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Impact of catchment properties on aquatic chemistry in the rivers of Latvia

Ilga Kokorite, Maris Klavins and Valery Rodinov

ABSTRACT

The relationships between land use characteristics and aquatic chemistry (nutrient concentrations, major inorganic ions and indicators of organic matter concentrations) were analyzed to determine factors controlling the runoff of dissolved substances, spatial variability of water chemical composition and possible impacts of pollution sources in Latvia. Groups of factors were found to determine the variability of nutrient, organic matter and major inorganic ions concentrations. Bedrock geology and weathering of soil minerals affect the concentrations of inorganic ions, but the nature of the relationships between nutrient concentrations and those of land use are good indicators of human impact.

Key words | catchment properties, land use, Latvia, water quality

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INTRODUCTION

The chemical composition of surface waters can be regarded as a sensitive indicator, which reflects the intensity of geochemical, geological, hydrological and biological processes, as well as the anthropogenic impacts within the catchment area. It is evident that the impacts of these factors overlap and, as a consequence, the natural processes interfere with human-induced processes to a large degree.

The chemical composition of surface waters and flows of dissolved substances have been studied worldwide, particularly with respect to human loading, global warming and forest logging. Climatic factors (precipitation and air temperature) affect flows of dissolved organic carbon (Correll *et al.* 2001) and chemical weathering and fluxes of dissolved substances (White & Blum 1995).

Currently, due to increased anthropogenic pressure, the influence of the natural factors on aquatic chemistry can be substantially altered especially with respect to concentrations of nutrients and trace elements (Domburg *et al.* 1998; Thornton & Dise 1998; Jarvie *et al.* 2002). Increased nitrogen and phosphorous concentrations are typically linked to a more intensive agriculture and urbanization

(Thornton & Dise 1998; Rantakari *et al.* 2004). Furthermore, intensive agricultural practices on large areas of arable land facilitate suspended sediment loads along with adsorbed pollutants (Vervier *et al.* 1999; Ekholm *et al.* 2000; Gomez-Gutierrez *et al.* 2006).

It is clear that close links between land-use patterns and water chemical composition exist. In large, heterogeneous catchments, identification of one particular pollution source becomes difficult, however; relationships between different processes within a catchment area (e.g. changes in anthropogenic loading, land use types, hydrological regime and climate) and water quality are not straightforward (Edwards *et al.* 2000; Jarvie *et al.* 2002; Stålnacke *et al.* 2003; Iital *et al.* 2005). These relationships are also specific to the region (Rantakari *et al.* 2004). There is insufficient evidence of relationships between catchment properties and water chemical compositions in large- or medium-sized river basins.

Studies carried out in small agricultural river basins in Latvia (Vagstad *et al.* 2000; Jansons *et al.* 2003) have proven that water quality is affected by agricultural land use type

and farming practice, especially with respect to nutrient concentrations. A specific situation in this regard arises in Eastern Europe and also Latvia, which have experienced a substantial reduction of human loads to the environment due to socio-economical and political crises in the early 1990s. For example, fertilizer and manure use has dropped by a factor of five and the number of livestock has decreased to around two-thirds (Lofgren *et al.* 1999). It has also been assumed that these changes have substantially reduced the loading of nutrients to the surface water (Klavins & Rodinov 2001; Stålnacke *et al.* 2003). Subsequently, the recent socio-economical recovery has increased anthropogenic pressure (Agriculture Census 2008).

In heterogeneous large- and medium-size catchments, evaluation of the current impact of anthropogenic pressures and diffuse pollution sources on water quality allows future water quality changes to be predicted and the best management practices to be selected (Klavins & Rodinov 2001; Jarvie *et al.* 2002; Klavins *et al.* 2002).

The aim of this study is to evaluate relationships between land use characteristics and water chemistry in Latvia in order to determine factors controlling the runoff of dissolved substances, spatial variability of water chemical composition and possible impact of various pollution sources.

