

Stream water chemistry between 1984–1990 and 2010 reflects declining acidic deposition and bark beetle induced ecosystem changes

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Abstract

Streamwater chemistry in the Šumava National Park (Czech part of the Bohemian Forest) was observed in three periods: 1984–1990, 2003–2004, and 2010. Declining acidic deposition of S and N followed by decline of sulphate and nitrate concentration was driving force for recovery from acidification until years 2003–2004. Later, forest disturbance have led to changes in soil chemistry and have altered N soil availability resulting in enhanced nitrogen leaching from soil to surface waters between 2003–2004 and 2010.

Key words: stream water chemistry, sulphate, nitrate, acidity, bark beetle infestation, Bohemian Forest

INTRODUCTION

Significant acidification of mountain regions of the Czech Republic occurred during the second half of the 20th century. Contrary to widespread forest dieback and surface water acidification in the northern part of the country, only stream water and lake acidification was observed in the Bohemian Forest. Since the 1980s, emissions of SO₂, NO_x, and NH₄ in Europe have declined following the implementation of international agreements on reduction of air pollutants (UNECE 2013). In response to the decreased sulphur (S) and nitrogen (N) deposition, surface waters have begun to recover from acidification (e.g. HELIWELL et al. 2014). In the Czech Republic, acidic deposition have declined substantially (KOPÁČEK & VESELÝ 2005), which has been mirrored in the reversal trends in surface water sulphate (SO₄) and nitrate (NO₃) concentrations across small forested catchments (OULEHLE et al. 2008, CHUMAN et al. 2013).

Streamwater chemistry mapping has been performed repeatedly since the 1980s to provide insight into the various geochemical and biological processes operative in catchments (e.g. VESELÝ & MAJER 1996, MAJER & VESELÝ 2005, MAJER et al. 2012). The Bohemian Forest headwaters are naturally predisposed for research of anthropogenic acidification impacts on biogeochemical cycling – e.g. chemically resistant bedrock, shallow soils, homogenous forest cover, and historically high acidic deposition.

Under conservation management, natural spread of bark beetle (*Ips typographus* L.) in a mosaic of strictly natural and human altered forests started to develop, which led to the gradual disturbance of mature spruce forests (ČÍŽKOVÁ et al. 2011). This process has been further triggered in 2007 after the hurricane Kyrill. Subsequent large-scale windthrow and bark beetle outbreak may be considered as a natural feature of the forest cycle in this area (SVOBODA et al. 2012). The forest disturbance have led to changes in soil chemistry (KAŇA et

al. 2012) and have altered N soil availability (TAHOVSKÁ et al. 2010). The main aim of our study is to assess the long-term changes in stream chemistry since the 1980s/1990s with the special focus on (i) the effect of the declining acid deposition on water acidification reversal and (ii) the effect of forest disturbance on the stream chemistry.

MATERIALS AND METHODS

Sampling

Within the three periods 1984–1990, 2003–2004 and in 2010, stream water samples were collected in the territory of the Šumava National Park and its close vicinity (Fig. 1). These 196 samples were collected at identical locations (Fig. 1). In the periods 1984–1990 and 2003–2004, samples were not filtered. During the 2010 campaign, they were filtered (0.45 µm). Samples were analysed for the following: anions – Cl, F, NO₃, SO₄; cations – Ca, Fe, Mg, Al, Mn, K, Na and Si; trace elements – Pb, Cd, As, Be, Li, Sr, Zn, Cu; total dissolved phosphorus (TDP, 2010 only); pH; conductivity and absorbance at 254 nm (ABS₂₅₄, 2010 only). The conductivity and pH were measured on the day of the collection using a portable conductometer (Cond 315i WTW GmbH, Weilheim, Germany) and a portable pH meter PHM201 with a combination glass electrode (pHC2085, with temperature sensor), both Radiometer, Denmark. All laboratory analyses were performed in the laboratory of the Czech

