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Solute fluxes in headwater catchments with contrasting anthropogenic impact

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A R T I C L E I N F O

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A B S T R A C T

Understanding the response of headwater catchments to increasing anthropogenic influences is one of the key issues in hydrological and geomorphological research. Two headwater catchments with contrasting human impacts on the environment were chosen to determine changes in surface water chemistry and solute fluxes. In one catchment, 22 % of the forest area was cleared in 2013 and in the other, 75 % of the arable lands was converted to grassland and forest in the last 25 years. Atmospheric input and solute mass balance were analysed using homogeneity Pettitt test. It seems that in both areas, a very important factor affecting solute fluxes was most likely changes, or lack thereof, in soil erosion. In the partially clear-cut catchment, a small clear-cut area and adequate protection of the soil cover had little effect on the stream water chemistry, and the total solute mass balance remained unchanged during the study period. In this catchment, the more pronounced effect on solute fluxes was using de-icing salts in winter, which contributed to a 62 % increase in total solute flux (mainly by supplying Na^+ and Cl^-, but also Ca^{2+}, Mg^{2+} and K^+). In a catchment with a decrease in arable lands, there was a 55 % decrease in total solute mass balance (including mass balance of Ca^{2+}, Mg^{2+}, Na^+, K^+, NH_4^+, SO_4^-, NO_3^-, Cl^-) in the stream likely associated with a decrease in soil erosion and fertilization. In both catchments there was a decrease in total monthly atmospheric input (especially in input of NH_4^+, SO_4^- and NO_3^-) of 53 % and 21 %, respectively, over the study period. To summarize, the road salting has increased the amount of transported solutes in the stream and deteriorated surface water chemistry, while the reduction of arable land area has reduced the amount of transported solutes in the stream and improved surface water quality.

1. Introduction

Water quality is affected by a number of cumulative natural and anthropogenic factors, including industrialization, wastewater, land use, agricultural activity, fertilization, road salting, atmospheric deposition and climate change (Diamantini et al., 2018; Szklarek et al., 2022). Despite numerous publications on the determination of water quality changes (e.g. Stålnacke et al., 2004; Ahearn et al., 2005; Chuman et al., 2012), the relation between different factors and water quality parameters has not yet been fully understood, especially in headwater areas (Wohl, 2017). Understanding the catchment's response to the changes taking place will enable appropriate water and land use management strategies to be adopted, especially in the presence of climate change and increasing anthropogenic impacts.

One of the most important factors affecting water quality and thus the solute fluxes in a catchment is land use and land cover (LULC) changes (Baker, 2006). Currently, two trends of LULC changes in mountainous areas are dominant in Europe: reduction of forest area (Lundmark et al., 2017; Senf et al., 2020) and reduction of arable lands (Kuemmerle et al., 2008; Keenleyside and Tucker, 2010). Generally, deforestation covers up to 0.2 % of the Earth's surface per year (Chakravarty et al., 2012). One reason for reduction in forest area is forest management, droughts, wildfires, pests and pathogens (Overpeck and Breshears, 2021). A special case of forest area reduction is clear-cut, which involves removing all the trees in a certain area and it is a common management practice for timber harvesting worldwide (Zerva and

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Mencuccini, 2005). The impact of clear-cut harvesting on water quality is not fully recognised, especially as some studies show contrasting trends of change, i.e. an increase in concentrations and loads of most ions (especially NO_3^- and base cations) over a period of time (Huber et al., 2010; Deval et al., 2021; Palviainen et al., 2022; Webster et al., 2022) or a decrease in concentrations of base cations (Płaczkowska et al., 2023). This issue therefore requires further detailed research and identification of the factors responsible for these differences.

The second direction of LULC change is related to decreasing arable land, caused e.g. by socio-economic transformations. After 1989 in countries that were part of the communist system in Central and Eastern Europe including Poland (Bucała-Hrabia, 2018), the Czech Republic (Bičík et al., 2001), Slovakia (Šebo and Nováček, 2014), Romania (Munteanu et al., 2014) and East Germany (Baessler and Klotz, 2006) the transition from a centrally planned to a free market economy was observed. The arable lands have mostly been replaced by grasslands and forests, especially in mountainous regions (Kozak, 2010; Kijowska-Strugała et al., 2018). This has already led to a reduction in soil erosion and mechanical denudation in the catchments (Kijowska-Strugała, 2019). Catchments with a high proportion of urban and agricultural land have high concentrations of most ions, especially nutrients (Chetelat et al., 2008; Li and Bush, 2015). Therefore, it can be expected that as the proportion of arable land decreases, the concentration of ions in the surface water will also decrease. This issue needs to be addressed in detail to enable an understanding of the impact of socio-economic changes on solute fluxes in such catchments.

Studies from different parts of the world show that roads are also an important factor affecting water quality (Buzás and Lomlyódy, 1997; Kelly et al., 2008; Corsi et al., 2010). Although they usually occupy only a small percentage of the catchment area, they significantly modify the quantity, direction and quality of surface runoff. Asphalt roads are a source of heavy metals and other substances from traffic (Dall'Osto et al., 2014) delivered to the catchment area, but it is the application of de-icing salts that has the greatest impact on surface water quality (Kelly et al., 2008). In some areas, the length of roads increased more than four times in the last 200 years (Nilson, 2006), often crossing even the headwater areas. De-icing salts used in winters to ensure road safety can have negative consequences for the aquatic ecosystem, through increased salinization of surface water (Szklarek et al., 2022).

In order to recognize the impact of different forms of human activity on the environment, two contrasting headwater catchments were chosen for the study: i) Wüstebach in the Eifel National Park, where 22 % of the spruce forest area was clear-cut in 2013 (Płaczkowska et al., 2023), and ii) Bystrzanka in the Polish Carpathians, where arable land decrease by 75 % in the last 25-years (Kijowska-Strugała and Bochenek, 2023). Solute fluxes in a stream consist of chemical denudation, atmospheric input and eventually other anthropogenic inputs. We expect that the above-mentioned LULC changes will significantly affect the amount of chemical denudation in the catchment, which is reflected by the solute mass balance (difference between solute fluxes and atmospheric input). We hypothesize that the ion concentrations and solute mass balance, especially nitrogen compounds, will increase in a partially clear-cut catchment as a result of reduced nutrient uptake and increased nitrogen leaching. On the other hand, in a catchment with a decrease in the area of arable lands and an increase in the area of forest, we expect a decrease in ion concentration and solute mass balance, especially nitrogen compounds, as a result of less use of fertilizers and a decrease in soil erosion. In addition, the contribution of other anthropogenic input, i.e. the application of de-icing salts, to solute fluxes from the catchment will be determined using the Wüstebach catchment as an example.

2. Materials and methods

2.1. Experimental catchments and history of LULC changes

The Wüstebach experimental catchment area of 0.5 km^2 (50°30′20"N 6°20′01″E) is located in the western part of the Eifel National Park and consists of the main catchment area and a control catchment area which is a tributary of the Wüstebach stream (Fig. 1a; Table 1). Bedrock is composed of the Lower Devonian shales of very low hydraulic conductivity (10^{-9}–10^{-7} m s^{-1}) with occasional sandstone inclusions (Meyer, 2013) and is covered with 1–2 m thick periglacial solifluction sediments (Bogena et al., 2015). Cambisols can be found on the slope and Gleysols and Planosols occur in the valley below. The climate is temperate oceanic with an average annual precipitation of approx. 1200 mm, of which 56 % is runoff and 44 % – evapotranspiration (Bogena et al., 2015). Due to the low permeability of the bedrock, the deep percolation of water may be neglected. Low flows occur mostly in summer periods while winter periods are characterized by high flows (Bogena et al., 2021).

Potential natural vegetation in this area would have been broadleaf forest dominated by beech (*Fagus sylvatica* L.), but intensive logging and the demand for fast-growing timber has resulted in the area being covered with spruce (*Picea abies* L.). Second World War brought the large-scale destruction of forests in the region especially heavy fighting during the Battle of the Bulge which took place at the turn of 1944 and 1945. For this reason, massive spruce reforestation was carried out in the Eifel in the 1950s including the Wüstebach catchment (Fig. 2; Lehmkuhl et al., 2010). This results in the presence of a monoculture spruce forest in large areas of the Eifel today. Although at first the choice of spruce may seem justified because due to its fast growth, it effectively protected the soil from erosion. However, recent years have shown that spruce is not resistant to disturbances, especially to droughts that hit Europe in 2018–2020 followed by bark beetle infestation. These events caused high spruce mortality, 45 % of spruce trees in Eifel in 2020 were classified by the forest statistics as damaged (Montzka et al., 2021). The managers of the Eifel National Park, established in 2004, decided to transform the forest into mixed and deciduous stands by planting beeches in the park including the Wüstebach and the control catchment (Röös and Mauerhof, 2014). To prepare for beech planting, forest thinning was carried out in both catchments. In the Wüstebach catchment itself, the condition of the spruce stands has not deteriorated, but in August/September 2013, spruce felling was carried out on an area of 9 ha (22 % of the catchment area; Fig. 1a) in order to regenerate a near-natural deciduous forest (Baatz et al., 2015). The felling was carried out using the cut-to-length method, which involved leaving the root system in the soil and removing only the trunk. In addition, skid trails were protected with branches, effectively limiting mechanical disturbance of the soil cover (Siebers and Kruse, 2019). These activities have resulted in short-term increases in concentrations of K^+ and NO_3^-, lasting 2–3 years, as well as longer-term decreases in concentrations of base cations (Ca^{2+}, Mg^{2+}, Na^+) and chlorides in stream water (Robinson et al., 2022; Płaczkowska et al., 2023).

Another anthropogenic impact in the Eifel is quite a dense network of traffic roads. The upper part of the Wüstebach catchment is crossed by the federal highway (Fig. 1a) which, due to difficult driving conditions, is salted in winter for 5–6 months a year (data of the Landesbetrieb Straßenbau Nordrhein-Westfalen). Long-term application of de-icing salts on the roads transformed surface water ionic composition in the Wüstebach from Ca-Mg-SO_4 dominant ions to Na-Cl (Płaczkowska et al., 2023).

The Bystrzanka catchment (49°37′51"N 21°07′02″E) has an area of 13 km^2 and is located in the central part of the Polish Carpathians (Fig. 1b; Table 1). The catchment is underlain by alternating layers of sandstone and shale of varying thickness. The dominant soil type in the catchment is sandy clay loam and clay loam Cambisols with a relatively low water capacity. Sandy clay Fluvisols cover the valley bottom (Ditzler et al., 2017). The lithological conditions, the energy of relief, and the erosive activity of the streams as well as precipitation make the study area susceptible to landslides, which cover 27 % of the catchment. The study area has a warm, humid, continental climate with an average annual precipitation of approx. 900 mm, of which 44 % is runoff and 56

