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Ivan DIADOVSKI¹, Maya ATANASSOVA¹
and Vasil SIMEONOV²

**ASSESSMENT OF CLIMATE IMPACT
ON THE TRANSBOUNDARY STRUMA RIVER FLOW
IN BULGARIAN TERRITORY USING INTEGRAL INDICES**

**OCENA WPŁYWU ZMIAN KLIMATYCZNYCH NA PRZEPIY W
TRANSGRANICZNEJ RZEKI STRUMA PRZEZ TERYTORIUM BUŁGARII
Z WYKORZYSTANIEM WSKAŹNIKÓW ZINTEGROWANYCH**

Abstract: The present work considers the Struma River on the Bulgarian territory using the integral method for evaluation of climatic and anthropogenic impacts on the river flow average annual water volume and maximum and minimum water flow.

The level of this impact is determined by the index K_i (flow module), the index C_i for the deviation of the average annual water flow Q_i from the flow norm Q_0 , the index $K_{i,max}$ for the deviation of the maximum water flow $Q_{max,i}$ from the flow norm Q_0 , the index $K_{i,min}$ for the deviation of the minimum water flow $Q_{min,i}$ from the flow norm Q_0 , the index $M_{i,max}$ for the deviation of the maximum water flow from the maximum flow norm $Q_{max,0}$, the index $M_{i,min}$ for the deviation of the minimum water flow from the minimum flow norm $Q_{min,0}$.

The new approach offered includes the introduction of more specific indicators for assessment of climatic impacts on the river water flow like indices for flow module ($K_{i,av}$), for deviation of average (C_i). The use of the indices suggested makes possible to estimate the role of different climatic changes by $K_{i,av}$, $K_{i,min}$, $K_{i,max}$, $M_{i,min}$, $M_{i,max}$, C_i , h_i and $h_{i,max}$. This is made for the first time in assessment of climatic impacts and has been checked at Pernik and Krupnik for the period 1948–2006.

The indices are integral in their nature because they reflect specific climatic caused events like abundant years, dry years, floods and draughts.

Keywords: integral indices, climate impact, river flow

The transboundary Struma River flows in the western part of Bulgaria and has a catchment area of 107.97 km² and length of 290 km. The catchment follows a mountain pattern and is characterized by a relatively low forestation level. The river

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water sources are in the high mountain part of the Vitosha and Rila Mountains. The Struma River flows through Bulgaria and Greece to the Aegean.

The Struma River catchment area is a part of a region that experiences the influence of European continental climate. The southernmost part of the river valley serves as a corridor for the Mediterranean climate impact. After Krupnik, the Struma River flow formation depends on the Mediterranean climate impact.

The EU Water Framework Directive [1] prescribes good water quality as a goal for all water bodies within a given catchment. To achieve this status, each EU country should develop an optimal management strategy [2–4].

The water quantity of the Struma River is controlled at 6 hydrometric stations – Pernik, Razhdavitsa, Dupnitsa, Boboshevo, Krupnik and Marino Pole, four of them being situated along the Struma River. The atmospheric precipitation is controlled at 7 stations – Pernik, Kyustendil, Dupnitsa, Blagoevgrad, Sandanski, Krupnik and Kulata. The characteristics of the Struma River flow are basically assessed according to the information coming from the Pernik and Krupnik stations (Fig. 1).



Fig. 1. Catchment of the Struma River in Bulgaria

The relief of the investigated area is diverse: the difference between the highest point (2180 m) and the lowest point at the Greek border (270 m) is significant. Preliminary studies have shown that the natural state of the river flow formation depends on the altitude [5].

The natural conditions of the Struma River flow formation are due to the climate impact, while the effect of the economic activity is insignificant. The Struma River is used for industrial water supply and for irrigation.

In the recent years many researchers focused their attention on climate changes due to anthropogenic activity [6–8].

Many authors believe that a period of warming will characterize the coming decades. Others are more reserved on the issue [9–10]. What can be pointed out is that the natural climate dependencies are disturbed by the anthropogenic impacts [3, 11].

Therefore, we believe that difficult for prediction climate changes at regional and global level are possible. The topic of risk assessment of flood events is a priority for all EU countries. A special Framework Directive 2007/60/EU of the European Parliament and Council for management of the flood risk has been recently accepted. The present work considers a particular regional problem with the goal of managing the waters in a transboundary river basin.

The main objectives of this research are to study:

- the tendency of the annual average value dynamics of the Struma River water during the period 1948–2006 with respect to climate impact assessment,
- the tendency of the multi-annual dynamics of the absolute maximum values of the river flow with respect to the risk assessment of flood events,
- the tendencies of the multi-annual dynamics of the absolute minimum values of the river flow with respect of drought events,
- the tendencies of the annual average atmospheric precipitation in the Bulgarian Struma River section during the period 1948–2006 with respect to climatic factors assessment,
- the tendencies of the multi-annual dynamics of the absolute maximum values of the atmospheric precipitation.

Materials and methods

The retrospective analysis of the river water flow dynamics is performed on the basis of information collected at the Pernik and Krupnik hydrometric stations. For this purpose the Origin 6.0 software [12] has been applied for data analysis.

Different functions were considered in the trend analysis for certain periods – linear, exponential, second and third degree polynomials. The type of the function describing the trend was determined on the basis of statistical criteria as correlation coefficients and Fisher's tests [13, 14]. The function representing the trend can be used for short-term (up to 1 year) prediction of the river flow dynamics, when it describes a significant trend.

Statistical methods are used in hydrology for the assessment of climatic and anthropogenic impact on the river flow formation in a specific cross-section of the river basin [15–17].

In the present work, an integral approach to evaluating the level of climate impact on the river flow formation is applied [18,19]. The proposed approach is based on the average multi-annual river flow Q_0 (flow norm), the ratios between the annual average flow Q_i and the flow norm [19]. With respect to the risk assessment of flood events and drought events new specific integral indicators are introduced, which are based on the ratios between the highest water discharge for the year $Q_{\max,i}$ and the flow norm Q_0 , as well as on the ratios between the maximum water discharges with respect to the annual-average value of the maximum water discharge $Q_{\max,0}$ and on the ratio between the minimum water discharge $Q_{\min,i}$ to the multi-annual-average value of the minimum water discharge $Q_{\min,0}$.

These relations represent indices, on the basis of which the effect of the climatic and anthropogenic factors on flow formation has been determined. The proposed approach is applied to the Struma River catchment on Bulgarian territory.

The flow norm Q_0 , the K_i index for the run-off modulus in the catchment area, the index C_i for the degree of diversion of Q_i from Q_0 [19], and the new index $K_{i,\max}$ index, representing the ratio between the maximum water flow $Q_{\max,i}$ and the flow norm Q_0 , the $K_{i,\min}$ index, representing the ratio between the minimum river flow $Q_{\min,i}$ and the flow norm Q_0 , the $M_{i,\max}$ index, representing the ratio between the maximum river flow $Q_{\max,i}$ and the average multi-annual value of the maximum water flow $Q_{\max,0}$ and the $M_{i,\min}$ index, representing the ratio between the minimum river flow $Q_{\min,i}$ and the average multi-annual value of the minimum river flow $Q_{\min,0}$, have been determined.

The proposed indices are found according to the equations:

$$K_i = Q_i / Q_0 \quad (1)$$

$$C_i = (Q_i - Q_0) / Q_0 \quad (2)$$

$$K_{i,\max} = Q_{\max,i} / Q_0 \quad (3)$$

$$K_{i,\min} = Q_{\min,i} / Q_0 \quad (4)$$

$$M_{i,\max} = Q_{\max,i} / Q_{\max,0} \quad (5)$$

$$M_{i,\min} = Q_{\min,i} / Q_{\min,0} \quad (6)$$

The fluctuations of the K_i , C_i [3, 4, 20], $K_{i,\max}$, $K_{i,\min}$, $M_{i,\max}$ and $M_{i,\min}$ indices for a certain period give the possibility of making integral assessment of the climatic and anthropogenic impact on the river flow formation on a river basin scale.

The dynamics of the annual average river flow, the absolute maximum river flow and the absolute minimum river flow at the points of Pernik and Krupnik, is studied for the period 1948–2006 (Fig. 1).

The climate could influence the river water flow formation by atmospheric precipitation. An integral index h_i is proposed for evaluating the impact of atmospheric precipitation on river flow formation. The index h_i can be presented as the ratio between the annual average atmospheric precipitation per year (H_i) at a control point in the river

basin and the multi-annual average atmospheric precipitation (H_0) for more than 30 years. The index $h_{i,\max}$ can be presented as the ratio between maximum atmospheric precipitation per year ($H_{i,\max}$) and the multi-annual average maximum atmospheric precipitation $H_{\max,0}$.

The index is determined according to the equation:

$$h_i = H_i / H_0 \quad (7)$$

$$h_{i,\max} = H_{i,\max} / H_{\max,0} \quad (8)$$

The influence of climate on river flow formation is determined on the basis of the multi-annual flow and atmospheric precipitation dynamics for a certain period. They are compared with the average multi-annual water flow (flow norm) and with the average multi-annual value of atmospheric precipitation, respectively.

The fluctuation of the h_i index, the $h_{i,\max}$ index, together with the variation of the K_i , C_i , $K_{i,\max}$, $K_{i,\min}$, $M_{i,\max}$, $M_{i,\min}$ indices allows more precise integral assessment of climate impact on river flow formation on river basin scale.

The dynamics of the h_i index at the Pernik and Krupnik stations is analyzed. The dynamics of the $h_{i,\max}$ index at the Pernik and Blagoevgrad stations is analyzed, because of lack of monitoring data for the Krupnik station. The Blagoevgrad station is situated at a distance of about 20 km above Krupnik.

The anthropogenic impact on the Struma River flow formation is insignificant and for this reason it is not considered further on.

Based on the results, one can specify different levels of correlation. Although no exact numbers are given, according to one of us [21] and his experience from environmetric studies indicates that correlation could be interpreted for the values:

for $0.0 < r < 0.1$ – no tendency,

for $0.1 < r < 0.2$ – insignificant tendency,

for $0.2 < r < 0.3$ – slight tendency,

for $0.3 < r < 0.5$ – moderate tendency,

for $0.5 < r$ – significant tendency.

These values have significance and interpretation only if the number of observations is above 30. In order to check the significance of the correlation coefficient, the calculated value is compared with the theoretical one, which represents in fact the r significance test [21].

A preliminary qualitative estimation of the relationship between the integral indicators is achieved by interpretation of the cross correlation table of the variables. All values of the correlation coefficient higher than 0.5 are accepted as statistically significant and are interpreted as a measure for high level of correlation. For values $0.2 < r < 0.5$ the statistical interpretation is more difficult but could be accepted provisionally as a moderate level of correlation [21].

By the use of the integral indices (K_i , C_i , $K_{i,\max}$, $K_{i,\min}$, $M_{i,\max}$, $M_{i,\min}$, h_i , $h_{i,\max}$) for assessment of the climatic factors on the stream dynamics, it could be possible in future studies to estimate the role of climate on determination of high-water and low-water events and, hence, the risk of draught or flood. It might be assumed by our preliminary

results that the indices are limited exactly in two latent factors – one explaining flood events and the other – draught events. This approach will resemble the study performed by [22, 23], dealing with river water quality of the Struma River catchment.

Results and discussion

According to Amoros [8] and Sing [17], the fluctuations of climate and physical geographic characteristics provoke trends, including leap-like (catastrophic) events.

In our study the trends of the basic characteristics of the river flow (K_i , C_i , $K_{i,max}$, $K_{i,min}$, $M_{i,max}$, $M_{i,min}$ indices) and the atmospheric precipitation (h_i index and $h_{i,max}$ index) at the Pernik and Krupnik stations are determined.

The theoretical correlation coefficient of the trend functions at degrees of freedom $No = 59$ and a probability of error $\alpha = 5\%$ has a value $r = 0.253$. The calculated values of the correlation coefficients for the investigated period are in the interval 0.2–0.59. This fact shows that the model for the trend characterizes adequately clearly expressed tendency and significant tendency.

The assessment of the flow change in the hydrometric stations of Pernik and Krupnik is made on the basis of integral parameter dynamics.

The multi-annual average river water flow for a period of 59 years (Q_0) at the Pernik point is $2.11 \text{ m}^3/\text{s}$.

The multi-annual average river water flow for a period of 59 years (Q_0) at the Krupnik point is $45.90 \text{ m}^3/\text{s}$.

The analyses of the K_i index dynamics at the Pernik and Krupnik points during the period 1948–2006 are presented in Figs. 2–3.

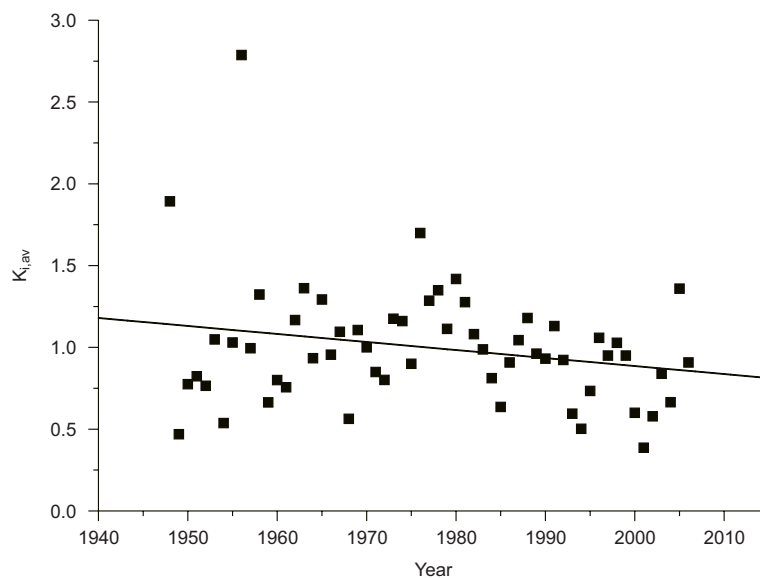


Fig. 2. Dynamics of the $K_{i,av}$ index for the Struma River at the Pernik point

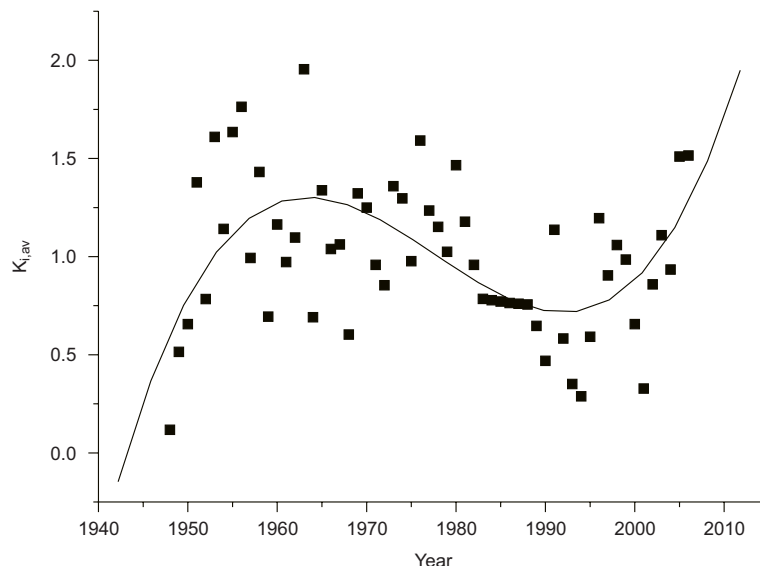


Fig. 3. Dynamics of the $K_{i,av}$ index for the Struma River at the Krupnik point

The trend of the K_i index dynamics for the Pernik point is described by a linear function with a value of the correlation coefficient $R = -0.22$. The trend of the K_i index tends to increasing and it exhibits a slight tendency.

The trend of the K_i index dynamics for the Krupnik point is described by a 3rd order polynomial with a value of the correlation coefficient $R = 0.31$. The trend shows variable tendency to increasing during the interval 1948–1965 and to decreasing during 1966–1990 and increasing during 1991–2006. The observed trend exhibits a moderate tendency.

The trend in the dynamics of the C_i index for the Pernik point is described by a linear function with a value of the correlation coefficient $R = -0.22$. The observed trend to increasing exhibits a slight tendency. (Fig. 4).

The trend in the dynamics of the C_i index for the Krupnik point is described by a third order polynomial with a value of the correlation coefficient $R = 0.31$. The trend shows variable tendency to increasing for 1948–1965, decreasing for 1966–1990 and increasing for 1991–2006 (Fig. 5). The trend exhibits a moderate tendency.

The influence of climate and physical geographic characteristics (Pernik and Krupnik) is determined by retrospective analysis of the K_i and C_i indices. The dynamics of the C_i index at the Pernik point changes within the range from 1.50 to -0.7 , while the dynamics of the K_i index – from 2.8 to 0.3. The dynamics of the K_i index for Krupnik changes from 1.8 to 0.1, while the dynamics of the C_i index changes from 0.8 to -0.9 . Three typical periods are determined for the Pernik and Krupnik points: first (1948–1972) with years of lower water resources ($C_i < 0$, $K_i < 1$); and second (1972–1995) with years of higher water resources ($C_i > 0$, $K_i > 1$) and third (1996–2006) with years of lower water resources ($C_i < 0$, $K_i < 1$).

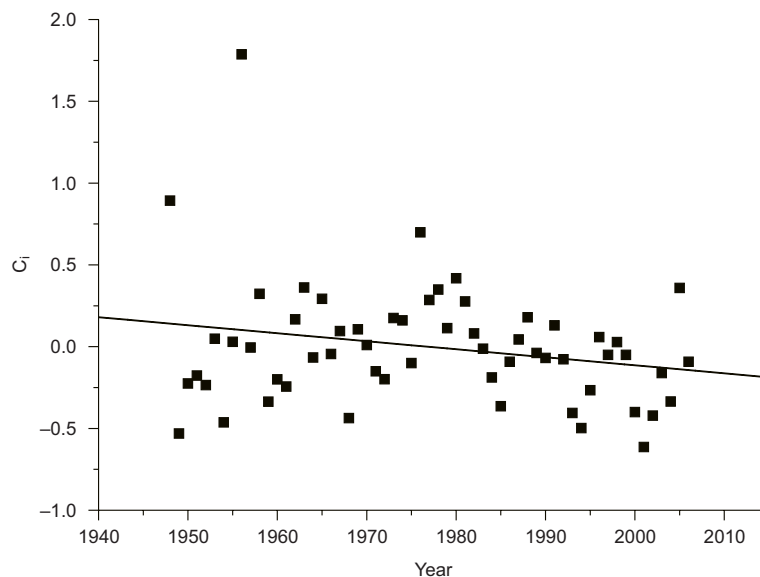


Fig. 4. Dynamics of the C_i index for the Struma River at the Pernik point

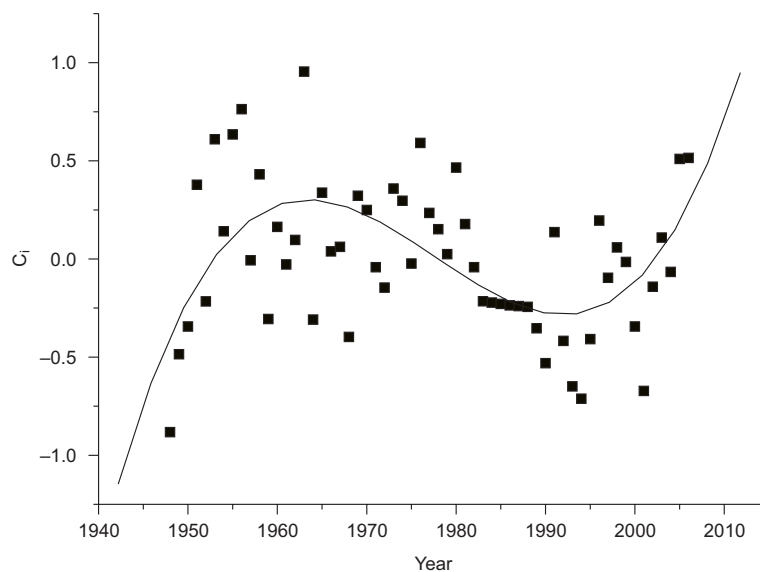


Fig. 5. Dynamics of the C_i index for the Struma River at the Krupnik point

The period 1948–1972 is characterized by a corresponding run-off reduction with respect to the norm Q_0 ($C_i < 0$, $K_i < 1$). The period 1973–1995 is characterized by run-off increase with respect to the norm Q_0 ($C_i > 0$, $K_i > 1$). During the next period 1996–2006 decreasing of run-off is observed compared with the norm.

Cycles of one-three water abundant years, followed by several low water years are outlined. These cycles are:

- for the first low-water period the years 1963–1965 (water abundant) and the years 1966–1969 (low water);
- for the second water abundant period – 1975–1979 (water abundant years) and the years (1981–1984) (low water);
- for the third low-water period – 1997–1999 (water abundant) and the years 2000–2003 (low-water).

These run-off variations could be explained with the influence of climatic factors, typical for the considered region.

For the integral assessment of the impact of climatic factors on extreme river flow formation, flood and drought events, the dynamics of the maximum and minimum water discharge is considered for the single years during the period 1948–2006. The dynamics of the $K_{i,max}$, $K_{i,min}$, $M_{i,max}$ and $M_{i,min}$ indices is analyzed.

The trend in the dynamics of the $K_{i,max}$ index for the Pernik point is described best by a linear function with a correlation coefficient $R = -0.52$. At the Krupnik point the trend is given by a linear function with a correlation coefficient $R = -0.58$ (Figs. 6, 7).

The trend in the dynamics of the $K_{i,max}$ index for both points exhibits a significant tendency to decreasing for the considered period. The values of $K_{i,max}$ in the Pernik point vary within the interval 2–86 for the considered period. This indicates that significantly higher maximum water flow exceeding the run-off norm Q_0 is observed, especially in the years 1948–1953, 1963–1968, 1990–1993 and 2003–2005.

The values of $K_{i,max}$ in the Krupnik point vary within the range 1.5–17. This shows that at this point the observed maximum water flow exceeds the run-off norm but the extent of rising is lower than that of the Pernik point.

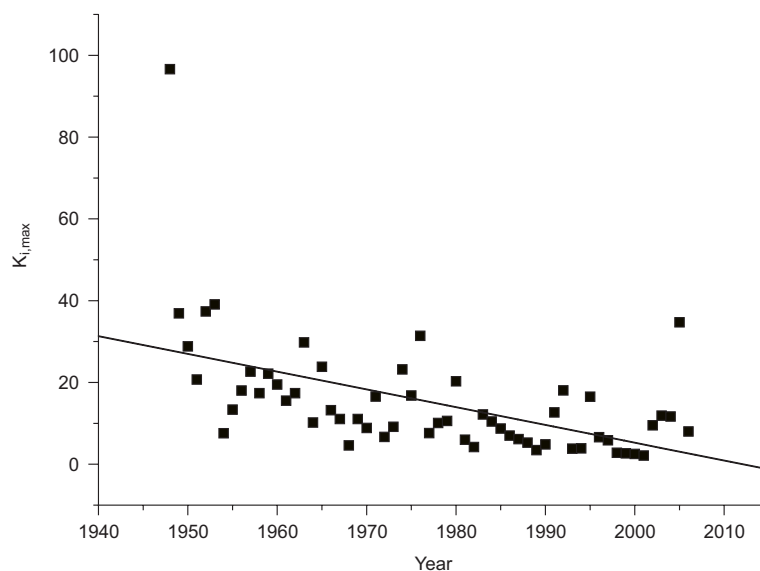


Fig. 6. Dynamics of the $K_{i,max}$ index for the Struma River at the Pernik point

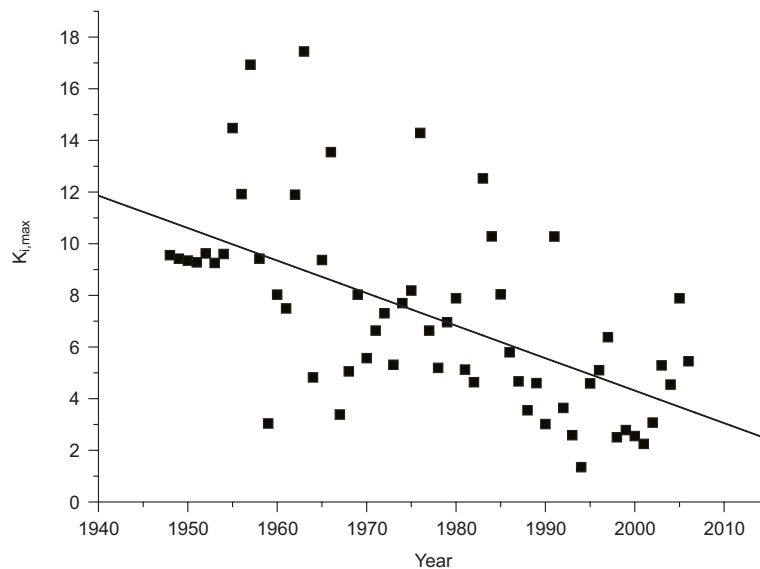


Fig. 7. Dynamics of the $K_{i,max}$ index for the Struma River at the Krupnik point

The trend in the dynamics of the $M_{i,max}$ index is described best by a linear function with a correlation coefficient $R = -0.52$ for Pernik (Fig. 8) and $R = -0.58$ for Krupnik (Fig. 9).

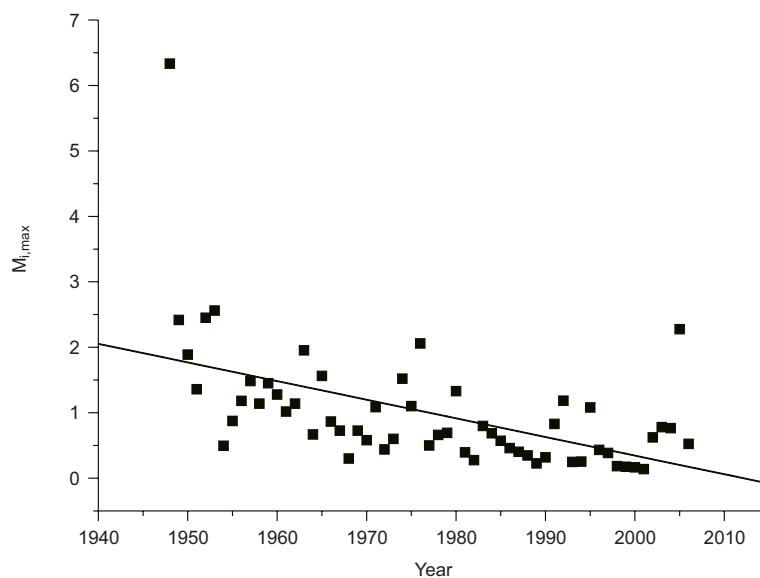


Fig. 8. Dynamics of the $M_{i,max}$ index for the Struma River at the Pernik point

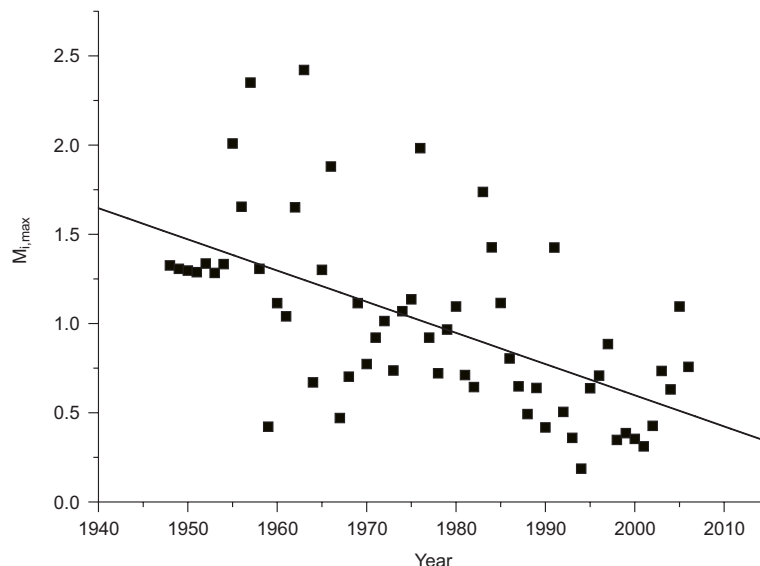


Fig. 9. Dynamics of the $M_{i,max}$ index for the Struma River at the Krupnik point

A significant trend towards decreasing of the $M_{i,max}$ index is outlined, which corresponds to the trend towards diminution of the maximum water flow $Q_{max,i}$ for both points.

Similar results are obtained when investigating the character of the changes in the values of the $K_{i,max}$ index.

The values of $M_{i,max}$ in the Pernik point vary within the range 0.3–6.2, which indicates that both higher and lower maximum water flow than the norm (average multi-annual value of the maximum water flow) is observed.

Years with hazardous flooding are outlined ($M_{i,max} > 2$), for example 1949–1953, 1960, 1975–1976, 1982 and 2005. It has to be noted that the years with values of the maximum water flow $Q_{max,i}$, which are lower or insignificantly higher than the norm of the maximum water flow for the considered period, are predominant.

The values of $M_{i,max}$ in Krupnik vary within the range 0.25–23, which indicates that in certain years the maximum water flow $Q_{max,i}$ significantly exceeds the norm of the maximum water flow $Q_{max,0}$, forming in this way hazardous floods. Years with hazardous flooding are outlined as 1950–1960, 1975–1976, 1982, 1986 and 2005.

The trend in the dynamics of the $K_{i,min}$ index for the Pernik point (Fig. 10) is described by a 3rd order polynomial with a value of the correlation coefficient $R = 0.54$ and by a linear function with $R = 0.21$ for the Krupnik point (Fig. 11).

A stable tendency is observed towards increasing the minimum water flow in the considered period for the Krupnik point. The trend shows variable significant tendency to increasing during the interval 1948–1988 and to decreasing during the period 1989–2006 for the Pernik point.

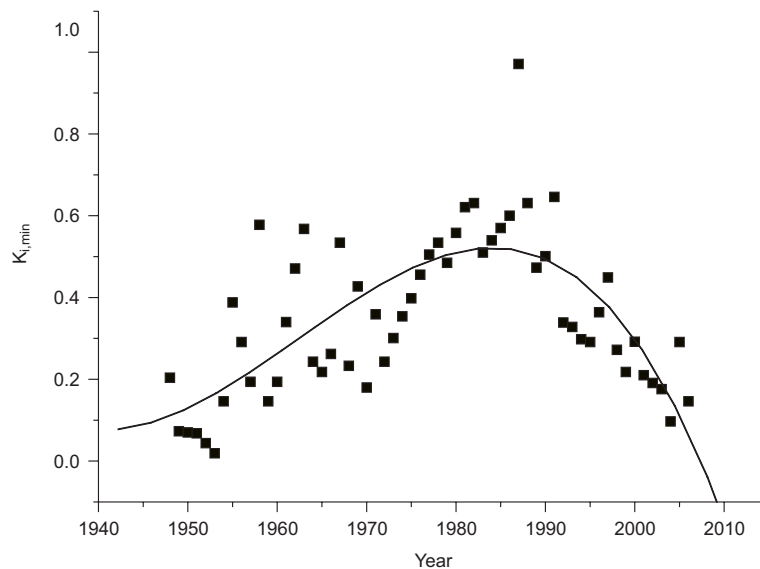


Fig. 10. Dynamics of the $K_{i,min}$ index for the Struma River at the Pernik point

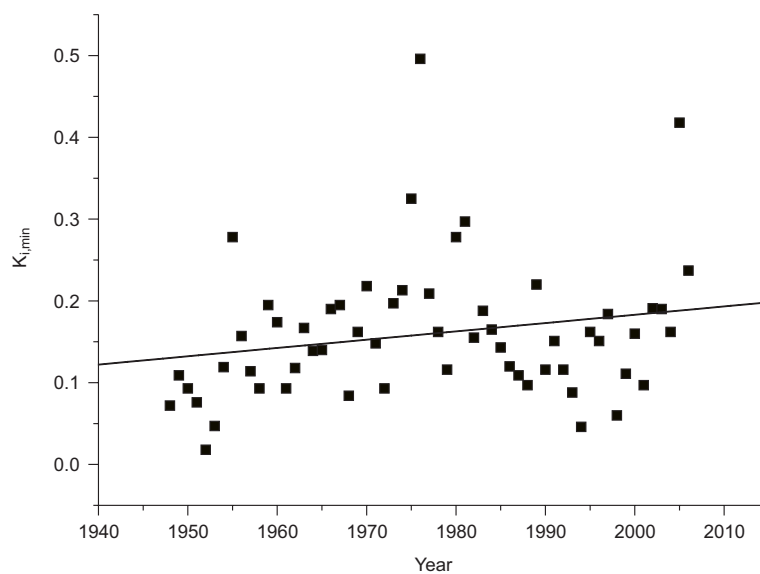


Fig. 11. Dynamics of the $K_{i,min}$ index for the Struma River at the Krupnik point

The values of $K_{i,min}$ in Pernik vary within the interval 0.05–0.8, indicating that years are observed with minimum water flow, which is significantly lower than the run-off norm (Q_0).

The values of $K_{i,\min}$ in Krupnik vary within the range 0.02–0.48, indicating that minimum water flow significantly lower than the run-off norm (Q_0).

The trend in the dynamics of the $M_{i,\min}$ index for Pernik (Fig. 12) is described by a 3rd order polynomial with a value of the correlation coefficient $R = 0.54$ and by a linear function with $R = 0.21$ for Krupnik (Fig. 13).

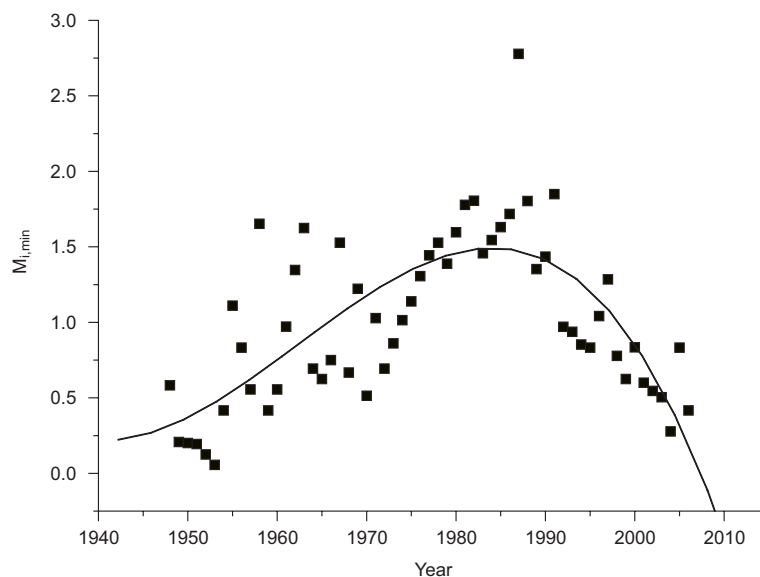


Fig. 12. Dynamics of the $M_{i,\min}$ index for the Struma River at the Pernik point

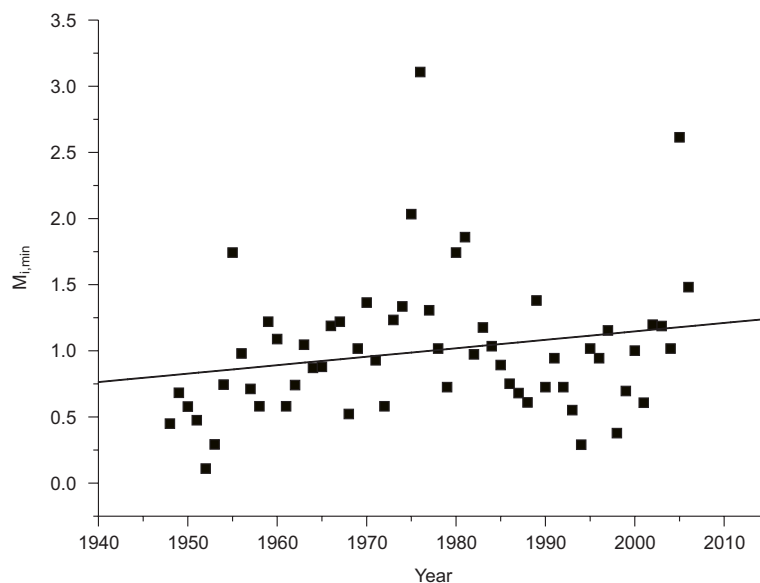


Fig. 13. Dynamics of the $M_{i,\min}$ index for the Struma River at the Krupnik point

A significant trend towards increasing values of the $M_{i,\min}$ index is outlined, which corresponds to the trend towards increasing of the minimum water flow $Q_{\min,i}$ for the Krupnik point. The trend shows variable tendency to increasing during the interval 1948–1988 and to decreasing during the period 1989–2006 for the Pernik point.

The conclusion can be made that a trend is established towards increasing the values of the ratio between the minimum water flow $Q_{\min,i}$ and the average multi-annual value of the minimum water flow $Q_{\min,0}$ for the considered period.