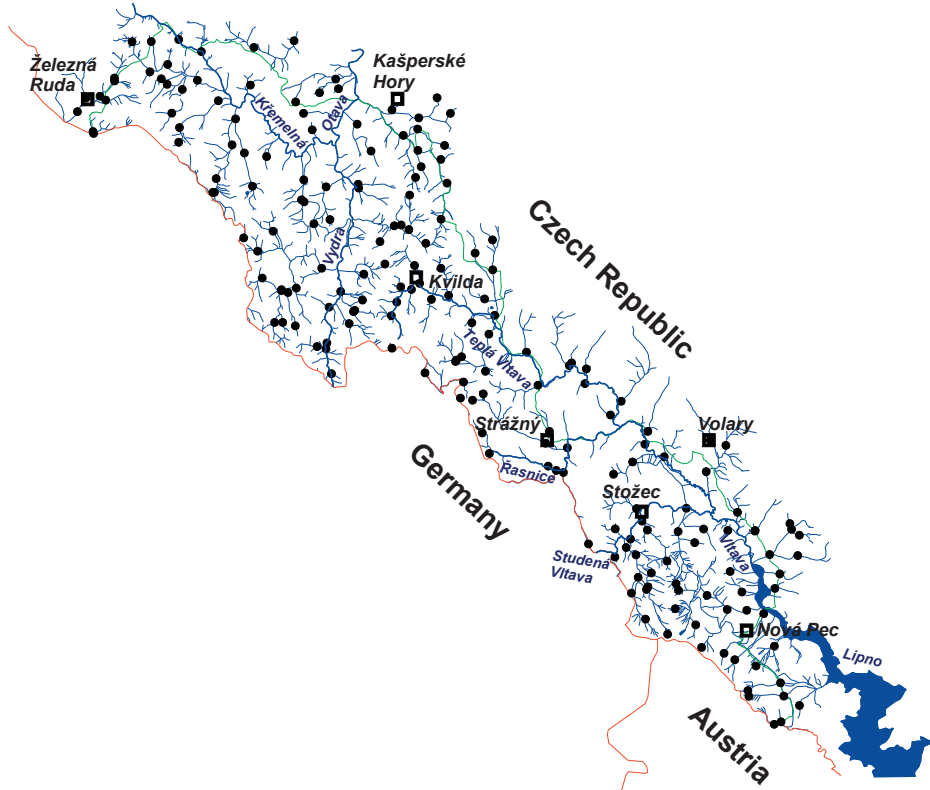


Fig. 1. Location of the sampling sites within the Šumava National Park.

Geological Survey (ISO 9001). The Cl, NO₃, SO₄ concentrations were determined by high pressure liquid chromatography with conductivity detection; F concentrations were determined with an ion-selective electrode (ISE); Na, K, Ca, Mg, SiO₂, Al, Fe, Mn, Sr, Zn, and Li were determined by flame atomic absorption spectrometry (FAAS); and As, Be, Cd, Cu, and Pb were determined by graphite furnace atomic absorption spectrometry (AAS). All the samples for the cation analyses were acidified with purified HNO₃ 1:1 (10 ml.l⁻¹) after filtration in the field. The dissolved organic carbon (DOC) concentrations of 20% of the samples were determined using platinum-catalysed high temperature oxidation by exploiting the non-purgeable organic carbon method (Apollo 9000 Tekmar-Dohrmann). The total dissolved phosphorus (TDP) was determined spectrophotometrically after perchloric acid digestion (KOPÁČEK & HEJZLAR 1993). The analytical quality was controlled by intercomparison between laboratories as per Youden, which was organized by ICP Waters (DAHL & HAGEBØ 2011).

Sampling scheme

All samples were collected during the vegetation growing season (April 15–October 15).

The seasonal and hydrological sample variabilities were minimized through sampling during stable hydrological conditions, i.e., when discharge at the nearest hydrological station of the Czech Hydrometeorological Institute (www.chmi.cz) was between 50% and 200% of the long-term average discharge, following the same methodology as VESELÝ et al. (1998).

Data analysis

Solute concentrations distribution was log-normal, thus non-parametric statistics was applied for statistical data treatment. Logarithm of concentration was used for the map creation. Maps of individual solutes were created using SURFER (Golden Software Inc. Data). Solute concentrations were re-calculated into regular grid (500×500 m) using kriging. We used a kriging method within 5 km radius divided onto 4 search sectors when interpolating grid nodes. Within each search sector maximum of four sampling points was used for interpolation, with total number of 10 nearest sampling points from all sectors. In case there was no sampling point within the search radius, the value was not interpolated for that particular grid node. Then isolines were generated and contour maps produced.

RESULTS AND DISCUSSION

The Bohemian Forest streams show generally lower concentrations of solutes compared to the whole Czech Republic (Table 1). Data taken by MAJER et al. (2012) are generally higher even for altitude >500 m a.s.l. representing mountain regions. Conductivity, the measure of the total amount of dissolved ions, was seven times lower in the Bohemian Forest compared to the median of the Czech Republic. Also pH was significantly lower (ca. 0.6 pH unit). There are several reasons for these differences: (i) the Bohemian Forest is a rainy and cold region, thus all solutes are diluted due to high stream runoff; (ii) low weathered igneous and metamorphic rock (schist, granite, and quartzite) dominate in the region; (iii) agriculture and inhabitation of the region is low in comparison with the rest of the country, thus source of municipal and agricultural contamination are very limited; and (iv) the upper mountain plateau is rich in peatlands, thus humic and fulvic acids contribute to natural acidity of many stream.

Acidity

Acidic areas (pH <5.5) were distributed at high elevated areas with peat bogs in central and

Table 1. Median, 25% and 75% quantiles of solute concentration in the Šumava National Park for the periods 1984–1990, 2003–2004, 2010, and solutes median concentration for the Czech Republic in 2007–2010. Data for the Czech Republic are for the whole territory, as well as just for the altitudes >500 m a.s.l. Quant: quantiles, Cond: conductivity (in $\mu\text{S}\cdot\text{cm}^{-1}$), ABS: absorbance (in cm^{-1}), all solute concentrations are expressed (in μg or mg) per litre.