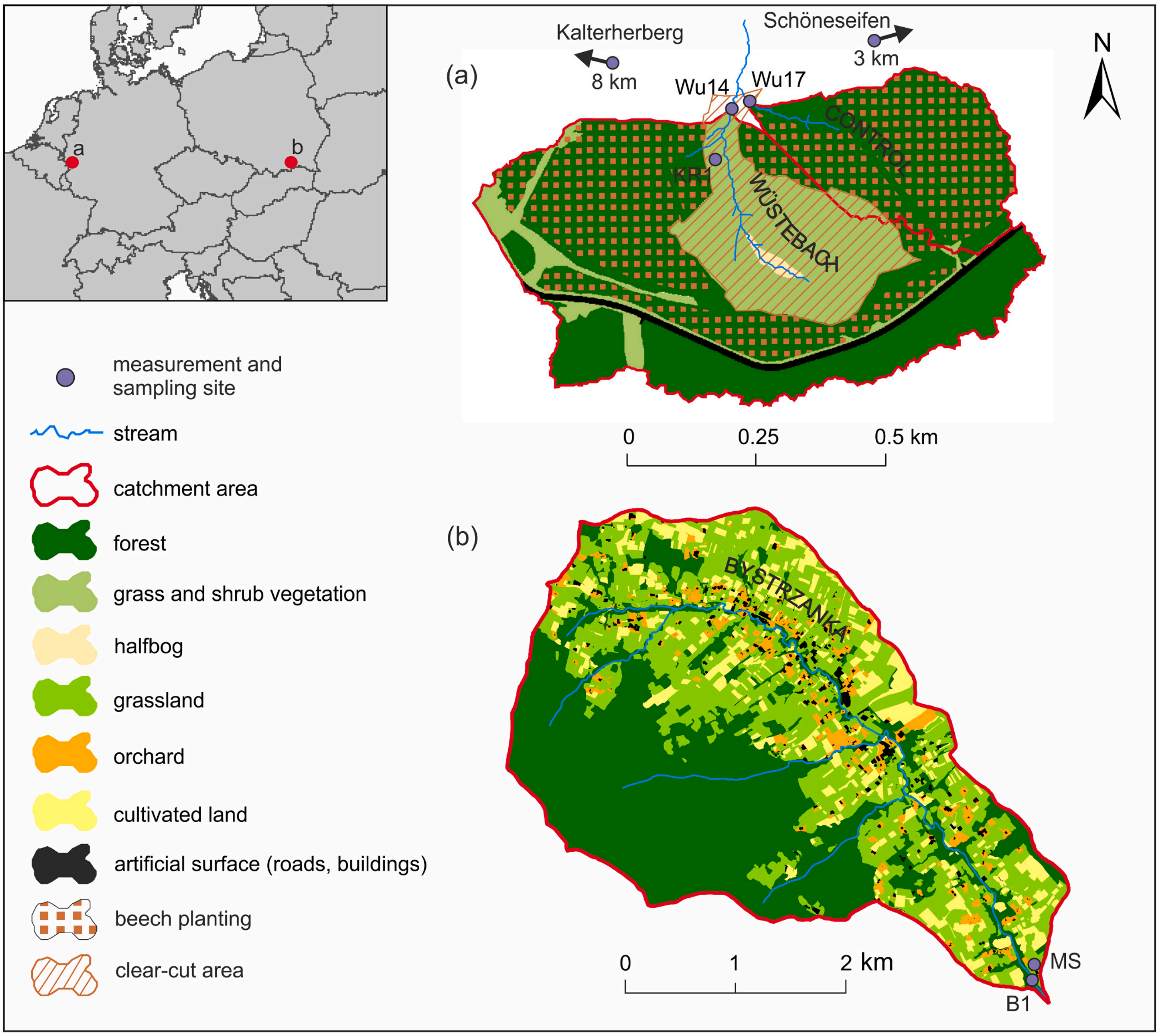

Fig. 1. Contemporary land cover of (a) the Wüstebach (https://www.geoportal.nrw) and (b) Bystrzynka (Kijowska-Strugała et al., 2020) catchments.

Table 1
Characteristics of the studied catchments.

Catchment characteristics	Unit	Eifel		Carpathians
		Wüstebach	Control	Bystrzanka
Area	km^2	0.38	0.11	13.00
Elevation:	m			
Minimum		595	596	300
Maximum		631	630	753
Slope inclination:	%			
Average		9	8	10
Maximum		67	38	31
Forest cover	%	62	96	46
Climate[1]	–	Cfb	Cfb	Dfb
Precipitation total	mm a^{-1}	1156	1156	870
Average discharge	L s^{-1}	9.05	2.18	162.00
Dominant ions	–	Na-Cl	Ca-Mg-SO_4	Ca-HCO_3

[1] According to the Köppen-Geiger climate classification (Peel et al., 2007).

% – evapotranspiration. The hydrological regime is characterized by two flood seasons: in spring connected with snowmelt and in summer connected with heavy rainfall (Kijowska-Strugała, 2019).

Natural vegetation occurs mainly in the highest part of the catchment and includes linden-oak-hornbeam forests (*Tilio-Carpinetum betuli*) up to 450–500 m a.s.l. and Carpathian beech forest (*Fagetum carpaticum;* Staszkiewicz, 1973). Some of the forest stands in the catchment are covered by planted spruce monocultures. Currently, forest covers 46 % of the catchment area while the rest of the catchment is occupied mostly by grasslands (35 %) and arable lands (mainly with potatoes and cereals, 7 %; Fig. 1b).

Nearly five thousand people live in two small villages located partly in the Bystrzanka catchment area (Central Statistical Office of Poland, 2022). Before the economic system transition in 1989, the inhabitants were mainly dependent on agriculture. In 1969, 48 % of the Bystrzanka catchment was occupied by arable land. The proportion of forest and grassland in the catchment area cover at that time was 36 % and 3 % respectively (Fig. 3). After the transformation from a centrally planned economy (communist system) to a free-market economy, most of the residents were abandoning farmlands and found employment outside

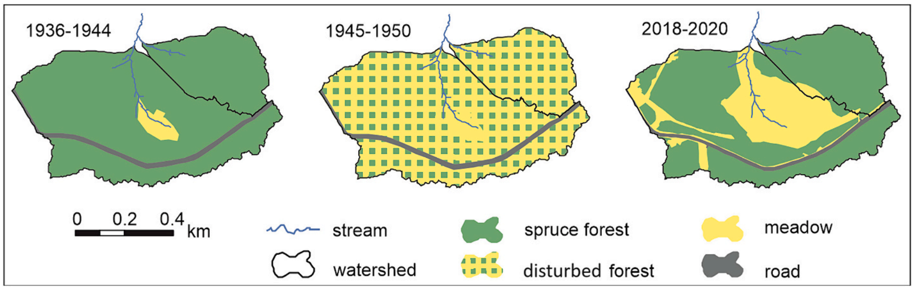

Fig. 2. Land cover changes in the Wüstebach catchment during and after Second World War (https://www.bezreg-koeln.nrw.de/geobasis-nrw/tim-online).

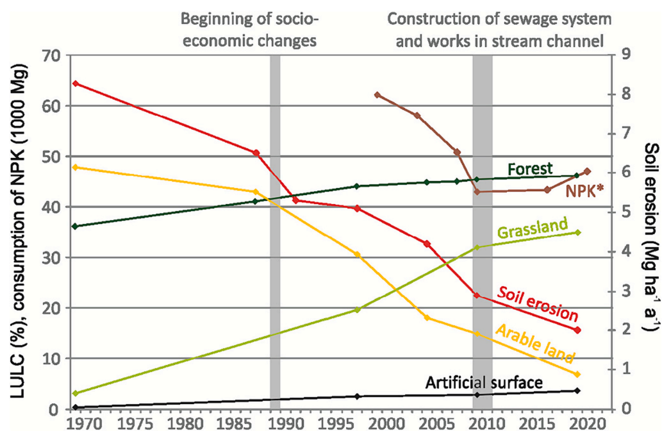

Fig. 3. Changes in LULC (% of catchment area) and soil erosion in the Bystrzanka catchment between 1969 and 2019 (Kijowska-Strugała, 2019) and changes in total consumption of mineral fertilizers (NPK) between 1999 and 2020 (Statistics Poland, 2019, 2022). *data for the entire Małopolskie region located in the central part of the Polish Carpathians and including the studied catchment area.

the agricultural sector (Central Statistical Office of Poland, 2022). The most dynamic changes in LULC occurred during the 1990s. After 2000, which includes the accession of Poland to the European Union in 2004, the general tendencies in LULC changes remained the same with slower dynamics (Bucała-Hrabia, 2018). Approximately 42 % of the catchment has experienced LULC changes leading to a decrease in soil erosion through the conversion of arable land to grassland. The average annual soil erosion in the Bystrzanka catchment decreased from 8.3 Mg ha^{-1} a^{-1} in the 1980s to 2.2 Mg ha^{-1} a^{-1} in 2010s, with the fastest decrease in the late 1990s (Fig. 3; Kijowska-Strugała, 2019). LULC and population density changes contributed to the change in road surface area and spatial pattern. Construction of new paved roads mainly in the valley bottom accompanied the abandonment of agricultural fields and cart roads on slopes. During the research period the total road density increased by 19 %, but the density of cart roads and roads crossing streams decreased by 22 % and 11 % respectively.

Accession to the EU and the implementation of the Water Framework Directive necessitated the improvement of surface water quality through the construction of a sewerage system in the catchment area by 2010. However, the sewerage system still does not cover the entire catchment area. Intensified construction work, co-financed by European Union funds, near and in the stream channel occurred during the second half of 2009 and the beginning of 2010. In that time, drain holes were drilled and ditches along the main road were waterproofed, six landslides were stabilized, and the largest bridge on the main stream was rebuilt. As a result of regulatory work, the two-kilometer mouth section of the Bystrzanka channel was reinforced by concrete.

2.2. Data acquisition

The Wüstebach experimental catchment is part of the Eifel/Lower Rhine Valley Observatory of the German network TERENO (Terrestrial Environmental Observatories), where complex monitoring of hydrological, climatological, and soil characteristics has been carried out since 2007 (Bogena et al., 2015). Stream discharge was measured in 10-min intervals based on two weir types: V-notch for low water levels and Parshall flume for high water levels. Water temperature, pH, and electrical conductivity referenced to 25 °C were measured using multiprobes (YSI 6820, YSI Inc., USA) in 15-min intervals. The hydrochemical characteristics of stream water were measured at two gauging sites: in the Wüstebach catchment (Wu14) and in the control catchment (Wu17; Fig. 1). The following ions were determined in stream water in weekly intervals: Cl^-, SO_4^-, NO_3^-, PO_4^{2-}, NH_4^+ (with ion chromatography, Dionex ICS-3000, Thermo Scientific, Waltham, MA, USA), Al^{3+}, Ca^{2+}, Fe_{tot}, Mg^{2+}, Mn^{2+}, Na^+, K^+ (with inductively coupled plasma – optical emission spectrometry, iCAP-7400, Thermo Scientific, Waltham, MA, USA). The air temperature was measured in 10-min intervals in the Wüstebach catchment (KR1). Rainwater sampling for chemical analysis was done at the TERENO Schöneseiffen site located 3 km east of the study area. More information on field measurements and sampling at TERENO can be found in Bogena et al. (2015, 2022). The daily precipitation totals were obtained from the Kalterherberg meteorological station of the German Weather Service, located 8 km west of the study area. Data on the application of de-icing salts were obtained from North Rhine-Westphalia State Road Construction Authority, Road Maintenance Department Simmerath (Landesbetrieb Straßenbau Nordrhein-Westfalen, Straßenmeisterei Simmerath) for 2018–2021.

The Bystrzanka experimental catchment belongs to the Szymbark Research Station of the Institute of Geography and Spatial Organization Polish Academy of Sciences (IGiPZ PAN). Continuous environmental monitoring (meteorological and hydrological parameters) is carried out here since 1980. Water levels of the Bystrzanka stream were recorded continuously at site B1 (Fig. 1b) using limnigraph KB2 and converted into the flow rate. Water temperature, pH, and electrical conductivity referenced to 25 °C were measured in situ in daily intervals using Elmetron CX701. Water samples for chemical analysis were taken since 1995 once a month during normal water levels at the B1 site. After filtering water samples, using 2.7 μm Whatman (GF/D) glass microfiber filters, ionic composition was determined (Cl^-, SO_4^-, NO_3^-, PO_4^{2-}, NH_4^+) using ion chromatography and (Ca^{2+}, Mg^{2+}, Na^+, K^+) atomic absorption spectrophotometer (VARIAN). Since 2015 all ions were determined using ion chromatography (Dionex ICS 1100). Studies carried out in different regions indicate that the precision and accuracy of spectrophotometric and ion chromatographic methods are very similar. A study by Thienpont et al. (1996) comparing these methods for the determination of Ca^{2+}, Mg^{2+}, Na^+ and K^+ yielded very similar results, and thus a change in measurement method should not affect the results. The concentration of HCO_3^- in stream water was measured using titration with 0.1 M HCl. The meteorological station (MS) is located in the Bystrzanka catchment at an altitude of 325 m a.s.l., at a distance of ca. 200 m from the B1. Precipitation totals and air temperature were measured there in 10-min intervals, respectively. Precipitation samples were collected after each rain event (bulk precipitation) and poured into a monthly sample to determine ionic composition (Clarke et al., 2022).

