

# Content of Nitrogen Compounds in Waters Flowing Out of Small Agricultural Catchments

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## Abstract

Research on the content of nitrogen compounds in waters flowing out of small ( $A=4.4-36.6 \text{ km}^2$ ) agricultural catchments in Lower Silesia has shown their high content of nitrate nitrogen, ranging from 1.69 to 9.43 mg N- $\text{NO}_3^-$ , while maximum concentrations often exceeded 11.3 mg N- $\text{NO}_3^-$  (50 mg of  $\text{NO}_3^- \cdot \text{dm}^{-3}$ ), and thus these waters should be considered highly polluted. Total nitrogen content was directly linked to that of nitrate nitrogen and varied, on average, from 3.21 to 16.85 mg of N·dm<sup>-3</sup>. As the pressure is of a local nature, the assessment of the real influence of agricultural areas on the content of nitrates in surface waters requires monitoring of small water-courses that directly collect water from these areas. Research shows a positive correlation between the share of agricultural land in the catchment and the concentration of nitrates flowing out of it. The lack of a strong correlation might be caused by two different reasons. These catchments have a relatively similar share of agricultural land, but first of all, the intensity of agriculture is relatively low.

The use of statistical analysis of the data collected in the process of water quality monitoring is significantly limited by the discrepancy between the distribution in the analyzed data collection and normal distribution.

Conducted analysis has shown that the concentration of  $C_{90\%}$  is significantly dependent ( $r=0.8910$  and  $p<0.01$ ) on the maximum concentration ( $C_{\text{max}}$ ), whereas the correlation coefficient for relationship  $C_{\text{max}-10\%} = f(C_{\text{max}})$   $r=0.6392$  and  $p>0.01$ . The analysis of the relationship between characteristic concentrations ( $C_{90\%}$ ,  $C_{\text{max}-10\%}$ ) and the average concentration ( $C_s$ ) has shown an inverse proportion. The results of the analysis clearly show that the concentration of  $C_{90\%}$  has a stronger correlation with the maximum concentration  $C_{\text{max}}$ , whereas the concentration  $C_{\text{max}-10\%}$  correlates more strongly with the average concentration  $C_s$ . The concentration marked here as  $C_{\text{max}-10\%}$  (similarly to the 90<sup>th</sup> percentile) can constitute a good statistical measure for the general assessment (classification) of waters. The concentration  $C_{90\%}$  is a more restrictive measure, as its value also takes into account the extreme values that are not taken into account during the application of other statistical measures, and it can be used for classifications requiring high guarantee.

**Keywords:** water, catchment, nitrogen, descriptive statistics

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## Introduction

One of the fundamental tasks faced by institutions responsible for water protection is to ensure sufficient quantity and quality of water to meet the needs of municipal utilities, agriculture and industry. To acknowledge the scale of the problem, the European Parliament adopted the Water Framework Directive (WFD) in 2000. The actions undertaken to preserve water resources affect a broad spectrum of water users. Among the many sectors of economy that seriously influence the quality of water, the impact of agriculture is particularly significant [1].

The threat to the quality of water posed by agriculture is related to the use of pesticides and to the increase in the load of nitrogen (mainly in the form of nitrate nitrogen) flowing out of agricultural catchments. Water bodies are often assigned the lowest quality class because of their content of nitrate nitrogen [2]. The share of agriculture in the overall balance of the load of nitrogen, e.g. flowing out of the catchment area, is rather varied. Research carried out in Finland shows that the average share of agriculture in the total load of nitrogen is 38% and varies from 0 to 85%, depending on the region [3]. The direct relationship between the share of agricultural land in the total catchment area and the concentration of nitrates in water flowing out of the catchment has been confirmed by numerous analyses [4, 5]. Moreover, the considerable increase of the content of nitrate nitrogen in water flowing out of such catchments is caused by intensified drainage [6-8]. Large animal farms have an especially disadvantageous influence on the quality of water [9]. In order to calculate the concentrations and loads of nitrogen flowing out of agricultural land, various models are used, such as multiple regression, artificial neural networks, and more [10, 11].

The size of the nitrogen load running off from the basin, apart from how it is used, is affected by climatic conditions, particularly annual precipitation, which largely determines the volume of water outflow from the catchment [8, 12].

Agricultural catchments produce from several to a few dozen kilos per hectare of nitrogen, of which  $N-NO_3^-$  accounts for ca. 90% [7, 8, 13].

