

Advanced power generation technologies include *supercritical* (SC) and *ultrasupercritical* (USC) giving outlet steam temperature of 540÷566°C at 250 bar and over 590°C under pressure over 250 bar, respectively. Increased thermal efficiency of up to 45% at present and 50% expected in the future (with IGCC or *Pressurised Fluidized Bed Combustion*, PFBC) results in lower levels of CO_2, which would have to be captured per kWh produced.

The IGCC technology has been under development for about thirty years now. The level of operating expertise required for its economic competitiveness still has not been reached, though there are examples of commercial-scale facilities operating worldwide.

In the gasification process known since the 19th century coal is converted into synthesis gas.

The first step of gasification process is pyrolysis, taking place at temperatures above 400°C, resulting in carbon-rich char and hydrogen-rich volatiles production in the absence of oxygen. In the second step, at temperatures over 700°C, the char is gasified. In the IGCC process the *water gas shift* (WGS) step is introduced to convert CO into CO_2 and thus increase the CO_2 content in the final gas. The following reactions between coal and gasifying medium, like oxygen and/or steam can be distinguished (the heats of reactions are calculated for 850°C using HSC Chemistry ver.3.0 [7]):

$$C + O_{2(g)} \rightarrow CO_{2(g)} \quad \Delta H = -394.9\ \text{kJ/mol} \tag{1}$$

$$C + 0.5O_{2(g)} \rightarrow CO_{(g)} \quad \Delta H = -113.0\ \text{kJ/mol} \tag{2}$$

$$CO + 0.5O_{2(g)} \rightarrow CO_{2(g)} \quad \Delta H = -281.9\ \text{kJ/mol} \tag{3}$$

$$C + H_2O_{(g)} \rightarrow CO_{(g)} + H_{2(g)} \quad \Delta H = +135.7\ \text{kJ/mol} \tag{4}$$

$$CO_{(g)} + H_2O_{(g)} \rightarrow CO_{2(g)} + H_{2(g)} \quad \Delta H = -33.2\ \text{kJ/mol} \tag{5}$$

$$2CO_{(g)} \rightarrow CO_{2(g)} + C \quad \Delta H = -168.9\ \text{kJ/mol} \tag{6}$$

$$CH_{4(g)} + H_2O_{(g)} \rightarrow CO_{(g)} + 3H_{2(g)} \quad \Delta H = +226.7\ \text{kJ/mol} \tag{7}$$

$$C + 2H_{2(g)} \rightarrow CH_{4(g)} \quad \Delta H = -91.020\ \text{kJ/mol} \tag{8}$$

$$CH_{4(g)} + CO_{2(g)} \rightarrow 2CO_{(g)} + 2H_{2(g)} \quad \Delta H = +259.942\ \text{kJ/mol} \tag{9}$$

In general, gasification technology and IGCC in particularly, offers higher potential efficiencies, wider variety of feedstock and products (eg electricity, synthetic natural gas SNG, H_2, chemicals) when compared with SC or USC.

The CCT focus is moving in developed countries from conventional pollutants emission control to decarbonization of coal processing by increasing efficiency and CO_2 capture and storage.

CCS technologies are of special importance in the light of Kyoto Protocol targets, increasing energy demand and role of fossil fuels in energy supply.

The technologies for CO_2 separation have been used in industry for a century now but with and aim of producing pure CO_2 streams rather than of its emission mitigation. CO_2 capture is performed among the others in purification of natural gas and in chemical plants for ammonia, alcohols and liquid fuel production. One of the processes of CO_2 separation from methane in natural gas treatment is chemical absorption. Amine scrubbing could be also used in post-combustion CO_2 capture processes, applicable for conventional coal-fired power generation and gas-fired power generation using combustion turbines. In this case, however, the CO_2 concentration in the gaseous mixture is lower, about 14%, and the relevant energy cost for new power plants is 20÷25% of plant output, resulting from the energy requirements of the process (for CO_2 desorption from the amine solution, dehydration and compression) and reduced plant efficiency. The chemical absorption and other components of the post-combustion capture systems, although operated commercially, have not been used and optimized for large scale of coal-fired plants yet. Still, they are attractive in terms of modernization of the existing plants.

In oxyfuel combustion process, operated in a number of system worldwide, coal is burned in oxygen. The flue gas is mostly CO_2 and thus the cost of amine scrubbing is about half the cost of CO_2 capture from conventional plants. The cost of air separation unit operation for oxygen production is however considerable. It is applicable to *pulverized coal* (PC) oxygen-fired combustion in an enriched oxygen environment using pure oxygen diluted with recycled CO_2 or H_2O. In the oxy-combustion process with flue gases recirculation: O_2/CO_2, fuel is combusted in the mixture of oxygen and CO_2, which is next recycled with flue gases for combustion temperature control. In a result the flue gases contain mainly CO_2 and steam, which can be condensed. The resulting gas stream contains high concentration of sequestration ready CO_2.

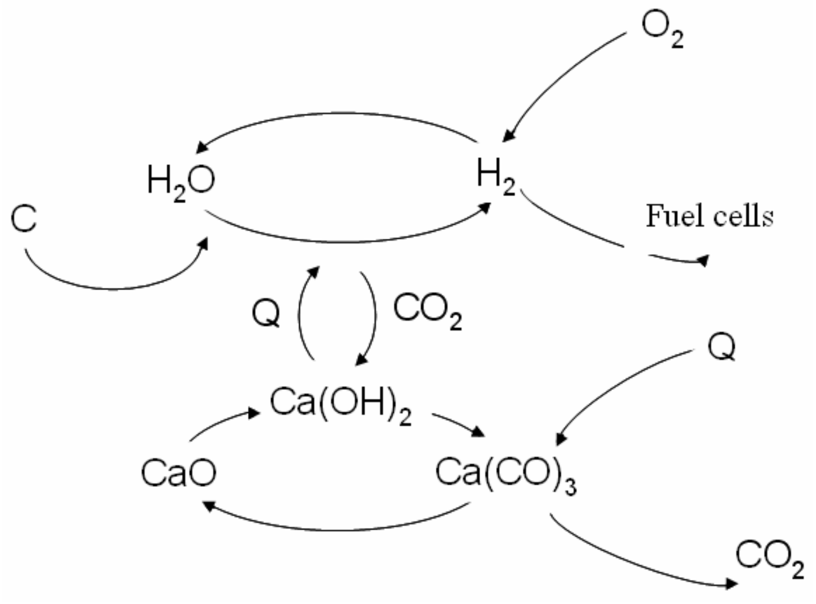

Fig. 1. The idea of the HyPr-RING process. Based on [10]

The pre-combustion CO_2 capture is applicable to gasification plants. It is suitable to be used in the IGCC plants where coal is gasified with steam to gas composed of hydrogen and carbon monoxide, which is further converted in WGS reactors to hydrogen and carbon dioxide mixture. After separation hydrogen is used as a fuel and carbon dioxide is ready for sequestration. Still no commercial scale system of this type is operated yet.

A novel method of the pre-combustion CO_2 capture is under development consisting in CO_2 absorption by CaO [8-16]. The idea of the coal-based hydrogen production and CO_2 capture in a single step is presented in Figure 1.

In the process coal is gasified in a presence of calcium oxide at 600÷700°C and under the pressure of 3 MPa [9].

The summary reactions may be presented as follows:

$$C + 2H_2O + CaO = CaCO_3 + 2H_2 \quad \Delta H_{700} = -69.420\,\mathrm{kJ/mol} \tag{10}$$

Calcination reaction used to produce CaO and regenerate it for cyclic application should also been taken into account in a heat balance of the process:

$$CaCO_3 \rightarrow CaO + CO_2 \quad \Delta H_{900} = 166.786\,\mathrm{kJ/mol} \tag{11}$$

Other materials ($CaOSiO_2$, MgO) have also been tested as CO_2 sorbents in the process but it was calcium oxide which was proved to produce gas of the best quality and highest volume (H_2 75%, CH_4 24%) [17].

Table 1

Selected CO_2 storage sites operated or planned [19-25]

Location, reservoir name and process type, scale	**Injection start [year]**	**Average injection rate [ton of CO_2/d]**	**Total planned storage [ton of CO_2]**
Fenn Big Valley, Canada, ECBM, pilot	1998	50	200
Sleipner, Norwey, Utsira saline formation, commercial	1996	3,000	20,000,000
Weyburn, Canada, EOR, commercial	2000	3,000÷5,000	20,000,000
Minami-Nagoaka, Japan, aquifier, gas filed, demonstration	2002	40	10,000
Recopol, Poland, ECBM, pilot	2003	1	10
Qinshui Basin, China, ECBM	2003	30	150
Yubari, Japan, ECBM, demonstration	2004	10	200
In Salah, Algeria, depleted gas field, commercial	2004	3,000÷4,000	17,000,000
Frio, USA, saline formation, pilot	2004	177	1,600
K12B, the Netherlands, EGR, demonstration	2004	100	8,000,000
Salt Creek, USA, EOR, commercial	2004	5,000÷6,000	27,000,000
CSEMP, canada, ECBM, pilot	2005	50	10,000
Pembina, Canada, EOR, pilot	2005	50	50,000
Teapot Dome, USA, EOR, demontration	2006	2,600,000/year	
Snohvit, Norway, saline formation	2007	1900	23,000,000
Ketzin, Germany, saline formation	2008	100	60,000
Otwey, Australia, saline formations and depleted gas field, demonstration	2008	126,5	100,000
Gorgon, Australia, saline formation	planned for 2009	10,000	120,000,000
Belchatow, Poland, onshore saline aquifiers, commercial	planned for 2015	-	over 500,000

In summary, CO_2 concentration from the post-combustion process (13÷15% vol. in coal-fired systems and 3÷4% vol. in gas-fired turbines) and pressure is low, which implies the need for treatment of high volumes of gas and impurities such as particulate matter, SO_2 and NO_x present in flue gas degrade sorbents. The pre-combustion and oxy-combustion processes utilize air separation units to combust coal in an oxygen-enriched environment, but the amount of oxygen required in oxy-combustion is significantly higher than in the pre-combustion process, increasing CO_2 capture costs.

In the pre-combustion process CO_2 stream is much more concentrated than in the post-combustion flue gas, and less oxygen is required in comparison with the oxy-combustion process, which makes the CO_2 capture less expensive. At present, however, there are few gasification plants in full-scale operation and capital costs are higher than for PC plants [6, 18].

Captured CO_2 can be commercially utilized for enhanced oil and gas recovery or for enhanced coal bed methane recovery from deep unminable coal seams.

The CO_2 storage capacity is estimated to be on the levels of 675÷900, 3÷200, 1,000÷10,000 $GtCO_2$ for oil and gas fields, unminable coal seams and deep saline formations, respectively [19]. The first industrial-scale CO_2 storage was started at Sleipner gas field in the North Sea (Norway), where compressed liquid CO_2 separated from methane is injected into a deep saline aquifer below the sea bed. In Table 1 selected CO_2 storage sites operated or planned are listed [19-25].

Role of coal in energy mix of Poland

Poland is listed among the major world coal producers. Its energy system depends heavily on coal with 58% of electricity generated on hard coal and 32% on lignite (data for 2007) [26], while as much as 70% of natural gas and 95% of crude oil is imported [27]. Polish proved reserves of crude oil in 2007 amounted to 0.096 billion bbl and of natural gas 5,820 billion cubic feet [28].

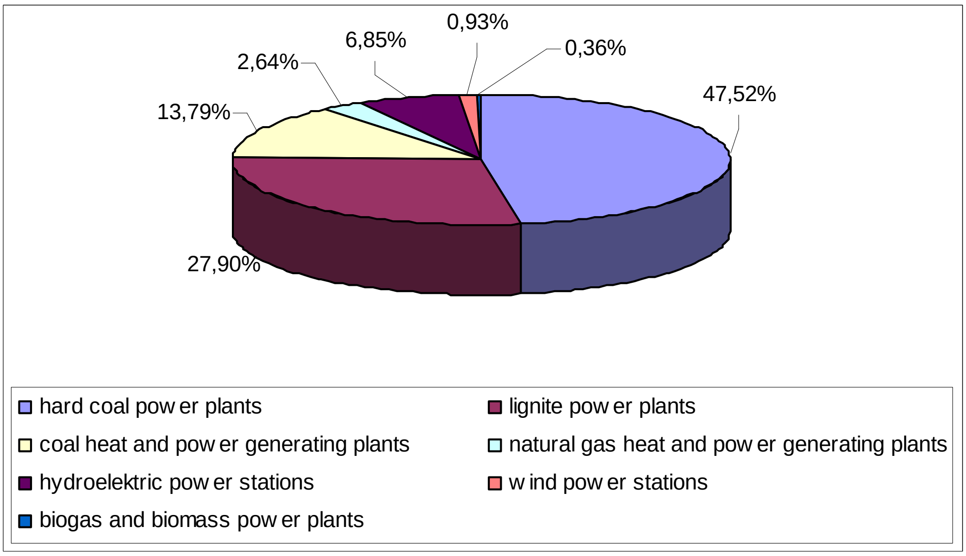

Fig. 2. Total installed electricity capacity for Poland (2008) [26]

The production, consumption and capacity of electricity generation in Poland in years 1998-2008 are given in Figures 2 and 3. The total installed electricity capacity in Poland in 2008 was 35,850 GW. The prognosis of power generation structure up to 2020 is given in Figure 4. The total electricity generation is expected to amount to 128.7, 140.10 and 156.10 TWh in years 2010, 2015 and 2020, respectively [26].

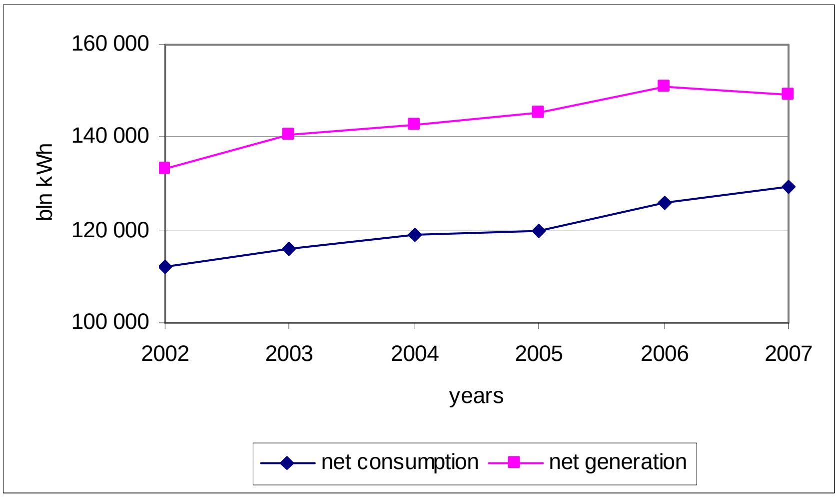

Fig. 3. Net electricity generation and consumption in Poland (2002-2007) [5]

The investments in Polish energy system planned for the next ten years are given in Table 2.

Table 2

The planned investments in Polish energy system [26]

Company	**Location**	**Capacity [MW]**	**Start date (year)**	**Technology / Fuel**
Polska Grupa Energetyczna	Opole	460	2012	hard coal
	Opole	460	2013	hard coal
	Turow	500	2014	lignite
	Dolna Odra	400	2016	combined cycle gas turbine (CCGT)
	Dolna Odra	400	2019	CCGT
Poludniowy Koncern Energetyczny	Halemba	up to 440	2012	hard coal
	Blachownia	100÷200	2012	hard coal or coke oven gas
	EC Bielsko-Biala	100	2012	hard coal
Vatenfall	Vatenfall Heat Poland Warsaw	400	2013	hard coal
CEZ	Skawina	600÷1,000	2014	hard coal
Polish Power	Zarnowiec	1,600	2013-2014	hard coal (gasification)

As can be seen their majority are coal-based plants, which comes as no surprise, taking into account the domestic fossil fuel resources and energy police principles specified below.

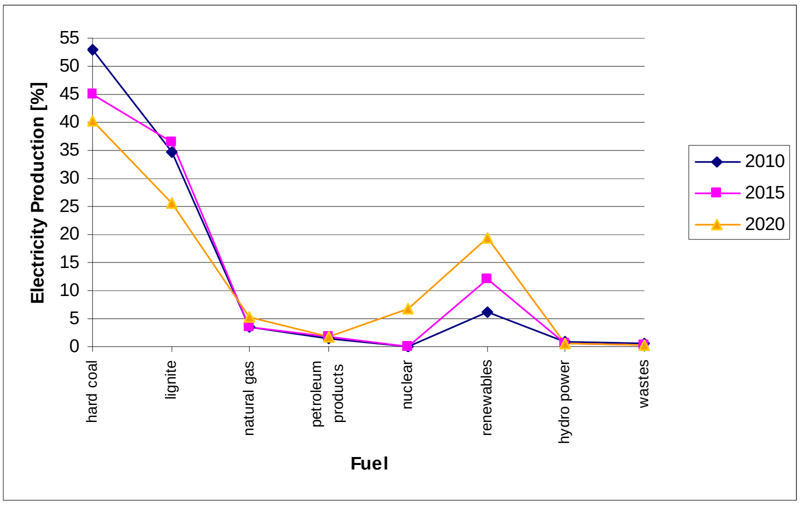

Fig. 4. Prognosis of electricity generation structure by fuel in Poland [26]

The documented balance resources of hard coal in Poland are estimated on the level of 43 201 million tons (31.12.2008) with 75% of steam coals and 25% coking coals (see Table 3). The resources located in operating deposits constitute 37.2% of the balance resources and amounts to 16,082 million tons. The resources are located in three basins with the largest being the Upper Silesian Coal Basin (Gornoslaskie Zaglebie Weglowe - GZW) with the area of 5,800 km^2 and over 78% of total domestic hard coal deposits, of which 19% are classified as exploited, 24% reserve and 27% prospective.

Table 3

Hard coal resources in Poland (2008) [29]

	No. of deposits	**Geological resources [million tons]**		**Industrial**
		balanced	**off balance**	
Total	**138**	**43,201**	**24,667**	**4,338**
of which resources of exploited deposits:				
Operating plants	47	16,082	8,464	4,166
of which resources of off balance deposits:				
Total	50	26,493	12,291	171
1. Deposits explored	37	13,569	5268	171
2. Deposits pre-explored	13	12,923	7,023	-
of which resources of abandoned deposits:				
Total	41	626	3,922	-

The Lublin Coal Basin (Lubelskie Zaglebie Weglowe - LZW) covers the area of 9,100 km^2 with 21.5% of the total domestic hard coal deposits of which only 0.8% are exploited, 10% reserve and the majority - prospective. The identified and exploited deposits of the Lower Silesian Coal Basin (Dolnoslaskie Zaglebie Weglowe - DZW), abandoned for technical and economic reasons, are placed in the area of 350 km^2 and amounts to about 150 million tons.

The documented balanced lignite reserves in the total amount of 13,563 million tons are located in Belchatow, Turow, Patnow and Adamow [29]. The levels of geological and industrial lignite resources are given in Table 4.

Table 4

Lignite resources in Poland (2008) [29]

	No. of deposits	**Geological resources [million tons]**		**Industrial**
		balanced	**off balance**	
Total	**77**	**13,5623**	**4,599**	**1,371**
of which resources of exploited deposits:				
Total	13	1,744	104	1,371
1. Operating plants	12	867	90	751
2. Plants under construction	1	877	14	620
of which resources of off balance deposits:				
Total	59	11,810	4,491	-
1. Deposits explored	29	2,791	715	-
2. Deposits pre-explored	30	9,019	3,776	-
of which resources of abandoned deposits:				
Total	5	9	4	-

The principles of Polish Energy Policy by 2030

The primary directions of Polish energy policy until 2030 include strengthening the fuels and energy supplies security, improvement of energy efficiency and mitigation of the hazardous environmental impact of power industry. In the light of unquestionable leading role of coal in domestic energy mix and limited potentiality for import of liquid and gas fuels and electricity (up to 10%) the energy and fuels supplies security is defined as ensuring stable supplies to meet domestic needs at acceptable prices and with optimal use of own resources, that is coal as the main fuel for power industry. The meaning of diversification of liquid and gas fuels supply was widened and now takes into account not only diversification of supply directions but also diversification of technologies. The latter one refers to a development of coal-based technologies of liquid and gas fuels production. Meeting the expected increasing demand for electricity by creation of new generation capacity is to be performed using low-emission technologies of coal-based energy generation to ensure meeting the required pollutants emission levels, including SO_2, NO_2, dust and CO_2, in line with climate protection and climate-energy package adopted by EU [30]. The reduction of CO_2 emission is to be performed to the extent technically feasible, while avoiding too strong dependence on imported fuels. The above mentioned technologies include coal gasification to synthetic natural gas (SNG) and coal liquefaction to liquid fuels as well as efficient coal-pretreatment technologies. Construction of new, highly efficient power generation units and cogeneration technology by 2020 is also declared among the policy objectives. CCS technologies are planned to be implemented to enhance fuel recovery in gas and crude oil extraction. New ways of CO_2 industrial utilization are to be subject of R&D activities in terms of CCS development. At least two demonstration CCS installations are expected to be located in Poland. The electricity transmission system is to be modernized and extended to enable cross-border exchange of at least 15% by 2015 and 25% by 2030 of electricity used. But at the same time independence in terms of electricity and heat generation is expected to be maintain based almost entirely on domestic coal resources.

The preparatory works in terms of legal, social acceptance and technical aspects of nuclear energy systems are to be undertaken. The renewable energy production in Poland nowadays takes place mainly in small local power generation units and for local users. An increase in renewable energy sources in the final energy use to the level of 15% in 2020 and 20% in 2030 and biofuels in the transport fuels market to 10% by 2020 is, however, to be strongly supported.

The importance of CCT should therefore be recognized, especially in countries with the energy systems dependent on coal and commitments in terms of international activities aiming at sustainable development and GHG emission reduction in particularly. The technical advances within CCT development can not be achieved without partnership and cooperation between enterprises and local governments as well as between companies and scientific and research communities. Creation of the Innovative Silesian Cluster of Clean Coal Technologies, constituting the platform for R&D and policy activities, aimed at promotion of such wide cooperation in terms of CCT development in Poland [31].

Summary and conclusions

The Clean Coal Technologies are of special interest and importance in the light of increasing energy demand and stable role of coal in ensuring energy security. The focus of CCT development has changed and nowadays the efforts in this regard are more devoted to optimization and implementation of highly efficient, zero-emission coal-based power generation technologies. The importance of CCT development, as a part of sustainable energy system, is recognized worldwide as over 40% of continuously increasing electricity demand is and will be generated in coal processing systems. Considerable financial support is secured for R&D projects worldwide within national and international programs.

The need for undertaking intensive activities in the field of CCT is also acknowledged in Poland. This should come as no surprise considering the structure of Polish energy system, characteristics of domestic fossil fuel resources base as well as national commitments in terms of European climate package. Targets and means aiming at facilitating development of CCT are included in the Energy Policy for Poland by 2030. There is also a considerable level of know-how and expertise available from the R&D institutes and industry traditionally related to mining and power generation fields. Coordination and support of future and already undertaken efforts as well as cooperation between different stakeholders of research and development, scientific and industry circles have, however, to be ensured. Some activities in this regard have already been initiated.

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PRZYJAZNE ŚRODOWISKU TECHNOLOGIE PRZETWÓRSTWA WĘGLA DLA ZRÓWNOWAŻONEGO ROZWOJU POLSKIEGO SEKTORA ENERGETYCZNEGO

Zakład Oszczędności Energii i Ochrony Powietrza, Główny Instytut Górnictwa, Katowice

Abstrakt: Według analityków, światowa produkcja energii elektrycznej wzrośnie z $18{,}0 \cdot 10^{12}$ kWh w 2006 do $31{,}8 \cdot 10^{12}$ kWh w 2030. Udział węgla jako surowca do produkcji energii elektrycznej pozostaje największy od lat i w roku 2030 ma osiągnąć 43%. Ocenia się, że z uwagi na najbogatsze zasoby i konkurencyjność rynkową dostępne zasoby węgla mogą zaspokoić światowe zapotrzebowanie na energię w perspektywie około 120 lat przy obecnym poziomie zużycia. Istnieje jednak konieczność doskonalenia technologii produkcji energii z wykorzystaniem węgla w zakresie ich sprawności i oddziaływania na środowisko. Tak zwane czyste technologie węglowe (CTW) umożliwiają wysoko sprawne i przyjazne środowisku użytkowanie węgla i obejmują: technologie wzbogacania węgla, poprawy sprawności istniejących elektrowni węglowych, zaawansowane technologie produkcji energii elektrycznej, technologie zeroemisyjne oraz technologie transportu i składowania CO_2. W pracy przedstawiono przewidywaną rolę węgla w energetyce ze szczególnym uwzględnieniem polityki energetycznej Polski oraz główne tendencje w zakresie technologii przetwarzania węgla w aspekcie czystych technologii węglowych.

Słowa kluczowe: węgiel, przetwarzanie, energia

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FUNCTIONAL PETROLEUM RESINS BASED ON PYROLYSIS BY-PRODUCTS AND THEIR APPLICATION FOR BITUMEN MODIFICATION

WYKORZYSTANIE FUNKCYJNYCH ŻYWIC NAFTOWYCH Z PIROLIZY PRODUKTÓW UBOCZNYCH DO MODYFIKACJI BITUMU

Abstract: The possibility of petroleum resins with epoxy, hydroxyl and carboxyl groups application for modification of bitumen properties has been shown. It has been suggested to modify bitumen by resins *via* joint oxidation of tars and petroleum resins, as well as *via* compounding of functional resins with oxidated bitumen.

Keywords: petroleum resin, functional group, petroleum bitumen, modification, adhesion

Wastelessness and ecological compatibility are the main problems of modern technological processes in petrochemistry. Therefore, the rational use of petrochemical by-products is a guarantee of environmental protection.

Hydrocarbon pyrolysis is the main source of ethylene and propylene production. A series of polymeric materials are produced on their basis. The main problem of pyrolysis is the presence of liquid by-products. Their yield ranged from 25 to 30% depending upon process conditions and raw material.

It is known that the C_9 hydrocarbon fraction of pyrolysis liquid products contains a great amount of unsaturated compounds, *viz* styrene, vinyltoluenes, dicyclopentadiene, indene, *etc*. We have developed a method obtaining of petroleum resins (PRs) with different functional groups (epoxy, hydroxyl and carboxyl) on the basis of the C_9 fraction. PRs with functional groups were obtained *via* initial cooligomerization of unsaturated compounds present in the C_9 fraction in the presence of azodinitrile or peroxy initiators at 353÷393 K for 10÷40 h [1-3]. Functional groups in petroleum resins improve their properties and allow to use them more widely.

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One of the perspective ways of PRs with functional groups practical application is their use for bitumen modification. Previous investigations confirmed such possibility [4, 5]. Bitumen may be modified by introduction of PRs into the raw material (tar) for oxidation process or into finished bitumen. The industrial petroleum resin “Pyroplast-2” was used for modification. The drawback of mentioned modifier is an absence of functional groups. Bitumen materials of improved quality may be obtained to our mind using PRs with functional groups for modification.

Experimental

Reactants and their characteristics

The residuum after, tar vacuum distillation was used as a raw material for bitumen production. Tar was produced at JSC “Ukrtatnafta” (Kremenchuk, Poltava region) from the mixture of Russian oils. Tar softening temperature was 299 K.

For the investigation of bitumen modification *via* compounding two different types of commercial oxidated bitumens were used: building bitumen BN-70/30 by DSTU 4148-2003 obtained at JSC “NPK-Galychyna” (Drogobych, Lviv region) and road bitumen BND-60/90 by DSTU 4044-2001 obtained at JSC “Ukrtatnafta” (Kremenchuk, Poltava region). Bitumen characteristics are represented in Table 1.

Table 1

Characteristics of initial bitumens

Factor	**BN-70/30**	**BND-60/90**
Needle penetration depth at 298 K (0.1 mm)	15	81
Softening temperature by “ring and ball” method [K]	345	325
Ductility at 298 K	3	77
Solubility in toluene or chloroform [%]	99.0	99
Mass change after heating [%]	1.0	0.85
Flash point [K]	503	518

Following PRs were used as modifiers:

PR with epoxy groups was obtained according to the procedure described in [1]. Its characteristics: molecular mass (M_n) = 850; epoxy number (e.n.) = 8.2; bromine number (br.n.) = 9.3 g Br_2/100 g.

PR with carboxyl groups was obtained according to the procedure described in [2]. Its characteristics: M_n = 1320; br.n. = 23.8 g Br_2/100 g; acid number (a.n.) = 51.9 mg KOH/g.

PR with hydroxyl groups was obtained according to the procedure described in [3]. Its characteristics: M_n = 610; unsaturation is 26.5%; hydroxyl number (h.n.) = 155.3 mg KOH/g.

“Pyroplast-2” PR was a commercial product obtained *via* thermal oligomerization of the pyrocondensate C_9 fraction after hydrocarbon pyrolysis. Softening temperature is 358 K, M_n = 710. All resins used for modification were solid substances with light-yellow color.

Experimental and analysis methods

Joint oxidation of petroleum tar and petroleum resins was carried out at the laboratory plant consisting of a reactor block, air supply and cooling systems and system of volatile products recovery. The procedure is described in [6].

Bitumen-polymeric mixtures were prepared by mixing of components at the laboratory plant consisting of electric heater, metal vessel with mixer and thermometer [6]. The composition was mixed at 393 K till the mixture became homogeneous. The temperature must be higher than softening temperature of PR.

Ductility, penetration and softening temperature were determined using standard procedures [7]. The factor "adherence with glass" was determined using procedure described in [8].

Results and discussion

Polymeric and oligomeric products used for the modification of petroleum bitumen are introduced into the raw material directly before oxidation or mixed with bitumen after oxidation. Taking this fact into account bitumen was modified also by two methods:

- PR introduction into the raw material for bitumen production;
- PR introduction into the finished bitumen after oxidation.

Using method of PR introduction into the raw material bitumens were modified *via* joint oxidation of tar and different petroleum resins. PRs with epoxy and carboxyl groups were used as modifiers. For comparison bitumen was modified by Pyroplast-2 (resin without functional groups).

Table 2

Effect of PRs with epoxy groups amount on the properties of oxidated bitumens

Factor	**PRs amount in the initial mixture [mass %]**				
	0	**1**	**3**	**5**	**10**
Softening temperature by "ring and ball" method [K]	308	309	311	313	315
Ductility at 298 K [cm]	40	43	49	56	84
Penetration at 298 K (0.1 mm)	260	226	174	131	94
Penetration index	–1.3	–1.4	–1.5	–1.7	–1.9
Brittle temperature [K]	229	229	230	231	232
Plastic range [K]	79	80	81	82	83
Adherence with glass [%]	14.5	20.6	34.3	42.5	77.8
Acid number [mg KOH/g]	0.28	0.32	0.41	0.49	1.10

Table 3

Effect of PRs with carboxyl groups amount on the properties of oxidated bitumens

Factor	**PRs amount in the initial mixture [mass %]**				
	0	**1**	**3**	**5**	**10**
Softening temperature by "ring and ball" method [K]	308	309	310	312	318
Ductility at 298 K [cm]	40	43	47	66	92
Penetration at 298 K (0.1 mm)	260	226	197	153	72
Penetration index	–1.3	–1.4	–1.5	–1.6	–1.7
Brittle temperature [K]	229	229	230	231	236
Plastic range [K]	79	80	80	81	82
Adherence with glass [%]	14.5	20.9	34.7	39.5	79.4
Acid number [mg KOH/g]	0.28	0.33	0.42	0.51	1.14

The joint oxidation of tar and petroleum resins was studied at different ratios tar : PR. The resin was introduced into the raw material in amount from 1 to 10 mass %. The oxidation was carried out at 523 K for 3 h. The air space velocity was 2.5 min^{-1}. The experimental results are presented in Tables 2-4.

Table 4

Effect of "Pyroplast-2" PR amount on the properties of oxidated bitumens

Factor	**PRs amount in the initial mixture [mass %]**				
	0	**1**	**3**	**5**	**10**
Softening temperature by "ring and ball" method [K]	308	309	310	311	317
Ductility at 298 K [cm]	40	41	42	64	93
Penetration at 298 K (0.1 mm)	260	223	200	168	68
Penetration index	–1.3	–1.4	–1.4	–1.6	–2.1
Brittle temperature [K]	229	229	230	230	232
Plastic range [K]	79	80	80	81	85
Adherence with glass [%]	14.5	19.6	31.6	36.9	75.3
Acid number [mg KOH/g]	0.28	0.31	0.39	0.48	1.06

One can see from the results that introduction of PRs of different types into the raw material essentially affects the bitumen properties. The increase of PR amount increases the softening temperature from 308 to 315÷318 K depending upon modifier. The introduction of PR increases also bitumen ductility. The increase of PR amount from 1 to 10 mass % increases ductility from 40 to 84÷93 cm, whereas penetration decreases from 214 to 68÷94 mm.

In order to investigate the colloid degree of bitumen and its divergence from standard viscous state penetration index was determined. We can see from Tables 2-4 that the increase of PR amount slightly decreases penetration index. At the same time there is the increase in brittle temperature which characterizes bitumen properties in pavement. Following bitumen characteristics plastic range is a difference between softening and brittle temperature. Bitumens with wide plastic range have improved cracks formation resistance at low temperatures and shearing strength at high temperatures. The increase of PR amount in the raw material increases the plastic range in all the cases (*vide* Tables 2-4).

The change of acid number and "adherence with glass" also has been studied. It was established that the increase of PRs content from 1 to 10 mass % in the raw material the acid number of modified bitumen increases from 0.28 to 1.06÷1.14 mg KOH/g. It is a positive factor for the improvement of bitumen adhesion which is characterized by "adherence with glass". This index increases also from 14.5 to 75.3÷79.4%.

Comparing characteristics of bitumen obtaining *via* tar oxidation without modifier and that obtaining *via* tar oxidation with PRs of different types one can see that introduction of petroleum resin allows to increase bitumen adhesion essentially. The optimal amount of modifier is 5 mass %. Using greater amount of modifier is inexpediently from the economic point.

From the results presented in Tables 2-4 one can see that there is no essential difference between properties of bitumen modified by PR with epoxy or carboxyl groups and bitumen without functional groups. The possible reason is the fact that functional groups in PRs are unstable against high temperatures (the temperature of oxidated bitumen obtaining is 523 K). Therefore it is necessary to investigate the modification of bitumen by petroleum resins after oxidation.

In order to estimate the efficiency of bitumen modification the effect of PRs amount on the performance characteristics of commercial bitumens has been studied. Bitumens BN-70/30 from JSC "NPK-Galychyna" and BND-60/90 from JSC "Ukrtatnafta" were taken for investigations. Mentioned bitumens differ by operational performance, application field and initial raw material. For instance, building bitumen BN-70/30 was obtained *via* oxidation of tar extracted from the mixture of Ukrainian oils and road bitumen BND-60/90 - *via* oxidation of tar extracted from the mixture of Russian oils.

Petroleum resins with epoxy, hydroxyl and carboxyl groups were used for the modification. Obtained results were compared with results received during bitumens modification by "Pyroplast-2" resin without functional groups. PRs were introduced into finished oxidated bitumen. The PRs amount was within the range of 1÷10 mass %. The results are presented in Tables 5 and 6.

Table 5

Effect of PRs of different types on the properties of building bitumen BN-70/30 from JSC "NPK-Galychyna"

Factor	**PR amount in the composition [mass %]**					
	0	**1**	**3**	**5**	**7**	**10**
PR with hydroxyl groups						
Softening temperature by "ring and ball" method [K]	72	72	73	74	75	76
Ductility at 298 K [cm]	3	4	4	4	3	2
Penetration at 298 K (0.1 mm)	15	12	8	6	3	2
Adherence with glass [%]	81.9	83.1	86.3	87.8	90.4	91.4
PR with epoxy groups						
Softening temperature by "ring and ball" method [K]	72	72	73	74	75	76
Ductility at 298 K [cm]	3	3	3	3	2	2
Penetration at 298 K (0.1 mm)	15	14	12	9	6	4
Adherence with glass [%]	81.9	84.3	87.6	89.7	91.1	92.5
PR with carboxyl groups						
Softening temperature by "ring and ball" method [K]	72	72	73	74	75	76
Ductility at 298 K [cm]	3	3	3	3	2	1
Penetration at 298 K (0.1 mm)	15	13	11	8	5	3
Adherence with glass [%]	81.9	89.20	97.7	99.3	99.5	99.6
Acid number [mg KOH/g]	0.8	3.8	5.4	6.4	7.1	9.7
Pyroplast-2						
Softening temperature by "ring and ball" method [K]	72	73	74	75	76	77
Ductility at 298 K [cm]	3	4	4	4	2	1
Penetration at 298 K (0.1 mm)	15	13	9	7	6	4
Adherence with glass [%]	81.9	83.2	85.5	87.1	89.7	89.9

Table 6

Effect of PRs of different types on the properties of road bitumen BND-60/90 from JSC "Ukrtatnafta"

Factor	**PR amount in the composition, [mass %]**					
	0	**1**	**3**	**5**	**7**	**10**
PR with hydroxyl groups						
Softening temperature by "ring and ball" method [K]	325	325	326	328	329	330
Ductility at 298 K [cm]	77	78	79	80	81	80
Penetration at 298 K (0.1 mm)	81	79	75	72	66	60
Adherence with glass [%]	71.5	74.7	79.8	82.4	86.4	92.3
PR with epoxy groups						
Softening temperature by "ring and ball" method [K]	325	325	326	327	328	329
Ductility at 298 K [cm]	77	77	78	80	81	81
Penetration at 298 K (0.1 mm)	81	80	77	74	71	65
Adherence with glass [%]	71.5	74.0	80.1	82.8	88.3	93.4
PR with carboxyl groups						
Softening temperature by "ring and ball" method [K]	325	325	326	327	328	329
Ductility at 298 K [cm]	77	78	80	82	82	81
Penetration at 298 K (0.1 mm)	81	79	76	73	70	64
Adherence with glass [%]	71.5	75.3	80.8	84.1	89.7	95.5
Acid number [mg KOH/g]	2.6	3.9	5.1	6.5	8.2	10.4
Pyroplast-2						
Softening temperature by "ring and ball" method [K]	325	326	327	328	329	331
Ductility at 298 K [cm]	77	78	80	83	84	83
Penetration at 298 K (0.1 mm)	81	80	77	71	66	61
Adherence with glass [%]	71.5	73.6	78.9	81.6	85.4	91.3

We can see from Table 5 that bitumen softening temperature increases by 4-5 degrees after introduction of PRs. Bitumen ductility is practically constant (minimum ductility is 3 cm). The bitumen hardness characterized by "penetration" increases with the increase of PRs amount.

One of the main characteristics of building bitumens is their ability to hold out on the solid surfaces (adhesive property). This property is characterized by "adherence with glass". Mentioned factor increases with the introduction of PRs into the bitumen. Moreover, the greater amount of PRs, the greater value of "adherence with glass". It is interesting to note that petroleum resins with functional groups affect bitumen adhesion in a greater degree than "Pyroplast-2" resin. The best results are obtained using PRs with carboxyl groups. The introduction of 10 mass % of such oligomer increases the "adherence with glass" from 81.9 to 99.6%. The main regularities determined for building bitumen BN-70/30 are the same for BND-60/90 bitumen, except for ductility (Tables 5 and 6). Small amount of PRs increases bitumen ductility but when this value equal to 5÷7 mass %, the ductility decreases.