The values of $M_{i,\min}$ in Pernik vary within the interval 0.2–2.5, which indicates that years with minimum water flow, significantly lower than the norm of the minimum water flow ($Q_{\min,0}$), are observed, thus forming hazardous drought periods. These years are 1948–1953.

The values of $M_{i,\min}$ in Krupnik vary within the range 0.2–3, which indicates that years with minimum water flow, significantly lower than the norm of the minimum water flow ($Q_{\min,0}$), are outlined, thus forming hazardous drought periods. Such years are 1948–1953, 1954–1956, 1990, 1993, 1996 and 2002. During the considered period the years with minimum water flow higher than the norm of the minimum water flow ($Q_{\min,0}$) are predominant.

The dynamics of the K_i , C_i , $K_{i,\max}$, $K_{i,\min}$, $M_{i,\max}$ and $M_{i,\min}$ indices shows the influence of climate in the Struma River basin under natural conditions of river flow formation (with the assumption for insignificant water use, as already mentioned).

The years with $K_i > 1$ and $C_i > 0$ are years with high water resources and with $K_i < 1$ and $C_i < 0$ – years with lower water resources.

Flood effects during high water are observed during the years with $M_{i,\max} > 1$, while for the years with $M_{i,\max} < 1$ high water with possible negative effect may be observed.

Low water with possible negative effect is observed during the years with $M_{i,\min} > 1$, while for the years with $M_{i,\min} < 1$ low water with drought effect may be observed.

Atmospheric precipitation higher than the multi-annual average atmospheric precipitation is observed during the years with h_i index > 1 , while atmospheric precipitation, lower than the multi-annual average atmospheric precipitation, is observed for the years with h_i index < 1 .

During the years with $h_{i,\max}$ index > 1 (maximum atmospheric precipitation higher than the average multi-annual maximum precipitation) flood effects may be observed in the respective section of the river catchment.

The multi-annual atmospheric precipitation (H_0) at the Pernik station is 621 mm and at the Krupnik station – 633 mm.

The fluctuation of the h_i index at the Pernik station for the considered period (1948–2006) is shown in Fig. 14.

The trend is represented by a 3rd order polynomial with a correlation coefficient $R = 0.11$. An insignificant variable tendency to increasing during the period 1948–1960, decreasing during the period 1961–1985 and increasing during 1986–2006 is observed.

The dynamics of the h_i index changes within the range from 0.50 to 1.55. Two typical periods are determined: first (1948–1990) of low atmospheric precipitation ($h_i < 1$), and second (1991–2006) with years of higher atmospheric precipitation ($h_i > 1$). Cycles are outlined with one – four water abundant years ($h_i > 1$), and several

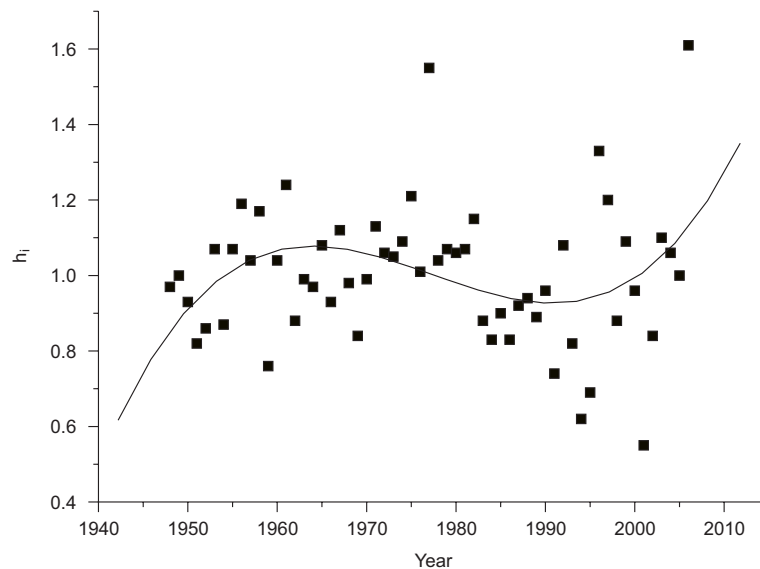


Fig. 14. Dynamics of the h_i index for the Struma River at the Pernik point

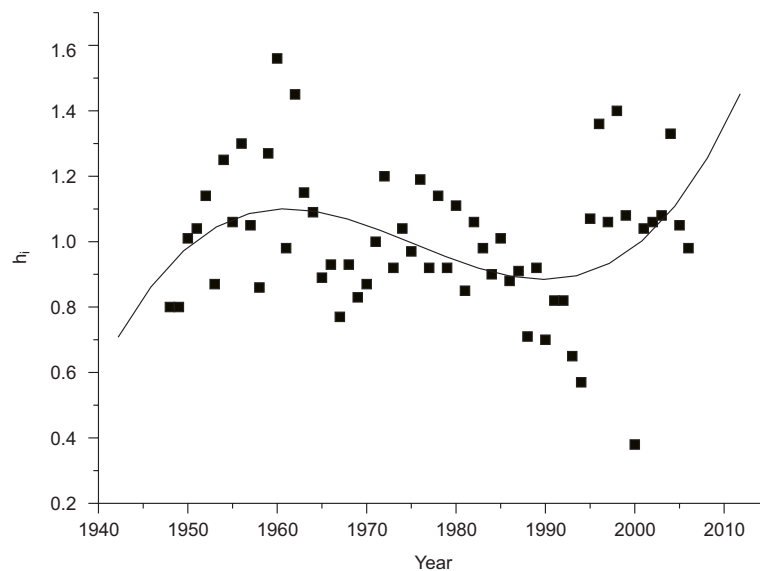


Fig. 15. Dynamics of the h_i index for the Struma River at the Krupnik point

low-water years ($h_i < 1$). The dynamics of the h_i index is not similar to that of the K_i and C_i indices for the period 1948–2006, which may be explained with the specific impact of the climatic factors in the region.

The trend of the h_i index dynamics at the Krupnik point is presented by a third order polynomial with a correlation coefficient $R = 0.14$. The trend shows variable tendency to increasing during the period 1948–1960, decreasing during 1961–1985 and increasing during 1986–2006 (Fig. 15).

The dynamics of the h_i index at the Krupnik point is similar to that of the K_i and C_i indices at the Krupnik point for the period 1948–2006.

A stable variable tendency is observed in the studied region (Krupnik) towards increasing, followed by decreasing and subsequent increasing of the annual average values of the Struma River flow (K_i , C_i) corresponding to the increasing-decreasing and increasing tenor of the average annual precipitation (h_i index).

The trend of the $h_{i,max}$ dynamics at the Pernik point is presented by a linear function with a correlation coefficient $R = -0.14$ (Fig. 16). An insignificant trend towards decreasing values of the $h_{i,max}$ index is outlined, which corresponds to the trend towards decreasing of the maximum water volume ($K_{i,max}$, $M_{i,max}$).

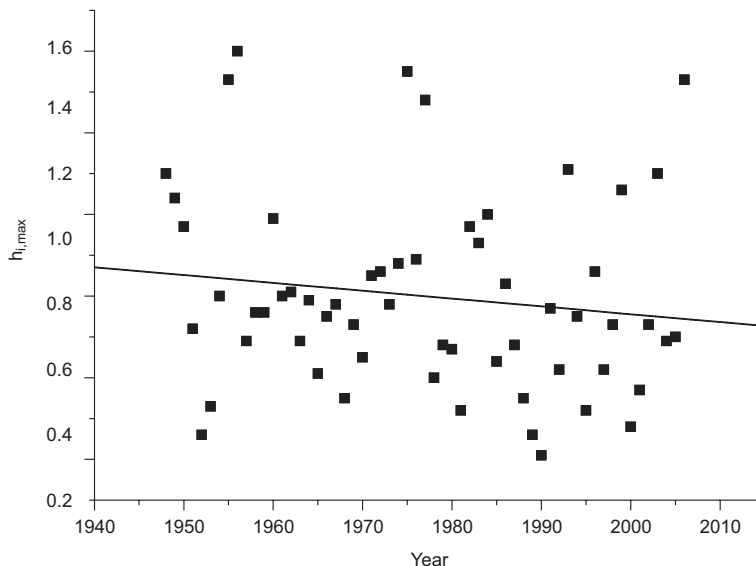


Fig. 16. Dynamics of the $h_{i,max}$ index for the Struma River at the Pernik point

The dynamics of the $h_{i,max}$ index at the Blagoevgrad station is analyzed, because of lack of monitoring data for the Krupnik station. The Blagoevgrad station is situated at about 20 km above Krupnik. The trend of the $h_{i,max}$ dynamics at the Blagoevgrad point is represented by a third order polynomial with a correlation coefficient $R = 0.17$. The trend shows variable tendency to increasing during the period 1948–1960, and to decreasing during the period 1961–1978 with subsequent increasing during 1979–2006.

The dynamics of the $h_{i,max}$ index at the Blagoevgrad point is similar to that of the K_i and C_i indices at the Krupnik point for the period 1948–2006 and is not similar to that of the $K_{i,max}$ and $M_{i,max}$ indices.

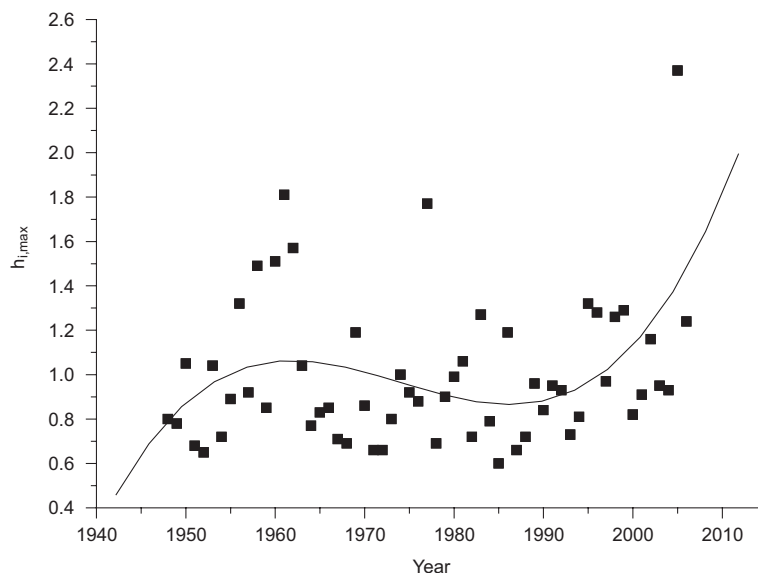


Fig. 17. Dynamics of the $h_{i,max}$ index for the Struma River at the Krupnik-Blagoevgrad point

The following conclusions may be drawn on the basis of the performed assessment of the integral indices dynamics.

A stable trend is observed towards decreasing of the maximum water flow ($M_{i,max}$, $K_{i,max}$) during the considered period for both points (Pernik, Krupnik).

A stable trend is observed towards increasing the minimum water flow during the considered period for the Krupnik point. A trend showing variable tendency towards increasing and decreasing of the minimum water flow during the considered period is established for the Pernik point.

A preliminary qualitative estimation of the relationship between the integral indicators – $K_{i,av}$, $K_{i,max}$, $K_{i,min}$, $M_{i,max}$, $M_{i,min}$, h_i and $h_{i,max}$ is achieved by interpretation of the cross correlation table of the variables (Table 1, 2).

Table 1

Correlation matrix for Pernik point

	$K_{i,av}$	$K_{i,min}$	$K_{i,max}$	$M_{i,min}$	$M_{i,max}$	h_i	$h_{i,max}$
$K_{i,av}$	1.00	0.29	0.37	0.29	0.37	0.35	0.26
$K_{i,min}$	0.29	1.00	-0.31	1.00	-0.31	0.04	-0.09
$K_{i,max}$	0.37	-0.31	1.00	-0.31	1.00	0.01	0.13
$M_{i,min}$	0.29	1.00	-0.31	1.00	-0.31	0.04	-0.09
$M_{i,max}$	0.37	-0.31	1.00	-0.31	1.00	0.01	0.13
h_i	0.35	0.04	0.01	0.04	0.01	1.00	0.44
$h_{i,max}$	0.26	-0.09	0.13	-0.09	0.13	0.44	1.00

Table 2

Correlation matrix for Krupnik point

	$K_{i,av}$	$K_{i,min}$	$K_{i,max}$	$M_{i,min}$	$M_{i,max}$	h_i	$h_{i,max}$
$K_{i,av}$	1.00	0.45	0.50	0.45	0.50	0.53	0.33
$K_{i,min}$	0.45	1.00	0.20	1.00	0.20	0.27	0.27
$K_{i,max}$	0.50	0.20	1.00	0.20	1.00	0.26	0.10
$M_{i,min}$	0.45	1.00	0.20	1.00	0.20	0.27	0.27
$M_{i,max}$	0.50	0.20	1.00	0.20	1.00	0.26	0.10
h_i	0.53	0.27	0.26	0.27	0.26	1.00	0.52
$h_{i,max}$	0.33	0.27	0.10	0.27	0.10	0.52	1.00

All values of the correlation coefficient higher than 0.5 are accepted as statistically significant and are interpreted as a measure for significant level of correlation. For values $0.2 < r < 0.5$ of the correlation coefficient the statistical interpretation is more difficult but could be accepted as a moderate level of correlation between the integral indicators.

The presented results confirm the importance of using the integral assessment of the climatic and anthropogenic impact within a catchment as a reliable tool for water management.

Conclusions

1. Two periods are outlined in the tenor of the changes in the average annual water flow for the investigated river points: first period – 1948–1972, second period – 1973–1995 and third period 1996–2006.

The period 1948–1972 is characterized by average annual river flow, which is lower than the average multi-annual water flow (flow norm) – dry years ($C_i < 0$, $K_i < 1$).

The period 1973–1995 is characterized by average annual water flow, which is higher than the flow norm – high water years ($C_i > 0$, $K_i > 1$). The period 1996–2006 is characterized by annual average river flow, which is lower than the flow norm – dry years ($C_i < 0$, $K_i < 1$).

In a long standing average of the annual water flow, determined cycles of wet and dry years in the identified water period are shown. Cycles with one-three wet years and a few dry years are outlined as well.

2. The character of the changes in the maximum water flow at the two river points with respect to the average multi-annual value of the maximum water flow $Q_{max,0}$ does not differ from the character of the changes in the average annual water flow with respect to the flow norm Q_0 .

Two periods are outlined for the two points: first 1948–1975 and second 1976–2006.

The 1948–1975 period is characterized by maximum water flow, which is higher than the average multi-annual value $Q_{max,0}$ ($M_{i,max} > 1$; high water and flood effect). For the two points a four-year cycle is outlined (1955–1958), when the maximum water flow is lower than the average multi-annual value $Q_{max,0}$.

The period 1976–2006 is characterized by maximum water flow, which is lower than the average multi-annual value $Q_{\max,0}$ for both points ($M_{i,\max} < 1$; high water, possible negative effect). For the two points a three-year cycle is outlined (1976–1978), when the maximum water flow is higher than the average multi-annual value $Q_{\max,0}$.

3. Two periods are outlined at the river points for the changes in the minimum water flow. The 1948–1972 period is characterized by minimum water flow, which is lower than the average multi-annual value $Q_{\min,0}$ ($M_{i,\min} < 1$; low water and drought effect). For the two points a three-year cycle is outlined (1961–1964), when the minimum water flow is higher than the average multi-annual value $Q_{\min,0}$.

The 1973–2006 period is characterized by minimum water flow, which is higher than the average multi-annual value $Q_{\min,0}$ ($M_{i,\min} > 1$). For the two points a three-year cycle is outlined (1998–2001), when the minimum water flow is lower than the average multi-annual value $Q_{\min,0}$.

4. Two periods are outlined in the change of the annual average atmospheric precipitation: first 1948–1990 of low atmospheric precipitation ($h_i < 1$) and second 1991–2006 with years of higher atmospheric precipitation for Pernik and Krupnik points. One to four water abundant years ($h_i > 1$) are outlined during the two periods.

5. Two periods are determined at the Pernik and Krupnik (Blagoevgrad) points for the changes in the maximum atmospheric precipitation. The period 1948–1990 is characterized by maximum atmospheric precipitation, which is lower than the average multi-annual value $H_{\max,0}$ ($h_{i,\max} < 1$, high atmospheric precipitation possible negative effect). For the two points a four years cycle is outlined (1948–1952 for Pernik and 1954–1959 for Krupnik/Blagoevgrad), when the maximum atmospheric precipitation is higher than the $H_{\max,0}$ ($h_{i,\max} > 1$, flood effect).

The period 1991–2006 is characterized by maximum atmospheric precipitation which is higher than $H_{\max,0}$. For the two points a four year cycle is outlined (1998–2002) when the maximum atmospheric precipitation is lower than $H_{\max,0}$ ($h_{i,\max} < 1$).

6. The proposed integral indices provide the possibility of evaluating the climate impact on the Struma River flow formation, but they may also be applied for other rivers on regional, national and transboundary level. Using integral indicators, high water years, dry years, maximum water flow and flood effect, minimum water flow and drought effect, are identified, which is a preliminary estimation of the risk assessment of flood events and drought events.

7. With the proposed integral parameters it is possible to investigate the influence of climate on the formation of the average annual maximum/minimum water flow and to establish and predict possible short-term negative effects.

Acknowledgement

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OCENA WPŁYWU ZMIAN KLIMATYCZNYCH NA PRZEPIŁYW TRANSGRANICZNEJ RZEKI STRUMA PRZEZ TERYTORIUM BUŁGARII Z WYKORZYSTANIEM WSKAŹNIKÓW ZINTEGROWANYCH

Abstrakt: Dokonano oceny wpływu zmian klimatycznych i antropogennych na średni roczny przepływ wody oraz wartość maksymalnego i minimalnego przepływu wody w rzece Struma przepływającej przez terytorium Bułgarii. Parametry te są określone przez indeks K_i (wskaźnik przepływu), wskaźnik C_i średniego odchylenia rocznego przepływu wody Q_i do normy przepływu Q_0 , indeks $K_{i,max}$ maksymalnego odchylenia przepływu wody $Q_{max,i}$ do normy przepływu Q_0 , indeks $K_{i,min}$ minimalnego odchylenia przepływu wody $Q_{min,i}$ do normy przepływu Q_0 , wskaźnik $M_{i,max}$ maksymalnego odchylenia przepływu wody do maksymalnej normy przepływu $Q_{max,0}$, indeks $M_{i,min}$ minimalnego odchylenia przepływu wody do minimalnej normy przepływu $Q_{min,0}$. Nowe podejście wprowadza bardziej szczegółowe wskaźniki oceny wpływu klimatu na wody rzeki, jak wskaźniki przepływu modułu ($K_{i,av}$), odchylenie średniej (C_i). Zastosowanie sugerowanych wskaźników umożliwia ocenę roli różnych zmian klimatycznych przez $K_{i,av}$, $K_{i,min}$, $K_{i,max}$, $M_{i,min}$, $M_{i,max}$, C_i , h_i i $h_{i,max}$. Metoda ta została zastosowana i sprawdzona w Perniku i Krupniku dla lat 1948–2006 w celu oceny skutków zmian klimatu. Indeksy te odzwierciedlają wywołane zmianami klimatycznymi szczególne wydarzenia, takie jak: lata suche, powódzie i wiatry.

Słowa kluczowe: wskaźniki zintegrowane, wpływ klimatu, przepływ rzeki

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and Andrzej ROCHWERGER

CALCIUM ION MIGRATION IN AGRICULTURAL AND AFFORESTED LAKE CATCHMENTS

MIGRACJA JONU WAPNIOWEGO W JEZIORNÝCH ZLEWNIACH ROLNICZO-LEŚNYCH

Abstract: The research on circulating of calcium in the agricultural-forest drainage areas were carried out on the Olsztyn lake district in 2004–2006 years. Three lakes were marked out for examinations about diversified anthropogenic interacting with their drainage areas.

Ardung lake is situated in the centre-western part of the Mazurian lake district, its surface amounts to 26.2 ha and the average depth is 1.8 m. The drainage area of examined lake has the surface of 1539 ha and forest communities are covering it in the form of pine forests about the high level of the naturalness.

Drainage area of Bukwałd lake is situated 20 km to the north of Olsztyn. Lake covers 36.2 ha of the surface and its average depth is 5.0 m. The total drainage area of lake is taking the surface of 1156 ha, in which the arable land constitutes the 60 % with the little surface area of the land filled by wasteland (9 %) and forests (31 %) and with low-density housing.

Lake Sunia is situated about 30 km to the north of Olsztyn. The surface area of lake amounts to 111.6 ha and its average depth is 3.9 m. The total surface of the drainage area amounts to 450 ha, out of which 97 % is going to the intensively agriculturally used lands, while the rest part constitute wastelands and forests.

Comparing the individual research years one should state that in 2005 the lowest values of flows were recorded in the rising tides and ebb tides from Lakes Sunia and Bukwałd, however the highest were observed in the year 2004; a situation developed differently in the drainage area of Ardung lake, in which, in the sequence of the entire research period, comparatively levelled values of flows were recorded in all rising tides and the ebb tide of lake.

Comparing flows off from the examined drainage areas one should state that the waters running off from the exploited agricultural drainage areas of Bukwałd lake were characterised by the highest Ca^{2+} contents (114.3–126.3 $\text{mg} \cdot \text{dm}^{-3}$), however the lowest were found in waters running off from the boggy area of the same lake (25.0 $\text{mg} \cdot \text{dm}^{-3}$).

Higher contents of calcium in the waters running off from the agricultural areas is connected with more intensive washing this element out of arable cultivated soils periodically deprived of the plant cover. Considerable de-equalisations occurring in the drainage areas of lakes can also contribute to the faster outflow of biogenes increasing this way their content in the waters flowing into the reservoir.

Keywords: lakes, catchment, biogenes, calcium

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The circulation of matter in the landscape, including pollutants, eutrophication substances and other vital components for ecosystems, takes place in the catchments. The runoff of biogenic substances from the catchment area to surface and underground water is determined by various factors, in particular relief features, soil coherence and fertility, land use type, water relations and climate conditions, primarily precipitation volume and distribution.

Together with magnesium, hydrogencarbonates and sulfates, calcium determines the hydrochemical type of most water resources in the catchment areas of young glacial zones. Intense leaching of calcium from the soil is responsible for the high calcium content in surface water [1]. Calcium is intensively washed out from farming areas in a moderate climate zone, mainly due to the acidification of precipitation water which also causes soil acidification. For this reason, calcium fertilizers should be applied to compensate for the loss of this nutrient and to create a supportive environment for plant growth. Calcium concentrations in water must be kept at an adequate level as calcium has buffering properties and it plays an important role in primary production by ensuring sufficient CO₂ concentrations for photosynthesis [2].

The objective of this study was to determine the effect of catchment use on calcium migration in surface water, in particular on its concentrations and load transported to the lake.

Materials and methods

The research on calcium migration in lake catchments was carried out in the Olsztyn Lakeland in the catchment areas of the lakes Sunia, Bukwałd and Ardung, between March 2004 and February 2007.

Lake Sunia (N 53°58', E 20°17') is situated around 30 km to the north of Olsztyn in the rural district of Świątki. The lake has an area of 111.6 ha and an average depth of 3.9 m. Its total catchment area is 450 ha, including a tributary area of 70 ha. It is surrounded mostly by arable land (97 %), with barren land and woodland accounting for only 3 % of the total area. The catchment area comprises predominantly loamy and sandy soils with heavy loamy sands and light sandy loams of soil quality class IVa, IIIa and IIIb.

The catchment of Lake Bukwałd (N 53°58', E 20°16') is in the vicinity of the village of Bukwałd, rural district of Dywity, around 20 km to the north of Olsztyn. The lake has an area of 36.2 ha with an average depth of 5.0 m. The lake catchment has an area of 1156 ha, and it is occupied by arable land (60 %), barren land (9 %), forests (31 %) and dispersed development. Lake Bukwałd is fed by 4 tributaries. Northern tributaries no. 1 and no. 2 intersect arable land and have a total catchment area of 322 ha. South-western tributaries comprise tributary no. 3, which flows through wasteland (catchment area of 63 ha) and emerges from a water-logged area, and no. 4 which flows mostly through woods (catchment area of 516 ha). The lake is fed from a hilly area with significant height differences reaching 23.5 m. The catchment area comprises mostly light and heavy loamy sands of soil quality class IVa, IVb and, locally, IIIa and IIIb.

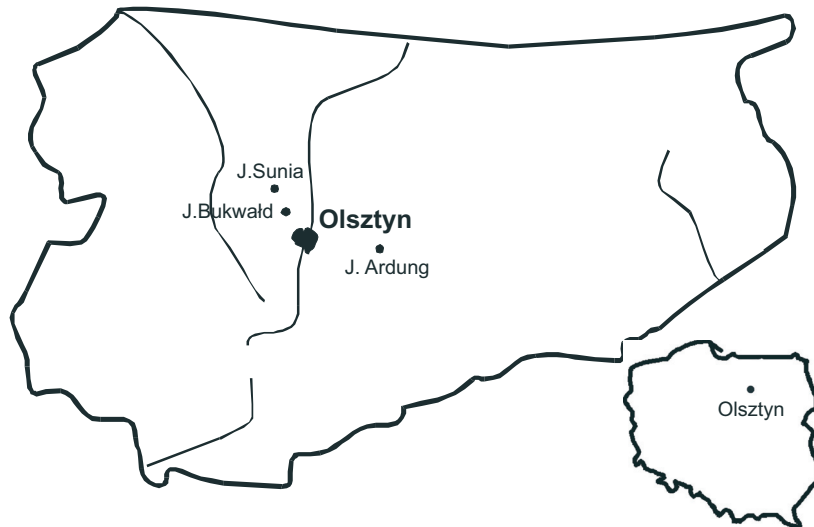


Fig. 1. Location of the study area

Lake Ardung (N 53°45', E 20°55') is situated in the central-western part of the Masurian Lakeland. It has an area of 26.2 ha and an average depth of 1.8 m. The lake catchment has an area of 1539 ha, of which 505 ha is occupied by the direct catchment. The lake is fed by 3 tributaries and 2 head streams. Tributaries no. 1 and 2 are found in the north-eastern part of the lake. Tributary no. 1 has an afforested catchment, while tributary no. 2 flows through an afforested catchment featuring a small number of settlements and a fish pond. Tributary no. 3 enters the lake on the south-eastern side. In the upper part, the catchment comprises several interior basins where seven small lakes play a focal function in the process of ground and underground water recirculation. The lower part of the catchment is afforested in 90 %. The predominant type of soils in this area are podzols overgrown with pine woods characterized by a high degree of naturalness. All three types of podzols are locally encountered in this area: podzolic soils, rusty soils and podzols of different morphological sub-types and varieties [3].

The study included hydrological measurements and laboratory analyses. The flow of watercourses feeding into the lake (4 into Lake Bukwałd, 1 into Lake Sunia, 2 into Lake Ardung) was measured once a week at approximately 50 m above the lake outlet. Flow measurements were performed with the use of a VALEPORT electromagnetic flowmeter and by the volumetric method at a low flow rate (below $2 \text{ dm}^3 \cdot \text{s}^{-1}$). Runoffs per area unit for each partial catchment area were computed based on mean annual measurements. Water was sampled for physical and chemical analyses once a month at the place of flow monitoring. The Ca^{2+} content of water was determined by atomic absorption spectrophotometry. Analyses were conducted in accordance with the universally accepted methodology [4].

The volume of calcium migration from the analyzed catchment was computed as the total product of calcium levels and the corresponding mean monthly flows.

Results and discussion

Water runoff from each catchment area was strongly determined by the type of land use. The lowest fluctuations were observed in the afforested catchment of Lake Ardung where the observed values were relatively stable in both the inflow and the outflow of this water body. The above could be attributed to the high retention capacity of the investigated catchment, covered by forest vegetation. In the catchments of the remaining lakes, the highest average flow values were noted in 2004, and the lowest – in 2005 which was marked by a complete absence of runoffs in the summer (Table 1).

An analysis of runoffs per area unit in each catchment showed the highest fluctuations in respect of outflows from the agricultural catchment of Lake Bukwałd ($0 \text{ dm}^3 \cdot \text{s}^{-1} \cdot \text{km}^{-2}$ in the summer and autumn of 2005 to $44.0 \text{ dm}^3 \cdot \text{s}^{-1} \cdot \text{km}^{-2}$ in the winter of 2006). The noted high variations in surface runoffs from the agricultural catchment could be due to a high level of water uptake by the farmed crops. The catchment's heavy soils inhibited surface water filtration into the soil profile. Runoff was supported by significant altitude differences and the periodic absence of vegetation cover.

An analysis of runoffs from the investigated lakes per area unit indicates the highest fluctuations in the outflow of Lake Bukwałd ($0 \text{ dm}^3 \cdot \text{s}^{-1} \cdot \text{km}^{-2}$ in the autumn of 2005 to $20.6 \text{ dm}^3 \cdot \text{s}^{-1} \cdot \text{km}^{-2}$ in the winter of 2004). Significantly lower fluctuations were observed in Lake Sunia ($0\text{--}13.4 \text{ dm}^3 \cdot \text{s}^{-1} \cdot \text{km}^{-2}$) and Lake Ardung ($4.2\text{--}8.8 \text{ dm}^3 \cdot \text{s}^{-1} \cdot \text{km}^{-2}$).

A comparison of runoffs per area unit in lake outflows and runoffs per area unit in lake inflows indicates that the lakes Ardung and Sunia were characterized by much lower runoff values in their respective inflows than in their outflows. The above could be attributed to the presence of water from the direct catchment or from internal feed sources in the lakes' water balance. A different situation was observed in the catchment of Lake Bukwałd where runoffs per area unit in the inflow were much higher than in the outflow. The above could be due to the lake's high retention capacity which eased the runoff wave from the catchment, as well as to intense evaporation of surface water.

A correlation analysis between the inflows and outflows of the lakes Bukwałd and Sunia points to a positive correlation within the range $r = < 0.81\text{--}0.93 >$ at $P \leq 0.05$ which is indicative of a very strong relationship between the quantity of water flowing in and out of the above water bodies. No correlation was observed between the inflows and outflows of Lake Ardung, most probably due to retention as well as other feed sources (eg underwater springs) in the lake's water balance. The above is validated by significant fluctuations in the inflows and outflows of the lake catchment in the winter and spring.

Mean calcium concentrations in the analyzed water samples were relatively stable throughout the year. Ca^{2+} leaching was most intense during the non-growing season when fluctuations in the levels of the investigated element were accompanied by limited biological sorption [5, 6].

Ca^{2+} leaching from the catchment area of Lake Ardung was most intense in the autumn of 2004 and 2005 when the highest calcium concentrations were reported in the majority of feeders into Lake Ardung. The only exception was the process observed in

Table 1
Seasonal fluctuations in runoffs per area unit in the inflows and outflows of the investigated lakes [$\text{dm}^3 \cdot \text{s}^{-1} \cdot \text{km}^{-2}$]

Catchment of lakes studied	(No. inflow)	2004					2005					2006				
		Spring	Summer	Autumn	Winter	Average	Spring	Summer	Autumn	Winter	Average	Spring	Summer	Autumn	Winter	Average
Ardung	Forest inflow No. 1	1.4	1.2	0.9	0.9	1.1	1.1	0.9	1.2	1.6	1.2	1.1	1.3	1.6	1.0	1.2
	Forest-fish-pond inflow	7.8	8.1	11.6	10.4	9.5	12.5	8.7	7.0	10.8	9.7	9.7	6.9	7.4	10.1	8.5
	Forest inflow No. 2	1.3	0.6	0.5	0.8	0.8	1.1	0.3	0.7	0.4	0.7	0.5	0.4	0.7	0.7	0.6
	Outflow	5.8	4.2	5.3	8.1	5.9	9.2	4.7	4.8	6.7	6.3	6.9	4.7	5.2	8.8	6.4
Bukwaid	Agricultural inflow No. 1	22.9	4.2	14.5	31.7	18.3	17.4	0.0	0.0	0.3	4.5	8.9	0.6	17.0	44.0	17.7
	Agricultural inflow No. 2	16.5	4.3	9.4	24.5	13.7	19.9	0.3	0.0	1.4	5.4	8.3	0.2	10.9	29.9	12.4
	Wetland inflow	10.2	0.6	3.2	19.4	8.4	6.3	0.0	0.0	0.0	1.6	3.2	0.0	14.8	31.3	12.4
	Forest inflow	3.4	1.2	1.8	8.4	3.7	2.6	0.0	0.0	0.0	0.6	2.2	0.1	3.7	8.8	3.7
	Outflow	12.8	3.6	5.0	20.6	10.5	5.4	0.2	0.0	0.1	1.4	5.9	0.4	5.8	14.2	6.5
Sumia	Agricultural inflow	5.0	4.3	1.0	4.9	3.9	2.0	0.0	0.0	0.0	0.7	2.6	0.4	1.4	4.7	2.3
	Outflow	12.9	3.9	1.0	7.9	6.4	9.4	1.1	0.0	0.0	2.6	1.7	0.4	3.4	13.4	4.7

2006, but the autumn concentrations of that year were only slightly below the winter concentrations. The highest fluctuations in calcium concentrations in the inflows to Lake Ardung were noted in feeder no. 2 ($42.6 \text{ mg} \cdot \text{dm}^{-3}$ in the spring of 2004 – $84.3 \text{ mg} \cdot \text{dm}^{-3}$ in the winter of 2004), while the lowest Ca^{2+} levels were observed in tributary no. 1 ($61.6 \text{ mg} \cdot \text{dm}^{-3}$ in the autumn of 2006 – $74.8 \text{ mg} \cdot \text{dm}^{-3}$ in the autumn of 2004) (Table 2). The highest calcium levels in the water of feeders to Lake Ardung were reported in the autumn of 2004, and the lowest – in the spring of 2004.

Calcium concentrations in feed water were clearly influenced by the type of catchment use, as shown by the agricultural catchment of Lake Bukwałd. The highest Ca^{2+} levels in all investigated watercourses were reported in the winter of 2005 in the agricultural runoffs from the catchment of Lake Bukwałd ($126.3 \text{ mg} \cdot \text{dm}^{-3}$ and $114.3 \text{ mg} \cdot \text{dm}^{-3}$). The above could result from soil leaching in the months preceding the beginning of the growing season, with limited phytosorption of calcium on arable land. High calcium levels in the inflows to Lake Bukwałd in the winter of 2005 could also be attributed to the intense leaching of this micronutrient from the catchment after the spring and summer draught. The lowest Ca^{2+} content in all investigated tributaries of Lake Bukwałd was observed in the winter of 2006 in the feeder from the lake afforested catchment area ($25.0 \text{ mg} \cdot \text{dm}^{-3}$), which was also the lowest concentration reported in all of the investigated watercourses.

Low Ca^{2+} levels in outflows from semi-natural areas in comparison with outflows from agriculturally used areas could be attributed mainly to low calcium concentrations in an environment where the investigated element is supplied by precipitation, mineral weathering, organic matter decomposition and calcium migration from the water environment due to sorption. Calcium is a vital macronutrient for plant growth in agricultural areas. In the non-growing season, calcium is intensively leached from the soil and large quantities of this element are also removed with farming crops. For this reason, calcium levels are supplemented by agrotechnical treatments to increase its concentrations in the soil and, consequently, in water which migrates from the area.

Based on a comparison of Ca^{2+} levels in the outflows of the investigated lakes, the highest Ca^{2+} concentrations were noted in the autumn and winter. The highest calcium levels were observed in the runoff from Lake Ardung (from $70.2 \text{ mg} \cdot \text{year}^{-1}$ in 2004 to $62 \text{ mg} \cdot \text{year}^{-1}$ in 2006), while the lowest concentrations were determined in the runoff from Lake Sunia ($58.2 \text{ mg} \cdot \text{year}^{-1}_{2004}$ – $47.0 \text{ mg} \cdot \text{year}^{-1}_{2005}$). Based on a seasonal analysis, the highest calcium levels were noted in the outflow from Lake Sunia in the winter ($99.3 \text{ mg} \cdot \text{season}^{-1}$), while the lowest – in the summer of 2004 ($40.4 \text{ mg} \cdot \text{season}^{-1}$) in the outflow of the same lake. Higher concentrations of calcium ions in the autumn and winter season could be attributed to intensified Ca^{2+} flow from the catchment area in the non-growing season. Small quantities of calcium ions are also absorbed by phytoplankton and shore plants [7].

Weather conditions were the main determinant of the quantity of calcium load washed out from the analyzed catchment areas, mostly precipitation intensity and spring thaw intensity. Thick snow cover and its fast thawing could lead to the formation of melt waves, thus increasing the quantity of biogenes which are leached out from the surface of the soil and are fed into the lakes.