The objectivity of results of environmental research depends both on the initial stage of research, consisting in the collection of samples for analysis [14], as well as on the applied analytic methods and the statistical analysis of obtained results. The choice of the statistical measure to determine the characteristic concentration for a given series to be analyzed is of great importance during the assessment of water pollution. One must bear in mind that in most such cases the analyzed series are not compatible with normal distribution [8].

The measures that are used most often in research work are the average and extreme values, whereas classification methods are relatively often based on the 90<sup>th</sup> percentile [2]. Other methods to determine the value of the characteristic concentration, based on the removal of a given percentage (e.g. 10%) of the most disadvantageous results that may be considered as random or obtained in extremely unfavourable conditions, are used less often.

The analysis of statistical data is impeded by the discrepancy between the distribution of samples, and normal distribution creates an impediment, and thus analysis requires the use of non-parametric methods such as the Spearman Rank Correlation [15].

This work aims to evaluate the content of nitrate nitrogen and total nitrogen in waters flowing out of small catchments used for agricultural purposes in Lower Silesia, and to assess the applicability of selected descriptive statistics for evaluation of nitrate content in surface waters.

## Methods and Scope of Research

Research carried out in Lower Silesia (Fig. 1) encompassed 15 catchments with a high percentage of agricultural land (Table 1) and diversified in terms of agricultural activity (Table 2). At the same time, no significant non-agricultural sources of nitrogen compounds have been identified.

Detailed characteristics of agricultural activity were analyzed based on the data obtained from the Agricultural Census conducted by the Central Statistical Office of Poland in 2002 [16]. The resulting selection of catchments is characterized by a high share of sown area – an exception is the catchment of the Gibiela River to the section Szklary Dolne, where 27.4% of the land is grassland (Table 2). Dominant crops are cereals (49.9-77.8%), and in the second position – corn, root plants, and rapeseed (Table 2). These catchments are characterized by low intensity of animal farming. The stock of animals ranged from 0.15 to 0.53  $LSU \cdot ha^{-1}$ .

As 5 years had passed since the agricultural census and there were insufficient detailed data for individual communes, the analysis covered all available data for the whole Lower Silesia Voivodship (Table 3). These data show the changes in the structure of agricultural land, crops, and the stock of farming animals as compared to 2002 (where the results from 2002 constitute 100%). The analysis of data

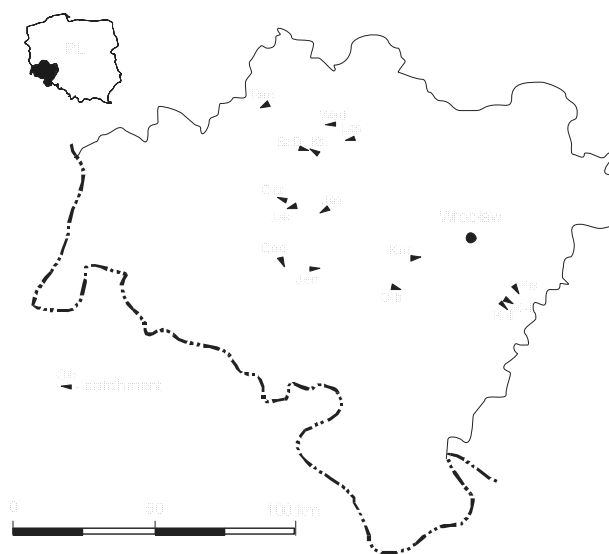


Fig. 1. Location of the analyzed catchments – marked as in Table 1.

Table 1. Basic parameters of the analyzed catchments.