METHODS

The study site stretches over the entire territory of Latvia (Figure 1). Latvia is located on the north-western part of the East European Plain and on the coast of the Baltic Sea. The territory of Latvia occupies approximately 64,000 km². The Precambrian basement of crystalline rocks and the succeeding Upper Proterozoic and Paleozoic sediments underlay the area. Rocks of the Middle and Upper Devonian directly underlie the Quaternary surficial sediments and outcrops occur throughout Latvia, particularly in river valleys. Carboniferous, Permian, Triassic and Jurassic sediments are found only in small areas of the SW part of Latvia. Middle and Upper Devonian rocks composed mainly of sandstone, siltstone and clay form sub-Quaternary surface areas in the north, east and southeast parts of Latvia (basins of the Rivers Salaca, Gauja, Irbe). Upper Devonian rocks composed mainly of dolomite and domerite occur in the central and eastern part (e.g. basin of the Rivers Lielupe and Daugava). Bedrock is covered by Quaternary deposits (thickness from a few metres to up to 100–160 m) consisting of moraine material, limnoglacial or fluvioglacial deposits (Dreimanis & Karklins 1997). The moraine material is usually rich in carbonates and calcareous rocks are common, as are sand

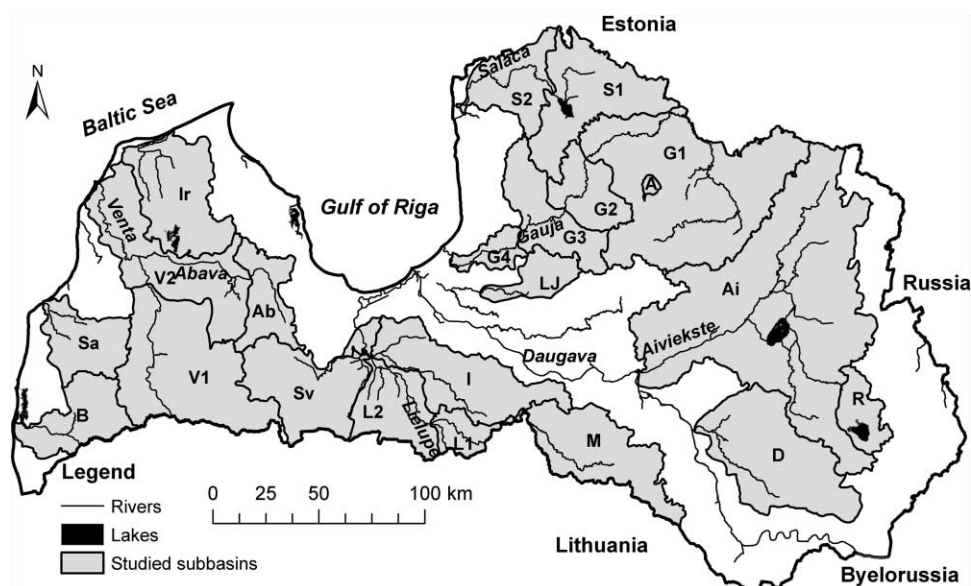


Figure 1 | Map of the studied area with the sub-basin codes selected for this study.

and gravel deposits. Limnoglacial deposits consist of glaciolacustrine clays, clays and silt loam.

Soil types in Latvia show a large diversity, but the key facet in soil formation is the moraine material. The most common soil type is podzolic soils, which are abundant both in agricultural land and forests. Eroded soils are widespread in agricultural territories with hilly topography, particularly in uplands in the east and southeast part of the country. Gleyish soils are common in lowlands in East Latvia, coastal regions and in depressions between hills. Carbonate soils are common in the middle part of Latvia (basin of the River Lielupe), and are intensively used for agricultural production. About 10% of the territory of Latvia is occupied by hydromorphic soils. These soils are common in coastal regions, east Latvia Lowland and in the northern part of Latvia (basin of the River Salaca) (Skujans & Mezals 1996).

The climatic conditions in Latvia can be characterized as humid and mean annual precipitation is about 700 mm. Mean temperature in January varies from -2.6°C to -6.6°C and in July from $+16.8^{\circ}\text{C}$ to $+17.6^{\circ}\text{C}$ (Klavins *et al.* 2002).

Data on water chemical composition (monthly concentrations of N/NH_4^+ , N/NO_2^- , N/NO_3^- , total N, $\text{P}/\text{PO}_4^{3-}$, total P, HCO_3^- , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , Na^+ , K^+ , total mineralization, pH and chemical oxygen demand or COD) and monthly mean river discharges used in this study were obtained from the monitoring data carried out by the Latvian Environmental, Geological and Meteorological Agency for the period from 1991 to 2001. In Rivers Salaca (S1, S2), Gauja (G2, G4), Lielupe (L1, L2), Venta (V1) and Aiviekste (Ai), 12 samples per year were taken for analysis of COD and N and P compounds and 6 samples for major inorganic ions. In Rivers Saka (Sa), Barta (B), Liela Jugla (LJ) and Irbe (Ir) as well as in stations G1 and G3 (the River Gauja), 6–9 samples per year were taken for all compounds. In other stations the sampling frequency decreased from 10–12 samples per year in the first years of the study period to 5–6 samples annually. For each site, water samples were taken from the midstream at depth 0.5 m using a Ruttner bathometer. During the study period, sampling and analytical methods adhered to the standard methods (Standard Methods 1973; Tsirkunov *et al.* 1992). National and international intercalibration carried out during 1992–1994 demonstrated general acceptability of

the methods used (Stålnacke 1996). Since 1997, national analytical methods based on ISO standards have been introduced. The brief description of analytical methods is given in Table 1.