Conclusions

On the basis of obtained results it has been established that petroleum resins may be used as active additives for bitumen-polymeric compositions. It has been shown that introduction of PRs with functional groups in amount of 5 mass % increases softening temperature by 5÷13 K, decreases penetration by 12÷29 0.1 mm and decreases oxidation time by 1.5÷2 times. The best result is achieved using PRs with carboxyl groups. The presence of carboxyl functional groups improves bitumen adhesion by 21.5÷33.6%.

Comparing two investigated methods of bitumen modification their advantages and disadvantages have been determined.

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WYKORZYSTANIE FUNKCYJNYCH ŻYWIC NAFTOWYCH Z PIROLIZY PRODUKTÓW UBOCZNYCH DO MODYFIKACJI BITUMU

Abstrakt: Badano możliwość wykorzystania żywic naftowych z grupami epoksydowymi, hydroksylowymi oraz karboksylowymi do modyfikacji właściwości bitumu. Zaproponowano modyfikowanie bitumu żywicami poprzez wspólne utlenianie smoły i żywic naftowych, a także poprzez przygotowanie mieszanek żywic z grupami funkcyjnymi z utlenionym bitumem.

Słowa kluczowe: żywice naftowe, grupy funkcyjne, bitum naftowy, modyfikacje, adhezja

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TEMPORAL VARIABILITY IN CONCENTRATION OF SELECTED PHYSICAL AND CHEMICAL PARAMETERS WITH RESPECT TO DISCHARGE IN A RIVER IN THE PUCK BAY BASIN

CZASOWA ZMIENNOŚĆ STĘŻEŃ WYBRANYCH WSKAŹNIKÓW FIZYCZNO-CHEMICZNYCH NA TLE NATĘŻENIA PRZEPŁYWU WÓD JEDNEJ Z RZEKI ZLEWISKA ZATOKI PUCKIEJ

Abstract: The goal of this work is to determine the concentration variability and the values of selected physical and chemical parameters, including the discharge values for the Plutnica River, as well as the causes for changes in these values. When it comes to physical and chemical water quality, the downstream waters of the Plutnica are freshwaters with elevated chloride concentrations. This is due to the fact that the Baltic Sea acts on shallow groundwater along this part of the coast as well as to periodically occurring saltwater intrusions into inland surface waters. The concentrations of the remaining common ions were fairly stable during the course of the year and their annual variability levels were similar.

Keywords: water quality, discharge, temporal variability, physical and chemical parameters

The degradation of man's natural environment is one of the most important, if not the most important, problem of the modern world. Worsening water quality leads to limiting of its use, and it becomes a problem in many areas [1]. It is especially noticeable on a local basis. Although globally, the processes and natural phenomena adversely affecting water quality are still dominant with respect to anthropogenic processes and phenomena [2], locally it is just the opposite. The degradation of water quality, and related to it water deficits, including river discharge magnitude decreases, are always noticeable on the local scale first. Natural characteristics of river flow and initial quality of water are more and more often just an abstraction. At present, human beings significantly influence the natural environment causing the initiation, acceleration or slowdown of certain physical, geographic, and biochemical processes [3]. The Plutnica River is an example of a river on

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the Polish coast of the southern Baltic Sea, where many coexisting factors are observed, both natural and anthropogenic (Fig. 1).

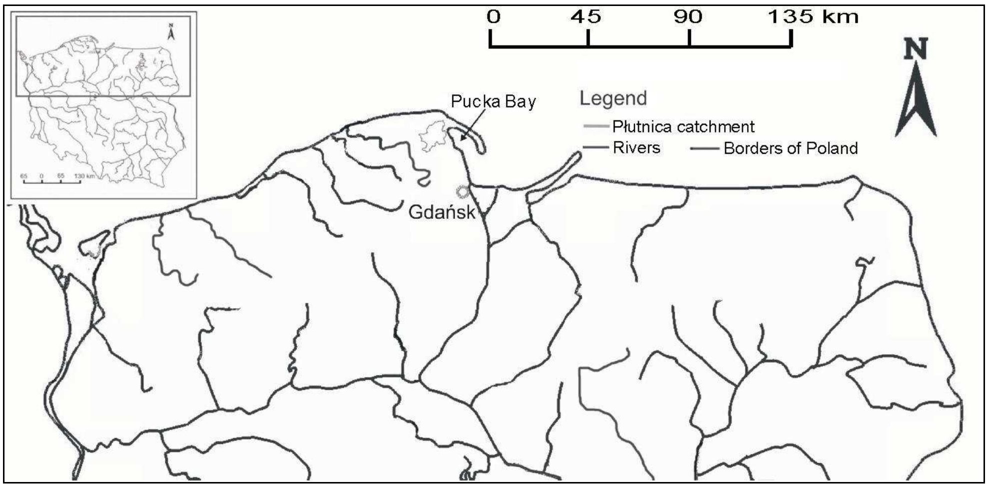

Fig. 1. Location of the research area in northern Poland

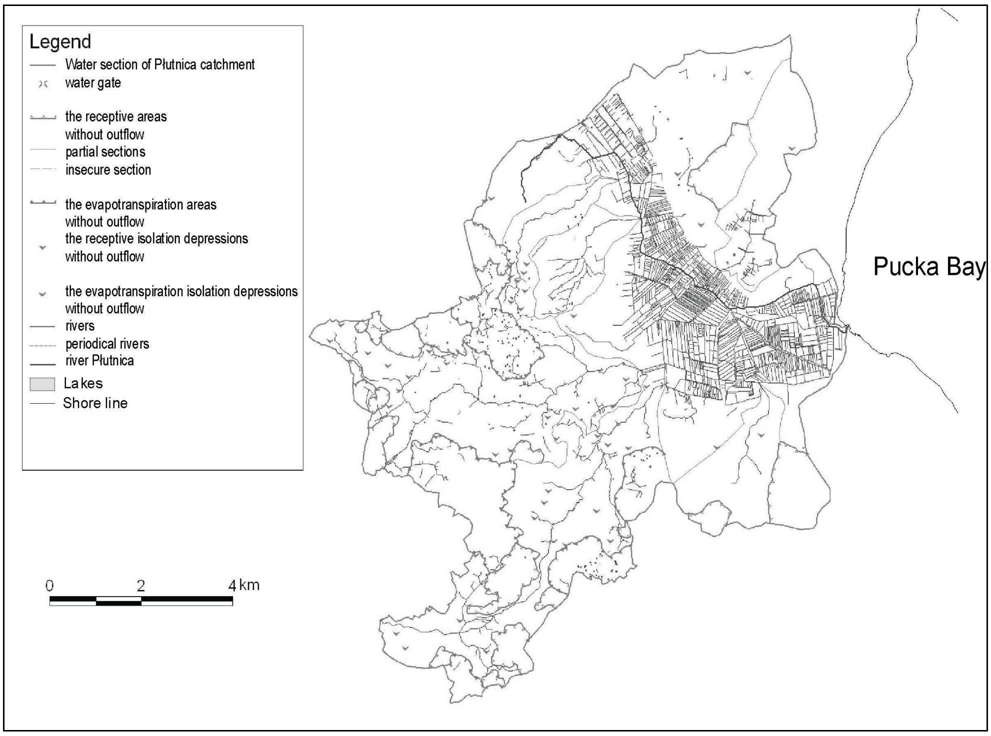

Fig. 2. Hydrographic map of the Plutnica River basin

Today, it is a hydrographic entity, whose surrounding environment has been modified by man to a lesser or greater degree. One should not forget that, once naturally formed, the environment still plays a fundamental role in the shaping of water relationships in this basin. The Plutnica River, in its downstream section, has been entirely reengineered by man, creating a polder system with forced water circulation (Fig. 2). Its headwaters and middle section have been significantly reengineered but water circulation remains gravity-based. The most natural conditions exist in the upland part of the basin, where the hydrological conditions are controlled primarily by natural processes.

The goal of this work is to determine the concentration variability and the values of selected physical and chemical parameters, the discharge values for the Plutnica River, as well as the causes for changes in these values.

Hydrological characteristics of the Plutnica River basin

The Plutnica is a small coastal river flowing across a lowland. It empties into the Bay of Puck (Fig. 1). The river originates in the Puck Hills in the vicinity of the town of Starzynski Dwor. It is 11.2 km in length and the area of its basin is 85.2 km^2. The Plutnica flows in a proglacial valley and drains the southern part of the Swarzew Hills as well as the northeastern part of the Puck Hills. The river drains the area’s autochthonous waters. The water level in the river influences the drainage of the basin. In the downstream section, the drainage of the basin depends on the water level in Puck Bay. With a heightened water level in the Bay, the outflow comes to a halt, and during storms, seawater intrusions into the river channel do occur. In its downstream section, the river flows through wetlands, called Puck Swamps. They cover an area of 1,600 hectares. A polder was created in the swamp area and is maintained by a pumping station that serves irrigation and drainage purposes. The station is located on the Pump Canal at its outlet to the Plutnica River. In this area, there are several operational locks and a weir that are used to control the drainage and irrigation system. There are no lakes in this basin, if a lake is defined as a reservoir whose area is greater than 1 hectare. In the Puck Upland, it is typical for numerous ponds and kettle lakes to be found (over 200), quite often functioning as fisheries. Several reservoirs were built in the river valley in the 1960s. Since 1992, seven new small reservoirs have been built on streams flowing down from the Puck Hills. The reservoirs’ area totals 0.14 km^2, which produces a low lake area to overall land area ratio, which equals 0.0016%.

Methods

Fieldwork was performed during the 2006 hydrological year. Water samples were collected monthly in the Plutnica River at a point located 400 m upstream from its mouth. The point was chosen because it lies downstream from all the tributaries and the influence of Puck Bay waters on river water quality can be detected here. The water samples were tested at the Hydrochemical Laboratory of the University of Gdansk Department of Hydrology in order to determine the basic ion content (chloride, sodium, potassium, calcium, magnesium, sulfate, bicarbonate, as well as BOD_5 and COD-Cr) in the waters of the Plutnica River. The methods used to perform applicable measurements are described in Table 1. The fieldwork for this project involved performing the following measurements:

- dissolved oxygen (DO) via the electrometric method using an oxygen electrode CellOx 325 made by WTW,

- water pH via the electrometric method using an SenTix 41-3 gel electrode made by WTW,
- electrical conductivity and water temperature via the TetraCon 325 conductometric probe made by WTW.

Table 1

Methods used to determine basic ion content of water, BOD_5 and COD

Parameter Being Determined	**Method**	**Standard Procedure Equivalent**
Chloride	Titration	PN-ISO 9297:1994
Sulfate	Colorimetry	None
Calcium	Titration	PN-ISO 6058:1999
Magnesium	Titration	PN-ISO 6059:1999
Sodium	Flame photometry	PN-ISO 9964-3/AK:1997
Potassium	Flame photometry	PN-ISO 9964-3/AK:1997
Bicarbonate	Titration	None
BOD_5	Electrochemistry	PN-EN 1899-2:2002
COD-Cr	Colorimetry	ISO 6060-1989

Concurrently to the collection of water samples, measurements of the discharge rate were conducted using a StreamPro Acoustic Doppler Current Profiler (ADCP). Measurements using this device are done as follows: ADCP emits acoustic waves and receives them after they are reflected off particles suspended in the water and in the river bed. The time needed for a wave to reflect and come back determines the distance from the suspended particle, while the frequency change of the reflected waves determines the direction of movement. Waves reflected by the river bed carry information about its shape. Waves reflected off suspended particles are used to measure discharge. The device does not measure discharge in the subsurface layer or close to the river bed; instead, it takes an average of it based on calculated flow velocity in adjacent layers. Today, this is the most accurate of discharge measurement methods.

The discharge irregularity coefficient **α** was also used in this work, where α is the ratio of maximum discharge to minimum discharge [4]:

$$\alpha = \frac{Q_{max}}{Q_{min}}$$

Based on the instantaneous discharge values measured during fieldwork, average monthly discharge values were calculated as follows: a graph was drawn on technical paper, where 1 mm corresponds to 1 day in a year. Then, the end of each month was marked with a vertical line and points were marked that represented the instantaneous discharge value for the particular day. The next step was to connect the points and read off the values for discharge at the points of intersection of the curve and the vertical lines marking the end of each month. Finally, an average of three numbers was taken: the discharge value read at the beginning of a particular month, the instantaneous discharge value, and the discharge value at the end of a particular month. In this manner, the monthly average discharge values were obtained.

Results and discussion

The direct cause that influences discharge variability in rivers is weather conditions, especially the amount of rainfall and its timing. These factors are further affected by the geographic characteristics of the natural environment of a basin [5]. Highly variable discharge is typical of basins with poorly permeable surfaces, a significant slope of land, and a scarce amount of forest. In basins with highly permeable surfaces, a small slope of land, large forested areas, and a significant presence of lakes, the rate of discharge is stable throughout the year [6].

The basin of the Plutnica River is dominated by low permeability surfaces (58%) and variable permeability surfaces (17%). Moreover, the lake to overall land ratio is low and equals 0.0016%, and the slope of land is rather steep. These factors lead to an irregular regime in the basin, as evidenced by a high coefficient of discharge irregularity (**α** = 11.4).

Table 2

Instantaneous discharge during the 2006 hydrological year

Date	**Instantaneous discharge [$m^3 \cdot s^{-1}$]**
30.11.05	0.617
15.12.05	0.993
30.01.06	0.128
23.02.06	0.56
30.03.06	1.1
13.04.06	1.12
27.04.06	1.08
17.05.06	0.197
22.06.06	0.782
20.07.06	0.098
30.08.06	0.959
27.09.06	0.865
25.10.06	1.1

Table 3

Average specific runoff during the 2006 hydrological year

Months	**Average specific runoff [$dm^3 \cdot s^{-1} \cdot km^{-2}$]**
XI	7.27
XII	9.08
I	4.03
II	5.55
III	11.05
IV	12.27
V	6.05
VI	6.94
VII	3.75
VIII	8.86
IX	10.75
X	11.88
Average	8.12

The instantaneous discharge rate (Table 2) for the Plutnica River during the 2006 hydrological year ranged from 0.098 $m^3 \cdot s^{-1}$ to 1.12 $m^3 \cdot s^{-1}$, and its specific runoff (Table 3) ranged from 1.165 $dm^3 \cdot s^{-1} \cdot km^{-2}$ to 13.317 $dm^3 \cdot s^{-1} \cdot km^{-2}$. The average discharge in the 2006 hydrological year was 0.68 $m^3\ s^{-1}$. Compared with 1988, it was lower by 0.23 $m^3 \cdot s^{-1}$, and compared with the year 2000, it was higher by 0.21 $m^3 \cdot s^{-1}$. The average specific runoff for the Plutnica River was 8.12 $dm^3 \cdot s^{-1} \cdot km^{-2}$. This value is close to the average specific runoff values for rivers such as the Reda (a.s.r. = 9.2 $dm^3 \cdot s^{-1} \cdot km^{-2}$) and the Radunia, whose average specific runoff is 7.9 $dm^3 \cdot s^{-1} \cdot km^{-2}$ [7].

Maximum discharge values, over 1.0 $m^3 \cdot s^{-1}$, occurred in mid-April, in March, and in October (Table 2). The lowest discharge rates were recorded in the Plutnica River in July and January (Fig. 3).

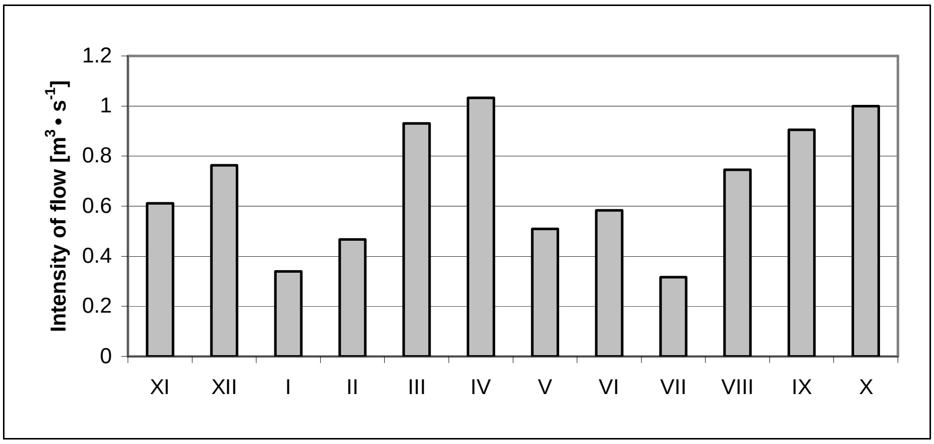

Fig. 3. Average discharge rate for the Plutnica River during the 2006 hydrological year

Comparing the winter half of the year (Nov.-Apr.) with the summer half of the year (May-Oct.), it can be concluded that the average discharge rate in the winter half of the year was greater and equaled 0.7 $m^3 \cdot s^{-1}$, and in the summer half of the year, it was slightly lower and equaled 0.68 $m^3 \cdot s^{-1}$.

The monthly discharge coefficient, which is a ratio of the average monthly discharge to the average yearly discharge, and is expressed as a percentage, shows an existence of two flood events that took place during the 2006 hydrological year - a spring flood event and an autumn flood event (Fig. 4). In the case of the Plutnica River, one can infer the existence of a spring and an autumn regime.

It should be mentioned, that the discharge rate in the Plutnica River depends on the operation of a pumping station, which is located at the outlet of the Pump Canal to the Plutnica River. In early spring and in autumn, the downstream part of the basin is drained, therefore the discharge values are higher. In late spring and summer, when high temperatures increase evaporation and a water deficit occurs, the irrigation system is turned on, which decreases the amount of water flowing out.

In order to determine the quality of the water in question, the water's hydrochemical type has to be determined first. Water type is based on the content of the following ions:

calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), bicarbonate (HCO_3^-), sulfate (SO_4^{2-}), chloride (Cl^-), and the ratios between them, expressed in the form of equivalents [8, 9].

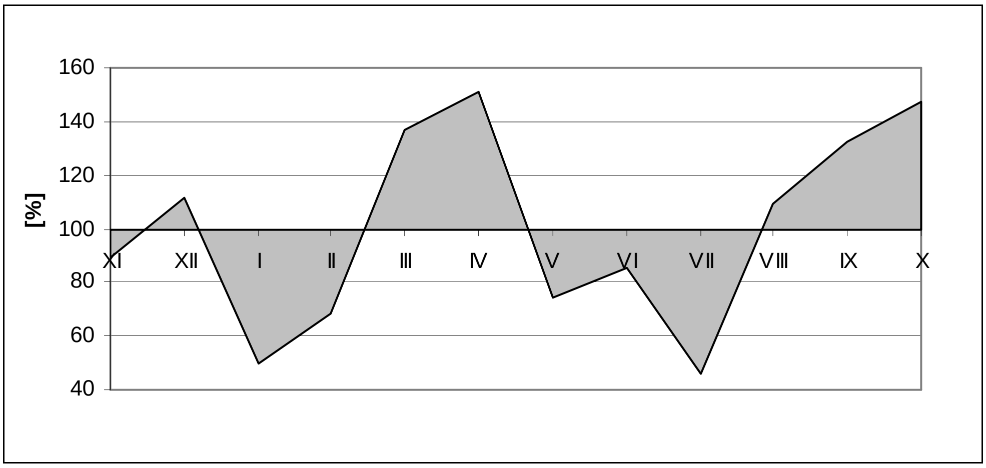

Fig. 4. Monthly discharge coefficient for the Plutnica River during the 2006 hydrological year

According to Alekin's classification system [10], water is divided into the following types: bicarbonate-, sulfate-, and chloride-type water, depending on the dominant anion. Plutnica River water is classified as bicarbonate water (Fig. 5). Groundwater belongs to this group and so does lake water and river water poor in mineral content [11]. Next, waters were divided into three groups, depending on the dominant cation: calcium, magnesium, and sodium. As shown in Figure 6, the dominant cation here is calcium (Ca^{2+}). The groups are then divided into three water types, which are determined by the ion concentration ratio. For the waters of the Plutnica River, the concentration ratio is as follows:

$$[HCO_3^-] < [Ca^{2+}] + [Mg^{2+}] < [HCO_3^-] + [SO_4^{2-}]$$

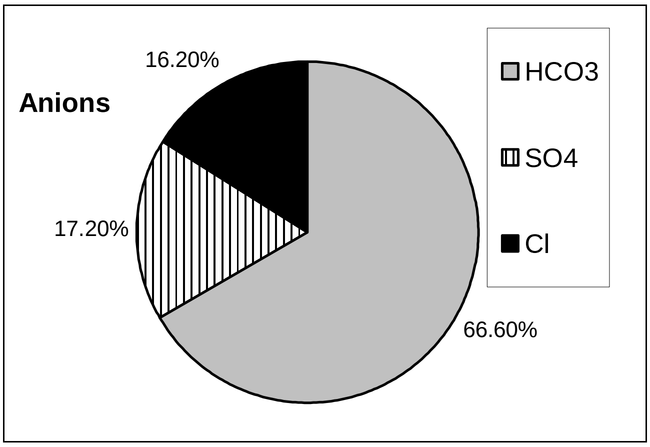

Fig. 5. Circle graph of common anions in Plutnica River waters during the 2006 hydrological year

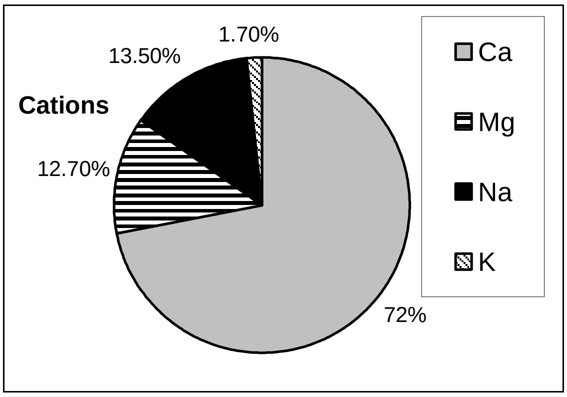

Fig. 6. Circle graph of common cations in Plutnica River waters during the 2006 hydrological year

The third ion, dominant for most of the year, is the sulfate ion (SO_4^{2-}). Only in autumn, this ion is replaced by the chloride ion (Cl^-), which may be related to storms taking place in that period of time, which in turn, cause saltwater intrusions [12]. Seasonal variability of sodium and magnesium with respect to one another may also be observed. Magnesium concentration reaches higher values in the winter and the spring, while sodium concentration does so in the summer and the autumn (Fig. 7).

Considering the results obtained for the selected chemical parameters, on a monthly basis, it can be observed that the lowest concentrations of most of the parameters occurred in March, and the highest in November (Fig. 8). Potassium reached one of its higher concentrations of the year in March only, and in November, one of its lowest. Usually, the potassium to sodium concentration ratio is about 1:4, but in this case, it was almost 1:2.

The concentrations of all the parameters considered during the research period are shown in Table 4.

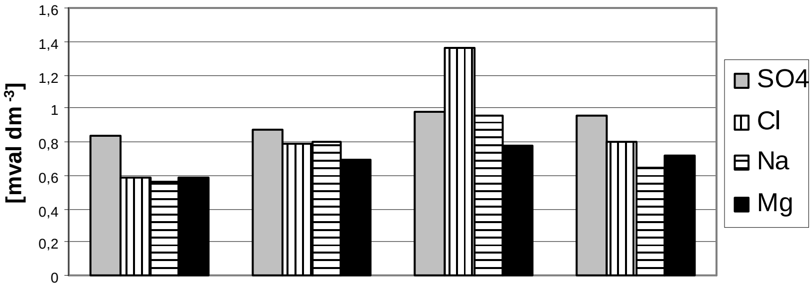

Fig. 7. Seasonal variability of sulfate, chloride, sodium, and magnesium concentrations during the 2006 hydrological year

The temperature variability of the Plutnica River water during the 2006 hydrological year corresponded to variability in air temperature. One unusual increase in water temperature was noted: from 2.5°C in November to 4.9°C in December. The average temperature of the river water was 9.9°C (Table. 4).

In the course of the year, pH ranged from 7.0 to 7.6, which is a range that falls within what is considered to be a neutral range for water (6.5÷8.5) (Table 4). Similarly, the average value of pH of the river water (7.3) was approaching neutral.

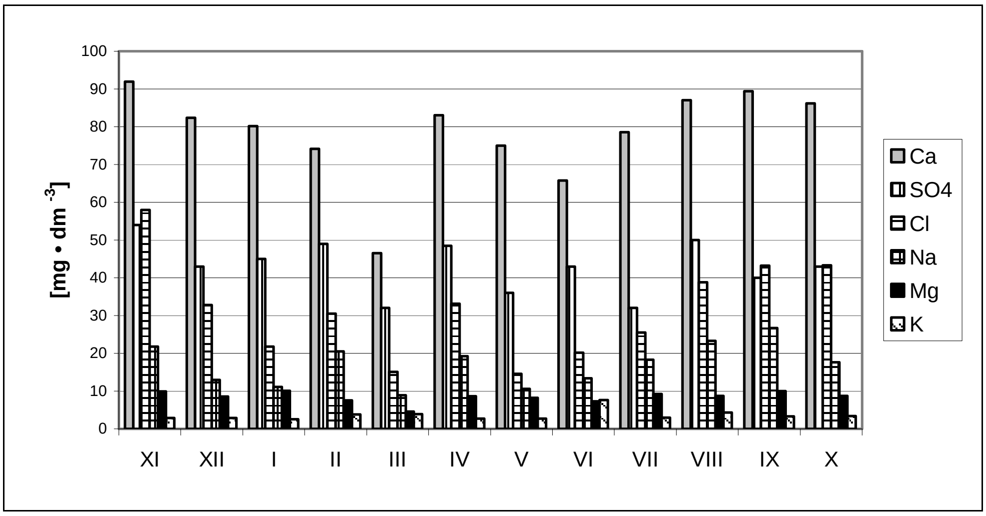

Fig. 8. Variability in the concentrations of common ions during the 2006 hydrological year

Table 4

Variability of selected physical, chemical, and biological parameters during the 2006 hydrological year

Months	**Temperature [°C]**	**pH**	**Conductivity [µS · cm^{-1}]**	**Dissolved oxygen [mgO$_2$ · dm^{-3} / %]**	**BOD$_5$ [mgO$_2$ · dm^{-3}]**	**COD [mgO$_2$ · dm^{-3}]**
XI	2.5	7.4	641.0	6.8 / 50.0	0.97	80.0
XII	4.9	7.6	478.0	9.4 / 73.5	1.82	-
I	1.0	7.2	461.0	-	-	-
II	2.6	7.4	470.0	-	-	-
III	5.5	7.4	284.0	11.1 / 88.0	3.65	34.3
VI	8.8	7.2	491.0	8.5 / 73.3	1.68	22.8
V	11.2	7.2	403.0	13.6 / 122.7	13.59	26.2
VI	18.9	7.2	405.0	3.3 / 35.6	2.72	46.9
VII	20.1	7.5	449.0	3.8 / 41.7	1.10	15.2
VIII	20.1	7.4	450.0	3.4 / 37.3	0.70	24.9
IX	11.8	7.4	547.0	3.9 / 35.7	0.98	16.4
X	11,0	7.1	484.0	3.5 / 31.9	0.37	18.8
Average	**9.9**	**7.3**	**463.6**	**6.7 / 59.5**	**2.76**	**31.7**

The conductivity of the waters of the Plutnica during the 2006 hydrological year ranged from 284 to 641 µS · cm^{-1}. In clean surface waters, conductivity is in the 50÷1000 µS · cm^{-1} range [13]. Higher values usually indicate the presence of wastewater pollution in analyzed water samples. Seawater intrusions are another potential reason for elevated values. The conductivity values calculated for the Plutnica River water indicate that it is clean.

Dissolved oxygen content in clean water usually corresponds to 100% saturation. The lower the value, the more polluted the water. Reduction of dissolved oxygen content below 40% may be dangerous to equilibrium in natural habitats [14]. Plutnica River water is characterized by unfavorable living conditions, given that the average oxygen saturation during the 2006 hydrological year was 59.5%. The cleanliness of the river's water was unsatisfactory from June until October, with dissolved oxygen content below 42%. The best oxygen saturation was detected in the spring, when dissolved oxygen content was 94.7%, on average, as well as in May, when full oxygen saturation was noted.

In the case of BOD_5, its lowest values were recorded in the autumn, when the average value was 0.8 $mgO_2 \cdot dm^{-3}$ (Fig. 9), with a minimum of 0.37 $mgO_2 \cdot dm^{-3}$ in October (Table 4). The highest values of BOD_5 were recorded in the spring (the average value of 6.3 $mgO_2 \cdot dm^{-3}$), with a maximum of 13.59 $mgO_2 \cdot dm^{-3}$ recorded in May (Table 4).

The average value of COD during the 2006 hydrological year was 31.7 $mgO_2 \cdot dm^{-3}$. In the case of COD, it is difficult to speak of seasonal variability, because low and high values occur regardless of the season. However, the highest average values of COD were recorded in the autumn (38.4 $mgO_2 \cdot dm^{-3}$); specifically, 80 $mgO_2 \cdot dm^{-3}$ was recorded in November (Table 4).

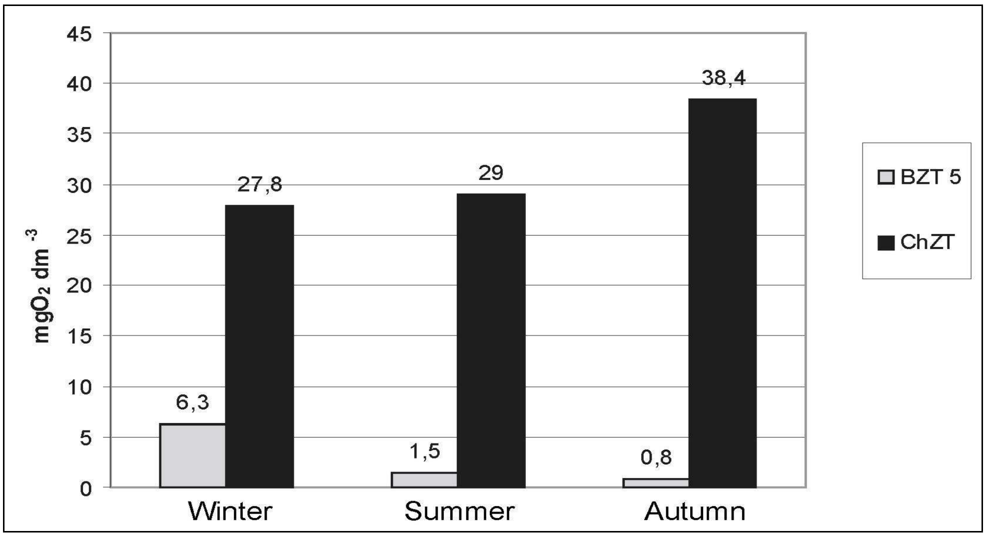

Fig. 9. Seasonal variability in BOD_5 and COD [$mgO_2 \cdot dm^{-3}$] in Plutnica River water

The average concentration of chloride in the Plutnica River was 31.5 $mgCl^- \cdot dm^{-3}$ and chloride concentration ranged from 14.5 to 58 $mgCl^- \cdot dm^{-3}$. Measured values of chloride concentration in Plutnica River water did not confirm a significant influence of Puck Bay on the water in the Plutnica River (no evidence of seawater intrusions). A chloride concentration above 100 $mgCl^- \cdot dm^{-3}$ was not observed at any time. However, there are periods of time during which values occur that exceed 30÷40 $mgCl^- \cdot dm^{-3}$ (Fig. 10). This is at least double the concentration values observed in inland waters [15].

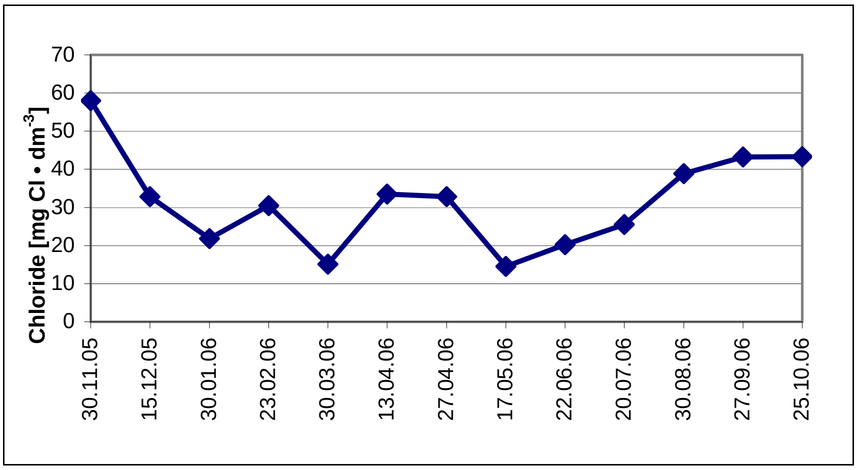

Fig. 10. Temporal variability of chloride concentration in Plutnica River water during the 2006 hydrological year

Conclusions

Human activity, concentrated primarily in the Plutnica Valley, is the reason why it is difficult to compare this river to any other river in the Pomerania coastal region. This applies not only to hydrographic or hydrological characteristics but to qualitative characteristics as well. The reengineered mouth of the Plutnica River may be compared with the mouth of the Reda River. The Reda, however, has been substantially reengineered only in its downstream stretch, while the Plutnica has been reengineered along its entire length.

When it comes to physical and chemical water quality, the downstream waters of the Plutnica are freshwaters with elevated chloride concentrations. This is due to the fact that the Baltic Sea acts on shallow groundwater along this part of the coast [16] as well as to periodically occurring saltwater intrusions into inland surface waters [12]. The concentrations of the remaining common ions were fairly stable during the course of the year and their annual variability levels were similar. For all common ions, except potassium, the lowest concentration values were noted in March, which can be linked to the spring snowmelt season. On the other hand, the highest values were detected in November, and this increase was due to storm weather conditions. An increase in the concentrations of chemical parameters commonly known as *maritime* normally takes place in November.

Water quality in the Plutnica River, as indicated by chemical parameters, is not the best. Human impact on the river's basin is significant, and the results of tests show that its water quality is bad. The cleanliness of Plutnica River water was unsatisfactory from June until October, with dissolved oxygen content below 42%. BOD_5 values for the autumn, with the minimum being in October, confirm the bad condition of the river water as far as its level of cleanliness is concerned. This is primarily due to wastewater pollution. The low COD values, determined during the entire research period, also confirm that the river's water quality is not as good as it could be.

In the 20th century, especially during its second half, the Plutnica River basin became more agricultural in nature, crop areas increased in size, and the amount of artificial fertilizers and pesticides being used increased. At present, arable land occupies 57% of the basin area. Due to the agricultural land use, primarily the use of fertilizer, a seasonal increase in potassium concentration is observed, regardless of discharge rate. This occurred in March, when potassium concentration reached one of the high values for the year, regardless of the high rate of discharge. This was due to the washing out of potassium fertilizer applied to crop fields in the autumn. The highest potassium concentration was recorded in June, which was related to fertilizer use on meadows following the first hay harvest of the year.

The monthly discharge coefficient values for the Plutnica River are different than those for other coastal rivers in Poland. For the Reda and Leba rivers, coefficient values were higher than 100% (which means that discharge was higher than average annual discharge) from November until April, but they were lower from May until October [17]. In the Lupawa River, discharge values that were higher than average annual discharge were noted from October until April. In the case of the Plutnica River, values of the monthly discharge coefficient that were higher than 100% occurred during different months of the year: in May, April, from August until October, and in December. Values lower than 100% were noted in January, February, from May until July, and in November. According to Bogdanowicz [17], coastal rivers are characterized by "negligible discharge variability and a high degree of discharge steadiness". Research on discharge rate variability during the 2006 hydrological year indicates that the above conclusion does not apply to the Plutnica River, where discharge is not steady.

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CZASOWA ZMIENNOŚĆ STĘŻEŃ WYBRANYCH WSKAŹNIKÓW FIZYCZNO-CHEMICZNYCH NA TLE NATĘŻENIA PRZEPŁYWU WÓD JEDNEJ Z RZEK ZLEWISKA ZATOKI PUCKIEJ

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Abstrakt: Celem niniejszej pracy było ustalenie zmienności stężeń i wartości wybranych wskaźników fizyczno-chemicznych oraz przepływów na rzece Płutnicy, a także określenie przyczyn tych zmian. Pod względem jakości fizyczno-chemicznej wody rzeki Płutnicy w jej dolnym biegu są wodami słodkimi o podwyższonych wartościach stężeń chlorków. Wpływa na to niewątpliwie sąsiedztwo morza, które oddziałuje na płytkie wody podziemne w tej części wybrzeża, a także okresowo występujące zjawisko intruzji wód słonawych drogą powierzchniową. Stężenia pozostałych głównych jonów w ciągu roku charakteryzowały się dużą stabilnością i podobną zmiennością roczną uzyskanych wyników.

Słowa kluczowe: jakość wody, natężenie przepływu, czasowa zmienność, wskaźniki fizyczno-chemiczne

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MODELLING TRANSPORT OF HYDROCARBONS IN SOIL-WATER ENVIRONMENT

MODELOWANIE TRANSPORTU WĘGLOWODORÓW W ŚRODOWISKU GRUNTOWO-WODNYM

Abstract: The paper deals with the diffusive model of hydrocarbons migration in porous medium. To assess the risk of groundwaters contamination by hydrocarbons migrating in the soil the mathematical model is applied. Incorporation of diffusion into the equation of mass transport enables the description of hydrocarbons transport deep into soil profile. The biodegradation equation makes it possible to consider the effect of microorganisms upon reduction of hydrocarbons content, especially oil fractions. To verify a theoretical model a series of experiments on the so-called soil filter were carried out. The parameters of theoretical model were determined for benzene, toluene, xylene, *n*-hexane, *n*-heptane and 2,2,4- trimethylpentane.

Keywords: petroleum derived products transport, transport in porous media, infiltration into the soil, organic compounds leakage, hydrocarbons transport in soil

Introduction

Although practically all petroleum constituents can infiltrate the soil the ones that do it most frequently are petroleum fuels as they have the major share in the turnover of petroleum products [1, 2].

Petroleum products spilt on the ground surface can penetrate deep into the ground. Their soluble components are the source of contamination and can reach as far as the underground water table threatening fauna, flora and underground water reservoir of drinking water [3].

Toxicity of petroleum products results from their physical and chemical properties. Thick, hydrophobic oils block soil pores limit the access of air to its deeper layers [4, 5].

Hydrocarbons enter human organism through respiratory system, skin and alimentary system [6-8].

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Aromatic hydrocarbons constitute a significant group of petroleum products. They are relatively volatile and widely applied in chemical and oil industry [9]. The percentage share of aromatic hydrocarbons in fuel oil is approx. 25%, but in ”Super” petrol it oscillates within 30÷50% [10].

