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Analysis of Precipitation and Runoff Against Quality Characteristics of Surface Water in Carpathian Areas (Based on Lysimetric Studies)

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ABSTRACT

The aim of the study was to analyse precipitation, subsurface runoff and concentrations of nutrients in water (NH_4^{+-}-N, NO_3^--N and PO_4^{3-} ions). The study was conducted at the lysimetric station in Jaworki (Małe Pieniny, Nowy Targ district, Malopolska province, 600 m a.m.s.l.). Measurements were carried out during vegetation periods, from April to September. The paper consists of an analysis of data in two periods – 2001–2018 and 2019–2022. Data in the historical years (2001–2018) showed that water quality as well as its quantitative variability was low, mainly until 2015. The year 2018 indicated slow changes in this regard. Analysis of the years 2019–2022 indicated that the outflow was almost identical. The years 2019 and 2022 were characterized by significantly higher leachate concentrations. Ammonium ion contents were similar. Analysis of nitrate ions in leachate showed an increasing trend over the years. Phosphates, on the other hand, showed a similar trend to nitrate ions. The study showed which types of land use have the greatest impact on both subsurface runoff volume and leachate water quality. In mountainous conditions, the type of use, as well as the climate and soil, have an extremely significant impact on the volume and quality of runoff, which affect the quality of groundwater and surface water.

Keywords: quality of rainwater and flowing leaches waters, nutrient concentrations, diversified use of meadows.

INTRODUCTION

In Poland, mountainous areas account for more than 8.7% of the country's total area. Grasslands predominate here, the acreage of which has exceeded 500 000 hectares [Twardy et al., 2015]. In the last decade of the 20th century. Europe's permanent grassland area has decreased [Burczyk et al., 2018, Huyghe et al., 2014]. In Poland, since 1989, there has been a decline in the profitability of agricultural production [Burczyk et al., 2018, Barszczewski et al., 2015, Regulation, 2013]. In the 1990's, more attention was paid to the non-productive importance of permanent grasslands (cultural and natural landscape, environment) [Burczyk et al., 2018]. Permanent grasslands also play climatic, hydrological, protective, filtering and phytosanitary functions [Wróbel et al., 2015]. They also protect soils from erosion and reduce post-surface runoff [Bielasik-Rosińska et al., 2013]. Through climate change there is a change of water runoff in the soil profile of mountainous areas, and this affects the water balance of the catchment and water quality. Therefore, permanent mountain grasslands should be kept in good condition [Wróbel et al., 2015].

The aim of the study was to hydrological parameters analyse (atmospheric precipitation and subsurface runoff) against the background of the quality of water draining from the soil profile in mountain areas. An additional aim was to demonstrate the best methods of developing mountain areas. This study is intended to fill a research gap regarding the impact of agricultural activities on surface and subsurface waters in the mountains under changing mail meteorological conditions.

There is a lack of studies comparing the situation in different periods of time.

STUDY MATERIALS AND METHODS

The purpose of this study was to analyse hydrological parameters (precipitation, subsurface runoff) against the quality of leachates from the soil profile in mountainous areas. The results of the quantity and quality of leachates obtained in lysimetric measurements, which were carried out during the growing seasons, from April to September, were analysed. The work consists of an analysis of data obtained in two study periods: the historical years 2001–2018 and the current years: 2019–2022. The work was conducted in the catchment area of the Grajcarek (84.9 km^2), a right-bank tributary of the Dunajec River, within the Western Carpathians [Kondracki, 2013].

Field research was conducted at the Research Station located in Jaworki in the Szczawnica municipality (Institute of Technology and Life Sciences National Research Institute). A lysimeter station located at an altitude of about 600 m a.m.s.l. was used for the research work (geographical coordinates: 49.407692, 20.558830).

The measurements use 26 metal lysimeters measuring 1.0 × 1.0 × 1.0 m (Table 1). At the bottom, the lysimeters have a bottom, made in the form of an inverted pyramid, which is filled with gravel. Such a design ensures even drainage of water from the entire soil profile. The lysimeters were filled with brown soil proper, preserving the natural layout of the soil profile (Figure 1). In the lysimetric experiment, a mixture of grasses was used (Meadow fescue 30%, Meadow timothy 20%, Blue grass 10%, Perennial ryegrass 30%, red fescue 10%). The fertilization depended on specific types of use. Leachate water was collected into tanks located in the basement under the lysimeters twice a month [Twardy, Kopacz, 2014].

Samples of rainwater, leachate from soil profiles lysimeters were analyzed to determine the following parameters: pH reaction, nutrient concentrations ($mg \cdot dm^{-3}$): ammonium nitrogen (NH_4^+-N), nitrate nitrogen (NO_3^--N) and phosphate (PO_4^{3-}). Reaction was determined using a pH-meter (WTW Xylem ALnalytics Brands). Concentrations of individual ions were determined by colorimetric methods.

In the first step, physico-chemical data of leachates from the soil profile, determined in 2001–2018, were analyzed. So this is a long-term analysis in this matter.