The loads of substances R were calculated as:

$$R = Wc,$$

where W is the volume of the runoff in a specific period (day, month, year) in m^3 (km^3) and c is the mean concentration of a substance in this period in mg l^{-1} (g m^{-3}).

The monthly water discharge was calculated using the formula

$$W = QT \times 8.64 \times 10^4$$

where Q is discharge ($\text{m}^3 \text{s}^{-1}$) and T is number of days per month.

Catchment boundaries were obtained from the digital database GIS Latvija 9.2, scale 1:500,000 (Envirotech 2004). Using the catchment boundaries, areas of different land use types within the river sub-basins were obtained from the GIS database Corine Land Cover Latvia (2003),

Table 1 | Methods of water chemical analysis

Parameter	Method of analysis
$\text{N}-\text{NO}_3^-$	Nitrate reduction to nitrite with metallic Cd and spectrometric determination of $\text{N}-\text{NO}_2^-$
$\text{N}-\text{NO}_2^-$	Spectrometric analysis with Griess reagent
$\text{N}-\text{NH}_4^+$	Spectrometric analysis with Nessler reagent
N_{tot}	Persulphate oxidation and spectrometric analysis
$\text{P}-\text{PO}_4^{3-}$	Spectrometric ascorbic acid method
P_{tot}	Oxidation with potassium peroxodisulfate and determination of P with spectrometric ascorbic acid method
COD	Oxidation with $\text{K}_2\text{Cr}_2\text{O}_7$ and subsequent back titration
Ca^{2+}	Titrimetric analysis with complexon III
Mg^{2+}	Calculated as difference between value of total hardness and Ca^{2+} concentration
Na^+ , K^+	Flame photometry analysis
HCO_3^-	Potentiometric titration
SO_4^{2-}	Turbidimetric method
Cl^-	Mercurimetric titration

scale 1:100,000. In this study, six land-use categories were distinguished: (1) agricultural land; (2) forests; (3) semi-natural territories (e.g. meadows, pastures); (4) bogs; (5) urban and industrial areas; and (6) areas covered by water. ArcMap 9.2 software was used to obtain land use data for each river sub-basin. The database contained information about mean concentrations and loadings of dissolved substances, yearly volume of water runoffs and land-use patterns for the study period in 22 river sub-basins (Figure 1). A general description of the studied river basins and sub-basins is given in Table 2.

The significance of relationships between land-use types and aquatic chemistry was determined using Pearson's r correlation coefficients and factor analysis. Factor analysis (principal component analysis or PCA) was applied to data on the proportions of different land use types in river sub-basins and mean concentrations for the period

1991–2001. Correlation and factor analysis was conducted using software SPSS 16.0 for Windows.

RESULTS AND DISCUSSION

Land-use characteristics are probably among the major factors influencing concentrations of dissolved substances in watersheds. However, links between aquatic chemistry and the land-use characteristics have usually been studied in small/medium-sized catchments by only evaluating those water parameters which have the greatest impact on aquatic biology: nutrients and organic matter.

Spatial variability of concentrations of dissolved substances in surface waters of Latvia can be considered to be comparatively high (Table 3). The highest concentrations of dissolved substances (especially nutrients and major