Table 2

Seasonal fluctuations in Ca^{2+} concentrations in the inflows and outflows of the investigated lakes [$\text{mg} \cdot \text{dm}^{-3}$]

Catchment of lakes studied	(No. inflow)	2004					2005					2006				
		Spring	Summer	Autumn	Winter	Average	Spring	Summer	Autumn	Winter	Average	Spring	Summer	Autumn	Winter	Average
Ardung	Forest inflow No. 1	48.7	71.1	86.1	77.8	71.0	67.5	74.7	74.5	65	70.4	69.9	74.7	67.4	68.8	70.2
	Forest-fish-pond inflow	53.6	72.2	88.3	60.2	68.6	63.7	76.7	79.9	62	70.6	69.1	71.0	66.3	78.3	71.2
	Forest inflow No. 2	42.5	61.6	76.4	84.3	66.2	57.9	65.1	72.2	50.5	61.4	66.8	66.3	60.4	69.9	65.9
	Sources No.1	66.2	62.8	74.8	74.6	69.6	65.2	65.2	72.2	64.2	66.7	65.9	67.4	61.6	68.5	65.8
	Sources No. 2	44.4	63.9	75.9	53.1	59.3	71.5	68.6	75.3	69.6	71.2	68.9	69.9	61.3	62	65.5
	Outflow	67.4	60.4	68.7	84.2	70.2	66.7	65.1	61.9	59.2	63.2	67.4	56.5	55.4	68.7	62.0
Bukwaid	Agricultural inflow No. 1	59.2	85.0	89.3	80.7	78.5	60.3	—	—	114.3	87.3	88.7	82.6	75.2	72.2	79.7
	Agricultural inflow No. 2	73.2	91.4	99.8	86.6	87.8	65.2	81.0	—	126.3	90.8	95.5	95.8	109.5	79.3	95.0
	Wetland inflow	36.1	32.0	28.4	44.0	35.1	36.4	—	—	—	36.4	27.7	—	39.8	25.0	30.8
	Forest inflow	42.0	62.9	71.9	62.8	59.9	45.2	—	—	77.1	61.1	44.8	49.8	53	42.7	47.6
	Outflow	55.6	60.4	64.6	79.4	65.0	48.1	55.4	—	60.2	54.6	58.4	62.8	54.1	57.2	58.1
Sunia	Agricultural inflow	60.5	60.2	74.2	84.0	69.7	47.1	—	—	—	47.1	59.4	63.5	65.2	77.0	66.3
	Outflow	44.2	40.4	48.9	99.3	58.2	47.0	47.0	—	—	47.0	42.9	65.2	64.5	50.7	52.9

An analysis of calcium supply and runoff from the lakes has shown that the calcium load in the catchment of Lake Arduńg was relatively balanced throughout the experimental period, reaching from 142792 kg · year⁻¹ in 2004 to 160429 kg · year⁻¹ in 2005 in the inflow, and from 195396 kg · year⁻¹ in 2005 to 205827 kg · year⁻¹ in 2004 in the outflow (Table 3). The inflow from the forest and pond catchment (81458–89641 kg · year⁻¹) as well as the inflow from tributary no. 2 (40299–56364 kg · year⁻¹), which accounted for 56–62 % and 28–34 % of the total calcium load respectively, had a significant share in Ca²⁺ transport to the lake. An estimated 90 % of total calcium load reached the lake from the two above feeders. A comparison of inflowing and outflowing loads indicates that 69 % to 82 % of total calcium is fed to the lake from the indirect catchment, while the remaining load is transported with water from the direct catchment and from underwater springs.

The lowest calcium load from the catchment area was reported in 2005, reaching 39 793 kg · year⁻¹ in Lake Bukwałd and 528 kg · year⁻¹ in Lake Sunia. The calcium runoff from Lake Bukwałd in 2005 was approximately 74–76 % lower than in other years of the experiment (169680 kg · year₂₀₀₄⁻¹ and 155305 kg · year₂₀₀₆⁻¹), and the runoff from the catchment of Lake Sunia was 91 % lower than in 2004 (5761 kg · year₂₀₀₄⁻¹) and 85 % lower than in 2006 (3492 kg · year₂₀₀₆⁻¹).

Agricultural feeders had the highest share of Ca²⁺ transport from the catchment to Lake Bukwałd and were responsible for the migration of 75–85 % of total calcium leaving the catchment area. The highest Ca²⁺ runoff was reported in the winter of 2006 (33 072 kg · season⁻¹ – tributary no. 1 and 35 543 kg · season⁻¹ – tributary no. 2).

Based on a comparison of experimental years, the highest runoff of calcium load was reported in 2004 from Lake Bukwałd (263500 kg · year⁻¹), followed by Lake Sunia (55168 kg · year⁻¹). According to a seasonal analysis, the highest Ca²⁺ migration from both lakes took place in the winter of 2004 (Lake Bukwałd – 149349 kg · season⁻¹ and Lake Sunia – 27779 kg · season⁻¹).

A comparison of outflowing and inflowing calcium loads in Lake Sunia shows that the latter had only a 3–10 % share of the load leaving the water body. The above could indicate that a significant part of the Ca²⁺ load was fed to the lake from other sources, including surface and underground runoffs from the direct catchment, precipitation and internal lake supply (sediment resuspension, underwater springs).

The highest level of calcium migration from all feed sources was determined in 2004 in the agricultural catchments of Lake Bukwałd at 455.5 kg · ha⁻¹ and in feeders from farming areas at 365.3 kg · ha⁻¹, while the lowest calcium concentrations were observed in 2005 in the afforested catchment of Lake Bukwałd at 9.3 kg · ha⁻¹ · year⁻¹ and in the agricultural catchment of Lake Sunia at 7.5 kg · ha⁻¹ · year⁻¹ (Table 4). The noted low level of migration was most likely caused by the draught observed in the investigated period and the resulting absence of surface runoffs. The agricultural catchment of Lake Bukwałd was also characterized by the highest seasonal fluctuations in Ca²⁺ runoff per area unit. The highest migration was noted in the winter of 2006 (244.4 kg · ha⁻¹ and 186.6 kg · ha⁻¹), and the lowest in the spring and summer of 2005 when no surface runoffs from the catchment to the lake were observed. An analysis of seasonal calcium runoffs from all catchments to the analyzed lakes shows the lowest inflow values from

Table 3

Seasonal fluctuations in Ca^{2+} load in the inflows and outflows of the investigated lakes [$\text{kg} \cdot \text{season}^{-1}$]

Catchment of lakes studied	(No. inflow)	2004					2005					2006				
		Spring	Summer	Autumn	Winter	Average	Spring	Summer	Autumn	Winter	Average	Spring	Summer	Autumn	Winter	Average
Ardung	Forest inflow No. 1	2361	2859	2629	2597	10445	2602	2267	3067	3639	11575	2581	3357	3746	2441	12125
	Forest-fish-pond inflow	14029	19534	34065	20915	88544	26567	22203	18618	22253	89641	22427	16345	16296	26390	81458
	Forest inflow No. 2	704	486	532	919	2642	860	265	677	229	2031	492	288	512	634	1925
	Sources No. 1	156	239	221	245	862	181	180	240	215	818	156	159	316	162	793
	Sources No. 2	7508	9018	14255	9517	40299	14287	13215	16722	12141	56364	14413	14742	7829	12440	49424
	Outflow	47824	31040	43818	83145	205827	74100	36937	36309	48050	195396	57450	31916	35084	73472	197922
Bukwaid	Agricultural inflow No. 1	14101	3663	13518	26577	57860	10942	0	0	378	11320	8170	543	13271	33072	55056
	Agricultural inflow No. 2	18113	5911	14072	31718	69814	19469	383	0	2683	22535	11842	302	17985	35543	65672
	Wetland inflow	1832	93	442	4241	6609	1134	0	0	0	1134	437	0	2918	3883	7238
	Forest inflow	5854	2963	5249	21332	35397	4716	0	0	88	4804	3962	196	7981	15200	27339
	Outflow	64765	20059	29326	149349	263500	23613	925	0	467	25004	31892	2195	28364	73846	136296
Sumia	Agricultural inflow	1646	1430	429	2255	5761	528	0	0	0	528	830	128	531	2003	3492
	Outflow	20162	5572	1655	27779	55168	15676	1797	0	0	17473	2623	994	7763	24063	35443

Table 4

Seasonal fluctuations in Ca^{2+} runoff per ha [$\text{kg} \cdot \text{ha}^{-1} \cdot \text{season}^{-1}$]

Catchment of lakes studied	(No. inflow)	2004					2005					2006				
		Spring	Summer	Autumn	Winter	Average	Spring	Summer	Autumn	Winter	Average	Spring	Summer	Autumn	Winter	Average
Ardung	Forest inflow No. 1	5.4	6.5	6.1	5.7	23.7	5.9	5.2	7.0	8.0	26.1	5.9	7.6	8.6	5.4	27.5
	Forest-fish-pond inflow	33.4	46.5	81.1	48.3	209.3	63.3	52.9	44.4	51.3	211.9	53.5	39.0	38.9	60.9	192.3
	Forest inflow No. 2	4.2	2.9	3.3	5.4	15.8	5.2	1.5	4.1	1.4	12.2	2.8	1.9	3.1	3.8	11.6
	Outflow	31.3	20.3	28.7	52.7	133.1	48.5	24.2	23.8	30.5	127	37.1	20.9	23.0	46.6	127.6
	Agricultural inflow No. 1	107.7	28.2	103.2	196.5	435.5	83.5	0.0	0.0	2.7	86.2	62.5	4.0	101.4	244.4	412.3
Bukwaid	Agricultural inflow No. 2	96.2	31.4	74.8	163.0	365.3	103.4	2.0	0.0	13.8	119.2	62.7	1.6	95.3	182.6	342.2
	Wetland inflow	29.1	1.6	7.2	65.5	103.4	18.4	0.0	0.0	0.0	18.4	7.0	0.0	46.7	60.0	113.7
	Forest inflow	11.5	5.8	10.3	40.3	67.9	9.2	0.0	0.0	0.1	9.3	7.7	0.4	15.6	28.8	52.5
	Outflow	56.4	17.5	25.6	126.0	225.5	20.6	0.8	0.0	0.4	21.8	27.3	1.9	24.7	62.3	116.2
	Agricultural inflow	24.1	20.5	5.9	31.4	81.8	7.5	0.0	0.0	0.0	7.5	12.1	2.2	7.4	27.9	49.6
Sumia	Outflow	45.2	12.4	3.7	60.2	121.5	35.1	4.1	0.0	0.0	39.2	5.9	2.2	17.4	52.2	77.7

the afforested catchment of Lake Ardung ($5.2 \text{ kg} \cdot \text{ha}^{-1}$ and $1.5 \text{ kg} \cdot \text{ha}^{-1}$ in the summer of 2005). The highest Ca^{2+} surface runoff from the catchment of Lake Ardung was noted in the feeder from the forest and pond catchment ($192.3 \text{ kg} \cdot \text{ha}^{-1} \cdot \text{year}^{-1}_{2006} - 211.9 \text{ kg} \cdot \text{ha}^{-1} \cdot \text{year}^{-1}_{2005}$). The above can be attributed to high flow intensity and the type of catchment use (the presence of human settlements and the use of tributary flow to feed a fish pond).

In view of an analysis of surface runoff per area unit measured in the outflows from each lake, the highest values were reported in 2004 in the outflow from Lake Bukwałd ($225.5 \text{ kg} \cdot \text{ha}^{-1} \cdot \text{year}^{-1}$), mostly due to the high share of Ca^{2+} load supplied from agricultural catchments in the lake total water balance. As regards seasonal fluctuations in Ca^{2+} levels, the highest load was noted in respect of the outflow from Lake Bukwałd ($0 \text{ kg} \cdot \text{ha}^{-1} \cdot \text{season}^{-1}$ in the autumn of 2005 – $126.0 \text{ kg} \cdot \text{ha}^{-1} \cdot \text{season}^{-1}$ in the winter of 2004), while the outflow from the mostly afforested catchment (more than 80 %) of Lake Ardung was marked by highest stability ($20.30 \text{ kg} \cdot \text{ha}^{-1} \cdot \text{season}^{-1}$ in the summer of 2004 – $52.7 \text{ kg} \cdot \text{ha}^{-1} \cdot \text{season}^{-1}$ in the winter of 2004).

Conclusions

1. Calcium migration from the catchment areas to the lakes was determined by runoff from feed sources, the type of catchment use, differences in altitude, soil type and weather conditions. The agricultural catchment of Lake Bukwałd was characterized by the highest and the most fluctuating runoffs per area unit ($0-44.0 \text{ dm}^3 \cdot \text{s}^{-1} \cdot \text{km}^{-2}$), while the lowest runoffs were noted in the afforested catchment of Lake Ardung ($0.9-1.6 \text{ dm}^3 \cdot \text{s}^{-1} \cdot \text{km}^{-2}$). The highest runoffs were observed in the winter, and the lowest – or the absence thereof – in the summer.

2. The type of catchment use strongly determined Ca^{2+} concentrations in water runoffs. The highest calcium levels were determined in the agriculturally used feeders (catchment of Lake Bukwałd – $126.3 \text{ mg} \cdot \text{dm}^{-3}$), and the lowest – in the runoff from the swampy catchment of Lake Bukwałd ($25.0 \text{ mg} \cdot \text{dm}^{-3}$).

3. Ca^{2+} concentrations in runoffs were also strongly determined by weather conditions. The highest calcium levels were noted in the autumn, and the lowest – in the spring.

4. Calcium runoff from the catchments to the lakes reached 12 to $436 \text{ kg} \cdot \text{ha}^{-1} \cdot \text{year}^{-1}$. The highest level of calcium migration in all feed sources was observed in the catchment of Lake Bukwałd in runoffs from agricultural catchments ($86-436 \text{ kg} \cdot \text{ha}^{-1}$), followed by runoffs from the swampy catchment ($18-114 \text{ kg} \cdot \text{ha}^{-1}$), while the lowest values were reported in respect of the lake afforested catchment ($9.3-68 \text{ kg} \cdot \text{ha}^{-1}$).

5. The average annual runoff from the investigated lakes ranged from 22 to 226 kg Ca per one hectare of catchment area. The magnitude of calcium migration was determined by the type of catchment use, and it was much higher and marked by the highest fluctuation in the agricultural catchment ($293 \text{ kg} \cdot \text{ha}^{-1}$ on average) than in the afforested catchment ($43 \text{ kg} \cdot \text{ha}^{-1}$ on average).

6. The highest seasonal fluctuations in calcium levels in runoffs were reported in Lake Bukwałd with a high share of the agricultural catchment ($0 \text{ kg} \cdot \text{ha}^{-1} \cdot \text{season}^{-1}$ in

the autumn of 2005 – $126.0 \text{ kg} \cdot \text{ha}^{-1} \cdot \text{season}^{-1}$ in the winter of 2004), and the lowest – in Lake Ardung with an afforested catchment ($20.30 \text{ kg} \cdot \text{ha}^{-1} \cdot \text{season}^{-1}$ in the summer of 2004 – $52.7 \text{ kg} \cdot \text{ha}^{-1} \cdot \text{season}^{-1}$ in the winter of 2004).

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MIGRACJA JONU WAPNIOWEGO W JEZIORNICH ZLEWNIACH ROLNICZO-LEŚNYCH

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Abstrakt: Badania nad krążeniem wapnia w zlewniach rolniczo-leśnych prowadzono na Pojezierzu Olsztyńskim w latach 2004–2006. Do badań wytypowano trzy jeziora o zróżnicowanym oddziaływaniu antropogennym na ich zlewnie.

Jezioro Ardung położone jest w środkowo-zachodniej części Pojezierza Mazurskiego, jego powierzchnia wynosi 26,2 ha, a średnia głębokość 1,8 m. Zlewnia badanego jeziora ma powierzchnię 1539 ha i porastają ją zbiorowiska leśne w postaci borów sosnowych o wysokim stopniu naturalności.

Zlewnia jeziora Bukwałd położona jest 20 km na północ od Olsztyna. Jezioro zajmuje 36,2 ha powierzchni, a jego średnia głębokość wynosi 5,0 m. Całkowita zlewnia jeziora zajmuje powierzchnię 1156 ha, w której grunty orne stanowią 60 % z niewielką powierzchnią terenu zajętej przez nieużytki (9 %) oraz lasy (31 %) i rozproszoną zabudowę.

Jezioro Sunia położone jest ok. 30 km na północ od Olsztyna. Powierzchnia jeziora wynosi 111,6 ha, a jego średnia głębokość 3,9 m. Całkowita powierzchnia zlewni wynosi 450 ha, z czego 97 % przypada na grunty intensywnie użytkowane rolniczo, a pozostałą część stanowią nieużytki oraz zadrzewienia.

Porównując poszczególne lata badawcze, należy stwierdzić, że w roku 2005 odnotowano najmniejsze wartości przepływów w dopływach i odpływach z jezior Sunia i Bukwałd, natomiast największe zaobserwowano w roku 2004, odmiennie kształtowała się sytuacja w zlewni jeziora Ardung, w którym w ciągu całego okresu badawczego odnotowano względnie wyrównane wartości przepływów we wszystkich dopływach i odpływie z jeziora.

Porównując spływy z badanych zlewni, należy stwierdzić, że największą zawartością Ca^{2+} odznaczały się wody odpływające ze zlewni użytkowanych rolnie jeziora Bukwałd ($114,3\text{--}126,3 \text{ mg} \cdot \text{dm}^{-3}$), natomiast najniższe stwierdzono w wodach odpływających z obszaru podmokłego tego samego jeziora ($25,0 \text{ mg} \cdot \text{dm}^{-3}$).

Większe zawartości wapnia w wodach odpływających z obszarów rolniczych jest związane z intensywniejszym wymywaniem tego składnika z gleb uprawianych ornie okresowo pozbawionych okrywy roślinnej. Znaczne deniwelacje występujące w zlewniach jezior mogą się także przyczyniać do szybszego odpływu biogenów, zwiększając tym samym swoją zawartość w wodach dopływających do zbiornika.

Słowa kluczowe: jeziora, zlewnia, biogeny, wapń

Anna RABAJCZYK¹

INFLUENCE OF THE ROAD TRAFFIC ON QUALITY OF THE WATER OF SILNICA RIVER

WPLYW RUCHU KOMUNIKACYJNEGO NA JAKOŚĆ WÓD RZEKI SILNICY

Abstract: Silnica River is a small river cutting through the city of Kielce from the North to the South-West. It has its source in Masłowskie Range at a height of 360 m a.s.l. and it flows into Bobrza River. It is ranked among mountain rivers at a 6.4 ‰ gradient. Its river-bed has belonged to Kielecki Protected Landscape Area since 2006. Next to Szydłówek estate the artificial water body was build – Kielecki Bay. Beneath Kielecki Bay, Silnica River flows in regulated river-bed. Because of no separated storm water drainage, the rainwater washes away pollutants among others from industrial plants, houses, pavements, and streets into Silnica River. The aim of this study is to present results of the research on influence of the road traffic on physiochemical properties of the water of Silnica River. Points of the heaviest traffic volume in Kielce located at the river were analysed. The research program included analysis of pH and heavy metals: Pb, Cd and Ni. Atmospheric conditions were observed at the same time. The obtained results showed that depending on analysed point the pollution of the Silnica River water reached different levels. This is a result not only of external factors such as praximity of roads and the road traffic volume but also the processes occurring in water environment.

Keywords: Silnica River, road transport, land use, biogenic compounds, heavy metals

Human activity contributes to degradation of individual components of the environment. Apart from industry, public utilities and farming the highest and at the same time the most negative influence is caused by the road traffic that emits 15 thousands of chemical compounds to the environment [1]. Noxious substances being a mixture of many substances occur in different states of aggregation [2]. Substances emitted from motor vehicles are dispersed in the air, water and soil causing pollution of particular environmental compartments. Their influence depends not only on means of transport and road traffic volume but also on processes shaping pollutant spread in the environment. Additionally the transportation causes deformation of the lie of the land, disturbance of bedrock structure and devastation of plant and animal life.

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The highest amount of exhaust gases is emitted during idle run for example when warming up a car in the winter and when waiting before a crossroad, accelerating and braking [3]. However depending on type of fuel used, an amount of noxious components in exhaust gases from vehicles after burning of 1 kg of fuel is different (Table 1).

Table 1

Amount of noxious components in exhaust gases from vehicles after burning of 1 kg of gasoline and diesel oil [4]

Type of components	Amount of components [$\text{g} \cdot \text{kg}^{-1}$ fuel]	
	Petrol	Diesel oil
Carbon oxide (CO)	465.69	20.81
Hydrocarbons (HC)	23.28	4.16
Nitrogen oxides (NO_x)	15.83	18.01
Sulphur trioxide (SO_3)	1.86	7.80
Aldehyde	0.93	0.78
Carbon black	1.00	5.00
Lead (Pb)	0.50	—

In Poland a typical car travelling 10 thousand kilometres a year consumes approx. 14.5 thousand kilograms of fuel and emits 328 kg of carbon oxides, 110 kg of hydrocarbons, 20 kg of nitrogen and sulphur oxides and 5 kg of carbon black [3]. However one has to remember that the amount of chemical compounds in atmosphere depends both on the number of motor vehicles, a number of kilometres they travel and fuel type, and on size, construction and working conditions of the engine [3, 5]. A concentration of automobile exhausts is variable in time and at the same time proportional to the road traffic volume. That is why a minimum concentration of pollutants is observed in night hours while maximum concentrations are found during the highest road traffic volume [4].

The chemical compounds in atmosphere are subject to various processes, especially physical, chemical and photochemical ones, which cause changes of pollutant concentration because of forming new substances or pollutant transportation. Wind speed,

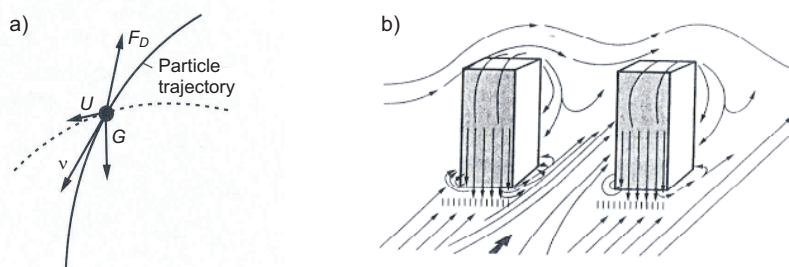


Fig. 1. Diagram: a) particle falling in the air, where U – wind speed, v – particle fall velocity, G – body force coming from gravitational acceleration, F_D – resisting forces of medium [5]; b) air flow above and around buildings [6]

particle fall velocity, body force coming from gravitational acceleration, resisting forces of medium should be taken into consideration (Fig. 1a) as well as medium viscosity in which a given particle is moving, diameter of falling particle, type, motion and thermodynamical parameters of medium and a presence of various obstacles during analysing a trajectory of particle falling in the air (Fig. 1b). Both meteorological conditions and development and use of the land near roads have tremendous influence on migration of pollutants.

Apart from land use, closeness of pollution source and meteorological conditions, the following hydrological factors significantly influence quality of water of surface streams:

- water depth, cross-section area, discharge and velocity distribution in a river,
- slope of energy drop line and a line of free surface of water and longitudinal profile of a river,
- formed free surface under constant atmospheric pressure,
- external body forces coming from terrestrial field of gravity, resisting force of flow caused by viscosity and hydrostatic pressure forces,
- type of flow – laminar flow, turbulent flow, transition form [5, 7].

An influence of air mass causes both positive and negative effects for the environment. Airing, accelerating the evaporation and preventing cool air from accumulation in sheltered and concave places influences positively the nature because it prevents dangerous substances to be deposited in one place. On the other hand a contamination of water and soil at closer or more distant locations to a source of emission of exhaust gases is an effect of negative wind influence [5, 8].

Study area

Silnica River flowing into Kielecki Bay and cutting through the centre of Kielce from the North to the South thus having profound importance for shaping hydrological conditions in the most urbanised part of the city was selected for the research [9]. It has its source in Masłowskie Range at a height of 360 m a.s.l. and it is the left-bank tributary of Bobrza River. The watercourse has 18.9 km in length. Silnica is ranked among mountain rivers at a 6.4 ‰ gradient. A catchment area is 49.9 km² and 44 % of this area is urbanized. A river-bed of catchment has belonged to Kielecki Protected Landscape Area since the second half of 2006 [10, 11].

A section of Silnica River including 4 crossroads of the city of Kielce has been selected for the research (Fig. 2).

The first measurement profile was located at Jesionowa St. that is a direction towards Łódź. It is a section of 950 m in length being at the same time a section of the state road No. 74 [12] cutting through the recreation ground located at Kielce Bay and Silnica River. Single- and multi-family building and an outbuilding is situated along the street.

Whereas IX Wieków Kielc St. with 2nd measurement point is located in the city centre. This street is a part of regional road No. 702, it is 1.1 km long and functions as the North section of the city centre ring road. Cross-section of this road is very expanded and comprises two roadways with two or three lanes each, and the number of

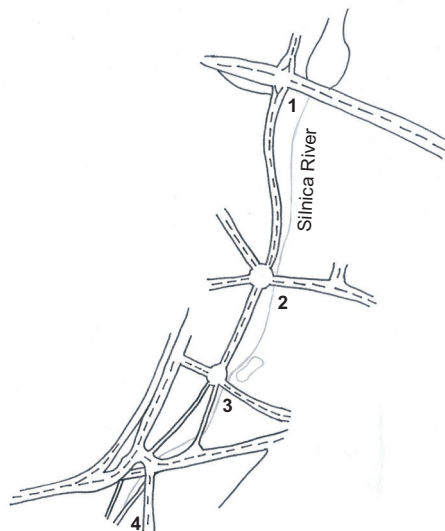


Fig. 2. Places of sample collection: 1 – Jesionowa Street, 2 – IX wieków Kielc Street, 3 – Oгородowa Street, 4 – Krakowska Street

lanes increases at exits of crossroads [12]. An outbuilding and multi-family building is situated at various distances to the street.

Oгородowa St. (3rd measurement point) is a section of DW regional road No. 760 on the way: Kielce – Piekoszów – Łopuszno, and at the same time it links the city centre with the Western residential area of the city [13]. The street goes through corridor-like way along which there are high trees separating the street from the public park on the one side, while there are the high outbuilding and single- and multi-family building on the other side of the street.

Krakowska St. is a section of DW regional road No. 762 on the way: Kielce – Małogoszcz towards Kraków [13]. 4th profile of sampling was located next to split level junction. On the East and South-eastern side of the street in the close neighbourhood there are recreation grounds (Kadzielnia Reserve) and single-family building, while on the North side there is a housing estate with the high multi-family building.

Experimental part

The research was carried out every first Monday each month starting from September to November 2007. It comprised an analysis of traffic volume in selected streets, and a quality of water and bottom deposits of Silnica River flowing close to selected measurement points. In defined hours, a number of motor vehicles moving on selected sections of the streets was counted taking into consideration a division into cars, trucks and buses. Atmospheric conditions with regard to such components as precipitation, insolation and wind speed were observed simultaneously.

The chemical analysis included both tests of water and bottom deposit samples. A solid material was collected from a layer located at a depth of 0–10 cm. Ground samples of deposits were dried to reach constant mass at 105 °C, and then it was triturated in agate mortar and sieved to obtain a fraction of grains of a diameter $\leq 100 \mu\text{m}$. 3 samples of 2 g in mass were collected for mineralization from a representative and homogeneous batch of the material and underwent mineralization supported by microwave radiation and concentrated trioxonitric(V) acid. The AAS method was used to determine heavy metals (Pb, Cd, Ni) in water samples and extraction solutions obtained from microwave mineralization of bottom deposits. A correctness of determination was confirmed by standard addition method with an accuracy of $\pm 4\%$. Statistica 6.0 computer application was used to compile the results.

Results and discussion

The motor transport is one of the factors that influence air quality in Kielce. The transport tremendously contributes to total amount of pollutants emitted to the atmosphere including dust containing heavy metals like Pb, Cd and Ni. In the city centre in rush hours during the highest traffic volume and the slowest traffic, huge emission of pollutants is reported what is linked to frequent starts and stops of vehicles [14].

The analysis of traffic volume was carried out in selected measurement points, and on the basis of tests of water and bottom deposit samples a cleanliness of Silnica River was evaluated. The selection of measurement points was dictated by the importance of particular streets for the city of Kielce and resulting increased road traffic. Additionally the closeness of watercourse was of significant importance in order to define an influence of the road traffic on quality of water of Silnica River.

On the basis of the research it was observed that traffic volume was the highest at the measurement point No. 1 and it was the lowest in the measurement point No. 4 while in measurement points No. 2 and 3 the number of all vehicles was comparable (Table 2). A quantitative distribution of cars and buses moving on the roads during the research coincides with total traffic volume in these days. However it was different in the case of trucks which volume is the highest in the measurement profile No. 4 and the lowest in the measurement point No. 2. It should be added that in the measurement point No. 3 the trucks were not reported at all.

Substances emitted to the atmosphere are spread by the wind and get mixed with a surrounding air. It leads to standardization of concentration of these compounds in the layer of turbulent atmosphere [5]. A level of dilution of a dangerous substance depends on development and use of the land, and on meteorological conditions in observed time.

Along with Silnica River course that is from the point No.1 to the point No. 4, a general fall of the ground is visible within the valley. Topographic features of the city show properties of depression what influences natural airing system of the city. A low wind speed or the weather calm favours formation of local concentrations of pollutants, whereas higher speed of the wind contributes to dispersion and decrease of local concentrations. However such situation takes place if there are possibilities for the

so-called airing of the city that is if there are corridors without building perpendicular to prevailing directions of the wind [14].

Table 2

Traffic volume (between the hours of 7.00 and 19.00) in the analysed streets of the city of Kielce during measurements performed from September to November 2007

Type of transport	Month	Streets			
		Jesionowa	IX wicków Kielc	Ogrodowa	Krakowska
Cars	IX	34232	27360	29039	23740
	X	30440	31740	28440	22816
	XI	33232	29976	31920	27000
Trucks	IX	1828	1038	0	1959
	X	1744	1156	0	1748
	XI	1382	1156	0	1864
Buses	IX	1226	626	647	528
	X	1248	664	607	588
	XI	1226	626	637	573
Total		106558	94342	91290	80812

It was observed that Western and South-western winds dominated in the analysed stands. The best conditions for pollutant spread were found in Krakowska St. where the area is open towards the North. However as far as Ogrodowa St. is concerned, because of the street location in a “tunnel” formed by trees and public park on the one side, and high building on the other side, pollutant spread is very limited. Such conditions cause that emitted substances are deposited in the area of their emission source.

The results of tests of water samples and bottom deposits of Silnica River (Table 3; Fig. 3) confirm the complexity of factors contributing to the quality of water of this watercourse. Chemical potential of hydrogen ions (pH) in water of the river in general amounts from 6.5 to 8.5 what indicates low aggressiveness. It should be also emphasized that high values of pH do not favour washing out the metals from the bottom deposits.

Average values of this factor in individual measurement points in Silnica river-bed ranged from 5.9 to 8.0, and extreme values amounted to 5.8 and 8.0. These values decreased along the course of the river that is from the measurement point No. 1 towards the measurement point No. 4. The lowest pH was reported in Krakowska St. profile located next to road interchange, whereas the highest pH was observed in the profile placed below the water basin – Jesionowa St. profile.

Based on the results it can be noted that the content of heavy metals is diverse both in water samples and in bottom deposits collected in the individual measurement points of tested river. An average lead concentration in water samples decreases along with the river course from 0.143 to 0.103 ppm. As far as cadmium is concerned, the opposite situation is observed. The content of this metal in the water increases from 0.004 ppm at the measurement point No. 1 to 0.011 ppm at the measurement point No. 3 whereas it decreases to 0.004 at the measurement point No. 4. The results of analyses for nickel

indicate a lower amount of this metal in water samples collected from measuring points No. 2 and 4 compared with samples collected from the points No. 1 and 3.

Table 3

The results of tests of water samples and bottom deposits of Silnica River collected from 4 measurement points from September to November 2007

Measurement points	Month	Analytes						
		Water				Sediment		
		pH	Pb [ppm]	Cd [ppm]	Ni [ppm]	Pb [ppm]	Cd [ppm]	Ni [ppm]
1	IX	8.1	0.049	0.001	0.040	155.1	18.2	15.10
	X	7.8	0.050	0.002	0.045	108.0	14.5	11.26
	XI	8.0	0.044	0.001	0.029	100.1	9.25	17.31
2	IX	6.8	0.036	0.003	0.033	122.1	34.1	31.22
	X	7.1	0.045	0.003	0.042	148.9	37.2	40.01
	XI	6.9	0.042	0.002	0.012	117.2	32.0	38.73
3	IX	6.8	0.030	0.002	0.031	102.2	21.67	38.90
	X	6.3	0.038	0.005	0.044	133.1	24.52	29.07
	XI	6.5	0.049	0.004	0.034	110.0	22.84	28.08
4	IX	5.9	0.035	0.001	0.029	87.22	9.22	11.02
	X	6.1	0.027	0.002	0.020	77.24	11.41	10.29
	XI	5.8	0.041	0.001	0.037	78.13	8.53	10.83
RSD [%]			19	22	16	18	19	21
RS			0.011	0.0005	0.014	21.34	3.92	5.23
Background			—			15	< 0.5	5

Together with samples of the water of Silnica River, the bottom deposits were also collected and analysed for Pb, Cd and Ni after mineralization supported by microwave radiation. Based on the results, at first the increase and then the decrease of the content of the metals in tested material can be found along with the watercourse. The highest

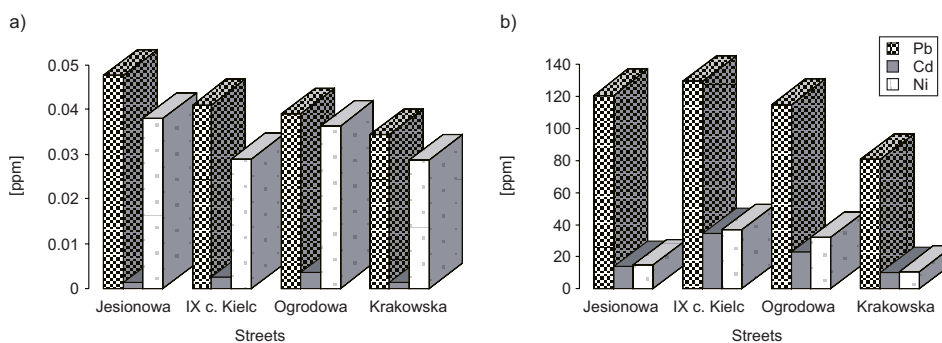


Fig. 3. Average concentration of heavy metals in water (a) and bottom deposits (b) of Silnica River in individual measurement points

average amounts of tested metals were observed at the measurement point No. 2 whereas the lowest ones at the point No. 4.

The concentrations of metals obtained in samples of bottom deposits and water indicate transportation of the material and accumulation of heavy metals at the measurement point No. 2, despite the highest traffic volume is observed in Jesionowa St. (point No. 1). After penetration to the water of Silnica River, heavy metals precipitate and then depose at the measuring point No. 1 because of high pH of water environment. However a fall of water from sluice and land slope causes that suspended material and eroded material are carried by the river from the deposition place for longer distances and that is why metals have accumulated in the bottom deposit at point No. 2.

Additionally a land use in individual measurement points is an important factor. As far as Jesionowa St. is concerned, the direction of deposition is parallel to the water course, while IX Wieków Kielc is characterized by falling the contamination in the place of generation. At the measurement point No. 3 in Ogradowa St. where the traffic volume is less at points No. 1 and 2, motion of the air-mass resulting from land use causes a migration of pollutants in direction perpendicular to the water course. It determines the amount of deposited substances in the river. The best conditions for dispersion of heavy metals emitted by transport were found in Krakowska St. what was confirmed by the results of water samples and bottom deposits collected from Silnica River.

Recapitulation

The migration of pollutants in the environment is a complex process what results from factors that contribute to the motion of particles in individual media. Compounds emitted to the air are subject to both physical and biological processes that cause deposition, transfer for long distances and transformation of these compounds.

Pollutants begin their travel in the watercourse during the exchange of substances between the air and the water. Most of heavy metals are fixed and transported in rivers with the suspension what leads to formation of bottom deposits in surface water characterized by fast and slower flow. One should remember that the material accumulated on the bottom of river-bed may be a source of secondary pollution of the ecosystem due to changing chemical properties and despite no inflow of pollutants.

Pollutants brought into water ecosystems undergo various processes including transportation and sedimentation causing their migration for diverse distances. Some part of compounds of heavy metals undergo more or less permanent deposition in the bottom deposits. Depending on properties of pollutants themselves as well as water environment properties and hydrological factors such as speed and characteristic of the flow or river-bed morphology, these compounds get decomposed. During Evaluation of the rates of heavy metal pollution of water basins, their content in bottom deposits in particular in the finest clayey layer is determined. They can be transported with clayey layers for long distances and join even sea sediments [15]. This aspect of bottom deposits makes them especially useful material for research on determining major

sources of pollution because they work as absorption column and provide clear picture of phenomena occurring in water above them [16].

Silnica River cutting through the centre of Kielce from the North to the South is cut by routes of high traffic volume. However the building found in tested area comprising 4 measurement points is very diverse determining the quality of water ecosystem. The concentration of heavy metals in the water samples and in the bottom deposits is a result not only of the close location of routes and the amount of moving vehicles but also of land use and meteorological conditions that determine the process of deposition or migration for long distances.