Quant	pH	Cond	ABS	DOC	P	NO ₃	F	SO ₄	Cl	Li	Na	Mg
				mg	μg	mg	mg	mg	mg	μg	mg	mg
Šumava National Park in 1984–1990:												
25%	6.10	24				0.12	0.02	2.8	0.9	<5	2.0	0.6
50%	6.60	36				1.18	0.03	4.6	1.2	<5	2.6	0.9
75%	6.89	50				3.07	0.05	7.6	2.0	<5	3.0	1.7
Šumava National Park in 2003–2004:												
25%	6.36	28				0.12	0.03	2.8	0.7	<2	1.9	0.5
50%	6.79	41				0.92	0.04	5.4	0.9	2	2.4	0.8
75%	6.98	61				2.61	0.05	9.5	1.4	3	3.2	1.4
Šumava National Park in 2010 (filtered 0.45 μm):												
25%	6.20	23	0.128	4.54	13.5	0.79	0.02	1.6	0.5	<2	1.6	0.5
50%	6.68	32	0.213	6.44	19.9	1.44	0.03	3.4	0.6	<2	2.1	0.8
75%	6.96	48	0.347	8.83	29.8	2.46	0.05	5.5	0.9	<2	2.9	1.3
Czech Republic in 2007–2010:												
50%	7.53	230		5.07	31.3	6.00	0.12	26.3	8.5	4	8.7	6.1
Czech Republic in 2007–2010 (>500 m a.s.l.):												
50%	7.30	137		5.03	25.0	3.40	0.09	17.2	3.1	3	5.6	3.6

western part of the Bohemian Forest and in high elevated south part underlined by granite (Fig. 2). pH generally increased between 1984–1990 and 2003–2004 as a result of pronounced decline of acidic deposition (OULEHLE et al. 2013) in the region. But significant pH decline was later observed for the difference between 2010 and 2003–2004, mostly in the western part of the NP. The reason for that was enhanced leaching of nitrates from soils (see below) after the hurricane Kyrill in 2007 and subsequent bark beetle infestation.

Sulphates

Sulphate was the dominant strong acid anion in the 1980s and its origin was almost exclusively from atmospheric deposition; bedrocks underling of the Bohemian Forest contain just traces of geogenic sulphur. Despite reduction of S deposition by 85% (OULEHLE et al. 2013), sulphate in stream waters decreased by average of ca. 30–40% between the 1980s and 2010 (Table 1, Fig. 3), pointing out that S retention in soil is a factor controlling the lag of surface water responses to declining S deposition at majority of streams. Average concentration 3.4 $\text{mg}\cdot\text{l}^{-1}$ is very low in comparison with the rest of the Czech Republic (cf. Table 1 and CHUMAN et al. 2013). The main reasons are high runoff and subsequent dilution, but also high SO₄ adsorption capacity of soil s in the region (e.g. HRUŠKA & MAJER 1996).

Nitrates

Nitrate concentration showed an interesting temporal pattern (Fig. 4). It declined at the ma-

Al	K	Ca	Mn	Fe	Zn	Sr	SiO ₂	Be	Cu	As	Cd	Pb
µg	mg	mg	µg	mg	µg	mg	mg	µg	µg	µg	µg	µg
147	0.3	1.4	9	0.14	<10	<0.05	8.5	0.02	<1	<1	<0.1	<1
219	0.7	2.5	21	0.28	<10	<0.05	10.5	0.05	<1	<1	<0.1	<1
340	1.1	4.0	42	0.45	<10	<0.05	12.8	0.12	<1	1.3	<0.1	<1
78	0.5	1.7	6	0.13	<10	<0.05	8.4	0.02	<0.2	<0.5	<0.04	<0.4
132	0.7	2.9	14	0.23	<10	<0.05	10.9	0.04	0.4	<0.5	0.04	<0.4
313	1.1	4.7	34	0.50	<10	0.05	14.0	0.13	0.8	1.3	0.06	0.4
76	0.5	1.2	6	0.08	<5	<0.05	9.3	<0.02	<0.2	<0.5	<0.04	<0.4
126	0.7	2.1	12	0.17	<5	<0.05	10.8	0.03	<0.2	<0.5	<0.04	<0.4
182	1.0	3.6	22	0.27	<5	<0.05	12.9	0.08	0.3	1.0	0.05	<0.4
15	2.4	23.7	29	0.07	<10	0.12	12.0	<0.02	0.8	<0.5	<0.04	<0.4
31	1.5	13.7	22	0.11	<10	0.07	13.2	<0.02	0.6	<0.5	<0.04	<0.4

jority of NP between the 1980s and 2003–2004 as a result of declining atmospheric deposition and enhanced microbial activity in soil (OULEHLE et al. 2013). But NO₃ increased in central part of NP as a result of bark beetle infestation and subsequent forest dieback in the 1990s. The enhanced NO₃ leaching started after the hurricane Kyrill in 2007 at many areas, resulting in significant increase of NO₃ concentrations in 2010 on the majority of NP. Forest disturbances have led to changes in soil chemistry (KAŇA et al. 2012) and have altered N soil availability (TAHOVSKÁ et al. 2010) resulting in enhanced nitrogen leaching from soil to surface waters between 2003–2004 and 2010. The NO₃ decline was observed between 2003–2004 and 2010 in the areas, where forest dieback occurred in the 1990s. As a result of this mixed pattern within NP, median concentration did not change significantly (1.18 mg.l⁻¹ in 1984–1990, 0.92 mg.l⁻¹ in 2003–2004, and 1.44 in 2010). Moreover, these concentrations are far below limit for drinking water (50 mg.l⁻¹ for adults and 15 mg.l⁻¹ for children), and there is no risk for drinking water quality.