Section	Location	Water-course length to the measuring section [km]	Surface [km <sup>2</sup> ]	Percentage of agricultural land [%]
Godziszowa (God)	Partial catchment of the Uszewnica, left tributary of the Wierzbak located in the Mściwojów and Jawor communes.	3.2	8.8	98.0
Grzymalin (Grz)	Catchment of the Dłuzeń, right tributary of the Skora, located in the Chojnów and Miłkowice communes.	6.0	6.9	96.4
Jakuszów (Jak)	Catchment of the Łopiennik, left tributary of the Lubiátówka, located in the Miłkowice commune.	7.1	7.7	97.7
Jaskowice Legnickie (Jas)	Catchment of the Dopływ spod Zimnicy, left tributary of the Dziewcza Struga, located in the Kunice commune.	3.8	4.8	99.0
Jenków (Jen)	Partial catchment of the Jania, left tributary of the Cicha Woda, located in the Udanin, Wądroże Wielkie and Mściwojów communes.	3.7	9.5	92.9
Korbielowice (Kor)	Catchment of the Dopływ ze Starego Dworu, right tributary of the Czarna Woda, located in the Kąty Wrocławskie and Kobierzyce communes.	4.0	7.0	99.0
Księgnice (Ksi)	Partial catchment of the Księgińska Struga, left tributary of the Zimnica located in the Lubin commune.	1.9	5.3	82.6
Kuchary I (K-I)	Catchment of the Dopływ spod Domaniówka, right tributary of the Żurawka, located in the Domaniów commune.	5.2	6.5	97.4
Kuchary II (K-II)	Partial catchment of the Żurawka, left tributary of the Mszana, located in the Domaniów, Wiązów, Strzelin, and Borów communes.	9.0	36.6	98.8
Lasowice (Las)	Partial catchment of the Widnica, right tributary of the Przychowska Struga, located in the Ścinawa and Rudna communes.	8.0	16.3	84.8
Olbrachtowie (Olb)	Catchment of the Dopływ spod Solnej, right tributary of the Barnica, located in the Kobierzyce commune.	2.7	4.4	92.2
Piskorzów (Pis)	Catchment of the Dopływ spod Polwicy, right tributary of the Mszana, located in the Oława and Domaniów communes.	3.7	11.1	97.4
Radwanice (Rad)	Partial catchment of the Szprotawa, right tributary of the Czarna, located in the Radwanice and Jerzmanowa communes.	5.3	9.2	82.8
Szklary Dolne (SzD)	Catchment of the Gibiel, left tributary of the Zielnica, located in the Chocianów and Lubin communes.	4.8	8.3	81.1
Wądroże (Wad)	Partial catchment of the Przychowska Struga, left tributary of the Odra, located in the Rudna and Ścinawa communes.	2.7	4.5	59.8

presented in this table leads to the conclusion that there have been no significant changes in the structure of agricultural land, but a slow decline in the area of grasslands has been observed. On the other hand, the structure of sown area shows a significant decrease of the root plants cultivation area, in favour of rapeseed (Table 3). The stock of farming animals has also been significantly reduced. The changes in plant production (the switch from root plants to the cultivation of rapeseed) should not have a significant impact on the outflow of nitrogen from agricultural land, as both these crops foster such processes. Root plants do not cover the soil sufficiently during the major part of the vegetation period, while rapeseed requires a high level of nitrogen fertilizers. The reduction of the stock of farming animals should rather limit the outflow of nitrogen of agricultural origin, although even higher stock, such as that observed in 2002, does not constitute a significant threat, so one should not have expected a significant influence on the outflow of nitrogen from the catchments covered by our

analysis. The level of fertilization (NPK) in the Lower Silesia Voivodship in 2008 was 171.8 kg·ha<sup>-1</sup>, including 93 kg·ha<sup>-1</sup> of nitrogen [16].

Research was conducted in the hydrological year 2007-08. This included the evaluation of total nitrogen and nitrate nitrogen concentrations. Samples of water for chemical analysis were collected twice a month; but due to unfavourable conditions during the winter season, 21 samples were collected from most of the sections. In the case of 3 catchments (K-I, Las, and Olb), this number was lower (10-14) as these watercourses did not carry any water during summer. Water for analysis was collected directly from the current (the bottom width of these courses does not exceed 1.5 m), to plastic containers of the capacity of 0.5 dm<sup>3</sup>. The samples were marked in the Water and Wastewater Laboratory at the Institute of Environmental Protection and Development of the Wrocław University of Environmental and Life Sciences using the following methods: nitrate nitrogen – the 2,6 dimethylphenol spectromet-

Table 2. Characteristics of agricultural activity in analyzed catchments (as for 2002).