Physico-chemical data from lysimetric measurements collected in the second stage of the study (2019–2022) were subjected to statistical analysis in R software with the RStudio overlay [R Core Team 2021]. The level of significance for all analyses was adopted as $\alpha = 0.05$. The purpose of the study was to analyze the observed changes in parameters (leachate volume, NH_4^+-N, NO_3^--N and PO_4^{3-} concentrations) measured in each year (2019, 2020, 2021, 2022) and to determine any correlations with the tillage methods used (fallow, self-seeding, unmoved, mowed 1x, mowed 2x, mowed 3x, mowed 4x).

The conformity to normal distribution (Shapiro-Wilk test) and homogeneity of variance (Lavenea test) were checked. Since the tests showed a distribution conforming to the normal

Table 1. Scheme of a lysimetry experiment

No	Four plots	Four plots	Four plots	Four plots	Four plots	Four plots	Two plots
	First combination	Second combination	Third combination	Fourth combination	Fifth combination	Sixth combination	Seventh combination
Use	Self-seeding	Un-mowed	1-mowed	2-mowed	3-mowed	4-mowed	Fallow

Figure 1. View of plots of lysimeter station Jaworki – prepared for the experience and during its implementation

distribution and equal variance, therefore ANOVA analysis of variance was used, and Tukey's HSD test was used as a post hoc test. For overall data comparison, the Euclidean distance measure was used on standardized data (Kim, 2017).

RESULTS

Simplified analysis from 2001 to 2018

Historical data, as well as current measurements, showed that precipitation totals varied markedly between them. The most precipitation was recorded in 2010 and the least in 2003 (Figure 2). The distribution of precipitation was uneven. The highest average monthly precipitation fell on the month of July (nearly 180 mm). In the years in question, decades with minimal precipitation were also recorded, as well as rainless decades. There was also a one-time monthly rainless period (August 2003), when only 15 mm of precipitation was recorded. The unevenness of precipitation is quite natural in this area and results from orographic peculiarities. The evapotranspiration was also taken into account in this respect [Kopacz, Twardy 2014].

Chemical composition of flowing leaches waters

An analysis of historical data on the content of individual mineral components in leachates proved their low overall mineralization, which, however, does not authorize downplaying the importance of precipitation in shaping the quality of the water and soil environment. Concentrations of NH_4^+-N remained on average at about 1 mg·dm^{-3} (Table 2), the maximum determined value was 2.92 mg·dm^{-3}.

Nitrate nitrogen occurred in concentrations ranging from 0.13 to 2.56 mg·dm^{-3}. In 20% of the measurement series, concentrations exceeded the value of 1 mg·dm^{-3}. The amount of phosphate in precipitation was low and did not exceed tenths of mg·dm^{-3}. Phosphate ions PO_4^{3-} is a biogenic component that contributes significantly to eutrophication. The permissible concentration of phosphate in flowing waters is 0.1 mg·dm^{-3} and total phosphorus up to 0.35 mg·dm^{-3} (Limits for surface water quality classes https://www.gov.pl/web/odra/wybrane-wartosci-graniczne-dla-klas-jakosci-wod-powierzchniowych). Exceeding the value of 0.25 mg·dm^{-3} of total phosphorus along

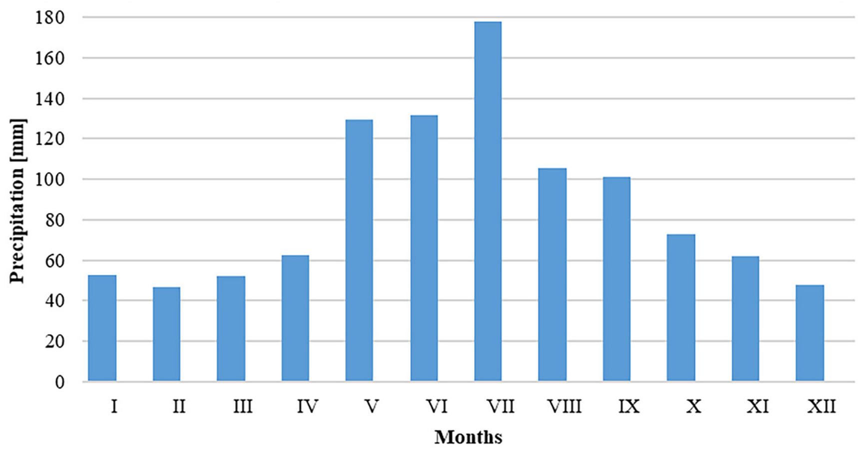

Figure 2. Monthly averages of precipitation from 2001–2018

Table 2. Historical parameters - average values of concentrations of nutrients (mg·dm^{-3}) in rainwater during the growing seasons (April–October) (2001–2018)

Physico-chemical parameter (mg·dm^{-3})	2001	2005	2010	2015	2018
NH_4^+-N	1.01	0.98	0.83	0.95	1.01
NO_3^--N	0.59	0.56	1.01	0.69	0.46
PO_4^{3-}	0.09	0.03	0.16	0.02	0.02

Note: source – own elaboration based on: Twardy, Kopacz [2014].

with nitrates above 10 mg·dm^{-3} and chlorophyll a - above 25 µg·dm^{-3} may indicate eutrophication.