Chlorides

Coherent decline of chloride was observed (Fig. 5), which was linked to the decline of Cl emissions from chemical and energy industry. The importance of Cl acidification potential could be of high relevance at sites where S and N are effectively immobilised (e.g. peat bogs or other environments with anoxic/reducing conditions) as pointed out by EVANS et al. (2011). Enhanced concentrations in the central and northern part of NP are associated with deicing salt application on the main roads crossing the Šumava NP.

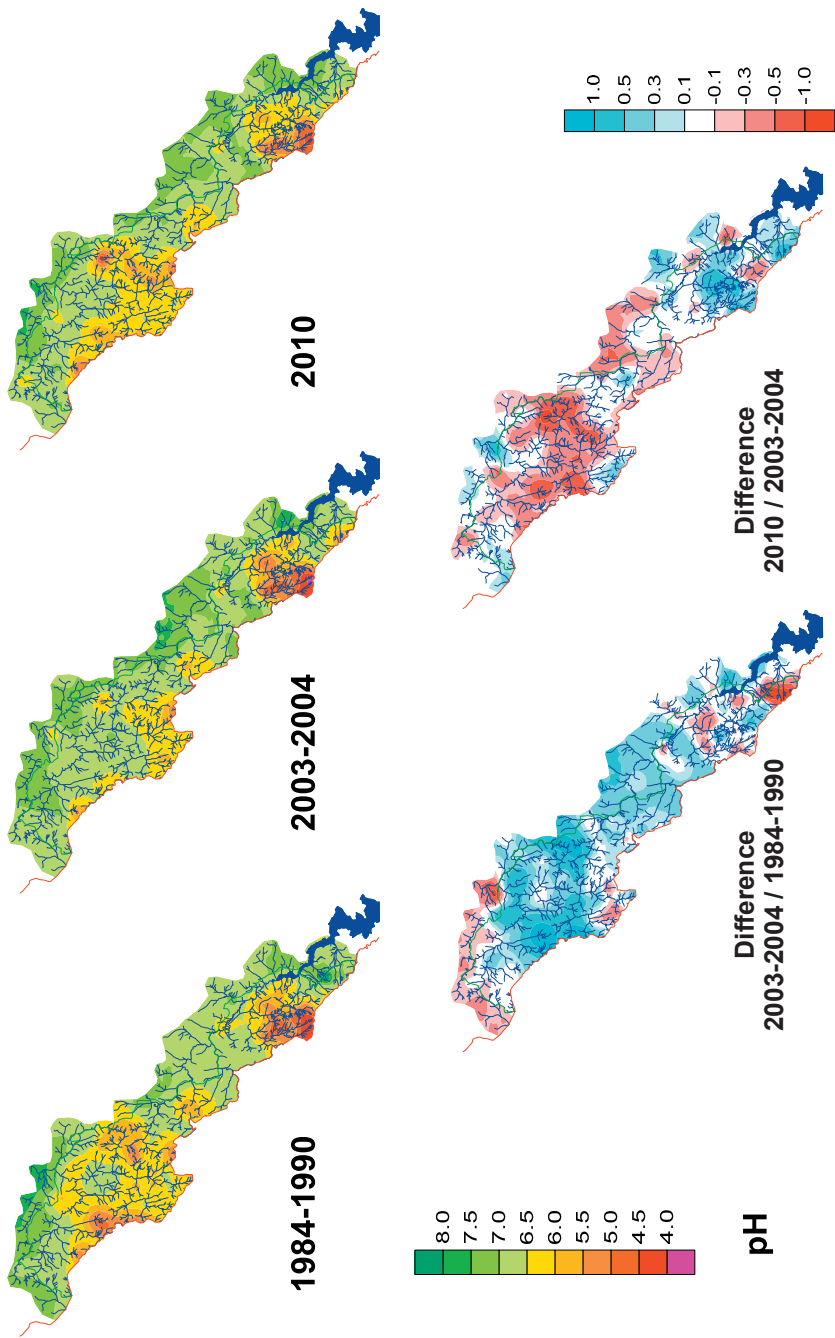


Fig. 2. Isoline maps of pH and differences between solute concentrations for the periods 1984-1990, 2003-2004, and 2010.