Based on performed analyses it was observed that the bus traffic volume and contamination of Silnica River by heavy metals was higher in IX Wieków Kielc St. than that of Jesionowa St. This is because apart from meteorological conditions, the building had considerable influence that limited the migration of pollutants and influenced deposition in the place of generation. However in Jesionowa St. despite higher car and truck traffic volume, the water of Silnica River was less contaminated by heavy metals. Open space typical for that section of Jesionowa St. contributed to that situation. Pollutants generated during road traffic migrate for long distances due to the wind what causes their less concentration in the place of formation.

The performed research indicates that further analysis is necessary including monitoring of the road traffic volume and physiochemical properties of the water and bottom deposits of Silnica River. It will allow to track trends of changes in the environment.

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WPLYW RUCHU KOMUNIKACYJNEGO NA JAKOŚĆ WÓD RZEKI SILNICY

Samodzielny Zakład Ochrony i Kształtowania Środowiska,
Uniwersytet Humanistyczno-Przyrodniczy Jana Kochanowskiego w Kielcach

Abstrakt: Silnica jest niewielką rzeką przecinającą miasto Kielce z północy na południowy zachód. Wypływa z Pasma Masłowskiego na wysokości 360 m n.p.m. i uchodzi do Bobrzy. Ma charakter rzeki górskiej ze spadkiem wynoszącym 6,4 ‰. Koryto rzeki od połowy 2006 r. wchodzi w skład Kieleckiego Obszaru Chronionego Krajobrazu. Na wysokości osiedla Szydłówek wybudowany został sztuczny zbiornik – Zalew Kielecki. Poniżej zalewu Silnica płynie w sztucznie uregulowanym korycie. Na skutek braku osobnej kanalizacji woda deszczowa spłukuje i wprowadza do Silnicy zanieczyszczenia m.in. z terenów placów zakładowych, posesji, chodników, ulic. Celem pracy jest przedstawienie wyników badań nad wpływem ruchu komunikacyjnego i zagospodarowania terenu na właściwości fizykochemiczne wód rzeki Silnicy. Przeanalizowane zostały punkty o największym natężeniu ruchu samochodowego dla miasta Kielce. Program badawczy obejmował analizę pH oraz metali ciężkich Pb, Cd i Ni. Równocześnie prowadzono obserwację warunków atmosferycznych. Wody rzeki Silnicy, w zależności od analizowanego punktu, charakteryzowały się różnym stopniem zanieczyszczenia, co jest efektem wpływu zarówno zagospodarowania terenu, jak i panujących warunków atmosferycznych.

Słowa kluczowe: Silnica, ruch komunikacyjny, zagospodarowanie terenu, związki biogenne, metale ciężkie

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**HEAVY METAL DISTRIBUTION
IN THE DIFFERENT PARTS OF MOLLUSKS
BY USING MULTIVARIATE ANALYSIS**

**OCENA AKUMULACJI METALI CIĘŻKICH
W RÓŻNYCH CZĘŚCIACH MIĘCZAKÓW
Z WYKORZYSTANIEM ANALIZY WIELOCZYNNIKOWEJ**

Abstract: The mollusk samples were obtained from several locations along the Black Sea coast (gulf of Varna and Gulf of Burgas, Bulgaria). The samples were dissected into five different soft tissues. The soft tissues and the shell were then analysed for heavy metals. It was found that the highest concentrations of Cu (112–178 µg/g dm) and Zn (117–161 µg/g dm) were found in the tentacle; the highest concentrations of Cd (4.41–5.37 µg/g dm), Pb (53.2–63.8 µg/g dm) and Ni (26.1–27.9 µg/g dm) were found in the shell. On the other hand, the highest Fe concentrations (910–2921 µg/g dm) were found in the operculum. The cluster analysis revealed that the accumulation of heavy metals were clustered into a few groups, where the metals found in the shell were significantly different from the other soft tissues. Results from the cluster analysis were further complimented by the correlation analysis and multiple stepwise linear regression which revealed that the accumulation by the different parts were interrelated with one another. It was also found that the soft tissue was the most influential part in accumulation of heavy metal studied. Thus, it indicates the ability of the mollusks to accumulate heavy metal, hence fulfilling the criteria as a good biomonitor.

Keywords: mollusks, heavy metal, multivariate analysis

Currently, the determination of heavy metal concentrations in whole individuals presents little interest, since the main metal accumulating organs such as gills, digestive gland and kidney are but a small part of a total soft tissue [1]. Besides, the spawning season of the mollusks and environmental factors may contribute to the wide variability of heavy metal concentrations in the total soft tissues, thus, the above points strongly

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evidenced the disadvantages of the use of the total tissue in monitoring of metal bioavailability in marine environment.

The present study focuses on the different parts of mollusks as a biomonitor of heavy metal contamination in coastal waters. They are found abundantly in the coastal areas and their ability to accumulate metals fulfilled the criteria as biomonitors of heavy metal contamination. In the literature, their reliability as biomonitors of heavy metal contamination had been studied by many researchers [2–5]. The literature above supported the application of mollusks as biomonitors of heavy metal pollution in the marine environment.

On the other hand, correlation and cluster analysis were applied in this study to observe the differences of metal distribution in the different tissues of the mollusks. Correlation and cluster analysis (CA) are the most usual multivariate statistical methods used in environmental studies [6–12] especially in the studies of heavy metals in sediment. A few studies reported on the use of cluster analysis in the determination of heavy metals in the marine mollusks were found in the literature [13–16].

The use of multivariate statistical techniques, such as cluster analysis (CA) is useful in the interpretation of complex data matrices to better understand the heavy metals and ecological status of the systems studied, allowing the identification of possible factors/sources that might influence heavy metals and can offer a valuable tool for reliable management as well as rapid solution to pollution problems [17–21]. Besides, the use of multivariate analysis, statistically, could assist in determining the potential biomonitor accurately, by referring to cluster groups of their different parts. Moreover, multivariate methods are recommended for the use in monitoring studies since they can help reduce the costs of carrying out further environmental surveys [22–23].

Therefore, present study aims to determine the distribution of heavy metal in the different parts of mollusks and to determine the possible significant relationships between the concentrations of the different parts by using cluster and multiple stepwise linear regression analyses.

Experimental

A sampling was conducted in the gulfs of Burgas and Varna. The identification of the species were followed the descriptions by Lim et al [24]. For the analysis, 30–40 individual mollusks with almost similar sized were randomly taken from the main sample and thawed at room temperature (26–29 °C) on a clean tissue paper. The soft tissues were then separated from the shell by crunching (using a clean pestle) the shell carefully. Due to the fragile characteristic of the shell, a mild force was sufficient to break the shell (strong force might destroy the internal organs of the snail). The soft tissues were then dissected and pooled into six different components namely ceacum, foot, muscle, operculum, remainder and tentacle besides the shell. The soft tissues and the shell were dried for 72 hours at 60 °C in an oven to constant dry weights. The whole analytical procedure was performed at Institute of Oceanology, Bulgarian Academy of Sciences.

About 0.5 gram of sample tissues were digested in 10 cm³ of concentrated nitric(V) acid (AnalaR Grade; 69 %). They were placed in a hot block digester first at low temperature (40 °C) for 1 hour and were then fully digested at high temperature (140 °C) for at least 3 hours. The digested samples were then diluted to a volume of 40 cm³ with double distilled water (DDW). The sample was then filtered through Whatman No. 1 filter paper (Dia: 110 mm; Schleicher & Schuell, Whatman International Ltd Maidstone England) and they were determined for Cd, Cu, Fe, Ni, Pb and Zn by using an air-acetylene flame Atomic Absorption Spectrophotometer (AAS) Perkin Elmer Model AAnalyst 800. The samples were analyzed in three replicates. The data were presented in µg/g dry mass (dm) basis. Multilevel calibration standards were analysed to generate calibration curves against which sample concentrations were calculated. Standard solutions were prepared from 1000 mg/dm³ stock solutions of each metal (Merck Titrisol).

All the glassware and plastic materials used were acid-washed in 10 % acid solution in order to minimize external contamination. Quality control samples made from standard solutions of Cu, Cd, Zn, Pb, Ni and Fe were analyzed once in every ten samples to check for the metal recoveries. The analytical procedures for the snail samples were checked with the Certified Reference Material (CRM) for dogfish liver (DOLT-3, National Research Council Canada) and the recoveries of all metal were satisfactory (Table 1).

Table 1

Analytical results for the Certified Reference Material (CRM) and its certified values for each metal [µg/g dry mass]

Metal	Sample	CRM values	Measured values	Percentage of recovery
Cd	DOLT-3 Dogfish-liver	19.4 ± 0.600	20.5 ± 0.439	106 ± 2.26
Cu	DOLT-3 Dogfish-liver	31.2 ± 1.00	26.5 ± 2.58	85.0 ± 8.28
Fe	DOLT-3 Dogfish-liver	1484 ± 57.0	1070	72.1
Ni	DOLT-3 Dogfish-liver	2.72 ± 0.350	2.77 ± 0.741	102 ± 27.2
Zn	DOLT-3 Dogfish-liver	86.6 ± 2.40	80.9 ± 1.94	93.4 ± 2.24

NA: Pb value is not available.

For the statistical analysis, the distributions of heavy metals in the different parts were determined by using cluster analysis. Multiple stepwise linear regression analysis was used to determine the influence of heavy metal in the different parts toward the allometric parameters. All data were log₁₀ (X + 1) transformed prior to the statistical analysis. STATISTICA 7 was used to conduct the cluster analysis, correlation and multiple stepwise linear regression analyses.

Results and discussions

Heavy metal concentrations in the different parts of the mollusks collected from the three sampling sites (V1 and V2 from Varna Gulf and B1 from Burgas Gulf) are shown in Table 2. In general, it was found that the tentacles were highly accumulative

Table 2

Heavy metal concentrations [$\mu\text{g/g dm}$, mean \pm SE] of (Cu, Cd, Zn, Pb, Ni and Fe) in the different soft tissues of mollusks

	Site	Cu	Cd	Zn	Pb	Ni	Fe
Caecum	V1	95.3 \pm 15.8	1.79 \pm 0.185	113 \pm 18.3	10.0 \pm 0.193	9.44 \pm 0.207	782 \pm 86.2
	V2	94.7 \pm 2.61	1.43 \pm 0.086	113 \pm 10.6	7.94 \pm 0.433	9.26 \pm 0.530	543 \pm 47.9
	B1	51.1 \pm 1.77	3.45 \pm 0.169	318 \pm 5.67	16.2 \pm 1.00	7.54 \pm 0.350	661 \pm 71.9
Foot	V1	118 \pm 4.21	1.48 \pm 0.071	74.4 \pm 8.77	5.94 \pm 0.234	2.80 \pm 0.192	177 \pm 15.9
	V2	113 \pm 11.3	0.984 \pm 0.096	97.7 \pm 2.67	5.10 \pm 0.606	3.58 \pm 0.269	121 \pm 4.07
	B1	124 \pm 9.36	1.22 \pm 0.115	113 \pm 0.183	14.0 \pm 0.553	5.79 \pm 0.615	255 \pm 3.47
Muscle	V1	64.8 \pm 7.72	1.16 \pm 0.111	82.4 \pm 6.21	5.88 \pm 0.434	0.660 \pm 0.086	156 \pm 12.1
	V2	83.4 \pm 3.79	0.901 \pm 0.141	92.4 \pm 3.30	4.12 \pm 0.178	3.33 \pm 0.539	124 \pm 10.0
	B1	77.3 \pm 0.526	1.39 \pm 0.075	79.0 \pm 1.57	13.7 \pm 0.548	5.08 \pm 0.137	254 \pm 5.11
Operculum	V1	51.7 \pm 0.000	2.78 \pm 0.000	43.9 \pm 0.000	9.45 \pm 0.000	0.222 \pm 0.000	2921 \pm 0.000
	V2	44.7 \pm 0.000	2.13 \pm 0.000	45.0 \pm 0.000	7.50 \pm 0.000	3.47 \pm 0.000	910 \pm 0.000
	B1	59.1 \pm 0.000	2.46 \pm 0.000	38.9 \pm 0.000	43.0 \pm 0.000	7.22 \pm 0.000	638 \pm 0.000
Remainder	V1	136 \pm 13.4	1.54 \pm 0.202	65.0 \pm 5.06	10.7 \pm 1.86	6.54 \pm 0.848	850 \pm 60.8
	V2	143 \pm 3.25	1.35 \pm 0.158	77.5 \pm 1.89	7.62 \pm 0.550	6.37 \pm 0.253	406 \pm 29.6
	B1	133 \pm 2.51	1.17 \pm 0.144	81.1 \pm 5.29	17.2 \pm 1.71	6.22 \pm 0.052	1137 \pm 123
Shell	V1	11.9 \pm 0.794	5.12 \pm 0.047	5.91 \pm 0.255	56.2 \pm 1.43	26.1 \pm 0.909	240 \pm 48.9
	V2	11.1 \pm 0.750	5.37 \pm 0.205	7.04 \pm 0.647	53.2 \pm 0.483	27.9 \pm 0.295	66.3 \pm 4.95
	B1	8.65 \pm 0.503	4.41 \pm 0.118	6.53 \pm 1.39	63.8 \pm 0.318	24.4 \pm 0.143	52.0 \pm 2.35
Tentacle	V1	178 \pm 0.000	0.962 \pm 0.000	117 \pm 0.000	5.70 \pm 0.000	20.1 \pm 0.000	240 \pm 0.000
	V2	173 \pm 0.000	1.36 \pm 0.000	130 \pm 0.000	4.54 \pm 0.000	16.2 \pm 0.000	177 \pm 0.000
	B1	112 \pm 0.000	2.32 \pm 0.000	161 \pm 0.000	34.2 \pm 0.000	27.9 \pm 0.000	283 \pm 0.000

of Cu and Zn from all the sites, where they ranged from 112–178 $\mu\text{g/g dm}$ and 117–161 $\mu\text{g/g dm}$, respectively. Meanwhile, the operculum were mostly accumulative of Fe, ranging between 638–2921 $\mu\text{g/g dm}$. On the other hand, the shell was highly accumulative of Cd (4.41–5.37 $\mu\text{g/g dm}$), Pb (53.2–63.8 $\mu\text{g/g dm}$) and Ni (24.4–27.9 $\mu\text{g/g dm}$).

Distribution of heavy metals in the different parts of the mollusks are better explained by cluster analysis as shown in Figure 1. Generally, the accumulation of Cu, Cd, Zn, Pb and Fe by the shell were significantly different from the other tissues as they were solely clustered into one group. This could be due to the fact that some trace metals are incorporated into the shells through substitution of the calcium ion in the crystalline phase of the shell or are associated with the organic matrix of the shell

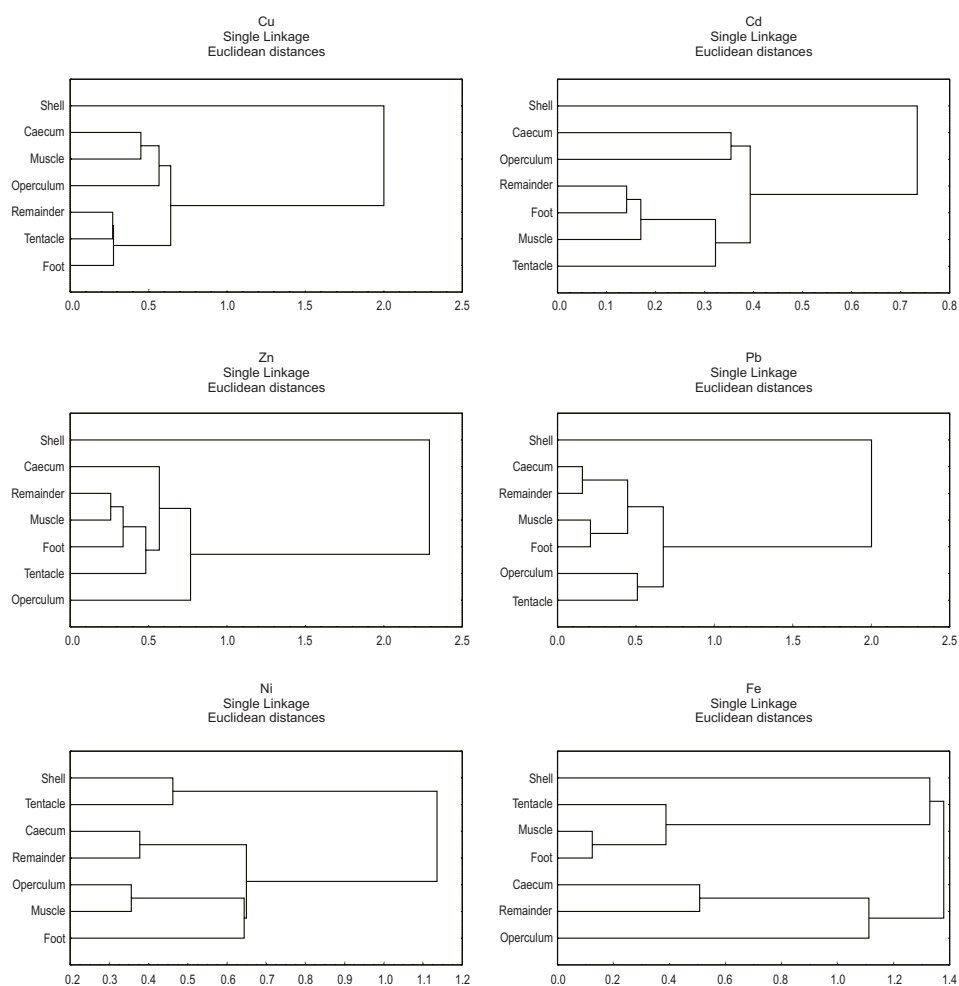


Fig. 1. Cluster analysis on the distribution of heavy metals (Cu, Cd, Zn, Pb, Ni and Fe) in the different parts of mollusks

instead of induction of metallothionein as being found in the soft tissues. However, for the accumulation of Ni, the shell and tentacle were significantly different from the other soft tissues. Besides, most of the soft tissues were found clustered into two distinct groups (by ignoring the shell). For the accumulation of Cu, the caecum, muscle and operculum were clustered as one group while another group consisted of the remainder, tentacle and foot. As for Cd, the first group consisted of the caecum and operculum while the second group consisted of the remainder, foot, muscle and tentacle. The accumulation of Zn by the operculum was significantly different from the remainder as it was solely clustered, while the caecum, remainder, muscle, foot and tentacle were clustered as one group.

For Pb, the caecum, remainder, muscle and foot were clustered into one group while the operculum and tentacle were clustered into another group. Meanwhile for Ni, the first group of the soft tissues consisted of the caecum and remainder and the second group consisted of the operculum, muscle and foot. Two distinct cluster groups were also observed in the accumulation of Fe by the soft tissues, where the first group consisted of the tentacle, muscle and foot while the second group consisted of the caecum, remainder and operculum. Generally, the cluster analyses indicated the differences of heavy metal accumulation by the different parts, in other words, each tissue accumulate different concentrations of metals.

The relationships between the different parts and the total soft tissues are explained in the multiple stepwise linear regression analysis (Table 3). The caecum was found to be the influential tissues in the accumulation of heavy metals studied besides the remainder and operculum.

Table 3

Multiple linear stepwise regression between the total tissues of mollusks and their different soft tissues

Metal	Multiple stepwise linear regression
Cu	Total tissue = $-9.861 - 0.033$ (Caecum) + 2.805 (Remainder) + 3.346 (Operculum)
Cd	Total tissue = $-0.053 + 0.634$ (Caecum)
Zn	Total tissue = $-1.479 + 1.492$ (Caecum)
Pb	Total tissue = no significant variables were selected
Ni	Total tissue = $-0.898 - 0.050$ (Caecum) + 1.322 (Remainder) + 0.405 (Operculum)
Fe	Total tissue = $-1.502 + 1.189$ (Caecum) + 1.264 (Remainder) - 0.917 (Operculum)

Conclusions

From the present study, it was found the ability of mollusks to accumulate and regulate heavy metal concentrations in their body as revealed by the multivariate analysis. From the correlation and cluster analyses, it was found that the accumulation of metal by the shell was significantly different from the remaining soft tissues. Multiple stepwise linear regressions also revealed that the caecum was the most influential organ in the accumulation of heavy metals by mollusks.

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OCENA AKUMULACJI METALI CIĘŻKICH W RÓŻNYCH CZĘŚCIACH MIĘCZAKÓW Z WYKORZYSTANIEM ANALIZY WIELOCZYNNIKOWEJ

Abstrakt: Próbkę mięczaków były pobierane w kilku miejscach wzdłuż wybrzeża Morza Czarnego (Zatoka Warna i Zatoka Burgas, Bułgaria). Z próbek wyodrębniono pięć różnych tkanek miękkich. W tkankach miękkich i skorupkach oznaczono metale ciężkie. Stwierdzono, największe stężenia Cu (112–178 µg/g s.m.) i Zn (117–161 µg/g s.m.) w mackach; a największe stężenie Cd (4.41–5.37 µg/g s.m.), Pb (53.2–63.8 µg/g s.m.) i Ni (26.1–27.9 µg/g s.m.) stwierdzono w skorupie. Z drugiej strony, największe stężenia Fe (910–2921 µg/g s.m.) stwierdzono w pokrywie skrzelowej. Analiza klastrów ujawniła, że akumulowane metale ciężkie były pogrupowane w kilka skupień, w których metale oznaczone w skorupkach były inne od tych zidentyfikowanych w tkankach miękkich. Wyniki analizy klastrów były weryfikowane przez analizę korelacji i regresji liniowej wielostopniowej, które wykazały, że akumulacja w różnych częściach była wzajemnie ze sobą powiązana. Stwierdzono również, że w tkankach miękkich kumuluje się najwięcej metali ciężkich. W związku z tym wskazano na zdolność mięczaków do kumulowania metali ciężkich, a tym samym stwierdzono, że spełniają one kryteria charakteryzujące dobre biomonitoring.

Słowa kluczowe: mięczaki, metal ciężki, analiza wieloczynnikowa

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CHRONOPOTENTIOMETRIC AND CHRONOAMPEROMETRIC ELECTROCOAGULATION OF WASTEWATER IN A STATIC SYSTEM

STATYCZNA ELEKTROKOAGULACJA ŚCIEKÓW MODELOWYCH

Abstract: This study presents the results of electrochemical treatment of model wastewater. It compares the parameters and the results of wastewater electrolysis performed by chronopotentiometric electrocoagulation (CHRP) at constant current intensity ($I = \text{const}$) and chronoamperometric electrocoagulation (CHRA) at constant voltage ($U = \text{const}$). Electrolysis was carried out in a static system with the use of an electrolyzer with aluminum electrodes. A six-electrode electrolyzer (three cathodes and three anodes) was applied. The chemical oxygen demand (COD), turbidity, color intensity, suspended solids and total phosphorus concentration of the solution were determined after electrocoagulation and sludge sedimentation.

Keywords: electrocoagulation, chronopotentiometry, chronoamperometry, static system, model wastewater

Waste treatment is one of the numerous environmental protection measures implemented to preserve the purity of surface and underground water resources. The main objective of waste treatment practices should be to modify the composition and properties of wastewater to ensure that when evacuated, it does not pose a threat to life forms residing in receiving water bodies or to the continued use of wastewater receivers [1, 2].

More stringent water protection requirements stimulate research efforts to improve the effectiveness of industrial and municipal wastewater treatment methods [3]. From among the available physical and chemical treatment methods, special emphasis should be placed on coagulation, electroflotation and electrocoagulation [4, 5]. In theory and practice, electrochemical coagulation could pose a specific alternative to wastewater treatment by coagulation. The reported attempts at electrolytic treatment of textile [6, 7], dye [8], pulp-and-paper wastewater [9], as well as the use of electrocoagulation in

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theoretical models [10, 11] indicate that this method could offer a viable alternative to chemical coagulation [12, 13].

This study presents the results of chronoamperometric and chronopotentiometric [14, 15] electrocoagulation with the use of aluminum electrodes as a method of model wastewater treatment [16].

Materials and methods

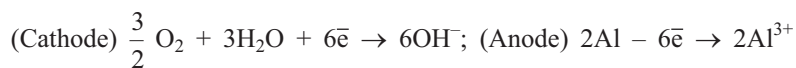
An analysis of model wastewater, with composition similar to that of dairy plant effluents, was carried out under laboratory conditions. Model wastewater was prepared for the experiment in accordance with the procedure described in previous chronopotentiometric and chronoamperometric studies [15, 16]. Electrochemical coagulation was performed in a static system with the use of an electrolyzer comprising six aluminum electrodes. To avoid excessive polarization of electrodes, the direction of current was changed every 256 s, and an environment supporting the self-cleaning of electrodes was established.

The chronopotentiometric electrolysis of wastewater (CHRP) was conducted at current intensity of 1.0, 0.5, 0.3, 0.1, 0.05, 0.03 and 0.01 A, respectively. Thousands of intensity readouts were registered each time, and the calculated average was applied in an equivalent chronoamperometric process (CHRA) at $U = \text{const}$. The treatment process was completed in 512, 1024 and 1536 s. The pH of wastewater was adjusted to 5.5–6.0 with the application of 2 M HCl. After 0.5 h of sedimentation, samples were collected from the above-sludge layer for the determination of wastewater parameters. Chemical oxygen demand (COD), total phosphorus concentrations [17], turbidity and suspended solids were determined by standard spectrophotometry with the use of a HACH DR 2000 spectrophotometer [1, 18], pH and temperature were measured with a HANNA HI 9025 pH-meter.

Results and discussion

As anticipated, the initial measurements of the relationship between pH, the time of electrocoagulation and the applied method (CHRP and CHRA) showed that the longer the electrocoagulation time, the higher the pH of treated wastewater. It was found that the pH of wastewater electrocoagulated at the highest current intensity (for CHRP) or voltage (for CHRA) reached up to > 11 regardless of electrolysis time.

The following diagram was proposed for the processes taking place in the solution during wastewater treatment by electrocoagulation with the use of aluminum electrodes:



where $x < 3$.

The above mechanism implies that the system's pH increases rapidly when Al^{3+} ions are involved in the process of pollutant coagulation and flocculation, as only some of the formed OH^- ions pass to the sludge. At the completion of this stage, successive Al^{3+} ions formed on the anode effectively capture OH^- ions and precipitate them in the form of sparingly soluble hydroxide sediment $\text{Al}(\text{OH})_3\downarrow$. At this point, the increase in pH is inhibited, and in addition to electrolysis parameters, ie current density in electrodes, current intensity (CHRP), current voltage (CHRA) and process time, the final pH of treated wastewater is determined by the possible sorption of OH^- ions on sludge flocs. To ensure optimal treatment results, pH was continuously adjusted in the wastewater solution with the use of 2 M HCl.

The results of wastewater treatment by CHRP and CHRA electrocoagulation are presented in graphic form below. Figures 1a and 1b show a decrease in pollution load that affects the color intensity of wastewater.

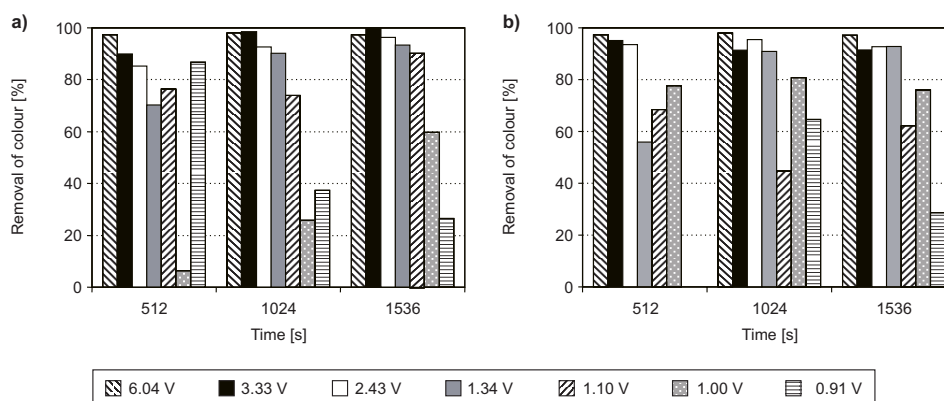


Fig. 1. a) Removal of color (CHRP); b) Removal of color (CHRA)

Figure 1a presents a decrease in pollution load affecting the color intensity of wastewater treated by CHRP electrocoagulation at different current intensity levels. Satisfactory color removal results (80–100 %) were achieved at current intensity of $I \geq 0.3\text{A}$ already at $t = 512\text{s}$. At the longest electrolysis time, similar results were reported at $I \geq 0.5\text{A}$. Minimal color removal was noted at low intensity levels for all three applied time parameters.

The application of constant voltage during electrocoagulation (CHRA) also produced highly satisfactory color removal results. Similarly to CHRP, the reported efficiency was determined by the time of electrolysis. Color removal was least efficient during CHRA electrocoagulation at $U = 0.91\text{V}$ and $t = 512\text{s}$. In the remaining cases, color removal values reached 60 % to 100 %, and the most satisfactory results were observed at the voltage of $\geq 1.31\text{V}$ (Fig. 1b).

As regards the turbidity of the treated model wastewater, the highest removal efficiency was reported at the highest current intensity levels (CHRP), as shown in Figure 2a. Turbidity removal was least efficient at $I = 0.01\text{--}0.03\text{ A}$, reaching only 8 %

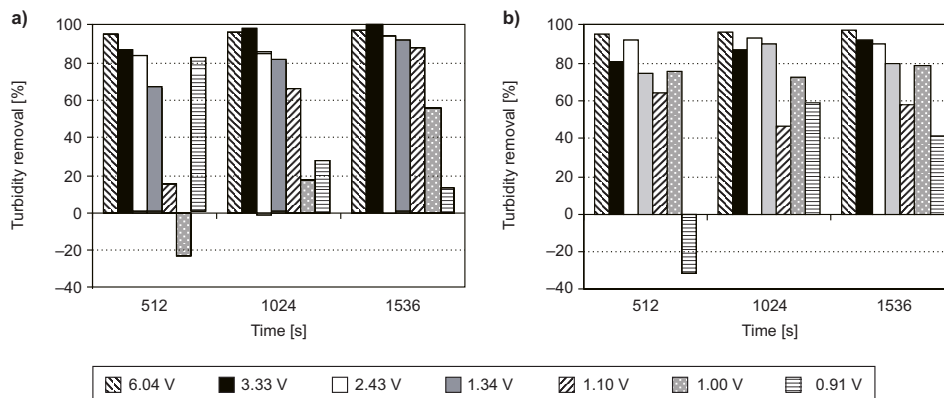


Fig. 2. a) Turbidity removal (CHRP); b) Turbidity removal (CHRA)

after electrolysis time of 1536 s with aluminum electrodes. In general, the effectiveness of turbidity removal reached 100 % at electrolysis time of 1024 s and current intensity of 0.5 A (Fig. 2a).

Figure 2b presents the relationship (CHRP-equivalent) between turbidity removal in CHRA electrocoagulated wastewater and electrolysis time at different voltage levels. Electrocoagulation time of 1536 s supported the achievement of the desired end result, ie 100 % turbidity removal. The application of low voltage levels at $U = 1.1$ V, 1 V and 0.91 V did not stimulate rapid electrolysis, and coagulation, aggregation and sedimentation processes were not visibly observed. The formation and destabilization of colloidal $Al(OH)_3$ were not highly effective under the applied conditions. The process of anodic dissolution of aluminum and cathodic oxygen polarization led to the formation of non-destabilizing sol, increasing the analyzed system's turbidity even by 40 %.

Similar results were observed in respect of suspended solids (Fig. 3a and 3b). Suspended solid concentrations increased during CHRA electrocoagulation at low

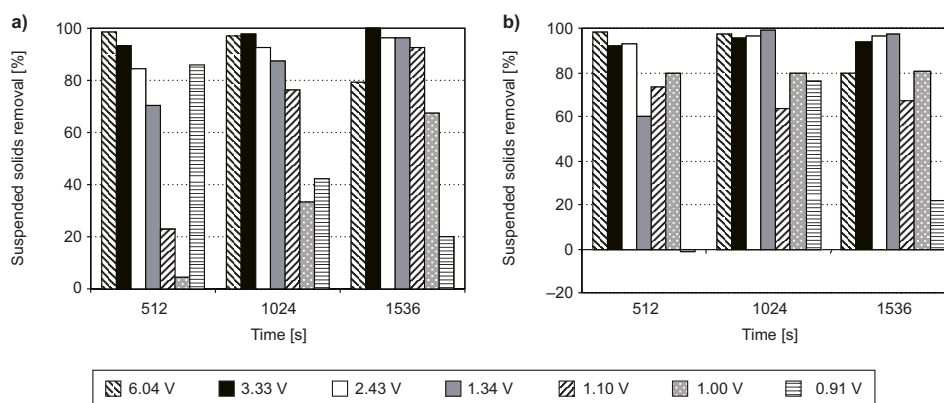


Fig. 3. a) Suspended solids removal (CHRP); b) Suspended solids removal (CHRA)

voltage parameters. The efficiency of suspended solids removal ultimately reached 80–100 % as a result of both CHRA and CHRP electrocoagulation.

COD removal in the treated model wastewater reached 60–65 % following CHRP electrocoagulation at $I \geq 0.3A$. Low current intensity parameters did not enhance removal efficiency, and much better results were noted in chronoamperometric electrocoagulation. Aluminum electrodes supported around 60 % COD removal from the investigated model wastewater already at $t \geq 1024s$.

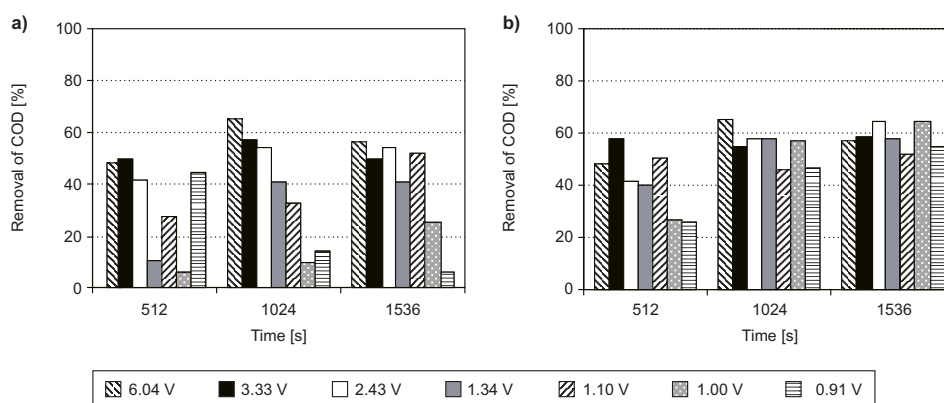


Fig. 4. a) Removal of COD (CHRP); b) Removal of COD (CHRA)

The results of phosphorus removal from wastewater are presented in Tables 1 and 2. For enhanced visualization of the process, the phosphorus removal index (PRI) was calculated each time as mg P removed from the system by 1 C moving charge.

Table 1

Phosphorus removal efficiency (ChRP)

Current [A]	Time [s]	Removal of P [%]	Q [$C \cdot dm^{-3}$]	PRI mg $P_{og}/1 C$
1.0	512	78.3	512	0.069
	1024	82.6	1024	0.036
	1536	78.3	1536	0.023
0.5	512	73.9	256	0.13
	1024	65.2	512	0.058
	1536	82.6	768	0.049
0.3	512	65.2	154	0.2
	1024	73.9	307	0.11
	1536	82.6	461	0.082
0.1	512	47.8	51	0.43
	1024	65.2	102	0.29
	1536	73.9	154	0.22

Table 1 contd.

Current [A]	Time [s]	Removal of P [%]	Q [C·dm ⁻³]	PRI mg P _{og} /1 C
0.05	512	56.5	26	1.0
	1024	56.5	51	0.51
	1536	65.2	77	0.39
0.03	512	52.2	15	1.56
	1024	47.8	37	0.88
	1536	73.9	46	0.72

Table 2

Phosphorus removal efficiency (ChRA)

Voltage [V]	Average current [A]	Time [s]	Removal of P [%]	Q [C·dm ⁻³]	PRI mg P _{og} /1 C
3.22	0.405	512	69.6	207	0.15
3.38	0.488	1024	65.2	500	0.062
3.39	0.452	1536	86.9	694	0.053
2.35	0.241	512	82.6	123	0.30
2.47	0.244	1024	91.3	250	0.17
2.38	0.249	1536	73.9	382	0.089
1.39	0.078	512	52.2	40	0.6
1.32	0.093	1024	65.2	95	0.31
1.31	0.092	1536	73.9	141	0.24
1.12	0.058	512	69.6	30	1.055
1.09	0.052	1024	73.9	53	0.63
1.07	0.022	1536	86.9	34	1.13
1.04	0.025	512	31.8	13	1.22
0.99	0.022	1024	65.2	22	1.33
0.98	0.022	1536	73.9	34	1
0.907	0.014	512	34.8	7	2.2
0.909	0.003	1024	30.4	3	5.1
0.911	0.003	1536	8.7	5	0.8

CHRP electrocoagulation involving aluminum electrodes resulted in 47–82 % total phosphorus removal from the treated wastewater at $I = 0.1$ – 1.0 A, with minimum phosphorus removal efficiency of 65 %. As expected, similarly to COD removal, the efficiency of total phosphorus removal increased with an extension of electrolysis time. Up to 91 % of total phosphorus was removed from wastewater during CHRA electrocoagulation. Removal efficiency at voltage levels higher than 0.98V reached 60–91 %.