Table 2 | Main properties of the studied river basins

River	Subbasin code as in Figure 1	Catchment area (km ²)	Volume of runoff (km ³ y ⁻¹)	Percentage (%) of land use types within the sub-basins				
				Agr. land	Forests	Urban	Bogs	Open waters
Salaca	S1	2,031	0.62	41.38	52.61	0.31	2.92	2.78
Salaca	S2	3,237	0.97	37.85	56.17	0.33	3.77	1.88
Gauja	G1	6,150	1.47	37.68	60.25	0.42	1.08	0.57
Gauja	G2	7,190	1.72	38.28	59.40	0.68	0.99	0.65
Gauja	G3	8,510	2.21	38.28	59.40	0.68	0.99	0.65
Gauja	G4	8,840	2.29	38.01	58.99	0.81	1.43	0.76
Abuls	A	59	0.02	56.01	41.56	1.31	0.70	0.42
Dubna	D	2,780	0.58	57.05	33.57	0.75	3.97	4.66
Aiviekste	Ai	9,052	1.68	47.97	45.78	0.67	2.94	2.64
Rēzekne	R	708	0.14	59.62	33.33	1.10	0.89	5.06
Lielā Jugla	LJ	667	0.18	33.76	58.99	3.60	1.89	1.76
Lielupe	L1	11,100	1.78	44.74	52.77	0.40	1.53	0.56
Lielupe	L2	16,540	2.78	55.34	42.16	0.84	1.17	0.50
Mēmele	M	3,680	0.91	42.63	54.89	0.25	1.63	0.60
Iecava	I	2,145	0.50	36.36	60.36	0.67	2.28	0.33
Svēte	Sv	2,320	0.40	67.50	30.03	0.96	0.76	0.75
Venta	V1	8,320	2.09	45.39	52.11	0.86	0.98	0.66
Venta	V2	11,267	2.76	44.74	52.53	0.84	1.23	0.66
Abava	Ab	875	0.23	49.82	48.76	0.20	0.89	0.33
Saka	Sa	1,074	0.34	53.39	44.43	0.56	0.58	1.04
Irbe	Ir	1,809	0.51	20.83	72.75	0.76	3.03	2.63
Bārta	B	1,750	0.64	53.13	44.81	0.76	0.95	0.35

Table 3 | Concentrations of dissolved substances in the studied rivers (average concentration for period 1991–2001 ± standard deviation)