Section	Structure of land usage %				Structure of sown area %					Stock of animals LSU·ha <sup>-1</sup>
	sown area	grasslands	orchards	fallows grounds	corn	maize	rape-seed	root plants	remaining	
Godziszowa (God)	93.3	4.5	0.4	1.8	64.7	7.1	12.8	10.4	5.1	0.32
Grzymalin (Grz)	84.2	13.5	0.4	1.9	74.5	9.1	5.4	7.7	3.4	0.49
Jakuszków (Jak)	84.4	12.7	0.4	2.5	76.3	4.6	4.8	9.1	5.2	0.48
Jaskowice Legnickie (Jas)	81.9	16.0	0.2	2.0	66.8	14.2	3.4	13.3	2.3	0.31
Jenków (Jen)	95.9	3.7	0.1	0.3	67.3	11.3	4.6	15.4	1.4	0.36
Korbielowice (Kor)	93.9	3.3	2.3	0.5	62.3	18.1	6.6	10.3	2.6	0.15
Księgnice (Ksi)	74.8	17.0	0.5	7.7	77.8	3.4	10.5	5.3	3.1	0.42
Kuchary I (K-I)	98.2	1.2	0.3	0.2	50.7	21.2	6.7	14.6	6.8	0.47
Kuchary II (K-II)	96.9	2.4	0.4	0.3	49.9	20.5	7.1	17.1	5.5	0.40
Lasowice (Las)	87.4	9.3	0.3	2.9	75.0	11.7	3.8	6.9	2.5	0.30
Olbrachtowie (Olb)	97.8	1.5	0.4	0.3	50.0	19.4	4.6	21.7	4.3	0.15
Piskorzów (Pis)	95.4	3.4	0.5	0.8	52.1	20.3	8.3	13.5	5.8	0.39
Radwanice (Rad)	77.1	20.7	0.4	1.9	77.1	3.6	1.8	12.5	5.0	0.53
Szklary Dolne (SzD)	67.0	27.4	0.2	5.4	61.1	23.4	6.6	6.6	2.3	0.34
Wądroże (Wad)	86.8	9.6	0.4	3.3	76.9	9.2	3.5	7.5	2.9	0.32

Table 3. Changes in land usage and structure of sown area in Lower Silesian Voivodship in 2002-08 (year 2002=100%) [16].

Year	Structure of land usage %				Structure of sown area %			Stock of animals %
	agricultural land	arable land	grassland	orchards	cereal	rapeseed	root plants	
2002	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
2003	99.7	100.6	100.0	100.0	100.2	100.6	92.0	95.3
2004	99.9	100.6	98.4	97.4	101.2	109.1	95.3	91.6
2005	100.0	100.6	98.0	88.1	101.2	138.7	91.2	92.6
2006	no data	no data	95.8	no data	100.1	156.5	90.1	87.4
2007	no data	no data	97.6	no data	96.0	195.0	80.9	87.1
2008	no data	no data	87.4	no data	96.8	210.1	67.0	75.1

ric method (ISO 7890-1:1986), total nitrogen – calculated as the sum of Kjeldahl nitrogen (PN-EN 25663:2001), nitrite nitrogen (PN-EN 26777:1999), and nitrate nitrogen. Each series consisted of 10 to 21 analyses.

Analysis of the relationships between characteristic concentrations was carried out using linear Pearson correlations. For the purpose of the correlation between the concentration of nitrate (V) nitrogen and the share of agricultural land in the catchment area, the Spearman Rank Correlation method also was applied, as the distribution of population consisting of average annual concentrations proved incompatible with normal distribution.

Statistical calculations were carried out with use of the package Statistica 8 [17].

## Research Results

Water flowing out of small agricultural catchments contained considerable amounts of nitrogen compounds, particularly in the form of nitrate nitrogen. The mean concentration of this form of nitrogen ranged from 1.69 to 9.43 mg of N-NO<sub>3</sub>·dm<sup>-3</sup> (Table 4). It is worth noting that the obtained results varied significantly – from below 0.01 mg

Table 4. Total nitrogen concentration and concentration of nitrates in water flowing out of agricultural catchments.