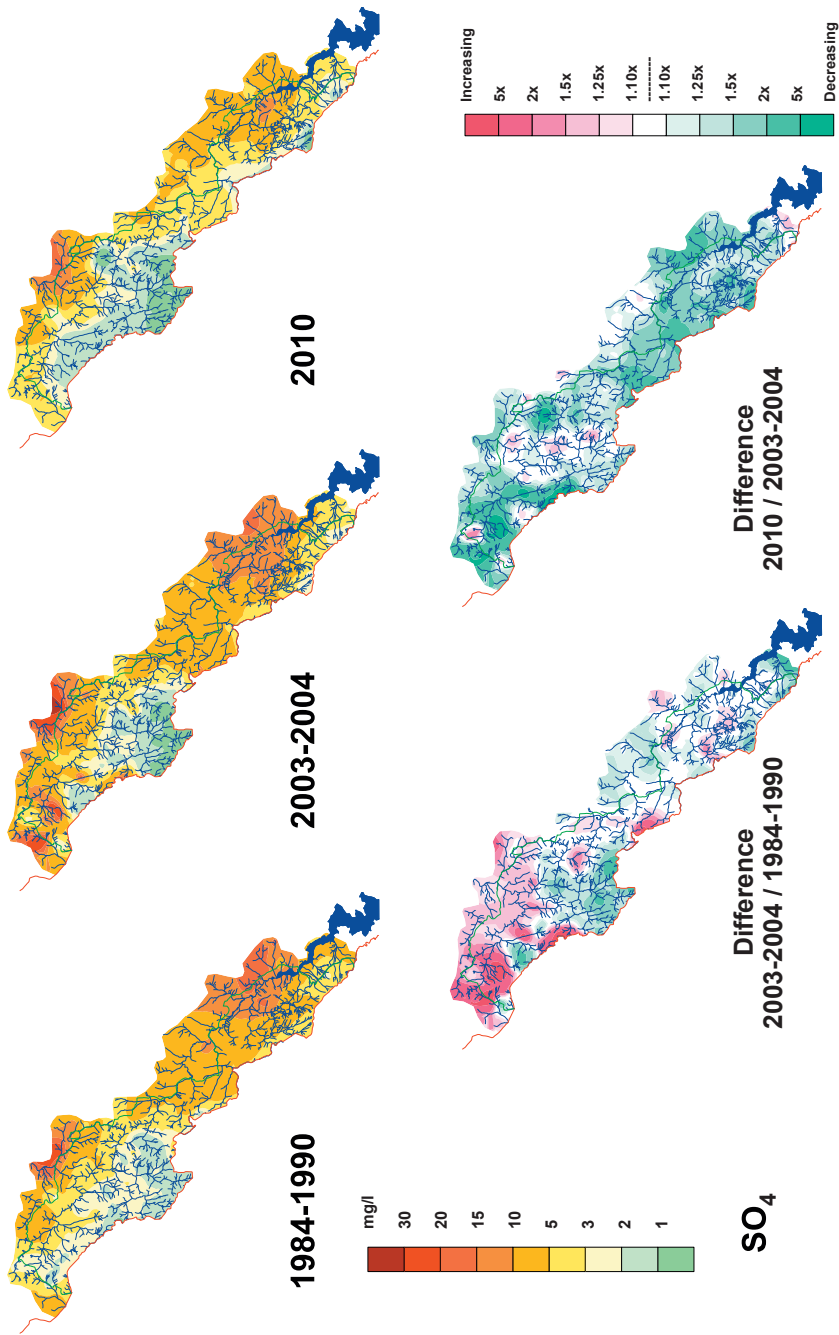


Fig. 3. Isoline maps of SO_4 and differences between solute concentrations for the periods 1984–1990, 2003–2004, and 2010.

