

Study of the Quality of Surface Waters in the Sącz Agglomeration

Emilia Basta^{1*}, Józef Ciuła¹

¹ Faculty of Engineering Sciences, University of Applied Sciences in Nowy Sącz, ul. Zamenhofska 1A, 33-300 Nowy Sącz, Poland

* Corresponding author's e-mail: ebasta@ans-ns.edu.pl

ABSTRACT

To evaluate the water quality in the Poprad, Kamienica, Dunajec river and the Łubinka stream in the Sącz agglomeration, two series of pilot studies were conducted on raw water samples, with a particular focus on both physical parameters (such as total suspended matter, turbidity, pH, and conductivity) and chemical parameters. The analysis presented increased concentrations of phosphorus, nitrogen, BOD₅, COD, chlorides, sulfates, permanganate value, orthophosphates, total suspended matter, specific electrolytic conductivity (PEW), pH levels, and various elements including lithium, magnesium, manganese, potassium, sodium, calcium, and iron. No exceedance of the detection limits for individual pesticides were observed in the waters of the Poprad, Kamienica rivers and the Łubinka stream. Nevertheless, increased concentrations of the insecticide imidacloprid and the fungicide imazalil were detected in the Dunajec river. The primary factors impacting water quality in the Sącz agglomeration are the use of fertilizers, the proximity of wastewater treatment plants, and the presence of landfill sites.

Keywords: surface water, physicochemical parameters, pesticides, metals.

INTRODUCTION

Water has recently become a major aspect of interest to researchers, in terms of its abundance and quality, and it is a key component of the environment also indicating environmental change. Water is used in every area of human functioning, thus being the most vulnerable to environmental pollution [Pekel et al., 2016]. Water quality may be affected by hydrological, atmospheric, climate, topographical and lithological factors [Jesuraja et al., 2021; Uddin et al., 2018]. One of the human activities negatively impacting the environment is the continuous increase in municipal waste [Przydatek and Basta, 2020; Zwolińska and Basta, 2024], but also increased sediment flow or soil erosion resulting from land use change [Lobato et al., 2015], heavy metal pollution and post-process water from wastewater treatment plants [Aquirre-Martínez and Martín-Díaz, 2020; Ciuła, 2022]. These threats should be eliminated to the highest extent possible and negative environmental impacts should be countered. Groundwater

accounts for only approx. 30% of the world's freshwater resources, and only 0.3% is concentrated in reservoirs such as lakes and rivers [Li and Qian, 2018]. Such factors as climate change and biodiversity also interfere with surface water [Pekel et al., 2016].

Surface waters (rivers, lakes, wetlands and artificial reservoirs), are the core of the world's water demand. Recent decades showcased a significant decrease in hydrological networks, and water bodies such as rivers, lakes, wetlands are markers and integrators of current climate change operating on the Earth [Cretaux et al., 2023; Zhao et al., 2022]. Contaminants entering surface and groundwater constitute an issue [Stephens et al., 2020; Derylo-Marczewski et al., 2019]. Riedo et al. [2022] estimated that pesticides applied directly to the soil reach non-target areas, especially along the edges of fields their amount may increase with the amount of precipitation. Reference is mainly made to pesticides used to control insects, fungi, bacteria, rodents, weeds and other pests that damage crops [Kruć-Fijałkowska et al.,

2022; Summerton et al., 2022] as well as other micropollutants, such as pharmaceuticals and microplastics [Puckowski et al. 2021; Titov et al., 2024]. The amount of water pollutants shows the ease of their migration to soils, waters and land, where the most persistent and mobile pesticides permeate [Derbalah et al. 2019; Montuori et al., 2014]. Pesticide contamination may result from water runoff, rainwater discharge from agricultural crops and runoff from irrigated fields [Aguirre-Martínez and Martín-Díaz, 2020; Masia et al., 2015]. These factors currently undeniably impact water quality as a result of agricultural activities determined by population growth, and thus the growing demand for agriculture-supported food production [Sadowski and Baer-Nawrocka, 2018; Srivastava et al., 2020].

Contaminants, particularly pesticides, are more and more frequently detected in drinking water, which may negatively impact human health [Klarich et al., 2017; Dragon et al., 2018]. Contaminants concentrations in water vary depending on their amount and exposure time [He et al., 2020; Fini et al. 2019]. They are susceptible, similarly to other micropollutants, to migration from rivers to wells [Kumar et al., 2018; Nsibande and Forbes, 2016] and accumulation in the human body. Pollutants elimination from hydrological sources depends on the distance and the time pollutants remained in the water – the longer the duration, the more demanding the process of pollutant removal becomes [Sallwey et al., 2020; Kruć et al., 2019]. An essential issue is to prevent leachate from infiltrating the soil and surface water, a task that, at landfill sites, is safeguarded through the use of plastic drainage systems [Przydatek et al., 2024; Wysowska et al., 2024]. In contemporary practice, advanced surface water treatment processes are increasingly employed for such purposes, including methods such as gamma irradiation, bioremediation, membrane filtration, oxidation, ozonation, and adsorption [de Souza et al., 2020].

BACKGROUND

The presence of pesticides in ecosystems induces adverse effects that vary based on the concentration, quantity, and duration of exposure to these contaminants. Furthermore, pesticides are regarded as highly toxic due to their persistence in the environment and their ability to bioaccumulate in organisms [Porter et al., 2018]. These

pollutants pose significant risks to human health, potentially causing serious conditions such as cancer, infertility, birth defects, and chromosomal abnormalities, which may result in DNA mutations and oxidative stress. Such effects are associated with aging and diseases like Parkinson's and Alzheimer's. Although pesticides are primarily applied to the soil, they can be transported over long distances through processes such as evaporation and precipitation. Additionally, pesticides can enter water bodies through surface runoff and infiltration into groundwater. Consequently, elevated concentrations of various compounds have been detected in surface waters on a global scale. [Sabarwal et al., 2018; Gronba-Chyła et al., 2024]. Due to runoff and soil erosion, phosphorus is also leached from agricultural fields, prompting farmers to apply fertilizers using specialized agricultural machinery and equipment to mitigate these deficits [Kowalski et al., 2022]. Plants, however, lack the ability to use the phosphorus supplied to them to the maximum extent, which results in excess phosphorus entering surface waters through erosion. Owing to the limited solubility of phosphate in the soil, it is transported 75%–90% with water runoff from farmland [Mekonnen and Hoekstra, 2017]. Excessive concentrations of nitrogen can also be detected in surface waters, of which the following are identified as the main sources: manure, domestic and industrial wastewater [Shi et al., 2019].

Chloride pollution of surface waters, in particular following the winter season, is on the increase. Sodium chloride (NaCl), commonly utilized as road salt in winter to enhance safety on roads and sidewalks, has detrimental long-term effects on soil and surface waters. Its prolonged use diminishes biodiversity among aquatic flora and fauna while encouraging the proliferation of phytoplankton, particularly cyanobacteria. Cl has also been observed to reduce water self-purification processes by decreasing the accumulation of nutrients in macrophytes, reducing the rate of denitrification and limiting the decomposition of organic matter [Szklarek et al., 2022a; Hajduga et al., 2019].

The concentrations of various phosphorus forms, including total phosphorus, orthophosphates, polyphosphates, and organic phosphorus, are of tantamount importance for water quality. As presented in the research of Wojtkowska and Bojnarowski [2018], the sources of such pollutants in rivers are wastewater treatment plant discharges, leaking septic tanks, surface runoff

from agricultural land and roads, landfill leachate [Ciula, 2021; Basta and Szewczyk, 2024]. A high level of phosphate contamination is indicative of significant eutrophication. A substantial proportion of orthophosphates within total phosphorus suggests that phosphorus compounds in rivers are, to some extent, undergoing self-purification processes [Wiewiórska and Rybicki, 2022; Wojtkowska and Bojanowski 2018]. Sources of organic phosphorus can also include substances originating from the decomposition of organic matter, mainly proteins – for instance they are formed as a result of inflow of wastewater with phosphorus-containing surfactants [Wiewiórska et al., 2023; Cruz-Alcalde et al., 2017]. Yet, orthophosphates may in turn be formed by leaching from the soil or by transformation of other forms of phosphorus in water through mineralization and hydrolysis. The range of phosphate concentrations is observed even in short stretches of rivers [Gebus-Czupyt and Wach 2022; Doydora et al., 2020].

Significant sources of water quality degradation also include area-based nitrate pollution from agriculture [Akhtar et al., 2021; Ciula et al. 2023]. Soil overfertilization is the main contributor to the phenomenon [Withers et al., 2014] as well as improperly balanced fertilization, i.e. inadequate mix of nitrogen to phosphorus and potassium [Ławniczak et al., 2016] and the use of fertilizers at inappropriate times of the year, for example, in Poland, nitrate exceedances in surface waters are mostly recorded in the winter season [Dębska et al., 2021; Kuczyńska et al., 2021] due to the limited (or lack thereof) uptake of nitrogen by vegetation outside of the vegetation period.

RESEARCH METHODS

The aim of the work was analysis was to analyze the physico-chemical parameters of surface waters of four major watercourses of the Sącz agglomeration/Beskid Sądecki (Chełmiec Commune, Nowy Sącz, Stary Sącz, Nawojowa Commune) in the context of industrialization and urbanization of urban-rural areas in Stary Sącz, Chełmiec and Nowy Sącz. The implementation of the research project is aimed at determining the surface waters quality of the Dunajec, Poprad, Kamienica rivers and the Łubinka stream, which are tributaries of the Dunajec river, flowing through Nowy Sącz in the context of urbanization

of the southern Polish region. The areas of Nowy Sącz, Stary Sącz and the Chełmiec commune are mountainous and heavily industrialized, yet also being agricultural areas. Such conditions are conducive to surface water pollution, both through the entry of pesticides contained in fertilizers and industrial waste. Nowy Sącz is located in the Outer Western Carpathians, the Western Beskids and the macro-region of the Sącz Basin, these lands are located in the river forks of: the Dunajec, Poprad and Kamienica rivers. The Łubinka stream also flows on the outskirts of the analyzed area.

Cumulatively, surface waters cover approx. 2.19 hectares, i.e. 3.8% of the city's total area. In terms of flows, the Dunajec river is the largest one (average annual flow 63.5 m³/s) followed by the Poprad river (24.5 m³/s) and the Kamienica river (3.67 m³/s). These rivers are of a mountainous nature, which means observable fluctuations of water levels throughout the year. The highest river levels are recorded following spring thaws and sudden intense summer downpours, whereas lower levels predominantly occur in winter, primarily due to prolonged snow cover. Occasional autumn or even summer lows occur. Within the boundaries of Nowy Sącz, the Dunajec river has flood embankment, while other watercourses in significant sections are regulated and partly have banks raised with earth dikes [Gryczko-Gostyńska and Olędzka].

Figure 1 presents an overview map of the analyzed area of Nowy Sącz, with surface water sampling points marked. Figure 1 presents the location of surface water sampling points selected based on own observations and field inspections. The exact sampling points location is presented in Table 1, along with the definition of geographical coordinates based on the 1992 coordinate system (EPSG 2180). The raw water samples represent pilot samples of surface water in the Sącz agglomeration, and studies will continue in the near future.