Section	Total nitrogen mg N·dm <sup>-3</sup>			Nitrate nitrogen mg N-NO <sub>3</sub> <sup>-</sup> ·dm <sup>-3</sup>		
	$\frac{C_{min} - C_{max}^*}{C_s}$	$\delta$	V	$\frac{C_{min} - C_{max}}{C_s}$	$\delta$	V
Godziszowa (God)	$\frac{3.37 - 9.20}{5.88}$	1.65	28	$\frac{1.84 - 6.18}{4.55}$	1.09	24
Grzymalin (Grz)	$\frac{3.00 - 12.11}{5.75}$	2.58	45	$\frac{1.18 - 10.38}{4.16}$	2.24	54
Jakuszków (Jak)	$\frac{1.52 - 9.40}{5.43}$	1.90	35	$\frac{0.74 - 6.96}{3.99}$	1.25	39
Jaskowice Legnickie (Jas)	$\frac{0.92 - 18.12}{5.16}$	4.47	87	$\frac{<0.01 - 17.14}{3.47}$	4.56	131
Jenków (Jen)	$\frac{2.02 - 10.50}{6.02}$	2.03	34	$\frac{0.10 - 4.86}{2.97}$	1.29	43
Korbielowice (Kor)	$\frac{0.69 - 8.26}{4.03}$	2.33	58	$\frac{<0.01 - 6.44}{1.69}$	1.90	112
Ksiegnice (Ksi)	$\frac{0.29 - 17.09}{3.34}$	4.28	128	$\frac{<0.01 - 16.10}{2.31}$	4.30	186
Kuchary I (K-I)	$\frac{8.61 - 17.01}{12.38}$	2.93	24	$\frac{5.62 - 14.40}{9.43}$	2.68	28
Kuchary II (K-II)	$\frac{6.17 - 53.39}{16.85}$	10.28	61	$\frac{<0.01 - 34.64}{4.30}$	7.69	179
Lasowice (Las)	$\frac{2.91 - 16.39}{6.93}$	4.57	66	$\frac{2.02 - 15.26}{6.06}$	4.63	76
Olbrachtowice (Olb)	$\frac{2.81 - 14.07}{7.51}$	3.64	48	$\frac{<0.01 - 8.84}{3.80}$	2.96	78
Piskorzów (Pis)	$\frac{2.71 - 36.47}{13.41}$	7.89	59	$\frac{<0.01 - 8.74}{6.21}$	6.33	102
Radwanice (Rad)	$\frac{1.10 - 10.83}{3.55}$	2.70	76	$\frac{<0.01 - 8.74}{2.13}$	2.57	121
Szklary Dolne (SzD)	$\frac{1.70 - 20.20}{5.29}$	4.31	82	$\frac{0.03 - 9.98}{2.87}$	2.82	98
Wądroże (Wad)	$\frac{0.38 - 9.96}{3.21}$	2.92	91	$\frac{<0.01 - 8.72}{2.00}$	2.89	145

\*C<sub>min</sub> – minimum concentration, C<sub>max</sub> – maximum concentration, C<sub>s</sub> – average concentration,  $\delta$  – standard deviation, V – coefficient of variability in %.

N-NO<sub>3</sub><sup>-</sup>·dm<sup>-3</sup> up to to 34.64 mg N-NO<sub>3</sub><sup>-</sup>·dm<sup>-3</sup>. The obtained results proved that the concentrations over the analyzed period were dynamic. Variability coefficients ranged from 24 to 186%, which significantly limited the possibility of assessment of water pollution based on average concentrations.

Total nitrogen content was directly linked to that of nitrate nitrogen and it ranged, on average, from 3.21 to 16.85 mg N·dm<sup>-3</sup> (Table 4). The considerable share of N-NO<sub>3</sub><sup>-</sup> in the total load of nitrogen compounds flowing out of the catchment may indicate that they were carried out with the water used in agricultural land where nitrogen fertilization is used. Assessment of the influence of agriculture on water quality often ignores the fact that in rural areas agricultural activity often is not the only direct cause of water pollution, but is often accompanied by incorrect water man-

agement. Similarly to the nitrate nitrogen, the maximum concentrations of total nitrogen reached considerable levels, ranging from 8.26 to 53.39 mg of N·dm<sup>-3</sup>, which indicated significant pollution of water by nitrogen compounds.

The analysis of the relationship between the average concentrations of nitrate nitrogen and the area of the catchment or the share of agricultural land showed no significant relationships. Such relationships do exist in the case of bigger catchments [5], while in the case of small catchments there is no relationship between the concentration of pollutants and flow rate [18-20].