The recorded phosphate concentrations (in precipitation) were significantly lower (even several times) than the values reported by Pawlik-Dobrowolski [1988] based on studies conducted in the 1970's, also the concentrations of ammonium and nitrate nitrogen were slightly lower (by about 20%).

Seeping waters

Ammonium nitrogen

Average N-NH_4 concentrations for the growing season were in the range of 0.02–0.11 mg·dm^{-3} at individual sites. Higher concentrations were found in leachates from the soil profile with uncut sward, especially in 2001 and 2010 (0.10 and 0.17 mg·dm^{-3} N-NH_4, respectively). This could be explained by all plant biomass remaining on the surface of such a site, which resulted in increased mineralization of organic matter (Figure 3).

Nitrate nitrogen

Significantly higher concentrations of N-NO_3 were recorded in leachates from black fallow. On average, they were at a level of about 8.1 mg·dm^{-3}. The highest concentrations of this component were in 2005–2015 (Figure 4). This was a consequence of the lack of vegetation using nitrate for its development.

Phosphates

In soils, free phosphate ions are bound with calcium, iron or clay into insoluble combinations and sorbed by soil colloids, which significantly limits their mobility in the water-soil environment. The content of phosphate in leachates ranged from a few hundredths of a part to more than 0.3 mg·dm^{-3}, although most often it did not exceed 0.2 mg·dm^{-3} (Figure 5). The lowest concentrations were measured in leachates from fallow soils. The highest concentrations

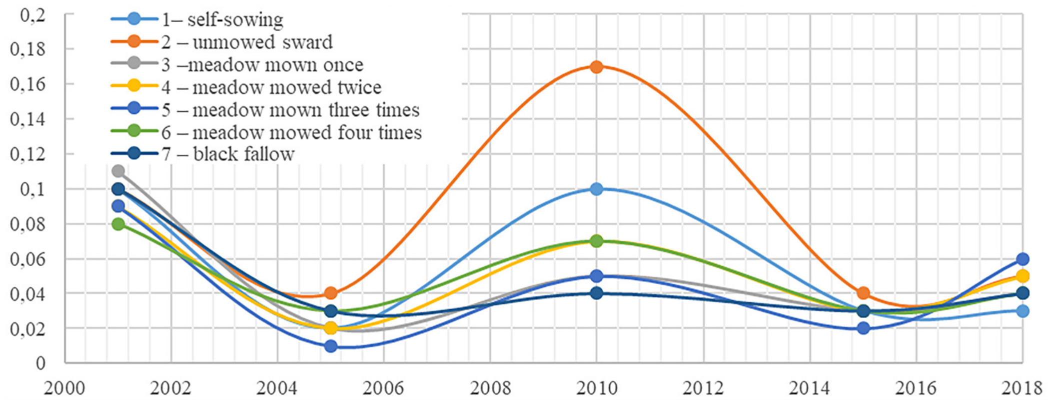

Figure 3. Historical parameters - average concentrations of NH4+-N (mg·dm–3) in water draining from soil profiles in sub-sequent growing seasons (April–October) (2001–2018)

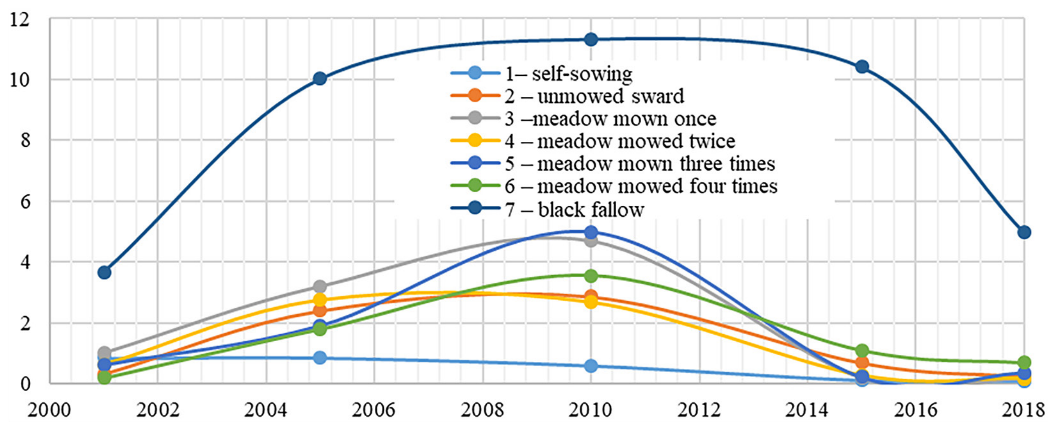

Figure 4. Historical parameters - average NO_3^--N concentrations (mg·dm^{-3}) in water draining from soil profiles in subse-quent growing seasons (April–October) (2001–2018)

were recorded from sites mowed once or twice and also unmoved. The lowest concentration of PO_4^{3-} was associated with sites with high depth runoff, and the highest with low leachate volumes, which is due to the dilution of the component in question. Monthly average PO_4^{3-} concentrations show a slight decrease in values from the beginning of the growing season until May, followed by an increase in July and August. The reasons for the first dependence can be traced to the intensive use of this component by vegetation, despite the spring release of large amounts of it from organic compounds.