The Poprad river is typologically classified as a medium eastern upland river [Journal of Laws of 2021, item 1475]. The Poprad river's total length amounts to 169.8 km, and its catchment area amounts to 2077.30 km². The Polish section amounts to 62.1 km, the catchment area amounts to 482.8 km², the river has no major tributaries, only mountain rivers and streams [Radecki-Pawlik et al., 2019]. Surface water quality analyses were performed at P1 and P2 points. The river has its source in the Slovak part of the High Tatra Mountains from the place of the Hińczowy stream joining the Krupa stream, and flowing into

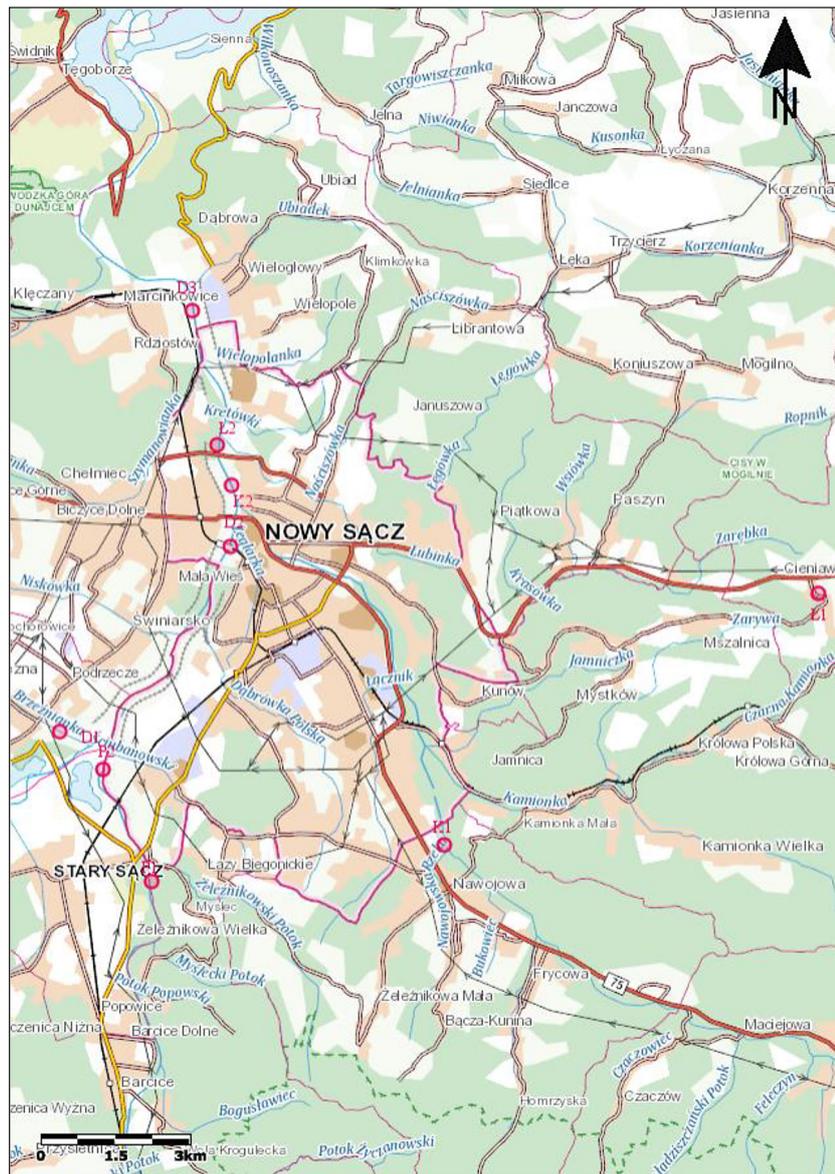


Figure 1. Overview map of surface water sampling points.
Source: own study based on <https://www.geoportal.gov.pl/>

the Dunajec river in Stary Sącz. As regards the Dunajec river, pilot raw water samples were collected at three points: D1, D2, D3. The Dunajec is a medium [Czerniawski and Bilski, 2019] eastern upland river, which flows through the entire Nowy Sącz agglomeration, with the Kamienica and Łubinka watercourses as its tributaries. Watercourses: the Kamienica and the Łubinka are included in the category of surface water as a flysch stream [Policht-Latawiec et al., 2014]. The Kamienica takes its source in the northern side of the Jaworzyna Krynicka mountains, where mountain streams flow, while it finds its outlet in the Dunajec river in the area of Nowy Sącz. The length of the Kamienica amounts to 33.079 km,

and the catchment area amounts to 237.83 km², it flows through a valley in a northwest direction, marking the border between the Beskid Niski and Beskid Sądecki. The predominant form of natural landscape in the catchment area is the Carpathian flysch, the flysch sediments mainly in the form of sandstone, shale and conglomerate. In terms of use, the predominant part of the catchment (58.7%) is forest-covered, the types of which are determined by soil conditions, terrain and climatic conditions, other forms of use include: developed areas (11.8%), grassland (7.4%), arable land (6.5%), wasteland (15.6%). The highest runoff volumes occur in March and April due to the thawing of the snow cover, and what characterizes

Table 1. Characteristics of surface water sampling points with their coordinates defined based on the 1992 coordinate system (EPSG, 2180)

Collection point marking	Name of the watercourse	Coordinates X	Coordinates Y	Location of the collection point
D3	Dunajec	201713.23	620813.87	The collection point is located in the Chelmiec commune
Ł2	Łubinka	198849.11	621620.80	The collection point is located in the City of Nowy Sącz
K2	Kamienica	197374.06	621951.59	The collection point is located in the City of Nowy Sącz
D2	Dunajec	196937.49	621759.76	The collection point is located in the City of Nowy Sącz
Ł1	Łubinka	195072.18	633566.82	The collection point is located in the City of Nowy Sącz
K1	Kamienica	190759.46	625979.87	The collection point is located in the Nawojowa Commune
P1	Poprad	189932.64	620066.44	The collection point is located in the Stary Sącz Commune
P2	Poprad	192274.20	619193.30	The collection point is located in the City of Nowy Sącz
D1	Dunajec	192565.25	618869.18	The collection point is located in the Stary Sącz Commune

the surges in the Kamienica river is short duration (2 days on average) [Wałęga et. al., 2016].

The source of the Łubinka is the village of Mogilno, where it initially flows in a southwesterly direction, from the mouth of Zarębianka, to change its direction to the west. The stream is 15 kilometers long, and the catchment area of the Łubinka and its tributaries is located in three geographic mesoregions. The largest part of the catchment area is located in the Beskid Niski, but some of the source streams flow from the Rożnowskie Foothills. The lower section of the Łubinka is already located in the Sądecka Basin, the main tributaries are streams: Krasówka, Łękówka, Naściszówka, Wsiówka and Zarębianka. The analyzed flysch stream flows into the Dunajec river on its right side, carrying pollutants from the surrounding agricultural areas, as well as industrialized areas, scrap metal dumps, and a wastewater treatment plant. Water samples were also taken from both watercourses at points for the Łubinka stream (L1, L2) and the Kamienica river (K1, K2), respectively.

The river accumulating all the watercourses analyzed is the Dunajec – the second largest river considered a Carpathian tributary of the Vistula (247 km). The Dunajec river's catchment area covers 6813 km², 1028 km² of which is outside Poland. It is formed by streams in Nowy Targ – large streams of the Czarny and Biały Dunajec, where the river flows along the northern bank of the Nowy Targ Basin, significantly forested with spruce, then flows through the small erosion

basin of Krościenko, flows from Jazowska with a funnel-shaped valley extension into the Nowy Sącz Basin. In this section two rivers flow into the Dunajec river – the Ochotnica (109.1 km²) and the Kamienica (128.5 km²) draining the Gorce Mountains. In the area of the flat, unfor-ested Sącz Basin, the Dunajec receives the waters of the Poprad river (2080.2 km²) flowing out of the High Tatras and breaking from the mountainous areas of Slovakia into Poland through the Beskid Sądecki. Furthermore, the Dunajec is supplied by a number of smaller tributaries and, in Nowy Sącz, by the Kamienica Nawojowska river, which collects water in the Beskid Sądecki. The rock substrate of the Dunajec river basin is quite diverse, as its Tatra area is composed of crystalline rocks and sedimentary rocks of different ages (Triassic, Jurassic, Cretaceous) and lithologies of the rift and conglomerate series. On its way, the Dunajec river flows through the rocks of the so-called Podhale flysch (older Tertiary), rocks of the Czorsztyń and Pieniny series (Jurassic, Cretaceous) shielded by a mantle of marls, shales and sandstones, flysch formations of the Magurian and Menilite series (Tertiary, Cretaceous), Miocene siltstones and gravels of the Orava-Nnowotarska fracation, which became the cause of their partial embolization. The bottom of the Sącz Basin and the sub-quadernary layers of the lower lowland part of the basin are Miocene formations [Wiewiórska, 2023].

The study was carried out using research materials comprising surface water samples collected

from nine sampling points, as shown in Figure 1 and Table 1. These samples served as preliminary material for pilot studies, which will be repeated and expanded, with additional intensified monitoring of specific parameters. The analyzed surface water samples will provide the foundation for subsequent research and a comprehensive investigation into the sources of watercourse pollution in the study area.

The work schedule for the research project included carrying out two series of surface water sampling in February and April, at nine points. The samples were subjected to a series of raw water laboratory tests for 16 non-metallic inorganic parameters (total phosphorus (P), Kjeldahl nitrogen, total nitrogen as N, nitrates (NO_3), nitrites (NO_2), chlorides (Cl), COD-Cr, phosphate phosphorus, sulfates (SO_4), total $\text{N-NO}_2 + \text{N-NO}_3$, permanganate value (COD-Mn), nitrate nitrogen (NNO_3), nitrite nitrogen (NNO_2), BOD_5 , orthophosphates (PO_4), total suspended matter), 5 physical parameters (turbidity, specific electrolytic conductivity (PEW), pH value, PEW measurement temperature, pH measurement temperature), 27 dissolved metals, including major cations (antimony (Sb), arsenic (As), barium (Ba), beryllium (Be), boron (B), chromium (Cr), zinc (Zn), total phosphorus (P), aluminum (Al), cadmium (Cd), cobalt (Co), lithium (Li), magnesium (Mg), manganese (Mn), copper (Cu), molybdenum (Mo), nickel (Ni), lead (Pb), potassium (K), mercury (Hg), selenium (Se), sodium (Na), silver (Ag), thallium (Tl), vanadium (V), calcium (Ca), iron (Fe)) and 239 pesticides, including herbicides, insecticides, fungicides, as well as all-purpose pesticides and plant growth promoters. The pesticides analyzed are used primarily in the fall to protect spring and winter cereal crops, as well as apple, corn, potatoes, canola (2-amino-N-(isopropyl) benzoamide, 2-hydroxyatrazine, 3-hydroxy-carbofuran, acetochlor, acclonifen, alachlor, ametryn, amidosulfuron, atrazine, atrazine-deisopropyl, atrazine-diethyl, benalaxyl, bentazonmethyl, bifenox, bromacil, chloridazone, chloridazon-desphenyl, chlorpropham, chlorsulfuron, chlortoluron, chlortoluron-desmethyl, clomazone, cybutryne (irgarol), desmethrin, difenoxuron, dimethachlor, diuron, domethenamid, epoxyconazoles, EPTC (s-ethyl dipropylthiocarbamate), ethofumesate, ethoprophos, fenuron, fipronil, florasulam, fluazifop-butyl (isomers), fluazifop, foramsulfuron, haloxyfopmethyl (isomers), haloxyfop, imazamox, imazamox, isoproturon, isoproturon-monodesmethyl,

isoproturon-desmethyl, carbetamide, carfentrazone, clodinafop, lenacil, linuron, mefenpyr-diethyl, metazachlor, metobromuron, metolachlor (isomers), metribuzin, metribuzin-deamino, mesosulfuron-methyl, mesotrione, napropamide, napalam, nicosulfuron, ethyl parathion, pendimethalin, picloram, pretilachlor, prime sulfuron-methyl, prodiamine, promethrin, propachizafop, propachlor, propanil, propoxycarbazonasodium, propyzamide, prosulfocarb, prothioconazole, quinclorac, quinoxifen, quizalofop, rimsulfuron, sulfosulfuron, simazine, simazine-2-hydroxy, terbuthylazine, terbutrin, terbuthylazine-diethyl-hydroxy-2-, terbuthylazine-hydroxy, terbuthylazine-diethyl, tifensulfuron-methyl, triasulfuron, tribenuron-methyl, triflurosulfuronmethyl, acetamiprid, aldicarb, atratone, bendiocarb, chlorfenvinphos, chlorpyrifos-methyl, chlorpyrifos, cyanazine, cyprazine, cyromazin, desmethrin, diazinon, dichlorvos, dichlormid, diethofencarb, difenacoum, diflubenzuron, diflufenican, dicrotophos, dimefuron, dimethoate, ethiofencarb, fenamiphos, fenarimol, phenoxaprop, phenoxycarb, fenpropidin, fensulfotion, phonophos, fosalon, phosphamidon, fosmet, furatiocarb, hexithiazox, hexazinone, imazethapyr, imidacloprid, indoxacarb, cadusafos, carbofuran, carboxin, clothianidin, krimidin, coumaphos, malathion, mecarbam, methamidophos, methami tron, methiocarb, methoxuron, methoxyphenoside, methomyl, metsulfuronmethyl, moline, monocrotophos, neuron, nuarimol, oxadixyl, oxamyl, omethoate, paclobutrazol, pencycuron, pyrimiphosmethyl, pyrimiphos-ethyl, pyrimicarb, profenofos, propoxur, pyriproxifen, sebumetone, sulfonaldicarb, sime-thrin, tebutiuron, teflubenzuron, thiabendazole, thiamethoxam, trialat, triazophos, tricyclazole, triforine, azoxystrobin, bitertanol, boscalid, bromophosetyl, carbaryl, chlorbromuron, chloroxuron, cymoxanil, cyprodinil, cyproconazole, difenoconazole, dimethomorph, fenhexamid, flusilazole, flutolanil, hexaconazole, iprodione, isopyrazam, carbendazim, kresoxim-methyl, mandipropamid, imazalil, metalaxyl (isomers), metconazole, picoxystrobin, pyrimethanil, prochloraz, propamocarb, spiroxamine, tebuconazole, thiophanatemethyl, triadimefon, triadimenol, trifloxysulfuronsodium, triticonazole, fenpropimorph urea, propiconazole, monuron, monolinuron, 2-chloro-2, 6-diethylacetoanilide, acybenzolar-S-methyl, azinphosetyl, azinphosmethyl, BAM (2,6-dichlorobenzamide metabolite), BDMC (bis-desmethoxycurcumin), dichlofention,

diuron, desmethylorapamycin (DCPMU), ethion, ethylparaoxon, forat, imazamethabenz-methyl, iprovalicarb, clomeprop, malaoxon, metabenzothiazuron, methidathion, methylparaoxon, penconazole, pyribenzoxime, profam, promecarb, prometon, propazine, sebuthylazine, sethoxydim, thioben carb).