2.3. Data analysis

The period analysed for the Wüstebach catchment was between June 2009 and April 2022 and for the control catchment – between January 2011 and April 2022. For the Bystrzanka catchment, the analysed period was between November 1994 and October 2022. The average monthly values of stream discharge (Q), water temperature (T_w), electrical conductivity (EC), water acidity (pH), and air temperature (T_a) and the monthly precipitation totals (P) were calculated for both study areas.

For both studied areas a reference evapotranspiration (ET_0) was estimated using the Penman-Monteith method (Allen et al., 1998) and meteorological data measured in both experimental catchments. In the Wüstebach catchment, the concentration of HCO_3^- was calculated as the difference in the equivalent sum of base cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) and acid anions (Cl^-, NO_3^-, SO_4^-). Concentrations of PO_4^{2-} in stream and rainwater in both study areas were excluded from analysis as they were very low, usually near or below the detection limit.

In this paper, solute fluxes are understood to be the total mass loss of dissolved solids transported in a stream from a catchment area. Input to a catchment is the mass of dissolved solids delivered to a catchment from natural and anthropogenic external sources. In this paper we consider atmospheric input, understood as dry and wet deposition of natural elements and pollutants, and non-atmospheric input from road salting. The solute mass balance is understood as the net dissolved solids mass loss transported in the stream and is the result of processes occurring in the soil that contribute to stream concentration of solutes defined as chemical denudation (Balogh-Brunstad et al., 2008). Solute flux in streams and total atmospheric input were calculated based on the weighted ion concentration multiplied by the stream flow or amount of precipitation. The solute mass balance transported from the catchment was calculated as the difference between solute fluxes in stream and atmospheric input. The input of road salting was calculated using two methods: i) based on data on the amount of de-icing salts applied provided by the NRW State Road Construction Authority (https://www.strassen.nrw.de/de), and ii) based on the difference in the share of atmospheric input to solute fluxes between the Wüstebach catchment and the control catchment.

The first method includes data on daily quantities of salt applied on all roads for which the local road service of the district of Simmerath is responsible without further information on the spatial distribution. To apply these data on the catchment area, a weighting factor was generated based on one-kilometer gridded weather service data of the average annual number of frost days for the period 1991–2020 (DWD, 2023) as an indicator for salting quantity and road data of the Federal Government (open.nrw, 2023) as a geometric basis. The 298.62 km of major roads in the road services area were divided into segments for which the number of frost days were extracted from the gridded frost day data and multiplied with the segment lengths respectively. The sum of these (19,715.93) divided by the total major road length results in a weighted average of frost days of 66.02 per year. The closest road segment to the Wüstebach catchment has a frost day raster value of 90 per year, which leads to the assumption that average salting in the road segment of the catchment follows a factor of 1.4 compared with the average salting amount in the overall road service area.

The second method of calculating input from road salting was used as a verification of the first method. The share of atmospheric input of the individual ions in the solute fluxes differs significantly between the Wüstebach and the control catchment (not affected by road salting), e.g. the share of atmospheric input of Na^+ in the control catchment was 56 % and in the Wüstabach only 5 % (Płaczkowska et al., 2023, see Table 3 there). Considering that the catchments are located next to each other (Fig. 1a) and have similar soil and bedrock conditions, this difference should not be so great. This indicates an additional non-atmospheric input of Na^+ ions into the Wüstebach catchment area. As both catchment areas are located within the Eifel National Park with hardly any settlement, the only non-atmospheric input is from salting of the road crossing the upper part of the Wüstebach catchment area. Based on the difference in atmospheric input between the Wüstebach and the control catchment, the possible supply of individual ions (Cl^-, Na^+, Ca^{2+}, Mg^{2+}, K^+) with road salting was estimated (Płaczkowska et al., 2023). The total ion input estimated in this way was consistent with the calculations of the first method, so that the input of individual ions was assumed correct.

Of the many methods for identifying artificial or natural discontinuities and changes in data series, the nonparametric homogeneity Pettitt test (Pettitt, 1979) is one commonly used in earth sciences (Conte et al., 2019). The Pettitt test identifies an abrupt change in the median of a series and is considered to be robust to changes in distributional form and relatively powerful (Kundzewicz and Robson, 2004) from which its widespread use stems. The Pettitt test has been so far widely used to identify change points in time series of climatological (precipitation, temperature, evapotranspiration, relative humidity, radiation), hydrological (runoff, water level, baseflow), and water quality (electrical conductivity, pH, total dissolved solids, sodium adsorption ratio, sediment loads) parameters (Conte et al., 2019 and cited there; Sattari et al., 2020; Manojlović et al., 2021; Tian et al., 2022). The method has also been used for spatial series in geomorphological studies such as the identification of changes in river channel morphometry (Toone et al., 2014; Liro, 2015; Płaczkowska, 2017). Due to its robustness and widespread use, the Pettitt test was used in this study to identify natural and anthropogenic changes in climatic, hydrological and water quality variables in both study areas.

The Pettitt test detects whether two sets of variables in one data sequence perform distinct distributions: $F_1(X_t)$, $t = 1, 2, \ldots, \tau$, and $F_2(X_t)$, $t = \tau + 1, \ldots, T$. The null hypothesis (H0) was that there is no change in data sequence and $F_1(X_t) = F_2(X_t)$. The alternative hypothesis (H1) was that there is a change point τ in the data sequence and $F_1(X_t) \neq F_2(X_t)$. The test uses the statistic $U_{t,T}$, similar to the Mann-Whitney test statistic (Mann and Whitney, 1947) for two samples to detect a change point, given by $U_{t,T} = \sum_{i=0}^{t}\sum_{j=t+1}^{T} sgn(Xi - Xj)$, $1 \leq t < T$ (Pettitt, 1979). The most probable change point τ is at max $U_{t,T}$, $1 \leq t < T$. The H0, that the two distributions are equal, was rejected when the p-value was >0.05. The p-value has been computed using 10,000 Monte Carlo simulations. The Pettitt test works best when the change point is in the middle of the data series (Conte et al., 2019), so we made cuts in the original dataset in order to identify all possible change points. The following periods were analysed for the Wüstebach catchment: entire study period (June 2009 – April 2022), pre-clear-cut period (June 2009 – September 2013), post-clear-cut period (October 2013 – April 2022), period excluding dry years (June 2009 – December 2017). The following periods were analysed for the Bystrzanka catchment: entire study period (November 1994 – October 2022), decades 1995–2004, 2005–2014 and 2015–2022.

3. Results

3.1. Change points in meteorological and hydrological parameters

Two main change points can be noted in the case of meteorological and hydrological data in the Wüstebach catchment area, one at the beginning of 2014 (CP1) and another in 2018–2019 (CP2; Fig. 4). In 2014, EC of the Wüstebach stream decreased by 17 % with the beginning of the growing season following clear-cut and increased to the same level as before clear-cut in 2018 (Fig. 4c). The second change point was characterized by a decrease in precipitation totals by 7 % in 2018 and pH by 5 % at the beginning of 2019. The average monthly air temperature and monthly ET_0 did not change significantly between 2009 and 2022,

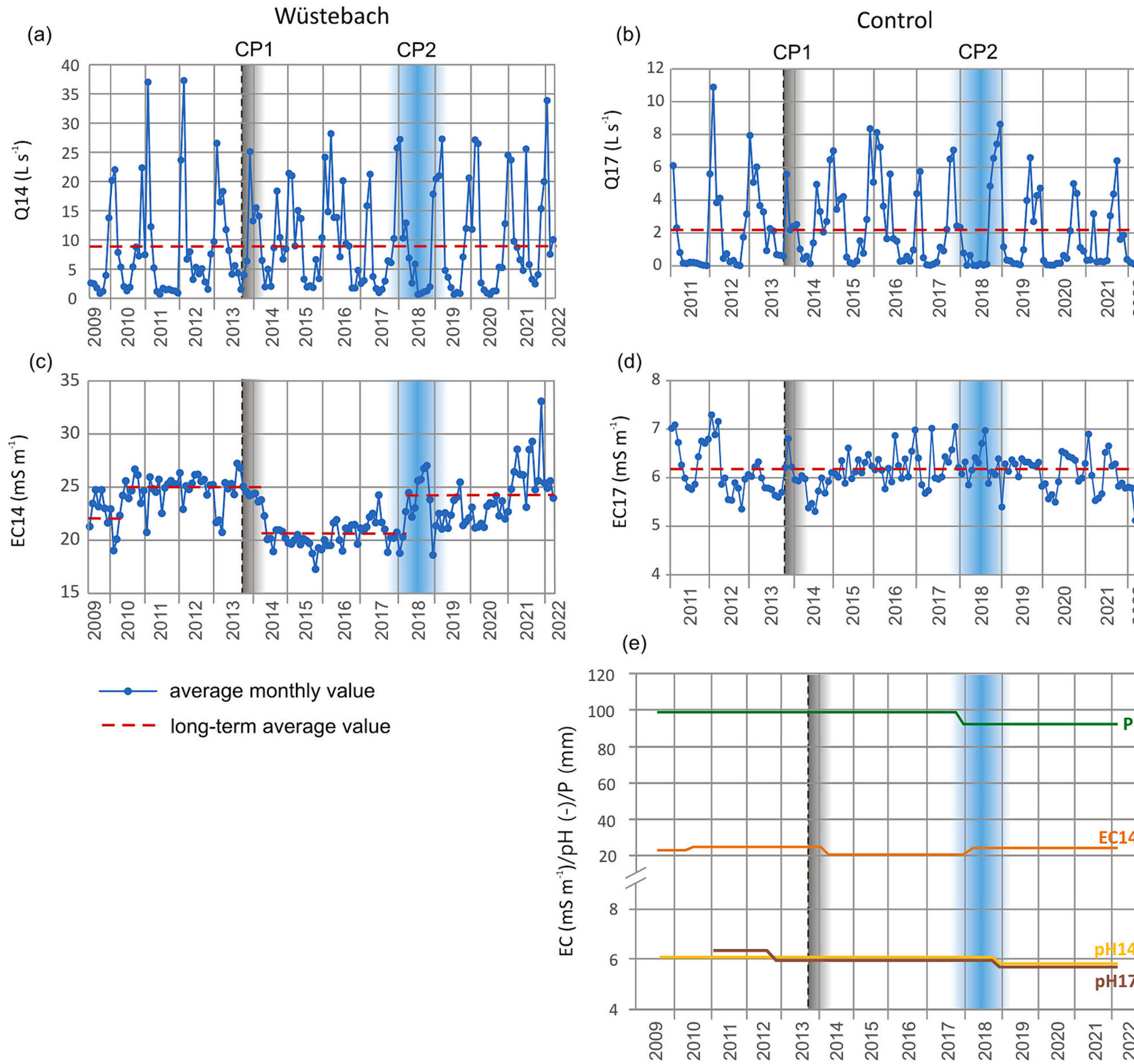

Fig. 4. Average monthly values and long-term average of chosen hydro-meteorological parameters in the Wüstebach experimental catchment: (a) water discharge of the Wüstebach stream (Q14), (b) water discharge of the control stream (Q17), (c) water electric conductivity of the Wüstebach stream (EC14), and (d) water electric conductivity of the control stream (EC17). (e) Long-term averages of all hydro-meteorological parameters in the Wüstebach catchment that showed a significant changes over the study period: Q14 – discharge of the Wüstebach stream (L s^{-1}), EC14 – water electric conductivity of the Wüstebach stream (mS m^{-1}), pH 14 – water acidity of the Wüstebach stream (–), pH 17 – water acidity of the control stream (–), P – precipitation totals (mm). Discharge of the control stream, water electric conductivity of the control stream, water temperature of the Wüstebach and control streams, air temperature and reference evapotranspiration exhibited no significant changes over the study period. CP1 and CP2 indicate the two main change points of hydro-meteorological parameters identified in the Wüstebach catchment.

nor did the stream flow. No significant changes in hydrological and hydrochemical parameters were recorded for the control stream, with the exception of pH, which decreased twice: in 2012 and during CP2 in 2018.