The potential sources of contamination with BTX (benzene, toluene, xylene) are refineries, petroleum storehouses, filling stations, coking plants, pulp and paper factories, dry-cleaners, pharmaceutical and metal works [10].

The health risk of VOCs like benzene, toluene, ethylbenzene, xylenes, formaldehyde and acetaldehyde even at low concentrations is well established and some of them have been identified as proven or probable carcinogens by the US Environmental Protection Agency [11].

Benzene exposure has the most serious effects. It is a volatile organic compound of a ring structure characteristic of homologous series of aromatic hydrocarbons. It is a natural constituent of crude oil with the percentage share in all distillations below 1%. To reduce knocking more hydrocarbons were added to petrol including benzene whose share rose to 5%. The areas exposed to the highest benzene contamination are filling stations and their surroundings [12, 13].

Benzene is a first group carcinogen. The research has proved that high concentration of benzene occurs in European cities. Thus, EC Directive 2000/69 specifies the permissible level of benzene in the atmospheric air as not exceeding 5 mg/m^3.

The toxic hazard caused by the leakage of petroleum products to the soil increases in lower temperatures due to decreased vapour pressure and lower ability of the system to biodegradate contaminants. The dynamics of physical and chemical processes and microbiological changes caused by petroleum hydrocarbons are dependent upon environmental factors. In hot and humid climate hydrocarbons decompose relatively fast while in the cold climate the process is much slower [14].

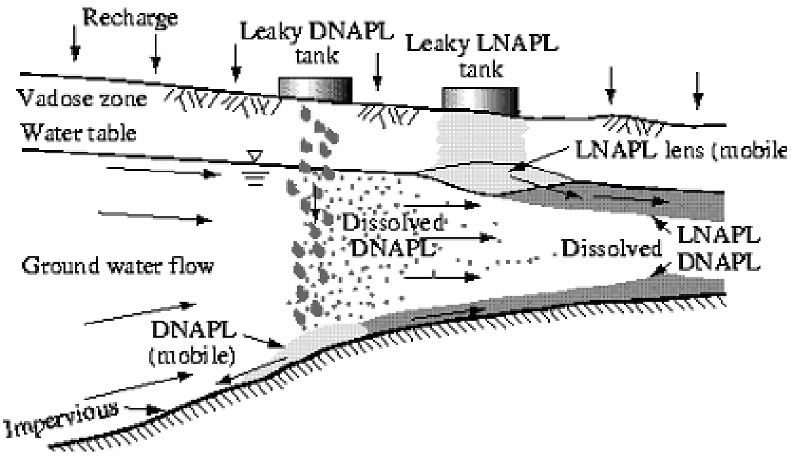

Fig. 1. Migration of petroleum products in aeration and saturation sphere [15]

Particular emphasis is laid upon the transport of petroleum products in atmospheric and soil - water environment. Understanding the process of transport in soil - water environment makes it possible to predict contamination risk and facilitate remedy when contamination occurs. It is difficult to use a mathematical model to illustrate the transport of petroleum products as their constituents in the soil environment are heterogeneous mixtures whose sorption on soil particles shows different characteristics and so does the dynamics of their migration in pores. To a large extent these processes are dependent upon structure and characteristics of the soil, that is, porosity, humidity, organic matter content etc.

The durability of petroleum contaminants in the soil is determined by [16] soil graining, climate as well as by their composition and concentration.

The description of petroleum hydrocarbons migration in soil should include penetration of light phase through aeration sphere and surface movement on the mirror of the underground water. During aeration phase the transport of volatile substances formed by the phase change of migrating hydrocarbons takes place.

In the soil porous space different phases coexist: soil air phase, water phase and organic phase which seeps to the ground. Spreading of petroleum products is the resultant of several single processes: convection, diffusion, dispersion, adsorption and biochemical degradation [17-19].

The starting point for theoretical diffusive models is Fick's second law [20, 21]:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} \tag{1}$$

In natural environment petroleum products undergo biochemical degradation. The ability of bacteria to decompose petroleum products has been built over centuries. Such bacteria are mostly found in the places where crude oil naturally occurs [22]. They produce enzymes biodegradating petroleum hydrocarbons. The appearance of enzymes is the reaction of microorganisms upon certain chemical compounds [23]. Since most hydrocarbons do not dissolve in water, microorganisms produce egzoenzymes allowing formation of hydrophilic structure.

In theoretical models the first-order model of biochemical reaction is frequently assumed [24]. However, the descriptions of more complex kinematics are also found [25]:

$$\frac{dC_i}{dt} = \mu_{max} \cdot \frac{B \cdot C_i}{Y \cdot C_{ks}} \tag{2}$$

where:

μ_{max} - maximum rate of bacteria multiplication $[s^{-1}]$

B - biomass concentration $[mg \cdot dm^{-3}]$

C_i - hydrocarbon concentration $[mg \cdot dm^{-3}]$

C_{ks} - hydrocarbon concentration for partial value μ_{max} $[mg \cdot dm^{-3}]$

Y - biomass produced for the unit of metabolized substrat

Biodegradation rate depends upon organic material content [25].

Another group of models is based on classical theory of multiphase flow and modified Darcy's formula for water - hydrocarbons [14]:

$$Q_i = k_i \cdot A \cdot \text{grad}\, \theta_i \tag{3}$$

where:

A - area of soil cross section $[m^2]$

k_i - intrinsic permeability $[m \cdot s^{-1}]$

Q_i - flow rate [$m^3 \cdot s^{-1}$]
θ_i - volume share of pores filled with free petroleum product [$m^3 \cdot m^{-3}$]

$$\frac{\partial \theta_i}{\partial t} = -K_i \frac{\partial}{\partial z}\left(\frac{\partial h}{\partial z} + 1\right) + \Delta LNAPL \tag{4}$$

where:
h - hydraulic pressure loss in porous matrix [m]
K_i - intrinsic permeability [$m \cdot s^{-1}$]
ΔLNAPL - mass gain of free product [$kg \cdot s^{-1}$]

The model consistent with equation (4) provides comprehensive description of transport in aeration and saturation spheres with regard to transport of volatile phase and sorption of contaminants. The model does not include biochemical degradation, migration in orthogonal direction to the main stream and does not allow for migration below saturation sphere.

A majority of petroleum products' transport models in porous matrix belong to the group of diffusive models. The diffusive model is presented in [14] with regard to heavy fractions and light ends concentration as well moisture and biochemical changes and chemisorption:

$$\begin{aligned} R_1 \frac{\partial c_1}{\partial t} + \frac{\partial a_1}{\partial t} &= -\mathrm{div}(v_1 \cdot c_1) + \mathrm{div}(D_1 \cdot \mathrm{grad}\ c_1) - n(V_1 + I_1) - \eta_1 \\ R_2 \frac{\partial c_2}{\partial t} + \frac{\partial a_2}{\partial t} &= -\mathrm{div}(v_2 \cdot c_2) + \mathrm{div}(D_2 \cdot \mathrm{grad}\ c_2) - n(V_2 + I_2) - \eta_2 \\ R_s \frac{\partial s}{\partial t} + \frac{\partial a}{\partial t} &= -\mathrm{div}(v_s \cdot s) + \mathrm{div}(D_w \cdot \mathrm{grad}\ s) \end{aligned} \tag{5}$$

where:
c_1 - concentration of oil heavy fractions [$kg \cdot m^{-3}$]
c_2 - concentration of oil light ends [$kg \cdot m^{-3}$]
v_1 - convection rate of oil heavy fractions [$m \cdot s^{-1}$]
v_2 - convection rate of oil light ends [$m \cdot s^{-1}$]
v_s - convection rate of water [$m \cdot s^{-1}$]
s - soil moisture [$kg \cdot m^{-3}$]
a - mass of adsorbed moisture per unit volume of soil [$kg \cdot m^{-3}$]
$a_{1,2}$ - mass of absorbed hydrocarbons [$kg \cdot m^{-3}$]
I_1 - rate of heavy fractions degradation caused by microbiological factors [$kg \cdot s^{-1}$]
I_2 - rate of light ends degradation caused by microbiological factors [$kg \cdot s^{-1}$]
η_1 - transformation rate of the adsorbed heavy fractions into other forms [$kg \cdot s^{-1}$]
η_2 - transformation rate of the adsorbed light ends into other forms [$kg \cdot s^{-1}$]
V_1 - transformation rate of heavy fractions in free state into other forms [$kg \cdot s^{-1}$]
V_2 - transformation rate of light ends in free state into other forms [$kg \cdot s^{-1}$]
R_i - retention constant
D_1 - dispersion coefficient of heavy petroleum products [$m^2 \cdot s^{-1}$]
D_2 - dispersion coefficient of light petroleum products [$m^2 \cdot s^{-1}$]
D_w - water dispersion coefficient [$m^2 \cdot s^{-1}$]

The left-hand side of equation (5) consists of the expression showing the mass accumulation in the balancing area. The right-hand side of the first two equations describes kinetics of the following processes: convection, dispersion, biodegradation and chemisorption. To these equations the equations of sorption kinematics [14] may be added:

$$\begin{aligned} \frac{\partial a_1}{\partial t} &= \beta_1 \cdot \left(c_1 - c_1^*\right) \\ \frac{\partial a_2}{\partial t} &= \beta_2 \cdot \left(c_2 - c_2^*\right) \\ \frac{\partial a}{\partial t} &= \beta \cdot \left(s - s^*\right) \end{aligned} \tag{6}$$

where:

β_1 - kinematic coefficient of oil heavy fractions' sorption [s^{-1}]

β_2 - kinematic coefficient of oil light ends' sorption [s^{-1}]

β - kinematic coefficient of water sorption [s^{-1}]

* - parameter values in state of equilibrium

The model presented in [14] contains heat balance:

$$C_p \cdot \rho_o \cdot \frac{\partial T}{\partial t} = \operatorname{div}\left(\lambda \cdot \operatorname{grad} T\right) \tag{7}$$

where:

C_p - heat capacity of hydrocarbons - soil system [$m^2 \cdot s^{-2} \cdot deg^{-1}$]

λ - heat conductivity [$kg \cdot m \cdot s^{-3} \cdot deg^{-1}$]

ρ_o - apparent density of soil [$kg \cdot m^{-3}$]

T - temperature [°C]

The disadvantage of model (5) is the necessity to determine several parameters.

The theoretical model described in [17] can be presented by means of the following boundary value problem:

$$\frac{\partial C \cdot \theta \cdot A \cdot dz}{\partial t} = \frac{\partial \theta \cdot AD_1 \cdot \frac{\partial C}{\partial z}}{\partial z} dz + \frac{\partial\left(-v_1 \theta \cdot A \cdot C\right)}{\partial z} dz + \psi \cdot Adz - \mu \cdot C \cdot \theta \cdot Adz \tag{8}$$

where:

ψ - mass adsorption rate [$kg \cdot m^{-3} \cdot s^{-1}$]

μ - rate constant [s^{-1}]

More complex theoretical models are presented in [26], where the authors discussed transport models in heterogenic environment on the basis of four scenarios with different combinations of uniform/heterogeneous rate-limited dissolution and uniform/heterogeneous rate limited sorption/desorption. The results show that both heterogeneous rate-limited sorption/desorption and heterogeneous rate-limited dissolution can significantly increase the time or pore volumes required to elute immiscible-liquid constituents from a contaminated porous medium. However, sorption/desorption has minimal influence on elution behaviour until essentially all of the immiscible liquid has been removed [26].

The alternative approach towards modeling the transport of polycyclic aromatic hydrocarbons (PAH) is shown in [27]. The authors prove the effect of adsorption upon petroleum hydrocarbons' dispersion in the porous matrix containing dissolved organic matter DOM. The presence of the dissolved organic matter in the matrix containing SiO_2 results in the increase of the retardation factor $R_i > 1$ [27].

The purpose of the model suggested here was to simplify mathematical operations. It was also verified on the research stand with the aim of using it in practice to assess contamination risk expressed by migration time of contaminants from the soil surface to the underground-water table. The suggested algorithm requires prior determination of ”input” parameters.

Research methodology

Basing upon literature, for example, [12, 28] the following assumptions were made to construct the model:

- soil medium is highly porous and permeable for liquid contaminants,
- sorption processes are neglected,
- biodegradation rate of hydrocarbons is greater than zero.

The next step was the experimental verification of the model. For that purpose dry, sand soil of three different grain sizes was used. In choosing petroleum hydrocarbons both their high toxicity and relatively good water solubility were taken into account as they effect contamination risk in the cases of oil leakage from ground objects [29-31]. The following hydrocarbons were selected: benzene, toluene, xylene (isomer mixture) *n*-hexane, *n*-heptane and 2, 2, 4-trimetylopentane.

The results of experimental research were statistically assessed with Student t and Snedecor F tests.

The model of petroleum hydrocarbons' transport

Ground modeling is most frequently conducted on sand filters simulating loose, permeable grounds. In the theoretical models the diffusive transport of hydrocarbons and convection resulting from water flow through aeration sphere are usually taken into account. These models properly describe the transport of hydrocarbons with viscosity $\upsilon > 2\cdot 10^{-6}$ m^2 · s^{-1}. To verify the results obtained experimentally, a diffusive model of hydrocarbons' transport (the initial boundary condition) in the sand - hydrocarbon system was proposed:

$$R_i \frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial z^2} - \mu_i C_i \qquad (9)$$

- $C_i\,(z,0) = 0 \quad \text{for} \quad 0 < z \le S$
- $C_i\,(0,t) = C_{0i} \cdot \exp(-\mu_i \cdot t)$ for $t \ge 0$
- $\frac{\partial C_i}{\partial t} = 0$ for $t > 0$ and $z = S$

The solution of the problem (1) describing the transport of petroleum product in the ground is the equation:

$$C_i(z,t) = \frac{C_{oi} \cdot S}{\sqrt{4 \cdot \pi \cdot D_i \cdot R_i^2 \cdot t}} \exp\left\{-\left[\frac{z^2}{4 \cdot D_i \cdot t} + \mu_i \cdot t\right]\right\} \qquad (10)$$

where:

μ_i - hydrocarbons' biodegradation coefficient [s^{-1}]

C_i - concentration of key component ”i” in the matrix [kg · m^{-3}]

C_{0i} - initial concentration of key component „i” in the matrix [$kg \cdot m^{-3}$]
D_i - equivalent diffusion coefficient of key component ”i” [$m^2 \cdot s^{-1}$]
S - the maximum depth of hydrocarbon penetration through the ground [m]
R_i - retardation factor of key component ”i” in the matrix
t - migration time [s]
z - direction of hydrocarbons' migration [m]

Sand soils usually do not contain organic matter and their sorptivity is smaller than that of migrating organic contaminants and heavy metals ($R_i \rightarrow 1$) [27].

On the basis of coefficients determined for model (9) and the solution (10), the maximum depth of hydrocarbon infiltration into sand soil after time *t* from the leakage can be calculated. The result shows to what degree hydrocarbons' transport is a menace to underground-water table.

Hence, the sought value is the concentration of hydrocarbons C_i which in time t cover the distance z. If z is the distance of contamination source from underground-water table the time of ecological disaster - groundwater contamination can be assessed.

The boundary-value problem (9) is the description of petroleum hydrocarbons' transport in the aeration sphere. The model was verified on the research stand simulating natural ground medium.

Experimental research

To simulate real conditions a propylene model of ground filter with diameter ϕ = 135 mm and height = 2000 mm, was constructed (Fig. 2).

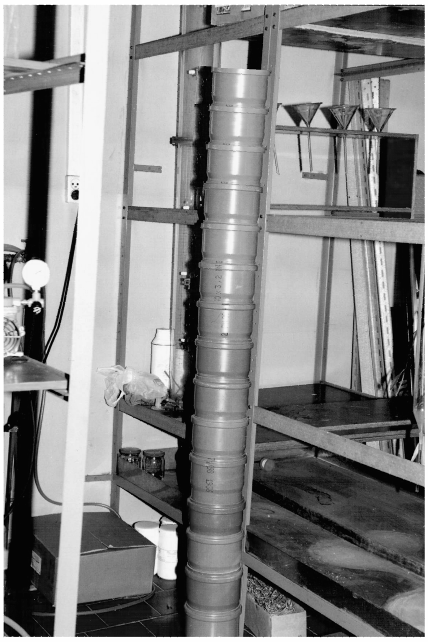

Fig. 2. Model of soil filter for examining the migration of hydrocarbons

The column is a segmented structure consisting of eighteen 100 mm high cylindrical elements filled with the sand and the base the height of 200 mm, filled with gravel (supporting layer).

Three ground matrices with high water permeability and small sorptivity were prepared.

The matrices were obtained by passing natural sand through sieves with diameters $d_1 = 2.0$ mm and $d_2 = 0.5$ mm. The porosity factor of the sorted sand fractions is shown in Table 1.

Table 1

Basic parameters of ground matrices used in research

Sorted sand fraction	**Minimum diameter of sand grain, d_{min} [mm]**	**Maximum diameter of sand grain, d_{max} [mm]**	**Porosity ε [%]**
Soil No. 1	0.5	2.0	34
Soil No. 2	0.25	0.5	33
Soil No. 3	0.033	0.25	31

Sand fractions of soil no. 1, soil no. 2 and soil no. 3 were obtained by sieve separation (according to PN-ISO98/B-04481).

Three aromatic hydrocarbons were used to examine the migration of petroleum contaminants:

- benzene,
- toluene,
- xylene (isomer mixture),

and two aliphatic hydrocarbons (octane numbers ON):

- *n*-hexane,
- *n*-heptane,
- 2,2,4-trimetylopentane.

The experimental research was conducted on the model of the ground filter filled with dry matrix in the following experimental conditions:

- ambient temperature t = (20 ± 0.5)°C,
- air relative humidity: (70 ± 2.5)%,
- atmospheric pressure.

The porosity ε of soil no. 1, soil no. 2 and soil no. 3 was determined in the measuring cylinder of the volume of 250 cm^3 containing 100 cm^3 of the tested hydrocarbons and 200 cm^3 of the previously weighted granular material. When the level of hydrocarbons was determined as value a_w the porosity of matrix ε in relation to petroleum hydrocarbons was calculated according to the formula (11):

$$\varepsilon = \frac{(200+100)-a_w}{200} 100 \quad [\%] \tag{11}$$

where a_w - hydrocarbon volume in the measuring cylinder [cm^3].

The minimum (close to zero) level of petroleum products' biodegradation was assumed. The assumption resulted from the method of preparing the sand to fill the columns (drying at the temperature of 105°C) to obtain dry matter. This system poses a risk - there is high probability that groundwaters will be contaminated with petroleum products due to lack of organic matter and low sorptivity in comparison with migrating oil derivatives ($R_i \rightarrow 1$) [27].

The hydrocarbon concentration in the model of ground filter $C_i(z, t)$ - the value from equation (10) - can be determined by measuring the content of hydrocarbon in each of 18 segments after the set migration time (Figs 3 and 4).

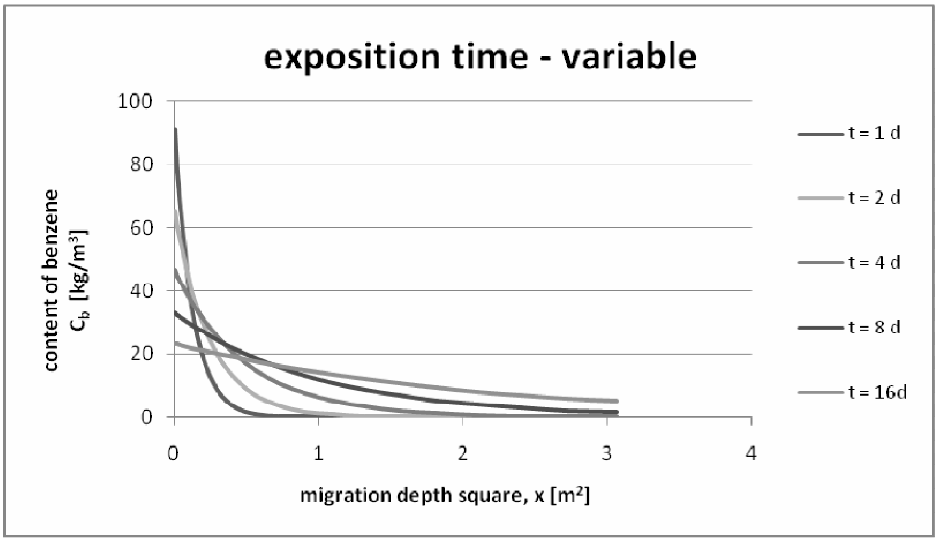

Fig. 3. Distribution of benzene content in the model of ground filter in relation to migration time (soil No. 1)

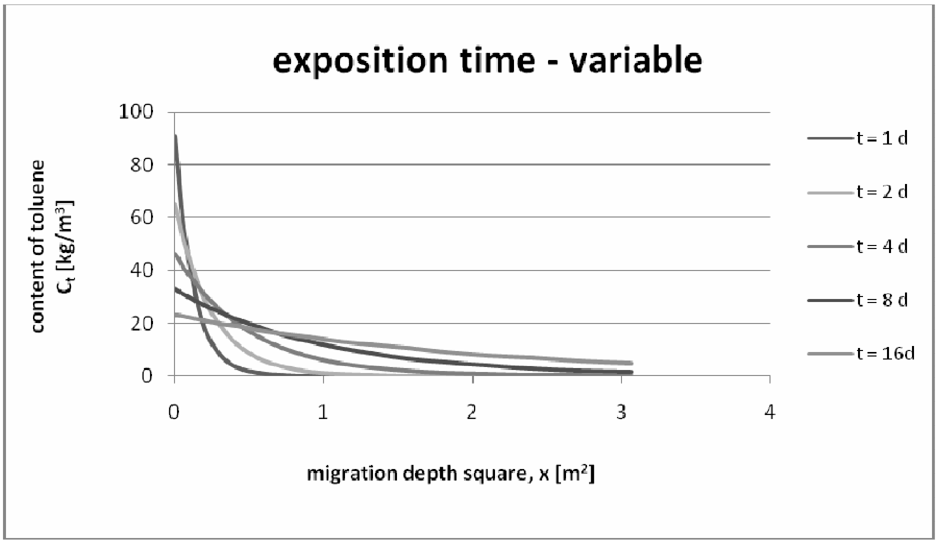

Fig. 4. Distribution of toluene content in the model of ground filter in relation to migration time (soil No. 1)

The biodegradation factor/coefficient μ_i of petroleum hydrocarbons was examined in the single cell of the soil filter where the sand matrix was filled with 290 kg/m^3 d.m., of hydrocarbons which corresponded to filling the pores in 100% volume. The cell was sealed from the top in order to eliminate the loss of hydrocarbons by evaporation (Fig. 5).

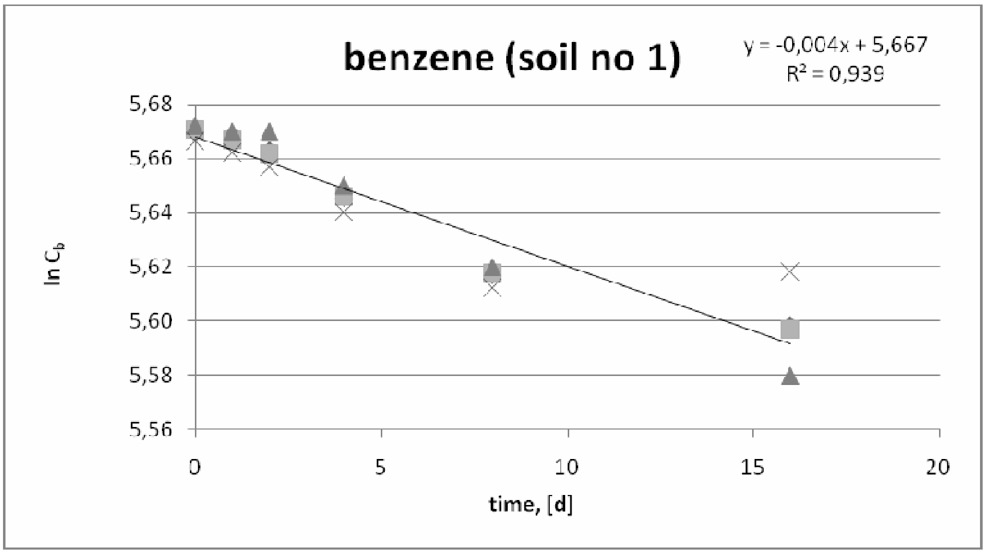

Fig. 5. Loss of benzene in relation to time in soil No. 1

The migration rate of petroleum products was established by determining their content in individual segments in the exposition time t for hydrocarbons: 24, 48, 96, 192 and 384 hours, respectively.

The equivalent diffusion coefficient D_i was determined by inserting 290 kg/m^3 d.m., 145 kg/m^3 d.m. lub 72 kg/m^3 d.m. of the tested hydrocarbon on the top of the column into the sand matrix.

To determine the content of petroleum hydrocarbons in the ground matrix gas chromatography was used. The content of aromatic hydrocarbons was determined by gas chromatograph of INCO N-503 type (a 2-metre column filled with 5% SP-1200 and 1.75% Bentone 34). The content of aliphatic hydrocarbons was determined by gas chromatograph of GCHF 183 type (a 2-metre column filled with 5% Apiezon L on chromosorb W 80/100 mesh).

Results of experimental research and discussion

The results of tests on the soil filter (Figs 3-5) allowed the authors to determine equivalent diffusion coefficient D_i (Fig. 6) and hydrocarbon biodegradation factor, μ_i (Fig. 7).

The value of equivalent diffusion coefficient D_i for petroleum hydrocarbons depends upon the type of sand soil and assumes values in the range $(3.3\div24)\cdot10^{-6}$ m^2 · s^{-1}.

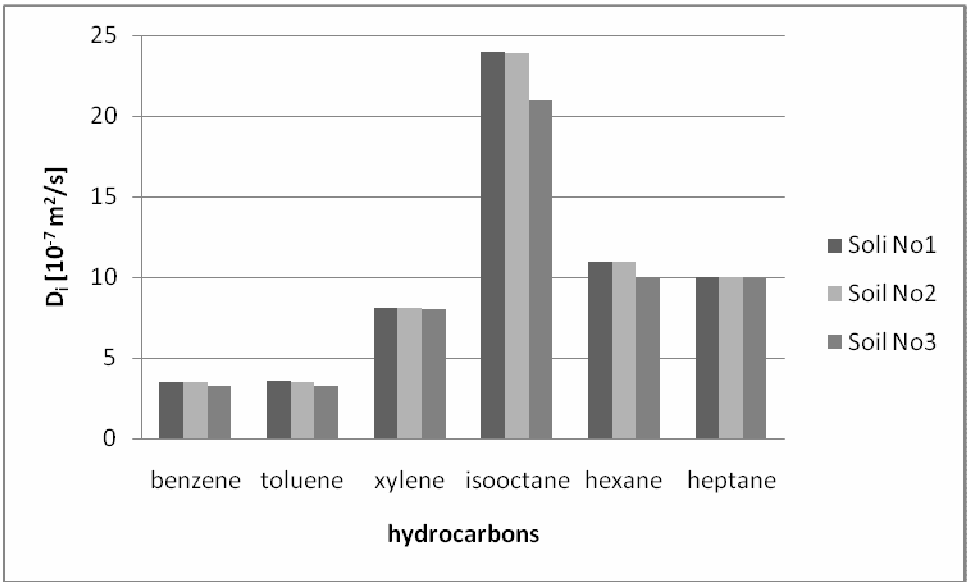

Fig. 6. Values of equivalent distribution coefficient D_i determined on the model of ground filter

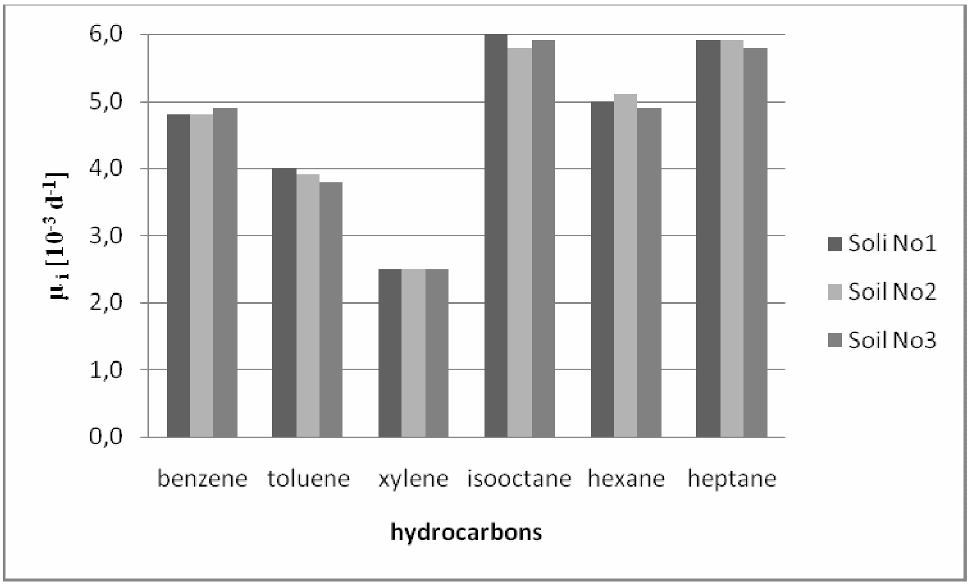

Fig. 7. Comparison of biodegradation coefficient μ_i determined on the model of ground filter

From among hydrocarbons examined benzene has the smallest equivalent diffusion coefficient, it equals $3.5 \cdot 10^{-7}$ m$^2 \cdot$ s^{-1} (Fig. 6).

In spite of that it may be considered the key component of petroleum hydrocarbon mixture. Despite low diffusion coefficient, benzene has the highest water solubility and acutest toxicity.

When predicting the transport of oil derivatives in sand, porous soils hydrocarbon distribution may be estimated as the transport of the key component - benzene.

The value of the biodegradation constant does not practically depend on the grain size of the soil matrix and for toluene oscillates in the range $(3.8 \div 4.0) \cdot 10^{-3}\ \mathrm{d}^{-1}$ (Fig. 7).

Summary and conclusions

The results obtained in the research on the model migration of petroleum hydrocarbons by means of soil filter enable prediction of petroleum hydrocarbons' migration.

It has been proved that function (10) may be used to practically evaluate actual menace caused by hydrocarbons migrating in the soil. On the basis of coefficients determined from model (9) and solution (10) the maximum depth of hydrocarbons' infiltration in the sand soil after time t from the onset of the leakage can be predicted. Basing upon prediction it can be assessed to what extent the transport of hydrocarbons poses threat to the underground water-table.

It has been confirmed that in the experimental conditions the presence of the biodegradation constant in the properly prepared soil matrix only insignificantly influences the concentration loss of the key component as the value of μ_i factor in the range $(2.5 \div 6.0) \cdot 10^{-3}\ \mathrm{d}^{-1}$ is very small.

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MODELOWANIE TRANSPORTU WĘGLOWODORÓW W ŚRODOWISKU GRUNTOWO-WODNYM

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Abstrakt: Przedstawiono dyfuzyjny model transportu węglowodorów w ośrodku porowatym. Model matematyczny pozwala na ocenę ryzyka skażenia wód gruntowych przez migrujące w gruncie węglowodory. Uwzględnienie dyfuzji w równaniu transportu masy pozwala opisać transport węglowodorów w głąb profilu gruntowego. Wprowadzenie równania biodegradacji pozwala na uwzględnienie wpływu mikroorganizmów na obniżenie zawartości węglowodorów, zwłaszcza frakcji olejowych. W celu weryfikacji modelu teoretycznego wykonano serię badań eksperymentalnych na tzw. filtrze gruntowym. Wyznaczono parametry modelu teoretycznego dla benzenu, toluenu, ksylenu, *n*-heksanu, *n*-heptanu oraz 2,2,4-trimetylopentanu.

Słowa kluczowe: transport produktów ropopochodnych, transport w ośrodku porowatym, infiltracja w gruncie, odcieki organiczne, transport węglowodorów w glebie

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USEFULNESS OF NATURAL ESSENTIAL OILS IN THE CONTROL OF FOXGLOVE APHID (*Aulacorthum solani* Kalt.) OCCURRING ON EGGPLANT (*Solanum melongena* L.)

PRZYDATNOŚĆ NATURALNYCH OLEJKÓW ETERYCZNYCH W ZWALCZANIU MSZYCY ZIEMNIACZANEJ (*Aulacorthum solani* Kalt.) WYSTĘPUJĄCEJ NA OBERŻYNIE (*Solanum melongena* L.)

Abstract: The purpose of the study was to determine the efficacy of natural essential oils, such as basil oil, citronella oil, eucalyptus oil, juniper oil and patchouli oil, in the control of foxglove aphid (*Aulacorthum solani* Kalt.) occurring on eggplant. The above-mentioned oils were used at concentrations of 0.02, 0.05 and 0.10%. The mortality of pest was evaluated 24, 48 and 72 hours after treatment. After application of citronella oil and patchouli oil at a concentration of 0.05 and 0.10% and juniper oil at 0.10%, 100% mortality of *A. solani* was observed. In the remaining combinations with the use of tested essential oils mortality amounted to 24.63÷89.40% (72 hours after treatment).

Keywords: natural essential oils, eggplant, *Aulacorthum solani*, control

Increasing problems have been observed in recent years in the control of pests found on crops, including aphids. These results first of all from the generation of pest biotypes resistant to applied chemical preparations. At the same time the range of admissible plant protection agents has been considerably reduced. In view of the Directive of the European Union many active substances of these preparations have been withdrawn from use in plant protection due to their being a hazard for human health and for the natural environment (Directive of the EEC Council of 15.07.1991, consolidated version of 01.08.2006, on the marketing of plant protection products - 91/414/EEC) [1]. Thus it is necessary to search for new, alternative methods of pest control. At present in plant protection we may observe increasing interest in the applicability of natural origin preparations, based on essential oils produced from different plant species. Essential oils are characterized by a complex chemical composition (Table 1) and many compounds they contain exhibit toxic or repellent action against pests.

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Table 1

A list of the most important chemical compounds found in natural essential oils used in the study and their contents [%] [2-6]

Essential oil	Monoterpenes	Monoterpenols	Sesquiterpenes	Sesquiterpenols	Esters	Ethers	Phenols	Aldehydes	Oxides
Basil oil	Ocimene 1-3 Limonene 1-2 Myrcene 0.1-2 Alpha-pinene 0.5-1 Beta-pinene <1	Linalool 35-54 Citronellol 2-4 Terpinen-4-ol 2-4	-	-	Methyl cinnamate 4 Geranyl acetate 1-2	Methyl chavicol 0-5	Eugenol 5-6		-
Citronella oil	Limonene 1-5	Geraniol 20-25 Citronellol 9-15	-	-	-	-	-	Citronellal 30-45 Geranial < 2 Neral < 2	-
Eucalyptus oil	Pinenes 3-30 Limonene 0-4	-	-	-	-	-	-	-	1,8 cineole 40-85
Juniper oil	Alpha-pinene 33-45 Myrcene 11-20 Beta-farnesene 10 Camphene 3-4 Carene 1-2 Limonene 1-2 Sabinene 3	-	-	-	-	-	-	-	-
Patchouli oil	-	-	Alpha patchoulene 22 Beta caryophyllene 20 Beta patchoulene 13	Patchoulol 30-40 Bulnesol 1-3 Pogostol 1-3	-	-	-	-	-

The aim of the study was to determine the efficacy of selected natural essential oils in the control of foxglove aphid (*Aulacorthum solani* Kalt.) occurring on eggplant (*Solanum melongena* L.).

Materials and methods

Experiments on the efficacy of natural essential oils in the control of foxglove aphid (*A. solani*) occurring on eggplant were conducted in 2009. The following essential oils were tested: basil (*Ocimum basilicum*), citronella (*Cymbopogon winterianus* Jowitt), eucalyptus (*Eucalyptus globulus*), juniper (*Juniperus communis*) and patchouli (*Pogostemon patchouli*) oils, which were applied at a concentration of 0.02, 0.05 and 0.10%. The above-mentioned aroma substances were produced by Pollena-Aroma Sp. z o.o., Warsaw, Poland. Leaves of eggplant cv. "Epic" infested by the pest were removed from plants and immersed for 3 s in the prepared solution (water emulsion) containing different combinations of essential oils at appropriate concentrations. After leaves were removed from the solution they were placed for several seconds in the vertical position for excess liquid to drip down. In order to obtain o homogenous emulsion an emulsifier, RO-1, was added to solutions of tested oils at a concentration of 0.0125%. In the conducted experiments the effect of the emulsifier RO-1 on mortality of foxglove aphid was also tested by treating the pest with its solution at the applied concentration. In the control combination no essential oils were applied and eggplant leaves infested by the bug were immersed in water with no addition of aroma substances. Each combination was performed in 10 replications. After the oils were spread, leaves were placed on glass dishes lined with moistened filter paper and next plastic plates with holes of 35 mm in diameter were placed on leaf surface. The number of pests was counted in the location of holes in these plates. After counting was completed plates with holes were covered with glass plates, constituting a physical barrier preventing migration of bugs. Filter paper was moistened with water daily in order to maintain leaf turgor.

The efficacy of tested essential oils was determined after 24, 48 and 72 h. Results were analyzed statistically using the Newman-Kels test at the significance level $p = 0.05$.

Results and discussion

In the conducted experiments high efficacy of natural essential oils was recorded in the control of foxglove aphid (*A. solani*). After the application of citronella and patchouli oils at a concentration of 0.05 and 0.10%, as well as juniper oil at 0.10% a 100% mortality of the examined pest was recorded at 72 h after treatment. In the other combinations of tested essential oils mortality of the bug on the last day of observations was 24.63÷89.40% (Table 2).

At the same time no effect on survival rates of foxglove aphids was found for the emulsifier RO-1 applied at a concentration of 0.0125%. No significant differences were found in terms of mortality between pests treated with an emulsifier solution and the control.

Literature contains information on the suitability of natural essential oils in the control of different pest species, although data concerning aphids are relatively scarce. Digilio et al [7] found high mortality of pea aphid (*Acyrthosiphon pisum* Harris) and green peach aphid (*Myzus persicae* Sulzer) following the application of oils produced from anise (*Pimpinella* *anisum* L.), basil (*Ocimum basilicum* L.) and fennel (*Foeniculum officinale* All.). Satisfactory results in the control of peach aphid were recorded by Chiasson et al [8] when applying oil from wormseed goosefoot (*Chenopodium ambrosioides* L.). In turn, Masotoshi [9] showed a strongly toxic action against peach aphid for oils from penny-royal (*Mentha pulegium* L.) and garden thyme (*Thymus vulgaris* L.). Usability of different essential oils, including thyme oil, in the control of cabbage aphid (*Brevicoryne brassicae* L.) was determined by Görür et al [10]. Thyme oil exhibited the strongest action, mainly due to the content of such compounds as carvacrol and thymol. High mortality of pests was also reported after the application of oil produced from drug speedwell (*Veronica officinalis* L.) and agrimony (*Agrimonia eupatoria* L.). Essential oils used in the control of cabbage aphid when applied at lower doses caused reduced fertility of the pest. As it was reported by Soliman [11], high efficacy in the control of cotton aphid (*Aphis gossypii* Glover) was observed for essential oils produced from two wormwood species, ie *Artemisia herba-alba* (Asso) and *Artemisia monosperma* (Delile), with the former exhibiting higher effectiveness.