The limit of quantification for the aforementioned pesticides amounted to 0.05 µg/l.

Forty-five organochlorine pesticides were also studied, and their limits of quantification amounted to: 0.005 µg/l (hexachlorobenzene (HCB), aldrin, sum of 5 hexachlorocyclohexanes), 0.01 µg/l (hexachloroethane, hexachlorobutadiene, 1,2,4,5-tetrachlorobenzene, pentachlorobenzene, trifluralin, hexachlorocyclohexane alpha, hexachlorocyclohexane beta, hexachlorocyclohexane gamma, hexachlorocyclohexane delta, hexachlorocyclohexane epsilon, alachlor, heptachlor, telodrin, isodrin, heptachloroepoxide-cis, heptachloroepoxide-trans, 2,4-DDE, alpha-endosulfan, 4,4'-DDE, dieldrin, 2,4-DDD, endrin, beta-endosulfan, 4,4'-DDD, 2,4-DDT, 4,4'-DDT, methoxychlor), 0.02 µg/l (1,2,3,5- & 1,2,3,4-tetrachlorobenzene, sum of endosulfan, quintozone & pentachloroaniline), 0.03 µg/l (sum of 3 tetrachlorobenzenes, dicofol, ketonendrin, aldehydendrin), 0.04 µg/l (sum of 4 hexachlorocyclohexanes, sum of 4 isomers of DDT), 0.05 µg/l (dichlobenil), 0.06 µg/l (sum of 6 isomers of DDT), 0.270 µg/l (sum of 25 OCPs + 3 CBs), 0.290 µg/l (sum of 27 OCPs + 3 CBs), 0.350 µg/l (sum of 29 OCPs + 3 CBs). A total of 332 parameters were studied in one series.

According to PN-EN 1899-2:2002, ISO 5815-2, SM 5210B standards, biochemical oxygen demand after 5 days (BOD_5) was determined. Per ISO 15923-1:2013(E), the following parameters were determined: ammonium ion, nitrate, nitrite, chloride, orthophosphate, sulfate. Silica was determined with the use of photometric method [NR – Journal of Laws of 2019 item 1747]. The permanganate index was determined with the permanganate method, chemical oxygen demand with the dichromate method (COD-Cr) and the spectrophotometric method. Per PN-ISO 15705:2005, the chemical oxygen demand index (SP-COD) was determined with the miniaturized method using sealed tubes. In accordance with PN-EN 27888:1999, the specific electrolytic conductivity was determined, whose result correction was carried out using a temperature-compensated device (PEW 25°C). Through fluorescence

spectrometry, mercury was determined. The sample was filtered through a microfilter with a porosity of 0.45 µm, and nitric acid was added before the analysis (CSN EN ISO 178 52). The amount of elements was determined by inductively coupled plasma atomic emission spectrometry and stoichiometric calculation of compound concentrations from the measured values, including total mineralization and calculation of total Ca+Mg. The sample was filtered through a microfilter with a porosity of 0.45 µm, and nitric acid was added before the analysis (CSN EN ISO 11885). The amount of Kjeldahl nitrogen was determined with the spectrophotometric method (ISO 7150-1 CSN). With the application of ISO 15923-1:2013 (E), the quality of selected parameters was determined with discrete analysis: ammonium ion, nitrate, nitrite, chloride, orthophosphate, sulfate.

Total nitrogen concentration was determined with calculation method based on the component results, and organochlorine pesticides and other halogen compounds were also determined by gas chromatography and liquid chromatography with ECD detection, and the sum of organochlorine pesticides and other halogen compounds was calculated from the measured values (CSN EN ISO 6468). Determination of pesticides, pesticide metabolites, drug residues and other contaminants was performed with liquid chromatography with MS/MS detection and calculation of the sum of pesticides, pesticide metabolites, drug residues and other contaminants from measured values. Per PN-EN ISO 10523:2012, water pH was determined by correcting the pH result with a temperature compensation device (20°C), and turbidity was determined with an optical turbidimeter.

Per ISO 15923-1:2013 (E) selected water quality parameters were determined with discrete analysis. (Ammonium ion, nitrate, nitrite, chloride, orthophosphate, sulfate and silica with photometric method). Per PN-EN ISO 6878:2006, the determination of phosphorus was carried out using the spectrophotometric method with ammonium molybdate. Per PN-EN 872:2007+Ap.1:2007, suspended matter was determined using filtration through glass fiber filters (CSN EN ISO 7027-1). Turbidity of the studied raw water was determined with an optical turbidimeter.

The results obtained were compared with the permissible parameters contained in the current legal act on surface water quality, i.e. the Regulation of the Minister of Infrastructure of 25 June 2021 on the classification of ecological status,

ecological potential and chemical status, and the method of classifying the status of surface water bodies, as well as environmental quality standards for priority substances [Journal of Laws 2021, item 1475].

RESULTS

The following tables present research results for selected parameters of the surface waters of the Poprad river (Table 2), Kamiénica river (Table 3), Łubinka stream (Table 4) and Dunajec river (Table 5). Surface water samples quality analysis and their classification was carried out pursuant to the Regulation of the Minister of Infrastructure [Journal of Laws of 2021, item 1475], which distinguishes 5 classes of surface water quality, with physico-chemical parameters falling into two classes:

- Class I means very good condition,
- Class II means good condition,
- failure to meet the requirements of Class II means condition below good, moderate condition.

The analytical results of water samples for all the aforementioned watercourses (at all sampling points), tested for the content of individual pesticides and organochlorine pesticides fall below limits of quantification (2.2). Concentration of only two of the studied pesticides exceeded their limits of quantification, i.e. in the Dunajec river, at D2 point (imidacloprid 0.099 µg/l) and D3 (imazalil 130 µg/l) (Table 5). The surface water quality class for indicators specified in the Regulation has not been determined, however, taking into account their low concentrations, the conclusion is that the waters of the Poprad river,

Table 2. Water quality indicators in the Poprad river

Non-metal inorganic parameters	Unit	P1		P2		Surface water quality class
		Draft 1 (February)	Draft 2 (April)	Draft 1 (February)	Draft 2 (April)	
Total phosphorus (P)	mg/l	<0.050	0.071	0.065	0.065	very good
Kjeldahl nitrogen	mg/l	<0.50	0.61	0.74	0.60	very good
Total nitrogen as N	mg/l	1.40	5.72	2.19	1.52	moderate
BOD ₅	mg/l	2.80	1.1	2.20	1.1	good
Chlorides (Cl)	mg/l	12.2	9.5	12.4	9.4	good
COD-Cr	mg/l	21.0	10.4	15.2	13.6	good
Sulfates (SO ₄)	mg/l	23.6	19.9	28.4	19.4	very good
Sum of N-NO ₂ + N-NO ₃	mg/l	1.40	5.12	1.45	0.919	unclassified
Oxidizability (COD-Mn)	mg/l	3.24	2.44	2.79	2.25	very good
Nitrite nitrogen (N-NO ₂)	mg/l	0.023	0.030	0.018	0.029	good
Orthophosphates (PO ₄)	mg/l	0.127	0.263	0.196	0.209	moderate
General suspension	mg/l	67.4	18.0	10.0	15.7	moderate
Physical parameters						
Specific electrolytic conductivity (PEW)	µS/cm	347.0	315.0	350.0	319.0	very good
pH value	-	7.7	8.1	7.6	8.1	good
Pesticides						
imidacloprid	µg/l	<0.050	<0.050	<0.050	<0.050	unclassified
imazalil	µg/l	<0.050	<0.050	<0.050	<0.050	unclassified
Dissolved metals/mainly cations						
Lithium (Li)	mg/l	0.0062	0.0084	0.0061	0.0088	unclassified
Magnesium (Mg)	mg/l	9.42	9.49	9.58	9.50	very good
Manganese (Mn)	mg/l	0.00170	0.00133	0.00570	0.00103	unclassified
Potassium (K)	mg/l	1.89	2.00	1.93	1.99	unclassified
Sodium (Na)	mg/l	8.27	8.16	8.28	8.38	unclassified
Calcium (Ca)	mg/l	41.9	40.8	43.5	39.4	very good
Iron (Fe)	mg/l	0.0206	0.0141	0.0193	0.0129	unclassified

Kamienica river and the Łubinka stream are not polluted with pesticides.

Increased concentrations of the indicators tested at P1, P2 points (Table 2), in the two pilot series, mainly result from the fact that the waters of the Poprad river flow from Slovakia, through mountainous, Tatra areas, where the tanning industry dominates, which may affect the elevated levels of cadmium and chromium, among others, in the watercourses [Wiśniowska-Węglarz, 2008]. Above the P2 point, the Poprad river flows through towns, agricultural fields, and in the vicinity of a landfill, which may further affect surface water quality through the risk of landfill leachate entering surface water. Account should also be taken of the runoff of excessive amounts of water from sudden snowmelt, deposited on the southern slopes of the Tatra Mountains.

Class I (very good) specifies the ecological status and quality of surface waters of the Poprad river in terms of total phosphorus concentration, whose values ranged from 0.050 to 0.071 mg/l, the highest concentration of this parameter was recorded in April at P1 point. Very good surface water quality was determined based on the results of sulfate analysis (from 19.4 to 28.4 mg/l), oxidation (COD-Mn) with results from 2.25 to 3.34 mg/l, electrolytic conductivity (PEW) (from 319 to 530 $\mu\text{S}/\text{cm}$), pH values (from 7.6 to 8.1), and magnesium and calcium concentrations, with values from 9.42 to 9.58, and 39.4 to 43.5 mg/l, respectively. Class II (good condition) was determined by the concentrations of chloride (from 9.4 to 12.2 mg/l), COD-Cr (from 10.4 to 21 mg/l) and nitrite nitrogen (from 0.018 to 0.030 mg/l). Condition above Class II was determined by such parameters as total nitrogen (from 1.40 to 5.72 mg/l), orthophosphates (from 0.127 to 0.263 mg/l, a concentration of 162 mg/l beyond the limit of Class II surface water quality classification values) and total suspended matter (from 10 to 67.4 mg/l, by 34.7 mg/l beyond the limit of Class II surface water quality values). These values may be classified as a moderate class of surface water quality. Values not classified in the Regulation [Journal of Laws of 2021, item 1475] are the sum of $\text{N-NO}_2 + \text{N-NO}_3$, pesticides, including imidacloprid and imazalil, lithium, manganese, potassium, sodium, iron. According to the data provided by the laboratory, the limit of quantification of the sum of $\text{N-NO}_2 + \text{N-NO}_3$ concentrations amounts to 0.050 mg/L. This value was exceeded 102 times at P1 point during the April sampling. Likewise, other

values were significantly exceeded at each of the sampling points on the Poprad river (Table 2).