In the case of the Bystrzanka catchment area, three change points in hydro-meteorological data can be distinguished, in the late 1990s to 2000 (CP3), in 2010–2012 (CP4), and in 2018–2019 (CP2; Fig. 5). The first change point (CP3) was characterized by a significant decrease in stream discharge by 29 %. A decrease in stream EC and pH was also observed. Between 2010 and 2012 (CP4), there was a further decline in stream discharge, EC and pH. The recent change point (CP2) appears to be similar to that in the Wüstebach catchment, as precipitation totals decreased by 4 % and the average monthly stream EC increased by 22 %.

3.2. Changes in ion concentrations in rainwater and atmospheric inputs

As atmospheric input is a component of solute fluxes it is also necessary to analyze changes in the ionic composition of precipitation. In the case of the Wüstebach catchment, significant changes in ion concentrations occurred in 2017 and 2020. The biggest changes occurred in 2017 when NH_4^+, SO_4^{2-}, and HCO_3^- concentrations declined by 53 %, 37 % and 57 %, respectively (Fig. 6a and c). In 2020, there was a further decrease in the concentration of ions (Mg^{2+}, K^+, Al^{3+}, Fe_{tot}, Mn^{2+} and NH_4^+) in the precipitation. The total monthly atmospheric input (TMAI) decreased gradually over the study period and was dependent on the concentration of ions in the precipitation on the one hand, and on the amount of the precipitation on the other (Fig. 6b). The first significant decrease of TMAI by 75 % occurred at the beginning of 2011 when almost all ion inputs decreased, and the last in 2020 when

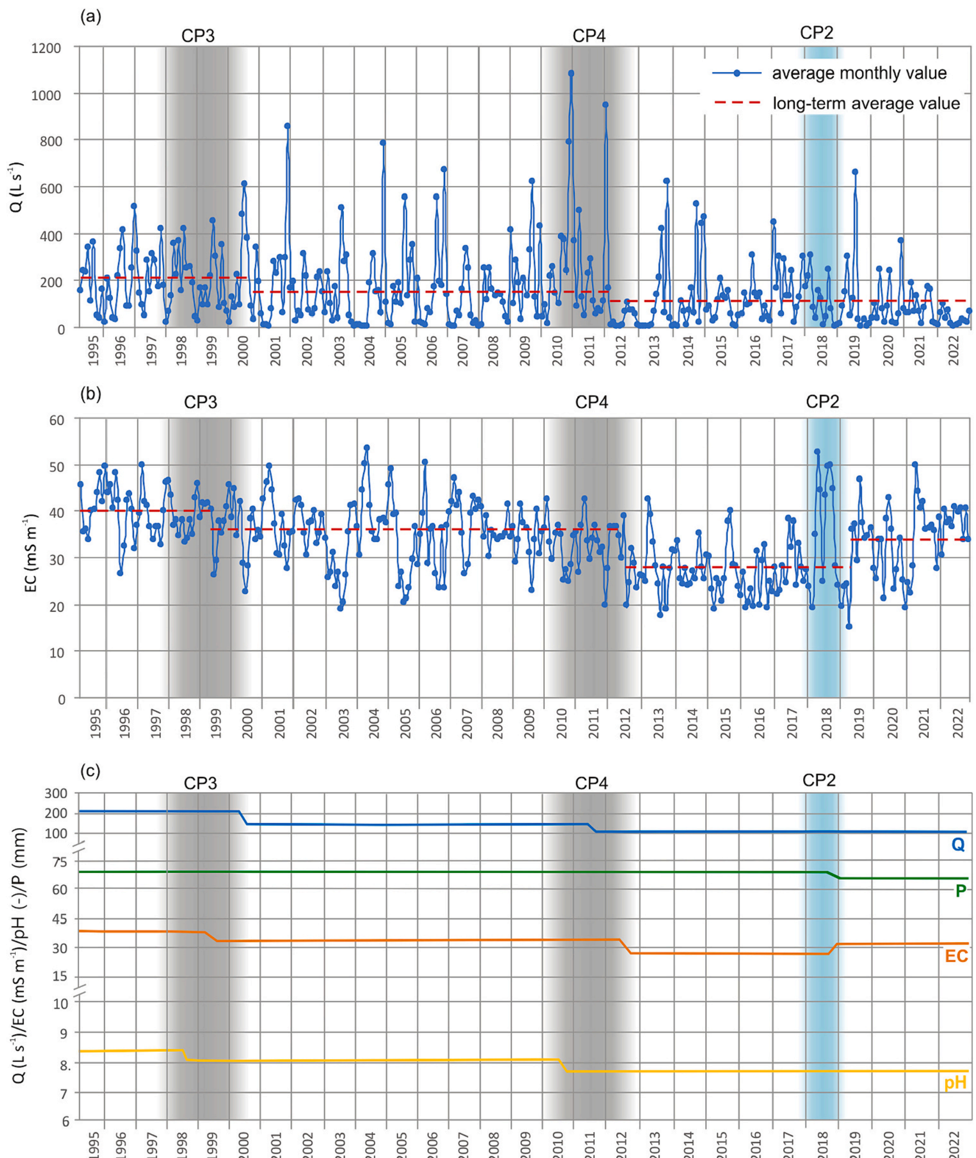

Fig. 5. Average monthly values and long-term average of chosen hydro-meteorological parameters in the Bystrzanka catchment: (a) water discharge of the Bystrzanka stream (Q), (b) water electric conductivity of the Bystrzanka stream (EC). (c) Long-term averages of all hydro-meteorological parameters in the Bystrzanka catchment that showed a significant changes over the study period: Q – stream discharge ($m^3\ s^{-1}$), EC – water electric conductivity ($mS\ m^{-1}$), pH – water acidity (−), P – precipitation totals (mm). Water and air temperatures and reference evapotranspiration exhibited no significant changes over the study period. CP3, CP4 and CP2 indicate the three main change points of hydro-meteorological parameters identified in the Bystrzanka catchment.

TMAI decreased by 53 % (Fig. 6d).

In the case of the Bystrzanka catchment, ion concentrations in precipitation changed significantly in three periods: the late 1990s and early 2000s, in 2010–2011 and late 2010s (Fig. 7a). In the first period there was a decrease in the concentration of some ions (Na^+, NH_4^+, SO_4^{2-}) and an increase in others (Ca^{2+}, NO_3^-, Cl^-). In 2010–2011, NO_3^- concentration decreased by 50 % and Ca^{2+} concentration increased by 2 %. In the recent period of change, there has been mainly an increase in the cation concentration of Mg^{2+}, Na^+ and K^+ in precipitation, which contrasts with the Wüstebach catchment, where ion concentrations in precipitation have mainly decreased. Despite an increase in the concentration of some ions in precipitation, the total mass of atmospheric input decreased by 21 % in the Bystrzanka catchment in 2003. The input of Mg^{2+}, NH_4^+, NO_3^- and SO_4^{2-} decreased similarly. In contrast, the atmospheric input of Ca^{2+}, Na^+, K^+ and Cl^- ions increased (Fig. 7b).

3.3. *Change points in ion concentration and solute mass balance in stream water*

In the case of ion concentration and solute mass balance in the control and Wüstebach catchments, most of the changes occurred in similar periods as in the case of hydro-meteorological parameters, i.e. at the turn of 2013–2014 (CP1) and in 2018–2019 (CP2).

In the control catchment, the first period of change (CP1) lasted even until the second half of 2015, and mainly included an increase in the concentration of many ions (Na^+, K^+, Fe_{tot}, Mn^{2+}) in the stream (Fig. 8a), which was the opposite of the partially clear-cut Wüstebach catchment, where a decrease in some ion concentrations (Na^+ and Cl^-) was rather observed (Fig. 8b). The exceptions were the concentrations of Ca^{2+} and Mg^{2+}, which decreased in both catchments: by 5 % and 4 % in the control catchment, and by 12 % and 15 % in the Wüstebach catchment. The concentrations of NH_4^+ increased in both catchments (by 100 % in the control catchment and by 360 % in the Wüstebach catchment).

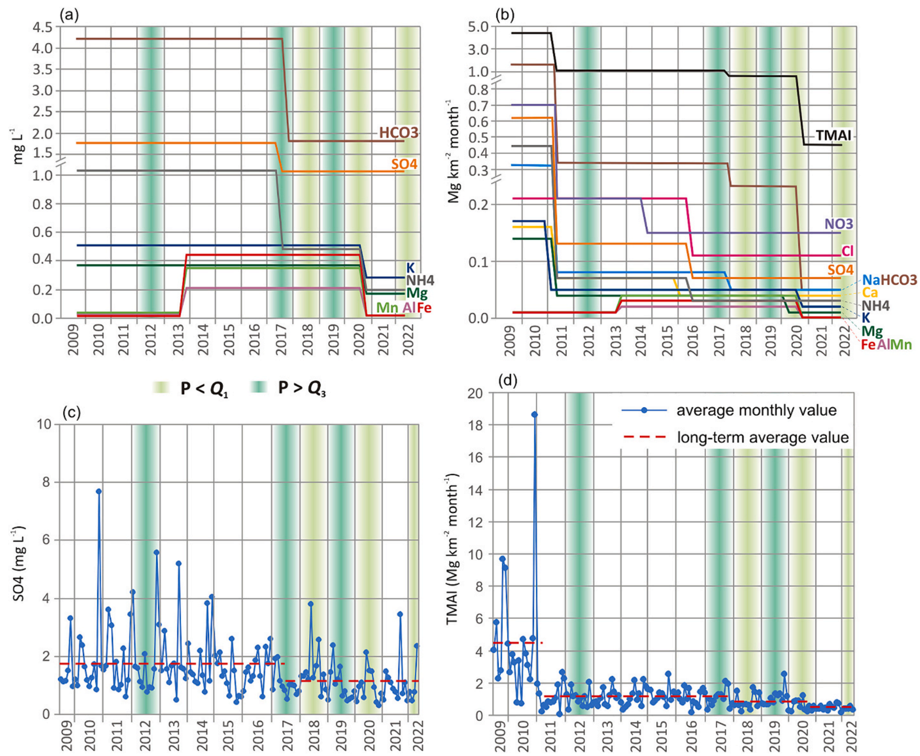

Fig. 6. Long-term averages of rainwater chemical characteristics that showed significant changes over the study period in the Wüstebach catchment: (a) ion concentrations (mg L^{-1}) and (b) atmospheric input (Mg km^{-2} $month^{-1}$). Concentrations of Ca^{2+}, Na^{+}, NO_3^{-}, and Cl^{-} exhibited no significant changes over the study period. Years with exceptionally low (P below 25th-quantile, Q_1) and high (P above 75th-quantile, Q_3) precipitation totals are highlighted. Average monthly values and long-term average of chosen rainwater chemical characteristics in the Wüstebach catchment: (c) SO_4^{2-} concentrations and (d) total monthly atmospheric input (TMAI).

The second change point covered 2018 and 2019 (CP2) when, in the control catchment, Ca^{2+}, Mg^{2+}, NH_4^{+}, and NO_3^{-} concentrations decreased (by 5 %, 7 %, 43 % and 42 % respectively), and Fe_{tot} and Cl^{-} concentrations increased (by 43 % and 12 %; Fig. 8a). Similarly, in the Wüstebach catchment, the average concentrations of NH_4^{+} and NO_3^{-} decreased by 65 % and 34 %, respectively, and Cl^{-} increased by 18 % (Fig. 8b). However, $Fe_{tot,}$ concentrations have decreased in the Wüstebach catchment by 30 %. Additionally, there were changes in 2020 in the Wüstebach catchment when the average concentrations of Al^{3+} and Mn^{2+} decreased by 76 %, and 63 % respectively, and the concentrations of Na^{+} increased by 10 %.