Precipitation and runoff analysis for 2019–2022

In the present study, after a preliminary analysis of the data from 2001–2018, the parameters of precipitation, subsurface runoff and water quality characteristics in the study area were evaluated. Precipitation in 2019–2022, varied seasonally, while it did not differ markedly from the data of previous years. The highest precipitation values were for the summer months. Extreme precipitation values concerned the years 2020 and 2021. The average of precipitation values (in mm), its distribution is shown in Figure 6. Individual precipitation values strongly deviate from monthly averages. Figure 7 shows the cumulative precipitation values (in mm). The increases in precipitation over the course of the calendar year can be seen here. The largest occurred in the summer months, especially in 2020, and the smallest in 2022. However, the differences are not statistically significant here, although 2022 was characterized by a noticeably wetter autumn period.

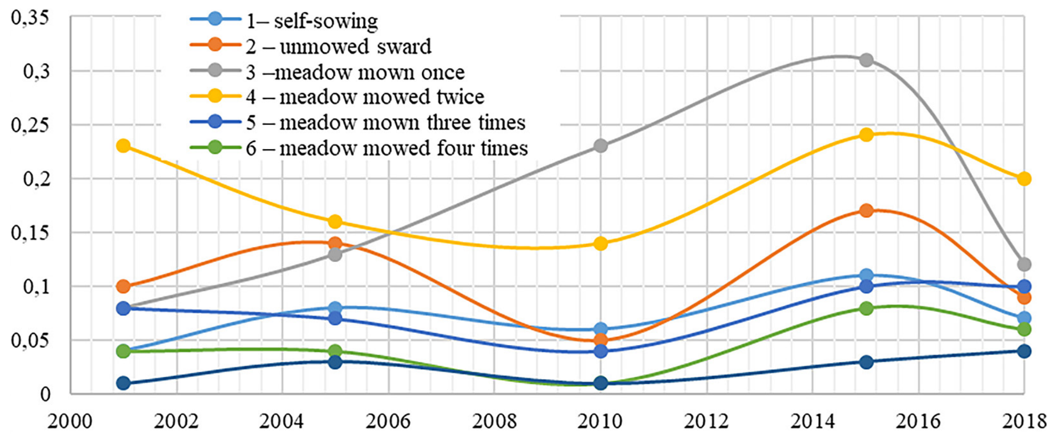

Figure 5. Historical parameters – average PO_4^{3-} concentrations ($mg \cdot dm^{-3}$) in water draining from soil profiles in subsequent growing seasons (April–October) (2001–2018)

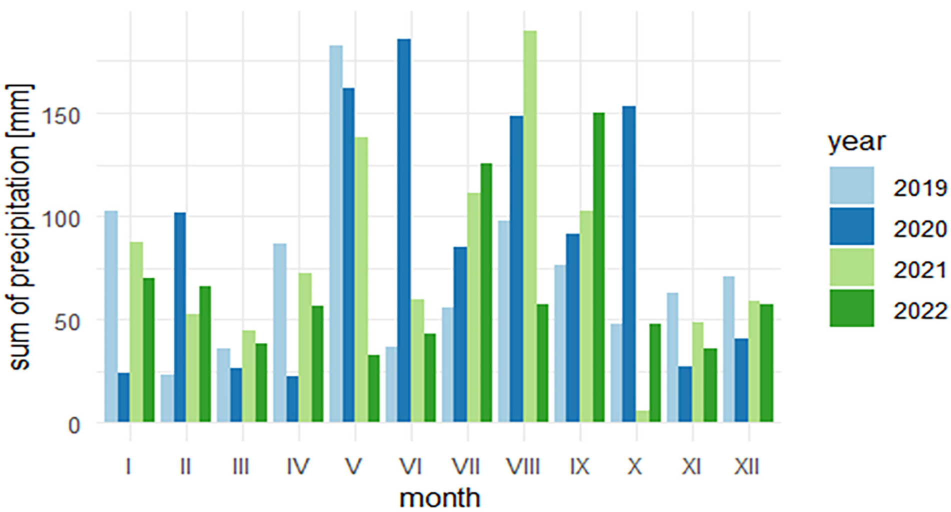

Figure 6. Total precipitation in 2019–2022 (mm)