The Kamienica river's water quality analysis showed no pesticide pollution, however, exceedance of the values of Kjeldahl nitrogen concentrations (from 0.50 to 0.75 mg/l), orthophosphates (from 0.030 to 0.206 mg/l), electrolytic conductivity (from 276 to 394 $\mu\text{S}/\text{cm}$) and calcium (from 35.1 to 52.2 mg/l) were particularly observed. Taking into account the Regulation [Journal of Laws of 2021, item 1475], the abovementioned indicators should be classified in class below II (moderate condition), since exceeding surface water quality limits of individual parameters varies from several to more than a dozen times. Class II classified parameters such as BOD_5 (from 1.0 to 2.5 mg/l), chlorides (from 6.5 to 11.4 mg/l), total nitrogen (from 1.02 to 1.59 mg/l), COD-Cr (from less than 5.0 to 12.8 mg/l), sulfates (from 15.2 to 20.6 mg/l), nitrite nitrogen (from 0.005 to 0.014 mg/L), total suspended matter (exceeded the limit of the permissible concentration only at K1 point in April; 7.5 mg/L), pH value (from 7.4 to 8.2) and magnesium (from 6.83 to 9.98 mg/L). Indicators such as total phosphorus (less than 0.050 mg/L), COD-Mn oxidation (from 1.36 to 2.27 mg/L) may be described as very good condition (Class I). Quality parameters studies results for the Kamienica river stem from the terrain through which it flows, and additionally the Kamienica river is characterized by a complex hydrological regime, which means that its surges occur most often in March and from May to June.

The analyzed surface water quality indicators for the Łubinka stream are classified as Class I for parameters such as COD-Cr (from 7 to 10 mg/l), permanganate value COD-Mn (from 1.65 to 2.27 mg/l). Indicators such as Kjeldahl nitrogen (below 0.050 to 0.59 mg/l), total nitrogen (less than 1 to 2.90 mg/l), BOD_5 (below 1 to 2.9), pH value (from 7.5 to 8.2), total suspended matter (Ł1 point, standard 17.3 mg/l, value 16.9 mg/l) and nitrite nitrogen (0.005 to 0.017 mg/l), can be described as good condition (Class II). The highest index values are found for total phosphorus (Ł1 point, February, limit 0.14 mg/l, value 0.146 mg/l), chloride (Ł2 point, limit 12.8 mg/l, value 20.1 mg/l and 24.2 mg/l), sulfate (Ł1 and Ł2 points, limit 28.2 mg/l, values from 25.4 to 29.2 mg/l), orthophosphate (Ł1 and Ł2 points, limit 0.067 mg/l, values from 0.077 to 0.160 mg/l), electrolytic conductivity (Ł2 point, limit 309, value from 261 to 520 $\mu\text{S}/\text{cm}$), magnesium (Ł2

Table 3. Water quality indicators in the Kamienica river

Non-metal inorganic parameters	Unit	K1		K2		Surface water quality class
		Draft 1 (February)	Draft 2 (April)	Draft 1 (February)	Draft 2 (April)	
Total phosphorus (P)	mg/l	<0.050	<0.050	<0.050	<0.050	very good
Kjeldahl nitrogen	mg/l	0.75	0.59	<0.50	0.59	moderate
Total nitrogen as N	mg/l	1.59	1.21	1.02	1.30	good
BOD ₅	mg/l	2.50	<1.0	1.40	1.4	good
Chlorides (Cl)	mg/l	6.5	8.0	7.9	11.4	good
COD-Cr	mg/l	12.8	8.3	<10.0	<5.0	good
Sulfates (SO ₄)	mg/l	15.2	18.9	17.1	20.6	good
Sum of N-NO ₂ + N-NO ₃	mg/l	0.840	0.618	1.02	0.716	unclassified
Oxidizability (COD-Mn)	mg/l	1.36	1.46	1.56	2.27	very good
Nitrite nitrogen (N-NO ₂)	mg/l	0.006	0.005	0.006	0.014	good
Orthophosphates (PO ₄)	mg/l	<0.030	0.031	0.032	0.206	moderate
General suspension	mg/l	<5.0	7.5	<5.0	<5.0	good
Physical parameters						
Specific electrolytic conductivity (PEW)	µS/cm	276.0	382.0	291.0	394.0	moderate
pH value	-	7.9	7.4	8.0	8.2	good
Pesticides						
Imidacloprid	µg/l	<0.050	<0.050	<0.050	<0.050	unclassified
Imazalil	µg/l	<0.050	<0.050	<0.050	<0.050	unclassified
Dissolved metals/mainly cations						
Lithium (Li)	mg/l	0.0032	0.0049	0.0031	0.0056	unclassified
Magnesium (Mg)	mg/l	6.83	9.84	6.86	9.98	good
Manganese (Mn)	mg/l	0.00050	0.00323	<0.00050	0.00213	unclassified
Potassium (K)	mg/l	1.47	2.46	1.48	2.62	unclassified
Sodium (Na)	mg/l	5.76	8.64	6.20	10.7	unclassified
Calcium (Ca)	mg/l	35.1	52.2	35.9	52.8	moderate
Iron (Fe)	mg/l	0.0058	0.0039	0.0050	0.0124	unclassified

point, limit 11.7 mg/l, value from 9.32 to 13.8 mg/l) and calcium (41 to 64.7 mg/l). These values should be classified as moderate, a class above II (Table 4). Sulfates in water occur concurrently with large amounts of calcium and magnesium ions making the water a non-carbonate hardness.

The Dunajec river flows through areas used mainly as agricultural areas, as well as developed with small-scale production facilities for construction materials and agri-food products, among others. The share of arable land amounts to 37%, orchards 2.5%, meadows and pastures 13.4%, agricultural land in total 52.9% and forests 37.8%. As regards the section from the Czorsztyn–Niedzica lake and Sromowce Wyżne up to the intake in Stary Sącz and Podegrodzie, the Dunajec receives tributaries of such watercourses as: Grajcarek, Krośnica, Obidzki Potok, Kamienica,

Czarna Woda, Jaworzynka, Jarzabka and Słomka. [Wiewiórska et al., 2023]. There is a wastewater treatment plant between sampling points D1 and D2, and before D3 point there is a municipal wastewater treatment plant and a landfill.

The Dunajec river is characterized by the highest recorded concentrations of studied surface water quality indicators among all the analyzed ones. In terms of total suspended matter (from 5.4 to 28.6 mg/l) and pH values (from 6.8 to 7.4), the Dunajec falls in Class II of surface water quality, being a good quality class. The values analyzed, such as total phosphorus (from below 0.050 to 0.433 mg/l), Kjeldahl nitrogen (from below 0.50 to 3.29 mg/l), total nitrogen (from below 1 to 4.59 mg/l), BOD₅ (from 0.600 to 6.00 mg/l), chloride (from 10.9 to 146.0 mg/l), COD-Cr (from below 5.0 to 43.6 mg/l), sulfate (from

Table 4. Water quality indicators in the Łubinka stream

Non-metal inorganic parameters	Unit	Ł1		Ł2		Surface water quality class
		Draft 1 (February)	Draft 2 (April)	Draft 1 (February)	Draft 2 (April)	
Total phosphorus (P)	mg/l	0.146	<0.050	<0.050	<0.050	moderate
Kjeldahl nitrogen	mg/l	<0.50	<0.50	<0.50	0.59	good
Total nitrogen as N	mg/l	1.74	<1.00	1.58	2.15	good
BOD ₅	mg/l	2.60	<1.0	2.90	1.1	good
Chlorides (Cl)	mg/l	16.2	18.3	20.1	24.2	moderate
COD-Cr	mg/l	<10.0	7.0	<10.0	7.9	very good
Sulfates (SO ₄)	mg/l	25.4	28.6	28.8	29.2	moderate
Sum of N-NO ₂ + N-NO ₃	mg/l	1.74	0.787	1.58	1.56	unclassified
Oxidizability (COD-Mn)	mg/l	1.65	1.81	1.65	2.27	good
Nitrite nitrogen (N-NO ₂)	mg/l	0.005	0.008	0.005	0.017	good
Orthophosphates (PO ₄)	mg/l	0.103	0.160	0.077	0.103	moderate
General suspension	mg/l	<5.0	16.9	<5.0	<5.0	good
Physical parameters						
Specific electrolytic conductivity (PEW)	µS/cm	361.0	456.0	430.0	520.0	moderate
pH value	-	8.1	8.1	8.2	7.5	good
Pesticides						
Imidacloprid	µg/l	<0.050	<0.050	<0.050	<0.050	unclassified
Imazalil	µg/l	<0.050	<0.050	<0.050	<0.050	unclassified
Dissolved metals/mainly cations						
Lithium (Li)	mg/l	0.0039	0.0060	0.0045	0.0070	unclassified
Magnesium (Mg)	mg/l	9.32	12.1	10.6	13.8	moderate
Manganese (Mn)	mg/l	0.00480	0.00203	0.00830	0.00653	unclassified
Potassium (K)	mg/l	2.16	2.68	2.45	3.32	unclassified
Sodium (Na)	mg/l	12.2	16.0	12.6	17.6	unclassified
Calcium (Ca)	mg/l	41.0	55.7	47.9	64.7	moderate
Iron (Fe)	mg/l	0.0055	0080	0.0056	0.0077	unclassified

19.0 to 59.1 mg/l), COD-Mn oxidation (from 1.75 to 9.05 mg/l), nitrite nitrogen (from below 0.0030 to 0.216 mg/l), orthophosphates (from 0.068 to 0.146 mg/l), electrolytic conductivity (from 328 to 1130 µS/cm), pH value (from 6.8 to 7.4), magnesium (from 8.06 to 14.1 mg/l) and calcium (from 39.8 to 94.0 mg/l) are classified below Class II, as moderate condition. All the analyzed surface waters flow into the Dunajec river, and the most frequent limits exceedance, particularly by several times the limit value, may be observed at D3 point, at the second, April, water sampling. As regards the Dunajec river, exceeding the limit was also observed for such pesticides as imidacloprid (limit <0.050, value 0.130 µg/l) and imazalil (limit <0.050, value 0.099 µg/l) (Table 5). Imidacloprid, due to its varied structure, exhibits high toxicity. Its application includes, i.a. a seed spray on winter

wheat and winter barley, spray against aphids, potential vectors of viral diseases. It is a potent insecticide, attacking the nervous system of insects [Michel, 2020]. Imazalil is a fungicide to prevent mold, to improve yield, in Poland it is used primarily to reduce the development of silver scab (in potato cultivation) – imazalil may be used in the fall after harvesting vegetables [Osowski and Urbanowicz, 2023].