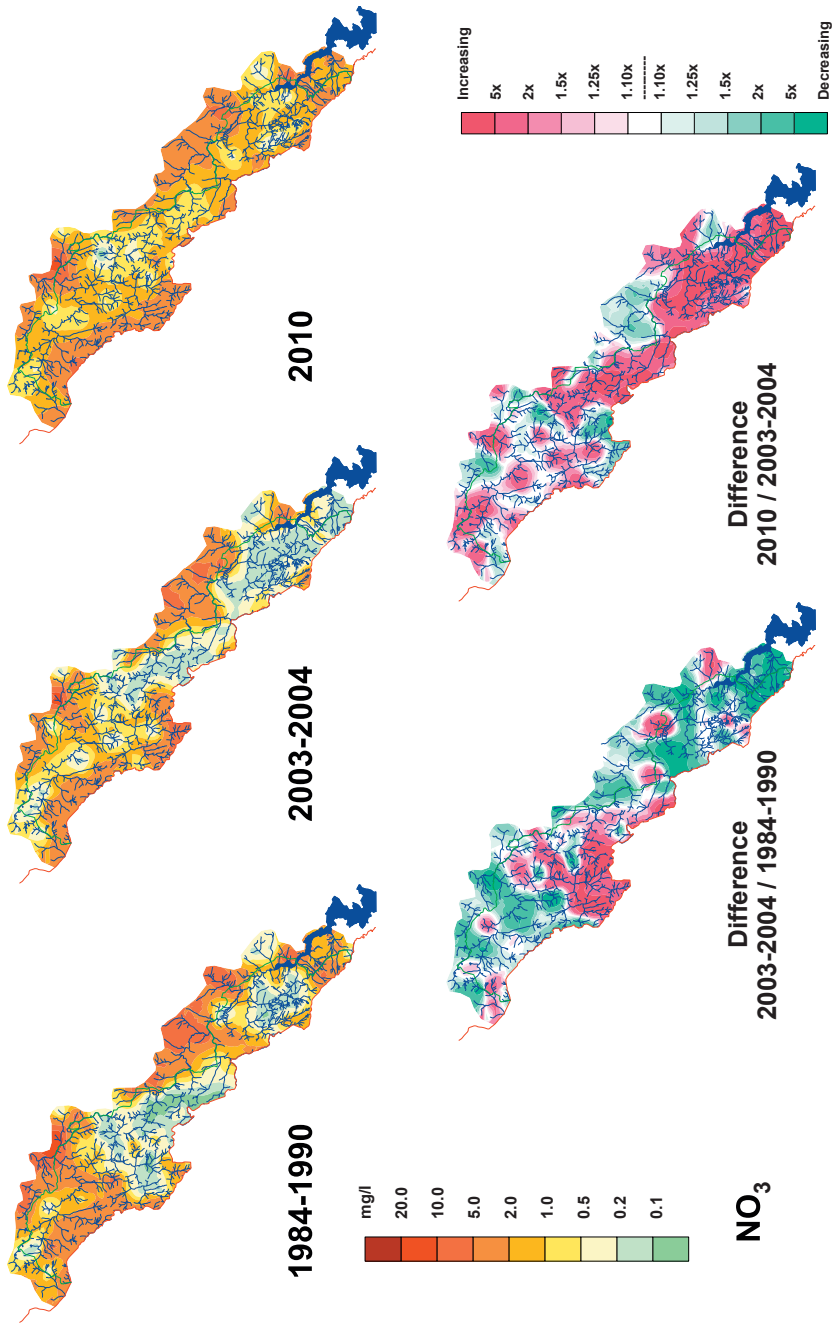


Fig. 4. Isoline maps of NO_3 and differences between solute concentrations for the periods 1984–1990, 2003–2004, and 2010.

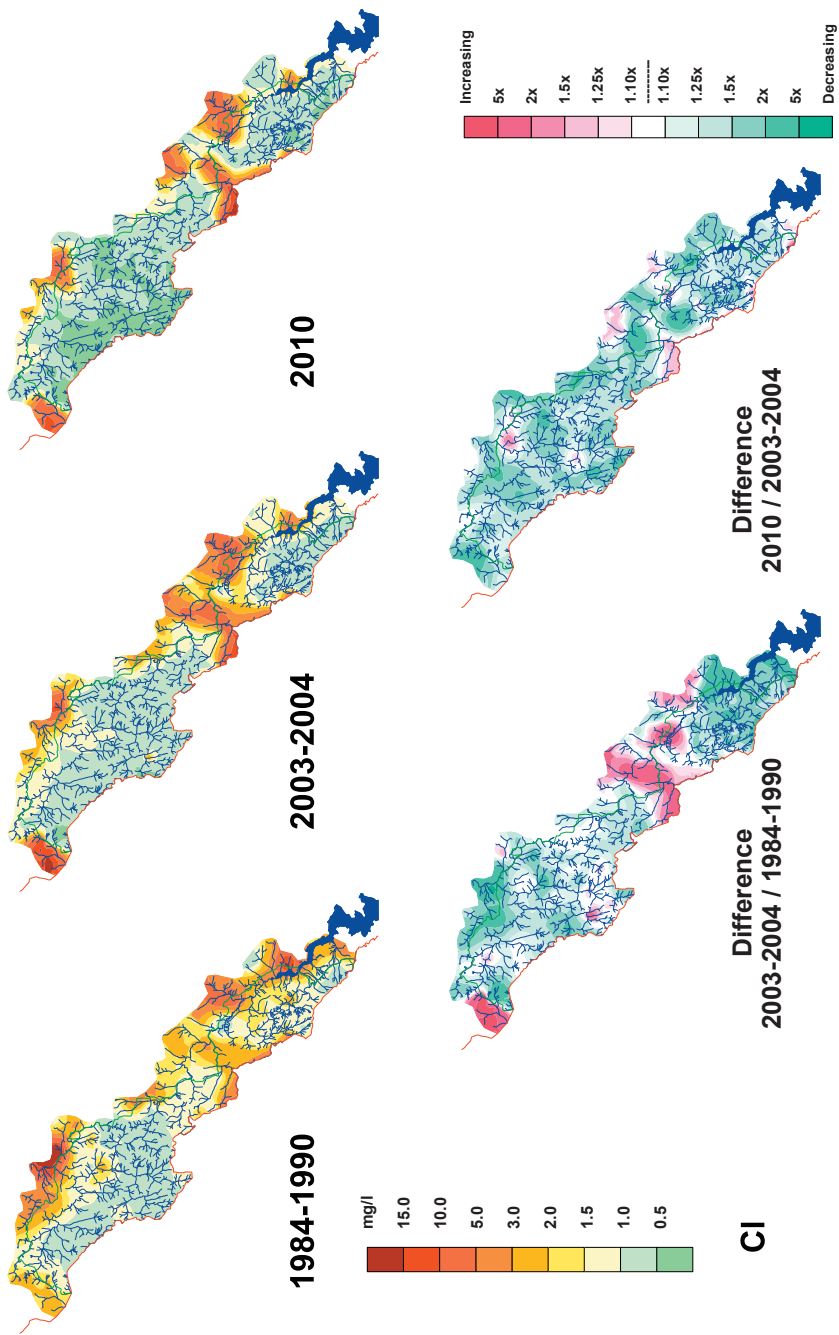


Fig. 5. Isoline maps of Cl and differences between solute concentrations for the periods 1984–1990, 2003–2004, and 2010.