Table 2

Average mortality of foxglove aphid (*Aulacorthum solani* Kalt.)
occurring on eggplant after application of natural essential oils

Essential oil	**Concentration [%]**	**No. of hours after treatment**		
		24	**48**	**72**
		mortality [%]		
Patchouli oil	0.02	31.38 ab*	35.50 ab	36.03 a
	0.05	91.04 d	100.00 d	100.00 c
	0.10	96.40 d	100.00 d	100.00 c
Citronella oil	0.02	35.29 ab	53.96 bc	58.90 ab
	0.05	59.66 bc	96.44 cd	100.00 c
	0.10	96.57 d	100.00 d	100.00 c
Juniper oil	0.02	22.28 a	34.47 a	39.22 a
	0.05	26.71 ab	54.01 bc	71.60 ab
	0.10	92.18 d	100,00 d	100,00 c
Basil oil	0.02	21.33 a	46.56 bc	49.84 a
	0.05	39.68 ab	59.08 bc	84.24 b
	0.10	69.11 c	85.00 cd	89.40 b
Eucalyptus oil	0.02	16.55 a	20.07 a	24.63 a
	0.05	17.69 a	44. 26 ab	67.53 ab
	0.10	37.54 ab	61.00 bc	68.69 ab
Emulsifier RO-1	0.0125	21.55 a	24.45 a	28.05 a
Control	–	21.43 a	24.56 a	28.71 a

* Means in columns denoted with identical letters do not differ significantly ($p = 0.05$) according to Newman-Keuls' test

Natural essential oils not only exhibit toxic action against aphids, but also may have a repellent activity. Masotoshi [12, 13] reported that such properties in relation to peach aphid (*M. persicae*) are shown by ginger (*Zinigiber* spp.), lavender (*Lavandula officinalis* Chaix), peppermint (*Mentha piperita* L.), spear-mint (*M. spicata* L.), thyme (*Thymus vulgaris* L.) and rosemary (*Rosmarinus officinallis*) oils. At the same time that author found that among the 13 tested chemical compounds contained in rosemary oil a repellent action in relation to *M. persicae* is exhibited by such compounds as linalool, d,1-camphor and terpineol. According to Masotoshi [12] rosemary oil also shows repellent action in relation to cotton aphid (*A. gossypii* Glover) and potato aphid (*Macrosiphum euphorbiae* Thomas), also repelled by ginger oil.

Conclusions

1. Natural essential oils such as citronella oil, juniper oil and patchouli oil may be useful in the control of foxglove aphid (*Aulacorthum solani* Kalt.). After application of these oils 100% mortality of the pest was recorded.
2. A lower efficacy in the control of *A. solani* was found for the other tested natural essential oils, which exhibited 24.63÷89.40% efficacy (72 hours after treatment).

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PRZYDATNOŚĆ NATURALNYCH OLEJKÓW ETERYCZNYCH W ZWALCZANIU MSZYCY ZIEMNIACZANEJ (*Aulacorthum solani* Kalt.) WYSTĘPUJĄCEJ NA OBERŻYNIE (*Solanum melongena* L.)

Katedra Metod Ochrony Roślin, Uniwersytet Przyrodniczy w Poznaniu

Abstrakt: Celem badań było określenie skuteczności naturalnych olejków eterycznych, takich jak: bazyliowy, cytronelowy, eukaliptusowy, jałowcowy i paczulowy w zwalczaniu mszycy ziemniaczanej (*Aulacorthum solani* Kalt.), występującej na oberżynie. Wyżej wymienione olejki stosowano w stężeniach 0,02; 0,05 i 0,10%. Śmiertelność szkodnika określono po 24; 48 i 72 godzinach po zabiegu. Po zastosowaniu olejków: cytronelowego i paczulowego o stężeniach 0,05 i 0,10% oraz jałowcowego - 0,10% zanotowano 100% śmiertelność *A. solani*. W pozostałych kombinacjach z użyciem testowanych olejków śmiertelność wynosiła 24,63÷89,40% (72 godziny po zabiegu).

Słowa kluczowe: naturalne olejki eteryczne, oberżyna, *Aulacorthum solani*, zwalczanie

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STUDY OF INTERACTION BETWEEN HUMIC ACIDS AND FULLERENE C_{60} USING FLUORESCENCE QUENCHING APPROACH

BADANIE ODDZIAŁYWAŃ MIĘDZY KWASAMI HUMINOWYMI I FULERENAMI C_{60} Z WYKORZYSTANIEM SPEKTROSKOPII FLUORESCENCYJNEJ

Abstract: The interaction between buckminsterfullerene C_{60} and humic acids (HA) of different origins was compared using fluorescence spectroscopy as a function of pH, humic acid concentration, ionic strength. Binding constants between fullerene and humic acids were calculated. It can be suggested that the complexation was driven by hydrophobic interactions depending on the properties of the interacting compounds. Hydrophobic interaction model as indicated by linear Stern-Volmer plots and high K_d values is characterizing the interaction between buckminsterfullerene C_{60} and humic acids The results of this study support the development of understanding of the fate of nanomaterials in the environment as well as the development of analytical methods for nanomaterials in waters and wastewater treatment approaches.

Keywords: humic acid, fluorescence spectroscopy, fullerene C_{60}, binding

The growth of nanotechnology applications requires environmental impact assessment of elaborated nanomaterials to reduce environmental risks in case of their releases and possible pollution. Buckminsterfullerene C_{60} is an example of carbon containing nanomaterials with diversity of potential applications [1, 2], but also possible environmental and health effects [3, 4]. Poor solubility of C_{60} in natural waters is a major factor controlling environmental transport and biological interactions. However in several studies toxic impacts on living organisms has been found related to necrotic and apoptic cellular damage and impacts on fish embryos [5], but also other types of the toxic action might be identified [6]. The first phase of the action on living organisms in the aquatic environment could be the action of nanoparticles, carbon nanomaterials and also C_{60} with natural organic matter - humic substances [7, 8].

Humic substances in surface waters have a key role in terrestrial and aquatic biogeochemistry [9]. Humic substances (HS) are the most widely found naturally occurring

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organic substances [10]. Humic substances are a general category of naturally occurring, biogenic, heterogeneous organic substances that can generally be characterized as being yellow to black in color, of high molecular weight and refractory. Humic substances can be divided in three fractions: a) humin is the fraction of humic substances that is not soluble in water at any pH; b) humic acid (HA) is the fraction of humic substances that is not soluble in water under acidic conditions (below pH = 2), but becomes soluble at greater pH values; c) fulvic acid is the fraction of humic substances that is soluble under all pH conditions [10]. Humic substances influence mineral weathering, nutrient cycling, aggregation and photochemical reactions in waters and they are a substrate for bacterial growth in hydroecosystems and control light absorption [11-14].

The interaction of humic substances with xenobiotics may modify the uptake and toxicity of these compounds, and affect the fate of pollutants in the environment [15, 16].

It is found that aquatic humic substances (HA) can solubilise fullerene C_{60} and their apparent water solubility in presence of HAs can be ~ 500 times higher than in pure water. A significant stage in the solubilisation process plays the adsorption of C_{60} on humic substances and this process might influence the behaviour of nanoparticles in the environment [17].

To study interaction between humic substances and buckminsterfullerenes high performance liquid chromatography on a humic acid stationary phase has been suggested [18], but also dynamic light scattering has been used [19]. However, as a tool to study complex formations with humic substances, a fluorescence spectroscopic method (fluorescence quenching due to complex formation) has found widespread application [16, 20]. This method has an advantage in that it is a simple, quick and reliable method avoiding the complicated separation of the complex from individual substances [21].

The aim of the present study is to analyse the complex formation between humic substances and fullerene C_{60}, the impact of environmental factors and properties of humic substances.

Materials and methods

Analytical quality reagents were used without further purification. All chemicals used in this study were of analytical quality. For the preparation of solutions, high purity water Millipore Elix 3 (Millipore Co.) 10÷15 MΩ/cm was used throughout.

Table 1

Composition and characteristics of the humic acids used in this study

	Aldrich HA	**Leonardite HA**	**Daugava HA**	**Gagu HA**
Elemental analysis [%]				
C	60.70	63.81	51.42	54.32
H	3.70	3.70	4.48	5.03
N	1.50	1.23	0.97	2.36
O	34.10	31.27	40.21	36.78
Functional analysis				
COOH [mEq/g]	2.15	3.16	4.34	4.15
Total acidity [mEq/g]	3.32	5.77	5.39	5.63
O/C	0.65	0.37	0.59	0.51
H/C	1.13	0.69	1.04	1.10
E_4/E_6	4.51	3.65	8.97	5.84

The fullerene was purchased from TCI Europe nv Belgium.

Humic acids from Gagu bog (Latvia) peat were extracted and purified using procedures recommended by the International Humic Substances Society (IHSS) [22]. Humic acids from waters of the River Daugava (Latvia) were obtained as suggested by Thurman and Malcolm [23]. Reference humic acids were purchased from Sigma-Aldrich Co (Aldrich HA) and the International Humic Substances Society (Leonardite HA). The properties of the studied humic substances are as reported in Table 1.

Fullerene solutions were made as previously described [24] in dimethyl sulfoxide because of its poor solubility in water. Stock solution concentration of fullerene was 10 mg/dm^3. Solution of Aldrich HA was prepared by dissolving necessary amount of HA in water, however Leonardite, Gagu and Daugava HA were dissolved in 0.1 M NaOH and then diluted to the necessary concentration. Aliquots of the stock solutions of HS and fullerene were mixed 1:1. Final concentration of HA was 5 mg/dm^3, but final concentrations of fullerene were 5, 4, 3, 2, 1, 0.5 and 0.1 mg/dm^3. The solution of HS and fullerene was poured into a quartz cell. The fluorescence spectra were obtained on a spectrofluorometer Perkin Elmer LS55 at room temperature (25°C). The fluorescence emission spectra results were recorded at a speed of 500 nm/min, at a excitation $\lambda = 350$ nm, 8 nm (Ex) and 8 nm (Em) slit widths.

Influence of pH on interactions of HA-fullerene. Aldrich HA was dissolved in water, and Leonardite HA was dissolved in 0.1 N NaOH (final concentration of HA was 5 mg/dm^3) and mixed with the stock solution of fullerene to reach a final concentration of fullerene (5 mg/dm^3); pH values were adjusted to fixed values from pH 3.09 to pH 8.98 with 0.1 N HCl and 0.1 N NaOH. Conditions for fluorescence analyses were as previously mentioned.

Influence of ionic strength on interactions of HA-fullerene. Binding sites of HS were investigated using a solution of HA, fullerene and $NaNO_3$ so that the concentrations of $NaNO_3$ were 1 mol/dm^3, 0.75 mol/dm^3, 0.5 mol/dm^3, 0.25 mol/dm^3, 0.1 mol/dm^3 and 0.05 mol/dm^3, while the final concentrations of HA was 5 mg/dm^3 and the fullerene was also 5 mg/dm^3. Solutions were well mixed and fluorescence emission spectra were then recorded.

Results and discussion

The synchronous-scan fluorescence excitation emission spectra (SSFS) of humic substances are shown in Figure 1 and they differ significantly depending on the origin of the humic acids: spectra of highly humified HAs (IHSS reference humic acids: Leonardite HA, the industrially produced Aldrich HA, peat HA and aquatic HA) were characterized by two major fluorescence peaks. Aquatic humic acid isolated from water of the River Daugava was characterized by one peak ($\lambda \sim 375$ nm), but peat humic acid (isolated from Gagu sphagnum bog peat) was characterized by two peaks ($\lambda \sim 345$ and 375 nm). Synchronous scan spectra of humic substances isolated from highly humified organic material (leonardite, coal) had an intensive fluorescence peak $\lambda \sim 475$ nm that was determined by the presence of conjugated unsaturated bond systems bearing carbonyl and carboxyl groups (substituting aromatic core structures), but its intensity differed with respect to aromaticity of the humic acid selected [25].

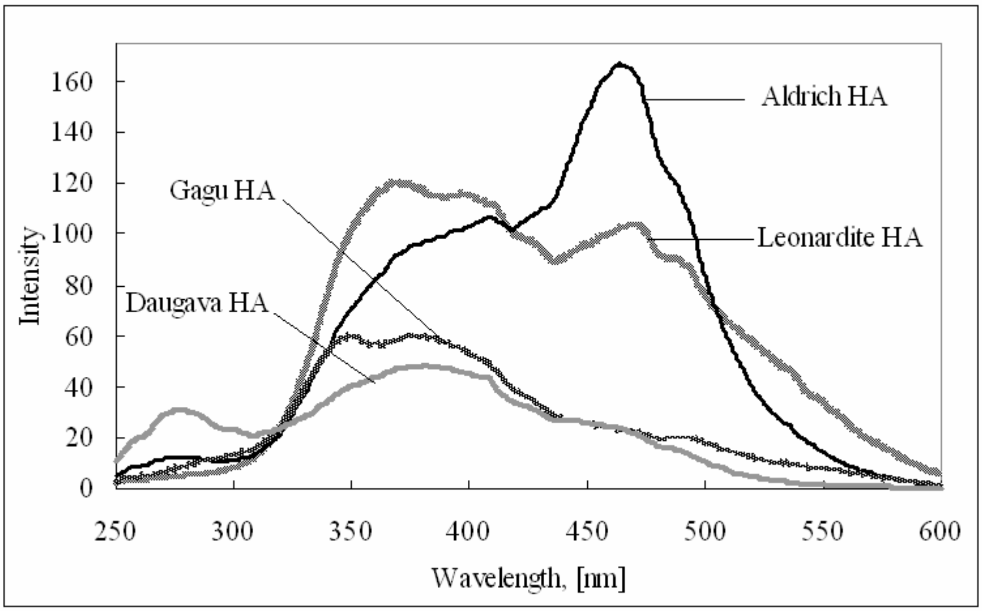

Fig. 1. Fluorescence synchronous spectra of humic acids used in the study (γ_{HA} = 25 mg/dm^3, pH = 7)

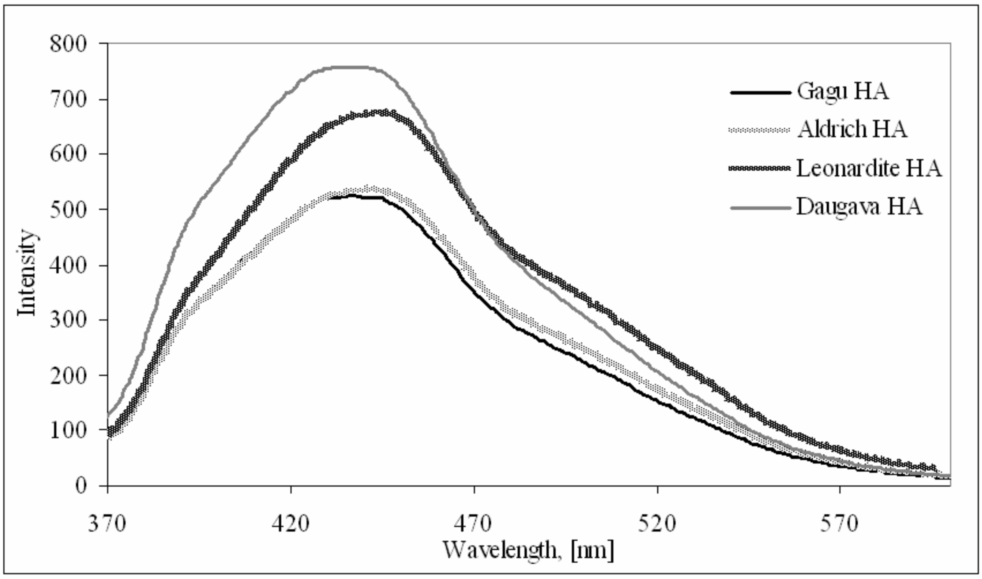

Fig. 2. Fluorescence emission spectra of humic acids used in the study (γ_{HA} = 5 mg/dm^3, excitation λ = 350 nm)

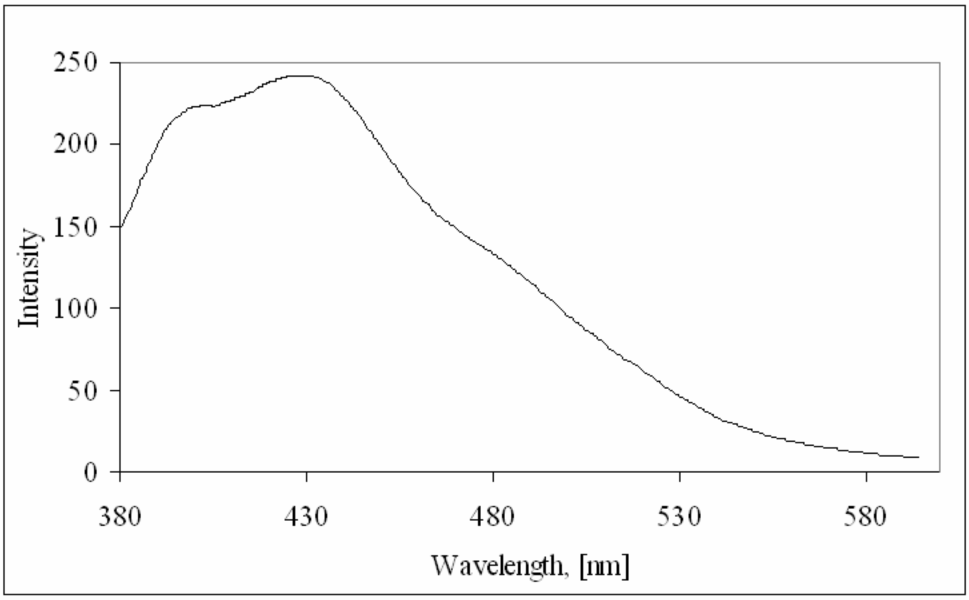

Fig. 3. Fluorescence emission spectra of fullerene (γ_{C60} = 5 mg/dm^3, excitation λ = 350 nm)

Fluorescence emission spectra of studied humic acids are shown in Figure 2. However in comparison to SSFS emission spectra does not show great differences - their main differences are intensity and wavelengths where is located fluorescence maxima of each humic substance. This may be attributed to the different modifications of the fluorophoric structures in humic molecules.

Fluorescence emission spectra of fullerene C_{60} (Fig. 3) is similar to that of humic substances, but comparatively intensity of fullerene emission spectra is lower and also fluorescence maxima peaks were slightly shifted towards the shorter wavelengths.

The fluorescence emission spectra of the studied humic acid in the presence and absence of fullerene demonstrated quenching of the fluorescence peak λ ~440 nm, associated with the presence of aromatic structures in humic molecules (Fig. 4). Thus, the fluorescence quenching methodology in our study differs from the approach used to study binding between humic substances and polyaromatic hydrocarbons [15]. As far as this case is concerned, the fluorophore structures in the humic molecules were quenched and the fullerene was the quencher. In this respect the interaction between humic acids is similar to that with metal ions [26] and carbamazepine [20] and such an approach supports the interaction analysis between humic substances and a large number of substances of interest. The fluorescence intensities of peaks at λ ~440 nm exhibited a successive decrease as the concentrations of the fullerene increased (Fig. 4).

The intensity of the fluorescence quenching is supposed to be proportional to the concentration of the formed humic substance - substance of interest complex according to the Stern-Volmer equation [27]. The fluorescence of the humic acids quenching mechanism by fullerene is considered in the 1:1 interaction model.

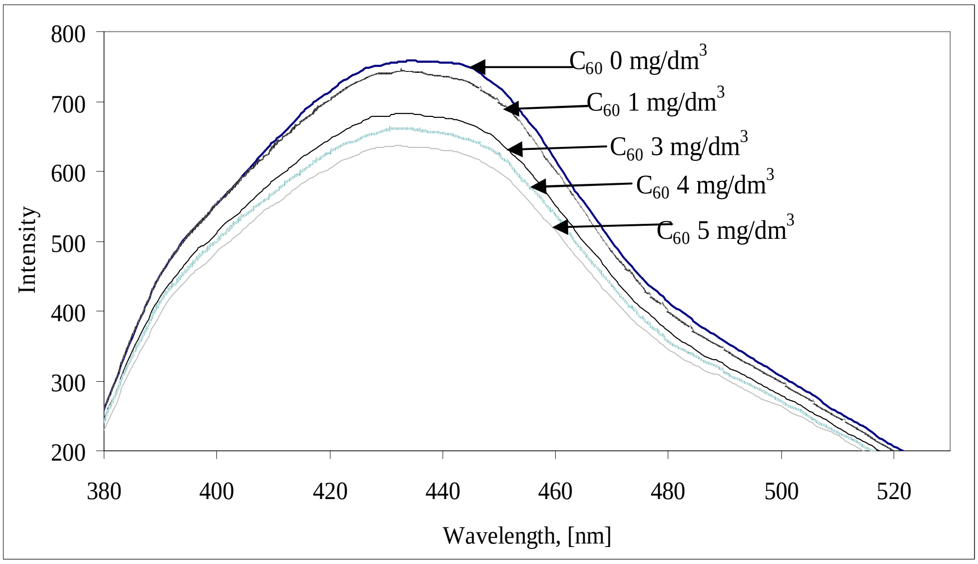

Fig. 4. Fluorescence emission spectra of Daugava HA in the absence and presence of fullerene (γ_{HA} = 5 mg/dm^3)

The binding constants are obtained by steady-state fluorescence quenching measurements and are given as a slope in the Stern-Volmer plot. The interaction between humic substances and fullerene (C_{60}) can be described as follows:

$$C_{60} + HA = C_{60}–HA \tag{1}$$

With the corresponding binding constant K_b:

$$K_b = \frac{[C_{60} - HA]}{[C_{60}][HA]} \tag{2}$$

The total concentration of the humic acid HA_t can be expressed as a sum of free HA_f and bound to humics HA_b:

$$HA_t = HA_f + HA_b \tag{3}$$

By substituting Eq (2) into Eq (3) we obtain:

$$HA_t = HA_f + HA_f K_b[C_{60}] \tag{4}$$

$$\frac{HA_t}{HA_f} = 1 + K_b[C_{60}] \tag{5}$$

As far as fluorescence intensity ratio of the initial substance and fluorescence in the presence of quencher, I_0/I is proportional to HA_t/HA_f then Eq (5) can be modified to:

$$\frac{I_0}{I} = 1 + K_b[C_{60}] \tag{6}$$

However, for practical application the equilibrium concentration of fullerene $[C_{60}]$ can be replaced by the total concentration C_{C60} as the concentrations of the C_{60} bound to humic substances under the experimental concentrations were much lower than the concentrations of the humic substances:

$$\frac{I_0}{I} = 1 + K_b C_{C60} \tag{7}$$

And thus the binding constant can be calculated:

$$K_b = \frac{\frac{I_0}{I} - 1}{C_{C60}} \tag{8}$$

The character of the relationships from modified Stern-Volmer plots (Fig. 5) offer strong support for the 1:1 complex ($r^2 > 0.97$).

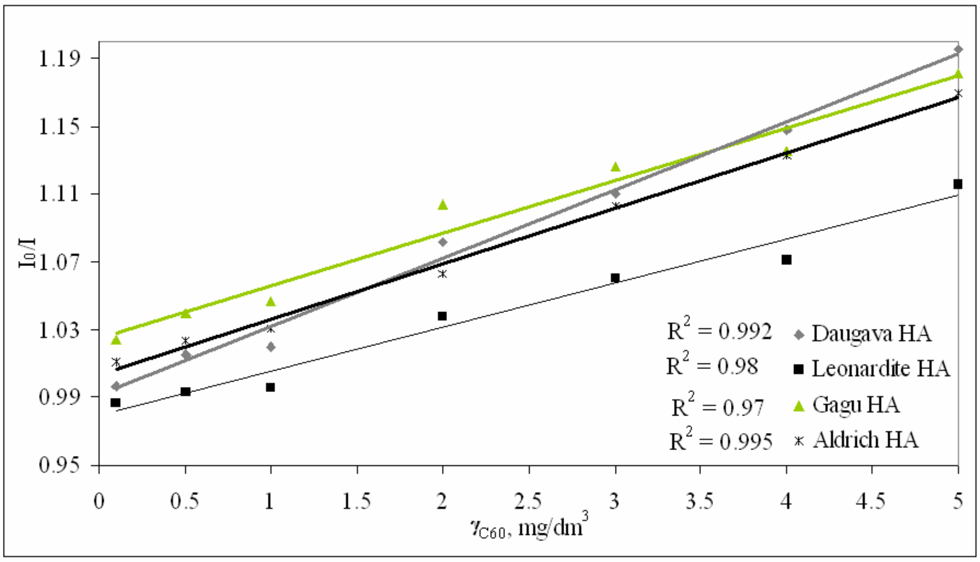

Fig. 5. Stern-Volmer plots: the ratio of I_0/I of HA-C_{60} as a function of γ_{C60} (γ_{HA} = 5 mg/dm^3)

Quenching may occur by a wide range of mechanisms as either static or dynamic quenching. Dynamic quenching is a process where the fluorophore and the quencher come into contact during the lifetime of excited state and involves energy transfer, while static quenching is a process where non-fluorescent complex of the ground state fluorophore are formed. For monodisperse systems fluorescence quenching data have a linear dependence when presented as a Stern-Volmer plot. By plotting I_0/I against concentration of quencher and deviations from linearity carry information on the nature of the quenching process and fluorophore-quencher interaction [28]. If the linear Stern-Volmer plot is indicative of a single class of fluorophores with equal accessibility to the quencher, then a combination of dynamic and static quenching typically produces non-linear Stern-Volmer plots [29]. Therefore it is very important reason to explore the linearity of Stern-Volmer plots; it is an excellent tool to understand organic matter interactions with fullerene nanoparticles.

Fluorescence quenching of humic acid by fullerene was described by linear Stern-Volmer plots (Fig. 5), therefore it is possible that there is only one quenching process, on a base of HA - fullerene interaction. This quenching most likely involves one - static or dynamic quenching mechanism. In comparison with interaction of other nanoparticles (for example iron nanoparticles) and humic substances, Stern-Volmer plots is non-linear - indicating more than one quenching process [28], but interaction between humic substances - pyrene and its derivatives shows linear Stern-Volmer plots [16] as well as interaction between phenanthrene and humic substances, which also suggest that either static and dynamic fluorescence quenching mechanism dominate [30]. However interaction between fullerene (C_{60}) and cryptophanes A and E shows linear Stern-Volmer plots and similar to our study fluorescence of the studied substance is quenched by fullerene. It is suggested that fullerene may interact with natural organic matter due hydrophobic interaction model [31, 32].

The calculated log K_b, values for different humic acids and fullerene are shown in Figure 6.

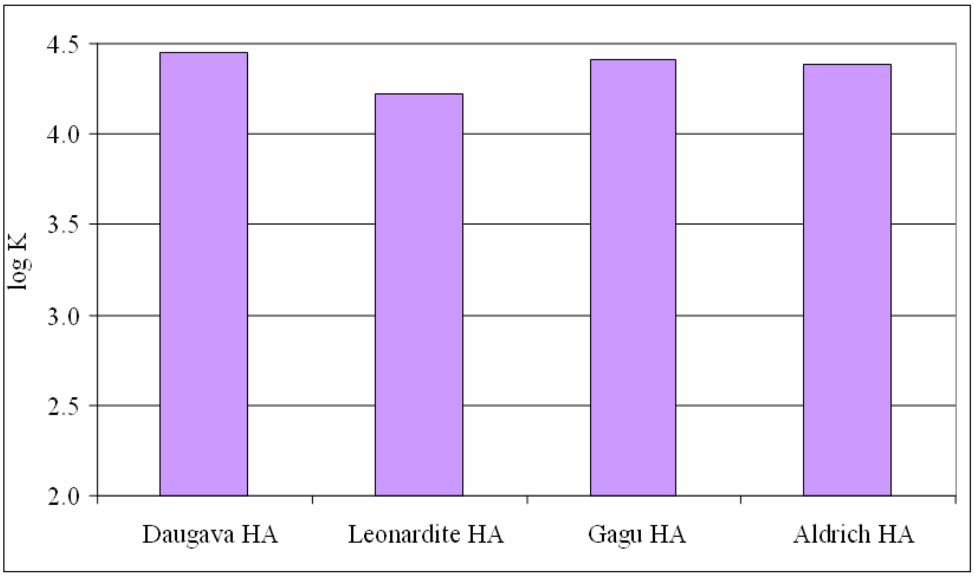

Fig. 6. Stern-Volmer binding constants (K_b, dm^3/mol) between the studied humic substances (γ_{HA} = 5 mg/dm^3) and fullerene (γ_{C60} = 5 mg/dm^3)

For the studied humic substances and fullerene, the log K value ranged from 4.11 to 5.25 dm^3/mol. The observed log K_b values for the interaction between fullerene and studied humic acids was similar with the value found in a previous study (log K_b = 3.85 – 4.82 dm^3/mol) using soil humic acid and polycyclic aromatic compounds [15] and also interaction between fullerene and cryptophanes shows log K values from 4.93 to 5.93 dm^3/mol [31]. Strong binding was found in the case of the interaction between Gagu HA and fullerene. The lower log K value was for the interaction between fullerene (γ_{C60} = 4 mg/dm^3) and Leonardite HA (γ_{HA} = 5 mg/dm^3) log K_b = 4.11.

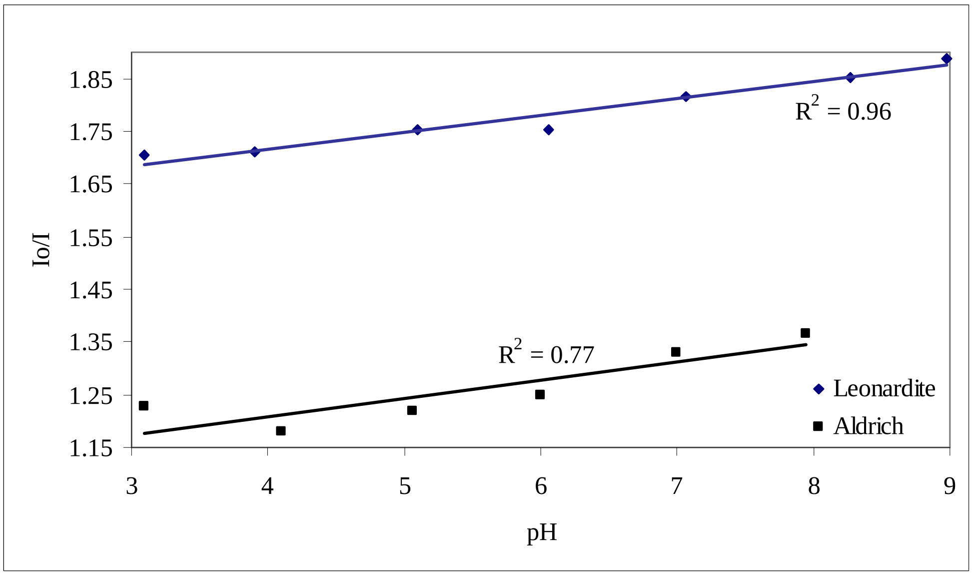

Fig. 7. Influence of pH on fluorescence quenching of humic acids by fullerene (γ_{HA} = 5 mg/dm^3, γ_{C60} = 5 mg/dm^3)

To understand the likely fate and behavior of nanoparticles in environment it is important to understand their interaction with natural environment components under a variety of physicochemical conditions, for example pH, a type and concentration of natural organic macromolecules. It is suggested that the aggregate size increases with increasing humic acid concentration and pH. It could have one or more reasons, for example increased particle aggregation, increased humic acid adsorption, because of the increase of surface coating thickness, changing humic acid conformation, additional formation of nanoparticle layers on the existing particles by further hydrolysis with the increase in pH [8]. It also could be related to pH based chemical changes, leading to electronic changes in humic acid molecules, full deprotonation of carboxylic and other functional groups leading to charge repulsion and change in the conformation of the humic acid as pH increases [28]. The pH will affect dissociation of functional groups and develop differences in amount of negative charge on the humic substances. At lower pH values there is less dissociation, at neutral pH humic substances reduce electrostatic forces by aligning hydrophobic structures together in a core and aligning charged functional groups in the molecule towards solvating water molecules. On higher pH, there will be more dissociation but it will be energetically more favourable for the hydrophobic groups to align on a surface [33].

Obviously in Figure 7 fluorescence quenching at a constant nanoparticle and constant humic acid concentration is highly pH dependent. It could be suggested that humic - C_{60} interaction is influenced by the conformation changes of humic substances.

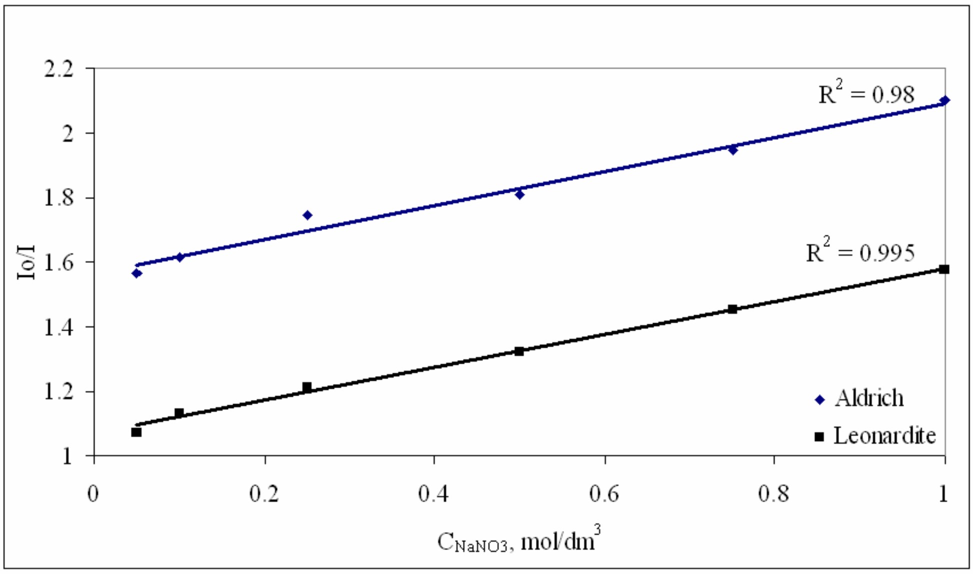

Fig. 8. Influence of ionic strength on fluorescence quenching by fullerene. γ_{HA} = 5 mg/dm^3, γ_{C60} = 5 mg/dm^3

Figure 8 shows that with increasing ionic strength the fluorescence intensity of HA - C_{60} complex significantly decreased. As mentioned earlier pH affects particle size and also ionic strength can alter size of particles and thus the stability of the formed complexes as it is found on example of humic-polyaromatics interaction [33]. This may indicate the preferential binding of highly hydrophobic fullerene (C_{60}) to more hydrophobic structures, with consecutive changes in the conformation of humic macromolecules.

Conclusions

C_{60} buckminsterfullerene causes quenching of the fluorescence signal of humic substances and the intensity of the quenching is proportional to C_{60} concentration. Thus the ratio I_0/I can be used to estimate the complex forming process as known in metal - humic interaction studies.

We have determined the binding constants between fullerene and studied humic acids, using fluorescence quenching technique. Obtained values are similar to that determined in other studies between humic substances and polycyclic aromatic hydrocarbons. Our findings suggest that a hydrophobic interaction plays a dominant role in the complex formation between humic acids and fullerene C_{60}. The importance of the hydrophobic attraction between humic acids and fullerene C_{60} was also confirmed by a salt effect and pH dependence of the fluorescence quenching effect. The hydrophobic interaction between fullerene C_{60} and HA was weakened at low pH, resulting in a decrease in the binding constants. The results of this study support the development of an understanding of the fate of nanomaterials in the environment as well as the development of analytical methods for nanomaterials in waters and wastewater treatment approaches.

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BADANIE ODDZIAŁYWAŃ MIĘDZY KWASAMI HUMINOWYMI I FULERENAMI C_{60} Z WYKORZYSTANIEM SPEKTROSKOPII FLUORESCENCYJNEJ

Abstrakt: Porównywano oddziaływania między buckminsterfulerenami C_{60} i kwasami huminowymi (HA) różnego pochodzenia w zależności od pH, stężenia kwasów huminowych i siły jonowej. Do badań stosowano spektroskopię fluorescencyjną. Obliczono stałe trwałości związków kwasów huminowymi i fulerenów. Można przypuszczać, że kompleksowanie jest powodowane oddziaływaniami hydrofobowmi, zależnymi od właściwości związków. Model interakcji hydrofobowych wskazanych przez liniowe zależności Sterna-Volmera i duże wartości K_d charakteryzują interakcje między buckminsterfulerenami C_{60} i kwasami huminowymi. Wyniki opisanych badań są ważne dla poznania losu nanomateriałów w środowisku, a także dla rozwoju metod analizy zawartości nanomateriałów w wodach oraz metod oczyszczania ścieków.

Słowa kluczowe: kwasy huminowe, spektroskopia fluorescencyjna, fulereny C_{60}, wiązanie

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Alicja KOLASA-WIĘCEK[1]

EXPLOITATION OF WATER RESOURCES OF THE OPOLE PROVINCE - FORECASTING WITH THE USE OF ARTIFICIAL NEURAL NETWORKS

EKSPLOATACJA ZASOBÓW WODNYCH WOJEWÓDZTWA OPOLSKIEGO - PROGNOZOWANIE Z WYKORZYSTANIEM SZTUCZNYCH SIECI NEURONOWYCH

Abstract: The paper performs forecasting based on Flexible Bayesian Models on Neural Networks. On the basis of changing factors like number of population and industrial water consumption the amount of underground and surface water resources was predicted. The prognosis was performed for the Opole province and for its for individual districts. Teaching series were real data taken from the Central Statistical Office. The likelihood of these results is 94% by checking the verification data.

Keywords: water resources, underground water, superficial water, forecasting, artificial neural networks

Water plays an exceptional part in nature. Unfortunately, water resources are insufficient in compared with the demand. If we are supposed to prevent ourselves from possible problems in the nearest future, the current water management should mainly take into consideration economic development and forecasted climate changes. It is estimated that in the nearest decades the shortage of water resources due too climatic changes will increase by 20% [1]. Moreover, it is further estimated that an increase in temperature may result in a variety of changes, among others, those concerning the form and model of precipitation, adjustment and capacity of outflow [2].

The basic way of using the water resources which have a special impact on their state of quantity and quality is water consumption for economic and industrial usage and using the reservoirs and watercourses as sewage receivers. One of the more important actions accepted for realisation in the nearest years by the EU member states is the Water Framework Directive which seems to be the most important directive concerning appropriate water management and water policy. A number of EU countries, in spite of the

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valid Directive, have problems related to the effective water resources management. The problem is even more significant because the global changes essentially modify water problems which are different in the course of time. Changes in water sector management are necessary [3]. Water pollution is increasing gradually and the quality of water environment is deteriorating. Hence, steps towards appropriate strategies of water management and exploration are invariably essential [4].