River	N _{tot} (mg/l)	P _{tot} (mg/l)	N/NH ₄ ⁺ (mg/l)	N/NO ₃ ⁻ (mg/l)	P-PO ₄ ³⁻ (mg/l)	COD (mg/l)	Mg ²⁺ (mg/l)	Cl ⁻ (mg/l)	SO ₄ ²⁻ (mg/l)	Na ⁺ (mg/l)	HCO ₃ ⁻ (mg/l)	Ca ²⁺ (mg/l)
Salaca	2.05 ± 0.97	0.045 ± 0.019	0.08 ± 0.05	1.12 ± 0.82	0.027 ± 0.035	33 ± 6	13.9 ± 2.9	7.9 ± 1.8	30.6 ± 5.2	3.4 ± 0.9	171.7 ± 42.9	51.7 ± 11.1
Salaca	1.72 ± 0.70	0.036 ± 0.009	0.06 ± 0.04	0.82 ± 0.68	0.016 ± 0.012	34 ± 5	12.3 ± 2.6	8.9 ± 3.3	31.2 ± 3.6	4.7 ± 1.3	181.6 ± 36.5	52.8 ± 8.6
Gauja	1.87 ± 0.82	0.071 ± 0.045	0.15 ± 0.06	0.90 ± 0.74	0.058 ± 0.039	33 ± 5	13.7 ± 3.1	8.7 ± 2.2	33.1 ± 4.5	4.9 ± 1.5	201.4 ± 46.5	58.1 ± 11.0
Gauja	1.92 ± 0.95	0.049 ± 0.066	0.10 ± 0.10	1.01 ± 0.70	0.037 ± 0.033	32 ± 5	13.9 ± 3.1	9.1 ± 2.5	33.9 ± 4.5	5.0 ± 1.7	201.1 ± 44.9	58.8 ± 10.8
Gauja	1.90 ± 0.80	0.052 ± 0.020	0.10 ± 0.05	0.99 ± 0.71	0.040 ± 0.035	32 ± 5	13.8 ± 3.1	8.7 ± 1.8	33.7 ± 4.5	4.7 ± 1.3	200.5 ± 47.1	64.0 ± 11.3
Gauja	1.78 ± 1.01	0.038 ± 0.032	0.08 ± 0.05	0.88 ± 0.68	0.026 ± 0.024	30 ± 5	14.5 ± 3.0	9.5 ± 3.4	33.1 ± 4.7	5.4 ± 2.2	207.7 ± 43.4	59.4 ± 10.0
Abuls	3.39 ± 1.00	0.265 ± 0.313	0.25 ± 0.25	2.37 ± 1.08	0.242 ± 0.277	32 ± 5	16.4 ± 3.5	16.8 ± 8.9	42.8 ± 7.8	7.8 ± 6.0	246.4 ± 45.1	75.7 ± 11.3
Dubna	2.28 ± 0.86	0.066 ± 0.025	0.13 ± 0.08	1.05 ± 0.65	0.046 ± 0.024	40 ± 6	16.7 ± 2.7	11.0 ± 3.1	34.8 ± 4.3	6.4 ± 1.7	210.7 ± 34.5	58.5 ± 6.3
Aiviekste	2.26 ± 0.59	0.059 ± 0.016	0.11 ± 0.07	1.16 ± 0.61	0.038 ± 0.026	41 ± 6	14.6 ± 3.5	9.8 ± 4.0	37.7 ± 15.0	5.7 ± 1.7	201.9 ± 43.2	58.9 ± 14.5
Rēzekne	2.81 ± 0.92	0.142 ± 0.144	0.19 ± 0.13	1.72 ± 0.97	0.138 ± 0.127	32 ± 6	12.6 ± 5.1	8.4 ± 5.1	28.6 ± 5.0	6.2 ± 3.5	193.2 ± 41.7	54.8 ± 10.3
Lielā Jugla	2.15 ± 0.96	0.046 ± 0.021	0.08 ± 0.05	1.22 ± 0.84	0.029 ± 0.015	34 ± 6	15.5 ± 3.6	7.2 ± 2.8	49.1 ± 19.1	3.7 ± 1.2	211.3 ± 47.3	65.6 ± 15.4
Lielupe	3.87 ± 1.87	0.119 ± 0.066	0.15 ± 0.17	2.47 ± 1.69	0.098 ± 0.061	36 ± 5	29.9 ± 4.4	29.9 ± 9.2	201.4 ± 45.8	20.6 ± 6.5	330.1 ± 50.3	148.4 ± 23.1
Lielupe	3.49 ± 1.94	0.126 ± 0.048	0.19 ± 0.12	2.04 ± 1.65	0.088 ± 0.051	37 ± 5	23.8 ± 4.1	19.5 ± 9.1	104.0 ± 38.3	10.2 ± 6.0	297.8 ± 47.0	103.5 ± 18.4
Mēmele	2.71 ± 1.13	0.068 ± 0.034	0.10 ± 0.06	1.35 ± 0.97	0.040 ± 0.029	38 ± 5	21.7 ± 4.6	15.6 ± 5.5	70.3 ± 23.3	7.5 ± 3.0	273.7 ± 46.4	85.7 ± 15.9
Iecava	2.83 ± 1.63	0.073 ± 0.037	0.29 ± 0.24	1.89 ± 0.95	0.049 ± 0.025	47 ± 6	19.0 ± 4.1	24.3 ± 9.1	78.1 ± 19.9	12.3 ± 6.9	220.0 ± 44.9	77.1 ± 13.1
Svēte	3.67 ± 1.96	0.056 ± 0.024	0.10 ± 0.07	2.32 ± 1.78	0.039 ± 0.027	33 ± 4	26.3 ± 4.7	20.6 ± 6.5	80.1 ± 18.2	8.6 ± 2.4	298.0 ± 39.4	93.1 ± 15.1
Venta	2.50 ± 1.37	0.038 ± 0.026	0.09 ± 0.08	1.35 ± 1.12	0.031 ± 0.024	27 ± 5	18.7 ± 3.0	16.0 ± 3.8	44.0 ± 6.5	7.8 ± 2.0	255.8 ± 34.5	75.6 ± 9.2
Venta	1.74 ± 0.86	0.037 ± 0.024	0.08 ± 0.07	0.71 ± 0.69	0.023 ± 0.023	-	-	-	-	-	-	-
Abava	2.63 ± 0.60	0.051 ± 0.021	0.10 ± 0.05	1.83 ± 0.97	0.033 ± 0.019	28 ± 5	23.4 ± 4.2	12.0 ± 3.9	47.4 ± 9.2	5.3 ± 1.2	295.9 ± 46.9	83.1 ± 12.4
Saka	1.94 ± 0.90	0.051 ± 0.024	0.11 ± 0.076	0.97 ± 0.71	0.033 ± 0.021	24 ± 6	13.0 ± 3.5	9.4 ± 20.2	33.0 ± 5.8	5.3 ± 9.9	210.3 ± 41.7	62.5 ± 9.3
Irbe	1.44 ± 0.73	0.036 ± 0.018	0.08 ± 0.05	0.51 ± 0.38	0.020 ± 0.012	37 ± 7	8.8 ± 2.1	8.2 ± 1.6	26.7 ± 3.6	4.2 ± 0.86	135.4 ± 27.2	41.9 ± 6.4
Bārta	2.17 ± 0.98	0.045 ± 0.022	0.10 ± 0.08	1.14 ± 0.84	0.028 ± 0.018	23 ± 5	12.9 ± 3.3	9.4 ± 2.8	31.9 ± 7.3	5.5 ± 1.3	229.7 ± 40.5	68.1 ± 10.1

inorganic ions) have been recorded for rivers in the Lielupe basin (the Rivers Lielupe, Svēte, Iecava), which is located in the middle part of Latvia.