Two water samples were collected for each of the analyzed raw water sampling points of the watercourses (P1, P2, K1, K2, Ł1, Ł2, D1, D2, D3), one in February and the other one in April. In February, water level indicated runoff from the mountains related to snowmelt, as no precipitation was observed, while in April, water was collected during precipitation. The initial raw water sampling points were those located on the Poprad

Table 5. Water quality indicators in the Dunajec river

Non-metal inorganic parameters	Unit	D1		D2		D3		Surface water quality class
		Draft 1 (February)	Draft 2 (April)	Draft 1 (February)	Draft 2 (April)	Draft 1 (February)	Draft 2 (April)	
Total phosphorus (P)	mg/l	<0.050	<0.050	<0.050	<0.050	<0.050	0.433	moderate
Kjeldahl nitrogen	mg/l	0.66	<0.50	<0.50	0.63	1.30	3.29	moderate
Total nitrogen as N	mg/l	1.85	<1.00	1.41	3.66	2.48	4.59	moderate
BOD ₅	mg/l	0.600	1.1	1.80	1.2	6.00	4.1	moderate
Chlorides (Cl)	mg/l	10.9	11.2	11.7	11.2	92.6	146.0	moderate
COD-Cr	mg/l	<10.0	<5.0	16.4	9.4	22.2	43.6	moderate
Sulfates (SO ₄)	mg/l	26.0	19.8	19.8	19.0	49.9	59.1	moderate
Sum of N-NO ₂ + N-NO ₃	mg/l	1.19	0.716	1.41	3.03	1.18	1.30	unclassified
Oxidizability (COD-Mn)	mg/l	1.87	1.75	2.35	2.00	7.18	9.05	moderate
Nitrite nitrogen (N-NO ₂)	mg/l	<0.0030	0.004	0.004	0.014	0.190	0.216	moderate
Orthophosphates (PO ₄)	mg/l	0.037	0.088	0.068	0.146	0.143	0.065	moderate
General suspension	mg/l	5.4	6.1	10.0	21.1	8.3	28.6	good
Physical parameters								
Specific electrolytic conductivity (PEW)	µS/cm	328.0	334.0	339.0	331.0	817.0	1130.0	moderate
pH value	-	6.8	6.8	7.0	7.1	7.4	7.1	moderate
Pesticides								
imidacloprid	µg/l	<0.050	<0.050	<0.050	<0.050	<0.050	0.130	unclassified
imazalil	µg/l	<0.050	<0.050	<0.050	0.099	<0.050	<0.050	unclassified
Dissolved metals/ mainly cations								
Lithium (Li)	mg/l	0.0051	0.0062	0.0056	0.0066	0.0078	0.0120	unclassified
Magnesium (Mg)	mg/l	8.06	9.04	8.70	8.65	11.5	14.1	moderate
Manganese (Mn)	mg/l	0.00570	0.00583	0.00610	0.00203	0.0134	0.0549	unclassified
Potassium (K)	mg/l	1.73	1.84	1.85	1.82	12.7	24.4	unclassified
Sodium (Na)	mg/l	7.72	9.31	8.13	9.91	59.3	124.0	unclassified
Calcium (Ca)	mg/l	39.8	43.5	41.6	40.0	71.3	94.0	moderate
Iron (Fe)	mg/l	0.0074	0.0084	0.0114	0.0121	0.0442	0.104	unclassified

river (P1 and P2). Comparing the highest concentrations of the studied parameters at the different sampling points – P1 to P2, total phosphorus (0.015 mg/l), Kjeldahl nitrogen (0.24 mg/l), total nitrogen (0.79 mg/l), chloride (0.2 mg/l), sulfate (4.8 mg/l), orthophosphate (0.069 mg/l), specific electrolytic conductivity (3 µS/cm), magnesium (0.16 mg/l), manganese (0.004 mg/l), potassium (0.04 mg/l), sodium (0.01 mg/l), calcium (1.6 mg/l) increase, and a decrease in BOD₅ (0.60 mg/l), COD-Cr (5.8 mg/l), total N-NO₂ + N-NO₃ (0.05 mg/l), permanganate value (COD-Mn) (0.45 mg/l), nitrite nitrogen (0.005 mg/l), total suspended matter (57.4 mg/l), pH value (0.1), lithium (0.0001 mg/l), magnesium (0.16 mg/l), iron (0.0013 mg/l) as well as equal values of pesticide concentrations (below the

limit of quantification <0.05 mg/l) were observed in February. In April, a decrease was observed in the concentrations of total phosphorus (0.006 mg/l), Kjeldahl nitrogen (0.01 mg/l), total nitrogen (4.2 mg/l), chloride (0.1 mg/l), sulfate (0.5 mg/l), total N-NO₂+N-NO₃ (4.201 mg/l), permanganate value (COD-Mn) (0.19 mg/l), nitrite nitrogen (0.001 mg/l), orthophosphate (0.054 mg/l), total suspended matter (2.3 mg/l), specific electrolytic conductivity (4 µS/cm), manganese (0.003 mg/l), potassium (0.01 mg/l), calcium (1.4 mg/l), iron (0.0012 mg/l), equal concentration values for BOD₅ (1.1 mg/l), pH value (8.1), pesticides (below the limit of quantification <0.05 mg/l), and increases in COD-Cr (3.2 mg/l), lithium (0.0004 mg/l), magnesium (0.01 mg/l), sodium (0.22 mg/l).

The waters of the Poprad river merge with the Dunajec river right below sampling P2 point. Surface waters collected at D1 point merge with waters flowing from the Slovak side and accumulate at D2 point. Concentration analysis of the studied values between point D1 and D2 in February presented equal values of total phosphorus and pesticides (below the limit of quantification <0.05 mg/l), a decrease in Kjeldahl nitrogen (0.16 mg/l), total nitrogen (0.44 mg/l), sulfate (6.2 mg/l), an increase in BOD₅ (1.2 mg/l), chlorides (0.8 mg/l), COD-Cr (6.4 mg/l), total N-NO₂+N-NO₃ (0.22 mg/l), oxidation (COD-Mn) (0.48 mg/l), nitrite nitrogen (0.001 mg/l), orthophosphate (0.031 mg/l), total suspended matter (4.6 mg/l), specific electrolytic conductivity (11 μS/cm), pH value (0.2), lithium (0.0005 mg/l), magnesium (0.6 mg/l), manganese (0.0004 mg/l), potassium (0.12 mg/l), sodium (0.41 mg/l), calcium (1.8 mg/l) and iron (0.004 mg/l). The values in April were also comparable for total phosphorus and imidacloprid (below the limit of quantification <0.05 mg/l), chlorides 11.2 mg/l, an increase in imazalil (0.044 mg/l), Kjeldahl nitrogen (0.13 mg/l), total nitrogen (2.66 mg/l), BOD₅ (0.1 mg/l), COD-Cr (4.4 mg/l), total N-NO₂+N-NO₃ (2.314 mg/l), permanganate value (COD-Mn) (0.25 mg/l), orthophosphate (0.058 mg/l), total suspended matter (15.0 mg/l), pH value (0.3), lithium (0.0004 mg/l), sodium (0.6 mg/l), iron (0.0037 mg/l), decrease in sulfate (0.8 mg/l), specific electrolytic conductivity (3 μS/cm), magnesium (0.39 mg/l), manganese (0.0038 mg/l), potassium (0.02 mg/l) and calcium (3.5 mg/l) content.

The Kamienica river is the tributary of the Dunajec river and its waters were studied at K1 and K2 points. The observation was that in February, comparing K1 to K2 points, the concentration of total phosphorus, pesticides (below the limit of quantification <0.05 mg/l), total suspended matter (below the limit of quantification <5.0 mg/l), nitrite nitrogen (0.006 mg/l), manganese (0.0005 mg/l) remained at a constant level, the concentration of Kjeldahl nitrogen (0.25 mg/l), total nitrogen (0.57 mg/l), BOD₅ (1.10 mg/l), COD-Cr (2.8 mg/l), lithium (0.0001 mg/l), magnesium (0.03 mg/l), iron (0.0008 mg/l) decreased, chloride content (1.4 mg/l), total N-NO₂+N-NO₃ (0.18 mg/l), permanganate value (COD-Mn) (0.3 mg/l), orthophosphate (0.002 mg/l), specific electrolytic conductivity (15 μS/cm), pH value (0.1), potassium (0.01 mg/l), sodium (0.44 mg/l) and calcium (0.8 mg/l) concentration increased. In April,

the concentration of total phosphorus, pesticides (below the limit of quantification <0.05 mg/l) as well as Kjeldahl nitrogen (0.59 mg/l) remained at a constant level, the concentration of total nitrogen (0.09 mg/l), BOD₅ (0.4 mg/l), chlorides (3.4 mg/l), sulfates (1.7 mg/l), total N-NO₂+N-NO₃ (0.098 mg/l), COD-Mn (0.81 mg/l), nitrite nitrogen (0.009 mg/l), orthophosphate (0.175 mg/l), specific electrolytic conductivity (12 μS/cm), pH value (0.8), lithium (0.0007 mg/l), magnesium (0.14 mg/l), potassium (0.16 mg/l), sodium (2.06 mg/l), calcium (0.6 mg/l), iron (0.0085 mg/l) increased and the COD-Cr content (3.3 mg/l), total suspended matter (2.5 mg/l) and manganese (0.00110 mg/l) content decreased.

The Łubinka stream was also studied at raw water sampling points from the Cieniawa side (Ł1) to the Łubinka flowing into the Dunajec river (Ł2). Compared to the content of the studied substances in Ł1 to Ł2 points in February, the content of total phosphorus (0.096 mg/l), total nitrogen (0.16 mg/l), the sum of N-NO₂+N-NO₃ (0.16 mg/l), orthophosphate (0.26 mg/l) decreased, the content of chloride (3.9 mg/l), sulfate (3.4 mg/l), specific electrolytic conductivity (69 μS/cm), pH value (0.1), lithium (0.00064 mg/l), magnesium (1.28 mg/l), manganese (0.00350 mg/l), potassium (0.29 mg/l), sodium (0.4 mg/l), calcium (6.9 mg/l), iron (0.0001 mg/l) increased, and Kjeldahl nitrogen (0.09 mg/l), COD-Cr (below the limit of quantification <10.0 mg/l), COD-Mn (1.65 mg/l), nitrite nitrogen (0.005 mg/l), total suspended matter (below the limit of quantification <5.0 mg/l), pesticides (below the limit of quantification <0.05 mg/l) remain at a constant level. In April, the content of total phosphorus and pesticides remained at a constant level (below the limit of quantification <0.05 mg/l), the content of Kjeldahl nitrogen (0.09 mg/l), total nitrogen (1.15 mg/l), chloride (5.9 mg/l), COD-Cr (0.9 mg/l), sulfate (0.6 mg/l), total N-NO₂+N-NO₃ (0.773 mg/l), COD-Mn (0.46 mg/l), nitrite nitrogen (0.009 mg/l), specific electrolytic conductivity (64.0 μS/cm), lithium (0.0010 mg/l), magnesium (1.7 mg/l), manganese (0.00450 mg/l), potassium (0.64 mg/l), sodium (1.6 mg/l), calcium (9.0 mg/l) increased and orthophosphate content (0.57 mg/l), total suspended matter (11.9 mg/l), pH content (0.6) and iron (0.0003 mg/l) decreased.

The analysis of the last section of surface water studied, from Ł2 to D3, the connection area of the Łubinka stream with the Dunajec river, presented in February the same concentrations of total phosphorus and pesticides (below the limit

of quantification <0.05 mg/l), an increase in Kjeldahl nitrogen (0.80 mg/l), total nitrogen (0.9 mg/l), BOD₅ (3.10 mg/l), chlorides (72.5 mg/l), COD-Cr (12.2 mg/l), sulfate (21.1 mg/l), COD-Mn (5.56 mg/l), nitrite nitrogen (0.185 mg/l), orthophosphate (0.066 mg/l), total suspended matter (3.3 mg/l), specific electrolytic conductivity (387 μ S/cm), lithium (0.0033 mg/l), magnesium (0.9 mg/l), manganese (0.0051 mg/l), potassium (10.25 mg/l), sodium (46.7 mg/l), calcium (23.4 mg/l), iron (0.0386 mg/l), a decrease only in the case of total N-NO₂+N-NO₃ (0.4 mg/l) and pH value (0.8). In April, an increase was observed in total phosphorus (0.383 mg/l), Kjeldahl nitrogen (2.7 mg/l), total nitrogen (2.44 mg/l), BOD₅ (3.0 mg/l), chlorides (121.8 mg/l), COD-Cr (35.7 mg/l), sulfate (29.9 mg/l), COD-Mn (6.78 mg/l), nitrite nitrogen (0.199 mg/l), total suspended matter (23.6 mg/l), specific electrolytic conductivity (610 μ S/cm), imidacloprid pesticide (0.18 mg/l), lithium (0.005 mg/l), magnesium (0.3 mg/l), manganese (0.04837 mg/l), potassium (21.08 mg/l), sodium (106.4 mg/l), calcium (29.3 mg/l), iron (0.0963 mg/l), a decrease in total N-NO₂+N-NO₃ (0.26 mg/l), orthophosphate (0.038 mg/l), pH value (0.4), constant value of imazalil pesticide (below the limit of quantification <0.05 mg/l). The analyzed watercourses exhibit elevated concentrations of non-metallic inorganic compounds, physical parameters, and dissolved

metals, particularly cations. During the study period, low pesticide concentrations were recorded in the Poprad and Kamienica rivers, as well as the Łubinka stream. The Dunajec river, which receives inflows from the Poprad and Kamienica rivers and the Łubinka stream in the Sącz region, showed the highest concentrations of substances such as phosphorus, nitrogen, BOD₅, COD, chlorides, sulfates, permanganate value, total suspended matter, magnesium, manganese, potassium, sodium, calcium, iron, and pesticides. These substances primarily originate from agricultural and horticultural runoff, urban surface runoff, leaking septic systems, and discharges from wastewater treatment plants. Notably, the value for specific electrolytic conductivity should be considered, as it reflects the watercourse's ability to conduct electrolysis. A higher conductivity value indicates a reduced capacity for the watercourse to self-purify [Wysocka-Czubaszek and Wojno, 2014].