The total solute mass balance transported from the control and the Wüstebach catchments did not change over the study period (Fig. 9c and d), but the individual ion mass balances did. In the control catchment there were two change points of the ion mass balances, in 2013 (CP1) and in 2020 (Fig. 9a). Mass balance of Al^{3+}, $Fe_{tot,}$ and Mn^{2+} decreased 6, 69 and 83 fold at the end of 2013 and then increased in 2020 by 99 %, 93 % and 102 % respectively as did the mass balance of HCO_3^{-} by 140 %. Only the mass balance of NH_4^{+} increased by 57 % in the control stream at the beginning of 2018 associated with CP2. In the Wüstebach catchment there were also two change points of the ion mass balances, one in 2013–2014 (CP1) and another in 2016 (Fig. 9b). At the end of 2013 and at the beginning of 2014 mass balance of Al^{3+}, $Fe_{tot,}$ and Cl^{-} (Fig. 9d) decreased (by 233 %, 93 %, and 22 % respectively), while mass balance of NH_4^{+} and SO_4^{-} increased (by 78 % and 87 %). In 2016 mass balance of Mn^{2+} and HCO_3^{-} decreased (by 200 % and 54 %), while the mass balance of Al^{3+} increased by 175 %. No changes have been registered in relation to CP2 in the Wüstebach catchment.

In the case of the Bystrzanka catchment, changes in ion concentrations in stream water occurred at a similar time to changes in hydrometeorological parameters: in the late 1990s to 2000 (CP3), in 2009–2011 (CP4) and in 2017–2019 (CP2; Fig. 10a). In the first period of change (CP3), from the late 1990s to 2000, there was a decrease in Mg^{2+}, SO_4^{2-} and Cl^{-} concentration and an increase in K^{+} concentrations. In the second period (CP4), 2009–2010, there was a further decrease in SO_4^{2-} and Cl^{-} concentrations and a decrease in K^{+} and NO_3^{-} concentrations. In contrast, the concentrations of NH_4^{+} and HCO_3^{-} increased. In the third period of change (CP2), 2017–2019, the concentrations of SO_4^{2-} decline again, decreasing by 47 % over the study period. Cl^{-} concentrations increased back to almost the same level as at the beginning of the study period. Concentrations of Ca^{2+} and Na^{+} increased by 22 % and 17 %, respectively, and NH_4^{+} concentrations were reduced by 80 % to 0.04 mg L^{-1}.

The mass balance of ions transported from the Bystrzanka catchment has changed during two change points, in the late 1990s (CP3) and 2009–2011 (CP4; Fig. 11a). In both change points there was a decrease in the total solute mass balance (TSMB), by 54 % over the study period, as well as a decrease in the individual ion mass balance (Fig. 11b).

3.4. Impact of de-icing salts on total solute flux in the Wüstebach catchment

In the upper part of the Wüstebach catchment area 150 m from the stream, there is a 1272 m asphalt road on which de-icing salts are applied during the winter season. According to data from the North Rhine-Westphalia State Road Construction Authority between 2018 and 2021, de-icing salts were mostly applied from November to April for 34–87 days a year. Each year 8–14 Mg of de-icing salt were applied to each kilometer of roads in the road service area. Taking into account that the Wüstebach catchment is located at the highest point in the road service area, where there are 1.4 times more days with frost than on average in the road service area (see Section 2.3.), at the same time 14–25 Mg of de-icing salt was applied to the road in the Wüstebach catchment area each year. The road salting input accounted for an

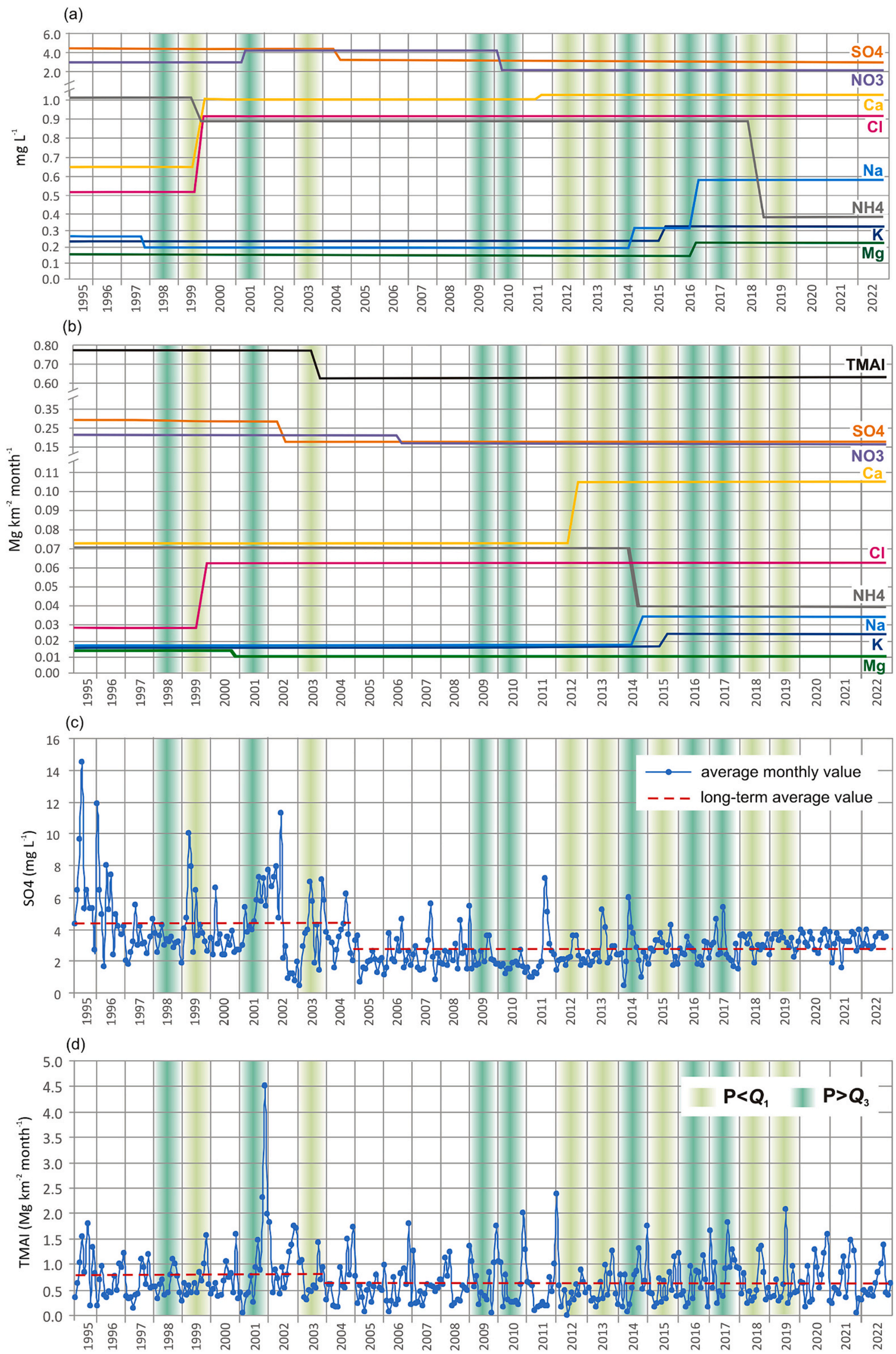

Fig. 7. Long-term averages of rainwater chemical characteristics that showed significant changes over the study period in the Bystrzanka catchment: (a) ion concentrations (mg L^{-1}) and (b) atmospheric input (Mg km^{-2} $month^{-1}$). Years with exceptionally low (P below 25th-quantile, Q_1) and high (P above 75th-quantile, Q_3) precipitation totals are highlighted. Average monthly values and long-term average of chosen rainwater chemical characteristics in the Bystrzanka catchment: (c) SO_4^{2-} concentrations and (d) total monthly atmospheric input (TMAI).

average of 62 % (19 Mg a^{-1}) of total solute flux from the catchment area annually (Fig. 12).

This stays in line with the estimations based on the differences in the share of atmospheric input of ions to solute fluxes from the catchment between the control and Wüstebach catchment (Płaczkowska et al., 2023 see Table 3). According to these estimates, on average 87 % of the Cl^- flux, 84 % of the Na^+ flux, 46 % of the Ca^{2+} flux, 15 % of the Mg^{2+} flux, and 9 % of the K^+ flux could be supplied from road salting, giving an average of 62 % of road salting input and 15 % of precipitation input in total solute flux in the Wüstebach catchment (Fig. 13). Thus, chemical

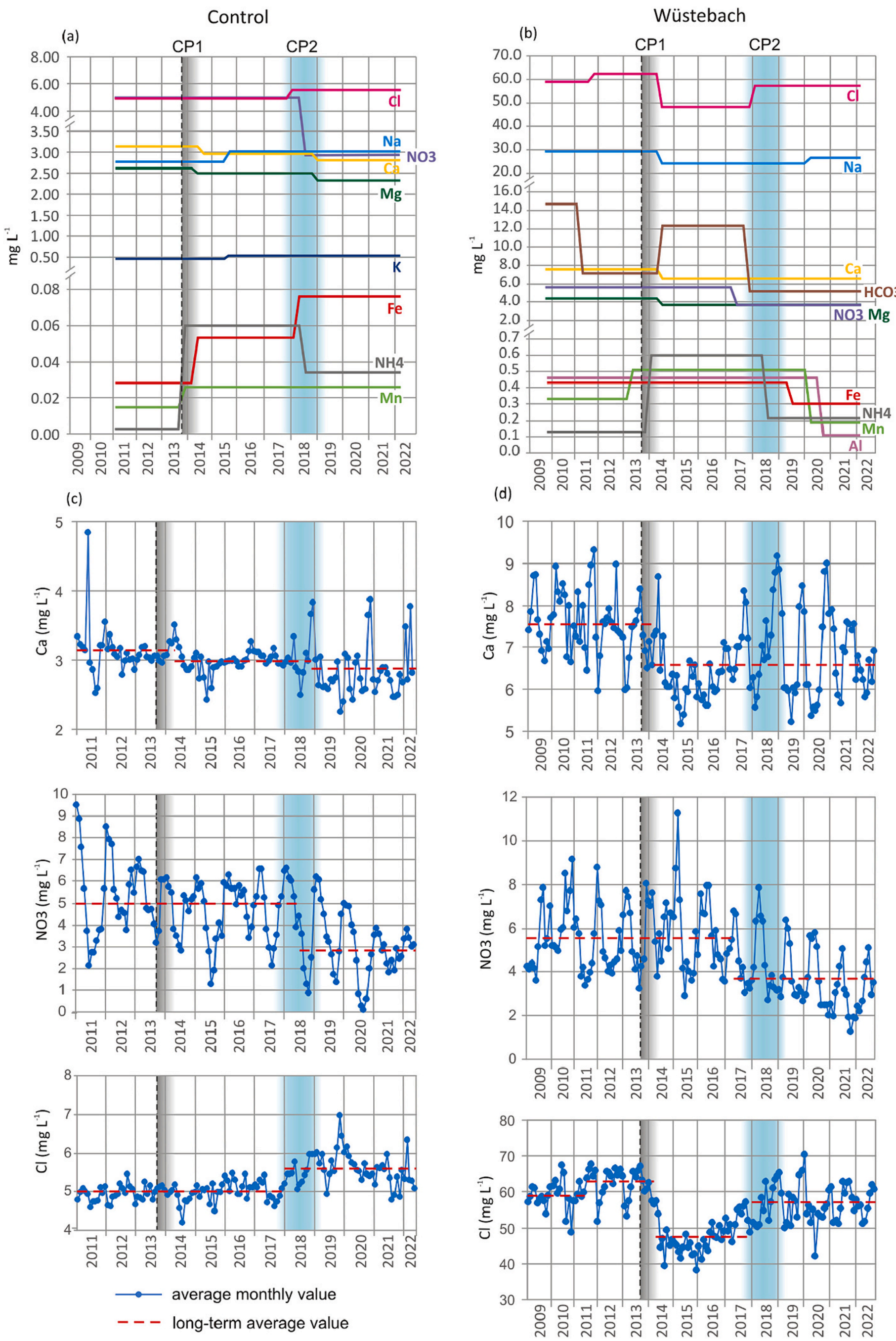

Fig. 8. Long-term averages of concentrations (mg L^{-1}) of ions that showed a significant changes over the study period in the control stream (a) and in the Wüstebach stream (b). Concentrations of Al^{3+}, SO_4^{2-}, HCO_3^- in the control stream and concentrations of K^+, SO_4^{2-} in the Wüstebach stream exhibited no significant changes over the study period. Average monthly values and long-term average of concentrations of chosen ions (Ca^{2+}, NO_3^-, Cl^-) in the control catchment (c) and in the Wüstebach catchment (d).

denudation would account for only 23 % (19.4 Mg km^{-2} a^{-1}) of the total solute flux (83.8 Mg km^{-2} a^{-1}).