PRI values support an evaluation of the analyzed process with regard to its energy efficiency and economic feasibility. Higher PRI values are indicative of increased

phosphorus removal efficiency of 1 C and, consequently, lower energy consumption of the process. The relationship between PRI, current intensity and electrolysis time is reversely proportional. In CHRA electrocoagulation with aluminum electrodes, PRI values are even 2–3 times higher than in the CHRP method. The reported results could suggest that CHRA is superior to CHRP. The highest RPI and phosphorus removal efficiency values for this method were reported already at the voltage range of 0.98–1.12V.

Conclusions

1. Static electrocoagulation of wastewater, carried out with the application of aluminum electrodes and pH adjustment, facilitated more than 50 % COD removal, more than 70 % total phosphorus removal, and nearly 100 % color, turbidity and suspended solids removal from the treated model wastewater.

2. With the application of optimal process parameters, chronoamperometric and chronopotentiometric electrocoagulation proved to be highly efficient methods for the treatment of model wastewater.

3. Satisfactory treatment results were reported when chronopotentiometric electrocoagulation was performed at electrolysis time of $t = 1024\text{s}$ and current intensity of $I \geq 0.3\text{A}$.

4. Optimal conditions for chronoamperometric electrocoagulation were determined at $U = 0.98\text{--}1.39\text{V}$ and $t \geq 1024\text{s}$.

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STATYCZNA ELEKTROKOAGULACJA ŚCIEKÓW MODELOWYCH

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Abstrakt: Przedstawiono wyniki elektrochemicznego oczyszczania ścieków modelowych. Porównano parametry oraz efekty elektrolitycznego oczyszczania ścieków w warunkach chronopotencjometrycznych (CHRP), tj. przy stałym natężeniu prądu ($I = \text{const}$) oraz chronoamperometrycznych (CHRA), tj. przy stałym napięciu ($U = \text{const}$). Elektrolizę prowadzono w układzie statycznym z użyciem elektrolizera z elektrodami glinowymi. Zastosowano 6-elektrodowy (3 katody i 3 anody) elektrolizer. Po elektrokoagulacji i sedymentacji osadu w roztworze oznaczano chemiczne zapotrzebowanie na tlen ChZT, mętność, barwę, zawiesiny oraz stężenie fosforu ogólnego.

Słowa kluczowe: elektrokoagulacja, system statyczny, ścieki modelowe

Magdalena BANACH-SZOTT¹ and Bożena DĘBSKA

**ROLE OF PLANT LITTER
IN DEVELOPING THE CONTENT
OF PHENOLIC COMPOUNDS IN HUMIC SUBSTANCES**

**ROLA OPADU ROŚLINNEGO
W KSZTAŁTOWANIU ZAWARTOŚCI ZWIĄZKÓW FENOLOWYCH
W SUBSTANCJACH HUMUSOWYCH**

Abstract: The aim of the present paper was to determine the content of phenolic compounds in the extracts of fulvic acids and hydrolysates of humic acids depending on the properties of plant litter. The research involved sampling from organic and mineral horizons of forest soils located in the area of the Arboretum in Mlyniany in Slovakia. To identify and to determine the quantity of phenolic compounds the chromatographic method (HPLC) was used. The research demonstrated that the content of phenolic compounds in hydrolysates of fractions of humic acids was generally lower as compared with their content in the extracts of fulvic acids. The content of phenolic compounds both in the extracts of fulvic acids and in the hydrolysates of humic acids decreased with an increase in the degree of the organic matter transformation. It was also shown that the basic parameter which differentiated the properties of newly-formed humic acids under different tree species was the ratio of vanillyl, syringyl and cinnamyl compounds. The extracts of humic acids of O1 subhorizon on the oak stand demonstrated a similar share of vanillyl and syringyl compounds (40:42:18), while the extracts of humic acids of O1 subhorizon on the spruce and thuja stands showed a considerable advantage of vanillyl compounds.

Keywords: humic acids, fulvic acids, phenolic compounds, forest soils

An essential part of organic matter is made up of humus which is produced as a result of very complex processes of transformation of organic residue in soil. The main component of humus are humic substances, being the most common and, at the same time, one of the least known groups of organic compounds in nature.

In forest soils one of the basic factors determining the properties of not only the organic horizon but also deeper horizons is the species composition of the tree stand species composition [1, 2].

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The chemical composition of the plant litter, its decomposition rate and the humus resources have been known very well [1, 3–5], however, it is also essential to study the properties of humus substances which play an important role in soil operation.

The present study of the structure demonstrated that the molecules of humus acids include non-decomposed fragments of lignins [6–9]. Lignins, unlike proteins and carbohydrates, next to which they occur in plant cells, are more resistant to decomposition due to the effect of microorganisms and so they can accumulate temporarily in soil. The lignins accumulated can be included to humus acids or undergo chemical and biological transformations leading to the formation of humus substances [7, 9–12]. Therefore these compounds are considered as one of the main precursors of aromatic carbon in the molecules of humus substances [13].

The changes in the content of lignins and their degree of transformation in the plant material undergoing decomposition can be evaluated by the oxidation of plant materials or the soil samples with CuO or with acidic hydrolysis [7, 11, 13–16].

The methods facilitate the release of aldehydes and phenolic acids from lignins in a form of:

- vanillyl compounds (V – total content of vanillin and vanillic acid), derived from coniferyl alcohol,
- syringyl compounds (S – total content of syringaldehyde and syringic acid), derived from sinapyl alcohol,
- cinnamyl compounds (C – total content of ferulic acid, caffeic acid and coumaric acid), derived from coumaryl alcohol [7, 10].

The mutual proportions of coniferyl, sinapyl and coumaryl alcohol in lignins depend on the plant species [10, 17]. Lignins of angiospermous plants contain approximately the same amounts of vanillyl and syringyl compounds as well as little cinnamyl compounds (49:46:5), while the lignins of gymnospermous plants demonstrate a clear advantage of vanillyl compounds over the others (80:6:14).

Kögel [7] suggests that the indices of the degree of lignin decomposition can be changed in the content of vanillyl, cinnamyl and syringyl compounds and thus the total content of vanillyl, syringyl and cinnamyl compounds (V + S + C), released during the oxidation of plant materials, is applied as a measure of undisturbed uncondensed lignin structures [15, 16, 18]. In forest soils parameter V + S + C usually drops from subhorizon O1 to subhorizon Oh [18–20].

One of the state-of-the-art analysis methods for investigating humus substances is the high performance liquid chromatography (HPLC). The results provide much precious information on the processes of humification of organic matter as well as facilitate obtaining data on the degree of plant residue decomposition in soil and suggest the relationships between the chemical composition and the plant species. Therefore defining the proportions between phenolic compounds in humic acids facilitates determining the relationships between the properties of soil humus and its sources [14, 16, 19–26].

The aim of the present paper was to determine the content of phenolic compounds in the extracts of fulvic acids and hydrolysates of humic acids depending on the plant litter properties in the Arboretum at Mlynany (Slovakia).

Materials and methods

The research involved the use of forest soil sampled in the Arboretum at Mlynany (Slovakia). The Arboretum is found in the northern end of the Poddunajska Lowland, in the left-bank part of the Žytawa valley, between 48°21' of the northern latitude and 18°21' of the eastern longitude. The above-sea-level height ranges from 160 to 208 m. The area morphology and the existing formations are created considerably by the river valley. The soils which occur here have been considered to represent Stagnic Luvisols. The Arboretum covers an area of 67 ha, and the entire collection takes about 2500 of woody plant species [27, 28]. The vegetation period at Mlynany takes about 240 days.

Table 1

Description of soil samples

Sample	Depth [cm]	Horizon	Sample	Depth [cm]	Horizon	Sample	Depth [cm]	Horizon
Oak stand			Spruce stand			Thuja stand		
MD01	5–4	O1	MS01	6–4.5	O1	MT01	4–3	O1
MD02	4–0	Ofh	MS02	4.5–2	Of	MT02	3–1	Of
MD1	0–3	A	MS03	2–0	Oh	MT03	1–0	Oh
MD2	3–15	AE	MS1	0–5	A	MT1	0–5	A
MD3	15–50	E	MS2	5–20	Bt ₁	MT2	5–18	AE
			MS3	20–30	Bhs	MT3	18–45	E
			MS4	30–50	Bt ₂			
Soil type	Stagnic Luvisols		Stagni-Albic Luvisols			Stagnic Luvisols		

The forest soil was sampled according to the scheme given in Table 1 under the following tree stands:

– oak (*Quercus cerris* L.); the trees about 90 year-old, 65 % tree layer cover, 25 % shrubby layer cover and 15 % herbaceous layer cover,

– spruce (*Picea abies* L. Karsten), the trees about 90 year-old, 75 % tree layer cover, 50 % shrubby layer cover, 10 % herbaceous layer cover and 5 % of Bryophytes layer cover,

– thuja (*Thuja plicata* D. Don. ex. Lamb.) the trees about 90 year-old, 70 % tree layer cover, 20 % shrubby layer cover and 10 % herbaceous plant layer cover.

The extraction of phenolic compounds was made following the pattern given in Fig. 1. The chromatographic division of solutions containing phenolic compounds was performed with the use of flow chromatograph HPLC Series 200 by Perkin-Elmer equipped with DAD detector. The analytical column by Waters X-Terra C18 of the molecule size of 5 µm and the size of 250 × 4.6 mm I.D. The filling of the pre-column was identical with the filling of the analytical column.

The mobile phase consisted of: eluent A: H₂O : CH₃CN : CH₃COOH (84:14:2) and eluent B: CH₃CN. The injection was 20 mm³. The detection was made at

the wavelength $\lambda = 254$ nm. The gradient division program was applied at the rate flow of $1 \text{ cm}^3/\text{min}$. The initial composition of the mobile phase accounted for 100 % of eluent A, the concentration of eluent B was increasing linearly during the analysis. The gradient was completed after 49 min when the content of eluent B was 10 %.

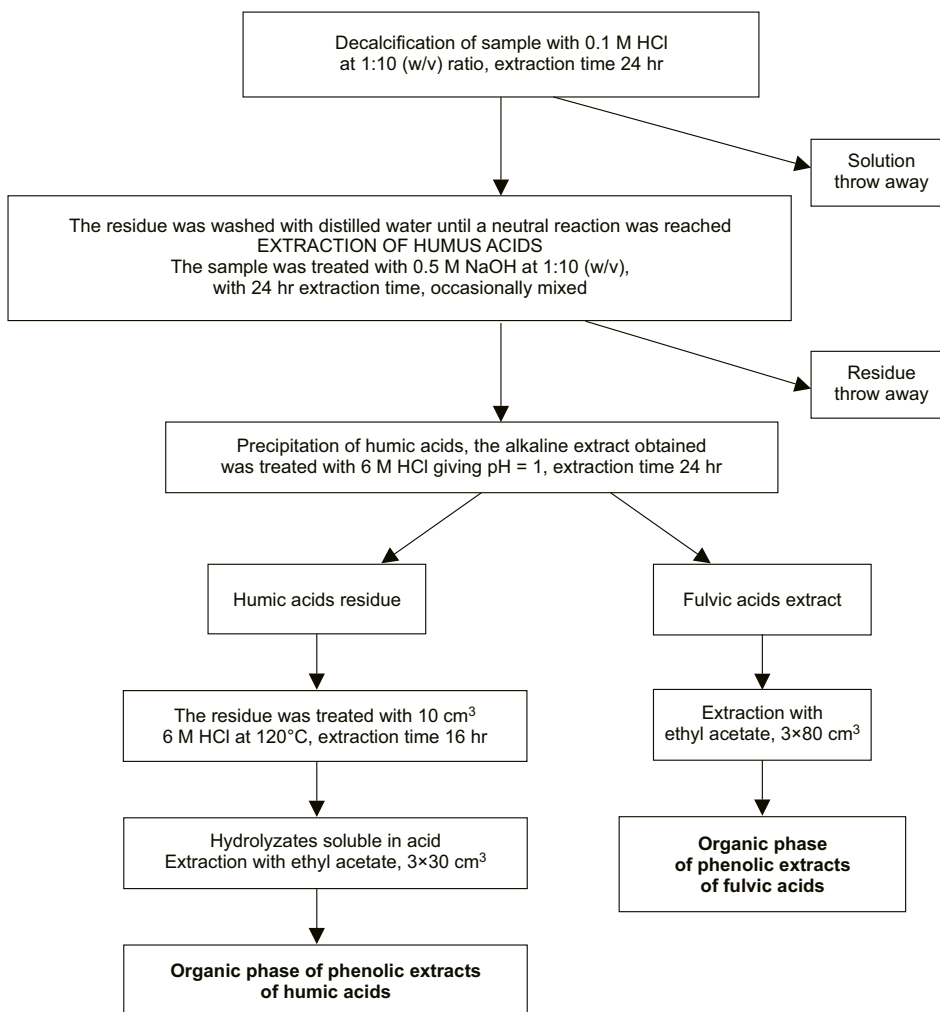


Fig. 1. Scheme of extraction procedure of phenolic compounds

The identification and the quantitative determination of phenolic compounds were performed based on the model solutions of phenolic compounds at the concentration of $0.6 \text{ g}/\text{dm}^3$. The list of the models applied is given in Table 2.

Table 2

List of models applied in qualitative and quantitative analysis of phenolic extracts

No.	Compound	Symbol
1.	Gallic acid (3,4,5-trihydroxybenzoic acid)	GA
2.	Protocatechuic acid (3,4-dihydroxybenzoic acid)	PA
3.	Vanillic acid (4-hydroxy-3-methoxybenzoic acid)	VA
4.	Syringic acid (4-hydroxy-3,5-dimethoxybenzoic acid)	SYA
5.	<i>p</i> -Hydroxybenzoic acid (4-hydroxybenzoic acid)	p-HBA
6.	Caffeic acid (3,4-dihydroxy-trans-cinnamic acid)	CA
7.	Vanillin (4-hydroxy-3-methoxybenzaldehyde)	VAN
8.	Syringaldehyde (4-hydroxy-3,5-dimethoxybenzaldehyde)	SYAL
9.	2,4-Dihydroxybenzoic acid	DHBA
10.	Ferulic acid (4-hydroxy-3-methoxy-trans-cinnamic acid)	FERA
11.	Salicylic acid (2-hydroxybenzoic acid)	SA
12.	<i>p</i> -Coumaric acid (4-hydroxy-trans-cinnamic acid)	p-CA

The model curves plotted were used to calculate the phenolic compounds content ($\mu\text{g}/\text{cm}^3$) in the extracts of fulvic acids and hydrolysates of humic acids [14, 21, 24, 25]. The content of vanillyl (V), syringyl (S) and cinnamyl compounds (C) was calculated:

– V – total content of vanillin (VAN) and vanillic acid (VA), (VAN + VA),
 – S – total content of syringaldehyde (SYAL) and syringic acid (SYA), (SYAL + SYA),

– C – content of ferulic acid (FERA) and caffeic acid (CA), coumaric acid not determined and the following parameters were calculated:

V + S + C – sum of phenols of vanillyl, syringyl and cinnamyl type,

V : S : C – ratio of the share of respective compounds [7, 8, 29].

Results

The concentrations of the aldehydes and phenolic acids in hydrolysates of the fraction of humic acids and extracts of fulvic acids determined with the model curve method are given in Tables 3 and 5. Fig. 2 presents sample chromatograms of solutions containing phenolic compounds.

Table 3
Content of phenolic compounds in the extracts of fulvic acids. For symbols, see Table 2

Sample	Horizon (Depth) [cm]	µg/cm ³										
		GA	PA	VA	SYA	p-HBA	VAN	SYAL	DHBA	CA	FERA	SA
Oak stand												
MD01	OI	27.7	123	22.9	nd	37.4	8.02	16.9	nd	nd	24.5	8.70
MD02	Ofh	41.6	101	17.6	nd	14.0	5.41	7.01	nd	nd	7.31	6.46
MD1	A (0-3)	16.9	139	1.47	nd	1.23	0.477	0.597	nd	nd	0.529	nd
MD2	AE (3-15)	13.9	129	0.571	nd	0.863	0.219	0.153	nd	nd	0.100	nd
MD3	E (15-50)	9.56	nd	nd	nd	0.113	nd	nd	nd	nd	nd	nd
Spruce stand												
MS01	OI	22.3	14.7	0.682	0.600	39.7	10.3	6.20	24.0	nd	0.607	99.1
MS02	Of	14.0	8.29	0.119	0.413	40.7	8.36	3.93	11.5	nd	0.770	62.6
MS03	Oh	22.0	7.54	1.25	0.247	44.1	2.42	2.87	3.48	nd	nd	23.4
MS1	A (0-5)	4.40	5.23	2.17	0.161	45.8	0.242	0.339	5.36	nd	nd	17.6
MS2	Bt ₁ (5-20)	4.23	2.81	nd	nd	42.8	nd	nd	0.631	nd	nd	12.6
MS3	Bhs (20-30)	nd	7.03	1.38	nd	1.55	nd	nd	1.26	nd	nd	8.29
MS4	Bt ₂ (30-50)	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Thuja stand												
MT01	OI	17.1	11.7	17.7	nd	nd	6.85	1.07	0.742	nd	4.14	15.1
MT02	Of	11.8	4.12	13.4	nd	nd	4.32	0.864	0.508	nd	3.82	12.2
MT03	Oh	2.49	1.15	4.75	nd	nd	1.68	0.497	0.366	nd	2.77	11.6
MT1	A (0-5)	0.891	0.411	2.79	nd	nd	1.16	0.304	nd	nd	0.059	10.8
MT2	AE (5-18)	0.472	0.171	1.07	nd	nd	0.438	nd	nd	nd	nd	3.84
MT3	E (18-45)	0.237	nd	0.419	nd	nd	0.229	nd	nd	nd	nd	1.23

nd – not detected

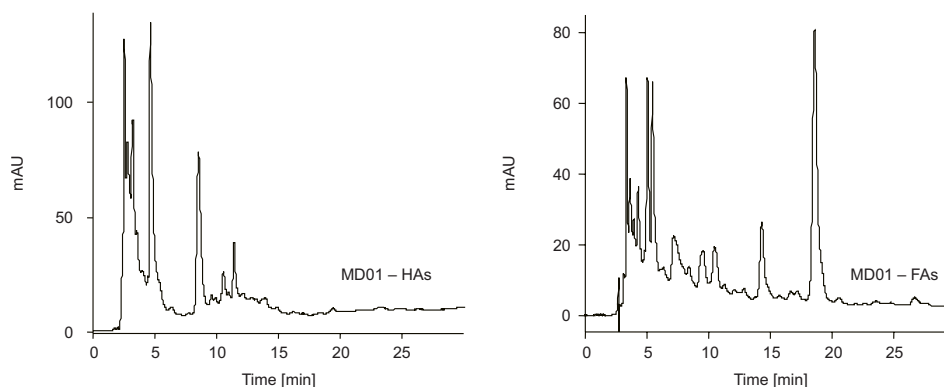


Fig. 2. Sample chromatograms of phenolic compounds which occurred in the extracts of fractions of humic acids (HAs) and fulvic acids (FAs)

Content of phenolic compounds in the fraction of fulvic acids

The extracts of fulvic acids isolated from the soil sampled from the organic horizon demonstrated a richer composition of phenolic compounds as compared with the extracts of fulvic acids of mineral horizons.

No caffeic acid (CA) was identified in any extracts of fulvic acids.

As for the quantitative characteristics, one shall consider that the concentration of phenolic compounds determined in respective fractions does not only result from the amount of these compounds which occur in the molecules of fulvic and humic acids but it is also connected with the content of FAs and HAs fractions in soils. With that in mind, one cannot directly refer the amount of the phenolic compounds obtained in FAs and HAs extracts to the amount of these compounds which occur in the molecules of fulvic and humic acids.

The extracts of fulvic acids, in general, demonstrated a decrease in the concentration of phenolic compounds deep in the soil profile (Table 3).

Similarly, it was observed that the highest content of GA, PA, SYAL and FERA was noted for FAs extracts on the oak stand. The other phenolic compounds identified, except for vanillic acid, occurred in greatest amounts in the FAs extracts in soil on the spruce stand.

Changes in the content of phenolic compounds in the extracts of fulvic acids of vanillic (V), syringic (S) and cinnamyl (C) type are given in Table 4.

The extracts of fulvic acids of the organic horizon of soils demonstrated higher contents of phenolic compounds V, S and C type and, as a result, V + S + C, as compared with FAs extracts of mineral horizons of soils. Besides, these contents decreased with the sampling depth. One shall stress that the extracts of fulvic acids from the soil sampled on the spruce stand contained the phenolic compounds C type (cinnamyl compounds) only in horizons O1 and Of.

Table 4

Content of vanillyl, syringyl and cinnamyl compounds and the values of parameter V + S + C in the extracts of fulvic acids

Sample	Horizon (Depth) [cm]	V	S	C	V + S + C
		$\mu\text{g}/\text{cm}^3$			
Oak stand					
MD01	O1	30.9	16.9	24.51	72.31
MD02	O1h	23.0	7.01	7.31	37.35
MD1	A (0–3)	1.95	0.597	0.529	3.08
MD2	AE (3–15)	0.790	0.153	0.100	1.04
MD3	E (15–50)	nd	nd	nd	nd
Spruce stand					
MS01	O1	11.0	6.20	0.607	17.8
MS02	Of	8.48	4.34	0.770	13.6
MS03	Oh	3.67	3.12	nd	6.79
MS1	A (0–5)	2.17	0.339	nd	2.41
MS2	Bt ₁ (5–20)	0.242	0.161	nd	0.40
MS3	Bhs (20–30)	1.38	nd	nd	1.38
MS4	Bt ₂ (30–50)	nd	nd	nd	nd
Thuja stand					
MT01	O1	24.5	1.07	4.14	29.7
MT02	Of	17.7	0.864	3.82	22.4
MT03	Oh	6.43	0.497	2.77	9.68
MT1	A (0–5)	3.95	0.304	0.059	4.31
MT2	AE (5–18)	1.51	nd	nd	1.51
MT3	E (18–45)	0.647	nd	nd	0.647

Content of phenolic compounds in the hydrolysates of HAs fractions

The content of phenolic compounds in the hydrolysates of fractions of humic acids is given in Table 5.

Hydrolysates of humic acids fractions of organic horizon of soils showed higher contents of phenolic compounds as compared with the hydrolysates of HAs fraction of mineral horizons. It was observed that the spruce and thuja stands, in general, identified the highest contents of phenolic compounds for the humic acids fractions hydrolysates of subhorizon Of (Table 5).

Changes in the content of phenolic compounds of vanillic (V), syringic (S) and cinnamyl (C) type in the humic acids fractions hydrolysates are provided in Table 6. In mineral soil horizons, similarly as in the organic horizon, vanillyl compounds were dominant. The cinnamyl compounds in mineral horizons were observed only in the hydrolysates of HAs fraction of the layer adjacent to the organic horizon on the spruce stand.

Table 5
Content of phenolic compounds in the extracts of humic acids. For symbols, see Table 2

Sample	Horizon (Depth) [cm]	µg/cm ³										
		GA	PA	VA	SYA	p-HBA	VAN	SYAL	DHBA	CA	FERA	SA
Oak stand												
MD01	Oi	43.5	33.6	20.2	21.5	38.6	13.1	27.4	nd	nd	4.79	nd
MD02	Ofh	9.36	13.8	23.1	1.35	2.92	3.77	3.40	nd	nd	0.699	nd
MD1	A (0-3)	1.70	0.281	3.21	nd	0.195	0.248	0.249	nd	nd	nd	nd
MD2	AE (3-15)	3.52	nd	0.674	nd	nd	nd	nd	nd	nd	nd	nd
MD3	E (15-50)	1.52	nd	0.283	nd	nd	nd	nd	nd	nd	nd	nd
Spruce stand												
MS01	Oi	14.2	3.13	34.3	0.733	1.05	0.714	2.37	0.324	0.663a	1.49	4.10
MS02	Of	16.2	5.79	58.8	0.781	2.07	1.22	1.56	0.796	2.32c	1.73	7.23
MS03	Oh	10.9	5.23	54.8	0.789	1.52	1.11	1.11	1.63	0.667a	0.614	13.2
MS1	A (0-5)	5.61	2.10	0.871	0.341	2.67	0.833	2.72	nd	1.79b	nd	1.07
MS2	Bt ₁ (5-20)	4.30	1.76	0.336	0.098	1.22	0.380	0.412	nd	nd	nd	0.724
MS3	Bhs (20-30)	3.20	0.621	0.278	0.038	0.512	0.139	0.704	nd	nd	nd	nd
MS4	Bt ₂ (30-50)	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Thuja stand												
MT01	Oi	1.32	4.46	21.2	0.731	nd	0.778	0.147	nd	nd	nd	2.01
MT02	Of	2.09	6.31	27.0	1.03	nd	0.961	0.164	nd	nd	0.108	1.90
MT03	Oh	0.397	0.720	8.9	0.342	nd	0.511	0.092	nd	nd	nd	nd
MT1	A (0-5)	0.245	nd	1.02	0.103	nd	nd	0.057	nd	nd	nd	nd
MT2	AE (5-18)	nd	nd	0.384	nd	nd	nd	nd	nd	nd	nd	nd
MT3	E (18-45)	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

nd – not detected

Table 6

Content of vanillyl, syringyl and cinnamyl compounds and the values of parameter V + S + C in hydrolysates of the fraction of humic acids

Sample	Horizon (Depth) [cm]	V	S	C	V + S + C
		μg/cm ³			
Oak stand					
MD01	OI	33.3	48.9	4.79	87.0
MD02	Ofh	26.9	4.75	0.699	32.3
MD1	A (0–3)	3.46	0.249	nd	3.71
MD2	AE (3–15)	0.67	nd	nd	0.674
MD3	E (15–50)	0.28	nd	nd	0.283
Spruce stand					
MS01	OI	35.0	3.10	2.15	39.6
MS02	Of	60.0	2.34	4.05	64.1
MS03	Oh	55.9	1.90	1.28	58.4
MS1	A (0–5)	1.70	2.82	1.79	6.31
MS2	Bt ₁ (5–20)	0.716	0.753	nd	1.47
MS3	Bhs (20–30)	0.417	0.742	nd	1.16
MS4	Bt ₂ (30–50)	nd	nd	nd	nd
Thuja stand					
MT01	OI	22.0	0.878	nd	22.8
MT02	Of	27.9	1.19	0.108	29.2
MT03	Oh	9.43	0.434	nd	9.87
MT1	A (0–5)	1.02	0.160	nd	1.18
MT2	AE (5–18)	0.380	nd	nd	0.384
MT3	E (18–45)	nd	nd	nd	nd

The values of V + S + C parameter recorded for HAs hydrolysates of organic horizons of soils were definitely higher than in the HAs extracts of mineral horizons (Table 6). The highest value of V + S + C parameter was noted for HAs fraction of subhorizon OI on the oak stand.

One shall stress that the content of phenolic compounds in the hydrolysates of humic acids fraction was generally lower, except or vanillic acid, as compared with their content in the extracts of fulvic acids. Vanillic acid, irrespective of the tree species and the sampling depth, occurred always in bigger amounts in the hydrolysates of humic acids.

Discussion

The source of much precious information on the humification processes of the organic matter inflow into soil can be phenolic compounds. As seen from the literature reports [14, 16, 19–26], both the qualitative and the quantitative composition of phenolic compounds depend on the type of the material researched and the decomposition degree of organic matter inflow to soil.

The present results demonstrate the differences in the qualitative and quantitative composition between hydrolysates of humic acids and extracts of fulvic acids. The hydrolysates of humic acids did not include dihydroxybenzoic acid (DHBA), and in the FAs extracts, in general, there was no syringic acid (SYA). Besides, it was shown that the content of phenolic compounds in the hydrolysates of humic acids was lower as compared with their content in the extracts of fulvic acids, except for vanillic acid.

Similarly, with the present results, it was noted that the content of aldehydes and phenolic acids identified in the extracts of fulvic acids and humic acids isolated from forest soils samples depended not only on the tree species but also the sampling depth (Tables 3 and 5). It is essential that in the extracts of humic and fulvic acids of mineral horizons the qualitative composition of phenolic compounds was changing, while the concentration of aldehydes and FAs present in the extracts were much lower than in the fractions of humus acids of the organic horizon.

The humification progress can be seen from the changes in the V + S + C parameter values determined as a measure of undisturbed uncondensed lignin structures. The present results (Tables 4 and 6) coincide with the literature reports [15, 16, 18–20] according to which the V + S + C parameter value decreases with soil profile depth, and thus it decreases with the increase in the degree of humification of the material researched. The values of V + S + C parameter obtained for the fraction of fulvic acids and the fraction of humic acids of subhorizon O1 were determined also by the plant litter properties. The highest content of V, S and C type compounds was found for the extracts of humus acids (HAs + FAs) of ectohumus on the oak stand.

The basic parameter differentiating the properties of newly-produced humus acids under different tree species is the ratio of vanillyl compounds (V), syringic (S) and cinnamyl (C) compounds. The proportions of these compounds obtained for a total of HAs + FAs, hydrolysates of humic acids and the extracts of fulvic acids are given in Table 7. The compounds discussed occur in lignins in specific proportions.

The reports by Higuchi et al [17] and Crawford [10] demonstrated that mutual proportions of coniferyl, sinapyl and coumaryl alcohols in lignins depend on the plant species.

The extracts of humus acids (HAs + FAs) of subhorizon O1 on the oak stand showed a similar share of vanillyl and syringyl compounds and a low share of cinnamyl compounds (Table 7), while the extracts on the spruce stand and thuja stand identified a considerable advantage of vanillyl compounds over the others. Therefore for the extracts being the sum: HAs + FAs, isolated from the soil sampled from subhorizon O1, there were reported similar values of the ratio of V, S and C compounds to the value of the ratio of these compounds in lignins [10, 17], which suggests a high share of lignins in the processes of humus acids formation in forest soils.

The proportions of the V, S and C type compounds in the extracts of humic acids isolated from the soil sampled from the organic horizon on all the stands showed, in general, a considerably greater share of vanillyl compounds over the others, except for the oak stand, subhorizon O1 (Table 7).

Table 7

Ratios of the share of vanillyl, syringyl and cinnamyl compounds in humus, humic and fulvic acids

Sample	V : S : C		
	HAs + FAs	HAs	FAs
Oak stand			
MD01	40:42:18	38:56:6	43:23:34
MD02	72:17:11	83:15:2	61:19:20
MD1	80:12:8	93:7:0	63:20:17
MD2	85:9:6	100:0:0	76:15:9
MD3	100:0:0	100:0:0	nd
Spruce stand			
MS01	79:16:5	87:8:5	62:35:3
MS02	86:8:6	90:4:6	62:32:6
MS03	90:8:2	95:3:2	54:46:0
MS1	40:22:38	40:18:42	42:58:0
MS2	51:49:0	27:45:28	60:40:0
MS3	71:29:0	36:64:0	100:0:0
MS4	nd	nd	nd
Thuja stand			
MT01	88:4:8	96:4:0	82:4:14
MT02	88:4:8	95.6:4:0.4	79:4:17
MT03	81:5:14	96:4:0	66:5:29
MT1	90:8:2	86:14:0	92:7:1
MT2	100:0:0	100:0:0	100:0:0
MT3	100:0:0	nd	100:0:0

The extracts of fulvic acids isolated from soil sampled from subhorizon O1 on oak stands were as follows: 43:23:34, while the extracts of fulvic acids of subhorizon O1 on the spruce and thuja stands, just like the extracts of humus acids and humic acids, revealed a considerable advantage of vanillyl compounds over the others, 62:35:3 and 82:4:14, respectively. It was noted that the greater the depth, the greater the changes in the ratio of respective compounds present. Johansson et al [11] report on the spruce needle decomposition process involving an increase in the share of vanillyl compounds and a slight decrease in the share of cinnamyl compounds. Similar relationships for HAs and FAs were observed also by Banach-Szott [19] and Banach-Szott and Dębska [20] in earlier reports.

Conclusions

1. The qualitative and quantitative composition of phenolic compounds in humus acids were determined by the kind of plant litter and the soil sampling depth. The humus acids of organic horizon demonstrated a much higher content of phenolic compounds as compared with the humus acids of mineral horizons.

2. The highest contents of vanillyl, syringyl and cinnamyl compounds were found in humus acids of subhorizon OI on the oak stand. The lowest content of V, S and C compounds in organic horizons was recorded for humus acids on the thuja stand.

3. Humus acids of subhorizon OI on the oak stand showed a higher share of the total of syringyl and cinnamyl compounds to the share of vanillyl compounds, while humus acids on the coniferous tree stands (spruce, thuja) – a considerable advantage of vanillyl compounds. The values of the V : S : C ratio recorded suggest a high share of lignins in the processes of humus acids in forest soils.

4. The fraction of fulvic acids demonstrated, in general, a higher content of the aldehydes and phenolic acids identified as compared with the hydrolysates of humic acids fractions. Only the content of the vanillic acid was higher in the hydrolysates of humic acids as compared with its content in the extracts of fulvic acids.

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ROLA OPADU ROŚLINNEGO W KSZTAŁTOWANIU ZAWARTOŚCI ZWIĄZKÓW FENOLOWYCH W SUBSTANCJACH HUMUSOWYCH

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Abstrakt: Celem pracy było określenie zawartości związków fenolowych w ekstraktach kwasów fulwowych i hydrolizatach kwasów huminowych w zależności od właściwości opadu roślinnego. Do badań pobrano próbki z poziomów organicznych i mineralnych gleb leśnych zlokalizowanych na terenie Arboretum w Młynianach na Słowacji. Do identyfikacji oraz ilościowego oznaczenia związków fenolowych zastosowano metodę chromatograficzną (HPLC). Wykazano, że zawartość związków fenolowych w hydrolizatach frakcji kwasów huminowych była generalnie mniejsza w porównaniu z ich zawartością w ekstraktach kwasów fulwowych. Zawartość związków fenolowych zarówno w ekstraktach kwasów fulwowych, jak i hydrolizatach kwasów huminowych zmniejszała się wraz ze wzrostem stopnia transformacji materii organicznej. Wykazano również, że podstawowym parametrem odróżniającym właściwości nowo powstałych kwasów humusowych pod różnymi gatunkami drzew jest stosunek jednostek wanilinowych, syryngowych i cynamonowych. Ekstrakty kwasów humusowych podpoziomu surowinowego (OI) na stanowisku dębu cechowały się zbliżonym udziałem jednostek wanilinowych i syryngowych (40:42:18). Natomiast ekstrakty kwasów humusowych podpoziomu OI na stanowiskach świerka i tui charakteryzowały się znaczną przewagą jednostek wanilinowych.

Słowa kluczowe: kwasy huminowe, kwasy fulwowe, związki fenolowe, gleby leśne

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DEHYDROGENASE ACTIVITY AS AN INDICATOR OF SOIL CONTAMINATION WITH HERBICIDES

AKTYWNOŚĆ DEHYDROGENAZ JAKO WSKAŹNIK ZANIECZYSZCZENIA GLEBY HERBICYDAMI

Abstract: The effect of soil contamination with the following herbicides: Harpun 500 SC, Faworyt 300 SL, Akord 180 OF and Mocarz 75 WG on the activity of soil dehydrogenases was estimated in a laboratory and pot experiment, in which dehydrogenase activity was determined repeatedly in soil (loamy sand) samples. The herbicides were applied to soil at the manufacturer's recommended doses, and at doses that were 10-, 50-, 100-, 150- and 200-fold higher than recommended. An attempt was also made to alleviate the negative influence of herbicides on dehydrogenases by the addition of bentonite in the amount of 60 g kg⁻¹ d.m. of soil.

It was found that all analyzed herbicides inhibited the activity of soil dehydrogenases. The adverse impact of herbicides was positively correlated with the level of soil contamination, and their inhibitory effect on dehydrogenases was observed over the entire experimental period (112 days) and decreased at a very slow rate. Dehydrogenase activity proved to be a good indicator of the degree of soil contamination with herbicides. Bentonite enhanced the inhibitory effect of herbicides on dehydrogenases.