Further analysis of the results showed that the lack of such correlation may depend on individual results, such as those obtained for the Korbielowice section, although, based on the characteristics of the catchment, no grounds were found to reject this result. The analysis of compatibil-

ity of the distribution of average concentrations obtained for 15 catchments did not show a compatibility with normal distribution ( $\chi=28.78$ ,  $\alpha=0.026$ ). The removal of the result obtained for the Korbielowice section does reduce the value of  $\chi$ , but not to such extent that would allow us to adopt null hypothesis for  $\alpha=0.05$ . Due to this lack of compatibility, Spearman Rank Correlation was determined. For the full series of measurements no significant relationship was obtained for the significance level  $\alpha=0.05$ . Only the removal of the result obtained for Korbielowice led to a positive result in the form of rank correlation indicator of 0.6631, significant for  $\alpha=0.05$ .

The conducted research proves the existence of a positive correlation between the share of agricultural land in the catchment, and the concentration of nitrates in water flowing out of it. The lack of strong correlation might be caused by two factors. First, these catchments have a similar share of agricultural land, and second, the intensity of agriculture is relatively low.

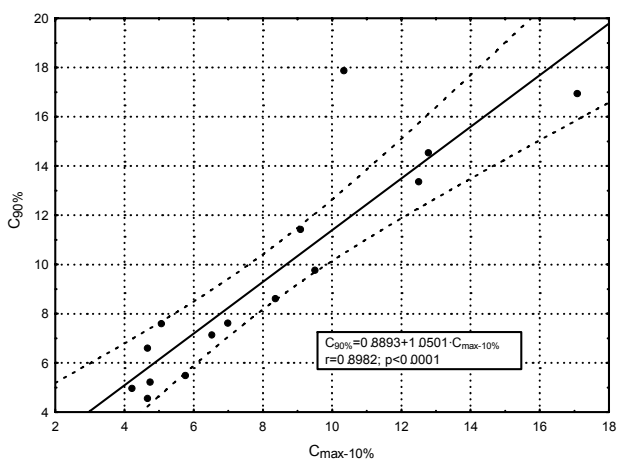


Fig. 2. Concentration with 90% probability of occurrence, including that of occurrence of lower values ( $C_{90\%}$ ) versus the maximum concentration with 10% of highest results excluded ( $C_{\max-10\%}$ ).

The subject of the analysis was the relationship between the concentration determined as the value occurring, together with lower values, with the probability of 90% ( $C_{90\%}$ ) and the concentration calculated by means of removal of 10% of most unfavourable results in the measurement series ( $C_{\max-10\%}$ ). In practice the removal of 10% of most unfavourable results meant exclusion of the 1 or 2 highest values (Fig. 2). The obtained relationship is significant ( $r=0.8982$ ,  $p<0.01$ ), deviation was observed only at one point. Fig. 3 shows that it concerned section K-II, where a very high value of maximum concentration of  $36.64 \text{ mg N-NO}_3^- \cdot \text{dm}^{-3}$  was observed, whereas the average concentration at this section was  $4.30 \text{ mg N-NO}_3^- \cdot \text{dm}^{-3}$  and did not significantly diverge from other sections. At this section,  $C_{90\%}$  was significantly higher than  $C_{\max-10\%}$  (Fig. 3). This allowed us to adopt the initial thesis that the value of  $C_{90\%}$  depends considerably on the highest results, which we want to omit by using the characteristic concentration calculated with use of this method. Next, the relationships between the characteristic concentrations ( $C_{90\%}$ ,  $C_{\max-10\%}$ ) and the maximum ( $C_{\max}$ ) and average ( $C_s$ ) concentrations were analyzed. Results of this analysis are shown in Figs. 4-7. Analysis revealed that the  $C_{90\%}$  concentration was significantly related ( $r=0.8910$ ,  $p<0.01$ ) to the maximum concentration ( $C_{\max}$ ), whereas the correlation coefficient for relationship  $C_{\max-10\%}=f(C_{\max})$   $r=0.6392$  and  $p>0.01$ . The analysis of the relationship between the characteristic concentrations ( $C_{90\%}$ ,  $C_{\max-10\%}$ ) and the average concentration ( $C_s$ ) showed the opposite – the correlation between  $C_{90\%}$  and  $C_s$  was insignificant for  $p=0.01$ , while the correlation between  $C_{\max-10\%}$  and  $C_s$  was significant ( $p<0.01$ ) with the correlation coefficient  $r=0.6878$ . This analysis clearly shows that the  $C_{90\%}$  concentration demonstrates a stronger correlation with the maximum concentration  $C_{\max}$ , whereas the concentration  $C_{\max-10\%}$  is more strongly correlated with the average concentration  $C_s$ . These results suggest that the use of the descriptive statistic in the form of the characteristic concentration of a definite probability of occurrence to determine the water quality may be questionable.