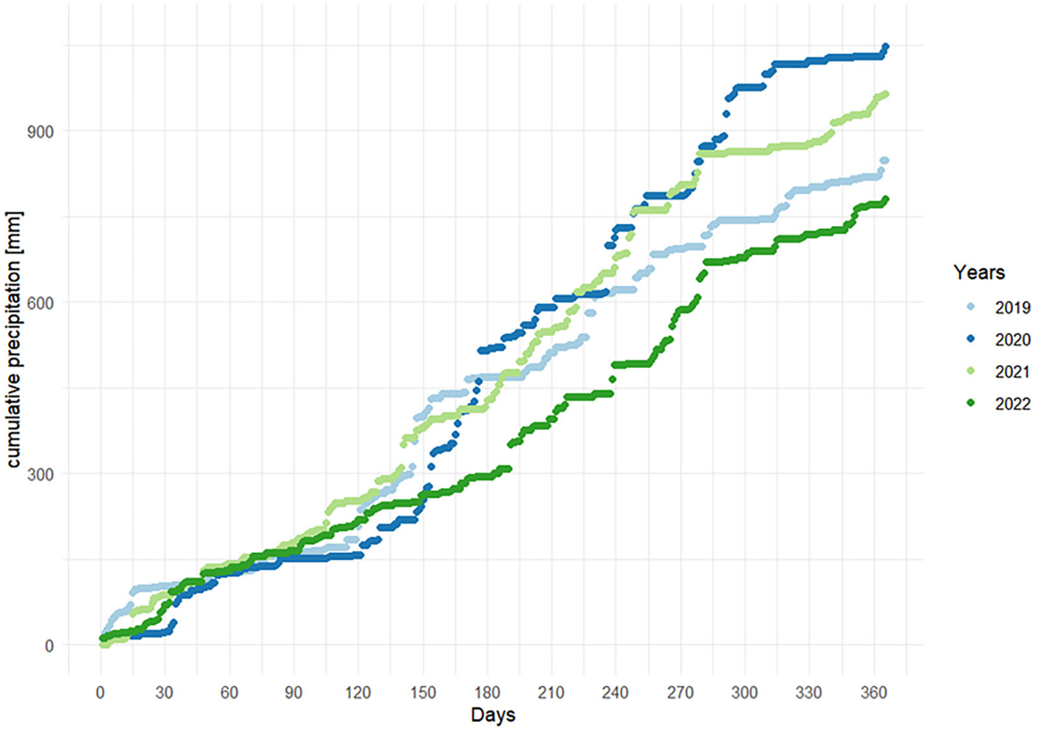

Figure 7. Cumulative rainfall in 2019–2022 (mm)

Characteristics of lysimeter leachates in 2019–2022

Lysimeter studies conducted in 2019–2022 showed that the leachate volumes from the soil profile of individual lysimeters were similar for all forms of use. The years 2019, 2021 and 2022 were characterized by significantly higher leachate values. Only in 2020 the upper value of measurement above 60 mm for all forms of use. The year 2020 was very abundant in precipitation, which translated directly into the amount of runoff.

It turns out that the form of use (the so-called fallow land) is the parameter that indicates the greatest scatter and the greatest minimum in the volume of leachate (Figure 8). This form of use, also generates the highest emissions of nutrients into the environment. We note here that fallow land causes the greatest and adverse changes in water chemistry. The bars and black dots indicate statistical values above 3 sigma. The variability and chemical level of waters is an important element in assessing the quality of leachates waters. Hence, the analysis of basic biogenic components (N-P-K) allowed a preliminary assessment of the biogenic quality of waters in the study basin. Figure 9 illustrates the variability of nitrogen in the ammonium form. Nitrate ion and ammonium ion