Keywords: herbicides, soil contamination, dehydrogenase activity, bentonite

The soil environment accumulates a wide variety of synthetic (man-made) chemical substances. The continuous introduction of excessive quantities of xenobiotics into the soil may lead to numerous undesirable changes including the disturbance of the biological balance of soil, which in turn alters the total number of living organisms and the enzymatic activity of soil [1–3]. The group of xenobiotic substances comprises also plant protection chemicals, including herbicides. Apart from their beneficial influence, herbicides can also cause negative sideeffects leading to a decrease in soil fertility [4,

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5]. Although herbicides are usually designed to be biodegradable, they may nevertheless pose a threat to the natural environment [6]. The adverse impact of herbicides on the soil environment is dependent primarily on the dose applied, frequency of use, environmental persistence, the physicochemical properties of soil, temperature, moisture content, pH and sorption capacity [7]. The toxic effects of herbicides are most often reflected in changes in the quantitative and qualitative composition of microorganisms and in the enzymatic activity of soil [8–13]. Apart from microbial counts, also enzymatic activity is a good measure of the biological activity of soil, since it provides information about changes taking place under the influence of external factors [14–18]. One of the most commonly applied indicators of soil biological activity is the activity dehydrogenases which are most susceptible to biocides [4, 19]. Dehydrogenase activity is also an indirect indicator of soil microbial biomass. Dehydrogenases belong to the group of intracellular enzymes which actively catalyze the oxidation of organic compounds found in the cells of microorganisms. In addition, dehydrogenases represent the class of oxidoreductases, which means that their activity is related to the process of soil microbial respiration [20], and it is affected by soil type and changes in the soil profile depth. These enzymes are also considered to be sensitive indicators of soil quality and key biomarkers of alterations in soil metabolism caused by anthropogenic factors [21]. The analysis of dehydrogenase activity is particularly recommended when newly developed herbicides are to be introduced to agricultural practice.

In view of the above, the objective of this study was to determine the effect of soil contamination with new generation herbicides, Harpun 500 SC, Faworyt 300 SL, Akord 180 OF and Mocarz 75 WG, on the activity of soil dehydrogenases.

Material and methods

The study consisted of two experiments, a laboratory experiment and a pot experiment. Both experiments were designed to determine the effect of four herbicides, Harpun 500 SC, Faworyt 300 SL, Akord 180 OF and Mocarz 75 WG, on dehydrogenase activity. The characteristics of the tested herbicides are presented in Table 1. The experimental materials comprised samples of soil classified under natural conditions as typical brown soil developed from loamy sand, with the following physicochemical properties: $\text{pH}_{\text{KCl}} - 6.5$, hydrolytic acidity $- 8.25 \text{ mmol}(+) \text{ kg}^{-1}$, sum of exchangeable cations $- 78 \text{ mmol}(+) \text{ kg}^{-1}$, organic carbon content $C_{\text{org}} - 6.3 \text{ g kg}^{-1}$.

The laboratory experiment was performed in three replications. 100 cm³ beakers were filled with 100 g of air-dried soil. Variable experimental factors were as follows: I – herbicide type: Harpun 500 SC, Faworyt 300 SL, Akord 180 OF, Mocarz 75 WG; II – herbicide dose: 0 – control, 1 – manufacturer's recommended dose, doses 50-, 100-, 150- and 200-fold higher than recommended; III – soil incubation time (days): 28, 56, 84 and 112. Soil was mixed with herbicides in beakers and moisture content was brought to 60 % of the capillary water capacity with the use of deionized water. Samples were incubated at a temperature of 25 °C for a specified period of time (experimental factor III) and dehydrogenase activity was determined.

Table 1

Characteristics of the herbicides used in the study

Herbicide	Active ingredient		Recommended dose [dm ³ ha ⁻¹] [kg ha ⁻¹]	Recommended dose [mm ³ kg ⁻¹] [μg kg ⁻¹]
	Name	[%] [g kg ⁻¹]		
Harpun 500 SC	isoproturon	500 g	2.5 dm ³	0.83 mm ³
Faworyt 300 SL	chloryralid	300 g	0.35 dm ³	0.12 mm ³
Akord 180 OF	phenmediphan desmediphan ethofumesate	60 g 60 g 60 g	5 dm ³	0.16 mm ³
Mocarz 75 WG	tritosulphuron dicamba	25 % 50 %	0.2 kg	6.66 μg

The pot experiment was performed in five replications. Polyethylene pots were filled with 3 kg of soil. The first two experimental factors, ie the type and dose of herbicides, were identical as in the laboratory experiment, while the third factor – time of analysis – was limited to 25 and 50 days. The fourth variable experimental factor was bentonite dose: 0 and 60 g kg⁻¹ d.m. of soil. Before filling the pots, soil was mixed with an appropriate dose of herbicides and with mineral fertilizers. Spring barley cv. Rabel (12 plants), spring rape cv. Sponsor (12 plants), oat cv. Kasztan (12 plants) and carrot cv. Kalina (5 plants), were sown in pots containing soil contaminated with the herbicides Harpun 500 SC, Faworyt 300 SL, Mocarz 75 and WG Akord 180 OF, respectively.

In the experiment with spring rape, spring barley and oat, fertilization levels were as follows [mg kg⁻¹ soil]: N – 100 (CO(NH₂)₂), P – 35 (KH₂PO₄), K – 100 (KH₂PO₄ + KCl), Mg – 20 (MgSO₄ · 7H₂O), Cu – 5 (CuSO₄ · 5H₂O), Zn – 5 (ZnCl₂), Mn – 5 (MnCl₂ · 4H₂O), Mo – 5 (Na₂MoO₄ · 2H₂O) and B – 0.33 (H₃BO₄). In the experiment with carrot, fertilization levels were almost identical as in the experiments with cereals and spring rape, only the rates of P and K were increased to 44 mg kg⁻¹ and 120 mg kg⁻¹, respectively.

Over the experimental period soil moisture content was maintained at a stable level equal to 60 % of the capillary water capacity. On day 25 and 50 soil samples were assayed for dehydrogenase activity. Both in the laboratory and pot experiment the activity of these enzymes was determined by the Lenhard method modified by Öhlinger et al [22], and it was expressed in [cm³ H₂ kg⁻¹ d.m. soil d⁻¹].

The results were processed statistically by Duncan's test. A statistical analysis was performed with the use of Statistica software [23].

Results and discussion

In the laboratory experiment the activity of dehydrogenases in soil not contaminated with weed killers was dependent on the duration of the experiment (Table 2). In control treatments the highest and the lowest activity of these enzymes was observed on day 28 and 112, respectively. On day 112 dehydrogenase activity was 2.2-fold lower than on day 28.

Table 2

Dehydrogenase activity in soil contaminated with herbicides as dependent on herbicide type and dose, and time of analysis, $\text{cm}^3 \text{H}_2 \text{kg}^{-1} \text{d.m. d}^{-1}$ (laboratory experiment)

Herbicide dose*	Time of soil incubation [days]			
	28	56	84	112
Harpun 500 SC				
0	3.57 ± 0.08	3.23 ± 0.05	3.05 ± 0.05	1.74 ± 0.04
1	3.56 ± 0.07	2.83 ± 0.06	2.43 ± 0.06	1.73 ± 0.07
50	3.73 ± 0.08	2.74 ± 0.05	2.40 ± 0.08	1.46 ± 0.05
100	3.83 ± 0.12	2.02 ± 0.14	2.06 ± 0.10	1.32 ± 0.08
150	3.83 ± 0.12	1.88 ± 0.06	1.84 ± 0.10	1.22 ± 0.04
200	3.72 ± 0.11	1.76 ± 0.10	1.61 ± 0.10	0.91 ± 0.07
r	0.60	-0.95	-0.97	-0.95
Faworyt 300 SL				
0	3.57 ± 0.08	3.23 ± 0.05	3.05 ± 0.05	1.74 ± 0.04
1	1.46 ± 0.07	2.47 ± 0.07	2.14 ± 0.07	1.69 ± 0.04
50	1.43 ± 0.06	2.45 ± 0.09	2.11 ± 0.10	1.59 ± 0.06
100	1.38 ± 0.05	2.38 ± 0.05	2.05 ± 0.11	1.55 ± 0.08
150	1.36 ± 0.07	1.74 ± 0.12	2.07 ± 0.10	1.51 ± 0.09
200	1.36 ± 0.04	1.70 ± 0.06	1.98 ± 0.09	1.48 ± 0.04
r	-0.64	-0.94	-0.70	-0.93
Akord 180 OF				
0	3.57 ± 0.08	3.23 ± 0.05	3.05 ± 0.05	1.74 ± 0.04
1	1.92 ± 0.05	2.34 ± 0.07	2.32 ± 0.08	1.78 ± 0.11
50	1.67 ± 0.04	1.62 ± 0.07	1.61 ± 0.08	1.81 ± 0.05
100	1.67 ± 0.04	1.25 ± 0.07	1.44 ± 0.06	1.72 ± 0.07
150	1.67 ± 0.07	1.16 ± 0.09	1.39 ± 0.04	1.64 ± 0.09
200	1.68 ± 0.09	1.07 ± 0.06	1.11 ± 0.03	1.26 ± 0.09
r	-0.65	-0.85	-0.86	-0.83
Mocarz 75 WG				
0	3.57 ± 0.09	3.23 ± 0.05	3.05 ± 0.05	1.74 ± 0.04
1	2.21 ± 0.03	2.14 ± 0.05	1.76 ± 0.03	1.59 ± 0.06
50	2.11 ± 0.05	2.15 ± 0.07	1.65 ± 0.04	1.58 ± 0.06
100	2.03 ± 0.07	2.15 ± 0.08	1.27 ± 0.10	1.34 ± 0.05
150	2.00 ± 0.09	2.12 ± 0.08	1.19 ± 0.07	1.29 ± 0.05
200	1.77 ± 0.06	1.93 ± 0.09	1.17 ± 0.02	1.28 ± 0.10
r	-0.77	-0.72	-0.82	-0.94
LSD _{0.01} **	<i>a</i> - 0.01; <i>b</i> - 0.02; <i>c</i> - 0.01; <i>a</i> · <i>b</i> - 0.03; <i>a</i> · <i>c</i> - 0.03; <i>b</i> · <i>c</i> - 0.03; <i>a</i> · <i>b</i> · <i>c</i> - 0.07			

* 0 – control sample (not contaminated with herbicides); 1 – manufacturer's recommended dose; doses 50-, 100-, 150- and 200-fold higher than recommended;

** LSD for: *a* – herbicide type; *b* – herbicide dose; *c* – time of analysis;

r – coefficient of correlation.

Soil contamination with herbicides had an adverse effect on dehydrogenase activity, which was found to vary over time (Table 2). At the beginning of the experiment (day 28), the herbicide Harpun 500 SC applied at doses 50- and 200-fold higher than recommended stimulated dehydrogenase activity. When applied at the highest dose (200-fold higher than recommended), this herbicide increased dehydrogenase activity by 4 %, as compared with the control treatment. Only the manufacturer's recommended dose did not cause significant changes in the activity of these enzymes. On day 56 the optimum dose of the herbicide decreased dehydrogenase activity by 12 %, while the dose 200-fold higher than the optimum dose – by as much as 46 %. On day 84 and 112 the adverse effect of Harpun 500 SC on dehydrogenases was similar as on day 56, as confirmed by negative coefficients of correlation between herbicide dose and enzymatic activity.

The second of the tested herbicides, Faworyt 300 SL, decreased dehydrogenase activity even when applied at the recommended dose: by 59 % on day 28, by 24 % on day 56, by 30 % on day 84 (Table 2). The negative impact of this dose was not observed only on day 112 of the experiment. Dehydrogenase activity was adversely affected by higher doses of this herbicide during the entire experiment, although their effect diminished considerably over the soil incubation period.

Dehydrogenases were also sensitive to Akord 180 OF (Table 2). On experimental day 28 all analyzed doses of this herbicide decreased dehydrogenase activity approximately twofold, in comparison with the control treatment. The highest dose of Akord 180 OF reduced dehydrogenase activity threefold on day 56, 2.7-fold on day 84 and 1.4-fold on day 112.

Mocarz 75 WG was also found to be a strong inhibitor of dehydrogenases (Table 2). The inhibitory effect of this herbicide on dehydrogenase activity was reported following the application of both the manufacturer's recommended dose and increased doses. In soil contaminated with the highest dose of Mocarz 75 WG (200-fold higher than recommended), dehydrogenase activity was inhibited by 38 % on day 28, by 40 % on day 56, by 62 % on day 84 and by 26 % on day 112.

All tested herbicides strongly inhibited the activity of dehydrogenases also in the pot experiment (Table 3). Their adverse impact was observed with respect to both increased and recommended doses. In this experiment Faworyt 300 SL exerted the slightest negative effect. Harpun 500 SC applied at the lowest dose decreased enzymatic activity by 37 % on average on day 25 and by only 8 % on day 50. In treatments contaminated with a dose 200-fold higher than recommended, dehydrogenase activity decreased 2.8-fold and 2.5-fold on day 25 and 50 respectively, compared with the control sample.

Akord 180 OF and Mocarz 75 WG, applied at the recommended dose, decreased dehydrogenase activity on average by 44 % and 50 % respectively, regardless of the time of analysis and bentonite addition. Higher doses of the above herbicides had an even greater negative influence on dehydrogenases. The adverse impact of the tested herbicides on dehydrogenase activity was enhanced by the addition of bentonite which was also found to be a strong inhibitor of these enzymes under the experimental conditions.

Table 3

Dehydrogenase activity in soil contaminated with herbicides as dependent on herbicide type and dose, time of analysis and bentonite dose, $\text{cm}^3 \text{H}_2 \text{kg}^{-1} \text{d.m. d}^{-1}$ (pot experiment)

Herbicide dose*	Bentonite dose [g kg^{-1} soil]			
	0		60	
	Time of analysis [days]			
	25	50	25	50
Harpun 500 SC				
0	3.12 ± 0.05	2.65 ± 0.06	1.73 ± 0.06	1.68 ± 0.06
1	3.03 ± 0.03	2.54 ± 0.06	0.59 ± 0.06	1.42 ± 0.06
10	1.57 ± 0.09	1.98 ± 0.06	0.53 ± 0.06	0.96 ± 0.06
50	1.51 ± 0.06	1.51 ± 0.06	0.50 ± 0.06	0.95 ± 0.06
100	1.30 ± 0.03	1.28 ± 0.06	0.49 ± 0.03	0.56 ± 0.06
150	1.28 ± 0.03	1.26 ± 0.06	0.49 ± 0.03	0.55 ± 0.03
200	1.26 ± 0.06	1.20 ± 0.06	0.47 ± 0.03	0.51 ± 0.06
r	-0.75	-0.84	-0.56	-0.88
Faworyt 300 SL				
0	3.12 ± 0.05	2.65 ± 0.06	1.73 ± 0.06	1.68 ± 0.06
1	2.51 ± 0.03	2.76 ± 0.06	1.64 ± 0.06	1.63 ± 0.03
10	2.42 ± 0.06	3.28 ± 0.06	1.57 ± 0.03	1.66 ± 0.09
50	1.98 ± 0.03	3.76 ± 0.09	1.49 ± 0.03	1.94 ± 0.06
100	1.94 ± 0.03	3.14 ± 0.03	1.48 ± 0.03	1.96 ± 0.06
150	1.78 ± 0.07	3.51 ± 0.07	1.47 ± 0.06	2.46 ± 0.03
200	1.60 ± 0.06	3.48 ± 0.07	0.91 ± 0.06	2.44 ± 0.06
r	-0.87	0.59	-0.88	0.93
Akord 180 OF				
0	3.12 ± 0.05	2.65 ± 0.06	1.73 ± 0.06	1.68 ± 0.06
1	1.24 ± 0.06	1.93 ± 0.06	0.44 ± 0.06	1.50 ± 0.03
10	0.96 ± 0.06	1.79 ± 0.03	0.37 ± 0.03	1.25 ± 0.06
50	0.73 ± 0.06	1.71 ± 0.03	0.32 ± 0.03	1.17 ± 0.06
100	0.71 ± 0.03	1.71 ± 0.06	0.34 ± 0.06	1.16 ± 0.03
150	0.68 ± 0.06	1.70 ± 0.03	0.34 ± 0.06	1.00 ± 0.03
200	0.67 ± 0.03	1.64 ± 0.03	0.36 ± 0.03	1.00 ± 0.03
r	-0.59	-0.61	-0.53	-0.87
Mocarz 75WG				
0	3.12 ± 0.05	2.65 ± 0.06	1.73 ± 0.06	1.68 ± 0.06
1	1.22 ± 0.07	1.84 ± 0.03	0.68 ± 0.06	0.89 ± 0.03
10	1.12 ± 0.06	1.66 ± 0.03	0.33 ± 0.03	0.62 ± 0.06
50	0.95 ± 0.06	1.42 ± 0.09	0.30 ± 0.03	0.61 ± 0.06
100	0.95 ± 0.06	1.39 ± 0.10	0.26 ± 0.03	0.43 ± 0.06

Table 3 contd.

Herbicide dose*	Bentonite dose [g kg ⁻¹ soil]			
	0		60	
	Time of analysis [days]			
	25	50	25	50
150	0.74 ± 0.06	1.15 ± 0.06	0.26 ± 0.03	0.42 ± 0.03
200	0.63 ± 0.06	0.96 ± 0.03	0.13 ± 0.06	0.40 ± 0.06
r	-0.69	-0.86	-0.68	-0.74
LSD _{0.05} **	<i>a</i> - 0.02; <i>b</i> - 0.02; <i>c</i> - 0.01; <i>d</i> - 0.01; <i>a</i> · <i>b</i> - 0.04; <i>a</i> · <i>c</i> - 0.02; <i>b</i> · <i>c</i> - 0.03; <i>a</i> · <i>d</i> - 0.02; <i>b</i> · <i>d</i> - 0.03; <i>c</i> · <i>d</i> - 0.02; <i>a</i> · <i>b</i> · <i>c</i> - 0.06; <i>a</i> · <i>b</i> · <i>d</i> - 0.06; <i>a</i> · <i>c</i> · <i>d</i> - 0.03; <i>b</i> · <i>c</i> · <i>d</i> - 0.04; <i>a</i> · <i>b</i> · <i>c</i> · <i>d</i> - 0.08			

* 0 – control sample (not contaminated with herbicides); 1 – manufacturer's recommended dose; doses 10-, 50-, 100-, 150- and 200-fold higher than recommended;

** LSD for: *a* – herbicide type; *b* – herbicide dose; *c* – time of analysis; *d* – bentonite dose; *r* – coefficient of correlation.

Cases of soil metabolism disorders caused by crop protection chemicals, particularly when present in excessive concentrations, have been also reported by other authors [11, 24–28]. Soil enzymatic activities are reliable indicators of the state of the natural environment [12, 16]. The present study showed that dehydrogenase activity can be considered a good measure of the effect of herbicides (Harpun 500 SC, Faworyt 300 SL, Akord 180 OF, Mocarz 75 WG) on the soil environment, since the activity of these enzymes is usually positively correlated with microbial counts [11]. Changes in individual microbiological and biochemical properties of soil, especially those induced by the application of novel pesticide products, should be closely monitored. According to Singh and Singh [29], these agents act not only on the target organism, but also affect non-target organisms, thus contributing to environmental deterioration.

The results of this study indicate that excessive loads of the herbicides Harpun 500 SC, Faworyt 300 SL, Akord 180 OF and Mocarz 75 WG may disturb the biological balance of soil, and that their toxic effects are difficult to neutralize. The adverse impact of the above herbicides on dehydrogenase activity was observed for a relatively long time, ie for 112 days of the experiment, and the attempt to alleviate their negative influence on dehydrogenases by the addition of bentonite to soil proved unsuccessful.

Conclusions

1. The herbicides Harpun 500 SC, Faworyt 300 SL, Akord 180 OF and Mocarz 75 WG may significantly decrease dehydrogenase activity in the soil environment, particularly when applied in excessive quantities.

2. Bentonite was found ineffective for alleviating the negative impact of herbicides on dehydrogenases, since it proved to be a potent inhibitor of the activity of these enzymes.

3. The inhibitory effect of the tested herbicides on dehydrogenase activity diminished over time, but the process was not dynamic.

4. Dehydrogenase activity may be a good indicator of the level of soil contamination with herbicides.

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AKTYWNOŚĆ DEHYDROGENAZ JAKO WSKAŹNIK ZANIECZYSZCZENIA GLEBY HERBICYDAMI

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Abstrakt: W celu określenia wpływu zanieczyszczenia gleby herbicydami: Harpun 500 SC, Faworyt 300 SL, Akord 180 OF i Mocarz 75 WG na aktywność dehydrogenaz glebowych wykonano dwa doświadczenia: laboratoryjne i wegetacyjne (wazonowe), w których kilkakrotnie określano aktywność dehydrogenaz w glebie (piasku gliniastym). Herbicydy stosowano dogłębowo w dawkach zalecanych przez producenta oraz w dawkach: 10, 50, 100, 150 i 200-krotnie większej. Podjęto także próbę złagodzenia negatywnego oddziaływania herbicydów na dehydrogenazy poprzez dodanie do gleby bentonitu w ilości 60 g kg⁻¹ s.m. gleby.

W wyniku badań stwierdzono, że wszystkie herbicydy hamowały aktywność dehydrogenaz glebowych. Ich negatywne oddziaływanie było dodatnio skorelowane ze stanem zanieczyszczenia gleb, a inhibicyjne działanie na dehydrogenazy utrzymywało się przez cały okres badań (112 dni) i zmniejszało się bardzo powoli. Aktywność dehydrogenaz okazała się dobrym wskaźnikiem oceny stanu zanieczyszczenia gleb herbicydami. Zastosowany bentonit zwiększał inhibicyjne oddziaływanie herbicydów na dehydrogenazy.

Słowa kluczowe: herbicydy, zanieczyszczenie gleby, aktywność dehydrogenaz, bentonit

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EFFECT OF OIL DERIVATIVE SPILL ON EPIGEAL INVERTEBRATES

ODDZIAŁYWANIE WYCIEKU ROPOPOCHODNYCH NA BEZKRĘGOWCE NAZIEMNE

Abstract: The investigations aimed to find the answer to the question how long since the moment of the environment contamination with oil derivatives the effect of these compounds on the epigeal and soil fauna may be assessed.

The experiment was conducted in 2006–2007 in Czyżów village at the No.4 national road section where a road accident of cistern truck carrying crude oil happened in 2004 resulting in a spill of 12 000 dm³ of toxic substance into the ground. The reclamation of the contaminated area was conducted “in situ” using bioremediation method based on Trigger-2R fast liquidation of contamination technology, ie realized in the contaminated place by enzymes and bacteria specialized in oil-derivatives biodegradation to the required soil standards.

With time elapsing since the moment of soil contamination with oil derivatives their toxic effect on individual invertebrate groups diminished. Three years after the moment of pollution no negative effect on the occurrence of a majority of epigeal invertebrates was visible. However, a decrease in the numbers of beneficial *Bembidion* sp., *Pterostichus* sp. and *Harpalus* sp. may be notices seasonally. Two years after the moment of pollution a persistent decline in the numbers of caught *Oribatida* may be observed.

Keywords: oil derivative, soil pollution, *Carabidae*, *Staphylinidae*, *Formicidae*, *Oribatida*, biomarkers of environmental pollution

The effect of oil derivative pollution is one of the problems difficult to asses due to a complexity of these substances and their considerable mobility. They may cause acute and long lasting toxic effects [1]. The outcomes of this kind of pollution (mainly polycyclic aromatic hydrocarbons) were quite thoroughly researched for aquatic invertebrates. These substances may cause cell damage, lower immunity, they may lead to disturbances in the development and osmoregulation, etc. [2, 3].

Soil fauna is frequently used as an indicator of the extend of the environment degradation [4], however there is few data concerning the effect of oil derivatives on

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this animal group. A considerable diversification both in PAH metabolizing effectiveness and in their accumulation by various land invertebrate groups was revealed [5]. Usually, within a short period of time since the soil contamination either total damage of arthropod population or considerably limited occurrence may be observed. The length of time after which the polluted areas become re-settled depends on the kind of pollution, the speed of remediation process and on the invertebrate species.

The research aimed to answer the question whether any differences could be discernible in the species structure of the epigeal fauna between the polluted area and control (unpolluted area) after 2–3 years since the moment of the environment pollution by oil derivative substances.

Material and methods

The experiment was conducted in Czyżów village at the section of national road No. 4, where a road accident of a fuel cistern carrying crude oil happened in 2004. In result 12 000 dm³ of toxic substance spilled into the ground. The event was classified to class 4, ie to the events posing a grave environmental emergency. In result of a major emergency response action carried out on 5–8 April 2004 about 6 Mg of water and oil emulsion was gathered. It was estimated that the total area in need of reclamation was 3980 m². This terrain was bioremediated “in situ” using Trigger – 2R technique for fast liquidation of pollution carried out on the spot by enzymes and bacteria specialized in oil derivative biodegradation to required soil standards.

The insects were trapped during the May–August 2006 and March–June 2007 periods. In order to determine the course of soil arthropod succession in time, 8 Barber traps were placed on the whole analyzed area (4 in the contaminated area and 4 in the control – unpolluted area). Because of group occurrence in a given area, which is characteristic for epigeal fauna, the control area was designed close to the polluted area and comparability of the environmental elements (kind of vegetation, distance from the road, etc.) was maintained. The trap was a glass jar dug into the ground so that its upper edge was even with the soil surface. The traps were protected against rainwater by plastic roofs. They were emptied between every 7 and 10 days. The obtained fauna material was classified to orders and families and in case of *Col.*, *Carabidae* beetles to species or gender according to Freude, Harde and Lohse [6]. Collected data were subjected to one factor ANOVA and the means were verified by Duncan’s test at $p = 0.05$.

Polluted and control soils were also analyzed with respect to their concentrations of nonpolar aliphatic hydrocarbons, heavy metals and basic elements, and also considering soil pH and texture. The samples were collected on 10.07.2006 and the analyses were conducted in the laboratory of the Regional Chemical-Agricultural Station in Krakow and in the laboratory of the Malopolskie Provincial Inspectorate for Environmental Protection in Krakow. The results were presented in Tables 1–3.

Table 1

Contents of basic elements and heavy metals in contaminated and control soils

Area of sample collection	Soil mechanic group	pH in KCl	Content per mg/100 g of soil			Content per mg/kg d.m. soil				
			P ₂ O ₅	K ₂ O	Mg	Pb	Cd	Zn	Cu	Ni
Polluted soil	IV	7.24	4.3	7.7	> 15.0	31.84	0.78	103.20	18.67	17.22
Control soil	IV	6.43	2.7	3.7	> 15.0	32.07	1.17	123.26	18.23	17.67

Table 2

Percent content of fractions in the analyzed soil

Percent fraction content			
< 2 μm	2–20 μm	20–50 μm	50–2000 μm
4.87	35.18	33.60	26.34

Table 3

Content of nonpolar aliphatic hydrocarbons

Analyzed indicator	Polluted soil	Control
Nonpolar aliphatic hydrocarbons [mg/kg d.m.]	589.9	246.9

Higher content of aliphatic hydrocarbons in the polluted soil indicates that the terrains has not been completely cleared. However, the level of these substances two years after the event was already over 200 times lower than on the day of the accident (data MPIEP). Heavy metal contents in the soils from both analyzed areas were similar.

Results and discussion

A total of 1807 invertebrate specimens were trapped in 2006, of which 905 in the polluted area. 3496 specimens were caught in 2007 (1603 in the control area and 1893 in the polluted area). One of the most numerous invertebrate groups of fauna were arachnids. Two years after the catastrophe no significant differences were observed in total numbers of arachnids between the polluted and control areas, whereas a year later significantly more arachnids were trapped in the polluted area (Table 4). Former investigations did not register any negative effect of oil derivative substances, such as petrol or diesel oil (dosed 2 dm³/m²) on arachnid population numbers. Seasonally even larger numbers of these invertebrates were trapped in the petrol polluted area than on the control [7]. On the other hand, a negative effect was noted for diesel oil [8]. *Acari*, *Oribatida* are one of dominant groups among the soil mezofauna. Due to their species

Table 4

Representatives of epigeal fauna in control soil and in soil polluted with oil derivatives

Anthropoda	Mean number of caught invertebrates specimens/trap/week			
	Control		Polluted area	
	2006	2007	2006	2007
<i>Carabidae</i> – total	1.00 a	3.86 a	1.10 a	3.00 a
<i>Bembidion</i> sp.	—	1.20 a	—	1.02 a
<i>Pterostichus</i> sp.	0.38 a	0.80 a	0.52 a	0.40 a
<i>Harpalus</i> sp.	—	0.93 a	—	0.94 a
<i>Amara</i> sp.	—	0.31 a	—	0.30 a
<i>Agonum sexpunctatum</i> (L.)	0.10 a	0.18 a	0.08 a	0.21 a
<i>Carabus cancellatus</i> (Illig)	0.25 a	0.20 a	0.15 a	0.09 a
<i>Ophonus pubescens</i> (Mull.)	0.07 a	0.09 a	0.05 a	0.04 a
<i>Carabidae</i> larvae	0.18 a	0.42 a	0.05 a	0.26 a
<i>Staphylinidae</i>	0.13 a	1.62 a	0.18 a	1.09 a
<i>Formicidae</i>	0.60 a	1.96 a	0.50 a	4.02 a
<i>Collembola</i>	1.98 a	8.06 a	3.28 a	9.30 a
<i>Arachnida</i> – total	7.07 a	8.51 a	6.82 a	13.68 b
<i>Oribatida</i>	2.67 b	1.58 a	1.05 a	0.47 a

* means in lines for individual year marked with different letter are statistically different at $p = 0.05$

abundance they are considered as potentially good bioindicators of habitat quality and human impacts upon the environment [9]. Among the soil invertebrates they are considered as one of the most sensitive to the presence of eg heavy metals, which at high concentrations cause a decrease in density and diversity of these mites [10]. Almost twice greater amounts of these arachnids were caught on the control than in the polluted area in 2006. A year later larger numbers of these invertebrates were found on the control (differences ranged within an experimental error). No statistically significant differences in mean seasonal numbers of trappings between the control and polluted areas were assessed for other numerous present groups of invertebrates, such as *Col.*, *Carabidae*, *Col.*, *Staphylinidae* beetles, *Hym.*, *Formicidae* or *Collembola* (Table 4). Visibly higher numbers of these representatives of epigeal fauna were trapped in 2007. Former investigations on the influence of oil derivatives on the occurrence of beneficial *Col.*, *Carabidae* beetles revealed that a negative effect of soil contamination with oil derivatives, such as petrol, diesel oil and used engine oil (applied in a dose of $2 \text{ dm}^3/\text{m}^2$) persisted for the period of at least 4 months since the moment of contamination. The response of individual *Carabidae* species was also diversified. Repellent effect of oil derivative substances was longer lasting in case of species with smaller bodies (*Amara*

sp., *Bembidion* sp.) [11]. The same investigations determined that *Formicidae* may be sensitive biomarkers of the environmental pollution with oil derivatives. Their negative reaction to pollutant presence was observed in all years when the research was conducted [12]. Obviously negative quantitative reaction under conditions of oil derivative pollution was registered also for *Collembola* [7].

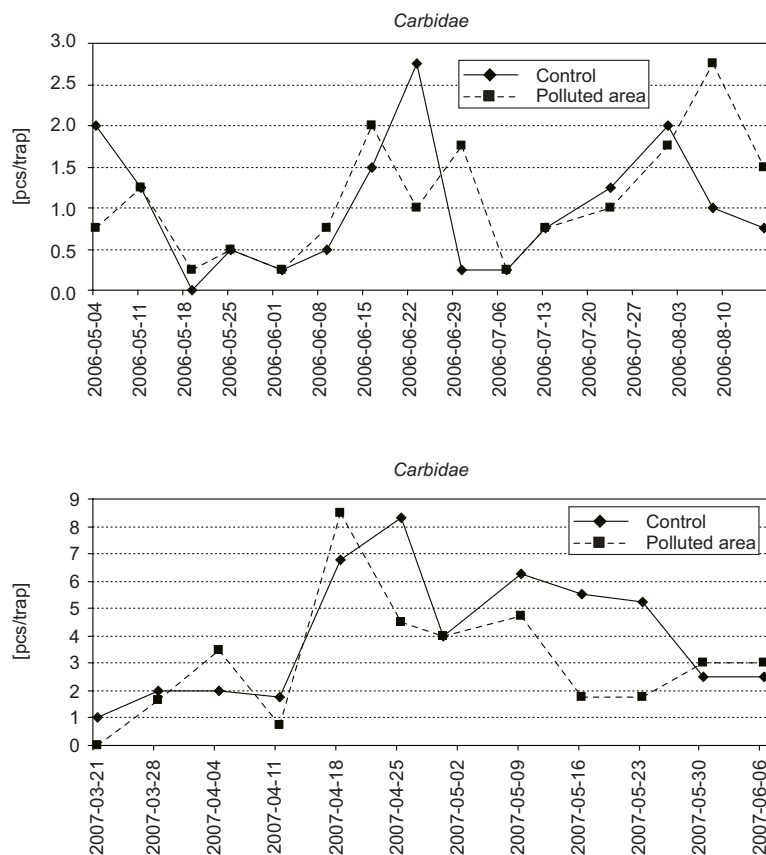


Fig. 1. Dynamics of *Col.*, *Carabidae* beetles occurrence under conditions of control (unpolluted) soil and in soil polluted with oil derivatives. Means for respective dates marked with different letters are statistically different at $p = 0.05$. Marking was used only if statistical differentiation existed, on the other observation dates differences were insignificant

The course of dynamics of *Carabidae* occurrence in both analyzed areas was similar. No statistically significant differences in the numbers of trappings on individual dates were registered between the control and oil polluted area (Fig. 1). However, if we follow the dynamics of occurrence of most numerously represented genera of beetles from this family, a seasonal decrease in the numbers of trappings in the polluted area is visible even in 2007. It refers to beetles of *Pterostichus* sp., *Bembidion* sp. and *Harpalus* sp. genera (Fig. 2–4).

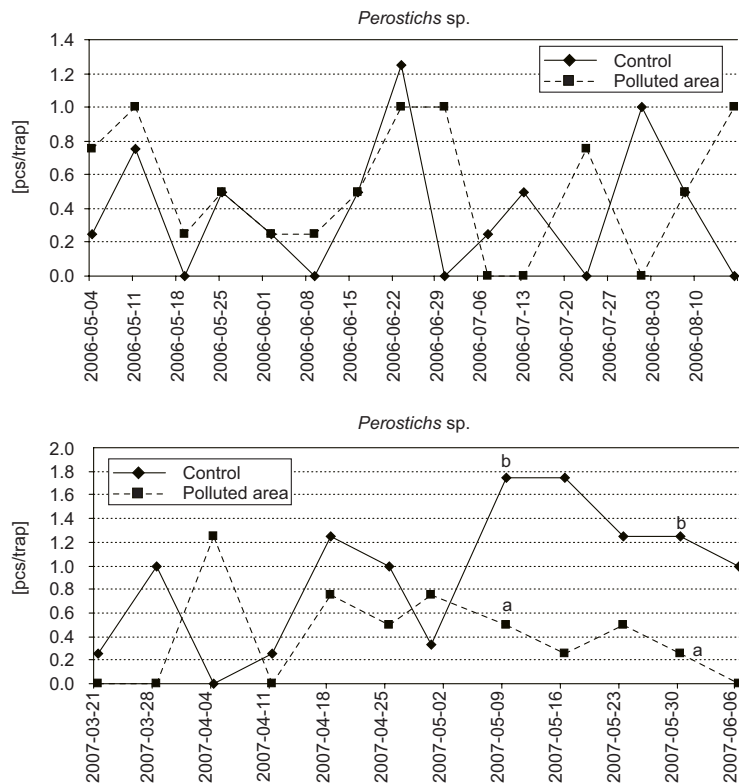


Fig. 2. Dynamics of *Pterostichus* sp. (*Col.*, *Carabidae*) beetles occurrence under conditions of control (unpolluted) soil and in soil polluted with oil derivatives. Means for respective dates marked with different letters are statistically different at $p = 0.05$. Marking was used only if statistical differentiation existed, on the other observation dates differences were insignificant

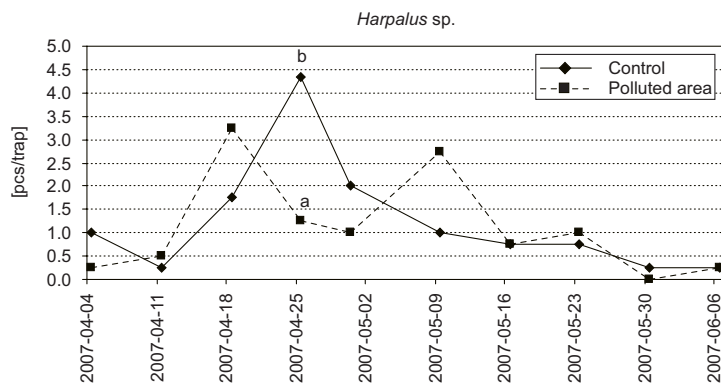


Fig. 3. Dynamics of *Harpalus* sp. (*Col.*, *Carabidae*) beetles occurrence under conditions of control (unpolluted) soil and in soil polluted with oil derivatives. Means for respective dates marked with different letters are statistically different at $p = 0.05$. Marking was used only if statistical differentiation existed, on the other observation dates differences were insignificant

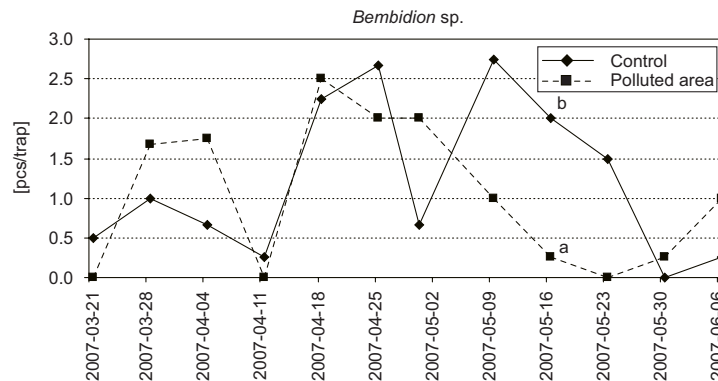


Fig. 4. Dynamics of *Bembidion* sp. (*Col.*, *Carabidae*) beetles occurrence under conditions of control (unpolluted) soil and in soil polluted with oil derivatives. Means for respective dates marked with different letters are statistically different at $p = 0.05$. Marking was used only if statistical differentiation existed, on the other observation dates differences were insignificant

Conclusions

1. Three years after the moment of pollution no negative effect on the occurrence of a majority of epigeal invertebrates was visible. However, a decrease in the numbers of beneficial *Bembidion* sp., *Pterostichus* sp. and *Harpalus* sp. may be noticed seasonally.