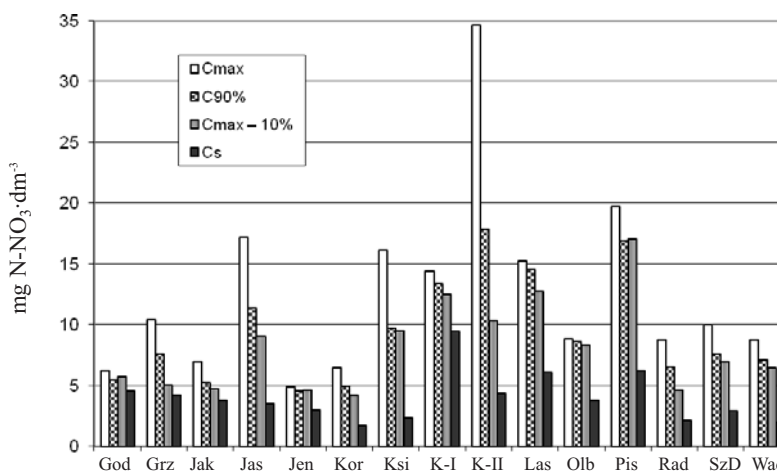


Fig. 3. Concentrations of nitrate nitrogen in water flowing out of small agricultural catchments: the maximum concentration ( $C_{\max}$ ) with 90% probability of occurrence, including that of occurrence of lower values ( $C_{90\%}$ ), the maximum concentration with 10% of highest results excluded ( $C_{\max-10\%}$ ) and the average concentration ( $C_s$ ).

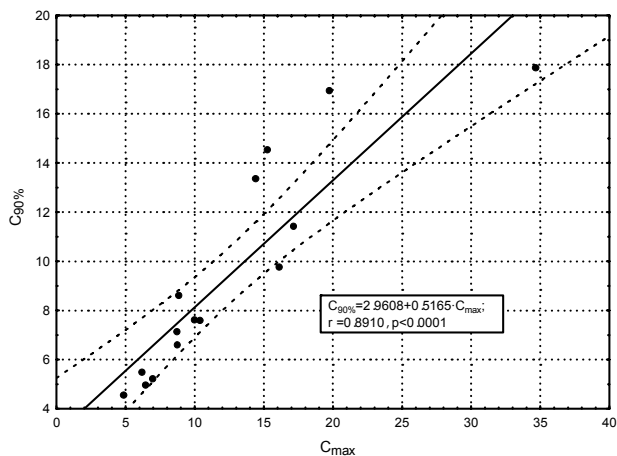


Fig. 4. Concentration with 90% probability of occurrence, including that of occurrence of lower values ( $C_{90\%}$ ) versus the maximum concentration ( $C_{max}$ ).

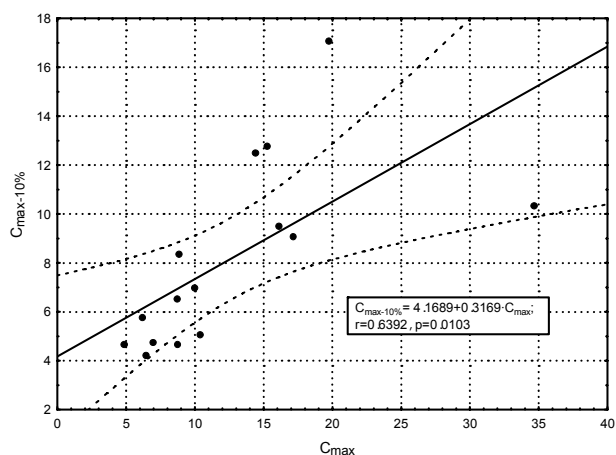


Fig. 5. Maximum concentration with 10% of highest results excluded ( $C_{max-10\%}$ ) versus the maximum concentration ( $C_{max}$ ).

For small measurement series (for water monitoring a yearly measurement series rarely consists of more than 12 analyses), the use of this method may cause an unjustified increase in the characteristic value calculated as  $C_{90\%}$  in the series with the highest value significantly divergent from the rest. In the case of application of the measure calculated as  $C_{max-10\%}$ , the highest value (often random) does not influence the obtained result.