Appropriate tools, eg those employing artificial tools and methods serve to solve problems associated with management through underground water optimisation. The method used by Chang-lei et al allows to calculate and adjust underground water resources. The authors suggest that it may be successively used in areas similar to the investigated one [5]. Nowadays, balanced water resources management should cover a wide variety of subjects concerning, among others, power issues and contaminants - mainly persistent chemicals [6]. Estimations indicate that over 40% of water stock in Western and Eastern Europe is acquired thanks to urban aquifers, efficient and cost-effective management tools [7]. That is why appropriate water resources management is so essential. The protected objects should be first of all non-renewable resources of underground water which are limited and have the highest market value, as well as fresh water of rivers and lakes [8]. In water consumption by population and economy, usage of water for production needs has the biggest percentage - 73%.

Polish water resources calculated for one inhabitant are significantly smaller than average in Europe and amount to ca 36% of the European average [9]. There have been settled middle-term goals for the ecological state policy by the year 2010, focusing mainly on the following issues:

1) continuation of actions in the scope of reasonable use of water,
2) reduction and elimination of underground water consumption for industrial needs,
3) all national water reaching a good state - by the year 2015,
4) reaching at least the level of 75% in biogenes removal in basins of the Odra and Vistula rivers,
5) modernisation, extension and construction of new municipal sewage plants,
6) reduction of contaminant emission from point sources [9].

Water resources of the Opole region

The Opole province is characterised by availability of rich resources of underground water and sufficient resources of surface water. The basic sources of water supply are underground water resources, accumulated in 14 main reservoirs of underground water. Surface water is used only in part. Generally, the state of water is insufficient. Providing all inhabitants of the province with an access to high quality, potable water is considered a task of priority. The target will be reached through stoppage of the underground water degradation, intensification of processes contributing to reasonable usage of the existing water resources and appropriate management of the protection areas around water reservoirs. The Regional Operational Programme for the years 2007-2013 assumes actions aimed at economical use of water and general decrease in water consumption [10]. At the territory of the province, water is collected from surface and underground intakes both for municipal and industrial purposes. Surface water resources of the province if calculated for one inhabitant amount to 796 m^3/M/year (almost twice as low as throughout the country).

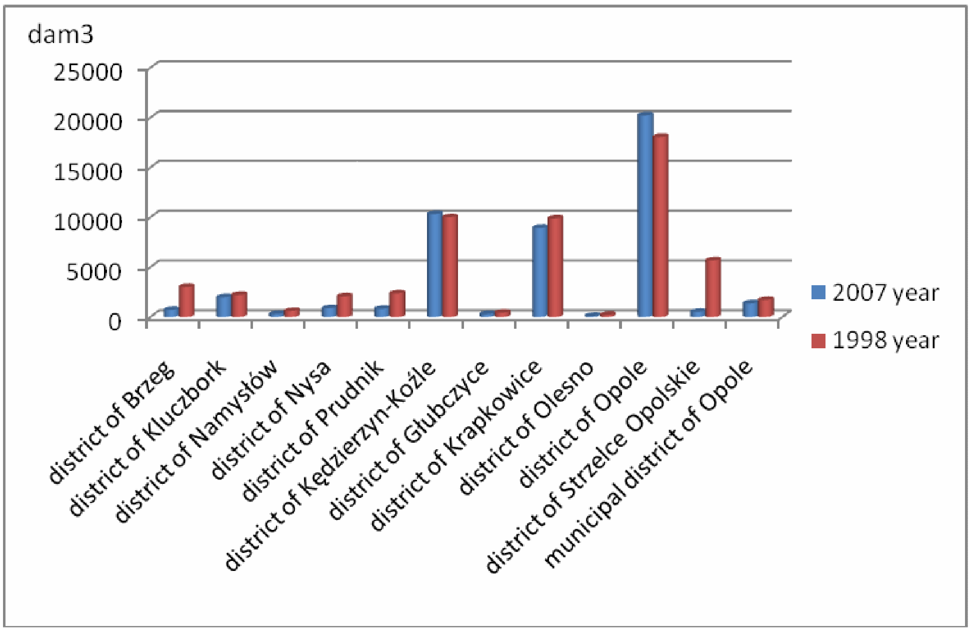

Fig.1. Water consumption by industry in districts of the Opole province [11]

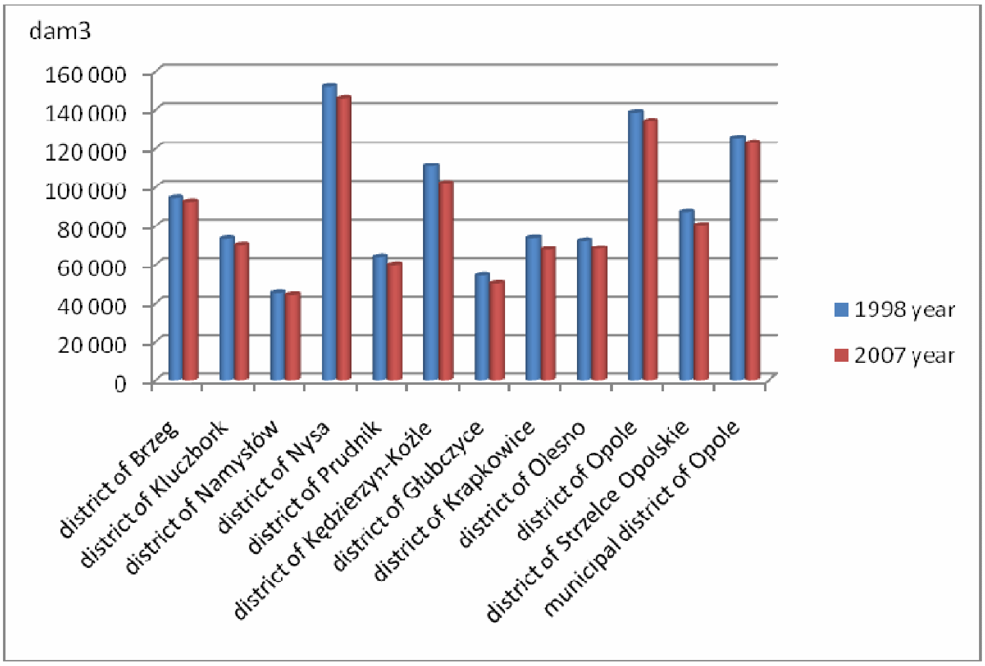

Fig. 2. Number of inhabitants of the Opole province in individual districts [11]

They are estimated in a border section with the province of Lower Silesia as 448.5 mln m^3 in the dry year and 860 mln m^3 in the normal year. Layout of surface water in unfavourable both in time and space, which along with low retention additionally results in temporary water shortages in some areas of the region, eg in the Glubczyce plateau or Olesnica plain. Usable resources of underground water are estimated as 469.3 hm^3 which corresponds to 2.8% of the total resources in Poland. The most valuable water reservoir due to its high usage advantages is the Main Underground Water Reservoir 333 Opole-Zawadzkie. Unfortunately, the reservoir in its southern part is characterised by low natural resistance to contaminants due to the lack of deposits insulating it from the impact of the environment [12]. Six reservoirs along with their supplying area have been classified as reservoirs of the highest protection against degradation and eight more - as areas requiring strict protection. Underground water resources are able to satisfy potential needs of municipal management, industry and agriculture in the province. The highest consumption of water by industry can be noticed in districts of: Opole, Kedzierzyn-Kozle and Krapkowice (Fig. 1).

The Opole province is characterised by a successive decrease in the number of population. This problem applies to all districts of the province (Fig. 2).

Research methodology

The research aimed at indicating the extent in which the development and water consumption in industry influences and may influence the consumption of underground and surface water resources in the Opole province in the nearest future. The modelling also took the human factor into consideration, yet the fall and rise of the number of inhabitants was considered. Several variants of solutions were examined, based on the quantity of water consumed by industry.

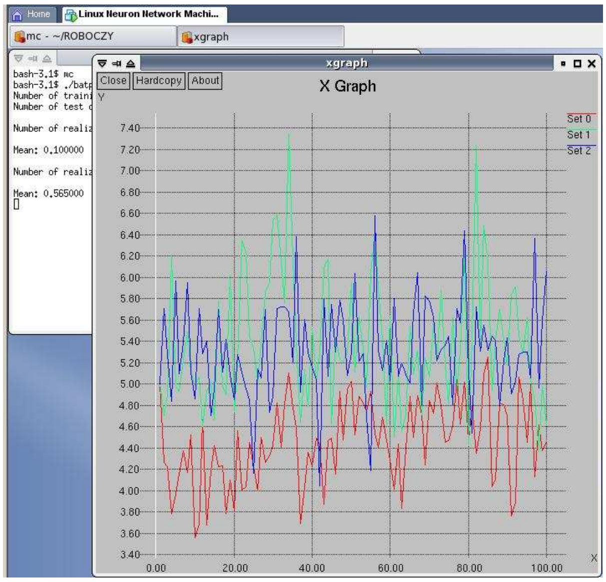

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Fig. 3. Chosen numerical and graphic parameters of learning neural network in FBM program

The artificial neural network of the Flexible Bayesian Models on Neural Networks [13] was employed for forecasting. Teaching series of real data from 1997 to 2007 were obtained from the Central Statistical Office database.

Flexible Bayesian methods allow complex neural network models to be used without fear of the "overfitting" that can occur in the case of traditional neural network learning methods [14].

The parameters are: number of population, industrial water consumption and surface and underground water consumption constituted a learning series [11]. The forecasting was executed for ten consecutive years for individual districts of the Opole province. Numerical and graphic parameters of the network learning quality indicate, among others: rejection index and diagrams of control values trajectory (weight hyperparameters) indicate an appropriate and relatively optimal process of network learning (Fig. 3).

Results and discussion

In view of the large number of options considered, below (Figs 4 and 5) exemplary modeling results reflect the scale exploitation of underground and surface water resources for changing conditions-decline or increase in population number and consumption of water for industrial use.

On the basis of the forecasts received, one may draw the following conclusions for individual districts of the Opole region:

- district of Brzeg - underground and surface water resources in the district will mainly depend on the amount of its industrial consumption and the human factor will affect the quantity of resources far more weakly,
- district of Kluczbork - the main factor conditioning the underground and surface water consumption is its industrial usage - along with its increase, water consumption increases as well. Similarly, water consumption increases in proportion to the increase in the number of inhabitants,
- district of Namyslow - an increase in water consumption by industry is the main factor influencing the quantity of underground water usage, yet the resources are used more extensively along with the simultaneous increase in the number of the local population,
- district of Nysa - the usage of water resources rises along with an increase in the industrial water consumption,
- district of Prudnik - the consumption of superficial water resources rises very significantly along with an increase of water consumption for industrial needs; the usage of underground water resources rises as well,
- district of Glubczyce - first of all, industrial usage of water will decide on the successive increase in the underground and surface water consumption, yet the rise of the surface water consumption is directly proportional to its usage for industrial needs,
- district of Kedzierzyn-Kozle - the both factors under investigation have a direct impact on the quantity of water resources usage; along with an increase in the number of inhabitants, the surface water consumption increases and an increase in water consumption for industrial needs means a rise of underground water consumption,
- district of Krapkowice - the number of the local population is the main factor influencing the quantity of surface and underground water consumption,

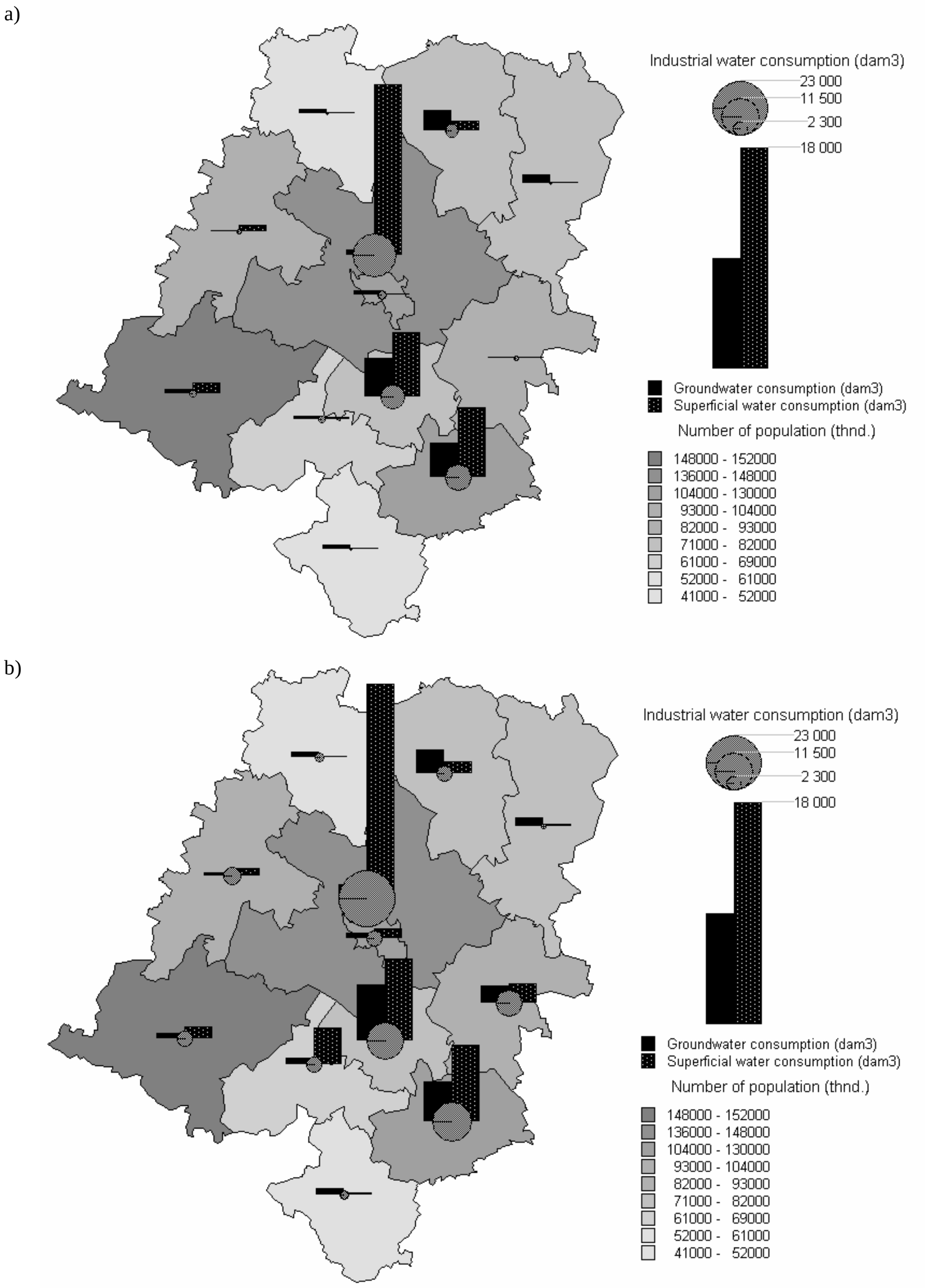

Fig. 4. The use of water resources in the Opole province in forecast 2009 year with an increase population: a) a decrease in the industrial water consumption, b) with an increase in industrial water consumption

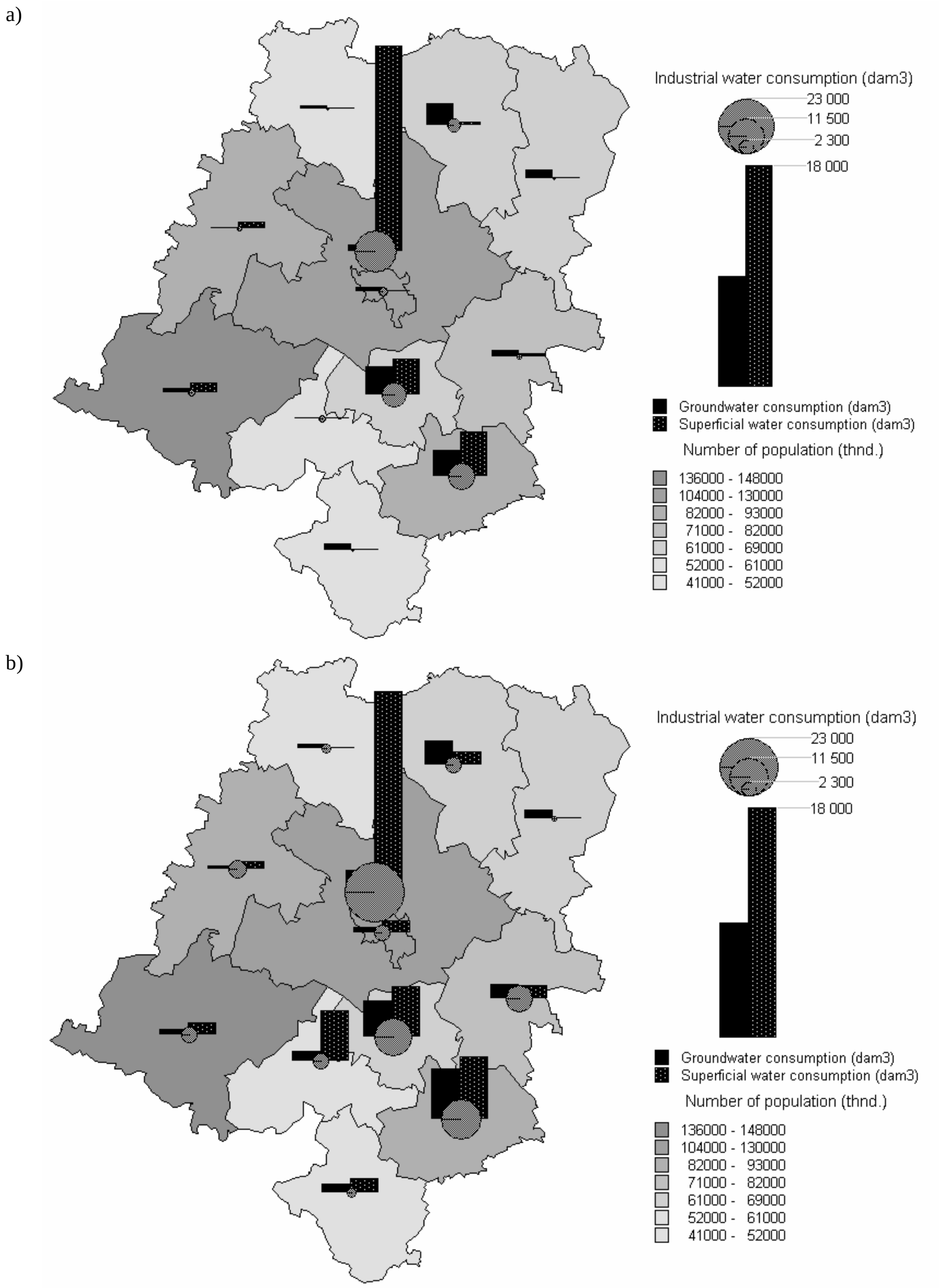

Fig. 5. The use of water resources in the Opole province in forecast 2017 year with a falling population: a) a decrease in the industrial water consumption, b) with an increase in industrial water consumption

- district of Olesno - underground water resources are mainly used in this area; the underground water consumption remains at a similar level in the period of years under analysis,
- district of Opole - a predominant influence of industry on the quantity of underground water consumption has been observed in this area,
- district of Strzelce Opolskie - the size of underground and surface water consumption is determined mainly by the quantity of water consumed by industry,
- municipal district of Opole - industry influences the consumption quantity of surface and underground water resources in this area.

Conclusions

Neural models, thanks to the process of learning on the basis of real data make it possible with satisfactory precision to forecast the state of water resources depending on their usage. The likelihood of the results amounts to 94%, which was checked by means of data verification.

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EKSPLOATACJA ZASOBÓW WODNYCH WOJEWÓDZTWA OPOLSKIEGO - PROGNOZOWANIE Z WYKORZYSTANIEM SZTUCZNYCH SIECI NEURONOWYCH

Katedra Ekonomii i Badań Regionalnych, Wydział Zarządzania i Inżynierii Produkcji, Politechnika Opolska

Abstrakt: W pracy dokonano prognozowania stopnia eksploatacji zasobów wód podziemnych i powierzchniowych w województwie opolskim, biorąc pod uwagę zmieniające się warunki - liczbę ludności oraz ilość wody pochłanianą przez przemysł. Serię uczącą stanowiły rzeczywiste dane uzyskane z bazy Głównego Urzędu Statystycznego. Modelowanie przeprowadzono z wykorzystaniem sztucznej sieci neuronowej. Prawdopodobieństwo wyników sprawdzono na podstawie weryfikacji danych i wynosi ono 94%.

Słowa kluczowe: zasoby wodne, wody podziemne, wody powierzchniowe, prognozowanie, sztuczne sieci neuronowe

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Teresa KORNIŁŁOWICZ-KOWALSKA[1*] and Kamila RYBCZYŃSKA[1]

DECOLORIZATION OF POST-INDUSTRIAL LIGNIN BY MUTANTS OF *Bjerkandera adusta* CCBAS 930 WITH ENHANCED LIGNINOLYTIC ACTIVITY

DEKOLORYZACJA LIGNINY POPRZEMYSŁOWEJ PRZEZ MUTANTY *Bjerkandera adusta* CCBAS 930 O ZWIĘKSZONEJ AKTYWNOŚCI LIGNINOLITYCZNEJ

Abstract: The paper describes the mutagenesis of the anamorphic fungus *Bjerkandera adusta* CCBAS 930 capable of decolorization and biodegradation of post-production lignin with participation of extracellular peroxidase. Seven mutants were isolated, out which 6 were characterized by shortened time of decolorization of model solutions of post-industrial lignin, from 21 to 7 or 14 days. The effect was caused by faster decomposition of the lignin polymer, as measured by decrease in the content of total phenols and of metoxyphenols. The process of biodegradation of lignin was catalyzed by an extracellular peroxidase that was not fully characterized. Two of the mutants studied, R59-2 and R59-5, were characterized by increased biosynthesis of that enzyme, coupled with accelerated transition of the fungus from the trophophase (primary metabolism) to the idiophase (secondary metabolism). This was accompanied by a drop in pH of the substrate that was more pronounced compared with the parental strain and to the other mutants.

Keywords: decolorization, lignin, *Bjerkandera adusta,* mutants, peroxidases

The primary source of contamination of waters is sewage, including industrial sewage, that from the pulp and paper industry being especially toxic and also produced in great quantities. In terms of the amount of contaminants released to the environment, that industry is ranked sixth in the world [1]. This is due to the scale of production of that industry, amounting to not less than 300 million tons of paper and paper products [2]. The composition of effluents from the pulp and paper industry, from various stages of pulping and bleaching of wood pulp, includes large amounts of chromatophores, mainly lignin and its derivatives, and partially tannins [2]. Depending on the technological processes applied - alkaline lignin and thiolignin in the Kraft process and lignin sulfonates in the sulfite (sulfate IV) method [3] - the amounts of effluents produced per 1 kg of paper are, respectively

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270÷450 dm^3 of effluent containing 40÷50 g of lignin or 300÷400 dm^3 of effluent containing 200÷250 g of lignin [2]. Migration of lignin-rich sewage to waters contributes to disturbance in the biological balance and to chemical contamination and colorization of waters [1].

Methods used so far for the decolorization of sewage containing post-industrial lignin are mainly of physicochemical character and involve adsorption with the use of activated carbon [4] and coagulation of lignin in the pulp and in paper industry sewage [5]. Those methods lead only to the transition of lignin from a water-soluble form to a solid form, and are considered to be costly and of low efficiency [6]. Decolorization of lignin-containing sewage with the method of chlorination, on the other hand, is conducive to the formation of colorless but resistant to biodegradation and strongly toxic and mutagenic chlorinolignins and other chlorino-aromatic complexes, including carcinogenic dioxins [1, 3]. The application of toxic chlorine can be limited through the use, for the purpose of decolorization of lignin-rich sewage, of selected effective microorganisms, mainly white rot fungi and ligninolytic enzymes - laccase and peroxidases [2, 7]. Until now, the greatest attention has been paid to the ligninolytic capabilities of such species of wood white rot fungi (*Basidiomycota*) as *Phanaerochaete chrysosporium*, *Trametes (Coriolus) versicolor* and *Pleurotus ostreatus* [6, 8-10]. Less researched in this respect are white rot fungi representing the genus *Bjerkandera* [11,12]. Our own studies [13] indicate that in stationary cultures, the anamorphic strain *Bjerkandera adusta* CCBAS 930, isolated from soil, decolorizes 0.2% solutions of lignin originating from the process of wood pulp pulping (alkaline fraction I). The process of decolorization was of enzymatic character and was dependent on the presence of extracellular peroxidase. Decolorization of lignin by the fungal strain *Bjerkandera adusta* CCBAS 930 was coupled with the production of aerial mycelium, which corresponded with the secondary metabolism of that fungus. Its maximum, observable as complete brightening of the substrate, became evident after 25 days of culturing [13].

The objective of the study presented here was an attempt at increasing the efficiency of post-industrial lignin decolorization by the above-mentioned strain of *Bjerkandera adusta* through mutagenesis. The criteria applied in the estimation of the decolorization activity of the mutants included the rate of decolorization of post-industrial lignin, changes in the total content of phenolic and methoxyphenolic substances (CH_3O - phenols), and the activity of extracellular peroxidase as compared with the parental strain.

Material and methods

Fungus strain

The anamorphic strain *Bjerkandera adusta* CCBAS 930 was isolated from samples of a soil (Phaeazems acc. FAO) collected in the region of south-east Poland. The isolation, identification and morphological and taxonomic characterization of the fungus have been described in the paper by Kornillowicz-Kowalska et al [14].

Lignin

Lignin (LG) precipitated from the first alkaline fraction (from wood extract) by acidification with H_2SO_4 was obtained from InterCell S.A. Ostroleka (Poland). Before usage the lignin was dissolved in sterile 0.1 M NaOH and adjusted to pH = 7 with 0.2 M HCl. Lignin contained (g · kg^{-1} d.m.) 408.2 of carbon, 40.4 of hydrogen, 0.2 of nitrogen and no ashes.

Isolation and selection of mutants of B. adusta CCBAS 930

Induction of mutants of *B. adusta* CCBAS 930 was conducted with the use of *N*-methyl-*N*'-nitro-*N*-nitrosoguanidine (MNNG) and UV radiation in accordance with the method of Kornillowicz-Kowalska and Iglik [15]. Selection of mutants was performed in the test of decolorization of 0.2% lignin in the Park and Robinson substrate [16]: 0.07% glucose, 0.05% $MgSO_4$, 0.02% KH_2PO_4, 0.01% NH_4NO_3, agar 2%, pH 6.5, after inoculation of plates (ø = 9 cm) with a circle of mycelium (ø = 0.5 cm) obtained from 7-day culture on glucose-potato agar (20% potato, 2% glucose, 2% agar). The alkaline lignin concentration applied corresponded to the content of that waste as encountered in the first fraction of wood pulp pulping with lye, called the black liquor. The culture was incubated at 26ºC, measuring the decolorization zone after 3, 7, 10 and 14 days. Mutants that decolorized agarized lignin faster than the parental strain were selected for further experiments.

Culture conditions

Liquid cultures of the parental strain and of the selected mutants were set up in 100 cm^3 Erlenmayer flasks with 50 cm^3 of mineral medium for f ligninolytic fungi [17] enriched with 0.2% of lignin and 0.25% of glucose. The inoculum were 3 circles of mycelium, 1 cm in diameter, obtained from 7-day culture on glucose-potato agar. Non-inoculated medium was used as control. The cultures and the control medium were incubated at 26ºC for 30 days under static conditions, with 3 parallel replications.

Analytical methods

Clear post-culture fluids, obtained after straining of mycelium and centrifuging at 3000 revs min^{-1} for 5 minutes, were used to determine the following:

- Degree of decolorization of lignin (LG) at λ = 430 nm (maximum of absorbance), calculated from the formula [18]:

$$\%\ \text{decolorization} = \frac{A\lambda i - A\lambda f}{A\lambda i} \cdot 100$$

where: % decolorization = degree of decolorization in %, Aλi - initial absorbance, Aλf - final absorbance.

- Content of phenolic (λ = 400 nm) and metoxyphenolic (λ = 500 nm) substances, with the method of Malarczyk [19], using standard curves prepared for protocatechuic acid and vanillic acid, respectively.
- Peroxidase activity, according to Maehly and Chance, with *o*-dianisidine as substrate [20].
- Laccase activity, according to Leonowicz and Grzywnowicz [21], using syringaldasine as substrate.
- Protein content in the substrate, with the method of Lowry [22] with beef albumin as protein standard.
- pH of medium.

Culture observations

Microscope observations of mycelium growth and development and of changes in the substrate comprised the morphology of the vegetative mycelium, formation of spore-producing aerial mycelium, substrate color changes, and mycelium color changes.

Evaluation of results

All results obtained are given as means from 3 replications for which standard deviations were calculated.

Results

Selection of mutants with enhanced post-industrial lignin decolorization activity

UV irradiation (UV-C, $\lambda = 200 \div 280$ nm) and treatment with nitrosoguanidine (MNNG) (0.01%, 5 min) of 10^5 cfu $\cdot$ cm^{-1} *B. adusta* CCBAS930 resulted in the survival of $44 \cdot 10^1$ cfu after treatment with MNNG and $0.6 \cdot 10^1$ cfu after ultraviolet irradiation. This indicated greater survivability of the fungus under study in the presence of MNNG than under UV irradiation, at 0.04% and 0.006%, respectively. Among the 50 colonies grown, seven were characterized by notable structural changes, consisting in "felting" of the mycelium, which produced colonies more flattened and compacted compared with the parental strain which grows in the form of fluffy colonies, with loose and wooly aerial mycelium.

Subsequent post-mutation selection took into account the rate of decolorization of post-industrial lignin (alkaline lignin) in cultures on Park and Robinson solid medium containing 0.2% of that substrate. That selection revealed that only three (R59-5, R59-9 and R59-14) out of seven morphological mutants decolorized lignin faster than the parental strain (Table 1). A characteristic phenomenon is that initially (cultures 1-3 days old) the clones mentioned above caused an increase in the intensity of coloring of the substrate (dark brown), and only afterwards its brightening. The most active decolorizer of lignin in the solid substrate was mutant R59-5 which, after 7 days, brightened ca 80% of surface area of substrate with 0.2% of alkaline lignin (Table 1).

Table 1

Decolorization of 0.2% lignin in solid substrate by selected mutants of *B. adusta* CCBAS 930 with modified morphology of colonies

Strains	**Days of culture**			
	3	**7**	**10**	**14**
CCBAS 930 (parent strain)	10* / 0**	60 / 10	90 / 40	90 / 50
R59-2	35 / 0	60 / 0	90 / 20	90 / 30
R59-5	35 / 0[1]	90 / 70	90 / 80	90 / 80
R59-9	20 / 0[1]	90 / 25	90 / 70	90 / 70
R59-14	40 / 0[1]	90 / 0	90 / 65	90 / 80
R59-28	0 / 0	25 / 0	50 / 0	70 / 20
R59-29	15 / 0	90 / 0	90 / 0	90 / 30
R59-30	20 / 0	65 / 0	90 / 0	90 / 0

Explanations: * - growth diameter in mm; ** - diameter of decolorization zone [mm]; 1- substrate darkening in growth zone of 15.10 and 10 mm; plate diameter - 9 cm

Decolorization of lignin by mutants of *B. adusta* CCBAS 930 in liquid cultures

Among the 7 mutants tested, only one (R59-30) decolorized 0.2% solution of post-industrial lignin at a rate similar to that of the parental strain (Fig. 1). The other mutants removed the coloring caused by the presence of that biopolymer at rates two- to three-fold faster than the parental strain. That effect became noticeable after 7-10 days of culturing, as 52÷83% (7 days) and 51÷85% (10 days) of substrate decolorization (measured by drop in absorbance), respectively. During the same time, the parental strain removed only 26÷27% of the coloring, and mutant R59-30 decolorized 17÷34% of lignin contained in the solution. Decolorization of solution containing 0.2% of alkaline lignin proceeded the fastest in cultures of mutants R59-2 and R59-29. After 7 days of culturing, both of those clones removed 73÷83% of the coloring. Mutant R59-5, that decolorized lignin the fastest in the solid substrate, was less efficient here - after 7 days of growth it removed 52% of the color.

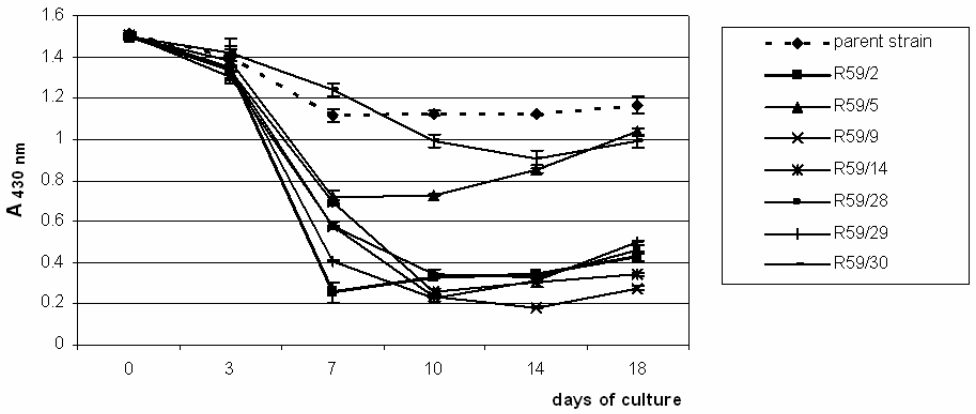

Fig. 1. Decolorization of 0.2% lignin by mutants *B. adusta* CCBAS 930

In culturing time of the mutants under study longer than 10 days, a recurring though less pronounced increase was observed in the substrate coloring as measured with increase of absorbance (Fig. 1). However, no biosorption of lignin was observed, either in the mutant cultures or in the non-mutated strain; their mycelia remained colorless (white).

Changes in the content of phenolics in the culture medium

In the course of decolorization of 0.2% solutions of alkaline lignin in the cultures of the mutants and of the parental strain of *B. adusta* CCBAS 930 the content of phenolic substances (λ = 400 nm) was decreasing (Fig. 2A). In the mutant cultures that decrease was 2-3-fold stronger than in the cultures of the parental strain. The exception were mutants R59-28 and R59-30 which displayed low effectiveness in the removal of phenolics (maximum 20%) - similar to that of the control (parental strain). The reduction of the total level of phenols was the fastest between days 7 and 14 (18) of culturing. That effect was the most pronounced in the cultures of mutant R59-2: 47% reduction of the concentration of phenolics after 7 days of growth. Whereas, the greatest decrease in the total phenolic content was observed in the case of the culture of R59-29 - 53% after 14 days of growth of the strain. The slowest decrease in the level of phenolic substances was observed in the cultures of mutants R59-28 and R59-30, with decrease rates of 21% and 24%, respectively, after 18 days of culturing (Fig. 2A).

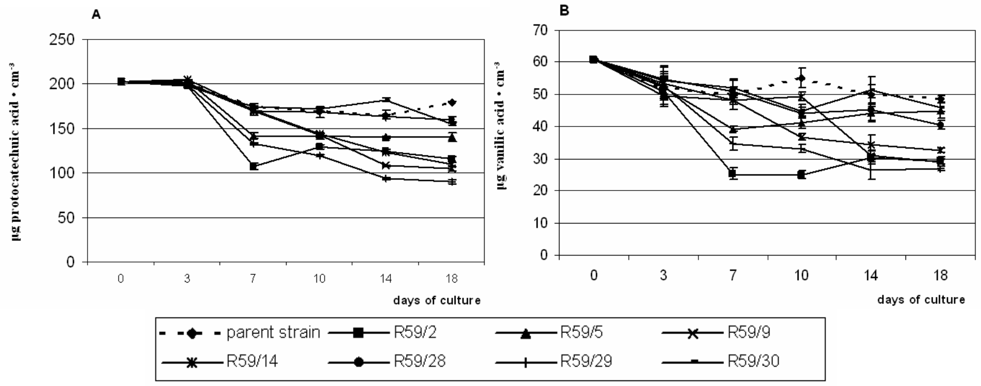

Fig. 2. Changes in the content of total phenolics (A) and methoxyphenolics (B) in culture fluids of mutants of *B. adusta* CCBAS 930 containing 0.2% of lignin

Initially, changes in the content of methoxyphenolics in the substrate had a run similar to that in the total content of phenols, but were more pronounced (Fig. 2A,B). The content of methoxyphenolic complexes decreased the fastest between days 7 and 14 (18). The most effective in this respect was the mutant R59-2 which, after 7 days, removed 58% of CH_3O - phenols, while the parental strain removed only 18%. Also relatively effective were mutants R59-29 and R59-5 - removal rates of 43% and 35%, respectively. The level of CH_3O - phenols-decreased the most slowly in cultures of the mutant R59-30 - 14% after 7 days (Fig. 2B).

Changes in peroxidase activity in the culture medium

Extracellular peroxidase activity of the parental strain of *B. adusta* CCBAS 930 and its 7 mutants became observable on the 3rd day of culturing on the substrate with 0.2% lignin and gradually increased from then on. The maximum of activity of that enzyme became evident in cultures of 10-14 (18) days old. However, the strain under study was notably varied in the level and dynamics of activity of that enzyme (Fig. 3). The highest levels of peroxidase activity were observed in cultures of mutants R59-2 and R59-5. The mean specific peroxidase activity in the cultures of those strains was 101.0 and 125.5 mU · mg^{-1} of protein, respectively. Those values were 20-25-fold higher with relation to the peroxidase activity of the parental strain. Considerably lower values of activity of the phenoloxidase under study were observed in the case of mutants R59-29 and R59-30 (12.5 and 46.9 mU · mg^{-1} of protein, respectively). Peroxidase activity of the remaining 3 clones, R59-9, R59-14 and R59-29, was at the same low level as in the culture of the parental strain (Fig. 3).

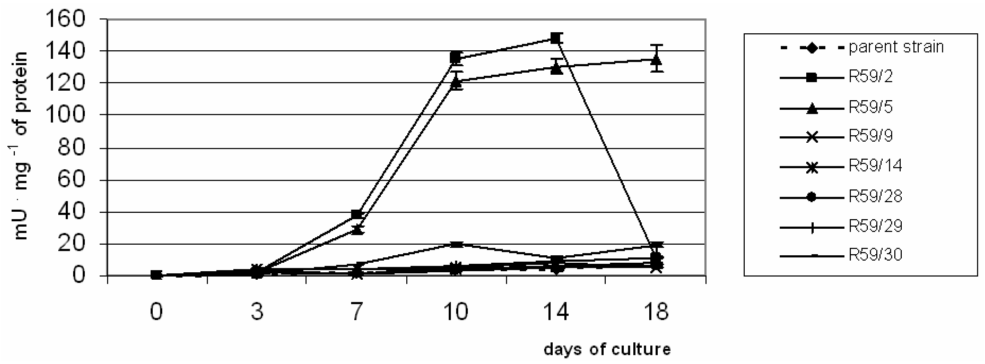

Fig. 3. Peroxidase activity in culture fluids of mutants of *B. adusta* CCBAS 930 containing 0.2% of lignin

Laccase activity

In the experimental design adopted in this study neither the parental strain nor its mutants produced any laccase.