2. Two years after the moment of pollution a persistent decline in the numbers of caught *Oribatida* may be observed.

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ODDZIAŁYWANIE WYCIEKU ROPOPOCHODNYCH NA BEZKRĘGOWCE NAZIEMNE

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Abstrakt: Celem badań było uzyskanie odpowiedzi na pytanie, jak długo od momentu zanieczyszczenia środowiska substancjami ropopochodnymi można mieć do czynienia z oddziaływaniem tych związków na faunę naziemną i glebową.

Doświadczenie zostało przeprowadzone w latach 2006–2007 w miejscowości Czyżów przy odcinku drogi krajowej nr 4, gdzie w 2004 r. miał miejsce wypadek cysterny przewożącej surową ropę naftową, czego efektem był wyciek do gruntu 12 000 dm³ substancji toksycznej. Przeprowadzono rekultywację zanieczyszczonego obszaru metodą bioremediacji “In situ” w technologii szybkiej likwidacji skażeń Trigger-2R, tj. realizowaną na miejscu skażenia przez wyspecjalizowane w biodegradacji substancji ropopochodnych enzymy i bakterie, do wymaganych standardów jakości gleby.

Wraz z upływem czasu od momentu skażenia gleby ropopochodnymi zmniejsza się ich toksyczne działanie na poszczególne grupy bezkręgowców. Po upływie 3 lat od momentu zanieczyszczenia można stwierdzić brak negatywnego wpływu na występowanie większości grup bezkręgowców naziemnych. Okresowo można jednak zaobserwować zmniejszenie liczebności pożytecznych chrząszczy z rodzajów *Bembidion* sp., *Pterostichus* sp. i *Harpalus* sp. Po upływie 2 lat od momentu zanieczyszczenia można zaobserwować nadal utrzymujące się zmniejszenie liczebności odłowów mechowców.

Słowa kluczowe: ropopochodne, zanieczyszczenie gleby, *Carabidae*, *Staphylinidae*, *Formicidae*, *Oribatida*, biomarkery zanieczyszczenia środowiska

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TRACE ELEMENT RATIOS IN PLANTS AS INDICATORS OF ENVIRONMENTAL HAZARDS

STOSUNKI PIERWIASTKÓW ŚLADOWYCH W ROŚLINACH JAKO WSKAŹNIKI ZAGROŻEŃ ŚRODOWISKOWYCH

Abstract: Study was carried out on 12 traffic circles in Lublin at four sites of every circle. The 28 element ratios on the studied roundabouts in a system of particular element to the subsequent ones were calculated and statistically worked out by variability and shape of experimental data distribution. Application of trace elements ratios in plants for evaluation of natural environment and environmental hazards may be considered as an important method of scientific and practical usefulness. The largest number of elements in plants should be determined when analyzing the state of environment. Meanwhile element ratios in the plants can be used as indices of anthropopression (an anthropopressure) and as the factors of the influences on the natural environment. However, not every influence is the pressure, though every pressure is the influence. The English terms anthropopression or anthropopressure mean human impact on the environment.

Keywords: anthropopression, anthropopressure, traffic circles (roundabouts), sward, trace elements, element ratios, environmental hazard

The occurrence of elements in the natural environment can provide important information about the influence of the civilization on the condition of the natural environment. That is why, determination of the content of elements in the soils and plants in the near road tracks environment were the object of numerous studies [1–7].

The content of elements are expressed in the unit of the mass or the unit of the amount of substance. There are the proper way of defining the content of elements, however the influence of elements on live organisms it is the completely different problem, because the elements influence the natural environment-essentially through the amount of atoms or ions. Elements are the special form of the substance and the every element has the definite molar mass and specific proprieties. So, the content of elements and the ratio of elements should define on the basis on the amount of

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substance, specially in environmental problems or the quality of the nature consideration.

The tests of the evaluation of the state and the hazard of urban environment on the basis on the unit of mass as well as units of amount of substance in soil or sward on traffic circles were also undertaken [8–11].

The aim of the investigations were calculated of the trace element ratios in the sward on traffic circles and the test of the qualification which could be the practically useful to the evaluation of hazard in the urban environment.

Methods

Study was performed on traffic circles in Lublin, Poland. Plant samples were taken from 12 traffic circles in 2000 and 2001 at four sites of every circle distant 1 m away from the circle edge. Plant samples consisted of the sward, ie aboveground parts of mainly grass species. Following trace elements were determined in the samples after digestion in concentrated sulfuric acid with addition of perhydrol at the end of process: Fe, Mn, Zn, Cu, Cr, Ni, Cd and Pb. Elements were determined by means of AAS methods applying Hitachi Z-8200 with Zeeman's polarization. Determinations of the elements were made in four replications in both years of study.

The contents of trace elements in sward on the unit of mass were recently published and statistically processed suitably to considered problems [9]. The results of trace element content in the sward on the traffic circles as the data were re-calculating into element ratios on the basis amount of substance unit. Trace element molar ratios in the sward were systematically calculated as a ratio of given element to subsequent elements and were statistically processed applying variance analysis, and were taken into account in statistics by the variability and shape of experimental data distribution.

Results

The plant analysis in environmental investigations is applied wide and has the specific methodical conditions [12], and determination of the trace elements are practically useful information in the agricultural and environmental human activity [2, 13, 14].

The sequence of the elements content in the author results, in sward on the studied roundabouts was $Fe > Zn > Mn > Cr > Cu > Cd > Ni > Pb$ [10], and in comparison with investigation in consideration on grasslands localized along traffic routes in the sward as fodder the element sequence were a little different, and the elements content were lower [3].

Only within plant analysis and in reference to the state and evaluation of natural environment, following questions may be asked: what would be a proper attempt to ratio composition idea? Or maybe more complex ratios including many elements in a single formula or only two of them would be better? Such a problem was discussed in some publications and it was suggested that ratios of two elements are more suitable for evaluation of natural environment or agrosystem state. However, selection of elements

Table 1
Trace element ratios in the sward on traffic circles

Traffic circle No.	Ratio													
	Fe : Mn	Fe : Zn	Fe : Cu	Fe : Cr	Fe : Ni	Fe : Cd	Fe : Pb	Mn : Zn	Mn : Cu	Mn : Cr	Mn : Ni	Mn : Cd	Mn : Pb	Zn : Cu
1	7.5	6.1	15.6	32.0	31.1	2142.8	705.3	0.8	2.0	4.2	4.1	284.4	93.6	2.5
2	7.6	6.2	23.3	26.8	26.7	875.7	616.8	0.8	3.0	3.4	3.4	114.0	80.3	3.7
3	13.7	10.2	30.3	35.1	42.3	2728.5	668.6	0.7	2.2	2.5	3.0	198.0	48.5	2.9
4	11.3	8.8	27.0	21.7	44.4	1808.3	562.6	0.7	2.3	1.9	3.9	158.9	49.4	3.0
5	15.0	20.2	28.1	22.2	75.1	3989.0	922.4	1.3	1.8	1.4	5.0	265.7	61.4	1.3
6	7.2	8.1	18.2	37.4	29.6	6898.8	553.1	1.1	2.5	5.1	4.0	948.0	76.0	2.2
7	10.8	14.5	39.2	24.6	46.9	10423.7	743.3	1.3	3.6	2.2	4.3	958.0	68.3	2.6
8	21.1	22.2	69.6	46.4	85.6	10332.4	979.9	1.0	2.2	2.1	4.0	489.1	46.3	3.1
9	22.3	19.1	69.3	46.1	85.2	10278.3	974.8	0.8	3.0	2.0	3.8	459.5	43.5	3.6
10	17.3	20.4	56.7	27.0	84.1	9308.8	1095.0	1.1	3.2	1.5	4.8	535.0	62.9	2.7
11	9.4	9.0	16.9	25.0	35.7	4384.0	721.2	0.9	1.7	2.6	3.7	464.0	76.3	1.8
12	6.5	7.1	18.7	29.5	26.6	4696.2	490.1	1.1	2.8	4.5	4.0	720.3	75.1	2.6
Mean ¹	12.4	12.6	34.4	31.1	51.1	5655.5	752.7	0.9	2.5	2.7	4.0	466.2	65.1	2.6
±L ²	±3.4	±3.9	±12.6	±5.4	±15.4	±2304.7	±124.2	±0.1	±0.3	±0.7	±0.3	±182.5	±10.0	±0.4
Variance ³	27.3	35.2	365.0	66.7	537.7	1.2 · 10 ⁷	3.5 · 10 ⁴	0.04	0.3	1.3	0.2	7.5 · 10 ⁴	229.8	0.4
Deviation ⁴	5.2	5.9	19.1	8.1	23.1	3472.9	187.2	0.2	0.5	1.1	0.4	275	15.1	0.6
Skewness ⁵	0.6	0.4	0.8	0.7	0.5	0.2	0.3	0.2	0.2	0.7	0.1	8.5	0.1	-0.3
Oblateness ⁶	-0.9	-1.5	-0.7	-0.6	-1.4	-1.5	-1.1	-1.2	-1.0	-0.8	-0.07	-0.8	-1.0	-0.2
Median ⁷	11.0	9.6	27.5	28.2	43.3	4540.1	713.2	0.9	2.4	2.3	4.0	461.7	65.6	2.6
Variability ⁸	43 %	49 %	57 %	27 %	47 %	64 %	25 %	22 %	23 %	44 %	13 %	61 %	24 %	25 %

Explanations: ¹ Arithmetic Mean; ² Confidence Interval at $\alpha = 0.05$; ³ Variance; ⁴ Standard Deviation; ⁵ Coefficient of Skewness; ⁶ Coefficient of Oblateness; ⁷ Median; ⁸ Coefficient of Variation.

Table 2

Trace element ratios in the sward on traffic circles

Traffic circle No.	Ratio													
	Zn : Cr	Zn : Ni	Zn : Cd	Zn : Pb	Cu : Cr	Cu : Ni	Cu : Cd	Cu : Pb	Cr : Ni	Cr : Cd	Cr : Pb	Ni : Cd	Ni : Pb	Cd : Pb
1	5.2	5.0	350.6	115.4	2.0	1.9	136.8	45.0	0.9	66.8	21.9	68.8	22.6	0.32
2	4.3	4.3	140.8	99.2	1.1	1.1	37.5	26.4	0.9	32.6	23.0	32.7	23.0	0.70
3	3.4	4.1	266.4	65.3	1.1	1.3	89.9	22.0	1.2	77.6	19.0	64.4	15.7	0.24
4	2.4	5.0	204.9	63.7	0.8	1.6	66.8	20.8	2.0	83.0	25.8	40.6	12.6	0.31
5	1.0	3.7	196.9	45.5	0.7	2.6	141.7	32.7	3.3	179.1	41.4	53.0	12.2	0.23
6	4.5	3.6	847.3	67.9	2.0	1.6	377.6	30.2	0.7	184.2	14.7	232.7	18.6	0.08
7	1.6	3.2	715.5	51.0	0.6	1.1	265.4	18.9	1.9	423.5	30.2	222.0	15.8	0.07
8	2.0	3.8	464.6	44.0	0.6	1.2	148.2	14.0	1.8	222.5	21.1	120.5	11.4	0.09
9	2.4	4.4	537.1	50.9	0.6	1.2	148.2	14.0	1.8	222.5	21.1	120.5	11.4	0.09
10	1.3	4.1	454.2	53.4	0.4	1.4	164.1	19.3	3.1	344.1	40.4	110.6	13.0	0.11
11	2.7	3.9	484.2	79.6	1.4	2.1	258.5	42.5	1.4	174.8	28.7	122.4	20.1	0.16
12	4.1	3.7	652.9	68.1	1.5	1.4	250.4	26.1	0.9	158.9	16.5	175.9	18.3	0.10
Mean ¹	2.9	4.0	442.9	67.0	1.0	1.5	173.7	25.9	1.6	180.8	25.3	113.6	16.2	0.20
±L ²	±0.8	0±.3	±140.9	±13.8	±0.3	±0.2	±61.7	±6.4	±0.5	±72.8	±5.4	±42.8	±2.7	±0.11
Variance ³	1.7	0.2	4.5 · 10 ⁴	437.1	0.2	0.2	8.6 · 10 ³	93.5	0.6	1.2 · 10 ⁴	67.2	4.1 · 10 ³	16.5	0.02
Deviation ⁴	1.3	0.4	212.3	20.9	0.4	0.4	93.0	9.6	0.8	109.8	8.1	64.5	4.0	0.01
Skewness ⁵	0.2	0.4	0.2	1.0	0.6	1.1	0.6	0.6	0.8	0.7	0.8	0.5	0.3	1.8
Oblateness ⁶	-1.2	-0.5	-0.9	0.1	-0.9	0.3	-0.3	-0.5	-0.4	-0.1	-0.3	-0.8	-1.2	2.7
Median ⁷	2.5	4.0	459.4	64.5	0.9	1.4	148.2	24.0	1.6	176.9	22.4	115.5	15.7	0.1
Variability ⁸	47 %	13 %	50 %	32 %	51 %	29 %	55 %	38 %	51 %	63 %	33 %	59 %	26 %	86 %

Explanations see Table 1.

for ratio composing should be thorough, which obviously also depends on the issue discussed. Ratios involving two elements, as a simple combination, seem to be the most proper and thus so long list of these ratios can be found in present paper. In the selection of the most suitable ratio, elements that have different reaction towards given properties, natural or civilization conditions resulting from chemical compounds conversion or changes of element valence due to the environment factors, should be taken into account. Molar ratios of eight determined trace elements in a form of a given elements to subsequent element made possible to calculate of 28 ratios which were presented in Table 1 and in the continuation Table 2. They are also the possibilities of the calculation of different ratios by the way calculation the reverse of the given ratio x as the relationship, for example $1 : x$, that is $1 : (\text{Zn} : \text{Ni}) = \text{Ni} : \text{Zn}$.

The analysis of the numerous statistical characteristics of the trace element ratios in the sward on the traffic circles shows, that if take into consideration, for example only, the standard deviation and coefficient of variability may be indicated the most interesting element ratios. The largest stability, it is easy to see in the element ratios on the basis Ni, and there are Mn : Ni, Zn : Ni, Cu : Ni and Cr : Ni they were the best indices to evaluate the environmental hazard in the studied traffic circles.

Conclusions

1. Application of trace elements ratios in plants for evaluation of natural environment state and environmental hazards may be considered as an important scientific and practical usefulness.

2. Possibly the largest number of elements in plants should be determined when analyzing the state of natural environment, meanwhile element ratios can be used for environmental hazard evaluation depending on specific environmental problem.

3. Element ratios of Mn : Ni, Zn : Ni, Cu : Ni and Cr : Ni in the sward were considered as particularly interesting environmental hazard indices on traffic circle, because they may be useful indices to assess of the anthropopression in the urban environment.

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STOSUNKI PIERWIĄSKÓW ŚLADOWYCH W ROŚLINACH JAKO WSKAŹNIKI ZAGROŻEŃ ŚRODOWISKOWYCH

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Abstrakt: Celem podjętych badań środowiskowych było określenie stosunków pierwiastków śladowych w roślinach jako wskaźników oceny stanu środowiska przyrodniczego i zagrożeń środowiskowych. Próbki roślinne pobierano z 12 rond drogowych w Lublinie z czterech miejsc każdego ronda. Obliczono 28 stosunki pierwiastków na badanych rondach drogowych w układzie kolejny pierwiastek z następnymi i opracowano statystycznie miarami położenia, zmienności i kształtu rozkładu danych eksperymentalnych. Uwzględnienie w badaniach środowiskowych stosunków pierwiastków śladowych w roślinach można uznać za praktycznie przydatny sposób w ocenie środowiska przyrodniczego i zagrożeń środowiskowych. Do rozpoznania stanu środowiska przyrodniczego powinno oznaczać się dużą liczbę pierwiastków w roślinach. Natomiast do oceny antropopresji jako zespołu czynników specyficznych oddziaływań człowieka na środowisko można wykorzystywać stosunki pierwiastków w roślinach jako wskaźników środowiskowych. Jakkolwiek nie każde oddziaływanie jest presją, to jednak każda presja jest oddziaływaniem. Angielskie terminy anthropopression lub anthropopressure oznaczają wpływ człowieka na środowisko.

Słowa kluczowe: antropopresja, ronda drogowe, ruń, pierwiastki śladowe, stosunki pierwiastków, zagrożenia środowiskowe

Tomasz KLEIBER¹

**NUTRITIONAL RESOURCES OF SOIL IN THE LOCALITIES
OF MONUMENTAL LARGE-LEAVED LINDEN
(*Tilia platyphyllos f. aurea*) ALLEYS**

**ZAWARTOŚĆ SKŁADNIKÓW W GLEBACH
NA STANOWISKACH ZABYTKOWYCH ALEI LIPY SZEROKOLISTNEJ
(*Tilia platyphyllos f. aurea*)**

Abstract: An estimation was carried out regarding the nutrient resources (macro- and micronutrients), sodium (ballast ion), heavy metals (cadmium and lead), soil reaction and salinity in soil samples taken from the monumental localities of large-leaved linden alleys (*Tilia platyphyllos f. aurea*) in Lubon (Wielkopolska province). It was found that among factors which could deteriorate the appearance (possible chloroses) and health of the studied plants was chemism of soil. The majority of the analysed soils was characterized by a decreased content of phosphorus and at the same time by an excess of potassium, calcium, and magnesium, as well as by the standard content of nitrogen. A high content of calcium in the soil contributed to a deterioration of the mutual quantitative proportion between calcium and magnesium which could have caused some difficulties in the uptake of magnesium, as well as potassium and the majority of micronutrients. Contents of metallic micronutrients (iron, manganese, zinc and copper) were within the range of standard. The determined contents of cadmium and lead did not exceed the admissible norms. In case of the alleys with a higher intensity of road traffic, excessive contents of sodium were found in the soil. However, the salinity of the studied soils was within the admissible range ($EC > 0.4 \text{ mS} \cdot \text{cm}^{-1}$). High content of alkalizing components (calcium, magnesium, potassium, sodium) exerted an influence on the soil reaction which was incorrect from the point of view of plant growth and nutrition, showing a strong alkalization (pH was in the range of 7.30 to 10.95).

Keywords: monumental alleys, soil, nutritive components, soil reaction

In Lubon (a town bordering with Poznan) including about 25 000 inhabitants, lying in the neighbourhood of a post-Evangelical Church devoted to St.Barbara (built in the years 1908–1912), there are seven monumental alleys of large-leaved linden (*Tilia platyphyllos f. aurea*) including totally 462 trees [1, 2]. The age of these monumental trees is estimated for 75–85 years.

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The objective of the presented studies was the estimation of the chemism of soils sampled from underneath the monumental linden trees from the point of view of their salinity (content of water soluble salts) and soil reaction, as well as the nutritive components (macro- and micronutrients), sodium (regarded as a ballast ion) and heavy metals (cadmium and lead). The recognition of the mentioned chemical soil parameters may supply an additional element in the elaboration of a protection program and even a fertilization program for the monumental alleys which could contribute to an improvement of their appearance and health conditions.

Material and methods

The estimation of the nutritive resources of soil (macro- and micronutrients), sodium, heavy metals, soil reaction and salinity in the localities of the monumental large-leaved linden alleys (*Tilia platyphyllos f. aurea*) localized in Luboń (Wielkopolska province) was carried out in the year 2008. In the moment of the nomination of these alleys as nature monuments (in 1995), in the Central Register of Nature Forms Protection, they included 462 trees grown along the following streets in Luboń: E. Bojanowski square (26 trees), 11 Listopada street (88 trees), J. Poniatowski street (89 trees), Lipowa street (94 trees), H. Kollataj street (66 trees), Szkolna street (56 trees) and Klonowa street (14 trees) [1, 2].

Soil samples from the layer of 0–20 cm were taken using Egner's stick, while for the deeper layers (20–40 cm and 40–60 cm), the soil auger was used. Because of an excessive hardness and density of soil, in case of two localities (at 11 Listopada street and on Bojanowski square), no samples were taken from the 40–60 cm layers. The roots of the large-leaved linden reach a depth exceeding 60 cm. Soil samples were taken under healthy, typical and randomly selected trees in the central part of the plantations, in 3 m distance from tree stems. Collected samples were chemically analysed by the universal method according to Nowosielski [3]. Extraction of macronutrients (N-NH₄, N-NO₃, P, K, Ca, Mg, S-SO₄), Cl and Na was carried out in 0.03 M CH₃COOH with a quantitative 1:10 proportion of soil to extraction solution. After extraction, the following determinations were made: N-NH₄, N-NO₃ – by microdistillation according to Bremer in Starck's modification; P – colorimetrically with ammonium vanadomolybdate; K, Ca, Na – photometrically; Mg – by atomic absorption spectrometry (AAS, on Carl Zeiss-Jena apparatus); S-SO₄ – nephelometrically with BaCl₂; Cl – nephelometrically with AgNO₃. Micronutrients (Fe, Mn, Zn and Cu) and heavy metals (Cd and Pb) were extracted from soil with Lindsay's solution containing in 1 dm³: 5 g EDTA (ethylenediaminetetraacetic acid); 9 cm³ of 25 % NH₄ solution, 4 g citric acid and 2 g Ca(CH₃COO)₂ · 2H₂O. Micronutrients and heavy metals were determined by AAS method. Salinity was identified conductometrically as a soil electrolytic conductivity (EC in mS · cm⁻¹), and pH – was determined by potentiometric method (soil : water = 1 : 2) [4].

Results and discussion

Results of soil chemical analyses referring to macronutrients content, pH and salinity are presented in Tables 1A and 1B. On the basis of our studies, one can state that the soil from the linden localities was characterized by a standard content of ammonium nitrogen which decreased with the increasing depth. A probable reason of this phenomenon could have been the washing out of this component caused by its sorption exchange [5]. In the studied soil samples, the determined values of nitrate nitrogen (N-NO_3) generally were slightly lower than those of ammonium nitrogen. This could have been caused by the washing out of nitrate nitrogen – resulting from its poor sorption [5].

In the studied soil profiles, differentiated phosphorus contents were found. The determined contents of phosphorus in the layer of 0–20 cm were distinctly higher in the layers lying lower (20–40, 40–60 cm) (except for the locality at E. Bojanowski square). This is a typical phenomenon occurring in mineral soils resulting, among others, from a greater content of organic matter in the 0–20 cm layer and from the chemical sorption of phosphorus with calcium and magnesium ions which occurred in the soil in excessive amounts [5, 6]. Generalizing, one can state that phosphorus content in some studied localities, particularly in the deeper soil layers, was insufficient ($< 40 \text{ mg P} \cdot \text{dm}^{-3}$) [7].

In the majority of the studied localities, there was an excessive content of potassium, particularly in the 0–20 cm layer. However, there appeared a typical tendency [5], resulting from sorption exchange, to the decrease of potassium in the deeper layers (20–40; 40–60 cm), except for the localities at Szkolna and H. Kołłątaj streets.

Soils in the studied localities were characterized by an excessive content of calcium [6], which was increasing with the increasing depth (exceeding even $5500 \text{ mg Ca} \cdot \text{dm}^{-3}$ in the 20–40 cm layer at Klonowa street). Excessive calcium content is unfavourable from the plant's point of view because it makes difficult the uptake of other nutritive components, among others of potassium, magnesium and micronutrients [6].

In the majority of the studied localities, increased or excessive contents of magnesium were determined. However, one can suppose that this fact exerted a positive effect on plant development by decreasing the mutual proportions between calcium and magnesium. Optimal for the growth and development of plants is the proportion between calcium and magnesium in soil which equals 6–9:1 [6], while the mean proportion from the studied samples – because of an excessive calcium content – was 17.2:1. In case of the majority of the studied localities, there was found a low or very low content of sulphate sulphur (S-SO_4) available to plants.

In consequence of excessive content of alkaline ions (calcium, magnesium, potassium and sodium) and a low content of sulphur, the soil reaction in the studied localities was incorrect: from a neutral one ($\text{pH} = 7.30$) to an alkaline one ($\text{pH} = 10.95$). A probable cause of a strong soil alkalization could have been the use of sodium chloride for ice melting on the road in winter, as well as the strongly alkaline dusts (containing among others: CaO , MgO , Na_2O , K_2O) as a side product from coal combustion in the households [8, 9]. Ash contains from 1.1 to 32.6 % of CaO . Soil alkalization certainly was caused by the production of calcium oxide and calcium

Table 1A
 Content of macronutrients, pH and salinity in the soils of the localities with a higher road traffic intensity

Locality (street)	Depth [cm]	N-NH ₄	N-NO ₃	P	K	Ca	Mg	S-SO ₄	pH (H ₂ O)	EC [mS · cm ⁻¹]
11 listopada	0-20	35.0	26.0	66.9	755.3	3959.8	324.6	84.9	7.32	0.13
	20-40	31.5	35.0	58.1	753.5	4113.2	355.1	67.9	7.30	0.05
Klonowa	0-20	49.0	28.0	81.5	736.0	3488.5	383.3	68.8	10.72	0.17
	20-40	24.5	24.5	4.7	135.3	5680.3	354.2	99.4	8.31	0.03
	40-60	21.0	28.0	7.8	197.4	5113.1	348.5	130.3	8.43	0.05
J. Poniatowski	0-20	24.5	17.5	61.1	730.7	2479.1	327.1	4.8	10.95	0.10
	20-40	28.0	24.5	Tr.	45.4	4103.1	71.4	4.6	8.72	0.03
	40-60	21.0	21.0	Tr.	28.1	4436.6	77.1	2.5	7.94	0.28
E. Bojanowski square	0-20	28.0	21.0	7.8	213.9	2270.7	101.7	7.1	10.77	0.94
	20-40	17.5	78.0	59.9	56.9	1100.1	294.1	4.9	8.01	0.04

Tr. – traces

Table 1 B
Content of macronutrients, pH and salinity in the soils of localities with a lower road traffic intensity

Locality (street)	Depth [cm]	N-NH ₄	N-NO ₃	P	K	Ca	Mg	S-SO ₄	pH (H ₂ O)	EC [mS · cm ⁻¹]
H. Koflataj	0-20	21.0	28.0	16.6	178.9	2964.3	234.9	2.7	7.67	0.03
	20-40	24.5	24.5	12.6	161.6	2643.0	250.0	15.1	10.83	0.20
	40-60	28.0	46.0	11.0	719.0	1566.4	406.0	6.5	7.81	0.03
Lipowa	0-20	14.0	24.5	24.8	128.2	3671.5	299.6	13.1	7.79	0.02
	20-40	10.5	17.5	15.2	110.3	4189.1	288.1	54.3	10.55	0.17
	40-60	14.0	10.5	19.4	62.4	4763.5	285.1	50.4	10.60	0.15
Szkolna	0-20	14.0	36.0	54.4	622.0	4140.7	313.4	8.5	10.66	0.16
	20-40	28.0	24.5	41.9	81.3	4857.4	153.6	19.1	7.64	0.17
	40-60	17.5	38.0	39.9	756.9	1100.1	294.1	4.9	8.02	0.04

hydroxide increasing the soil pH above 7.4 [6, 9]. Soil alkalization limits the availability of nutritive components [10, 11].

In spite of an excessive content of some components (calcium, magnesium, potassium, sodium), the majority of the studied localities – except for the 0–20 cm layer at E. Bojanowski square – was characterized by an admissible level of salinity ($EC > 0.4 \text{ mS} \cdot \text{cm}^{-1}$) [6].

The content of micronutrients, sodium (regarded as a ballast ion) and heavy metals: cadmium and lead (Tables 2A, 2B) were analysed as well. The determined iron contents were within the range of the standard [7]. There was a differentiation in the content of manganese, depending on the road traffic intensity. Excessive contents of manganese ($> 25 \text{ mg Mn} \cdot \text{dm}^{-3}$) [7] were found in the 0–20 cm layer in the locality at 11 Listopada street ($28.3 \text{ mg Mn} \cdot \text{dm}^{-3}$) and in the 20–40 cm layer in E. Bojanowski square ($41.0 \text{ mg Mn} \cdot \text{dm}^{-3}$). The studied localities were characterized by a standard (within the range from 5.0 to $50.0 \text{ mg Zn} \cdot \text{dm}^{-3}$) of zinc content [7]. The highest Zn content was found in the 20–40 cm layer in the locality of Szkolna street ($43.4 \text{ mg Zn} \cdot \text{dm}^{-3}$). Copper content in soil oscillated within the range of optimal contents, from 3 to $10 \text{ mg Cu} \cdot \text{dm}^{-3}$ [7]. Chlorides contents in the studied localities, independent of the road traffic intensity, were similar. In the majority of localities, they were within the admissible range, below $60 \text{ mg Cl} \cdot \text{dm}^{-3}$ [6]. The distinctly highest Cl content among the studied chloride samples was found in the 40–60 cm layer in the localities at Szkolna street ($223.0 \text{ mg Cl} \cdot \text{dm}^{-3}$) and at H. Kołłątaj street ($234.3 \text{ mg Cl} \cdot \text{dm}^{-3}$). Sodium content – regarded as ballast ion – in case of streets with a less intensive road traffic were within the admissible range ($< 60 \text{ mg Na} \cdot \text{dm}^{-3}$). However, they were distinctly higher in localities with intensive road traffic. The highest content of sodium was determined in the 40–60 cm layer in the locality at Klonowa street ($352.5 \text{ mg Na} \cdot \text{dm}^{-3}$). A probable reason of the excessive content of this ballast component was the use of the sodium chloride in winter for melting ice and snow layers. Sodium as a univalent cation exerts an unfavourable effect on soil structure. It destructs the crumble structure of soil which deteriorates the physical properties of soils and it can cause some disturbances in plant growth. In all studied localities, similar cadmium and lead values were found in soil and they were contained within the admissible limits [12].

Furthermore, in the studied localities, an excessive density of soil in its deeper layers (20–40 cm and 40–60 cm) was observed, as well as an increased soil dispersion in the 0–20 cm layer (in case of a higher road traffic indicating deteriorated air–water relations exerting a negative effect on the general plant conditions [9, 13]. Excessive soil covers around trees with materials which are not permeable or hardly permeable (like street asphalt or pavements) decrease the area in which tree root systems can easily develop [14, 15]. Generally, species of *Tilia* genus are rather more suited for plantation at streets with a less intensive road traffic or in a farther distance from the road [16]. An additional diagnostic instrument which can help in a better recognition of the mutual relations between the chemism of soil and the plants is the analysis of the content of nutritive components (sodium and heavy metals) in leaves sampled from the monumental linden alleys.

Table 2A
 Content of micronutrients (Fe, Mn, Zn, Cu, Cl), sodium and heavy metals (Cd, Pb) in localities with a higher road traffic

Locality (street)	Depth [cm]	mg · dm ⁻³									
		Fe	Mn	Zn	Cu	Cl	Na	Cd	Pb		
11 Listopada	0-20	57.5	11.9	40.4	3.1	138.2	327.2	0.10	3.6		
	20-40	56.5	28.3	37.6	1.8	145.3	329.3	0.08	2.6		
Klonowa	0-20	37.3	5.3	39.7	4.0	> 30.0	274.2	0.12	4.2		
	20-40	32.2	6.4	23.1	3.3	> 30.0	109.5	0.12	3.6		
	40-60	31.7	8.8	27.2	1.6	45.6	352.5	0.06	2.6		
J. Poniatowski	0-20	52.9	4.4	17.4	4.4	> 30.0	250.2	0.09	3.8		
	20-40	74.8	6.0	17.9	3.6	> 30.0	100.5	0.09	4.3		
	40-60	79.1	5.2	19.1	4.1	> 30.0	137.1	0.10	4.3		
E. Bojanowski square	0-20	95.1	18.1	23.5	3.0	55.5	43.8	0.11	4.2		
	20-40	135.5	41.0	17.2	2.4	> 30.0	223.0	0.10	3.6		

Table 2B
 Content of micronutrients (Fe, Mn, Zn, Cu, Cl), sodium and heavy metals (Cd, Pb) in localities with a lower road traffic

Locality (street)	Depth [cm]	mg · dm ⁻³									
		Fe	Mn	Zn	Cu	Cl	Na	Cd	Pb		
Lipowa	0-20	45.6	4.4	29.6	3.3	30.1	> 30.0	0.15	4.3		
	20-40	42.9	5.4	29.8	3.9	32.5	> 30.0	0.14	4.3		
	40-60	44.2	5.2	25.1	3.6	36.8	> 30.0	0.12	4.2		
Szkolna	0-20	30.7	3.8	15.8	2.5	185.8	> 30.0	0.10	3.5		
	20-40	40.6	3.4	43.4	3.4	63.1	> 30.0	0.16	4.2		
	20-40	35.5	4.0	17.2	2.4	223.0	> 30.0	0.10	3.6		
H. Kofłataj	0-20	60.4	4.8	29.6	4.4	41.0	55.9	0.13	4.0		
	20-40	74.9	4.8	28.6	4.7	44.4	35.7	0.15	3.7		
	40-60	80.8	6.2	24.3	4.3	234.3	> 30.0	0.13	4.0		

Summing up, one can state that it is advisable to apply a fertilization with magnesium (in the form of magnesium sulphate) in order to decrease the Ca:Mg proportion which should also increase the low level of sulphur in soil. It would be also beneficial to apply nitrogen fertilization (eg application of ammonium phosphate) in the spring period. Furthermore, it is asolutely necessary to stop using NaCl for melting snow layers in winter and to replace this treatment with the ecological CaCl₂ which can remove the excess of sodium from the soil by phytoremediation by plants. A beneficial action is also the tendency to use gas instead of using coal for house heating because it would decrease the amounts of alkalizing dusts. One can expect that after the consideration of the above suggestions, there will appear biological results improving the growth and development of the monumental linden alleys.

Conclusions

1. The studied soils were characterized by an insufficient content of phosphorus and at the same time by an excessive content of potassium, calcium, manganese and a standard content of nitrogen.

2. High content of calcium in soil exerted an influence on the deterioration of the mutual quantitative proportion between calcium and magnesium showing an average value of 17.2:1. An excessive wide proportion between these components causes impediments in the uptake of magnesium, as well as of potassium and micronutrients (ion antagonism).

3. Standard contents of metallic micronutrients (iron, manganese, zinc and copper) were determined in the soil.

4. Excessive sodium content in the soil of localities with a higher intensity of road traffic were shown. The studied soils were characterized by cadmium and lead content within the admissible range.

5. Salinity of the studied soils was within the admissible range ($EC > 0.4 \text{ mS} \cdot \text{cm}^{-1}$). Soil reaction was neutral to strongly alkaline (pH was within 7.30–10.95) which could have been an impediment in plant nutrition with magnesium, potassium and the majority of micronutrients.

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ZAWARTOŚĆ SKŁADNIKÓW W GLEBACH NA STANOWISKACH ZABYTKOWYCH ALEI LIPY SZEROKOLISTNEJ (*Tilia platyphyllos f. aurea*)

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Abstrakt: Dokonano oceny zasobności w makro- i mikroelementy, sód (jon balastowy), metale ciężkie (kadm i ołów), odczyn oraz zasolenia gleb pobranych ze stanowisk zabytkowych alei lipowych (*Tilia platyphyllos f. aurea*) w Luboniu (województwo wielkopolskie). Wykazano, że wśród czynników mogących powodować pogorszenie wyglądu (ewentualne chlorozy) i zdrowotności roślin jest chemizm gleby. Większość analizowanych gleb charakteryzowała się zmniejszoną zawartością fosforu, przy jednoczesnym nadmiarze potasu, wapnia i magnezu oraz standardowej zawartości azotu. Duża zawartość wapnia w glebie wpływała na pogorszenie wzajemnych relacji ilościowych między wapniem a magnezem, co powodować mogło utrudnienia w pobieraniu magnezu, a ponadto potasu i większości mikroelementów. Zawartości mikroelementów metalicznych (żelaza, manganu, cynku i miedzi) mieściły się zakresie standardowym. Oznaczone zawartości kadmu i ołowiu nie przekraczały dopuszczalnych norm. W przypadku alei o większym natężeniu komunikacyjnym wykazano nadmierne zawartości sodu w glebie. Zasolenie badanych gleb mieściło się jednak w zakresie dopuszczalnym ($EC > 0,4 \text{ mS} \cdot \text{cm}^{-1}$). Duża zawartość składników alkalinizujących (wapnia, magnezu, sodu, potasu) wpływała na odczyn gleb, który był wadliwy z punktu widzenia wzrostu i żywienia roślin, wykazując silną alkalizację (pH w zakresie 7,30–10,95).