4. Discussion

4.1. Anthropogenic impact on the atmospheric input to the catchment area

Air pollutant emissions are generally decreasing in Europe (European Environmental Agency, 2020), as can be seen in the decrease in concentrations and inputs of most ions and TMAI in rainwater in the Wüstebach catchment in 2017 and 2020 (Fig. 6c and d) and the decrease in concentrations and inputs of NH_4^+, NO_3^-, and SO_4^{2-} in the Bystrzanka catchment since 2003 (Fig. 6c and d). One of the natural sources of atmospheric deposition of Cl^-, Na^+, Mg^{2+}, Ca^{2+}, K^+, NO_3^-, and SO_4^- are sea spray aerosols (Bertram et al., 2018). The close location (220 km) of the Wüstebach catchment to the North Sea makes sea spray aerosol input common in this region (Sucker et al., 2011) which results in higher shares of Na^+ and Cl^- in rainwater ionic composition compared to the Bystrzanka catchment. The origin from sea spray aerosol could also explain why the concentrations of Ca^{2+}, Na^+, NO_3^- and Cl^- in rainwater remained unchanged in the Wüstebach catchment. However, both

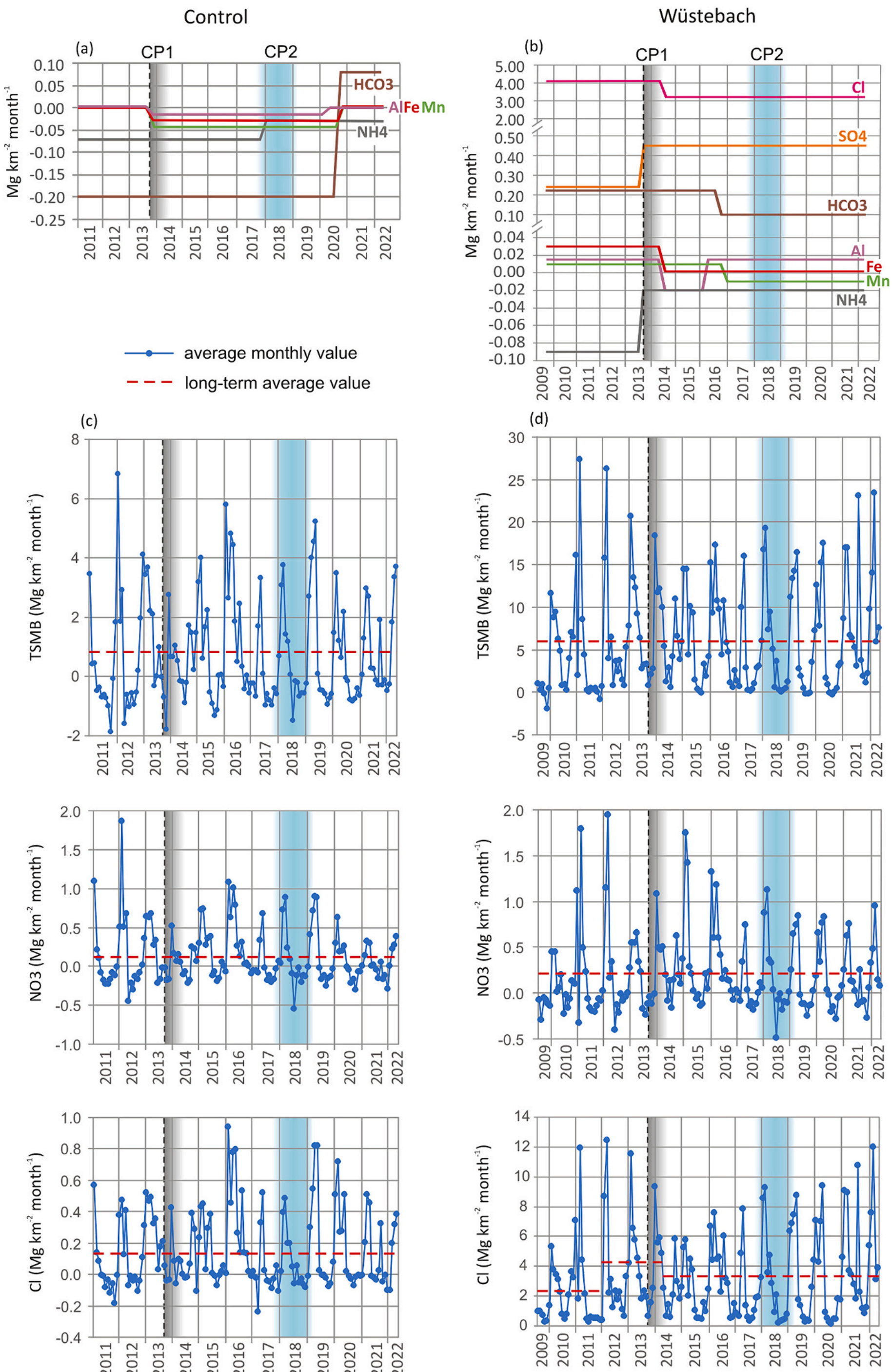

Fig. 9. Long-term averages of solute mass balance (Mg km^{-2} month^{-1}) that showed a significant changes over the study period in the control stream (a) and in the Wüstebach stream (b). Mass balance of Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, NO_3^- in both streams and mass balance of SO_4^{2-} and Cl^- in the control stream exhibited no significant changes over the study period. Average monthly values and long-term average of total solute mass balance (TSMB) and mass balance of the chosen ions (NO_3^-, Cl^-) in the control catchment (c) and in the Wüstebach catchment (d).

studied catchments are located close to industrial and densely populated regions which might be of particular importance for air quality, precipitation and surface water chemistry.

The Wüstebach catchment is located 100 km south of the Ruhr area and 35 km east of the Walloon area. With the dominance of W, NW and N winds in the Eifel region, these areas can be a potential source of air pollution. 3 % of the precipitation events had a total ion concentration higher than 30 mg L^{-1}, with a high contribution of $NO_3^-$and SO_4^{2-} and a low contribution of Cl^- which excludes sea spray aerosols as the only source. The only increase in ion concentrations and inputs in rainwater in the Wüstebach catchment occurred for Al^{3+}, Fe_{tot}, and Mn^{2+} in 2013. The most probable source for these ions is dust. The transport of Sahara dust to Europe is quite frequent even to the northern part of the continent which causes often the deterioration of air quality (Wang et al., 2020). However, most of the dust comes from local sources: open-pit mines in the Ruhr area (Krüger et al., 2022; Li et al., 2021) and road traffic (Dall'Osto et al., 2014). The main elements of dust are Si, Al, Fe, K, Ca, Mg, Na, P, Mn, and other heavy metals which are mostly of crustal

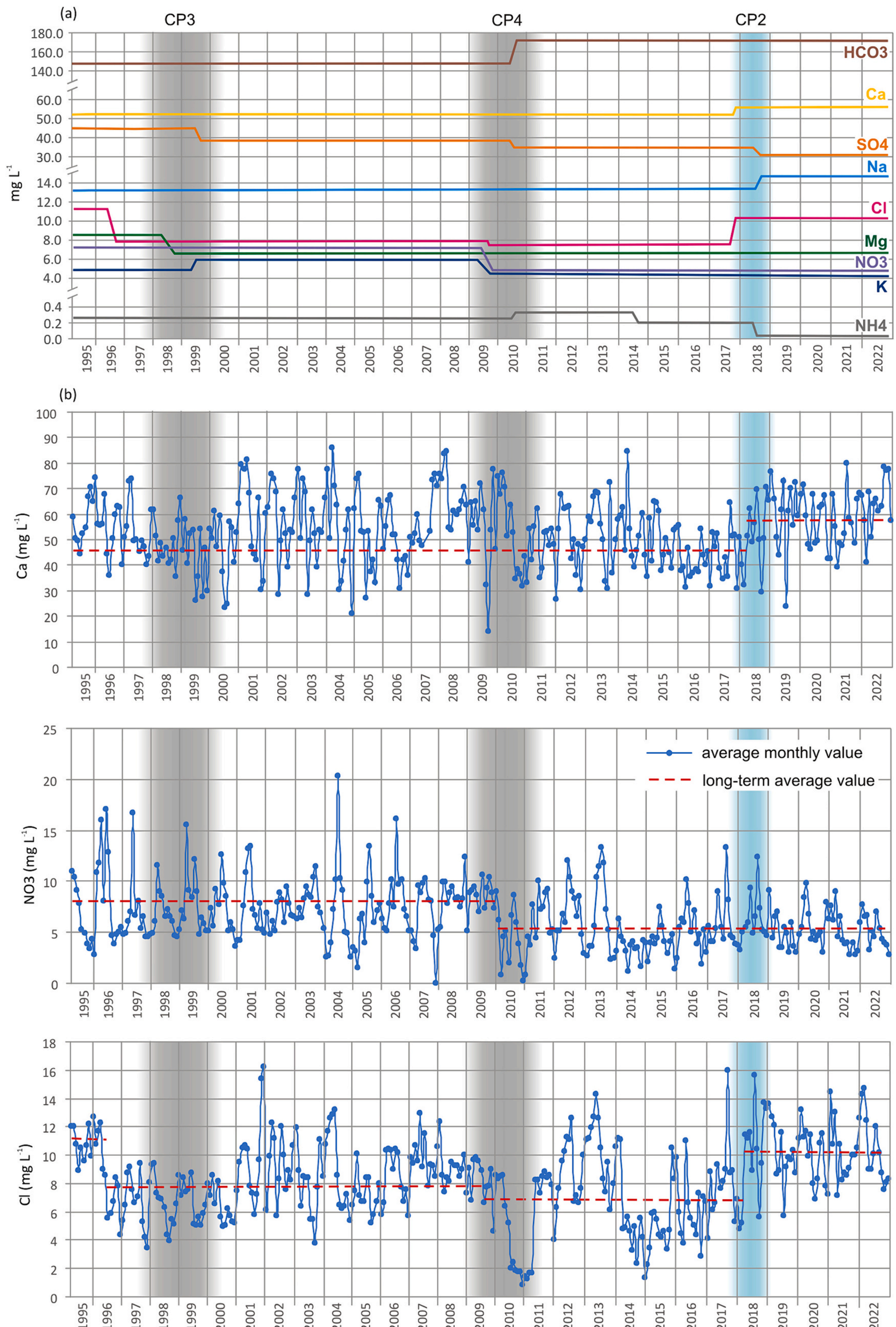

Fig. 10. (a) Long-term averages of concentrations (mg L^{-1}) of ions that showed a significant changes over the study period in the Bystrzanka catchment. (b) Average monthly values and long-term average of concentrations of chosen ions (Ca^{2+}, NO_3^-, Cl^-) in the Bystrzanka catchment.