Increase and changes in pH of the culture fluids

Under the conditions of stationary culture on substrate with 0.2% lignin, mutants of *B. adusta* CCBAS 930 were characterized by faster rate of growth and by the production of aerial mycelium, as compared with the parental strain. The process of aerial mycelium production (reflecting the transition of the fungus to the phase of secondary metabolism) in the mutant cultures began on the 7th day, while in the cultures of the parental strain on the 10th day of culturing (Tab. 2).

Table 2

Visual characterization of growth of mutants of *B. adusta* CCBAS 930 in liquid cultures enriched with 0.2% lignin

Strains	**Days of culture**			
	3	**7**	**14**	**18(21*)**
CCBAS 930 (parent strain)	- / -	++ / -	+++ / +	▒ +++ / +
R59-2	- / -	▓ ++ / +	▒ +++ / ++	▒ +++ / ++
R59-5	+ / -	░ +++ / +	▒ +++ / ++	▒ +++ / ++
R59-9	- / -	░ ++ / ++	▒ +++ / ++	▒ +++ / +
R59-14	- / -	░ +++ / +	▒ +++ / +	▒ +++ / +
R59-28	- / -	░ ++ / +	▒ +++ / +	▒ +++ / +
R59-29	+ / -	▓ +++ / ++	▒ +++ / ++	▒ +++ / ++
R59-30	- / -	+++ / +	+++ / +	▒ +++ / +

Explanations: - no growth; + mycelium growth 20%; ++ mycelium growth 50%; +++ mycelium growth 80÷100%; + / + ratio of vegetative mycelium to aerial mycelium

□	no decolorization
░	weak decolorization
▒	distinct decolorization
▓	strong decolorization

* - for parental strain

This was accompanied by visually observable gradual brightening of the substrate that progressed with the passage of the time of culturing. In the mutant cultures, its maximum was observed on the 14th day. Within a longer time-frame, a slight re-colorization of substrate was observed. Whereas, in the cultures of the parental strain, visually observable brightening of substrate was apparent as late as on the 21^{st} day of culturing (Table 2).

In the course of the growth of the parental strain and the mutants of *B. adusta* CCBAS 930, pH of the substrate (6.33÷6.40) decreased by ~0.7÷1.3 units, attaining values of 5.02÷5.59. The process of acidification was the fastest within the first week of culturing, which should be attributed to assimilation of glucose. Beginning with day 10 in the mutant cultures, and day 14 in the parental strain cultures, a gradual re-increase in pH values was observed, most pronounced in the case of the parental strain and of the mutant R59-14. The weakest re-increase of pH was noted in cultures of mutants R59-2 and R59-5, by as little as 0.15÷0.29 of a unit after 18 days of culturing (Fig. 4).

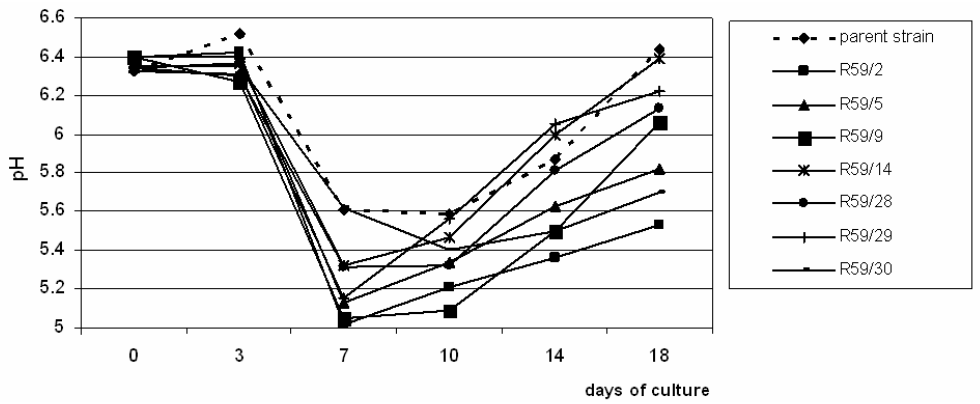

Fig. 4. Changes of pH in culture fluids of mutants of B. adusta CCBAS 930 containing 0.2% of lignin

Discussion

Decolorization of lignin solutions in stationary cultures of *Bjerkandera adusta* CCBAS 930 is an enzymatic process catalyzed by a non-fully characterized extracellular peroxidase of that fungus [13]. That extracellular peroxidase of *B. adusta* CCBAS 930 is also responsible for biodegradation and, in consequence, for decolorization of daunomycin (an anthracyclin antibiotic) and of pigments with aromatic structure, including anthraquinonic pigments [14, 15]. That enzyme is an enzyme of the secondary metabolism of *B. adusta* CCBAS 930, and the processes of decolorization and of biodegradation of lignin and of related compounds (humic acids, daunomycin, anthraquinonic pigments) are of cometabolic character, as they require the presence of an easily available source of carbon, such as glucose [14, 15].

In the present study, out of the 50 morphological mutants isolated after mutagenesis of homogenate of mycelium of *B. adusta* CCBAS 930 (1×10^5 cfu · cm^{-3}) under the effect of UV and nitrosequanisidine (MNNG) treatment, 7 mutants were selected that had increased capacity for decolorization of post-industrial lignin (first alkaline fraction). UV exerted a stronger lethal effect compared to MNNG - out of the 50 clones isolated only 6 were obtained after UV irradiation. Stronger fungicidal effect of UV radiation was also observed by Miura et al [23] during induction of mutants of non-sporification stage of white rot basidiomycete (des. as IZU-154) with increased ligninolytic activity. Out of the seven selected mutants of *B. adusta* CCBAS 930 (1 after UV mutagenesis, 5 after MNNG mutagenesis), two: R59-2 and R59-5 (both after treatment with MNNG) were characterized, on average, by 20-25x greater peroxidase activity compared with the parental strain. Stimulation of peroxidase activity (manganese-dependent peroxidase MnP) of mutants of non-sporifying fungus IZU-154 after mutagenesis of its ancestors with UV radiation and with MNNG has been reported earlier by Miura et al [23] who applied their capacity to decolorize synthetic melanin as the criterion of selection. Higher ligninolytic activity of mutants (UV induction) compared with the parental strain of the white rot fungus *Phanerochaete chrysosporium* was also observed by Kakar et al [24]. Those authors applied decolorization of chromatophores from the group Poly-R (polymeric pigments) as the criterion for the estimation of ligninolytic activity.

In our study, using the degree of decolorization of alkaline lignin as the index of ligninolytic activity of *B. adusta* CCBAS 930, we observed similar relationships. The selected mutants of the fungus decolorized water solutions of post-industrial lignin faster 3x compared with the parental strain. After 7 days of growth, the most efficient clones - R59-2, R59-5 and R59-29 - caused color reduction by 73%, 52% and 83%, respectively, while the parental strain rate of decolorization was 26%.

Our earlier study [13] showed that decolorization of alkaline lignin in stationary cultures of *B. adusta* CCBAS 930 was caused by biodegradation of that polymer, which was accompanied by a reduction in the level of total phenolics and of methoxyphenolic in the substrate. The decrease in the content of methoxyphenolic indicated demethylation of the lignin polymer under the effect of peroxidase [13]. Whereas, in cultures of *B. adusta* CCBAS 930 containing lignin no presence of laccase was detected. Laccase, like peroxidase, can catalyze the reaction of demethylation [25]. Also mutants of *B. adusta* CCBAS 930 did not synthesize laccase in stationary cultures containing lignin. Mutants (but not the parental strain) of *B. adusta* CCBAS 930, on the other hand, synthesized laccase in cultures containing synthetic dyes: carminic acid, erythrosine, and brilliant green, which was reported in the work by Kornillowicz-Kowalska and Iglik [15]. The process of decolorization of lignin in mutant cultures, as in cultures of the parental strain, proceeded along the cometabolic path, as indicated by its dependence on the presence of glucose [13]. Whereas, the mutants did not decolorize 0.2% solutions of lignin under conditions of absence of glucose (unpublished data). It was found, however, that the selected mutants R59-2 and R59-5, in cultures containing lignin and glucose, were characterized by faster growth of vegetative mycelium (trophophase) and transition to idiophase (secondary metabolism) compared with the parental strain. This involved faster absorption of glucose, causing increased acidification. The glucose metabolism in the parental strain cultures was notably weaker [13].

The study reported herein indicates that MNNG mutagenesis, increasing the biosynthesis of extracellular peroxidasae, accelerates the process of biodegradation of lignin. This was indicated by stronger than in parental strain cultures decrease in the content of phenolic substances, which caused faster decolorization of solutions of post-industrial lignin. The production of peroxidase by the parental strain and the mutants began on the 3rd day, but only in the case of the mutants R59-2 and R59-5 it intensified rapidly and remained at a considerable level throughout the period of culturing. The observed dynamics of peroxidase production in the cultures of mutants R59-2 and R59-5 was similar to that of peroxidase activity (lignin peroxidase, LiP) in cultures of mutants obtained after UV mutagenesis of conidia of *P. chrysosporium*, observed by Kakar et al [24].

The results of this study, therefore, indicate a possibility of improving the efficiency of decolorization and biodegradation of post-industrial lignin by the strain *B. adusta* CCBAS 930 through mutagenesis, as it leads to stimulation of growth and to biosynthesis of peroxidase catalyzing that process.

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DEKOLORYZACJA LIGNINY POPRZEMYSŁOWEJ PRZEZ MUTANTY *Bjerkandera adusta* CCBAS 930 O ZWIĘKSZONEJ AKTYWNOŚCI LIGNINOLITYCZNEJ

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Abstrakt: Opisano mutagenezę anamorficznego grzyba *Bjerkandera adusta* CCBAS 930 uzdolnionego do dekoloryzacji i biodegradacji ligniny poprodukcyjnej przy udziale zewnątrzkomórkowej peroksydazy. Wyizolowano 7 mutantów, z których 6 odznaczało się skróceniem czasu dekoloryzacji modelowych roztworów ligniny poprzemysłowej z 21 do 7 lub 14 dni. Efekt ten był wywołany szybszym rozkładem polimeru ligninowego, mierzonym zmniejszeniem zawartości fenoli ogółem i metoksyfenoli. Proces biodegradacji ligniny był katalizowany przez bliżej niescharakteryzowaną zewnątrzkomórkową peroksydazę. Dwa spośród badanych mutantów R59-2 i R59-5 odznaczały się wzmożoną biosyntezą tego enzymu, sprzężoną z przyśpieszeniem przejścia z trofofazy (metabolizm pierwotny) do idiofazy (metabolizm wtórny) grzyba. Towarzyszył temu silniejszy w stosunku do szczepu rodzicielskiego i pozostałych mutantów spadek pH podłoża.

Słowa kluczowe: dekoloryzacja, lignina, *Bjerkandera adusta,* mutanty, peroksydazy

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CHEMICAL, THERMAL AND LASER PROCESSES IN RECYCLING OF PHOTOVOLTAIC SILICON SOLAR CELLS AND MODULES

OBRÓBKA CHEMICZNA, TERMICZNA ORAZ LASEROWA W RECYKLINGU OGNIW I MODUŁÓW FOTOWOLTAICZNYCH Z KRYSTALICZNEGO KRZEMU

Abstract: In recent years, photovoltaic power generation systems have been gaining unprecedented attention as an environmentally beneficial method to solve the energy problem. From the economic point of view the pure silicon, which can be recapture from the used cells, is the most important material due to its cost and shortage. In the paper selected methods of used or damaged module and cells recycling and experimental results are presented. Advantages and disadvantages of these techniques are described, what could be helpful during the optimization of the method. The recycling process of PV module consists of two main steps: separation of cells and its refining. During the first step cells are separated due to the thermal or chemical methods usage. Next, the separated cells are refining. During this process useless layers are removed: antireflection, metallization and p-n junction layer, for silicon base - ready to the next use - gaining. This refining step was realized with the use of chemical and laser treatment as well.

Keywords: recycling, solar energy, silicon, photovoltaic solar cells, renewable energy

Production of photovoltaic modules on a commercial scale dates back to 1980's. PV module manufacturers provide a work warranty of 20-30 years, so modules produced back in the 1980's should be put out of commission and recycled during this decade, while modules manufactured in 2000 should be recycled by 2030. A particularly difficult task is developing an optimal technology of recycling and covering its high investment costs. This question is especially interesting because of the market's demand on silicon for PV cell production and - consequently - the need for its recycling.

This paper covers selected methods of recycling used or destroyed PV modules and photovoltaic cells and practical experiments results with chemical, thermal and laser

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recycling methods. Advantages and disadvantages of these methods, helpful in optimizing the recycling process for commercial use, were described.

PV recycling process requires two main stages:

- ***PV solar cell separation***. In this process, cells that are part of the commercial PV modules have been separated as a result of thermal or chemical processes;
- ***cleaning the surface of PV solar cells***. In this process, silicon solar cells separated from the PV modules underwent a process of purification, in which unwanted layers were removed (antireflection layer, metallization and a p-n semiconductor) - it was possible to recover the silicon substrate suitable for reuse. Stage surface cleaning of silicon PV cells was carried out using chemical and laser techniques.

Separation of silicon solar cells from damaged or used PV modules

In PV module production process, a predetermined number of silicon cells is hermetized with the use of such materials as EVA copolymer, Tedlar®, glass. The PV cell hermetization aims to secure it from harmful effects of atmospheric conditions or from mechanical damaging. EVA copolymer hermetiziation is done through covering both sides of cells with the polymer, while Tedlar® is used only on the bottom surface. Additionally, the front of a PV module is covered with glass (Fig. 1).

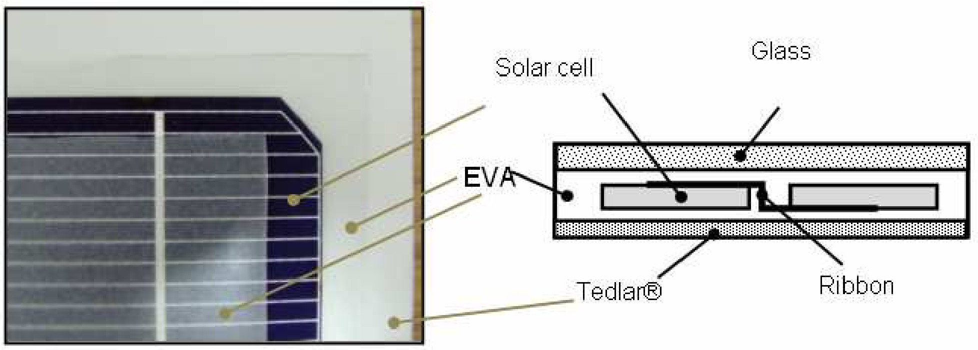

Fig. 1. Encapsulation of PV cells

In order to recycle silicon cells from damaged PV modules, it is required to introduce the delamination process [1]. In this process, the EVA is removed and materials such as glass, Tedlar, aluminum frame, steel, copper, and plastics are separated. Properties of the EVA copolymer have been thoroughly analyzed in paper [2]. The delamination process was conducted through two methods:

- Chemical treatment;
- Thermal treatment.

Chemical treatment in PV module recycling

As a result of the conducted chemical delamination with tetrahydrofurane (THF) (Fig. 2) it was possible to separate the materials from a damaged PV module.

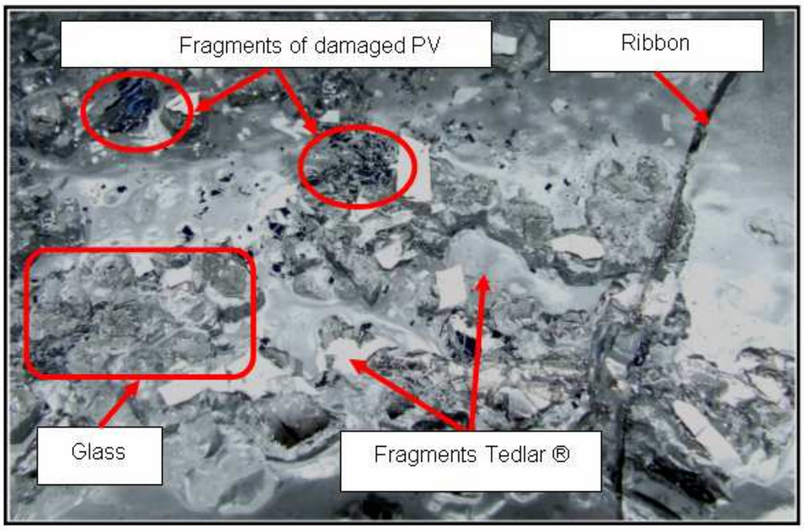

Fig. 2. The process of the removing of PV cell encapsulation using THF

The efficiency of the used method of chemical treatment was insufficient. Too long period of time needed for achieving satisfying results, in conjunction with a fairly high price of the solvent used, does not justify the use of this method for commercial PV cell and module recycling purposes. That is why, thermal treatment was proposed and investigated.

Thermal treatment in PV module recycling

In order to separate silicon photovoltaic cells from a damaged PV module, the module was placed in a SiO_2 bed which then was heated, to increase its temperature in time (Fig. 3).

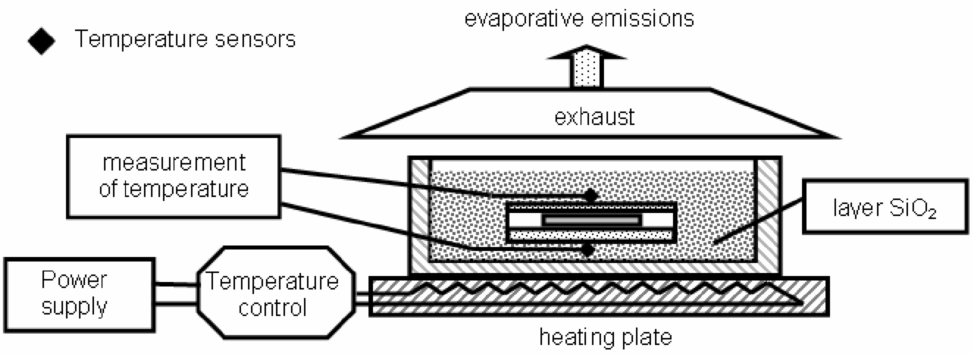

Fig. 3. The stand-up for the photovoltaic module lamination removing

In comparison to chemical treatment, the duriaton of the process is significantly shorter, also the problem of spent solvent does not occur. However, a disadvantage of thermal treatment is the emission of gas during EVA copolymer thermal degradation.

Nevertheless, this method, taking into account its simplicity and high efficiency, may be used in commercial PV recycling installations.

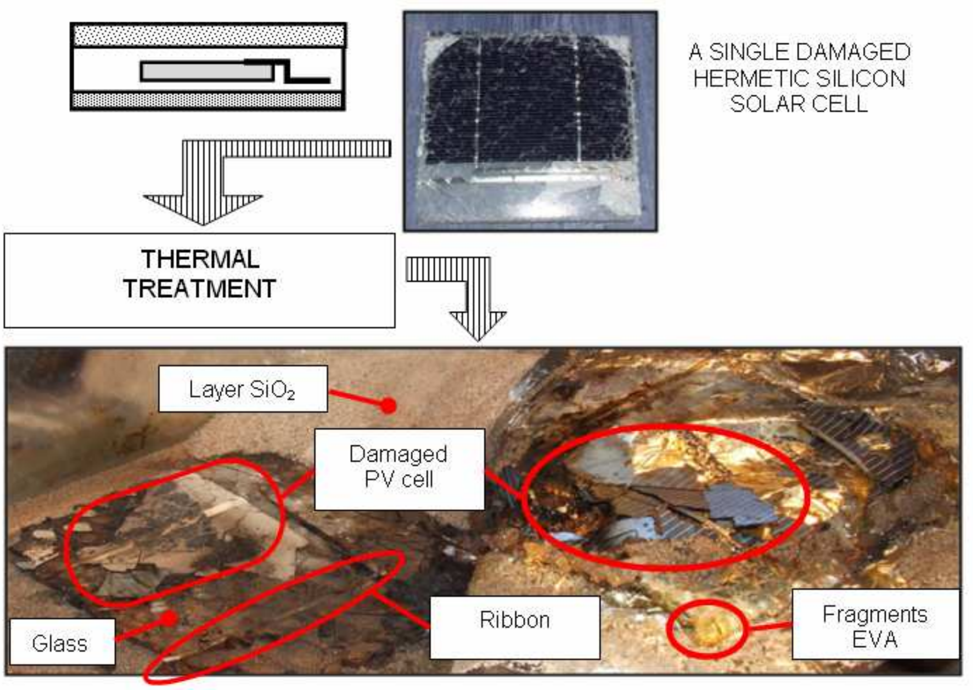

Fig. 4. The process of thermal removing of PV module encapsulation

When comparing chemical treatment with thermal treatment, it was found that for the delamination process, thermal treatment is a far more convenient method to use. With a moderate energetic cost, it is possible to obtain better process effectiveness. On the other hand, chemical treatment effectiveness is fairly low, the process lasts for a longer period of time, which additionally decreases effectiveness. The price of chemical compounds used, because of their type as well as their quantities, is high. Additional costs of waste solution disposal must also be taken into account in case of chemical treatment.

Surface purification of PV modules

Another stage of PV cell and module recycling - after cell separation - is the recovery of pure silicon. In order to extract the silicon base from exploited, obsolete or damaged PV cells, two methods were introduced: chemical treatment and laser surface cleaning.

Chemical treatment of silicon-based PV cells

After separating the cells from PV modules, in order to recover pure silicon, different layers of material, put on in the production process, must be removed in specific order: frontal metallization, bottom metallization, antireflective coating and n-p junction connector. A chemical process of removing different layer, needed for recovering the silicon bed, was designed (Fig. 5).

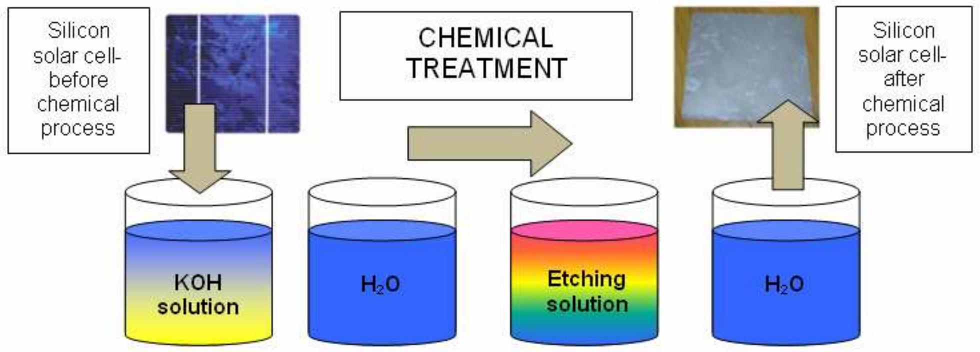

Fig. 5. Recovery of silicon base from the damaged PV cells

The main problem is choosing the proper composition of etching solutions, its concentration and optimal process temperature.

The application of laser technique for PV cell surface purification

Two types of PV cells were chosen for experiments - the samples for unnecessary layer removal originated from mono- and polycrystalline photovoltaic cells (Fig. 6).

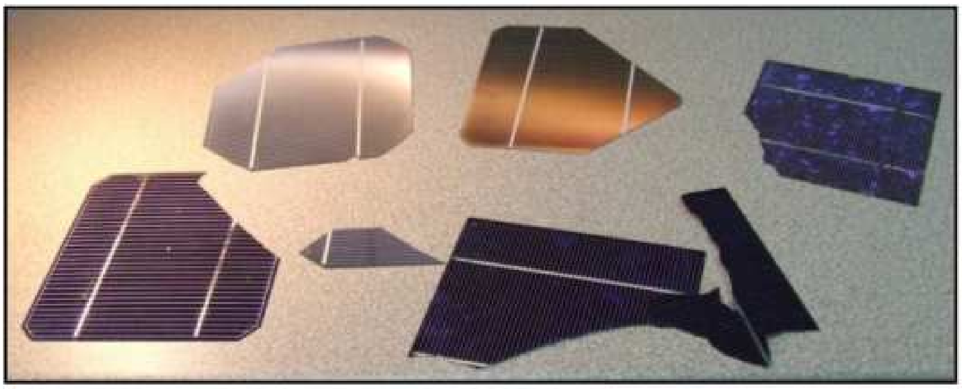

Fig. 6. Selected samples for the surface cleaning with the use of laser

The experiments were carried out with the use of neodymium impulse laser (wavelength λ = 1064 nm) Nd:YAG (*Yttrium-Aluminum-Garnet*), frequency up to 120 Hz, beam energy of 300 mJ per impulse, with 10 ns long impulses. It was possible to remove the aluminum bottom metallization and the antireflective coating from the PV cells. (Figs 7 and 8).

Fig. 7. Removing the ARC layer from PV cells using laser technology

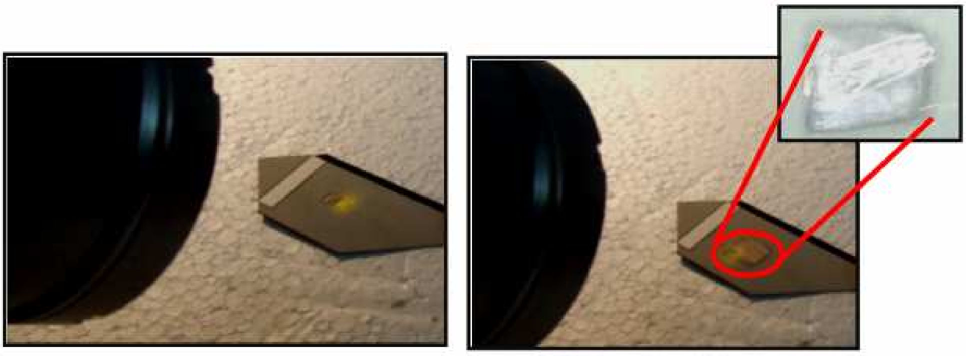

Fig. 8. Removing the back metallization from the PV cells, using laser technology

When comparing the methods used, it was determined that chemical treatment is far more advantageous. Because of the laser method's high price and low effectiveness, it is essential to further improve and optimize chemical methods of removing unwanted layers from PV cells. An estimated time of removing layers with the use of laser method is about 1 min/cm^2.

When utilizing chemical treatment, it is possible to purify the whole cell's surface during that time. For chemical purification, the following etching solutions may be applied: $HF/HNO_3/H_2O$, $H_2SiF_6/HNO_3/ H_2O$ or $H_2SiF_6/HNO_3/C_2H_4O_2$ [3-5].

Conclusion

The reason for conducting experimental work described in this paper was the effort to solve a more and more important problem of recycling obsolete, damaged or exploited PV devices with a minimal impact on the environment and with acquiring ecologically as well as economically worthy results.

The results of PV cell separation processes and unwanted layer removal processes, in order to recover pure silicon, show that recycling of PV modules is possible.

Separation of cells from damaged PV modules through chemical treatment is not economically worthwhile, a far more better solution is to use thermal treatment. Also, the implementation of laser techniques in unwanted layer removal stage, in comparison with chemical treatment, is also disadvantageous. An optimal solution is to use thermal treatment for cell separation and chemical treatment for removing the metallization, contacts, antireflective coating and the n-p junction.

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OBRÓBKA CHEMICZNA, TERMICZNA ORAZ LASEROWA W RECYKLINGU OGNIW I MODUŁÓW FOTOWOLTAICZNYCH Z KRYSTALICZNEGO KRZEMU

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Abstrakt: W ostatnich latach systemy fotowoltaiczne stają się bardzo popularne na całym świecie jako korzystne dla środowiska rozwiązanie problemów energetycznych. Zagadnienie zagospodarowania zużytych elementów systemów fotowoltaicznych, których ilość w przyszłości może być znaczna, nie zostało do tej pory opracowane. Konieczne jest znalezienie optymalnej metody recyklingu i ponownego wykorzystania wycofanych z użycia elementów składowych systemów PV. W artykule przedstawiono wybrane sposoby prowadzenia recyklingu zużytych lub uszkodzonych modułów i ogniw fotowoltaicznych oraz praktyczne wyniki prac eksperymentalnych z wykorzystaniem metod: chemicznych, termicznych oraz techniki laserowej. Opisano wady i zalety stosowanych technik, pomocne przy optymalizowaniu metody recyklingu dla zastosowań komercyjnych. Proces recyklingu modułów PV wymaga zastosowania dwóch zasadniczych etapów: separacji ogniw PV i oczyszczania ich powierzchni. W procesie separacji ogniwa - wchodzące w skład modułu PV - zostają rozdzielone w efekcie zastosowania procesów termicznych lub chemicznych. W następnej fazie ogniwa poddaje się procesowi, w którym usuwa się niepożądane warstwy: antyrefleksyjną, metalizację oraz złącze n-p, aby uzyskać podłoże krzemowe, nadające się do powtórnego zastosowania. Etap oczyszczania powierzchni krzemowych ogniw PV realizowano z zastosowaniem obróbki chemicznej oraz techniki laserowej.

Słowa kluczowe: ogniwa fotowoltaiczne, krzem, recykling, energia słoneczna, odnawialne źródła energii

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OZNACZANIE STĘŻEŃ JONÓW FLUORKOWYCH W PRÓBKACH WODY PITNEJ Z TERENU MIASTA MALBORKA

DETERMINATION OF FLUORIDE IONS IN DRINKING WATER SAMPLES COLLECTED FROM THE AREA OF THE TOWN OF MALBORK

Abstrakt: W pracy przedstawiono badania próbek wody pitnej z terenu miasta Malborka. Próbki wody pobierano sześciokrotnie (w miesięcznych odstępach - październik 2008, listopad 2008, grudzień 2008, styczeń 2009, luty 2009 oraz marzec 2009) w siedmiu punktach leżących w głównych dzielnicach miasta Malborka. Pobrane próbki podano analizie w celu oznaczenia następujących parametrów: zawartość anionów: F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}; zawartość kationów: Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}; przewodność; wartość pH. Uzyskane wyniki pozwoliły na jakościową i ilościową analizę składu próbek wody do picia. We wszystkich analizowanych próbkach zauważono większe niż dopuszczalne stężenie jonu fluorkowego, które na podobnym poziomie utrzymuje się od lat. Można również zaobserwować wyraźną zależność pomiędzy zawartością poszczególnych jonów a porami roku.

Słowa kluczowe: woda pitna, Malbork, jony fluorkowe

Wprowadzenie

Fluor jest pierwiastkiem, który w śladowych ilościach niezbędny jest do prawidłowego rozwoju. Aktywnie uczestniczy w metabolizmie zarówno roślin, zwierząt, jak i człowieka. Jednak ze wszystkich niezbędnych mikroelementów ma najmniejszy margines bezpieczeństwa pomiędzy niezbędną dla ustroju ilością a dawką, powyżej której występują objawy szkodliwego działania.

Powszechnie znany jest pozytywny wpływ fluoru na organizm człowieka. Fluor jest dodatkiem do różnego rodzaju preparatów stomatologicznych, stosowanych głównie do walki z próchnicą. Wzmacnia szkliwo zębów, niestety - zdaniem wielu naukowców - pozbawia zęby i kości wapnia, przez co stają się one bardziej kruche. Ciągle jednak za mało mówi się o jego szkodliwym, a wręcz toksycznym działaniu. Wśród skutków ubocznych stosowania fluoru naukowcy wymieniają zmiany szkieletowe, osteoporozę, zapalenie

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stawów, a nawet raka kości. Długotrwała ekspozycja organizmu na ponadoptymalne stężenie fluoru skutkuje ogólnoustrojową chorobą nazywaną fluorozą, która w końcowej fazie prowadzi do uszkodzenia wątroby, nerek, zaburzeń wzroku, a nawet ataksji. Fluor może też negatywnie oddziaływać na układ nerwowy, immunologiczny, a u dzieci powodować stałe zmęczenie, mały współczynnik inteligencji, ospałość, a nawet depresję.

Dla większości osób przyjmowanie produktów zawierających fluor w dopuszczalnych przez normy dawkach nie wiążą się z kłopotami, ale są osoby bardziej wrażliwe lub podatne na jego działanie niż pozostałe. Do nich należą przede wszystkim ludzie z zaburzeniami pracy nerek, gdyż to one właśnie są odpowiedzialne za wydalanie fluoru z organizmu.

Problem zanieczyszczenia środowiska przez związki fluoru został zauważony stosunkowo niedawno i związany jest głównie z przemysłową działalnością człowieka oraz z szerokim zastosowaniem jego związków w rolnictwie i profilaktyce stomatologicznej. Obecnie fluor obok ołowiu, rtęci, kadmu i arsenu traktowany jest jako jeden z najbardziej niebezpiecznych pierwiastków odpowiadających za skażenie środowiska. Dlatego tak ważne jest monitorowanie stężeń tego pierwiastka oraz prowadzenie badań pokazujących jego rzeczywisty wpływ na organizm ludzki.

Związki fluoru w wodzie

Fluor dość powszechnie występuje w wodach podziemnych, często w ilościach względnie dużych w porównaniu do zawartości innych mikroskładników. Najważniejszymi naturalnymi źródłami fluoru, które mogą prowadzić do zwiększenia jego stężenia w wodach podziemnych, są minerały (fluoroapatyt, fluoryt, kriolit oraz fluoronośne biotyty, hornblendy i turmaliny).

Podobnie jak w przypadku powietrza, do największego miejscowego wzbogacania wody w fluor dochodzi w strefach wulkanicznych oraz (dużo rzadziej) w przypadku wód kopalnych. Przykładowo stężenie 20 000 mg/dm^3 stwierdzono w kondensatach z wulkanu Kilauea [1]. Wody podziemne, choć w niewielkim stopniu, są również wzbogacane w fluor poprzez opady atmosferyczne (cykl obiegu fluoru). Wyraźną skłonność do koncentrowania się fluoru można zaobserwować w przypadku wód podziemnych w krajach o klimacie gorącym [1].

Podobnie jak w przypadku powietrza i gleby, również woda wzbogacana jest w fluor głównie w związku z przejawem antropopresji. Duże ilości fluoru przedostają się do wód podziemnych razem z atmosferycznymi zanieczyszczeniami gazowymi i pyłowymi, jak i wskutek przenikania ścieków oraz ługowania odpadów stałych [2]. W największym stopniu przyczyniają się do tego: produkcja superfosfatu, hutnictwo aluminium, ale także przemysł chemiczny, szklarski, emalierski i rolnictwo [1].

Stężenie fluoru w wodach podziemnych na terenie Polski zazwyczaj nie przekracza wartości 0,2÷0,5 mg F/dm^3. Wyjątkiem są regiony Gdańska, Malborka i Tczewa, gdzie zawartość fluoru przeciętnie wynosi 1,2÷3,2 mg/dm^3, natomiast lokalnie przekracza wartość 5 mg/dm^3 [3]. Największe dopuszczalne stężenie (NDS) tego pierwiastka w wodzie pitnej w Polsce wynosi 1,5 mg/dm^3 [4]. W większości krajów na świecie jest ono znacznie mniejsze. Przykładowo w USA wynosi ono 0,6 mg/dm^3, a w Indiach 0,5 mg/dm^3.

Wpływ fluoru na organizm ludzki

Korzystny wpływ fluoru

W organizmie człowieka fluorki ulegają absorpcji głównie poprzez przewód pokarmowy oraz płuca. Ich wchłanianie przez śluzówkę jamy ustnej jest ograniczone i stanowi mniej niż 1% dziennego wchłaniania. Główna absorpcja związków fluoru ma miejsce w żołądku i wynosi około 40÷50 % przyjętej dawki. Stopień i szybkość wchłaniania są odwrotnie proporcjonalne do pH treści żołądka. Pozostała ilości fluorków ulega absorpcji w górnej części jelita cienkiego. Wchłanianie w dużej mierze zależy od rodzaju związków fluoru (przede wszystkim ich rozpuszczalności). Obecność wapnia, magnezu i glinu w diecie ogranicza absorpcję fluorku w przewodzie pokarmowym, ponieważ tworzą one z nim nierozpuszczalne sole. Absorpcję zmniejsza również spożycie mleka, witaminy C i D, a zatem chroni przed jego przedawkowaniem. Stężenie fluoru w większości tkanek miękkich rośnie proporcjonalnie wraz ze wzrostem poziomu fluoru w osoczu, a później spada w sposób analogiczny. Głównym miejscem usuwania fluoru z ustroju są nerki.

Fluor w śladowych ilościach jest niezbędny do prawidłowego rozwoju kości i zębów. W dużym stopniu znaczny spadek próchnicy, obserwowany w świecie, można przypisać stosowaniu miejscowemu i ogólnemu związków fluoru. Profilaktyczny mechanizm jego działania jest wielokierunkowy. Zasadniczo jednak polega na wspomaganiu dwóch procesów: zmniejszaniu rozpuszczalności szkliwa oraz przyśpieszaniu jego remineralizacji.

Jony fluoru reagują z hydroksyapatytami szkliwa, wchodząc w miejsce jonów wodorotlenowych. W wyniku wymiany część hydroksyapatytów szkliwa przekształca się we fluoroapatyty, które mają lepsze właściwości krystaliczne oraz są słabiej rozpuszczalne w kwasach. Jon fluoru w apatycie tworzy silne wiązanie z grupą NH organicznego zrębu szkliwa, co warunkuje większą stabilność kryształów fluoroapatytu [5].

Druga możliwość profilaktycznego działania fluoru jest uwarunkowana jego zdolnościami stymulowania procesu demineralizacji [6]. Ta zdolność jest ściśle związana z obecnością tego jonu w ślinie oraz płytce nazębnej, a także na powierzchni szkliwa, gdzie może występować w postaci fluorku wapnia. Niekorzystne dla szkliwa i charakterystyczne dla procesu próchnicowego małe wartości pH śliny prowadzą do zwiększenia aktywności jonu fluorkowego. Dzięki swoim właściwościom fluor wpływa hamująco na tworzenie płytki bakteryjnej oraz produkcję kwasów przez bakterie tej płytki [5].

Dane literaturowe wskazują również, że ma on zdolność hamowania enolazy bakteryjnej - enzymu ważnego w przemianie węglowodanów. Możliwe też jest utrudnianie przez fluor transportu glukozy przez błony komórkowe bakterii kwasotwórczych. Prawdopodobnie miejscem inhibicji jest przenosząca protony ATP-aza błony bakteryjnej [5].