Aluminium

Aluminium is mobilised in acidic waters. The highest concentrations were observed in areas with low pH in the southern part of NP (Fig. 6). The decline between 2003–2004 and 2010 was proportional to observed pH changes (Fig. 2). Al is the toxic element for biota, mostly for fish and invertebrates (GENSEMER & PLAYLE 1999), and its toxicity is also regulated by presence of base cations and DOC. DOC complexes the toxic inorganic Al species to non-toxic complexes with humic and fulvic substances, divalent base cations (Ca^{2+} , Mg^{2+}) reduce physiological effects on gills and osmoregulation (GENSEMER & PLAYLE 1999). Potential toxic Al concentration (ca. $>300 \mu\text{eq.l}^{-1}$ of total Al) can be found in streams in the southern granitic part of the NP (Fig. 6). There is not clear trend in concentrations between the observed years.

Calcium

The concentrations of Ca (as well other major cations Mg, K, and Na) are mainly controlled by the topography (Fig. 7). Lowest concentrations were recorded at the highest altitudes in central and southern part of the NP and those highest in inhabited lower parts. There are no distinct differences between the observed periods; there is a slight increase between 1984–1990 and 2003–2004, and slight decrease between 2010 and 2003–2004. Generally, Ca concentrations are very low in comparison with the whole Czech Republic (Table 1), which is the result of low weathering bedrock, high altitude, and general absence of agriculture and inhabitation (CHUMAN et al. 2013).

Other solutes

Stream water chemistry (Table 1) shows general decline in majority of solutes between the 1980s and 2010, despite concentration decreasing was not very pronounced. Trace elements (Be, Cu, As, Cd, Pb, Sr, Li, and Zn) were always below the detection limits of apparent method of determination for all quantiles (25%, 50%, and 75%), major anions were described above, and major cations generally follows the trends of calcium.

CONCLUSIONS AND FUTURE PERSPECTIVE

There are two main factors driving changes of surface waters chemistry in the Bohemian Forest – the decline of acidic deposition and changes connected with bark beetle infestation and subsequent changes in soil biogeochemistry. The deposition decline was driving force for chemistry mostly between 1984–1990 and 2003–2004, when the quick and pronounced decline of sulphur and partial decline of N deposition occurred (KOPÁČEK & HRUŠKA, 2011). Since 2003–2004, the nitrate leaching as a result of bark beetle infestation became similarly important as decline of acidic deposition. For the future climate change, can be another important factor contributing to stream water chemistry changes. The expected runoff reduction, increased temperature, and soil and vegetation changes can significantly change stream waters hydrology and chemistry.

Within the ongoing Czech–Bavarian INTERREG 2015 project “SILVA GABRETA – Transboundary Monitoring of Mountain Ecosystems” another stream water sampling was organised in June 2015, this time also together with the Bavarian Forest NP using exactly the same methods and sampling scheme as described in this paper. New maps for the both NPs together and five years of restoration from bark beetle infestation will bring interesting information in respect of long-term development of protected mountain ecosystem of the Bohemian and Bavarian Forests.