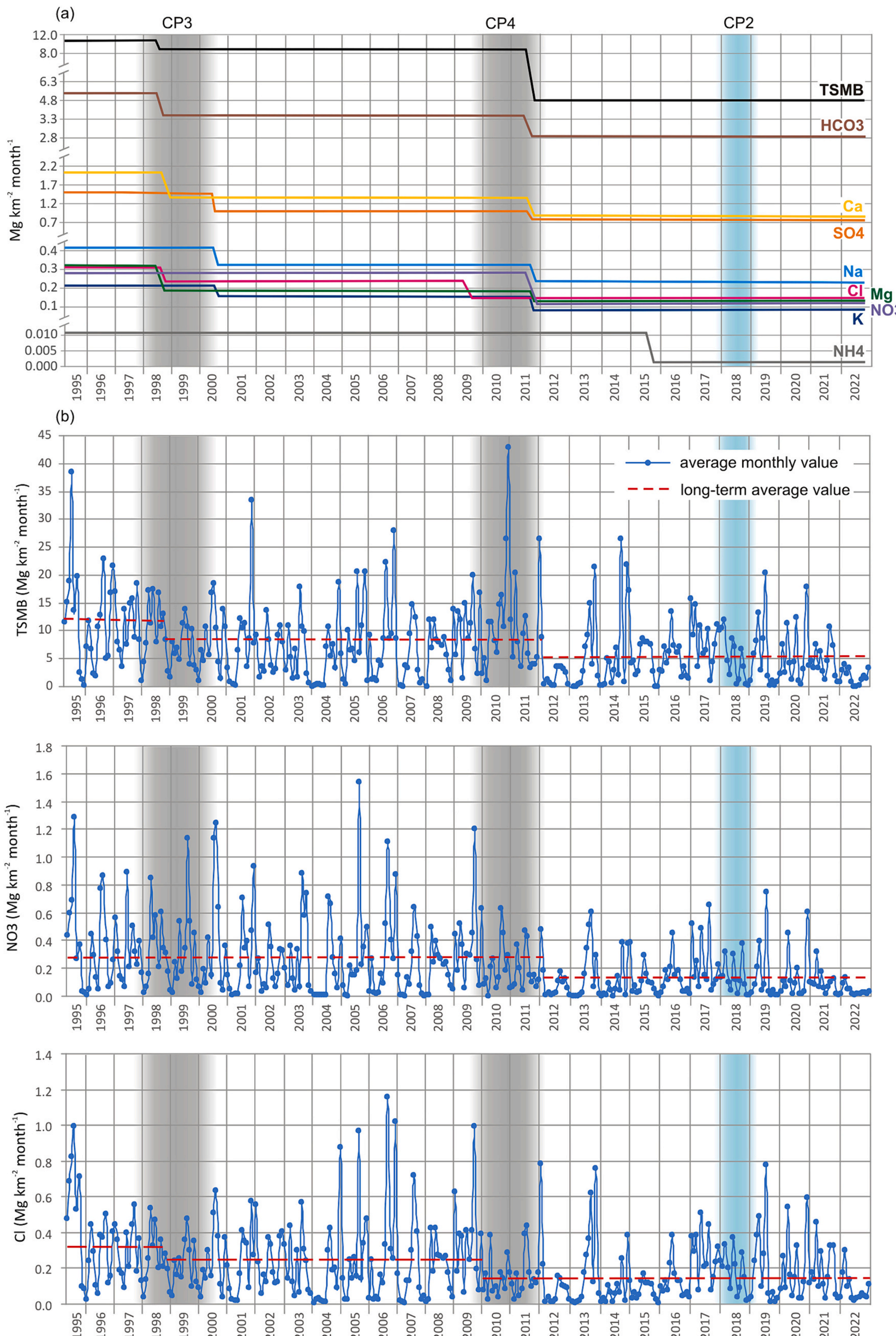

Fig. 11. (a) Long-term averages of solute mass balance (Mg km^{-2} month^{-1}) that showed a significant changes over the study period in the Bystrzanka stream. (b) Average monthly values and long-term average of total solute mass balance (TSMB) and mass balance of the chosen ions (NO_3^-, Cl^-) in the Bystrzanka catchment.

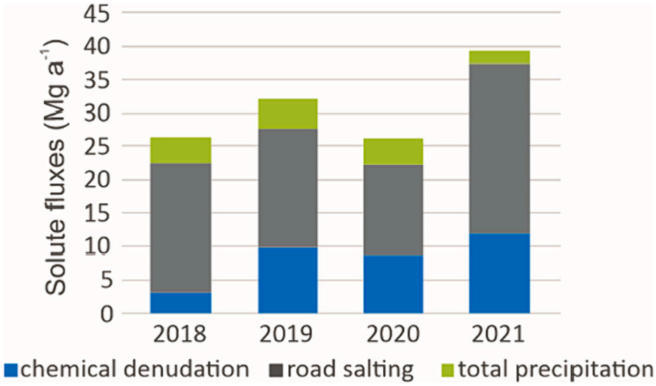

Fig. 12. Solute fluxes from the Wüstebach catchment area between 2018 and 2021 with partitioning to chemical denudation, road salting input and total precipitation input.

origin (Sharif, 1995). A significant decrease in the concentration and inputs of many ions in rainwater in the second half of 2020 may be due to reduced dust in the air as a result of limited traffic and lockdown during the COVID-19 pandemic.

The precipitation input seems to play a significant role in solute fluxes in the Eifel area. When excluding anthropogenic input (i.e. road salting) then the atmospheric contribution to the total solute flux in the Wüstebach catchment during the study period would be 39 %, with 91 % of K^+, 47 % of NO_3^-, 30 % of Na^+, 29 % of Cl^-, 25 % of Ca^{2+}, 23 % of SO_4^{2-}, 17 % of Mg^{2+} and 64 % of other ions (Al^{3+}, Fe_{tot}, Mn^{2+}, NH_4^+, HCO_3^-).

The Bystrzanka catchment is located in the direct vicinity of the Nowy Sącz-Gorlice-Tarnów area which used to be a large industrial center, with mainly engineering and petrochemical industries operating intensively until Poland's accession to the EU. More recently, the role of industry in the area has diminished, due to reduced demand for mining equipment and the end of production at the refinery in 2005. Despite the reduction of industry, the average annual concentration of particulate matter measured in the air in most Polish cities is high (EU Joint Research Center, 2018, 2021). In 2021, Nowy Sącz was the second worst city in Europe in this respect, exceeding EU annual target values (EU Joint Research Center, 2021). In the Bystrzanka catchment, SO_X and NO_X in the air in the summer season are lower by 61 % and 40 % respectively than in the winter season (Kijowska-Strugała and Bochenek, 2023). This indicates that air pollutants in the Bystrzanka catchment are mainly related to households' fuel combustions in the winter season. The increase in road traffic and the number of cars after Poland's accession to the European Union was not without significance for the change in pollution trends after 2004 (increase in NO_X pollution; Kijowska-Strugała and Bochenek, 2023). Both factors, industrial production in the region in the 1990s, households' fuel combustions in the winter, and intensified road traffic, most likely caused an increase in the concentrations and inputs of some ions in the precipitation in the Bystrzanka catchment in the late 1990s and in 2014–2016.

4.2. Impact of clear-cut on stream water chemistry and solute fluxes (CP1)

In the case of the Wüstebach catchment, the 2013–2014 change point (CP1) was clearly related to the clear-cut harvesting of 22 % of the catchment area. The clear-cut took place at the end of the 2013 growing season, which means that for some physical and chemical parameters the effect of clear-cutting was visible with the beginning of the next growing season in 2014. The control catchment has not been clear-cut, however the thinning of 84 % of the forest area before 2014 was done before beech planting (Płaczkowska et al., 2023). This might affect ion concentrations in the stream water similar to the Wüstebach stream, as Ca^{2+} and Mg^{2+} concentrations decreased and NH_4^+ increased in both catchments. The decrease in cation concentrations after clear-cutting or forest thinning can be explained by limited soil cover disturbance (Siebers and Kruse, 2019), lack of nutrient uptake by plants and increased soil leaching. However, these changes seem to have no effect on solute mass balance, except NH_4^+ but only in the Wüstebach catchment. Increasing concentrations and mass balance of NH_4^+ in the Wüstebach catchment stay in line with the other deforested areas where the nitrogen compounds increase in surface water after harvesting (Wang et al., 2006; Huber et al., 2010; Webster et al., 2022). In the case of NH_4^+ concentrations, this increase was rather short and lasted from two months to one year (Wang et al., 2006; Webster et al., 2022) while in the Wüstebach it lasted almost 5 years. Robinson et al. (2022) also found elevated nitrogen concentration values in the Wüstebach stream after clear-cutting, and determined from nitrogen and DOC concentrations that the effect of clear-cutting on water quality lasted for about five years. However, the Pettit test showed no significant change in NO_3^- concentration after clear-cutting. The monthly data show that the increase in NO_3^- concentration in the Wüstebach stream was very short-term, with a decrease in both catchments between 2017 and 2018 (Fig. 8c and d). At the same time, Robinson et al. (2022) observed a decline in nitrogen concentration in another catchment in the Eifel. This indicates that the decrease in NO_3^- concentration in the Wüstebach stream and the control stream 5 years after the time of the clear-cutting as well as the decrease in NH_4^+ concentration and changes in other ions (see Fig. 8), cannot be attributed solely to the clear-cutting. Another reason could be the forest thinning that has occurred in both catchments

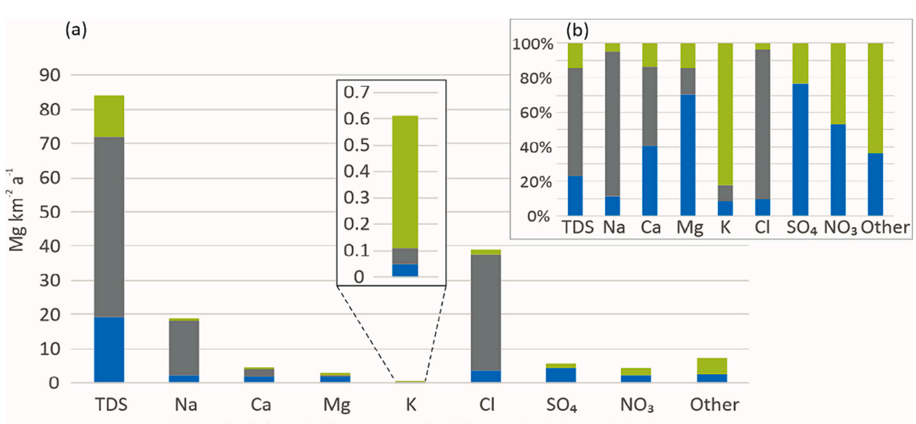

Fig. 13. Average solute fluxes in the Wüstebach catchment between 2010 and 2020 (a) with the contribution of chemical denudation, road salting input and precipitation input (b).

(Płaczkowska et al., 2023) or the changes in hydro-meteorological conditions in the region since 2018 and the associated lower atmospheric input (see Section 4.4.). The latter reason seems very likely, as NH_4^+, SO_4^{2-} and HCO_3^- concentrations in rainwater and TMAI have decreased over the same time, which corresponds with the long-term decrease in atmospheric input in Europe (Theobald et al., 2019; Templer et al., 2022).

In the catchment where partial clear-cut was carried out (Wüstebach catchment), there was also a decrease in EC and in the concentration of Na^+ and Cl^- in the stream water, which did not occur in the control catchment (with forest thinning). However, these changes seem to have only a slight effect on solute mass balance as only mass balance of Cl^- in the Wüstebach stream decreased. Cl^- has two main sources in the Wüstebach catchment: atmospheric with sea spray aerosols (Sucker et al., 2011) and anthropogenic with de-icing salts (Płaczkowska et al., 2023). Cl^- ions, which are delivered to the catchment area with sea spray aerosols or de-icing salts, are accumulated in soils and then washed out from the soils and recharged to the stream by interflow. In 2014, the first year after clear-cut, the Wüstebach runoff increased by 10 % (Wiekenkamp et al., 2016) resulting in dilution with shallow subsurface flow which increased in the Wüstebach catchment after clear-cut as the soil moisture at 5 cm depth increased by 15–20 vol% in the dry season (Wiekenkamp et al., 2016). In the control stream water, recharged mostly by groundwater (Bol et al., 2015), the changes in Cl^- concentrations were opposite despite the fact that at both sites the forest was thinned before planting beech trees. At both sites the Cl^- concentrations increased in 2018 when the precipitation totals decreased, and groundwater was diluted to a lesser extent by infiltrating rainwater.