For instance, a graphic representation of the results of specific electrolytic conductivity (PEW) in the form of a dot plot was prepared using Statistica software (Fig. 2).

Based on the results of the water samples collected in April, the variation in specific electrolytic conductivity may be observed. Specific electrolytic conductivity depends on chloride and sodium concentration in the water, among other

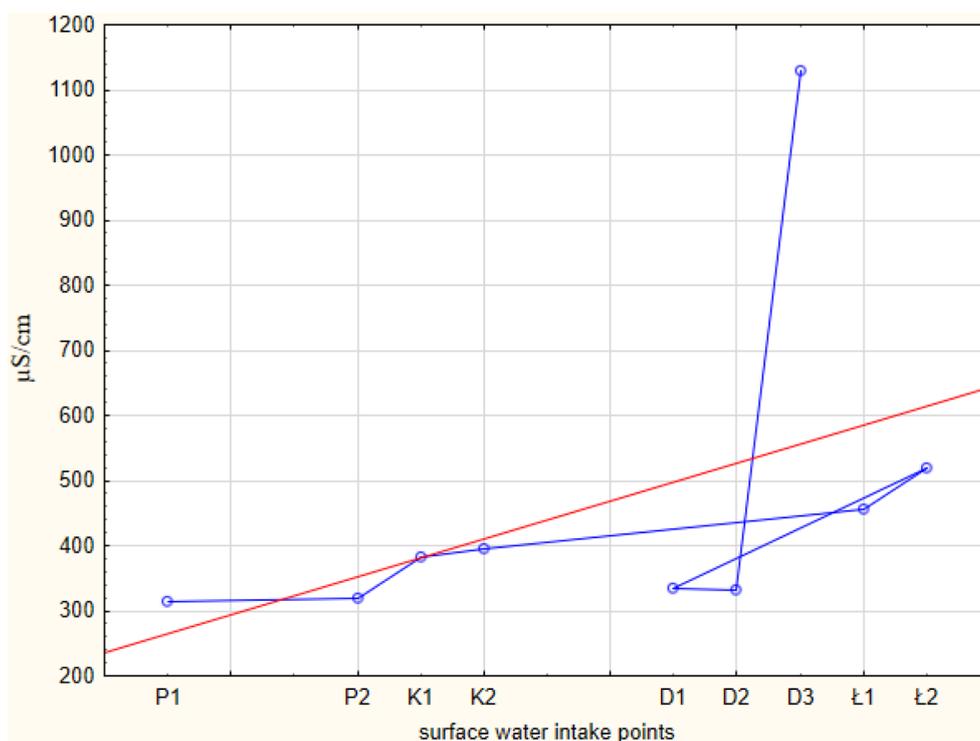


Figure 2. Results of the specific electrolytic conductivity measurements at individual points (April)

things (Fig. 3). Specific electrolytic conductivity concentration at P1, P2, D1 and D2 points is comparable and amounts to 315 $\mu\text{S}/\text{cm}$, 319 $\mu\text{S}/\text{cm}$, 334 $\mu\text{S}/\text{cm}$, 331 $\mu\text{S}/\text{cm}$, respectively, while increasing values may be observed at K1 (382 $\mu\text{S}/\text{cm}$), K2 (394 $\mu\text{S}/\text{cm}$), Ł1 (456 $\mu\text{S}/\text{cm}$) and Ł2 (520 $\mu\text{S}/\text{cm}$). The highest concentration may be found in the raw water sample from D3 point (1130 $\mu\text{S}/\text{cm}$). This value nearly doubles the recommended specific electrolytic conductivity concentration for Class II surface water quality [Journal of Laws of 2021, item 1475] and exceeds almost 3.5 times the lowest studied specific electrolytic conductivity value in April at P1 point. This relationship is directly proportional; as the concentrations of sodium (Na) and chloride (Cl) increase, the specific electrolytic conductivity correspondingly rises. Na and Cl values at individual sampling points graph analysis (Fig. 3) shows that similarly to specific electrolytic conductivity at P1 point (Na amounting to 8.16 mg/l, Cl amounting to 9.5 mg/l), P2 (Na amounting to 8.38 mg/l, Cl amounting to 9.4 mg/l), K1 (Na amounting to 8.64 mg/l, Cl amounting to 8.0 mg/l), K2 (Na amounting to 10.7 mg/l, Cl amounting to 11.4 mg/l), Ł1 (Na amounting to 16.0 mg/l, Cl amounting to 18.3 mg/l), Ł2 (Na amounting to 17.6 mg/l, Cl amounting to 24.2 mg/l), D1 (Na amounting to 9.31 mg/l, Cl amounting to 11.2 mg/l), D2 (Na amounting

to 9.91 mg/l, Cl amounting to 11.2 mg/l) sodium and chloride concentration values exceeded their limit of quantification, but remained at similar levels. Yet D3 point (Na amounting to 124 mg/l, Cl amounting to 146 mg/l) presented values clearly exceeding the other results, with the limit of their quantification amounting to 2 mg/l for chloride and 0.03 mg/l for sodium.

The results of this case study are influenced by the specific characteristics of the area under investigation, particularly the proximity of the analyzed watercourses to wastewater treatment plants, landfills, agricultural areas (such as those used for the cultivation of grain, corn, and potatoes), and orchards. The findings may vary with more frequent monitoring of raw water from these rivers, as fluctuations in the studied parameters and ecological status are likely to occur. Additionally, variations in medium to low flow rates, along with significant differences in low flow variability throughout the year within the same type of watercourse, may lead to the overestimation or underestimation of the seasonal study results [Madej and Grela, 2021].

DISCUSSION

The conducted studies revealed high contents of, among others, phosphorus, chlorides, PEW,

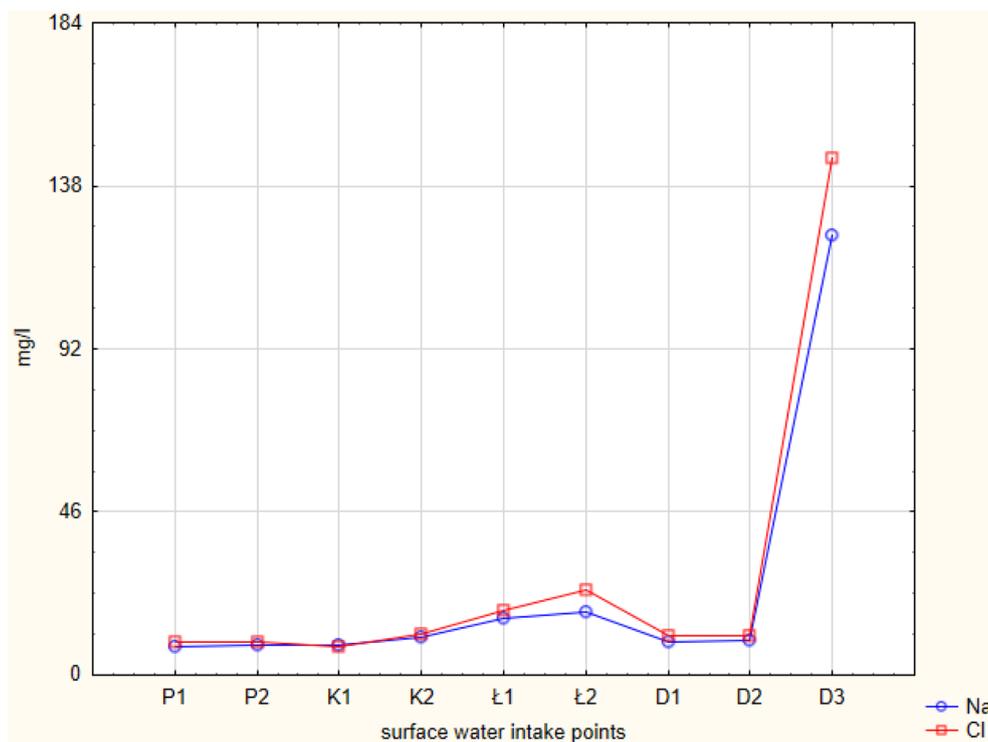


Figure 3. Measurement results of chloride and sodium concentrations at individual points (April)

oxidizability, pesticides in surface waters. Single increased phosphorus concentrations in the analyzed watercourses are due to overfertilization of agricultural fields adjacent to the river. Ayele and Atlabachew [2021] observed that significantly increased phosphorus concentration in the water contributes to the eutrophication of water bodies, yet these components are essential for life processes. Eutrophication is a global problem and should be controlled. A study conducted by Marsel et al. [2021] on the Citarum river, used for various anthropogenic activities, in the West Java province present nitrate levels of 0.13–0.33 mg/L and phosphate levels of 0.13–0.29 mg/L. Anthropogenic activities have a significant impact on water quality. A study of the Abadaba river in Nigeria, showed that nitrates ranged from 17.40 to 3.459 mg/L in the Abadaba during the rainy season to 26.748 to 6.536 mg/L in the Njaba river. Phosphates ranged from 40.204 to 6.024 mg/L in the Abadaba river. Comparing the results with World Health Organization (WHO) permissible limits showed that nitrate levels were low, and phosphate concentrations occurred only during the dry season [Isiuku and Enyoh, 2020].

As with the previously analyzed Poprad river, the elevated concentrations of the parameters listed in Table 3 can be attributed to the characteristics of the region and its level of industrialization. The Kamienica river is bordered by agricultural areas and flows through the city of Nowy Sącz, where traffic-related pollutants and elevated chloride levels, particularly from road salt, may enter the river during the winter season. Although sodium chloride (NaCl) is the most widely used de-icing agent, it has numerous adverse environmental impacts. In addition to water contamination, NaCl contributes to damage to vegetation, vehicles, and infrastructure. Ongoing research is exploring alternatives based on magnesium chloride ($MgCl_2$) and calcium chloride ($CaCl_2$); however, studies suggest that these alternatives may pose greater toxicity risks to freshwater species compared to NaCl and are generally more costly [Szkłarek et al., 2022b]. Most likely, the sources of the analyzed substances in the water are fertilizers used in agriculture, domestic and industrial wastewater, bottom sediments, decomposition products of organic substances of plant and animal origin permeating from the soil (Table 3). In the Dunajec River, particular attention should be paid to the detected concentrations of pesticides. The use of pesticides is widespread worldwide,

especially in China, where they are mainly used on rice crops. A study of surface water in the Nandu and Wanquan river basins, in Hainan, China, presented total concentrations that ranged from undetectable concentrations to 24.2 $\mu\text{g/l}$. The most common pesticides were carbendazim and imidacloprid, detected in 59.8% and 17.7% of surface water samples, respectively, at concentrations above 0.1 $\mu\text{g/l}$, as well as chlorpyrifos, detected in 9.0% of samples at concentrations above 0.05 $\mu\text{g/l}$, fungicides: difenoconazole and emamectin benzoate, herbicide: butachlor and the insecticide acetamiprid, which were present in $\geq 12.5\%$ of samples at concentrations above 0.1 $\mu\text{g/l}$ [Tan et al., 2021].

Similarly, nitrogen concentrations, pH value are commonly detected in surface waters. A study of nitrogen pollution sources in the Weihe river, located in northern China, presented a positive correlation between population, industrial wastewater, domestic sewage, livestock and nitrogen pollution concentrations. Forests and grasslands had a negative impact on nitrogen concentrations in surface water, with a total reduction effect of 55.8% [Shi et al., 2019]. Surface water was also tested for BOD₅ content. An analysis of 13 BOD-UV of surface water collected from Lake Taihu (TL, n = 23) and the Qiantang river (QR, n = 22) in China was conducted. The results showed that 5-chloro-2-(3,5-di-tertbutyl-2-hydroxyphenyl)-benzotriazole (UV-327) was consistently the predominant BOD-UV in water samples from TL (mean 16 ng/l; frequency detection 96%) and QR (14 ng/l; 91%). However, the sources of these pollutants have not been clearly established (Chen et al., 2024). The pH value of the water tested in the Rewa, India amounted to 7.61, this is the power concentration of H⁺ ions whose greater presence indicates an excessive concentration of carbon and bicarbonate. Chloride content in the river falls within the range of 20 mg/l, this concentration is due to a natural process, the flow of water through the natural formation of salts in the ground. Sulfate concentration amounted to 4.2 mg/l, no chloride content was recorded in the river. The highest concentration of magnesium in the river amounted to 8.16 mg/l. No nitrate content was observed in the river water samples, and the calcium content was below the desired limit [Solanki and Soni, 2022].