The average concentration of total nitrogen in the Lielupe basin reaches 3.87 mg l^{-1} , N/NO_3^- 2.47 , N/NH_4^+ 0.29 mg l^{-1} , total phosphorus 0.142 mg l^{-1} and $\text{P}/\text{PO}_4^{3-}$ 0.138 mg l^{-1} . This territory is characterized by intensive agricultural land use. In 2001, only 24% of total agricultural land in Latvia was fertilized. In districts within the Lielupe basin, however, up to 60% was fertilized (Agriculture Census 2008).

The average concentration of Mg^{2+} varies from 8.8 to 29.9 mg l^{-1} , Ca^{2+} from 41.9 to 148.4 mg l^{-1} , Na^+ from 3.4 to 20.6 mg l^{-1} , HCO_3^- from 135.4 to 330.1 mg l^{-1} , SO_4^{2-} from 26.7 to 201.4 mg l^{-1} and Cl^- from 7.2 to 29.9 mg l^{-1} . High concentrations of major inorganic ions can be explained by the bedrock geology, carbonate-rich soils and their intensive weathering (Klavins *et al.* 2002), but sea-borne aerosols, feeding with groundwater rich in sulphates and chlorides as well as industrial pollution could also be of importance. High total nitrogen (3.39 mg l^{-1}), total phosphorus (0.265 mg l^{-1}), N/NO_3^- (2.37 mg l^{-1}) and $\text{P}/\text{PO}_4^{3-}$ (0.242 mg l^{-1}) concentrations in the River Abuls are explained by the wastewater inflow from the town Smiltene and its milk production factory.

The highest concentrations of organic matter characterized by chemical oxygen demand (COD) are found in the Rivers Iecava (47 mg l^{-1}), Aiviekste (41 mg l^{-1}) and Dubna (40 mg l^{-1}). There are comparatively larger proportions of bog areas within these river basins (Table 2). High concentrations of organic matter are also common for the River Lielupe basin. An exception is the River Salaca, which also has a higher percentage of bogs but COD values of $33\text{--}34 \text{ mg l}^{-1}$. This could be due to differences in soil texture, soil types and other properties, which in turn affect adsorption capacity of dissolved organic matter (Maurice *et al.* 2002; Stutter *et al.* 2006). In this study, data on chemical oxygen demand is used for the approximate estimation of quantity of organic matter. However, for more reliable results, data on concentrations of total carbon and TOC or DOC are necessary.

Concentrations of dissolved substances, especially nutrients, have relatively large variability (Table 3). This is common for all studied rivers, as nutrient concentrations

exhibit strong seasonal changes. The highest concentrations of nitrogen and phosphorus compounds occur during the spring, largely because the surface runoff after snowmelt from the catchments dominates. The lowest concentrations of nutrients are observed in the summer, as the supply from catchments in the low-water phase is limited and nutrients are consumed in biological processes (Klavins *et al.* 2002). The highest concentrations of major inorganic ions are recorded in the summer and winter low-water phase, when rivers are fed mainly by groundwater. The lowest concentration occurs in spring, when river waters are diluted by snowmelt with low mineralization (Figure 2).

Knowledge of the relationships between different catchment properties and aquatic chemistry is important in predicting concentrations of dissolved substances (Table 4). The highest positive correlation was found between percentage of agricultural area and concentration of nitrogen compounds (N_{tot} $r = 0.61$, N/NO_3^- $r = 0.57$, $p = 0.01$) as well as bicarbonate ions ($r = 0.52$, $p = 0.01$). The significant negative correlation observed between forested area and