This analysis shows that the concentration determined as  $C_{max-10\%}$  (similarly to the 90<sup>th</sup> percentile) may be a good descriptive statistic for overall assessment (classification) of water. Its determination is much easier than that of  $C_{90\%}$ , which depends not only on the type of the probabilistic distribution being used, but also on the 1<sup>st</sup> extreme result. On the other hand, the concentration  $C_{90\%}$  is a more restrictive measure, and its value takes into account the extreme results as well, which are omitted when using the above-mentioned statistical measures. Thus, it may be used for the purpose of classifications requiring high guarantee, e.g. for the determination of water characteristics for consumption,

where not only the occurrence of values exceeding acceptable levels is important, but also the value of the excess itself.

### Conclusions

1. Water flowing out of small agricultural catchments contains considerable amounts of nitrate nitrogen, from 1.69 to 9.43 mg of  $N-NO_3^- \cdot dm^{-3}$ . Since the maximum concentrations often exceed 11.3 mg  $N-NO_3^- \cdot dm^{-3}$  (50 mg  $NO_3^- \cdot dm^{-3}$ ), these waters must be considered highly polluted.
2. The assessment of the real influence of agricultural areas on the content of nitrates in surface waters requires the monitoring of small water-courses that directly collect water from these areas, as the threat is of a local nature. Monitoring on the main rivers does not necessarily point out such local (and at the same time dangerous) enclaves.
3. The conducted analysis proves the existence of a positive correlation between the share of agricultural land in

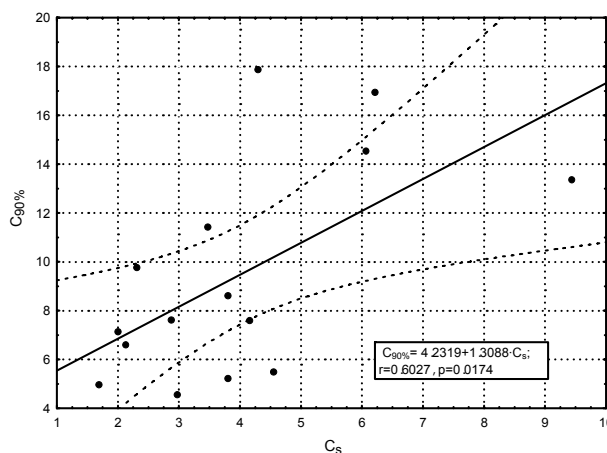


Fig. 6. Concentration with 90% probability of occurrence, including that of occurrence of lower values ( $C_{90\%}$ ) versus the average concentration ( $C_s$ ).

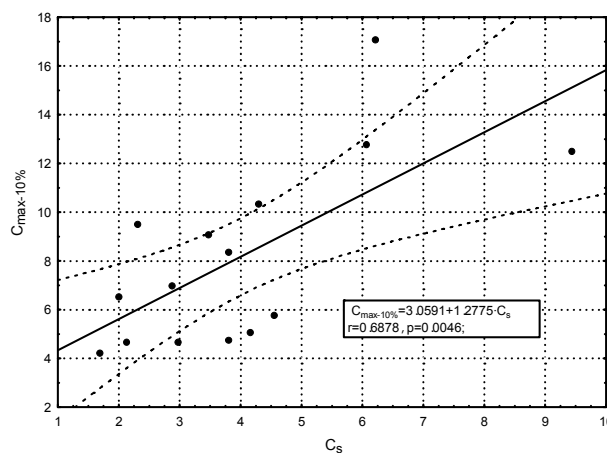


Fig. 7. Maximum concentration with 10% of highest results excluded ( $C_{max-10\%}$ ) versus the average concentration ( $C_s$ ).

the catchment and the concentration of nitrates flowing out of it. The lack of a strong relationship might be caused by two factors. First, these catchments have a similar share of agricultural land, and second, the agriculture is of relatively low intensity.

4. Statistical analysis has revealed that the concentration  $C_{\max-10\%}$  is more correlated with the average concentration  $C_s$  than with the maximum concentration  $C_{\max}$ , and that it can constitute (similarly to the 90<sup>th</sup> percentile) a good statistical descriptor for the purpose of general water assessment (classification).
5. The concentration  $C_{90\%}$  is a more restrictive measure, as its value takes into account the extreme results as well, which are not taken into account when using other statistical measures, so it can be used in classifications requiring high guarantee.

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