4.3. Impact of socio-economic changes on stream water chemistry and solute fluxes (CP3 and CP4)

In the Bystrzanka catchment, two change points in the physical and chemical parameters of the stream water can be identified, which are indirectly associated with socio-economic changes in the Carpathian region and in Poland, the first one in the late 1990s to 2000 (CP3), and the second one in 2009–2011 (CP4). The political transformation in the country in 1989 resulted in significant LULC changes in the Polish Carpathians and in the Bystrzanka catchment itself as described in the 2.1. section. The most important changes in the 1990s were a 4 % increase in forest area and a 17 % decrease in arable lands in the studied catchment (Kijowska-Strugała, 2019). Before these changes a large amount of sediments was transported on the Carpathian slopes by surface runoff and delivered together with dissolved solids to the riverbed (Halecki et al., 2018), often leading to water quality degradation (Giri, 2021; Mararakanye et al., 2022). Following the LULC changes in the 1990s, the amount of suspended solids transported in the stream decreased, which was directly linked to an 11 % decrease in soil erosion (Kijowska-Strugała, 2019). As in other areas, LULC changes and the distribution of arable lands have the greatest impact on changes in nutrient concentrations in the stream (Tasdighi et al., 2017).

Leaching of nutrients from agricultural land into surface water depends mainly on the type and intensity of agricultural production, as well as the susceptibility of soils to erosion and their permeability (Ilnicki, 2014). Crops absorb only part of the nutrients applied by fertilizers, on average 50–70 % of nitrogen and potassium from mineral fertilizers and about 20–30 % from natural fertilizers (Ilnicki, 2014), and the rest is washed out to the streams. After the introduction of the free market economy in Poland, the majority of farms in the Polish Carpathians reported a significant decrease in the use of mineral fertilizers and pesticides (Górka et al., 2002). After the year 2000, there was a further decline in mineral fertilizer consumption in the Carpathians (Fig. 3), which stays generally in contrast to other regions in Poland where mineral fertilizer consumption is on the increase (Piwowar, 2022). Thus, a reduction in the use of fertilizers resulting from a decrease in the area of arable land, together with a decrease in soil erosion were the reasons for the changes that occurred in the Bystrzanka stream from the late 1990s to 2000 (CP3): a decrease in EC, pH, concentration of Mg^{2+} and SO_4^{2-}, TSMB and mass balance of all individual ions. This is also confirmed by a statistically significant ($p < 0.05$) relationship between mineral fertilizer consumption and TSMB in the catchment ($r = 0.53$; Fig. 14).

The changes in LULC and soil erosion initiated in the 1990s have continued to the present day (Fig. 3), but the rate of change in later years has not always been as dynamic. Another driving factor was Poland's accession to the European Union in 2004, which enforced the improvement of the infrastructure of the domestic sewage network and building of the sewage system in the lower part of the Bystrzanka catchment. The most intensive work was carried out in this part of the catchment in 2009–2010 (Kijowska-Strugała, 2019). Studies conducted in other areas of the Carpathians indicate that before 2004 the vast majority of wastewater remained in catchments, and only 2 % of water sold to customers in rural areas by the water supply company was returned to the treatment plant as wastewater (Pietrzak, 2005). All the construction works in the Bystrzanka catchment in the first decade of the 21st century contributed to the improvement of sanitary conditions in the catchment and thus to the improvement of water quality. Therefore, another change point (CP4) in the chemical parameters of the stream water was identified in 2009–2011 when EC, pH, concentrations of many ions, TSMB and mass balance of all individual ions decreased.

Experimental studies conducted by Kijowska-Strugała and Bochenek (2023) in the Bystrzanka catchment using the SWAT model showed that if land use had not changed since 1997, simulated water runoff and nitrogen loads would have been 16 % and 67 % higher than observed values, respectively. This confirms the extremely significant impact of land use on nutrient content in the catchment area. According to Siwek (2021), an additional factor affecting water chemistry in the Carpathians is acid rain, which caused a very high deposition of acid sulphur and nitrogen in the second half of the 20th century. In the Carpathians, as in the Eifel Mountains, the loss of mainly spruce monocultures as a result of acid rain, wind, and bark beetle infestation has been observed (Siwek, 2021), which will lead to future changes in forest species in the region and thus also in surface water chemistry (Płaczkowska et al., 2023).

4.4. The 2018 hydro-climatic change point (CP2)

The changes in meteorological parameters in both study areas that

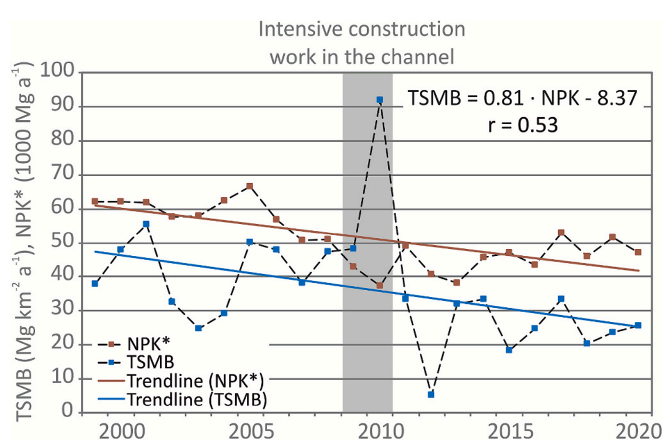

Fig. 14. Annual total solute mass balance (TSMB) in the Bystrzanka catchment and total consumption of mineral fertilizers (NPK) between 1999 and 2020. The trend lines of both parameters show the same direction of change. The high TSMB value in 2010, deviating from the generally decreasing trend, was related to the intensive construction work at the stream channel that year. *data for the entire Małopolskie region located in the central part of the Polish Carpathians and including the studied catchment area (Statistics Poland, 2019, 2022).

occurred in 2018 were likely initiated by the anomalous circulation that caused the summer 2018 heatwaves in the northern hemisphere and maintained by the global warming trend (Kornhuber et al., 2019). In both study areas, a decrease in precipitation totals was observed. Since 2018 the frequency of precipitation totals below the 25th-quantile (Q_1) in both study areas was higher. In the Wüstebach catchment, although the Pettitt test did not show significant changes in average monthly air and water temperatures, the previous studies demonstrated that annual air temperature has steadily increased since 2017 and both air and water temperatures were significantly higher in the post-clear-cut period than in the pre-clear-cut period (Płaczkowska et al., 2023). EC, which depends on the concentration of solutes in water (Marandi et al., 2013), also increased in both study areas during that time. The increase in EC in this case was associated with drier conditions in the catchment, as solute concentrations are related to stream discharge and when stream discharge decrease the solute concentrations increase (Knapp et al., 2020). In the Wüstebach catchment and many other European catchments the exceptionally low soil moisture values were observed in the period 2018–2020 (Bogena et al., 2022). Hence, 2018 can certainly be considered a natural change point for hydro-meteorological conditions in the studied catchments.

Reduced precipitation totals and drier catchment conditions have also affected surface water quality. Na^{+} and Cl^{-} concentrations in stream water increased in both catchments at similar times. This may be due to a similar mechanism (lack of dilution with rainwater) as for EC, as well as increased non-atmospheric inputs to the catchment, e.g. from road salting. In contrast, NH_4^+ concentrations in all the streams studied declined in 2018, as did NH_4^+ concentrations in rainwater.

4.5. Impact of road salting on stream water chemistry and solute fluxes

Data on the amount of de-icing salt applied to roads in the Wüstebach catchment was not included in the Pettitt test due to the short time of data availability (2018–2021). However, simply estimating the average annual input of de-icing salts to the catchment provides insight into the severity of this phenomenon and its contribution to the total solute flux in the catchment.

The effect of applying de-icing salts to roads on an increase in Cl^{-} and Na^{+} concentrations in soil and surface water is well known (Godwin et al., 2003; Bastviken et al., 2006; Kelly et al., 2008). However, the case of the Wüstebach catchment showed that headwaters are extremely prone to any human activity, and the application of salt even on a single asphalt road crossing a headwater area can completely change the ionic composition of the surface water (Płaczkowska et al., 2023) and significantly increase the solute flux from the catchment (by 62 %). The road salting input was on average 3 times higher than the fluvial chemical denudation rate. Even though the chloride concentrations in the Wüstebach did not exceed the water quality criteria, it was still 3 to 4 times higher than in rivers on average (Hong et al., 2023). This issue requires further thorough research on a regional scale.

5. Conclusions

Research indicates that the degree of soil cover disturbance is the most significant factor in determining solute flux from the catchment, regardless of the direction of LULC changes, such as reductions or increases in forest cover.

We expected to see an increase in ion concentration and mass balance after partial clear-cut of the Wüstebach catchment. Instead, the concentrations of some ions (Ca^{2+}, Mg^{2+}, Na^{+}, Cl^{-}) decreased significantly after logging. The hypothesis proved correct only in the case of nitrogen compounds (NO_3^- and NH_4^+), whose concentrations increased, but only temporarily. It seems that the minimal disturbance of the soil cover during the skidding works did not significantly impact solute fluxes in the catchment, and the total mass balance of solutes remained unchanged.

The Bystrzanka catchment has experienced a decrease in arable land and an increase in grassland and forest cover. This has led to a reduction in soil disturbance caused by ploughing and stabilization of the soil cover through revegetation. LULC changes in over 42 % of the catchment area resulted in a decrease in soil erosion and fertilization. As a consequence, concentrations of NO_3^- and NH_4^+ decreased by 33 % and 80 %, respectively, and the total solute mass balance transported from the catchment decreased by 55 %. In 2009–2010, a sewerage system was constructed in the lower part of the catchment area due to Poland's accession to the EU and implementation of the Water Framework Directive. This was another reason for the changes in ion concentration and solute mass balance.

The use of de-icing salts in winter was not without effect on total solute fluxes, as the example of the Wüstebach catchment showed. This confirms the observed pattern that headwater areas are very vulnerable to environmental modifications. The input of large amount of salt into the headwater catchment and its accumulation in the soil led to a 62 % increase in annual solute fluxes from the catchment, even if the water quality was within the defined standards.

In addition, the Pettitt test identified a change point in 2018 when the hydro-meteorological conditions in both catchments changed, manifested in particular in a decrease in precipitation totals. This relates to European trends and is most likely due to anomalous circulation in the northern hemisphere that occurred in 2018. In both study areas, decreases in total atmospheric input associated with improved air quality in Europe were observed. On the other hand, in both areas, the supply of pollutants from dust, road traffic or household fuel combustion cannot be excluded.

Finally, conducted studies have shown the possible limitations of the Pettitt test, such as not identifying gradual changes, i.e. air and water temperature, or brief changes, i.e. stream flow and NO_3^- concentrations after clear-cut. Despite this, the method has proven to be a very helpful tool in identifying human-induced changes in surface water quality.

CRediT authorship contribution statement

Eliza Płaczkowska: Writing – original draft, Visualization, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Małgorzata Kijowska-Strugała:** Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Gunnar Ketzler:** Writing – original draft, Methodology, Investigation, Formal analysis. **Heye Reemt Bogena:** Writing – review & editing, Investigation, Data curation, Conceptualization. **Michael Leuchner:** Writing – review & editing, Supervision, Investigation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The original datasets from the Wüstebach catchment (sites Wu14, Wu17, KR1) and from the Schöneseiffen site can be downloaded at the TERENO data portal www.tereno.net (accessed on 1 August 2023). The precipitation data at the Kalterherberg meteorological station of the German Weather Service are available at the Climate Data Center portal https://cdc.dwd.de/portal/ (accessed on 1 August 2023).

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