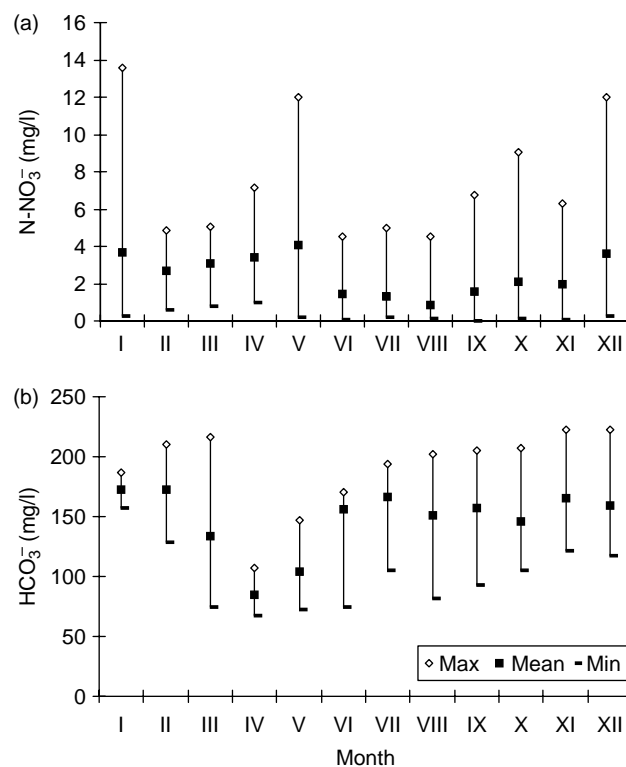


Figure 2 | Seasonal changes of (a) concentrations of N/NO_3^- in the River Lielupe and (b) HCO_3^- in the River Daugava (1977–1998).

Table 4 | Pearson's *r* correlation coefficients between land use types, concentrations of dissolved substances and percentage of land use types within the river basins

Parameters	Land use types within river basins				
	Agricultural	Forests	Urban	Bogs	Open water
Forests	−0.977**				
Urban land	−0.072	−0.001			
Bogs	−0.354	0.188	−0.077		
Open water	0.116	−0.310	0.117	0.563**	
N _{tot}	0.612**	−0.557**	0.019	−0.323	−0.187
P _{tot}	0.414	−0.395	0.111	−0.282	0.008
N/NH ₄ ⁺	0.259	−0.233	0.008	−0.182	−0.064
N/NO ₂ [−]	0.399	−0.376	0.075	−0.211	−0.051
N/NO ₃ [−]	0.572**	−0.509*	0.049	−0.367	−0.229
P/PO ₄ ^{3−}	0.407	−0.391	0.126	−0.313	0.047
COD	−0.227	0.137	−0.005	0.591**	0.252
Mg ²⁺	0.397	−0.309	−0.105	−0.280	−0.409
Ca ²⁺	0.319	−0.221	−0.090	−0.331	−0.456*
Na ⁺	0.197	−0.137	−0.171	−0.127	−0.274
K ⁺	0.336	−0.255	−0.184	−0.200	−0.382
HCO ₃ [−]	0.522*	−0.403	−0.085	−0.475*	−0.513*
SO ₄ ^{2−}	0.141	−0.083	−0.079	−0.122	−0.312
Cl [−]	0.224	−0.141	−0.141	−0.201	−0.415

Correlation is significant at the *0.05 level (2-tailed) and ** 0.01 level (2-tailed).

nitrogen compound concentration was due to co-variability of forest and agricultural area (Table 4). Nitrogen concentration has also previously been reported to be elevated due to larger proportions of agricultural lands (Vagstad *et al.* 2000; Rantakari *et al.* 2004).

The correlation between NO₃[−] and agricultural land coverage found by Van Herpe & Troch (2000) was stronger than reported in this study, perhaps due to less intensive agricultural practice in Latvia and the large, heterogeneous river basins examined in our study. In general, the correlation between N_{tot} concentration and land use pattern is closer than that between P_{tot} and land use pattern, which can be explained by differences in sources, transport and retention processes of these nutrients.

Ekholm *et al.* (2000) suggest that concentrations of total phosphorus reflect, to a great extent, erosion processes and are more linked to percentage of arable fields and relief. The established percentages of bog areas within the river basin provide an important factor that makes it possible to determine the concentration of chemical oxygen demand

(Pearson's $r = 0.59$, $p = 0.01$). With respect to the other parameters, however, no statistically significant negative correlations exist.

Research conducted in Finland showed a positive correlation of TOC with peatland coverage (consistent with this study) and a statistically significant negative correlation between area of upstream lakes and TOC, indicating retention of organic matter (mainly particulate matter) within lake bodies (Rantakari *et al.* 2004; Mattsson *et al.* 2005). In our study, the positive correlation ($r = 0.252$) between percentage of open water and COD was associated with the correlation between percentage of bogs and open water, as the partial correlation controlled for bogs was $r_p = -0.121$ ($p = 0.602$). A statistically significant negative correlation at level $p = 0.05$ was found between percentage area covered by open water and concentration of Ca²⁺ ($r = -0.46$) and HCO₃[−] ($r = -0.51$).