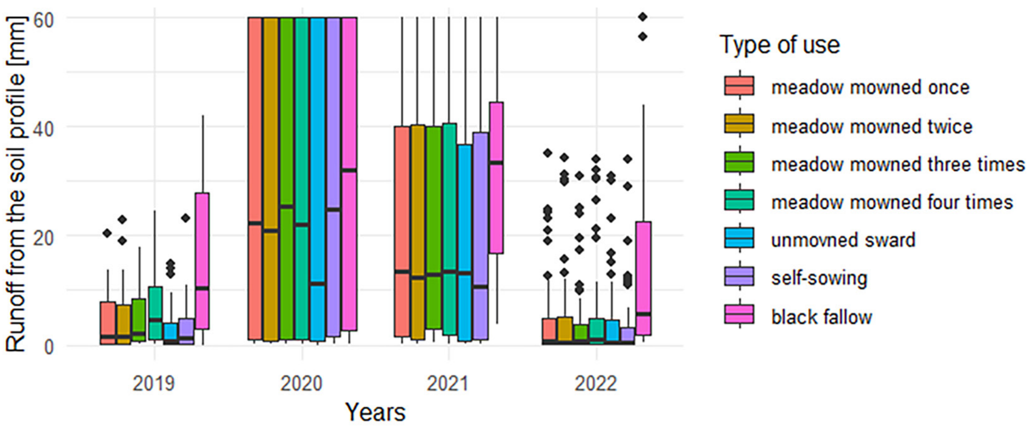

Figure 8. Runoff from the soil profile (mm) by year and type of use

are most readily absorbed by plants. However, the ammonium ion is retained periodically by soil colloids. The nitrate form, on the other hand, is found almost entirely in soil solution, while the ammonium form is retained periodically by soil colloids. This phenomenon, known as exchange sorption, prevents the leaching of this component deep into the soil profile and provides a periodic store from which nitrogen easily passes into the soil solution. Many studies show that some of the mineral nitrogen may be retained by soil microorganisms or lost in the form of ammonia to the atmosphere, and some of the NH_4^+-N may be oxidized to NO_3^--N (Twardy, Kopacz, 2014, Twardy et al., 2015). Figure 9 shows that the highest NH_4^+-N concentrations concern unmoved sward areas, or to a lesser extent, meadows moved once.

It is the ionic form that, like the nitrate ion, is best absorbed by plants. The nitrate ion remains in the soil solution, from which it can be easily leached, while the ammonium ion is retained by soil colloids, providing a periodic store from which it can pass into the soil solution. In addition, mineral forms of nitrogen can be assimilated by soil organisms or lost in the form of ammonia to the atmosphere. Under the conditions of the nitrification process, the ammonium ion can be oxidized to the nitrate ion, which also reduces its concentration in the soil solution. The cited relationships may account for the high variability of the obtained results of ammonium ion concentration in leachate and the lack of a noticeable correlation with the way the plots were cultivated or the amount of rainfall.

The cited relationships may explain the high variability of the obtained results of ammonium ion concentration in leachate and the lack of a noticeable correlation with the way the plots were cultivated or the amount of rainfall. Unlike ammonium forms of nitrogen (which are not stable in the external environment), the oxidized form of nitrogen in the form of NO_3^--N is a more stable form of mineral nitrogen but primarily remains in the soil solution, from which it can be easily leached.

Figure 10 shows the results of changes in the concentration of nitrogen in the nitrate form in the leachates studied. Comparing Figure 9 and 10, the differences between the ease of leaching of the ammonium and nitrate forms are clearly visible. In the case of ammonium, it poses little threat to the aquatic environment. Nitrate forms, on the other hand, represent a significant load of nutrients into the environment. The differences are mainly due to the properties of the two ions. The ammonium ion is susceptible to retention by the sorption complex, while the nitrate ion remains in the soil solution and readily enters groundwater and surface water.

In the case of phosphate ions (Figure 11), the situation is different. Analysis of leachates showed that the values of phosphate ion concentrations in leachates collected from lysimeters with different uses were at similar levels. The highest concentrations were recorded in 2022, especially when the sward was mowed two and three times. The minimum concentrations of PO_4^{3-} were determined (mainly but not only) in the case of leachates from fallow. The stability of phosphate ions, immobilized in the soil with calcium ions, for example, makes the value of ions carried away with leachate waters moderate even with varying runoff from the soil profile. Changes in the chemistry of water leaching from the soil profile due to the properties of nitrogen and phosphorus compounds in ionic form are as expected. Nevertheless, they are due to the characteristics of the current state of the soil profile and the use of the lysimeter plots studied. Euclidean distance analysis was used for comparisons of the total