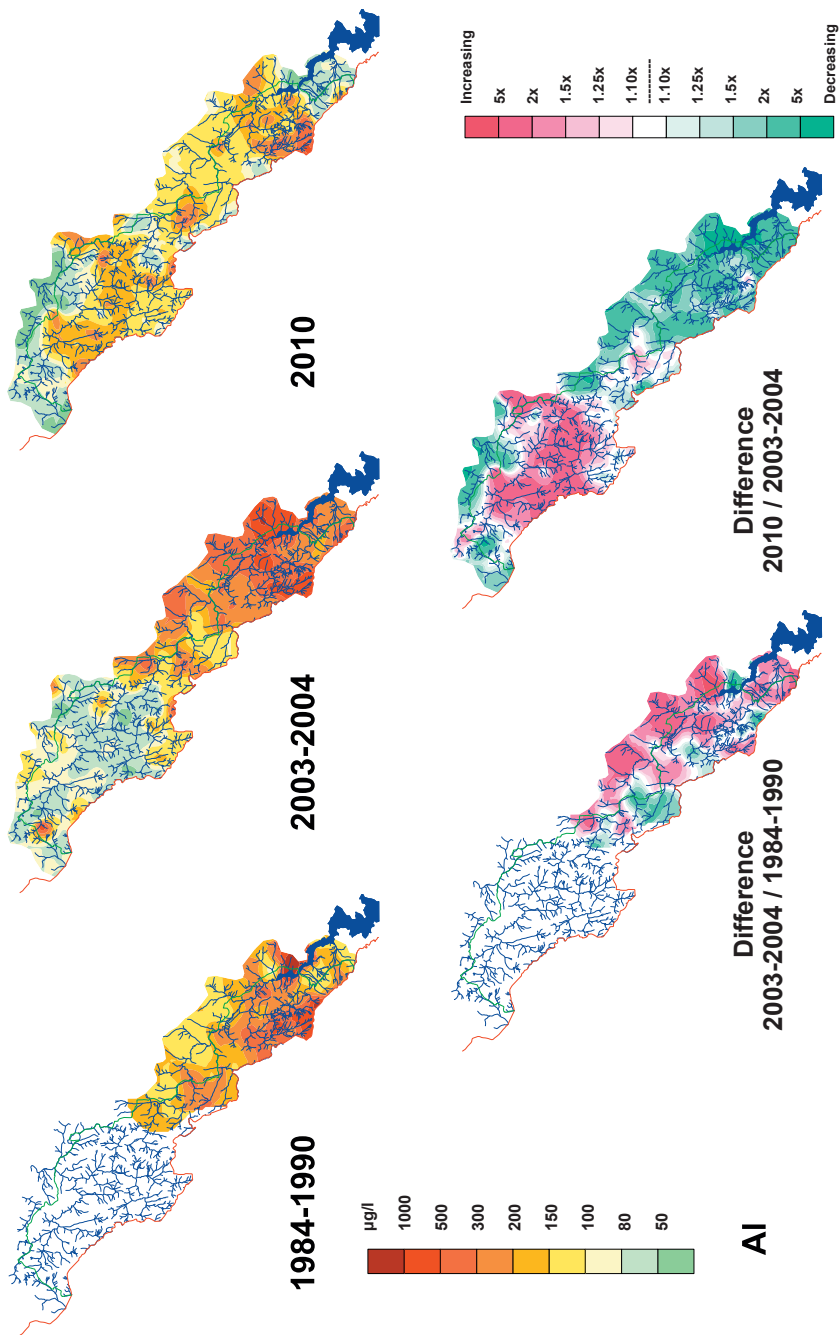


Fig. 6. Isoline maps of AI and differences between solute concentrations for the periods 1984–1990, 2003–2004, and 2010.

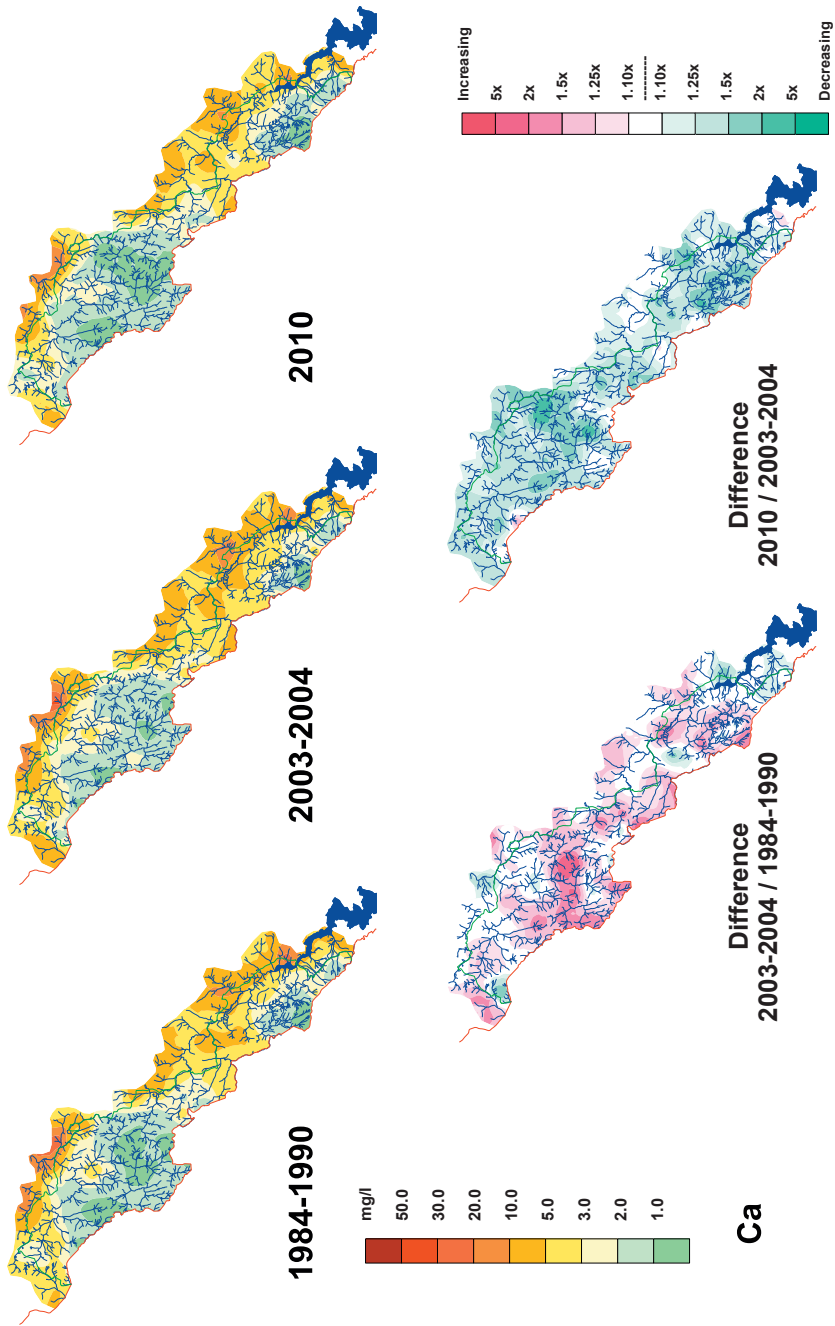


Fig. 7. Isoline maps of Ca and differences between solute concentrations for the periods 1984–1990, 2003–2004, and 2010.

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