Waters from the Obinna and Adada rivers located in Enugu, Nigeria, were tested for their irrigation needs potential. Testing forty-eight water

samples from four sampling points, physicochemical parameters were analyzed with standard methods, and the results presented average pH concentration indicating slight acidity of the river waters. The physicochemical parameters were found to present positive correlations, indicating ion exchange between the river waters and the surrounding soils [Abugu et al., 2023; Akhar et al., 2021].

CONCLUSIONS

The Poprad river, Kamienica river, Dunajec river and the Łubinka stream surface waters study results analysis facilitated the evaluation of surface waters quality in the Sącz agglomeration. As regards the Poprad river, study results indicate Classes I and II surface water quality for soluble metals, physical parameters, pesticides and non-metallic general inorganic parameters, excluding orthophosphates and total suspended matter. All the studied parameters in the case of the Kamienica river fall within Class I or II, except for orthophosphates and specific electrolytic conductivity. As regards the Łubinka stream, the studied raw water parameters values are classified as group I and II, except for phosphorus, chlorides, sulfates, orthophosphates, specific electrolytic conductivity, magnesium, manganese. The Dunajec river differentiates itself compared to the other analyzed watercourses – its study results present observable exceedance of standards and limits of quantification indicating a moderate state of surface water quality, especially for water sampling point D3. Study findings indicate that exclusive of total suspended matter, classified as Class II, all the parameters referred to in the Regulation fall below Class II.

The rivers presented in the study are mountainous in nature, and therefore, especially during the study period (February and April), the results were affected by surface water melt. Raw water samples in February were collected with no precipitation present, while in April, water collection was accompanied by precipitation on the water collection day and the days preceding it. The study finds that high concentrations of phosphorus, nitrogen, COD, BOD₅, sulfate, chloride, orthophosphate, total suspended matter, magnesium, manganese, potassium, sodium, calcium iron as well as pesticides (imidacloprid, imazalil), high concentrations of which were recorded at raw water sampling point D2 and D3 on the Dunajec river,

probably result from the entry of rainwater, water discharges from wastewater treatment plants, water flowing down from the mountains due to snowmelt, as well as salt used in the winter period for removing snow from roads, into the analyzed watercourses. The presented surface water quality in the Sącz agglomeration study results are based on pilot raw water. It is necessary to continue research in different seasons of the year and multiply it in order to precisely understand the causes of changes in the natural chemistry of the analyzed watercourses.

REFERENCES

1. Abugu H.O., Alum O.L., Ekere N.R., Eze I.S., Ucheana I.A., Ezugwu A.L., Ihedioha J.N. 2023. Hydrochemical Assessment of the Rivers Adada and Obinna in Enugu, Nigeria, for Irrigational Application. *Journal of Irrigation and Drainage Engineering*, 149(5). <https://doi.org/10.1061/JIEDDH.IRENG-9899>
2. Akhtar N., Ishak M.I.S., Bhawani S.A., Umar K. 2021. Various Natural and Anthropogenic Factors Responsible for Water Quality Degradation: A Review. *Water*, 13, 2660. <https://doi.org/10.3390/w13192660>
3. Aquirre-Martínez G.V., Martín-Díaz M.L. 2020. A multibiomarker approach to assess toxic effects of wastewater treatment plant effluents and activated defence mechanisms in marine (*Ruditapes philippinarum*) and fresh water (*Corbicula fluminea*) bivalve species. *Ecotoxicology*, 29, 941–958. <https://doi.org/10.1007/s10646-020-02216-1>
4. Ayele H.S., Atlabachew M. 2021. Review of characterization, factors, impacts, and solutions of Lake eutrophication: lesson for lake Tana, Ethiopia. *Environ Sci Pollut Res*, 28, 14233–14252. <https://doi.org/10.1007/s11356-020-12081-4>
5. Basta E., Szewczyk P. 2024. The Use of Methane from Landfill Gas to Generate Energy and its Management at the Plant as a Way to Reduce Climate Change. *Rocznik Ochrona Środowiska*, 26, 236–250. DOI10.54740/ros.2024.024
6. Chen Y., Guo R., Liao K., Yu W., Wu P., Jin H. 2024. Discovery of novel benzotriazole ultraviolet stabilizers in surface water. *Water Research*, 257, 121709, <https://doi.org/10.1016/j.watres.2024.121709>
7. Ciuła J. 2021. Modeling the migration of anthropogenic pollution from active municipal landfill in groundwaters. *Architecture Civil Engineering Environment*, 14, 81–90. <https://doi.org/10.21307/ACEE-2021-017>
8. Ciuła J. 2022. Analysis of the effectiveness of

- wastewater treatment in activated sludge technology with biomass recirculation. *Architecture Civil Engineering Environment*, 2, 123–134. <https://doi.org/10.2478/ACEE-2022-0020>
9. Ciuła J., Wiewiórska I., Banaś M., Pająk T., Szewczyk P. 2023. Balance and Energy Use of Biogas in Poland: Prospects and Directions of Development for the Circular Economy. *Energies*, 16, 3910. <https://doi.org/10.3390/en16093910>
 10. Cretaux J.F., Calmant S., Papa F., Frappart F., Paris A., Berge-Nguyen M. 2023. Inland Surface Waters Quantity Monitored from Remote Sensing. *Surv Geophys*, 44, 1519–1552. <https://doi.org/10.1007/s10712-023-09803-x>
 11. Cruz-Alcalde A., Sans C., Esplugas S. 2017. Priority pesticides abatement by advanced water technologies: The case of acetamiprid removal by ozonation. *Science of The Total Environment*, 599–600, 1454–1461. <https://doi.org/10.1016/j.scitotenv.2017.05.065>
 12. Czerniawski R., Bilski P. 2019. Functioning and protection of flowing waters. *Volumina*. (in Polish). Download from: <http://drawalifeplus.rdos.szczecin.pl/wp-content/uploads/2019/10/Funkcjonowanie-i-ochronaw%C3%B3d-p%C5%82yn%C4%85cych-2019-monografia.pdf>. Access date: 14.05.2024.
 13. de Souza R.M., Seibert D., Quesada H.B., Bassetti F. J., Fagundes-Klen M.R., Bergamasco R. 2020. Occurrence, impacts and general aspects of pesticides in surface water: A review. *Process Safety and Environmental Protection*, 135, 22–37. <https://doi.org/10.1016/j.psep.2019.12.035>
 14. Dębska K., Rutkowska B., Szulc W., Gozdowski D. 2021. Changes in Selected Water Quality Parameters in the Utrata River as a Function of Catchment Area Land Use. *Water*, 13, 2989. <https://doi.org/10.3390/w13212989>
 15. Derbalah A., Chidya R., Jadoo, W., Sakugawa H. 2019. Temporal trends in organo phosphorus pesticides use and concentrations in river water in Japan, and risk assessment. *Journal of Environmental Sciences*, 79, 135–152. <https://doi.org/10.1016/j.jes.2018.11.019>
 16. Derylo-Marczewska A., Blachnio M., Marczewski A.W., Seczkowska M., Tarasiuk B. 2019. Phenoxy-acid pesticide adsorption on activated carbon – Equilibrium and kinetics. *Chemosphere*, 214, 349–360. <https://doi.org/10.1016/j.chemosphere.2018.09.088>
 17. Doydora S., Mc Lamore E.S., Peters R., Sozzani R., Van den Broeck L., Duckworth O.W. 2020. Accessing Legacy Phosphorus in Soils. *Soil Systems*, 4(4), 74. <https://doi.org/10.3390/soilsystems4040074>
 18. Dragon K., Górski J., Kruć R., Drożdżyński D., Grischek T. 2018. Removal of natural organic matter and organic micro pollutants during riverbank filtration in Krajkowo, Poland. *Water*, 10, 1457. <https://doi.org/10.3390/w10101457>
 19. Fini M.N., Madsen H.T., Muff J. 2019. The effect of water matrix, feed concentration and recovery on the rejection of pesticides using NF/RO membranes in water treatment. *Separation and Purification Technology*, 215, 521–527. <https://doi.org/10.1016/j.seppur.2019.01.047>
 20. Gebus-Czupyt B., Wach B. 2022. Application of $\delta^{18}\text{O}$ -PO₄ analysis to recognize phosphate pollutions in eutrophic water. *Ecology & Hydrobiology*, 22, 21–39. <https://doi.org/10.1016/j.ecohyd.2021.05.005>
 21. Gronba-Chyła A., Generowicz A., Alwaeli M., Mannheim V., Grąz K., Kwaśnicki P., Kramek A. 2024. Municipal waste utilization as a substitute for natural aggregate in the light of the circular economy. *J. Clean. Prod.*, 440, 140907. <https://doi.org/10.1016/j.jclepro.2024.140907>
 22. Gryczko-Gostyńska A., Olędzka D. Regional report (in Polish). Download from: <https://www.pgi.gov.pl/psh/materialy-informacyjne-psh/informatory-psh/wody-podziemne-miast-polski/4165-nowysacz/file.html>, access date: 16.05.2024r.
 23. Hajduga G., Generowicz A., Kryłów M. 2019. Human health risk assessment of heavy metals in road dust collected in Cracow. *E3S Web of Conferences* 100, 00026. <https://doi.org/10.1051/e3sconf/2019>
 24. He X.S., Zhang Y.L., Liu Z.H., Wei D., Liang G., Liu H.T., Xi B.D., Huang Z.B., Ma Y., Xing B.S. 2020. Interaction and coexistence characteristics of dissolved organic matter with toxic metals and pesticides in shallow groundwater. *Environmental Pollution*, 258, 113736. <https://doi.org/10.1016/j.envpol.2019.113736>
 25. Isiuku B.O., Enyoh C.E. 2020. Pollution and health risks assessment of nitrate and phosphate concentrations in water bodies in South Eastern, Nigeria. *Environmental Advances*, 2, 100018. <https://doi.org/10.1016/j.envadv.2020.100018>
 26. Jesuraja K., Selvam S., Murugan R. 2021. GIS-based assessment of groundwater quality index (DWQI and AWQI) in Tiruchendur Coastal City, Southern Tamil Nadu, India. *Environmental Earth Sciences*, 80, 243. <https://doi.org/10.1007/s12665-021-09542-5>
 27. Journal of Laws of 2021, item 1475, Regulation of the Minister of Infrastructure of 25 June 2021 as applied to use in the utility, utility and emergency environment and in the basic version, which is part of the water surface (in Polish). Download from: <https://isap.sejm.gov.pl/isap.nsf/DocDetails.xsp?id=WDU20210001475>. Access date: 14.05.2024.
 28. Klarich K.L., Pflug N.C., De Wald, E.M., Hladik M.L., Kolpin D.W., Cwiertny D.M., LeFevre G.H. 2017. Occurrence of neonicotinoid insecticides in