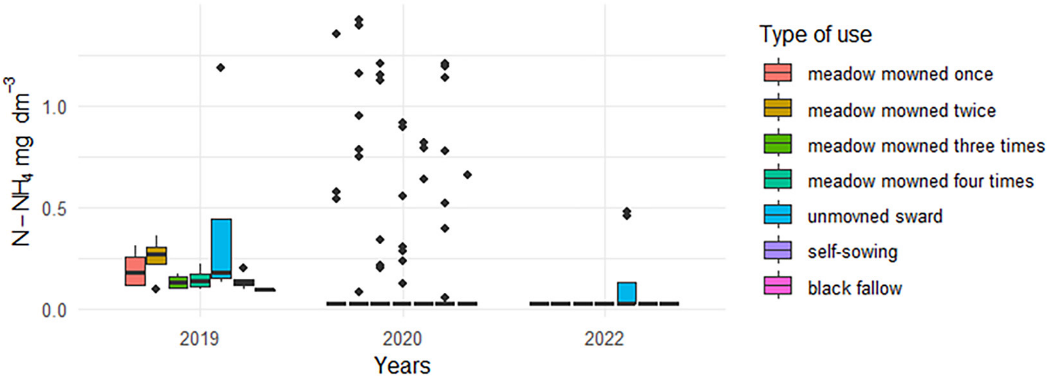

Figure 9. Changes in NH_4^+-N (mg·dm^{-3}) in various forms of use

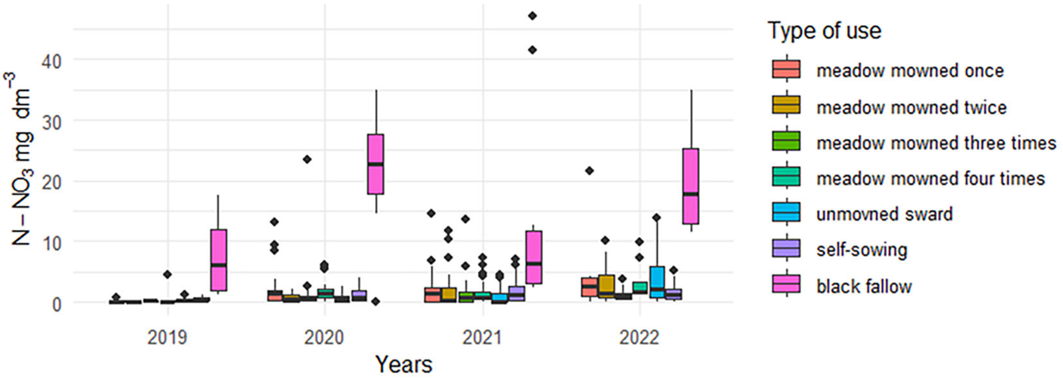

Figure 10. Changes in NO_3^--N (mg·dm^{-3}) in various forms of use

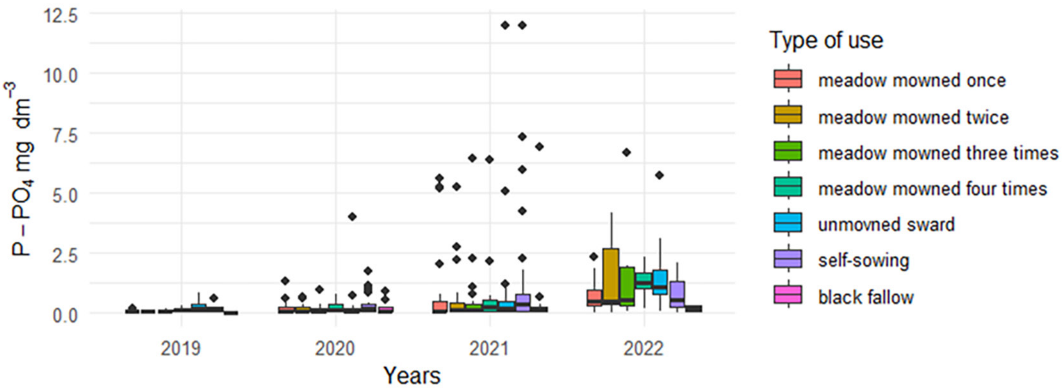

Figure 11. Changes in PO4^{3-} (mg·dm^{-3}) in various forms of use

data. The results of the analysis are presented in the form of a dendrogram (Figure 12). The analysis showed that, among the different use cases, the fallow from 2020 and the self-fertilization from 2021 stand out the most. The dendrogram shows that changes in leachate chemistry and leachate volume are the most variable here. The presented result of the cluster analysis showed that fallowing of the plot had the most destabilizing effect on environmental quality, i.e. the lack of proper use.

DISCUSSION

The article does not address the issue of climate change in detail. The aim of the work was only to show the relationship between runoff and nutrient concentrations in subsurface waters. A detailed climatic analysis of this problem will be presented in another study. A certain problem, mentioned earlier in the discussion chapter, is the accuracy of measurement and generalization of results from 1 m^2 of lysimeter surface to a larger area of agricultural use. In the presented studies, a particular type of use was repeated three times, and the black fallow area - twice. Increasing the number of repetitions, in the next studies, should improve the reliability of the result. Analysis of the volume and quality of the leachate from plots of different uses, equipped with lysimeters, perfectly reflects the influence of the agricultural land use on the quality of the leachate. Lysimeter measurements therefore provide important information on what type of management will be most effective in retaining water and, above all, in limiting the leaching of nutrients, and thus indirectly provide information on the quality of surface waters. Data obtained, among others, from lysimeter measurements on experimental plots are used to assess the effectiveness of agricultural practices introduced on the quality of surface waters. Lysimeter studies are burdened with a certain level of unevenness. This is due to the nature of lysimeter measurements. The measurement area of a lysimeter is 1 m^2, which, on a per hectare basis, causes this 10.000 – yr accuracy problem. Nevertheless - for the evaluation of the volume of runoff and the quality of leachate (these values do not depend