Toksyczny wpływ fluoru

Korzystne działanie związków fluoru spowodowało, że zaczęto szeroko stosować je w różnych dziedzinach medycyny (zwłaszcza stomatologii), rolnictwie oraz przemyśle. Przyczyniło się to do ich szczególnej popularności w drugiej połowie XIX w. Jednak obserwacje mówiące o pozytywnym działaniu związków fluoru przysłoniły rzeczywisty obraz ich oddziaływania na poziomie molekularnym [7]. Do chwili obecnej ukazały się tysiące prac na temat oddziaływania i zawartości fluoru w płynach ustrojowych (krew, mocz, płyn mózgowo-rdzeniowy, ślina), w tkankach miękkich (nerki, wątroba, mózg, łożysko), w tkankach twardych (kości, zęby, paznokcie, włosy, kamienie moczowe) potwierdzających ich negatywne, toksyczne i destrukcyjne działanie. Są to między innymi: ostra i przewlekła toksyczność, możliwość powstawania fluorozy zębowej i szkieletowej, liczne zaburzenia metaboliczne (np. cukrzyca fluorowa), osteoporoza, zaburzenia syntezy kolagenu, hamowanie aktywności niektórych enzymów, negatywny wpływ na procesy bioenergetyczne i oddychanie tkankowe, przyspieszanie procesów starzenia [7]. Poniżej, w sposób bardziej szczegółowy, przedstawiono negatywny wpływ jonów fluorkowych na wybrane elementy organizmu człowieka.

- **Skóra**

Efekt biologicznego oddziaływania jonu fluorkowego na tkankę łączną dotyczy: kolagenu, białek niekolagenowych oraz komórek tkanki łącznej. Efektem takim może być mineralizacja kolagenu, zmniejszenie zawartości białek kolagenowych oraz niewłaściwe usieciowane, zaburzenie struktury i regularności włókien kolagenu. W pierwszym etapie dochodzi do zaburzenia procesu syntezy białka kolagenowego (stanowiącego 30% wszystkich białek ustrojowych). Słabe wiązania wodorowe zostają zastąpione przez silniejsze wiązania fluorkowo-wodorowe, które zaburzają normalny proces jego powstawania. Zmiany konformacyjne takiego kolagenu prowadzą do zaburzeń w budowie przestrzennej matrycy, na której zachodzą procesy mineralizacji. W takiej sytuacji produkt mineralizacji również obarczony jest defektem. Pod wpływem fluoru dochodzi również do zwiększenia produkcji białek niekolagenowych (proteoglikanów i glikozaminoglikanów), mimo ogólnie hamującego wpływu fluorków na biosyntezę białka. Jest to powodem szybszego starzenia się skóry (jej zwiększonego pofałdowania i pokrycia zmarszczkami), głównie w grupie osób pomiędzy 30 a 40 rokiem życia [8].

- **Układ kostny**

Istotą patogenezy zmian w narządzie ruchu występujących pod wpływem fluoru jest szczególne powinowactwo jonu fluorkowego do hydroksyapatytu kości. Fluor ulega wbudowaniu w heksagonalny kryształ hydroksyapatytu. Do jednej molekuły hydroksyapatytu mogą wbudować się maksymalnie dwa jony fluorkowe, jednak jego całkowite wysycenie możliwe jest jedynie teoretycznie. Fluor może podstawić jedynie dwie grupy hydroksylowe ze względu na ograniczenia wynikające z budowy sferycznej. Pomimo niecałkowitego wysycenia (maksymalnie 3÷4%) w stosunku do całkowitej masy, hydroksyapatyt jest potężnym depozytem fluoru. W tych warunkach z części hydroksyapatytu (głównego nieorganicznego budulca tkanki kostnej) powstaje fluoroapatyt, który zmienia właściwości fizykochemiczne kości. Traci ona sprężystość i staje się mniej elastyczna, za to bardziej twarda, krucha i łamliwa. U ludzi obserwuje się wówczas pogrubienie kości oraz częste złamania kości kończyn górnych i dolnych. Fluoroza szkieletowa może prowadzić do trwałego inwalidztwa, bowiem fluor powoduje również mineralizację wiązadeł i tkanki chrzęstnej, przez co układ szkieletowy ulega deformacji, poruszanie zaś staje się bardzo utrudnione [8].

- **Przemiany biochemiczne**

Do zakłócenia szeregu przemian biochemicznych dochodzi z powodu tworzenia przez jon fluorkowy trwałych, jednak biologicznie nieczynnych kompleksów z kationami metali oraz wiązań wodorowych z ważnymi biologicznie grupami amidowymi. Jednym z ważniejszych metali w organizmie jest magnez, bowiem około 300 enzymów wymaga jego udziału, głównie w roli aktywatora. Jon fluorkowy, przenikając z krwi do komórek, wiąże jony magnezu, tworząc z nimi nierozpuszczalną sól. Inhibicja enzymów powodowanych przez jony fluorkowe może dotyczyć enzymów metalozależnych oraz takich, w których kofaktor nie jest potrzebny, a fluor blokuje bezpośrednio enzym (np. acetylocholinoesteraza). Udowodniono również, że wrażliwe na jon fluorkowy są składowe łańcucha oddechowego odpowiedzialne za transport elektronów: dehydrogenaza bursztynianowa, cytochrom C oraz oksydaza cytochromowa. Fluor odpowiedzialny jest również za hamowanie niektórych enzymów cyklu Krebsa, utlenienia kwasów tłuszczowych oraz przemiany glikolizy.

- **Płód**

Dowiedziono, że fluor pokonuje barierę łożyskową u ludzi, przedostając się z krwi matki do krwi płodu. Łożysko tylko częściowo spełnia rolę filtru dla jonów fluoru, głównie w częściach brzeżnych (ze względu na dużą zawartość w tej części jonów wapnia). Jak wykazały badania na obszarach skażeń związkami fluoru, badane łożyska charakteryzowały się spadkiem aktywności enzymatycznej. Na efektywność transportu fluoru przez łożysko wpływ mają następujące czynniki: stopień dojrzałości tkanki łożyskowej, prawidłowość przepływu maciczno-łożyskowego krwi oraz obecność zwapnień w tkance łożyskowej. Przyjmuje się, że około 99% fluoru w organizmie jest związane z tkankami twardymi. W młodych organizmach dochodzi do zwiększonej retencji fluoru w tkankach twardych. Jego retencja w szkielecie młodych organizmów jest około 2 razy szybsza niż u dorosłych. W trakcie ekspozycji na małe ilości fluoru dorośli magazynują około 10% wchłoniętego fluoru, natomiast rosnące dzieci mogą go magazynować nawet w 50%. Zwiększona ilość fluoru w łożyskach kobiet ciężarnych powoduje zaburzenia rozwojowe płodu, zmniejszenie masy urodzeniowej dziecka, a poprzez to zmniejszenie jego szans na przeżycie [9].

W chwili obecnej trwają badania nad powiązaniem wpływu ponadoptymalnych stężeń jonów fluorkowych na rozwój takich chorób, jak: rak kości, zespół Downa i choroba Alzheimera [7].

Fluoroza

Pierwszym widocznym objawem nadmiernej ekspozycji organizmu na ponadoptymalne stężenie fluorków pochodzących z wody, atmosfery oraz żywności bogatej w ten pierwiastek są przebarwienia szkliwa. Występują one w odcieniach od kredowobiałych do brunatnych, a nawet czarnych. W okresie rozwoju uzębienia efektem długotrwałego zatrucia fluorkami jest fluoroza zębowa, natomiast w okresie dorosłym - utrata uzębienia. Choroba ta poza wspomnianymi już przebarwieniami sprawia, że zęby stają się matowe, łamliwe i kruche, natomiast ich korzenie są krótkie. Dochodzi do zachwiania procesów mineralizacji, które bezpośrednio dotyczą układu kostnego. Powodują one zmiany w gęstości oraz strukturze kości [10].

Fluoroza zębów jest rodzajem zaburzeniem pochodzenia rozwojowego. Jest ona określana jako stan patologiczny, powstały w wyniku nadmiernej ekspozycji zęba na ponadoptymalne stężenie fluorków pochodzących z wody, atmosfery oraz żywności bogatej w ten pierwiastek w okresie rozwoju szkliwa. Pierwszym widocznym klinicznym objawem fluorozy zębów jest występowaniem zmian w szkliwie. W zależności od stopnia zaawansowania choroby zmiany te mogą występować w postaci pojedynczych lub zlewających się pasm lub plam opalizujących, kredowobiałych albo brunatnych, zagłębień, a także ubytków szkliwa, prowadzących w ciężkich przypadkach do zmiany kształtu zęba. W obrazie histopatologicznym stwierdza się nietypowe ułożenie i rozszczepienie pryzmatów szkliwnych oraz brak substancji międzypryzmatycznej, w miejscu której odkłada się barwnik brunatny. Zębina jest słabiej zmineralizowana i zawiera szerokie przestrzenie międzykuliste. Szkliwo może być matowe, nieprzezroczyste i chropowate. Stopień zaawansowania fluorozy zależy od stężenia związków fluoru w wodzie pitnej, czasu ekspozycji na fluor, od indywidualnej wrażliwości organizmu i czynników środowiskowych. Obecność wapnia i magnezu w diecie wpływa na ograniczenie wchłaniania fluoru. Niedobór tych pierwiastków w pożywieniu sprzyja występowaniu fluorozy.

Mechanizm powstawania szkliwa plamkowego nie jest dokładnie wyjaśniony. W niektórych pracach zawarto sugestie, iż pod wpływem jonów fluoru dochodzi do hamowania aktywności enzymów lizosomalnych w ameloblastach, może również dojść do bezpośredniego uszkodzenia ameloblastów. Uważa się, że szkliwo plamkowe występuje u osób, które w dzieciństwie spożywały wodę o stężeniu fluoru większym niż optymalne - czyli 1 mg/dm^3. Poglądy na temat występowania szkliwa plamkowego nie są jednak jednolite [10].

Do rozpoznania fluorozy zębów upoważnia nie tylko sam wygląd szkliwa, lecz także dodatkowe informacje uzyskane podczas wywiadu wskazujące na zwiększoną podaż związków fluoru lub potwierdzenie zwiększonej zawartości fluoru w tkankach (szkliwo, ślina).

Przyjmuje się, że fluoroza o średnim i dużym stopniu nasilenia występuje na terenach, na których fluor w wodzie pitnej osiąga stężenie około 3,5 mg/dm^3. Powstawanie fluorozy powoduje nadmierna podaż związków fluoru w okresie krytycznym, przypadającym na późne stadia przederupcyjnego rozwoju zęba. Równocześnie uważa się, że krytyczny okres dla uzębienia stałego występuje od okresu okołoporodowego do około 7 roku życia.

Fluoroza jest zwykle bardziej nasilona w przypadku zębów, dla których proces mineralizacji przypada na późniejszy okres życia. Najczęściej uszkodzonymi zębami stałymi są zęby przedtrzonowe, następnie drugie trzonowe, zęby sieczne górne i kły. Pierwsze trzonowce i dolne siekacze są zwykle najmniej dotknięte zmianami, z wyjątkiem przypadków o dużym stopniu zaawansowania choroby. Fluoroza częściej występuje w zębach stałych niż w zębach mlecznych. Uwarunkowane jest to prawdopodobnie dostarczaniem większych ilości związków fluoru do organizmu przez dzieci starsze. Fluoroza zębów mlecznych przebiega łagodniej niż fluoroza zębów stałych. Przyczyną tego faktu jest ponad 2-krotnie krótszy okres dojrzewania zębów mlecznych niż zębów stałych [10].

Wymagania stawiane wodzie pitnej w Polsce

Wykorzystanie wód do celów konsumpcyjnych związane jest ze spełnieniem przez nie określonych wymagań (tab. 1). W większości przypadków woda występująca w przyrodzie nie nadaje się do wykorzystania jako woda pitna. Wiąże się to z zawartymi w niej zanieczyszczeniami oraz zbyt dużą ilością związków mineralnych, organicznych i bakterii. W Polsce zgodnie z rozporządzeniem ministra ochrony środowiska (z dnia 11 lutego 2004 roku) obowiązuje pięciostopniowa klasyfikacja wód (jedynie wody pierwszej i drugiej z nich nadają się do wykorzystania jako woda pitna bez przeprowadzania zabiegów uzdatniających).

Tabela 1

Wymagania jakie powinna spełniać woda przeznaczona do picia [3]

Table 1

The requirements for drinking water [3]

Wskaźnik, nazwa substancji	Jednostka	Polska
Odczyn	[pH]	6,5÷9,5
Konduktywność	[μS/dm^3]	2500
Jon amonowy	[mg/dm^3]	0,5
Azotany(V)	[mg/dm^3]	50
Azotany(III)	[mg/dm^3]	0,5
Chlorki	[mg/dm^3]	250
Fluorki	[mg/dm^3]	1,5
Magnez	[mg/dm^3]	30÷125
Siarczany	[mg/dm^3]	250
Sód	[mg/dm^3]	200

Procesy wpływające na skład wód podziemnych

Ze względu na wysoki stopień zanieczyszczeń wód powierzchniowych główne źródło wody pitnej stanowić powinny wody podziemne. Procesy, które kształtują skład chemiczny wód podziemnych, nazywane są procesami hydrogeochemicznymi. Obejmują one udział ośrodka skalnego w tworzeniu chemizmu wód podziemnych. Poza skałami w skład układu wchodzą również: woda wraz z rozpuszczonymi w niej substancjami i zawiesinami oraz gazy. Na proces całościowy składa się wiele procesów jednostkowych, które można opisać prawami fizyki bądź chemii [8]. Wszystkie procesy hydrogeochemiczne można podzielić ze względu na efekty, jakie powodują:

- procesy, w których następuje przemieszczanie się substancji w wodach (np. dyfuzja),
- procesy, w których woda jest wzbogacana w określony składnik (np. ługowanie),
- procesy, w których woda jest zubażana w określony składnik (np. sorpcja),
- procesy, w których woda jest zarówno wzbogacana, jak i zubażana w określony składnik (np. wymiana jonowa).

Inna klasyfikacja, o dużym znaczeniu metodologicznym, za podstawowe kryterium, dzielące wszystkie reakcje chemiczne na dwie grupy, przyjmuje stosunki energetyczne reagujących układów oraz szybkość przebiegu reakcji. Do grupy pierwszej należą reakcje, których szybkość oraz zachodzące stosunki energetyczne sprzyjają ustalaniu się równowagi chemicznej - reakcje odwracalne (np. rozpuszczania, wytrącania). Analogicznie do drugiej grupy reakcji należą procesy trudniej odwracalne lub też nieodwracalne (np. procesy wietrzenia skaleni).

Przebieg określonych procesów, częstotliwość ich występowania oraz ich wpływ na kształtowanie chemizmu wód podziemnych w dużym stopniu zależą od warunków środowiska. Niektóre jednostkowe procesy zachodzą powszechnie i odgrywają ważną rolę w kształtowaniu chemizmu wód podziemnych. Należą do nich: hydratacja, hydroliza, sorpcja, wymiana jonowa, rozpuszczanie oraz wytrącanie, utlenianie i redukcja. Inne natomiast wywierają wpływ tylko w określonych warunkach (np. ultrafiltracja) lub też mają charakter wyłącznie lokalny (np. radioliza wody - w przypadku substancji promieniotwórczych) [8].

Ługowanie i wymywanie skał

Przykładem procesu powszechnie zachodzącego w środowisku jest ługowanie skał. Jest to proces definiowany szerzej niż rozpuszczanie. Ługowanie jest rozumiane jako rozpuszczanie minerału bądź też grupy minerałów i wynoszenie produktów rozpuszczania poza obszar występowania ługowanych skał. Jest to proces złożony, na który składa się wiele procesów jednostkowych: hydroliza, hydratacja, a także procesy utleniająco-redukcyjne. Duży wpływ na ługowanie ma obecność takich gazów, jak: CO_2, O_2, H_2S, oraz takie czynniki, jak pH, temperatura, ciśnienie. Do minerałów skał osadowych, które najłatwiej ulegają rozpuszczaniu, należą: halit, gips, anhydryt, kalcyt oraz dolomit. Nieco inaczej przebiegają procesy ługowania skał magmowych oraz metamorficznych. Tworzące je minerały są znacznie trudniej rozpuszczalne, natomiast wody krążące między nimi mają charakter szczelinowy, co w znacznym stopniu ogranicza kontakt z ośrodkiem skalnym.

Wymywanie jest procesem pokrewnym do ługowania, jednak odnosi się do większych kompleksów skalnych lub obszarów [11].

Wytrącane faz stałych

Czynnikiem inicjującym proces wytrącania się różnego rodzaju faz stałych w wodach podziemnych może być:
- zmiana warunków fizycznych (temperatura, ciśnienie),
- zmiana warunków chemicznych (stężenia, pH),
- działalność mikroorganizmów.

Pod pojęciem fazy kryją się zarówno minerały, jak i organiczne oraz nieorganiczne substancje amorficzne. Te drugie charakteryzują się dużo większą rozpuszczalnością niż krystaliczne minerały, a zatem ich wpływ na skład chemiczny wód podziemnych ma większe znaczenie. Jednak ich rola jest do dziś mało zbadana.

Wytrącanie minerałów jako faz stałych zmienia zarówno skład wód, jak i warunki środowiska (ich przepływ) poprzez zmianę rozmiaru i geometrii przestrzeni porowych. Powoduje to pogorszenie parametrów filtracji, a na znacznych głębokościach procesy wytrącania mogą prowadzić do przejścia osadu w litą skałę. Do wytrącania dochodzi w momencie trwałego przesycenia wody względem danego składnika, czyli po przekroczeniu jego iloczynu rozpuszczalności. Zatem kolejność wytrącania się faz stałych zależy od ich rozpuszczalności. W pierwszej kolejności wytrącają się minerały najtrudniej rozpuszczalne [11].

Mieszanie się wód o różnym składzie

Proces nazywany też: współdziałaniem hydrogeochemicznym wód różnego rodzaju w przyrodzie występuje powszechnie i ma podstawowe znaczenie w kształtowaniu się chemizmu wód podziemnych. Mieszanie zwykle zachodzi szybko i obejmuje znaczne masy wód. Efekty procesu zależą od chemizmu wód tworzących ten układ, proporcji ilościowej między nimi oraz od warunków środowiska (głównie hydrodynamicznych). Mieszanie się wód o różnym chemizmie zawsze prowadzi do przesunięcia równowag hydrogeochemicznych. Ogólnie można wyróżnić trzy podstawowe typy takich efektów:
- wytrącanie faz gazowych i stałych,
- rozpuszczanie faz gazowych i stałych,

- zastępowanie jednych minerałów w ośrodku skalnym przez inne.

W warunkach naturalnych następstwa mieszania się wód mogą wzajemnie przechodzić z jednych w drugie lub współwystępować [11].

Utlenianie i redukcja

Reakcje redoks (utleniania i redukcji) należą do najpowszechniej zachodzących w środowisku i mających ogromne znaczenie w kształtowaniu składu wód podziemnych. Utlenianie jest procesem, w którym dany pierwiastek podwyższa swój stopień utlenienia - poprzez utratę elektronów walencyjnych jego atomów. Analogicznie redukcja to obniżenie stopnia utlenienia poprzez przyjęcie elektronów przez atomy danego pierwiastka. Znaczenie tych procesów jest bezpośrednio związane ze zmianą zdolności migracyjnych poszczególnych pierwiastków przy zmianie ich stopnia utlenienia. Reakcje redoks mają wpływ na skład wód podziemnych zarówno w warunkach naturalnych, jak i zakłóconych antropopresją. Odgrywają one również ważną rolę w procesach samooczyszczania się wód. W wodach podziemnych najbardziej aktywnym utleniaczem jest tlen, jednak jego rolę mogą spełniać także: żelazo(III), mangan(IV), siarka(VI) oraz azot(V) [11].

Procesy sorpcyjne

Podobnie jak procesy utleniania i redukcji, są to procesy, które bardzo powszechnie zachodzą w przyrodzie i mają duży wpływ na kształtowanie się składu chemicznego wód podziemnych. Składają się na nie: adsorpcja, desorpcja i wymiana jonowa. Zachodzą one na granicy fazy stałej i ciekłej (np. minerału i wody). W znacznym stopniu zmieniają one skład gleb, skał, gruntu, a jednocześnie wód podziemnych. Podobnie jak procesy redoks, odgrywają one szczególną rolę w samooczyszczaniu się wód powierzchniowych i podziemnych. Adsorpcja to proces fizykochemiczny polegający na gromadzeniu się na powierzchni adsorbentów (minerałów) molekuł adsorbatu (molekuł rozpuszczonych w wodzie). Analogicznie desorpcja jest procesem odwrotnym i polega na przechodzeniu do roztworu uprzednio zaadsorbowanych molekuł. Na przebieg tych procesów wpływa wiele czynników, między innymi stężenie adsorbatu, rozdrobnienie i właściwości powierzchni adsorbentu oraz warunki środowiska (pH, temperatura, ciśnienie). W wodach podziemnych klimatów umiarkowanych dominują procesy adsorpcji kationów, natomiast w wilgotnych tropikach częściej do czynienia mamy z adsorpcją anionów. Podstawowymi adsorbentami kationów w wodach podziemnych są minerały ilaste, zeolity, substancja organiczna, wodorotlenki i tlenki szeregu metali. Adsorbentami anionów zaś głównie wodorotlenki glinu i żelaza. Szczególną uwagę poświęcić należy wymianie jonowej. Proces ten polega na adsorbowaniu z wody przez składniki fazy stałej jonów, na miejsce innych, które odłączają się i przechodzą do roztworu. Najczęściej jest to reakcja odwracalna i przebiega w ilościach równoważnych [11].

Czynniki abiotyczne i biologiczne wpływające na chemizm wód podziemnych

Skład wód podziemnych jest efektem współdziałania procesów oraz wielu czynników zachodzących w określonych warunkach środowiska. Możemy podzielić je na geograficzne, w skład których wchodzą:

- rzeźba terenu - wpływa na przebieg procesów warunkującej chemizację wód podziemnych, im bardziej urozmaicona rzeźba terenu, tym intensywniej zachodzą procesy mineralizacji;
- hydrografia - w dużym stopniu zależy od budowy geologicznej i warunków klimatycznych, najważniejsze znaczenie mają: gęstość sieci hydrograficznej, głębokość wcięć, kontakt wód powierzchniowych z podziemnymi oraz ingerencja wód morskich na terenach przybrzeżnych;
- klimat - pośrednio wpływa na chemizm wód podziemnych, największe znaczenie mają takie czynniki, jak: opady atmosferyczne, temperatura powietrza, parowanie, wiatr (na terenach morskich);
- gleby - jako strefa aktywna biologicznie dostarcza do wód łatwo rozpuszczalne związki, jej łatwość zmiany pH ma znaczący wpływ na migrację poszczególnych pierwiastków.

W przypadku czynników geologicznych należy również wymienić procesy: diagenezy, wietrzenia, magmatyzmu, tektoniczne, składu mineralnego oraz ciśnień geostatycznych.

Wody podziemne stanowią specyficzną, zróżnicowaną przestrzennie niszę ekologiczną dla wielu różnego rodzaju organizmów żywych, które w znaczący sposób wpływają na skład zamieszkałych przez nie wód. Największe znaczenie mają tutaj bakterie, ale w przypadku wód gruntowych można zauważyć również wpływ roślin naczyniowych. Bakterie występują w różnych środowiskach hydrogeochemicznych, od powszechnie występujących słabo mineralizowanych wód gruntowych po skrajnie kwaśne wody kopalniane czy wody termalne obszarów wulkanicznych. Bardzo aktywnie uczestniczą one w cyklu wielu przemian biogeochemicznych - obiegu pierwiastków, takich jak: węgiel, azot, siarka, żelazo, mangan, jod, miedź, kadm, a nawet rtęć. Dzięki zdolności biodegradacji materii organicznej odgrywają ogromną rolę w procesach samooczyszczania się wód [11].

Część eksperymentalna

Budowa geologiczna terenu Malborka

Pod względem geologiczno-tektonicznym teren Malborka należy do syneklizy perybałtyckiej i leży w peryferyjnej strefie platformy wschodnioeuropejskiej. Skały prekambryjskiego podłoża leżą głęboko (na głębokości ponad 3000 m) i podobnie jak zalegający na nich kompleks staropaleozoiczny (kambr, ordowik, sylur) nigdzie na terenie miasta nie zostały nawiercone. Ze skał mezozoicznego cyklu sedymentacyjnego rozpoczynającego się w cechsztynie nawiercono na terenie powiatu tylko najmłodsze - kredowe. Osady trzeciorzędowe są nieciągłe przestrzennie. W rejonie depresji podłoża czwartorzędu przebiegającej w rejonie koryta Nogatu osady czwartorzędowe zalegają bezpośrednio na osadach kredowych mastrychtu nawierconych w Malborku na głębokościach 87,0 i 94,5 m p.p.m. Dno depresji musi leżeć głębiej, gdyż w bezpośrednim sąsiedztwie miasta w kamienicy nawiercono kredę na głębokości 106,5 i 111,9 m p.p.m. Większe miąższości uzyskują osady trzeciorzędowe na wyniesieniach podłoża czwartorzędu (–60 do –70 m n.p.m.) i tam lokalnie występuje zarówno paleogen (pleocen i oligocen), jak i występujący wyspowo neogen-miocen. Na terenie miasta nawiercono utwory trzeciorzędowe w południowej, środkowej i wschodniej części miasta. Utwory miocenu udokumentowano w dwóch otworach na głębokości od 62,6 m p.p.m. do 80,1 m p.p.m. oraz od 73,8 do 81,0 m p.p.m. Utwory oligocenu przewiercono w czterech otworach na głębokościach odpowiednio 80,1÷88,5 m p.p.m., 83,5÷89,5 m p.p.m. i 87,8÷93,8 m p.p.m. oraz 96,7÷104,7 m p.p.m., a w piątym nawiercono oligocen na gł. 81,0 m p.p.m., nie osiągając spągu na gł. 88,7 m p.p.m. Tylko w ostatnim przypadku (Piaski) zostały udokumentowane utwory paleocenu na głębokości 93,8÷117,8 m p.p.m. W pozostałych głębszych wierceniach na terenie miasta, które osiągnęły spąg czwartorzędu, nie rozdzielono utworów trzeciorzędowych nawiercanych na głębokościach 64,0, 70,0 i 78,7 m p.p.m. W pierwszym przypadku osady kredowe podłoża stwierdzono na głębokości 102,0 m p.p.m., w pozostałych na głębokościach odpowiednio 132,0 i 108,2 nie osiągnięto jednak spągu trzeciorzędu [9].

Generalnie miąższość utworów czwartorzędowych jest duża (rzędu 70 i więcej metrów). Wykazują one duże zróżnicowanie genetyczne i litologiczne, gdyż obejmują osady lodowcowe i wodnolodowcowe, zastoiskowe, rzeczne, jeziorne, morskie i bagienne. Osady morskie i rozległy kompleks deltowych osadów rzecznych są charakterystyczne dla Żuław. W Malborku stwierdzono dobrze wykształcone osady interglacjalne interglacjału mazowieckiego o miąższości do 50 m i emskiego o miąższości dochodzącej do 40 m. W Kałdowie osady aluwialne, powszechnie dominujące wśród utworów powierzchniowych, przeważnie o dość ciężkim składzie mechanicznym, stały się skałą macierzystą dla żyznych gleb typu mad. Wysoczyzna polodowcowa Pojezierza Iławskiego w okolicy Malborka wykazuje dominację glin zwałowych i iłów zastoiskowych [12].

Zaopatrzenie Malborka w wodę

Mieszkańcy powiatu malborskiego na ogół są zaopatrywani w wodę z wodociągów. W Malborku pracują studnie głębinowe pobierające wody podziemne zarówno dla potrzeb przemysłu, jak i wodociągów komunalnych. Jakość ujmowanych tam wód jest lepsza, co leży u podstaw projektowanego przyłączenia tej sieci do sieci Centralnego Wodociągu Żuławskiego.

Tabela 2

Zwodociągowanie miasta Malborka na tle powiatu malborskiego [12]

Table 2

Water supply of the town of Malbork on the background of Malbork District [12]

Lp.	**Gmina**	**Długość sieci wodociągowej**	**Liczba przyłączy do budynków**	**Stopień zwodociągowania**
		[km]	**[sztuki]**	**[%]**
1	Miasto Malbork	135,80	2686	100
2	Gmina Malbork	35,90	572	96
3	Miłoradz	37,00	927	99
4	Lichnowy	46,80	525	98
5	Stare Pole	57,00	729	100
6	Nowy Staw	50,20	837	95
7	**Łącznie**	**362,7**	**6276**	**X**

Dotychczas jednak miasto posiada odrębną sieć wodociągową zaopatrywaną z własnego ujęcia (8 studni) czerpiącego wody z głębokości 190÷250 m p.p.t. i częściowo zaopatruje również podmiejskie miejscowości gminy Malbork. Według „Strategii rozwoju powiatu malborskiego” eksploatowanych jest 7 studni ujmujących wody z warstw kredowych (studnia nr 3, 4, 5, 6, 7) - 950 m^3/h i trzeciorzędowo-czwartorzędowych (studnia nr 8 i 9) - 389 m^3/h.

Zatwierdzone zasoby dla całego ujęcia miasta Malborka zgodnie z obowiązującym pozwoleniem wodnoprawnym na pobór wód podziemnych wynoszą 450 i 9800 m^3/d. Szczegółowe informacje na temat długość sieci w Malborku przedstawiono w tabeli 2.

Część gmin podłączona jest do Centralnego Wodociągu Żuławskiego (gminy Nowy Staw i Stare Pole w całości, gminy Malbork i Lichnowy - częściowo). Miasto Malbork jest w pełni zwodociągowane. Problemy sprowadzają się do dbałości o jakość wody dostarczanej wodociągiem (budowa stacji uzdatniania wody), modernizacji i przebudowy sieci oraz konserwacji urządzeń [12].

Zużycie wody na potrzeby gospodarki narodowej w 2003 r. w mieście Malbork wyniosło 1970,6 dam^3, z czego 1877,4 dam^3 na potrzeby gospodarstw domowych i socjalno-bytowe, reszta 93,2 dam^3 przypada na przemysł. W tabeli 3 przedstawiono dane dotyczące jakości wody do spożycia w mieście Malbork z ujęć wód podziemnych powiatu malborskiego (ocena GUS w 2001 i 2002 roku) [12].

Tabela 3

Jakość wody do spożycia w mieście Malbork z ujęć wód podziemnych powiatu malborskiego (ocena GUS w 2001 i 2002 roku) [12]

Table 3

Quality of drinking water in Malbork from intakes groundwater of Malbork District (Evaluation of the GUS in 2001 and 2002)

Miejscowość	**Rodzaj wodociągu**	**Rok 2001**	**Rok 2003**
		[mg/dm^3]	**[mg/dm^3]**
Malbork	publiczny	zła: fluorki 1,5÷3,5	zła: fluorki 1,5÷2,9
Malbork - szpital	lokalny	zła: żelazo 1,6÷6,0, mangan 0,06÷0,19, amoniak 0,9÷2,4, mętność 15÷37, barwa 5÷50	zła: żelazo 2,8, mętność 22, amoniak 1,79
Malbork - wytwórnia waty	lokalny	dobra	Dobra

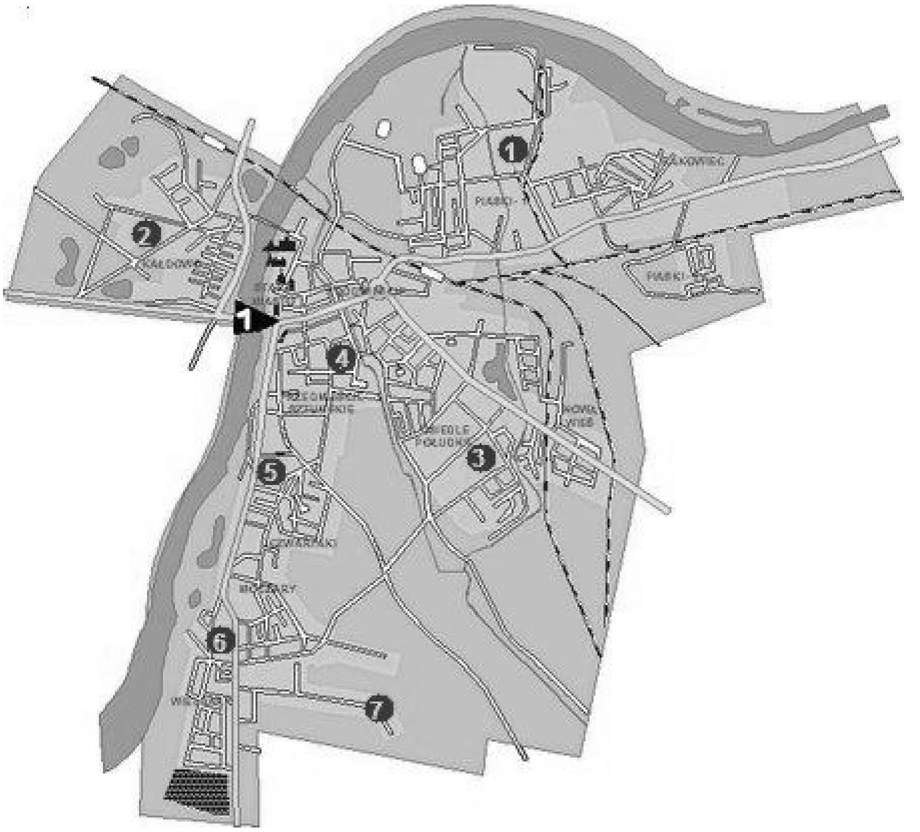
Wartości dopuszczalne: fluorki - 1,5 mg/dm^3; żelazo - 0,2 mg/dm^3; mangan - 0,05 mg/dm^3; amoniak - 0,5 mg/dm^3; mętność <dm^3

Lokalizacja miejsca pobierania próbek

Próbki wody pitnej pobierano z siedmiu odległych od siebie punktów (główne dzielnice) położonych na terenie miasta Malbork (rys. 1):

- miejsce pobrania próbek nr 1 - dzielnica Piaski, ulica Daleka,
- miejsce pobrania próbek nr 2 - dzielnica Kałdowo, aleja Rodła,
- miejsce pobrania próbek nr 3 - dzielnica Południe, ulica Kotarbińskiego,
- miejsce pobrania próbek nr 4 - dzielnica Śródmieście, ulica Kościuszki,
- miejsce pobrania próbek nr 5 - dzielnica Czwartaki, aleja Armii Krajowej,
- miejsce pobrania próbek nr 6 - dzielnica Wielbark, ulica Słupecka,
- miejsce pobrania próbek nr 7 - dzielnica Wielbark, ulica Głowackiego.

Próbki pobierane były sześciokrotnie: w październiku 2008, listopadzie 2008, grudniu 2008, styczniu 2009, lutym 2009 oraz marcu 2009. Pobierano je bezpośrednio z sieci wodociągowej do pojemników z tworzywa sztucznego pojemności 100 cm^3, a następnie zamrażano. Po przetransportowaniu ich do laboratorium przechowywano je w niskiej temperaturze i poddawano jak najszybszej analizie, ponieważ nie były one konserwowane za pomocą środków chemicznych.



Rys. 1. Plan miasta Malborka z zaznaczonymi miejscami pobierania próbek

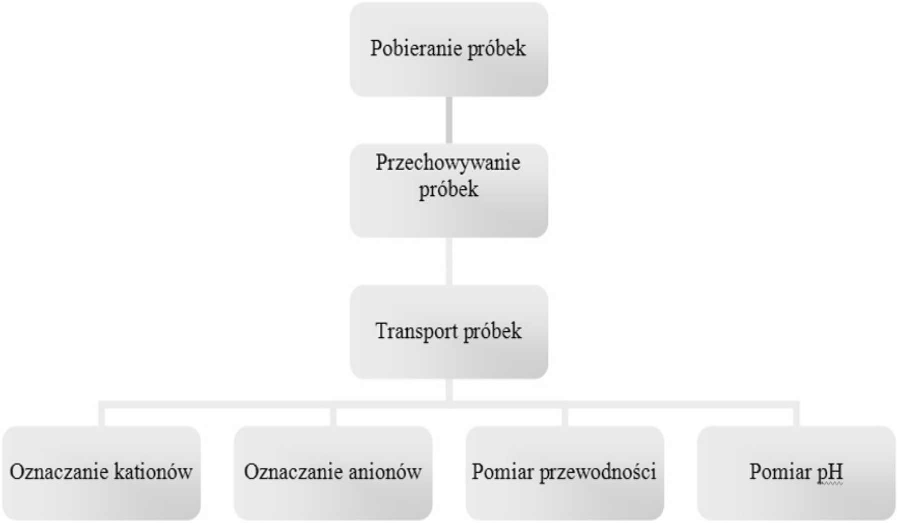
Fig. 1. The Malbork city map with marked sample collection places

Oznaczane związki i parametry

Badaniom poddano próbki wody pitnej pobrane z sześciu głównych dzielnic miasta Malborka. Dokonano ich analizy w celu oznaczenia następujących składników i parametrów fizykochemicznych:

- aniony: F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-},
- kationy: Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+},
- konduktywność (przewodnictwo właściwe),
- pH.

Uproszczony schemat postępowania z zebranymi próbkami wody pitnej przedstawiono na rysunku 2.



Rys. 2. Schemat postępowania z próbkami przeznaczonymi do badań

Fig. 2. Schema of the handling of samples undergoing analysis

Aparatura

W tabeli 4 przedstawiono zestawienie sprzętu używanego do oznaczania poszczególnych składników oraz parametrów fizykochemicznych.

Tabela 4

Wykaz aparatury pomiarowej wykorzystanej do przeprowadzenia badań

Table 4

List of measuring equipment used for analysis

Analizowana substancja lub parametr	**Aparatura**
Aniony	Chromatograf jonowy Dionex 500
Kationy	
Konduktywność	pH/tlenomierz mikrokomputerowy CX - 401 firmy ELMERTON
pH	Konduktometr mikrokomputerowy CX - 401 firmy ELMERTON

Wyniki i ich omówienie

Badaniom poddano 42 próbki wody pitnej pobrane w siedmiu odległych od siebie dzielnicach miasta Malbork. W tabeli 5 zestawiono otrzymane wyniki (zakres oraz wartości średnie) oznaczeń poszczególnych analitów oraz wartości zmierzonych parametrów fizykochemicznych. Ich graficzna interpretacja zamieszczona została na rysunkach 3-15, natomiast dyskusję uzyskanych wyników przedstawiono w tabeli 6.