- finished drinking water and fate during drinking water treatment. *Environmental Science & Technology Letters*, 4(5), 168–173. <https://doi.org/10.1021/acstlett.7b00081>
29. Kruć R., Dragon K., Górski J. 2019. Migration of pharmaceuticals from the Warta river to the aquifer at a riverbank filtration site in Krajkowo (Poland). *Water*, 11, 2238. <https://doi.org/10.3390/w11112238>
 30. Kruć-Fijałkowska R., Dragon K., Drożdżyński D., Górski J. 2022. Seasonal variation of pesticides in surface water and drinking water wells in the annual cycle in western Poland, and potential health risk assessment. *Scientific Reports*, 12, 3317. <https://doi.org/10.1038/s41598-022-07385-z>
 31. Kuczyńska A., Jarnuszewski G., Nowakowska M., Wexler S.K., Wiśniowski Z., Burczyk P., Durkowski T., Woźnicka M. 2021. Identifying causes of poor water quality in a Polish agricultural catchment for designing effective and targeted mitigation measures. *Science of the Total Environment*, 765, 144125. <https://doi.org/10.1016/j.scitotenv.2020.144125>
 32. Kumar P., Mehrotra I., Gupta A., Kumar I. S. 2018. Riverbank filtration: A sustainable process to attenuate contaminants during drinking water production. *Journal of Sustainable Development of Energy, Water and Environment Systems*, 6(1), 150–161. <https://doi.org/10.13044/j.sdewes.d5.0176>
 33. Ławniczak A.E., Zbierska J., Nowak B., Achtenberg K., Grześkowiak A., Kanas K. 2016. Impact of agriculture and land use on nitrate contamination in groundwater and running waters in central-west Poland. *Environmental Monitoring and Assessment*, 188, 172. <https://doi.org/10.1007/s10661-016-5167-9>
 34. Li P., Qian H. 2018. Water resources research to support a sustainable China. *International Journal of Water Resources Development*, 34(3), 327–336. <https://doi.org/10.1080/07900627.2018.1452723>
 35. Lobato T.C., Hauser-Davis R.A., Oliveira T.F., Silveira A.M., Silva H.A.N., Tavares M. R.M., Saraiva A.C.F. 2015. Construction of a novel water quality index and quality indicator for reservoir water quality evaluation: A case study in the Amazon region. *Journal of Hydrology*, 522, 674–683. <https://doi.org/10.1016/j.jhydrol.2015.01.021>
 36. Madej P., Grela J. 2021. Problems with the use of habitat methods for the development of a hydrological formula allowing the determination of the environmental flow. *Acta Scientiarum Polonorum serie Formatio Circumiectus – Environmental Processes*, 20(2), 41–54. DOI: <https://doi.org/10.15576/ASP.FC/2021.20.2.41>
 37. Marsela K., Hamdani H., Anna Z., Herawati H. 2021. The Relation of Nitrate and Phosphate to Phytoplankton Abundance in the Upstream Citarum River, West Java, Indonesia. *Asian Journal of Fisheries and Aquatic Research*, 11(5), 21–31. <https://doi.org/10.9734/ajfar/2021/v11i530216>
 38. Masia A., Campo J., Navarro-Ortega A., Barcelo D. Pico Y. 2015. Pesticide monitoring in the basin of Llobregat River (Catalonia, Spain) and comparison with historical data. *Science of The Total Environment*, 503–504, 58–68. <https://doi.org/10.1016/j.scitotenv.2014.06.095>
 39. Mekonnen M.M., Hoekstra A.Y. 2017. Global Anthropogenic Phosphorus Loads to Freshwater and Associated Grey Water Footprints and Water Pollution Levels: A High-Resolution Global Study. *Water Resources Research*, 54(1), 345–358. <https://doi.org/10.1002/2017WR020448>
 40. Michel, M. 2020. Neonicotinoids – systemic insecticides in plant protection. *Progress in plant protection*, 60 (1), 41–48. DOI: 10.14199/ppp-2020-006
 41. Montuori, P., De Rosa, E., Sarnacchiaro, P., Di Duca, F., Provisiero, D.P., Nardone, A., Triassi, M. 2014. Spatial distribution and partitioning of polychlorinated biphenyl and organochlorine pesticide in water and sediment from Sarno River and Estuary, Southern Italy. *Environmental Sciences Europe*, 32(132), 1–22. <https://doi.org/10.1186/s12302-020-00408-4>
 42. Nsibandé, S.A., Forbes, P.B.C. 2016. Fluorescence detection of pesticides using quantum dot materials – A review, *Analytica Chimica Acta*, 945, 9–22. <https://doi.org/10.1016/j.aca.2016.10.002>
 43. Osowski J., Urbanowicz J. 2023. Dry rot of tubers – agents, symptoms, and control. *Progress in plant protection*, 63(3), 137–148 (in Polish). DOI: 10.14199/ppp-2023-015.
 44. Pekel J., Cottam A., Gorelick N., Belward A.S. 2016. High-resolution mapping of global surface water and its long-term changes. *Nature*, 540, 418–422. <https://doi.org/10.1038/nature20584>
 45. Policht-Latawiec A., Kanownik W., Wójcik P. 2014. Quality and Sable values of water of flysch stream with low anthropo pressure. *PAN*, 3, 917–929. DOI: <http://dx.medra.org/10.14597/infraeco.2014.3.1.068>
 46. Przydatek G., Basta E. 2020. Systemic Efficiency Assessment of Municipal Solid Waste Management in the Suburban Municipality. *E3S Web of Conferences*, 154(2), 03001, 1–8. <https://doi.org/10.1051/e3sconf/202015403001>
 47. Przydatek G., Generowicz A., Kanownik W. 2024. Evaluation of the Activity of a Municipal Waste Landfill Site in the Operational and Non-Operational Sectors Based on Landfill Gas Productivity. *Energies*, 17(10), 2421. <https://doi.org/10.3390/en17102421>
 48. Puckowski A., Cwiąg W., Mioduszevska K., Stepnowski P., Białk-Bielińska A. 2021. Sorption of pharmaceuticals on the surface of micro

- plastics. *Chemosphere*, 263, 127976. <https://doi.org/10.1016/j.chemosphere.2020.127976>
49. Radecki-Pawlik A., Stypuła K., Radecki-Pawlik B., Brzęk M., N Plesiński, K. 2019. Filtration bed and stone riprap securing the banks of mountain streams. *Ekologia a Budownictwo*, <https://bibliotekanauki.pl/articles/161770.pdf>. (in Polish).
50. Riedo J., Herzog C., Fenner K., Walder F., van der Heijden M.G.A., Bucheli T.D. (2020), Concerted Evaluation of Pesticides in Soils of Extensive Grassland Sites and Organic and Conventional Vegetable Fields Facilitates the Identification of Major Input Processes. *Environmental Science & Technology*, 56(19), 13686–13695. <https://doi.org/10.1021/acs.est.2c02413>
51. Sadowski A., Baer-Nawrocka A. 2018. Food and environmental function in world agriculture -Interdependence or competition?. *Land Use Policy*, 71, 578–583. <https://doi.org/10.1016/j.landusepol.2017.11.005>
52. Sallwey A., Jurado A., Barquero F., Fahl J. 2020. Enhanced Removal of Contaminants of Emerging Concern through Hydraulic Adjustments in Soil Aquifer Treatment. *Water*, 12(9), 2627. <https://doi.org/10.3390/w12092627>
53. Shi P., Zhang Y., Song J., Li P., Wang Y., Zhang X., Li Z., Bi Z., Zhang X., Qin Z., Zhu T. 2019, Response of nitrogen pollution in surface water to land use and social-economic factors in the Weihe River watershed, northwest China. *Sustainable Cities and Society*, 50, 101658. <https://doi.org/10.1016/j.scs.2019.101658>
54. Solanki M.K., Soni S.K. 2022. Comparative Analysis of River, Underground and Pond Water during March 2022 in Rewa, (M.P.) India. *International Journal of Scientific Research in Science and Technology*, 9(2), 2395–6011. <https://doi.org/10.32628/IJSRST229215>
55. Srivastava A., Jangid N. K., Srivastava M. Rawat, V. 2020. Pesticides as Water Pollutants, Adverse Effect of Pesticide Pollution in Aquatic Eco system. Adverse Effect of Pesticide Pollution in Aquatic Eco system, IG Global. Download from: https://www.researchgate.net/publication/339447826_Pesticides_as_Water_Pollutants, Acces date: 15.05.2024.
56. Stephens G.L., Slingo J.M., Rignot E., Reager J.T., Hakuba M.Z., Durack P.J., Worden J., Rocca R. 2020. Earth's water reservoirs in a changing climate. *Royal Society*, 476, 2236. <https://doi.org/10.1098/rspa.2019.0458>
57. Summerton L., Greener M., Patterson D., Brown C.D. 2022. Effects of soil redistribution by tillage on subsequent transport of pesticide to subsurface drains. *Pest Management Science*, 79(2), 616–626. <https://doi.org/10.1002/ps.7229>
58. Szklarek S., Górecka A., Salabert B., Wojtal-Frankiewicz A. 2022b. Acute toxicity of seven de-icing salts on four zooplankton species—is there an “eco-friendly” alternative?. *Ecohydrology & Hydrobiology*, 22(4), 589–597. <https://doi.org/10.1016/j.ecohyd.2022.08.005>
59. Szklarek S., Górecka A., Wojtal-Frankiewicz A. 2022a. The effects of road salt on freshwater ecosystems and solutions for mitigating chloride pollution – A review. *Science of The Total Environment*, 805, 150289. <https://doi.org/10.1016/j.scitotenv.2021.150289>
60. Tan H., Zhang H., Wu Ch., Wang Ch., Li Q. 2021. Pesticides in surface waters of tropical river basins draining areas with rice–vegetable rotations in Hainan, China: Occurrence, relation to environmental factors, and risk assessmen. *Environmental Pollution*, 283, 117100. <https://doi.org/10.1016/j.envpol.2021.117100>
61. Titov I., Semerád J., Boháčková J., Beneš H., Cajthaml T. 2024. Microplastics meet micropollutants in a Central European river stream: adsorption of pollutants to microplastics under environmentally relevant conditions, *Environmental Pollution*, <https://doi.org/10.1016/j.envpol.2024.124616>
62. Uddin M.G., Moniruzzaman M., Quader M.A., Hasan M.A. 2018. Spatial variability in the distribution of trace metals in groundwater around the Rooppur nuclear power plant in Ishwardi, Bangladesh. *Groundwater for Sustainable Development*, 7, 220–231. <https://doi.org/10.1016/j.gsd.2018.06.002>.
63. Wałęga A., Górka A., Cupak A., Michalec B. 2016. Analysis of hydrological regime of the mountains catchment in multi-year 1985-2012 for example of the Kamienica river. *Acta Scientiarum Polonorum Formatio Circumiectus*, 15 (3), 177–186, DOI: <http://dx.doi.org/10.15576/ASP.FC/2016.15.3.177>
64. Wiewiórska I., Rybicki S. M. 2022, Analysis of a coagulation sludge contamination with metals using X-ray crystallography. *Desalination and Water Treatment*, 254, 151–159. <https://doi.org/10.5004/dwt.2022.28372>
65. Wiewiórska I., Labour M., Vovk M., Makara A., Kowalski Z. 2023. Analysis of the impact of changes in surface water quality on the dynamics of treatment processes in drinking water treatment technological systems. *Desalination and Water Treatment*, 315, 1–12. <https://doi.org/10.5004/dwt.2023.30053>
66. Wiśniowska-Węglarz R. The hydrological network of the Muszyna region from the Sądeczyzna river cycle (in Polish). Download from: https://www.almanachmuszynny.pl/spisy/2008/SIEC%20HYDROGRAFIC_ZNA.pdf. Acces date: 15.05.2024.
67. Withers P.J.A., Neal C., Jarvie H.P., Doody D.G. 2014. Agriculture and Eutrophication: Where Do We Go from Here?. *Sustainability*, 6(9), 5853–5875.

- <https://doi.org/10.3390/su6095853>
68. Wojtkowska M., Bojanowski D. 2018. Influence of catchment use on the degree of river water pollution by forms of phosphorus. *Rocznik Ochrona Środowiska*, 20, 887–904. <https://repo.pw.edu.pl/info/article/WU-T15934936a18b4f77adf688ed451ad8ba/>
69. Wysocka-Czubaszek A., Wojno W. 2014. Seasonal changes of water chemistry in a small River in an urban catchment. *Przegląd Naukowy – Inżynieria i Kształtowanie Środowiska*, 63, 64–76 (in Polish). Download from: <http://iks.pn.sggw.pl/PN63/A6/art6.pdf>. Access date: 15.05.2024.
70. Wysowska E., Wiewiórska I., Kicińska A. 2024. The Problem of Health Risk Resulting from the Presence of Pharmaceuticals in Water Used for Drinking Purposes: A Review. *J. Ecol. Eng.*, 25(5), 244-256. DOI: <https://doi.org/10.12911/22998993/186371>
71. Zhao G., Li Y., Zhou L., Gao H. 2022. Evaporative water loss of 142 million global lakes. *Nature Communications*, 13, 3686. <https://doi.org/10.1038/s41467-022-31125-6>
72. Zwolińska N., Basta E. 2024. Emissions of Gases and Dust into the Air as a Result of the Conversion of Landfill Gas into Electricity and Heat in a Cogeneration Plant. *Rocznik Ochrona Środowiska* 26, 94–105. <https://doi.org/10.54740/ros.2024.010>