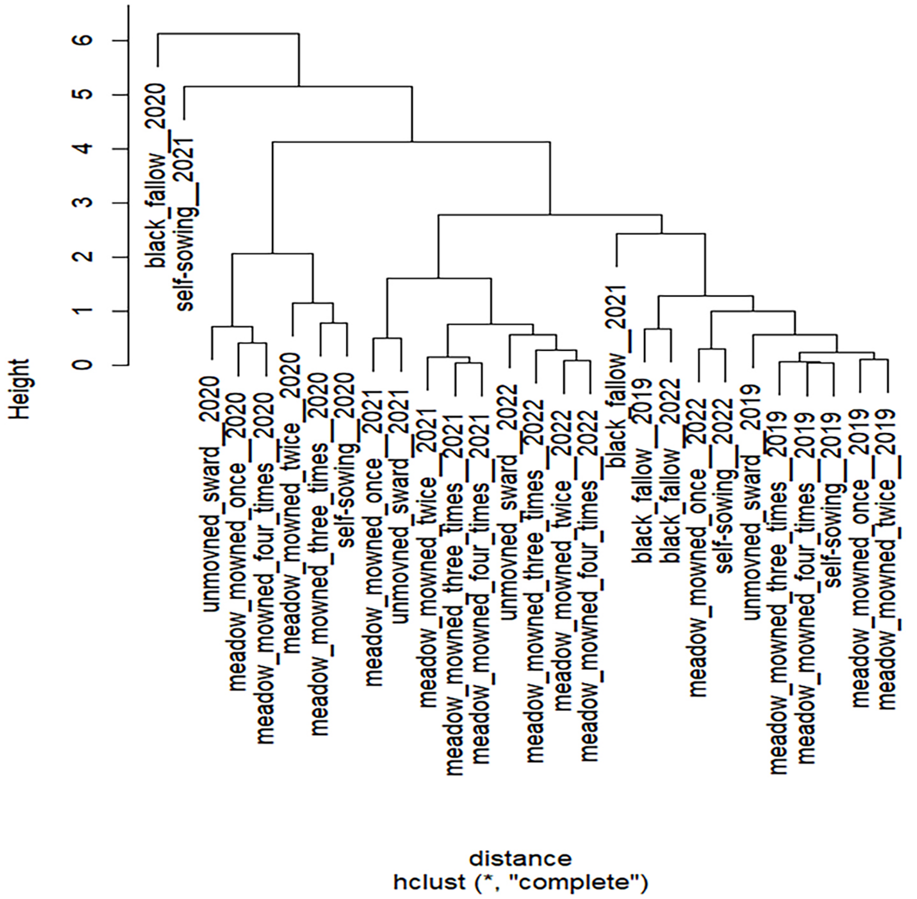

Figure 12. The relationship within the so-called cluster dendrogram („Tree of Distances" analysis)

directly on the surface area) it gives a fairly objective (albeit general) picture of the relationship between precipitation and subsurface runoff along with the average quality of these waters.

Analysis of leachate showed that only in the absence of mowing of the site (lysimeter plot) the value of NH_4^+-N concentrations was the highest. In other cases, the content of ammonium ions in the leachate was low. The existence of a sward in the absence of mowing probably limited the loss of ammonium ion to ammonia or nitrate ion.

In summary - data in the historical years (2001–2018) showed that water quality as well as its quantitative variability was low, mainly until 2015. The year 2018 indicated slow changes in this regard. The current analysis, which looked at the years 2019–2022, indicated that the years 2019 and 2022 are also almost identical in terms of outflow for total use. Only 2020 showed extremely high outflows.

The years 2020 and 2021 were characterized by much higher leachate values, for example, in 2020 the upper limit of subsurface leachate size takes a critical measurement value of more than 60 mm. These years were very abundant in leachate values ranging from 30 to 50 mm. Each time, fallow is the form of use here, causing the largest spread of leachate size and also the largest minimum.

Measured ammonium ion content in leachate showed that in all years (2019–2022) of the study (2019, 2020 and 2022) the concentration values were similar. The most varied year in terms of ammonium ion concentrations in leachates was 2019, with subsequent years presenting minimum values. No clear correlations were observed between the ways in which the plots with lysimeters were used with the concentrations of ammonium ion in leachates in successive years of the study. It is worth noting, however, that it was the form of use involving no mowing that indicated the highest values of ammonium ion.

Analysis of nitrate ions in leachate showed an increasing trend over the years. Only in the case of fallow in 2019 were NO_3- values minimal. On the so-called fallow land, nitrate nitrogen values were highest, which was due to the easiest leaching of nitrate ions not retained by the sorption complex. Phosphates, on the other hand, showed a similar trend to nitrate ions. While in 2019–2021 the values of phosphate concentrations did not exceed 1.5 $mg \cdot dm^{-3}$, in 2022 they were higher and were even above 2 $mg \cdot dm^{-3}$. Analyzing the use of lysimeter plots showed no statistically significant differences.

In order to check possible relationships between the forms of use of the plots and the composition of leachates, cluster analysis was used. Particularly noteworthy is the case of a fallow plot from 2020 and undergoing self-fertilization from 2021. Also noteworthy is the year 2020, in which the obtained parameters differ in values from other years.

CONCLUSIONS

In summary, the study showed - which types of use have the greatest impact on both the volume of subsurface runoff and the quality of leachate water. In mountainous conditions, the type of use, including meteorological (mainly precipitation) and soil conditions, have an extremely significant impact on the volume and quality of runoff, which also affect the quality of groundwater and surface water. Therefore, it is recommended to maintain a permanent plant cover, plough fields across slopes and maintain the plant cover as long as possible by using winter plants, using protective strips between fields, paths, rivers or water reservoirs, etc.

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