Słowa kluczowe: zabytkowe aleje, gleba, składniki pokarmowe, odczyn

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ALUMINUM, LITHIUM, AND COBALT CONTENTS IN ORGANIC MATERIALS OF DIFFERENT ORIGINS

ZAWARTOŚĆ GLINU, LITU I KOBALTU W MATERIAŁACH ORGANICZNYCH RÓŻNEGO POCHODZENIA

Abstract: The study included bovine manure, bovine manure composts, bovine manure vermicomposts, sewage sludge and peat vermicomposts, vermicomposts with sewage sludge, peat, and poultry droppings addition, as well as mushroom substrate. Mean aluminum, lithium, and cobalt contents were as follows (in $\text{mg} \cdot \text{kg}^{-1}$ d.m.): bovine manure 755, 18.30, and 0.76, manure composts 2775, 16.3, and 1.15, manure vermicomposts 1039, 21.9, and 1.03, sewage sludge vermicomposts with peat 7135, 5.96, and 3.77, sewage sludge, peat, and poultry droppings vermicomposts 6187, 5.58, and 3.19, mushroom substrate 1686, 26.3, and 6.42.

Keywords: compost, vermicompost, mushroom substrate

Concentration, mechanization, and specialization of plant and animal production, progressive development of city agglomerations along with more strict sanitary requirements make that more and more biomass is shifted from agricultural ecosystems to urbanized ones, where they are accumulated as post-processing wastes. Among many ways to neutralize wastes, namely organic, their agricultural utilization is probably the most common. Increasing number of new and modernized sewage treatment plants in Poland causes that enormous amounts of sewage sludge with varied chemical composition and different levels of toxicity are disposed to the environment every year [1]. Neutralization of sewage sludge at maximum utilization of nutrients contained along with meeting the environment protection requirements, is a main purpose of searching for efficient ways of their processing [2].

Composting and vermicomposting of organic wastes may be a solution for part of wastes processing problem, and at the same time fertilizers with advantageous physico-chemical properties can be produced [1, 3–5].

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The interests in mushroom production have recently grown in Poland, namely in the Siedlce region, which makes that larger quantities of mushroom substrate (or after the composting process – mushroom compost) are disposed to a subsoil. The mushroom substrate is a source of humus and nutrients for plants, it is characterized by good consistency and tolerated ground-like scent. Taking all these into account, Kryńska et al [6] recommended its utilization as an organic fertilizer. Due to the lack of wider reports referring to rational opportunities of utilizing that waste material, the need to undertake studies within that scope.

The study aimed at determining the aluminum, lithium, and cobalt contents in selected organic waste materials of different origin.

Material and methods

Experiments included the following organic materials:

- A – fresh bovine manure – 9 samples;
- B – composts made of bovine manure (composted for 2 and 4 months) – 6 samples;
- C – vermicomposts made of bovine manure (vermicomposted for 2 and 4 months) – 6 samples;
- D – vermicomposts made of sewage sludge (75 %) and peat (25 %) (vermicomposted for 2 and 4 months) – 6 samples;
- E – vermicomposts made of sewage sludge (75 %), peat (12.5 %), and poultry droppings (12.5 %) (vermicomposted for 2 and 4 months) – 6 samples;
- F – mushroom substrates – 18 samples.

Fresh bovine manure, sewage sludge from a mechanical-biological municipal sewage treatment plant in Siedlce, tall peat, and droppings from hatching hens were the main substrates for composts and vermicomposts production. After initial preparation, these materials were mixed in appropriate proportions and subjected to composting and vermicomposting by *Eisenia fetida* (Sav) earthworms.

Vermicomposts used in the present study were achieved by applying technology given in a patent by Kalembasa et al [7]. Under laboratory conditions (20–25 °C), corresponding organic mixtures were placed in boxes of 20 dm³ each and wetted to maintain the optimum humidity of 70–75 % (by weight). After several days of preliminary decomposition (to remove the ammonia excess), the acidity of the substrate was adjusted to pH 6.8–7.2 using calcium carbonate. Then, *Eisenia fetida* earthworms were introduced to such prepared subsoils. Two and four months later, earthworms were removed and achieved vermicomposts were used for further studies.

The mushroom substrate samples (mushroom compost) were collected from several mushroom-producing farms near Siedlce. All organic material samples (bovine manure, composts, vermicomposts, and mushroom substrate) were dried at 105 °C and ground.

To determine the contents of selected elements, the samples were combusted in a muffle furnace at 450 °C. Digested material was flooded in crucibles (placed on a sand bath) with hydrochloric acid solution (HCl : H₂O = 1:1) to decompose carbonates and separate silicates. Obtained chlorides were transferred using 10 % HCl solution into the

measuring flask of 100 cm³ capacity by separating silicates on a filter paper. Such prepared solutions were subjected to determinations for Al, Li, and Co contents by means of emission atomic spectrometry combined with inductively coupled plasma (ICP-AES) on OptimaRL device (Perkin Elmer).

Results and discussion

Contents of determined elements in analyzed organic materials can be ordered in a following sequence [mg · kg⁻¹]: Al (604–8490) > Li (3.36–27.1) > Co (0.56–5.67).

The highest mean aluminum concentration (Table 1) was found in vermicomposts made of the sewage sludge with peat addition (D) – 7135.0 mg · kg⁻¹ and peat plus poultry droppings addition (E) – 6187.5 mg · kg⁻¹. Aluminum level in vermicomposts made of sludge and peat (D) oscillated from 5150 to 8490 mg · kg⁻¹, while in vermicomposts made of sludge, peat, and droppings (E) from 3760 to 8070 mg · kg⁻¹ at the variability coefficients of 15.6 % and 24.7 %, respectively.

Table 1

The content of aluminium [mg · kg⁻¹] in analysed different waste organic materials

Organic materials	The content of aluminium [mg · kg ⁻¹]				
	Mean	Minimum	Maximum	Standard deviation	Variable coefficient
	[mg · kg ⁻¹]				[%]
A	755	604	906	151	20.0
B	2775	1010	4540	1123	40.4
C	1039	658	1230	232	22.4
D	7135	5150	8490	1111	15.6
E	6187	3760	8070	1530	24.7
F	1685	818	2065	456	27.0

Explanations: A – fresh bovin manure, B – compost made of bovin manure, C – vermicompost made of bovin manure, D – vermicompost made of sewage sludge and peat, E – vermicompost made of sewage sludge, peat and poultry droppings, F – mushroom substrate.

Bovine manure (A) contained the least aluminum (755 mg · kg⁻¹) at variability coefficient of 20 %. Its higher content (average) was recorded in composted manure (B) – 2775 mg · kg⁻¹ and vermicomposted manure (C) – 1039.0 mg · kg⁻¹.

The most varied aluminum contents were found in mushroom substrates (F) – 818–1686 mg · kg⁻¹, at mean level 1686 mg · kg⁻¹ and variability coefficient 27 %.

Lithium concentrations in analyzed organic materials greatly varied (Table 2) with mean level from 5.88 in vermicomposts made of sewage sludge, peat, and poultry droppings (E) to 26.3 in mushroom substrates (F). The variability coefficient for lithium concentrations in these materials amounted to 19.4 and 24.5 %, respectively.

Table 2

The content of lithium [$\text{mg} \cdot \text{kg}^{-1}$] in analysed different waste organic materials

Organic materials	The content of lithium [$\text{mg} \cdot \text{kg}^{-1}$]				
	Mean	Minimum	Maximum	Standard deviation	Variable coefficient
	[$\text{mg} \cdot \text{kg}^{-1}$]				[%]
A	18.3	17.4	19.2	0.90	4.92
B	16.3	3.36	25.3	7.81	47.9
C	21.9	18.0	27.1	3.34	15.2
D	5.96	4.26	8.22	1.30	21.8
E	5.88	3.98	6.83	1.14	19.4
F	26.3	4.30	17.2	6.46	24.5

Lithium levels in fresh bovine manure (A), composted manure (B), and vermicomposted manure (C) reached from $16.3 \text{ mg} \cdot \text{kg}^{-1}$ (B) to $21.9 \text{ mg} \cdot \text{kg}^{-1}$ (C), although variability coefficient value was the lowest for (A), and the highest for (B) (4.92 % and 47.9 %, respectively).

Among studied organic materials, the highest mean cobalt concentrations ($6.42 \text{ mg} \cdot \text{kg}^{-1}$) and its widest differentiation (from 0.62 to $16.3 \text{ mg} \cdot \text{kg}^{-1}$) at variability coefficient of 93.6 %, were recorded for mushroom substrate samples (F) (Table 3).

Table 3

The content of cobalt [$\text{mg} \cdot \text{kg}^{-1}$] in analysed different waste organic materials

Organic materials	The content of cobalt [$\text{mg} \cdot \text{kg}^{-1}$]				
	Mean	Minimum	Maximum	Standard deviation	Variable coefficient
	[$\text{mg} \cdot \text{kg}^{-1}$]				[%]
A	0.76	0.62	0.89	0.13	17.1
B	1.15	0.56	2.50	0.78	67.8
C	1.03	0.96	1.11	0.05	4.85
D	3.77	2.92	5.67	1.51	40.0
E	3.19	2.86	3.55	2.35	73.6
F	6.42	0.62	16.3	6.01	93.6

The least cobalt amounts were determined in fresh manure samples (A) $0.76 \text{ mg} \cdot \text{kg}^{-1}$, while slightly more in manure composts (B) and vermicomposts (C) (1.15 and $1.03 \text{ mg} \cdot \text{kg}^{-1}$, respectively). Similar average cobalt concentrations were recorded in vermicomposts made of sewage sludge with peat addition (D) $3.77 \text{ mg} \cdot \text{kg}^{-1}$ as well as peat plus poultry droppings (E) $3.19 \text{ mg} \cdot \text{kg}^{-1}$, at variability coefficients 40.0 and 73.6 %, respectively.

Contents of studied elements in analyzed composts and vermicomposts were similar to those determined by Gašior et al [8], Kalembasa [9], Kostecka and Kołodziej [10], as

well as Kotowska [11], while referring to mushroom substrates – to those found in earlier studies by Kalembasa and Wiśniewska [12].

Conclusion

Analyzed organic materials contained the most aluminum, while the least cobalt. Highest levels of aluminum were found in vermicomposts, whereas lithium and cobalt – in mushroom substrates. The lowest amounts of aluminum and cobalt were determined in fresh bovine manure. In most cases, composting and vermicomposting of manure increased aluminum, lithium, and cobalt contents.

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ZAWARTOŚĆ GLINU, LITU I KOBALTU W MATERIAŁACH ORGANICZNYCH RÓŻNEGO POCHODZENIA

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Abstrakt: Badaniami objęto obornik bydlęcy, komposty z obornika bydlęcego, wermikomposty z obornika bydlęcego, wermikomposty z osadu ściekowego i torfu, wermikomposty z dodatkiem osadu ściekowego, torfu i kurzeńca oraz podłoża po uprawie pieczarek. Średnia zawartość glinu, litu i kobaltu wynosiła odpowiednio ($\text{mg} \cdot \text{kg}^{-1}$ s.m.): w oborniku bydlęcym 755; 18,30 i 0,76; w kompostach obornikowych 2775; 16,3 i 1,15; w wermikompostach obornikowych 1039; 21,9 i 1,03; w wermikompostach z osadu ściekowego z dodatkiem torfu 7135; 5,96 i 3,77; w wermikompostach z osadu ściekowego, torfu i kurzeńca 6187; 5,58 i 3,19; w podłożu popieczarkowym 1686; 26,3 i 6,42.

Słowa kluczowe: kompost, wermikompost, podłoże popieczarkowe

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**ASSESSMENT OF LEAD AND CADMIUM CONTENT
IN FOOD PRODUCTS
IN ACCORDANCE WITH POLISH LAW IN FORCE**

**OCENA ZAWARTOŚCI OŁOWIU I KADMU
W PRODUKTACH SPOŻYWCZYCH
ZGODNIE Z OBOWIĄZUJĄCYM W POLSCE PRAWODAWSTWEM**

Abstract: The research covered the determination of Pb and Cd content in selected fruits and vegetables from the Lower Silesian Province area. The samples contained very low amounts of the pollutants (Cd, Pb) according to the European Commission Regulation (EC) No. 466/2001 of 8 March 2001 setting the maximum allowable levels for some pollutants in foodstuffs. The amounts do not pose health hazard to the cultivated plants and so they do not pose such hazard to living organisms. The random taking of samples of plant products for monitoring purposes shows that plant products from the Lower Silesian Province area satisfy the requirements for foodstuffs. They contain amounts of the toxic metals close to their natural content in cultivated plants.

Keywords: Lead, cadmium, toxicity, maximum allowable levels

In recent years the protection of the natural environment has become an increasingly important social, economic and global issue. Global solutions based on the idea of *sustainable development* are aimed at eliminating or reducing the hazards to the environment, arising from any interference into natural ecosystems. Agenda 21, adopted at the Earth Summit in Rio de Janeiro in 1992 by the governments of most countries, obligates the signatories to action for the improvement of the environment in a systematic way making it possible to monitor and assess the environment using proper tools and indexes [1–3]. As a result of industrial, municipal and transport emissions, waste and sewage disposal, etc., increasing quantities of pollutants and dangerous substances are introduced into the environment. Among them heavy metals pose a very serious danger. As opposed to socially dangerous microbiological contaminations of

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food, which immediately result in poisonings, chemical contaminations rarely cause acute poisonings. They may, however, cause diseases which manifest themselves much later. The largest amounts of metals (as much as 80 %) enter the body with food via the alimentary tract. Estimates of metal uptake in food rations show that over 30 % of the toxic compounds are supplied by vegetables [4, 5].

Besides microelements (highly valuable for human health), also elements having no nutritional value and posing a danger to health (because of their tendency to accumulate in the body) are ingested due to environmental contamination [6].

The consequence of the use of plant protectants and the accumulation of heavy metals products are deficient in natural nutrients, bioelements or vitamins and contain toxic elements (such as lead, arsenic, chromium, cadmium, mercury, nickel, tin, etc.) and other undesirable chemical compounds [6–8].

The main environment compartments from which trace elements pass to living matter are soil, water and air. Trace elements are particularly active and harmful because of their special role in biochemical processes and in the characteristic interactions of ions or chemical compounds as a result of which the biological effect of a given element depends on the occurrence and concentration of other ions or chemical substances. The interactions often disturb the chemical equilibrium in individual organisms or even in the ecosystem, which may lead to undesired biological consequences [4].

Heavy metals and their occurrence in soil

Soil is one of the vital links in the human food chain, which means that each change in its chemical composition brings about significant changes in the chemical composition of plants. Chemical soil pollutants are elements and chemical compounds which being not natural components of soil significantly affect its natural (formed long ago) properties. They may disturb the vegetation of plants and lower crops and the nutritional quality and technological usability of plant materials. Soil chemical contamination can be temporary, cyclic, long-lasting and practically irreversible. Particularly dangerous is soil contamination by such elements as: nickel, mercury, copper, cobalt, cadmium, beryllium and tin [9].

Soil is the main source of trace elements for plants. Trace elements are variously distributed among the particular components of soil, depending on: solubility, sorption, the formation of complex compounds, precipitation, occlusion, diffusion, oxidation, fixation by organic matter and uptake by microorganisms.

In the natural environment soil performs various functions, mainly filtration and buffering, which protect ecosystems against the excessive flow of trace elements into the other compartments of the biosphere [4].

The cycle of elements in soil and their transport to plant cells are highly complicated. They depend on, among other things, the soil pH, redox potential, mineral composition and moisture content, the kind of microorganisms and the abundance of organic compounds [8, 10].

Soil becomes contaminated with chemical compounds as a result of dust fall, sewage run-off and water migration of elements from solid waste heaps. Additional sources of heavy metal pollution are: the chemicalization of agriculture, some plant protectants and the transport and industrial wastes used for soil fertilization. The use of, for example, power plant ash as a mineral fertilizer brings about considerable chemical changes in soil – mainly the Mg and Ca content increases, which is beneficial for plants but at the same time a large load of heavy metals (particularly Pb, Zn and Cu) is introduced into the soil. Heavy metals easily migrate into the soil environment after its acidification [4, 11, 12].

A characteristic manifestation of soil contamination is the slow rate of change of the chemical compounds which do not naturally occur in it. This especially applies to heavy metals in cationic forms and to residues of some pesticides [9].

The soil reaction is one of the determinants of the agricultural usability of soils. In acid soils reduced plant growth, higher heavy metal concentrations and the loss of biological equilibrium are observed. The soil reaction regulates the uptake of nutrients and so it has a direct effect not only on the quality of the crops but also on their quantity. Increased soil acidity activates heavy metals in sparingly soluble compounds and blocks the uptake of beneficial forms assimilable by plants [13–15]. Soil liming is the most effective way of reducing the migration power of the existing and potential soil contaminations with heavy metals. Without improving the soil reaction it is impossible to achieve production objectives [16].

Heavy metals and their occurrence in plant products

Plants assimilate heavy metals occurring in the form of salts dissolved in soil solution or directly from atmospheric precipitation whereby there are differences in the heavy metal content between the aboveground and underground plant parts [17].

Heavy metals from dusts settle on plants, clogging their stomata and thereby reducing light absorption by plants and the rate of photosynthesis. Combined with water they form caustic compounds on the leaf's surface, damage the latter and after they get inside they change the structure of the cytoplasm and upset metabolism. Gaseous pollutants are even more harmful to plants than dusts. Dust pollutants on plants when ingested are harmful to consumers [8, 10].

The mechanism of trace elements uptake by the plant root system is complex, usually being the product of several processes such as cation exchange through the cell membrane, intracellular transport and rhizosphere processes. Ions (eg H^+ , OH^- , HCO_3^-) and different substances released by the roots into the surrounding environment directly affect the mechanism of nutrient uptake. The oxidation or reduction of cations and the reaction of the solutions in the vicinity of roots are major factors in the assimilability of trace elements.

In natural conditions the trace element content considerably varies between species, and even between varieties of plants. The content also depends on the part of the plant and its developmental stage [4, 11].

A common feature of heavy metals, particularly lead and cadmium, is their capacity to accumulate in the body and their long biological half-life causes chronic toxicity whereby they pose extremely serious danger. Heavy metals are intensively taken up by plants growing on acid soils with $\text{pH} < 6.5$ [12].

Heavy metals penetrate into plants from both soil (via roots) and atmospheric dust. In the case of lead and cadmium, the hazard of their uptake from soil persists even after the pollution sources have been removed (the two elements are characterized by very high environmental persistence). Plants store the taken up metals mainly in their roots, but cadmium, being highly mobile, also passes to the aboveground plant parts. The uptake of metals from the substrate is a complex process which depends on many factors, such as the substrate's composition and reaction, the element's chemical form, the species of the plant (its accumulation capacity), the atmospheric conditions and so on. However, the highest toxic substance concentrations are found in sewage and industrial waste. Such substances can also penetrate into soils and ground and surface waters.

Vegetables quickly respond to an increase in the heavy metal content in the environment, increasing the amount of heavy metals in their tissues. Thus they reflect the state of the environment and the potential danger to humans [12, 18].

Cadmium

Cadmium significantly contributes to environmental contamination. Because of its toxicological properties and increasing abundance in the natural environment, it is included among food contaminations which deserve special attention.

The absorption of cadmium compounds by the human body depends on their solubility. Cadmium accumulates mainly in the kidneys and its half-life in the human body is as long as 10–35 years. The kidneys are the organs which are most exposed to the toxic action of cadmium. Cadmium absorbed through the airways has been proved to be carcinogenic [19–21].

For many years cadmium has been on the list of the main environmental contamination factors. In the environment, cadmium occurs in small amounts. It gets into air, soil and other compartments of environment as a result of human activities. Generally, there are two sources of environmental pollution: the production and use of cadmium and other nonferrous metals and the cadmium containing sewage of various origin. Small amounts of cadmium occur in phosphatic fertilizers [22].

Environmental pollution is the main source of cadmium in food. Soil cadmium pollution is dangerous since plants very readily take up cadmium and accumulate it in their roots. Plants can accumulate considerable quantities of cadmium which directly or indirectly (through interactions with other heavy metals) acts toxically on them. Cadmium can also migrate from everyday articles (eg kitchenware) into food [9].

Plants can accumulate cadmium from soil and the industry has considerably contaminated the environment with this element. Cadmium metabolism to a large extent depends on the uptake of zinc, copper and other metals [6].

Cadmium is taken up by plants exceptionally readily, both by the root system and leaves, generally proportionally to its concentration in the environment. The roots of

plants readily take up cadmium in the form of cations Cd^{2+} , hydrated ions or chelates. Cadmium is assimilated by plants regardless of the properties of the soil. The transport of cadmium in plants is also easy but at its increased uptake it is accumulated mainly in roots, even when absorbed through leaf laminae. The exception are plants exposed to heavy atmospheric cadmium precipitation. Then cadmium accumulation in leaves is several times greater than in storage roots (eg carrot, beet). Plants resistant to high cadmium concentration form various protein compounds (phytochelatins) which by fixing this metal neutralize its phytotoxicity [4]. The ready assimilation of cadmium by plants entails a risk that excessive amounts of it will be incorporated into the human diet.

Lead

Lead is one of the dangerous heavy metals that have been more thoroughly researched. Liming and intensive phosphorous (with sulphur addition) fertilization can reduce lead uptake from soil by plants. Lead gets into the body through skin pores, the respiratory system and the alimentary canal and subsequently, into the blood, the bones and the body soft tissues, particularly the liver [6, 19, 21].

Lead is taken up by plants and accumulated mainly in their roots. But it also occurs in the aboveground parts of plants. Acid environment favours the migration of lead from technological containers and facilities into food. Lead acts on plants directly or through interaction with other components. It is highly toxic to animals [9, 15].

The harmful effect of lead on plants manifests itself mainly by photosynthesis, cell division and water balance disorders. The symptoms of toxicity include dark green colouring and withering of leaves and shortening of the roots.

The uptake of lead by roots is a passive process proportional to the occurrence of soluble forms in the substratum. As the lead concentration in the soil solution increases, so does its amount in plants, to a much higher degree in their roots than in their aboveground parts. The rate of lead uptake is determined by the properties of the plants and the soil conditions. The factors which markedly reduce lead uptake are: elevated soil reaction and lowered ambient temperature. Lead taken up by roots is stored in them and its transport to the green parts of the plant is very limited [19, 21].

Legal requirements

The maximum allowable levels (MAL) of heavy metals (Pb and Cd) are included in the Commission Regulation (EC) No. 466/2001 of 8th March 2001 setting the maximum allowable levels for lead (Pb) and cadmium (Cd) content in foodstuffs, section 3 [21]. The maximum allowable levels of lead (Pb) and cadmium (Cd) content in plant products are shown in Tables 1 and 2.

Table 1

MAL of lead (Pb) content in plant products [21]

Product	MAL of lead content [mg/kg of fresh product]
Vegetables, except for cabbage-like vegetables, leafed vegetables, fresh herbs and all mushrooms	0.1
Cabbage-like vegetables, leafed vegetables and all cultivated mushrooms	0.3
Fruits, except for berries and small fruits	0.1
Berries and small fruits	0.2

Table 2

MAL of cadmium (Cd) content in plant products [21]

Product	MAL of cadmium content [mg/kg fresh product]
Vegetables and fruits, except for leafed vegetables, fresh herbs, all mushrooms, stem vegetables, root crops and potatoes	0.05
Leafed vegetables, fresh herbs, root celery and all cultivated mushrooms	0.2
Stem vegetables, root crops and potatoes, except for root celery	0.1

Materials and methods

The aim of this research was to determine the heavy metal (Pb and Cd) content in plant products with regard to the current regulations. Commercial fruits and vegetables, coming from orchards and fields in Lower Silesia were tested for the content of the above contaminants.

The principles of taking up samples for the presence of Pb, Cd and Hg can be found in the Law Gazette No. 120 of 28th May 2004. This area is regulated by item 1257 of the Health Ministry Order of 30th April 2004 concerning the maximum allowable levels of chemical and biological pollutants, additives and processing aiding substances in food and food components or on the surface of food. The procedures and guidelines for taking and preparing samples are included in annex 1 to the Order [23].

Heavy metal content determination

Determination of lead and cadmium content in plant material

Samples for lead and cadmium content determination were mineralized in accordance with the 'Determination of Lead, Cadmium, Copper and Zinc Content in Food Products by the Flame Atomic Absorption Spectrometry Technique' [24].

The method consists in dry mineralizing samples and determining the metal content by the flame atomic absorption spectrometry (FAAS) technique after extracting Pb and Cd complexes from ammonium 1-pyrrolidinedithiocarbamate using methyl isobutyl ketone [24].

Prior to determining the Pb and Cd content the samples were subjected to dry mineralization. For this purpose, the product to be tested was homogenized and 10, 20, 50 g samples (depending on the plant material) were weighed out into quartz evaporating dishes. Since they contained much water (fruits, vegetables), the samples were dried and then carbonized. After incineration the samples were placed in a muffle furnace at a temperature of 250 °C. The temperature was gradually increased (at a step of 50 °C) up to about 400 °C (not exceeding 450 °C, which might result in losses of the elements to be determined). Incineration in the furnace was conducted until white ash was obtained. The residue was dissolved in 5 cm³ of 1 M solution of HNO₃ and heated up on a water bath. Then it was filtered into a 50 cm³ measuring flask and made up with 1 M solution of HNO₃.

30 cm³ of the tested mineralizate, 20 cm³ of deionized water, 100–200 mm³ of bromocresol green were measured out into an extraction flask with a capacity of 100 cm³. After mixing, 3 cm³ of citrate buffer were added, the whole was mixed and titrated with an ammonia solution until the colour changed from yellow to blue. Then again 3 cm³ of the buffer were added and the whole was mixed and heated up. 3 cm³ of 2 % solution of 1-pyrolidinedithiocarbamate were added to the hot solution, the whole was mixed and cooled down to room temperature. Then 4 cm³ of methyl isobutyl ketone were added and the whole was shaken for 0.05 h. Deionized water was added to the flask until the organic layer was in the upper part of the extraction flask neck. Then the organic layer was sucked in and the measurement was performed.

Results and discussion

The studies covered the determination of Pb and Cd content in selected vegetables and fruits coming from the Lower Silesian Province.

Pb and Cd in the product in [mg/kg] were calculated from this formula:

$$X_n = \frac{(C_n - C_{tr.}) \cdot V}{m}$$

where: C_n – the concentration of the element in the mineralizate;

$C_{tr.}$ – the concentration of the element in the reagent test, in µg/cm³;

V – the total mineralizate volume in the tested sample, in cm³;

m – the size of the analytical sample of the tested product, in g.

The arithmetic mean of the results from two simultaneously conducted determinations, differing from each other by no more than 15 % of the lower result, was adopted as the final result.

The results of the chemical analyses of the heavy metal content in the plant products are shown in the tables below.

The lead content in the selected fruit samples and vegetables is shown in Table 3 and Table 4, respectively.

Table 3

Lead content in fruits samples in mg/kg of fresh product

Fruits	Lead (Pb) [mg/kg of fresh product]
Apples	0.002
Peaches	0.000
Nectarines	0.000
Plums	0.000
Apricots	0.008

Table 4

Lead content in vegetables samples mg/kg of fresh product

Vegetables	Lead (Pb) [mg/kg of fresh product]
Soil-grown cucumbers	0.002
Mushrooms (<i>Agaricus</i>)	0.022
Carrots	0.008

No lead content was found in three of the eight tested samples. The other samples contain minimum amounts of the element with regard to the Commission Regulation (EC) No. 466/2001 of 8th March 2001 setting the maximum allowable levels for some pollutants in foodstuffs, section 3 [21].

The cadmium content in the fruit samples and in the vegetable samples is shown in Table 5 and Table 6, respectively.

Table 5

Cadmium content in fruits samples in mg/kg of fresh product

Fruits	Cadmium (Cd) [mg/kg of fresh product]
Apples	0.0000
Peaches	0.0004
Nectarines	0.0004
Plums	0.0024
Apricots	0.0010

Table 6

Cadmium content in vegetables samples in mg/kg of fresh product

Vegetables	Cadmium (Cd) [mg/kg of fresh product]
Soil-grown cucumbers	0.0030
Mushrooms (<i>Agaricus</i>)	0.0092
Carrots	0.0200

No cadmium was found in one of the eight tested samples while in the other samples cadmium content was minimal with regard to the Commission Regulation (EC) No. 466/2001 of 8 March 2001 setting the maximum allowable levels for some pollutants in foodstuffs, section 3.

Conclusions

The research covered the determination of Pb and Cd content in selected vegetables and fruits from the Lower Silesian Province area.

The elements were found to be absent in three of the eight plant material samples tested for Pb and Cd. The other samples contained minimum amounts of the pollutants with regard to the Commission Regulation (EC) No. 466/2001 of 8th March 2001 setting the maximum allowable levels for some pollutants in foodstuffs. The amounts do not pose health hazard to the cultivated plants and so they do not pose such hazard to living organisms.

The random taking of samples of plant products for monitoring purposes shows that plant products from the Lower Silesian Province area satisfy the requirements for foodstuffs. They contain minimum amounts of the toxic metals (close to their natural content in cultivated plants).

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OCENA ZAWARTOŚCI OŁOWIU I KADMU W PRODUKTACH SPOŻYWCZYCH ZGODNIE Z OBOWIĄZUJĄCYM W POLSCE PRAWODAWSTWEM

Instytut Technologii Nieorganicznej i Nawozów Mineralnych, Politechnika Wrocławska

Abstrakt: Przeprowadzone badania obejmowały oznaczenia zawartości pierwiastków chemicznych Pb i Cd w wybranych owocach i warzywach. Badaniu zostały poddane owoce i warzywa pochodzenia krajowego z terenu województwa dolnośląskiego. W trzech z ośmiu zbadanych próbek materiału roślinnego nie stwierdzono zawartości Pb i Cd, pozostałe próbki zawierają niewielkie ilości badanych zanieczyszczeń w porównaniu z zaleceniami Rozporządzenia Komisji (WE) Nr 466/2002 z dnia 8 marca 2001 r. ustalającego najwyższe dopuszczalne poziomy dla niektórych zanieczyszczeń w środkach spożywczych. Nie stanowią więc zagrożenia dla uprawianych roślin, a tym samym dla organizmów żywych.

Słowa kluczowe: ołów, kadm, toksyczność, najwyższy dopuszczalny poziom

Varia

INVITATION FOR ECOPOLE '09 CONFERENCE
CHEMICAL SUBSTANCES IN ENVIRONMENT



We have the honour to invite you to take part in the 18th annual Central European Conference ECOpole '09, which will be held in **14–17 X 2009** (Thursday–Saturday) on Wilhelms Hill at Uroczysko in Piechowice, PL.

The Conference Programme includes oral presentations and posters and will be divided into four sections – SI, SII, SIII and SIV:

- **SI Chemical Pollution of Natural Environment and Its Monitoring;**
- **SII Environment Friendly Production and Use of Energy;**
- **SIII Forum of Young Scientists and Environmental Education in Chemistry;**
- **SIV Impact of Environment Pollution on Food and Human Health.**

On the first day the debates of sections SI and SII will take place. The second day will be started with an ecological excursion. Afterwards the plenary Session with lectures on **environmental education** as well as **grants within the EU Programmes** and presentation of **EU Centres of Excellence** will be held. Then the **Forum of Young Scientists** – the presentation (lectures and posters) of young scientists work will take place.

The main topic of the third day is the influence of environment quality on the **human health**.

During the Conference an exhibition of publications concerned with conference topics will be also organised.

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)
 - extended abstracts (4–6 pages) in the semi-annual *Proceedings of ECOpole*;
- full papers will be published in successive issues of the *Ecological Chemistry and Engineering/Chemia i Inżynieria Ekologiczna* (Ecol. Chem. Eng.).

Additional information one could find on the Conference website:

ecopole.uni.opole.pl

The deadline for sending the Abstracts is **15.07.2009** and for the Extended Abstracts: **1.10.2009**. The actualised list (and the Abstracts) of the Conference contributions accepted for presentation by the Scientific Board, one will find (starting from 15.07.2009) on the Conference website.

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

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 15.08.2009), and a recommendation of his/her Professor.

Fees transferred after 15.09.2009 are 10% higher.

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).

Further information is available from:

Dr hab. Maria Waclawek, prof. UO

Chairperson of the Organising Committee
of ECOpole '09 Conference

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Date	Breakfast	Lunch	Dinner
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15 X			
16 X			
17 X			—



ZAPRASZAMY
DO UDZIAŁU W ŚRODKOWOEUROPEJSKIEJ KONFERENCJI
ECOpole '09
w dniach 14–17 X 2009

SUBSTANCJE CHEMICZNE
W ŚRODOWISKU PRZYRODNICZYM



Będzie to osiemnasta 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. Doroczne konferencje ECOpole mają charakter międzynarodowy i za takie są uznane przez Ministerstwo Nauki i Szkolnictwa Wyższego. Obrady konferencji ECOpole '09 będą zgrupowane w czterech Sekcjach SI–SIV:

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Materiały konferencyjne będą opublikowane w postaci:

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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 15 lipca 2009 r. Lista prac zakwalifikowanych przez Radę Naukową Konferencji do prezentacji będzie sukcesywnie publikowana od 15 lipca 2009 r. na stronie internetowej konferencji

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Aby praca (dotyczy to także streszczenia, które powinno mieć tytuł w języku polskim i angielskim, słowa kluczowe w obydwu językach) przedstawiona w czasie konferencji mogła być opublikowana, jej tekst winien być przygotowany zgodnie z wymaganiami

stawianymi artykułom drukowanym w czasopiśmie *Ecological Chemistry and Engineering*, które jest dostępne w wielu bibliotekach naukowych w Polsce i zagranicą. Są one takie same dla prac drukowanych w półroczniku *Chemia – Dydaktyka – Ekologia – Metrologia*. Zalecenia te są również umieszczone na stronie internetowej konferencji.

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 15.08.2009 r.**). Jest także wymagana opinia opiekuna naukowego. Sprawy te będą rozpatrywane indywidualnie przez Radę Naukową oraz Komitet Organizacyjny Konferencji. Członkowie Towarzystwa Chemii i Inżynierii Ekologicznej i Polskiego Towarzystwa Chemicznego (z opłaconymi na bieżąco składkami) mają prawo do obniżonej opłaty konferencyjnej o 25 zł. Opłaty wnoszone po dniu 15 września 2009 r. są większe o 10% od kwot podanych powyżej. Wszystkie wpłaty winne być dokonane na konto w Banku Śląskim:

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Po konferencji zostaną wydane 4–6-stronicowe rozszerzone streszczenia wystąpień w półroczniku *Proceedings of ECOpole*. Artykuły te winny być przesłane do **1 października 2009 r.** Wszystkie nadsyłane prace podlegają zwykłej procedurze recenzyjnej. Wszystkie streszczenia oraz program Konferencji zostaną wydane na CD-ROM-ie, który otrzyma każdy z uczestników podczas rejestracji. Program będzie także umieszczony na stronie internetowej konferencji.

Za Komitet Organizacyjny

dr hab. inż. Maria Waclawek, prof. UO

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14/15 X		15/16 X		16/17 X	
TAK	NIE	TAK	NIE	TAK	NIE

ZAMAWIAM POSILKI

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17 X			—



- - - - -



15th ICHMET



**15th International Conference on Heavy Metals
in the Environment
September 19–23, 2010
Gdańsk, Poland**

**Organized by
Chemical Faculty, Gdańsk University of Technology (GUT)
together with
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15th ICHMET – is a continuation of a series of highly successful conferences that have been held in major cities of the world since 1975. These conferences typically draw 500–1000 participants from countries in many parts of the world. Well over 5000 scientists have taken part in this series of conferences including most leaders in the field. Apart from the city's natural beauty, Gdansk is logical choice for the 15th Conference to highlight the outstanding work that is being done on heavy metals in central Europe. The venue for the meeting will be the Gdansk University of Technology (GUT) which features many tourist attractions.

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- Risk communication pertaining to heavy metals
- Life cycle analysis for metalliferous consumer products
- Soil quality criteria
- Remediation technologies
- Control strategies for heavy metal emissions and deposition
- Metal mixtures – mechanistic and epidemiological studies
- Nutrient-metal interactions
- Advancements in analytical tools (procedures and measurement devices)

- Toxicology of heavy metals, from cellular and genomic to ecosystem levels
- Heavy metals in foods
- Impact of global change on heavy metal cycle

For further information on the conference, please contact:

Professor Jacek Namieśnik (Conference Chairman)
Gdansk University of Technology,
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