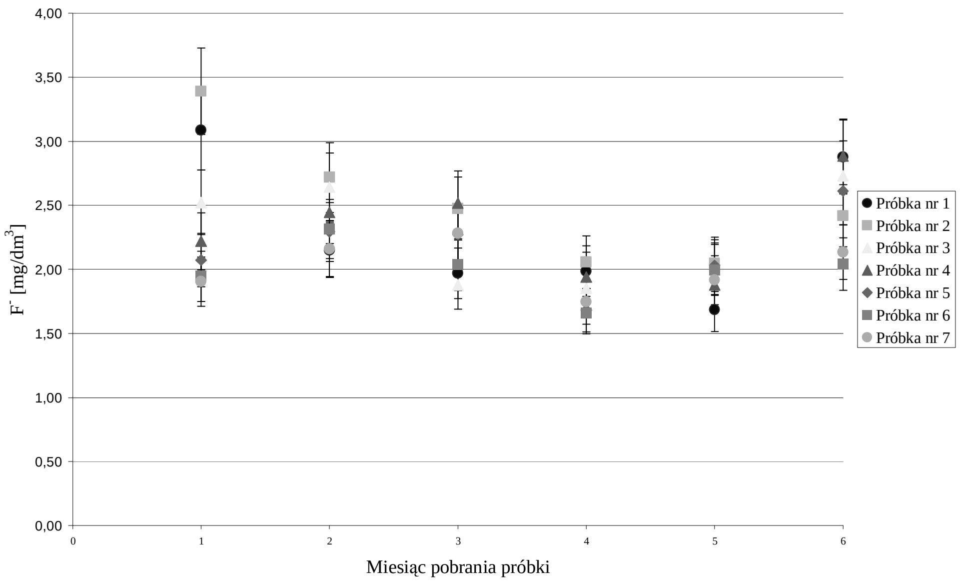
Tabela 5

Zestawienie uzyskanych wyników - zakres i wartość średnia

Table 5

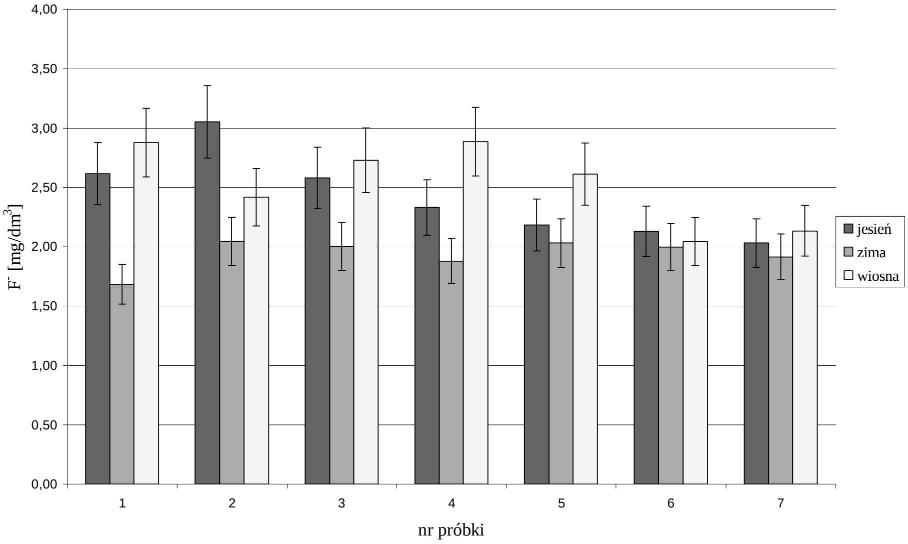
Summary of the obtained results - the range and average value

Parametr	**Jednostka**	**Jesień 2008**		**Zima 2008/2009**		**Wiosna 2009**	
		Zakres	**Wartość średnia**	**Zakres**	**Wartość średnia**	**Zakres**	**Wartość średnia**
pH	-	7,67÷8,62	8,10	7,54÷8,14	7,80	8,01÷8,34	8,10
Konduktywność	[mS/cm]	0,91÷1,21	1,08	1,01÷1,17	1,10	0,87÷1,04	0,99
F^-	**[mg/dm^3]**	**1,90÷3,39**	**2,42**	**1,66÷2,72**	**2,15**	**2,04÷2,88**	**2,53**
Cl^-	[mg/dm^3]	106,00÷ 143,00	118,38	86,37÷ 131,11	105,79	124,61÷ 159,67	137,13
NO_2^-	[mg/dm^3]	n.o.÷0,30	0,02	n.o.÷0,41	0,08	n.o.	n.o.
NO_3^-	[mg/dm^3]	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.
PO_4^{3-}	[mg/dm^3]	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.
SO_4^{2-}	[mg/dm^3]	n.o.÷0,65	0,24	n.o.÷0,18	0,03	n.o.÷0,42	0,14
Na^+	[mg/dm^3]	283,44÷360,53	325,08	287,76÷ 364,28	329,03	325,60÷ 397,21	371,87
NH_4^+	[mg/dm^3]	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.
K^+	[mg/dm^3]	5,95÷9,98	7,18	6,05÷9,96	7,72	9,07÷12,08	10,42
Mg^{2+}	[mg/dm^3]	7,61÷12,08	10,05	7,56÷13,03	9,96	8,04÷8,88	8,43
Ca^{2+}	[mg/dm^3]	9,92÷25,26	14,99	9,02÷22,55	13,75	1,72÷4,34	2,70



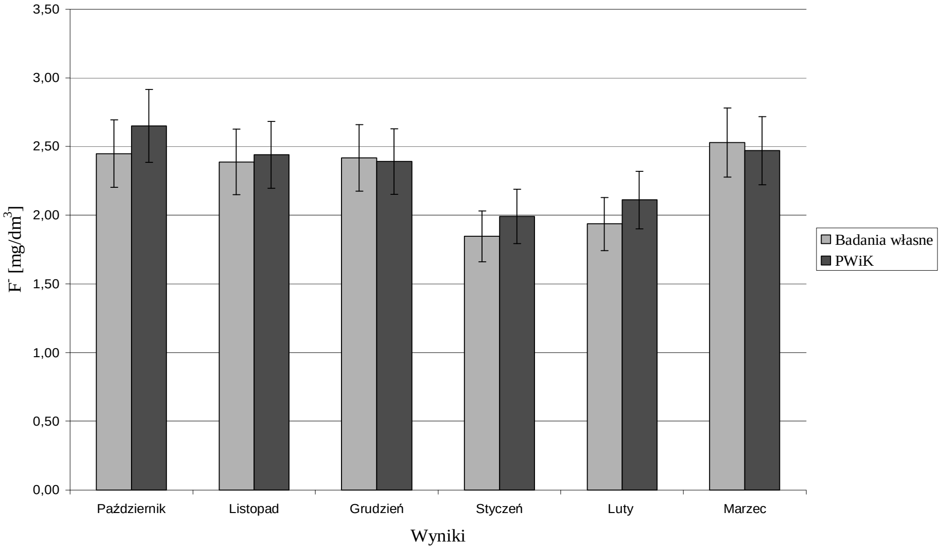
Rys. 3. Zmiany stężenia jonu fluorkowego w próbkach wód pitnych z obszaru miasta Malborka

Fig. 3. Changes in the concentration of fluoride ion in drinking water samples from the town of Malbork



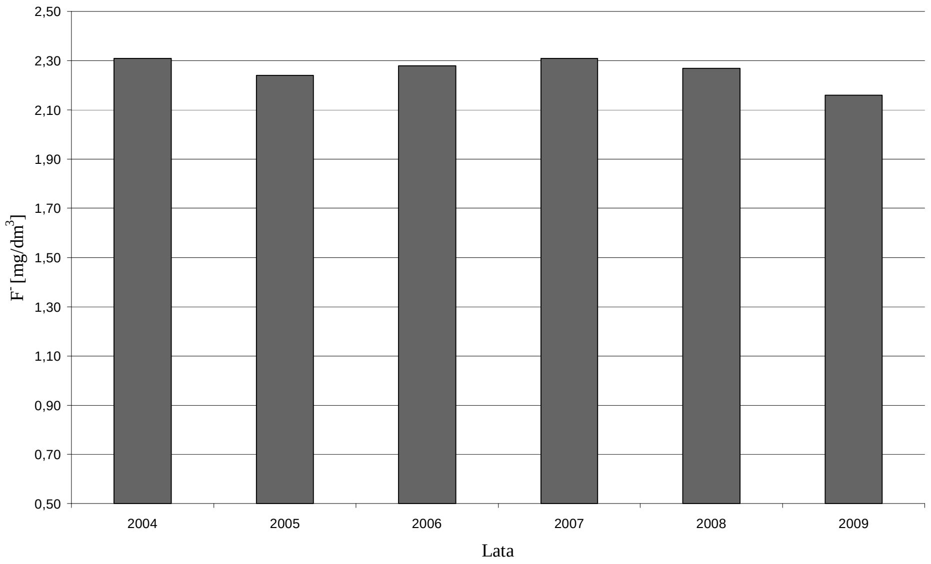
Rys. 4. Zmiany stężenia jonu fluorkowego w próbkach wód pitnych z obszaru miasta Malborka (z uwzględnieniem pór roku)

Fig. 4. Changes in the concentration of fluoride ion in drinking water samples from the town of Malbork (depending on the season)



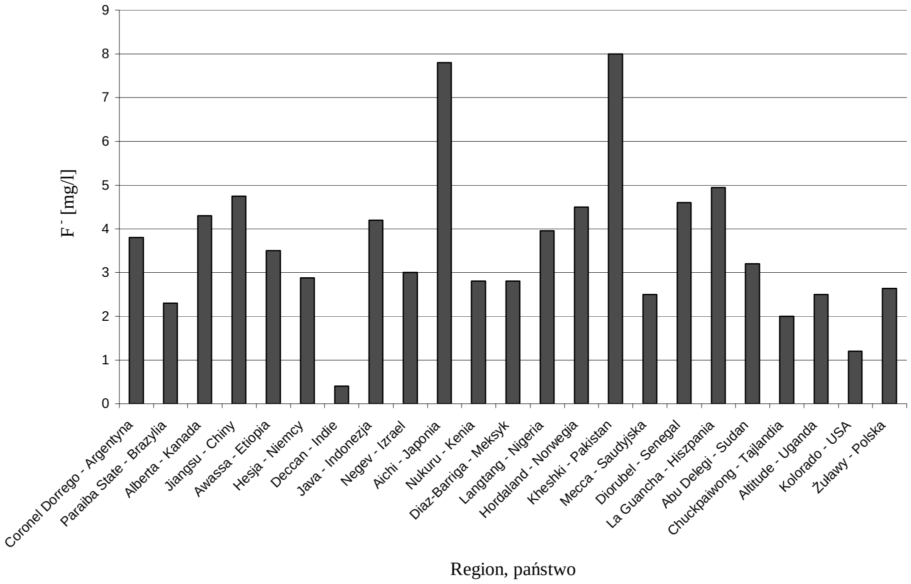
Rys. 5. Porównanie oznaczonych stężeń jonów fluorkowych w próbkach wód pitnych z obszaru miasta Malborka z wynikami pomiarów prowadzonych przez PWiK Malbork

Fig. 5. The comparison of concentrations of fluoride ion in drinking water samples from the town of Malbork with the results of measurements carried out by PWiK Malbork



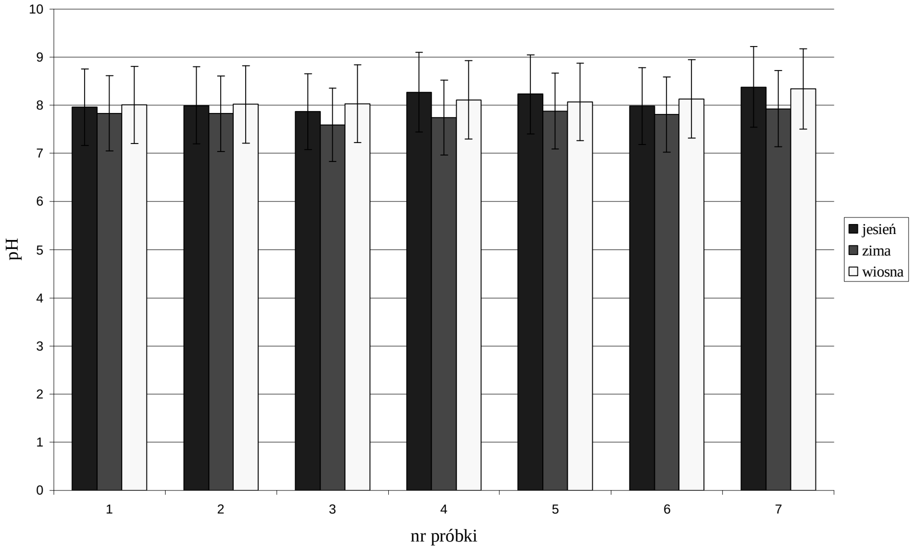
Rys. 6. Stężenie jonu fluorkowego w próbkach wód pitnych z obszaru miasta Malborka w okresie 2004-2009

Fig. 6. The concentrations of fluoride ion in drinking water samples from the town of Malbork city during the 2004-2009



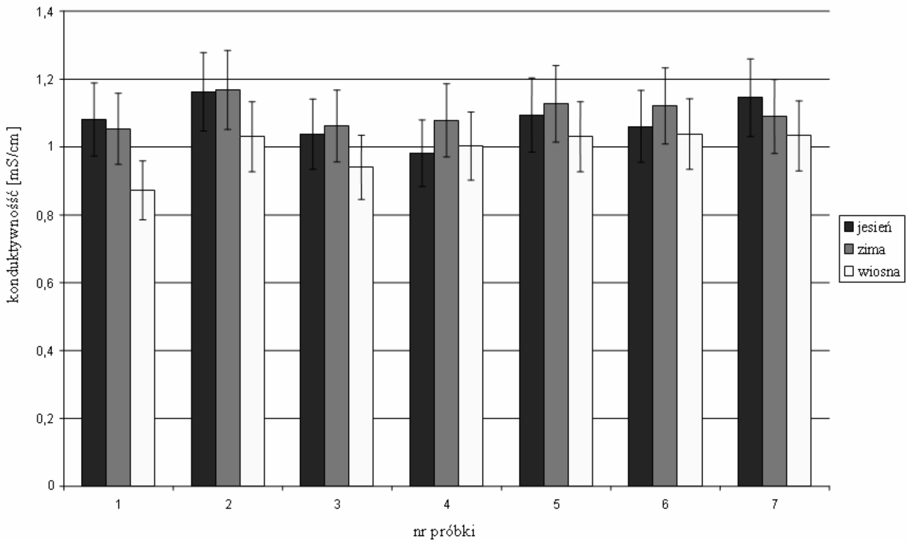
Rys. 7. Stężenie jonu fluorkowego w próbkach wód pitnych z różnych regionów geograficznych [13]

Fig. 7. The concentrations of fluoride ion in drinking water samples from various geografical regions



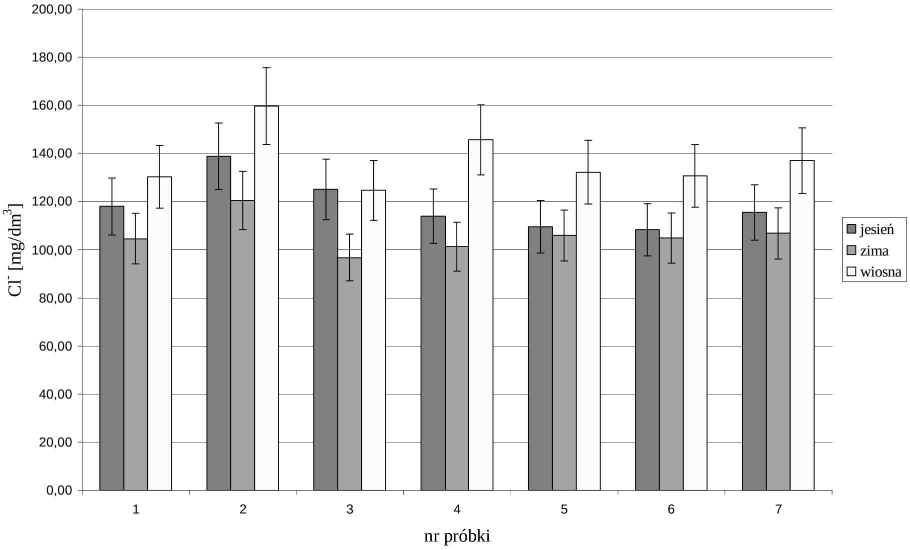
Rys. 8. Wartości pH próbek wód pitnych z terenu miasta Malborka (z uwzględnieniem pór roku)

Fig. 8. Value of pH in drinking water samples from the town of Malbork (depending on the seasons of the year)



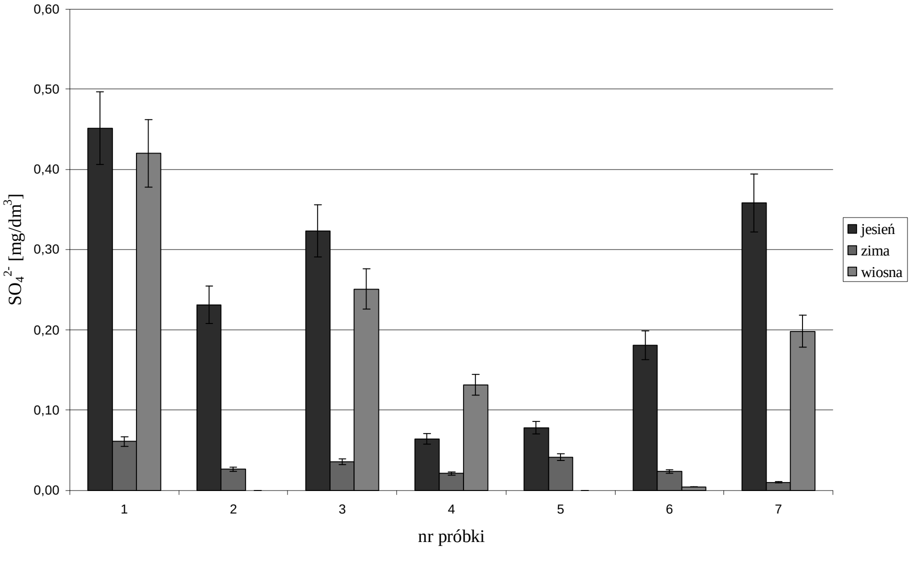
Rys. 9. Konduktywność próbek wód pitnych z terenu miasta Malborka (z uwzględnieniem pór roku)

Fig. 9. Conductivity of drinking water samples from the town of Malbork (depending on the seasons)



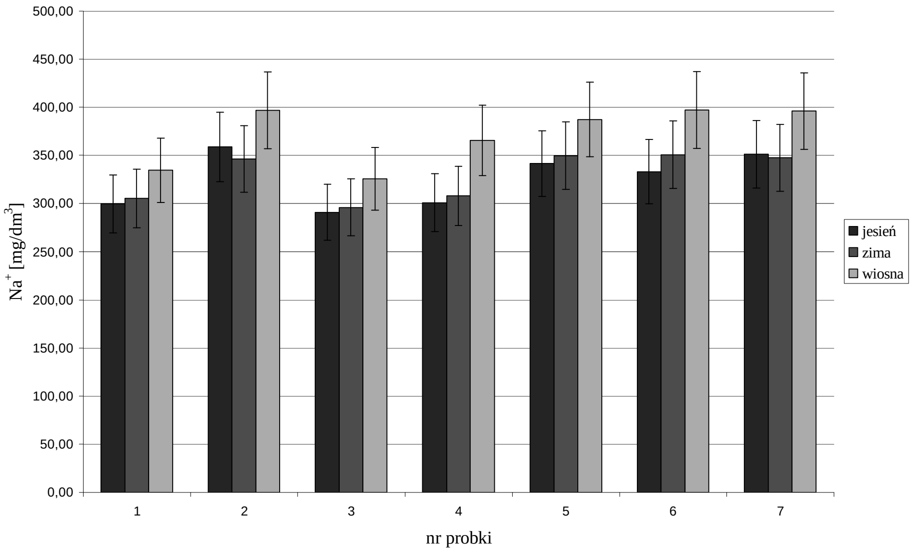
Rys. 10. Zmiany stężenia jonu chlorkowego w próbkach wód pitnych z terenu miasta Malborka (z uwzględnieniem pór roku)

Fig. 10. Changes in the concentration of chloride ion in drinking water samples from the town of Malbork (depending on the seasons)



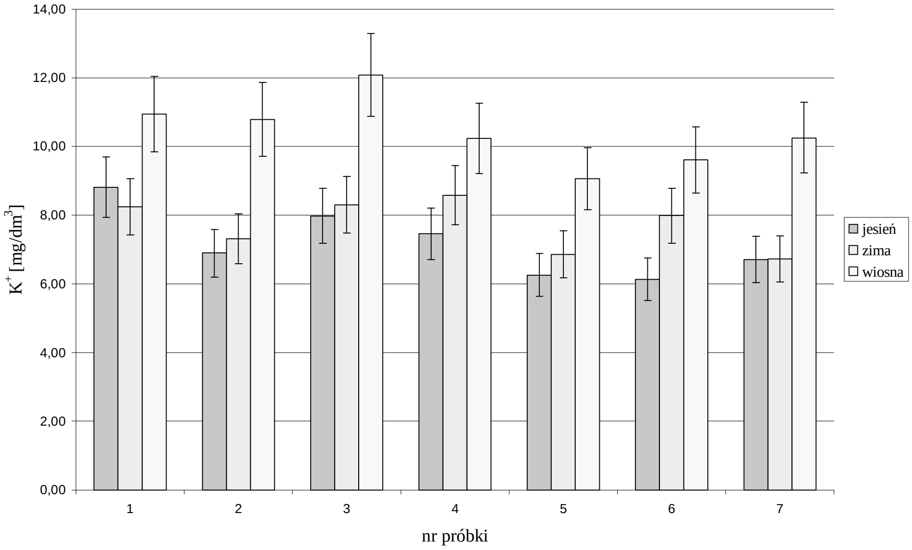
Rys. 11. Zmiany stężenia jonu siarczanowego w próbkach wód pitnych z terenu miasta Malborka (z uwzględnieniem pór roku)

Fig. 11. Changes in the concentration of sulfate ion in drinking water samples from the town of Malbork (depending on the season)



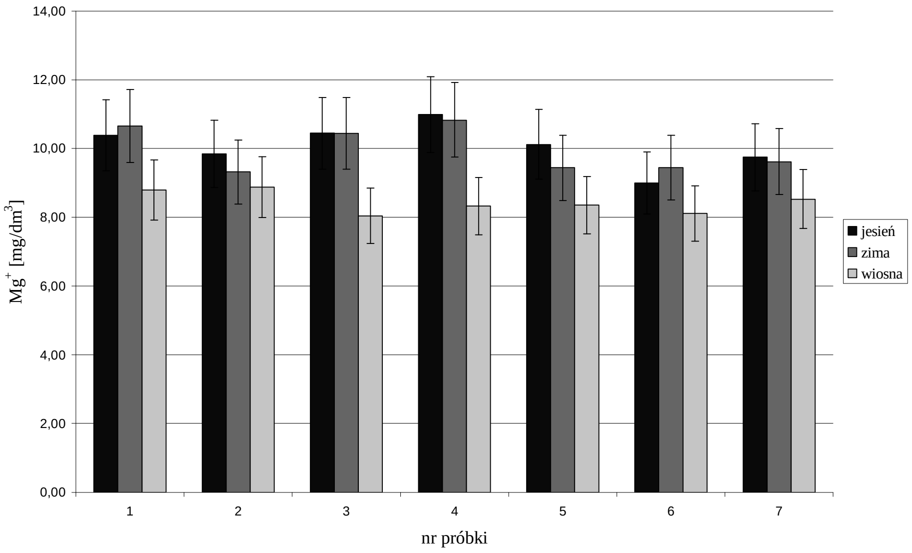
Rys. 12. Zmiany stężenia jonu sodowego w próbkach wód pitnych z terenu miasta Malborka (z uwzględnieniem pór roku)

Fig. 12. Changes in the concentration of sodium ion in drinking water samples from the town of Malbork (depending on the season)



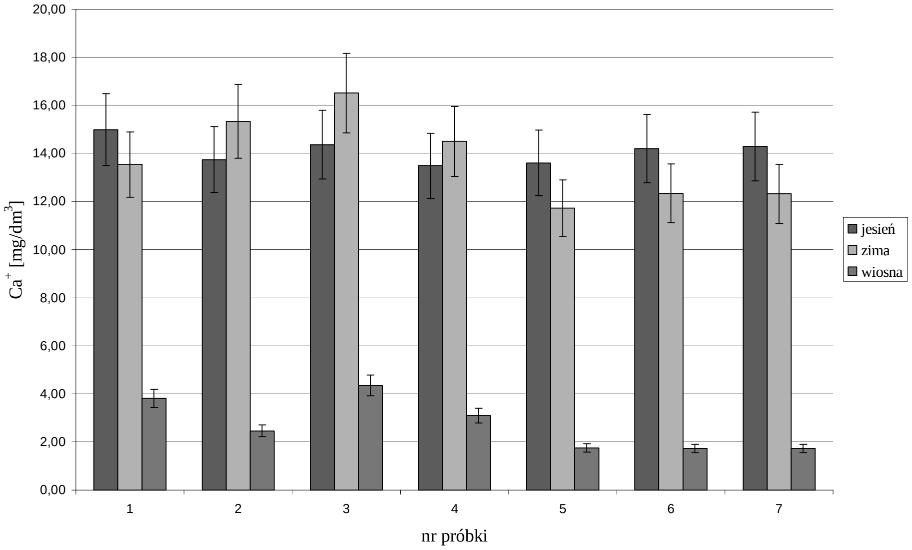
Rys. 13. Zmiany stężenia jonu potasowego w próbkach wód pitnych z terenu miasta Malborka (z uwzględnieniem pór roku)

Fig. 13. Changes in the concentration of potassium ion in drinking water samples from the town of Malbork (depending on the season)



Rys. 14. Zmiany stężenia jonu magnezowego w próbkach wód pitnych z terenu miasta Malborka (z uwzględnieniem pór roku)

Fig. 14. Changes in the concentration of magnesium ion in drinking water samples from the town of Malbork (depending on the season)



Rys. 15. Zmiany stężenia jonu wapniowego w próbkach wód pitnych z terenu miasta Malborka (z uwzględnieniem pór roku)

Fig. 15. Changes in the concentration of calcium ion in drinking water samples from the town of Malbork (depending on the season)

Tabela 6

Wyniki i ich omówienie

Table 6

Results and discussion

Parametr	**Omówienie wyników**	**Numer rysunku**
Jony fluorkowe	• obecność jonów fluorkowych stwierdzono we wszystkich analizowanych próbkach; • we wszystkich badanych próbkach wartość stężeń przekroczyła wartość 1,6 mg/dm^3 - przekraczając wartość dopuszczalną 1,5 mg/dm^3; • widać wyraźny spadek stężenia jonów w sezonie zimowym w przypadku punktów pomiarowych 1-5; • porównanie danych dotyczących wyników otrzymanych przez PWiK Malbork wskazuje, że nie różnią się one statystycznie istotnie na poziomie prawdopodobieństwa 95%; • oznaczony poziom stężeń utrzymywał się na podobnym poziomie w okresie 2004-2009.	3-6
pH	• wszystkie badane próbki miały odczyn powyżej 7,5; • wszystkie badane próbki spełniają wymagania dotyczące pH stawiane wodzie pitnej - zakres 6,5÷9,5; • uzyskane wartości są nieznacznie mniejsze w porze zimowej dla wszystkich punktów pomiarowych.	8
Konduktywność	• wszystkie próbki spełniają wymagania dotyczące wartości konduktywności dla wody pitnej - do 2,5 mS/cm; • uzyskane wartości nie zmieniają się znacząco w zależności od pory roku.	9
Jony chlorkowe	• obecność jonów chlorkowych stwierdzono we wszystkich analizowanych próbkach; • wszystkie badane próbki spełniają wymagania dotyczące jonów chlorkowych stawiane wodzie pitnej - 250 mg/dm^3; • widać wyraźny spadek stężenia jonów w sezonie zimowym w przypadku punktów pomiarowych 1-4.	10
Jony azotanowe(III)	• obecność jonów azotanowych(III) stwierdzono w 6 z analizowanych próbek; • wszystkie analizowane próbki spełniają wymagania dotyczące jonów azotanowych(III) stawiane wodzie pitnej - 0,5 mg/dm^3. • obecności jonów azotanowych(III) nie stwierdzono w żadnej z analizowanych próbek;	-
Jony azotanowe(V)	• wszystkie analizowane próbki spełniają wymagania dotyczące jonów azotanowych(V) stawiane wodzie pitnej - 50 mg/dm^3.	-
Jony siarczanowe	• obecność jonów siarczanowych stwierdzono w 25 analizowanych próbek; • we wszystkich analizowanych próbkach stężenie jonów nie przekroczyło wartości 0,65 mg/dm^3; • wszystkie analizowane próbki spełniają wymagania dotyczące jonów siarczanowych stawiane wodzie pitnej - 250 mg/dm^3.	11

Jony sodowe	• obecność jonów sodowych stwierdzono we wszystkich analizowanych próbkach; • stężenia jonów sodowych we wszystkich próbkach wody przekracza wartość 280 mg/dm^3; • wszystkie badane próbki nie spełniają wymagań dotyczących jonów sodowych stawianych wodzie pitnej - 200 mg/dm^3; • widać wyraźny wzrost stężenia jonów w sezonie wiosennym w przypadku wszystkich punktów pomiarowych.	12
Jony amonowe	• obecności jonów amonowych nie stwierdzono w żadnej z analizowanych próbek; • wszystkie analizowane próbki spełniają wymagania dotyczące jonów amonowych stawiane wodzie pitnej - 0,5 mg/dm^3.	-
Jony potasowe	• obecności jonów potasowych stwierdzono we wszystkich z analizowanych próbkach; • widać wyraźny wzrost stężenia jonów potasowych w sezonie wiosennym w przypadku wszystkich punktów pomiarowych.	13
Jony magnezowe	• obecności jonów magnezowych stwierdzono we wszystkich z analizowanych próbkach; • wszystkie badane próbki spełniają wymagania dotyczące jonów magnezowych stawiane wodzie pitnej - 125 mg/dm^3; • widać wyraźny spadek stężenia jonów w sezonie wiosennym w przypadku wszystkich punktów pomiarowych.	14
Jony wapniowe	• badaniu poddano 42 próbki wody pitnej; • obecności jonów wapniowych stwierdzono we wszystkich z analizowanych próbkach; • widać bardzo wyraźne zmniejszenie stężenia jonów w sezonie wiosennym w przypadku wszystkich punktów pomiarowych.	15

Wnioski

W ramach przyjętego programu badawczego poddano analizie 42 próbki wody pitnej z terenu miasta Malborka na zawartość wybranych jonów, wartości pH i konduktywności. Wykonano łącznie 168 analiz. Otrzymane wyniki porównano z wynikami uzyskanymi przez Przedsiębiorstwo Wodociągów i Kanalizacji (PWiK) Malbork (z okresu 10.08-03.09) oraz z danymi z lat 2004-2008.

Głównym odstępstwem od normy jakości badanej wody jest ponadnormatywne stężenie jonów fluorkowych. Niezadowalający stan jakościowy wód podziemnych na terenie powiatu malborskiego częściowo wynika z uwarunkowań naturalnych i stanowi ich trwałą cechę. W związku z tym woda dla zaopatrzenia ludności wymaga stałego i skutecznego uzdatniana. Wiąże się to z koniecznością modernizacji Centralnego Wodociągu Żuławskiego. Dodatkowo zły stan wody z wielu lokalnych ujęć wskazuje na konieczność ich modernizacji lub podłączenia wodociągów lokalnych do wodociągu centralnego, bowiem w dużym zakładzie uzdatniania wody łatwiej jest uzyskać odpowiednie dla niej parametry.

Dodatkowym źródłem zanieczyszczenia wód podziemnych jest również ich kontakt z zanieczyszczonymi wodami powierzchniowymi. Do przenikania zanieczyszczeń z powierzchni terenu dochodzi w wyniku działalności rolniczej, „dzikich” lub niedostatecznie zabezpieczonych składowisk i wylewisk odpadów, z nieodpowiednio składowanych nawozów, środków ochrony roślin i innych substancji chemicznych, z nieszczelnych zbiorników sanitarnych (szamb), spływów zanieczyszczonych wód z terenów komunikacyjnych i magazynowych. Przyczyną groźnego zanieczyszczenia wód podziemnych mogą być również katastrofy naturalne lub sztuczne: zalanie przez wody powodziowe terenów oczyszczalni ścieków, awarie komunikacyjne pojazdów przewożących substancje szkodliwe, awarie w zakładach przemysłowych i stacjach paliw.

Dla ochrony i poprawy stanu wód podziemnych konieczne jest:

- realizowanie programu związanego z ochroną wód powierzchniowych, w tym zwłaszcza programu skanalizowania powiatu, oczyszczania ścieków kanalizacji opadowej i zmniejszania zanieczyszczeń powierzchniowych;
- rygorystyczne przestrzeganie ograniczeń zagospodarowania i użytkowania terenu w strefie ochrony pośredniej ujęcia wody;
- właściwa polityka lokalizacyjna terenów i obiektów przemysłowych i magazynowych (m.in. poza zasięgiem zagrożenia powodziowego);
- likwidacja dzikich wysypisk i wylewisk, kontrola funkcjonowania składowisk odpadów;
- kontrola funkcjonowania składowisk i magazynów substancji chemicznych.

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DETERMINATION OF FLUORIDE IONS IN DRINKING WATER SAMPLES COLLECTED FROM THE AREA OF THE TOWN OF MALBORK

Department of Analytical Chemistry, Chemical Faculty, Gdansk University of Technology

Abstract: The analysis of drinking water samples collected from the area of town of Malbork was presented in this research study. The water samples were collected six times at one month intervals from October 2008 to March 2009 at seven sampling sites located in the main districts of town of Malbork. The parameters such as: the content of cations: Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}; the content of anions: F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-} and SO_4^{2-}; conductivity and pH were determined in the collected samples. The obtained results allowed to analyse the drinking water samples qualitatively and quantitatively. In all investigated samples, the concentration of fluoride ions was higher than the permissible limit, what is observed for years. The significant relationship between the concentration of selected ions and the season of the year was also noticed.

Keywords: drinking water, Malbork, fluoride ions

VARIA

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15th INTERNATIONAL CONFERENCE ON HEAVY METALS IN THE ENVIRONMENT

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INVITATION FOR ECOpole’10 CONFERENCE

CHEMICAL SUBSTANCES IN ENVIRONMENT

We have the honour to invite you to take part in the 19th annual Central European Conference ECOpole’10, which will be held in **13-16 X 2010** (Thursday-Saturday) on Wilhelms Hill at Uroczysko in Piechowice, the Sudety Mts., Lower Silesia, PL.

The Conference Programme includes oral presentations and posters and will be divided into five sections:

- **SI Chemical Pollution of Natural Environment and its Monitoring**
- **SII Environment Friendly Production and Use of Energy**
- **SIII Risk, Crisis and Security Management**
- **SIV Forum of Young Scientists and Environmental Education**
- **SV Impact of Environment Pollution on Food and Human Health**

The Conference language is English.

Contributions to the Conference will be published as:

- abstracts on the CD-ROM (0.5 page of A4 paper sheet format)
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Additional information one could find on the Conference website:

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The deadline for sending the Abstracts is **31.08.2010** and for the Extended Abstracts: **1.10.2010**. The actualised list (and the Abstracts) of the Conference contributions accepted for presentation by the Scientific Board, one can find (starting from 15.07.2010) on the Conference website.

The papers must be prepared according to the Guide for Authors on Submission of Manuscripts to the Journals.

The Conference fee is 300 € (covering hotel, meals and transportation during the Conference). It could be reduced (to 170 €) for young people actively participating in the Forum of Young Scientists. But the colleague has to deliver earlier the Extended Abstract (4-6 pages) of his/her contribution (deadline is on **15.08.2010**), and a recommendation of his/her Professor.

At the Reception Desk each participant will obtain a CD-ROM with abstracts of the Conference contributions as well as Conference Programme (the Programme will be also published on the Conference website).

Maria Wacławek

Further information is available from:
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SUBSTANCJE CHEMICZNE W ŚRODOWISKU PRZYRODNICZYM

Będzie to dziewiętnasta z rzędu konferencja poświęcona badaniom podstawowym oraz działaniom praktycznym dotycząca różnych aspektów ochrony środowiska przyrodniczego. Odbędzie się ona w ośrodku „Uroczysko” na Wzgórzu Wilhelma w Piechowicach koło Szklarskiej Poręby. Doroczne konferencje ECOpole mają charakter międzynarodowy i za takie są uznane przez Ministerstwo Nauki i Szkolnictwa Wyższego. Obrady konferencji ECOpole'10 będą zgrupowane w pięciu Sekcjach:

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Termin nadsyłania angielskiego i polskiego streszczenia o objętości 0,5-1,0 strony (wersja cyfrowa + wydruk) planowanych wystąpień upływa w dniu 31 sierpnia 2010 r. Lista prac zakwalifikowanych przez Radę Naukową Konferencji do prezentacji będzie sukcesywnie publikowana od 15 lipca 2010 r. na stronie webowej

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Aby praca (dotyczy to także streszczenia, które powinno mieć tytuł, treść i słowa kluczowe w języku angielskim) przedstawiona w czasie konferencji mogła być opublikowana, jej tekst winien być przygotowany zgodnie z wymaganiami stawianymi artykułom drukowanym w czasopismach *Ecological Chemistry and Engineering* ser. *A* oraz *S*, które są dostępne w wielu bibliotekach naukowych w Polsce i za granicą. Są one takie same dla prac drukowanych w półroczniku *Chemia-Dydaktyka-Ekologia-Metrologia*.

Koszt uczestnictwa w całej konferencji wynosi 1000 zł i pokrywa opłatę za udział, koszt noclegów i wyżywienia oraz rocznej prenumeraty Ecol. Chem. Eng. (razem blisko 2000 ss.) łącznie z materiałami Konferencji. Jest możliwość udziału tylko w jednym wybranym przez siebie dniu, wówczas opłata wyniesie 650 zł i będzie upoważniała do uzyskania wszystkich materiałów konferencyjnych, jednego noclegu i trzech posiłków (śniadanie, obiad, kolacja), natomiast osoby zainteresowane udziałem w dwóch dniach, tj. w pierwszym i drugim lub drugim i trzecim, winny wnieść opłatę w wysokości 800 zł. Opłata dla magistrantów i doktorantów oraz młodych doktorów biorących aktywny udział w Forum Młodych może być zmniejszona do 600 zł przy zachowaniu takich samych świadczeń. Osoby te winny dodatkowo dostarczyć: rozszerzone streszczenia (4-6 stron) swoich wystąpień (**do 15.08.2010 r.**). Jest także wymagana opinia opiekuna naukowego.

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Usilnie prosimy o stosowanie układu jednostek SI. Zwracamy uwagę, że osie wykresów oraz główki tabel powinny bezwzględnie zawierać jednostki stosownej wielkości. W przypadku artykułów pisanych po polsku podpisy tabel i rysunków powinny być podane w językach polskim i angielskim.

Polecamy symbolikę zalecaną przez PTChem (Symbole i terminologia wielkości i jednostek stosowanych w chemii fizycznej, Ossolineum, Wrocław 1989; Pure Appl. Chem., 1979, **51**, 1-41).

Materiał graficzny (rysunki, wykresy), obok wersji na papierze, powinien również być dostarczony w postaci cyfrowych plików wektorowych, np. za pomocą programów: CorelDraw wersja 9.0, Grafer dla Windows lub przynajmniej bitowe (TIF, JPG, PCX, BMP).

Przypisy i tabele, podobnie jak rysunki, zapisujemy jako osobne pliki.

Literaturę prosimy zamieszczać wg poniższych przykładów:

[1] Kowalski J. i Malinowski A.: Polish J. Chem., 1990, **40**(3), 2080-2085.
[2] Nowak S.: Chemia nieorganiczna. WNT, Warszawa 1990.

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