Multivariate methods such as principal component analysis and factor analysis can be applied in order to characterize processes both within the water body and

drainage area (e.g. Reisenhofer *et al.* 1995; Einax *et al.* 1998; Petersen *et al.* 2001). In this study, multivariate data analysis methods were applied to the average (1991–2001) concentrations of 14 different water quality ingredients obtained from 22 monitoring stations.

The first seven principal components describe 99.1% of the original dataset. Three principal components with eigenvalues greater than 1 explain 90.5% of the data variability. The first principal component explains 61.13% of the total variance, and the second and third account for 20.66% and 8.76% of the variance, respectively.

Factor loadings were calculated using *Varimax* rotation method for the first three components, which exceeded the eigenvalues of 1. Calculated factor loadings showed that the first factor was related to the changes in concentrations of major inorganic ions and, to a lesser extent, to concentrations of total N and N-NO₃⁻ (Table 5). The first factor can therefore mainly be explained by natural factors such as geology or weathering processes of soil in the catchment. The second factor, which had a stronger correlation with total P, PO₄³⁻, N-NH₄⁺ and N-NO₂⁻ and a weaker correlation with the total N and N-NO₃⁻ is likely forced by the pollution from point sources. Factors determining concentrations of total N and N-NO₃⁻ differed from those determining concentrations of N-NH₄⁺, N-NO₂⁻ and phosphorous compounds. The third factor was related to the COD concentrations and also (to a lesser degree) to the N-NH₄⁺ concentration in river water. This factor can probably be explained by the impact of wetlands on the water composition.

Factor scores can be used to show the significance of each factor among monitoring sites (Figure 3). Factor scores for the basins ranged from +4 to -4, with high positive values indicating a high influence of the factor on the sampling site. The Lielupe River at the monitoring site downstream from the city of Bauska had the highest score for the first factor (3.06). High scores were also found for all studied tributaries of the Lielupe River (Misa, Iecava and Svēte). The high concentrations of dominant inorganic ions found in the Lielupe River are also explained by the bedrock geology and weathering (Klavins *et al.* 2002), as well as intensive agricultural activities and larger proportion of arable fields (Agriculture Census 2008), which facilitates soil erosion. The lowest score was for the Irbe River where more

Table 5 | Matrix of rotated factor loadings of ingredients of water chemical composition of Latvian rivers (data from 22 monitoring stations, 1991–2001) on 3 PCA components (rotation method Varimax with Kaiser normalization converged in 4 iterations; factor loadings in bold are greater than 0.5)

Ingredients of water composition	Components		
	1	2	3
N _{tot}	0.761	0.564	0.031
P _{tot}	0.143	0.970	-0.017
N-NH ₄ ⁺	0.198	0.793	0.418
N-NO ₂ ⁻	0.207	0.950	0.140
N-NO ₃ ⁻	0.697	0.631	0.002
PO ₄ ³⁻	0.089	0.973	-0.056
COD	0.118	0.101	0.944
Mg ²⁺	0.952	0.027	-0.023
Cl ⁻	0.828	0.140	0.209
SO ₄ ²⁻	0.900	0.122	0.209
Na ⁺	0.847	0.253	0.299
K ⁺	0.924	0.231	0.238
HCO ₃ ⁻	0.921	0.152	-0.245
Ca ²⁺	0.964	0.172	-0.024

than 70% of catchment territory is occupied by forests and human impact can therefore be considered as relatively minimal. The highest scores on the second factor were found in the basins of the Abuls and Rēzekne rivers, which can be explained by pollution from point sources. The lowest influence on this factor was found in the Venta, Irbe and Salaca rivers. The highest values on the third factor were found in rivers with a comparatively larger proportion of wetlands and bog areas (the Iecava, Dubna, Aiviekste and Irbe rivers). Lowest values were found for the Abava, Saka, Bārta rivers, as well as for the Venta at the monitoring site downstream from the city of Kuldīga (Figure 3).

Factor analysis illustrated the differences in factors influencing aquatic chemistry. Considering the different combinations of factors affecting the river basins (Table 2) and consequently aquatic biota, the development of water quality criteria and basin management approaches should differ for the studied river basin groups (especially with respect to the major dissolved substances and the organic matter concentrations in the brownwaters) in order to reach good water quality requirements as set by the EU Water Framework Directive.

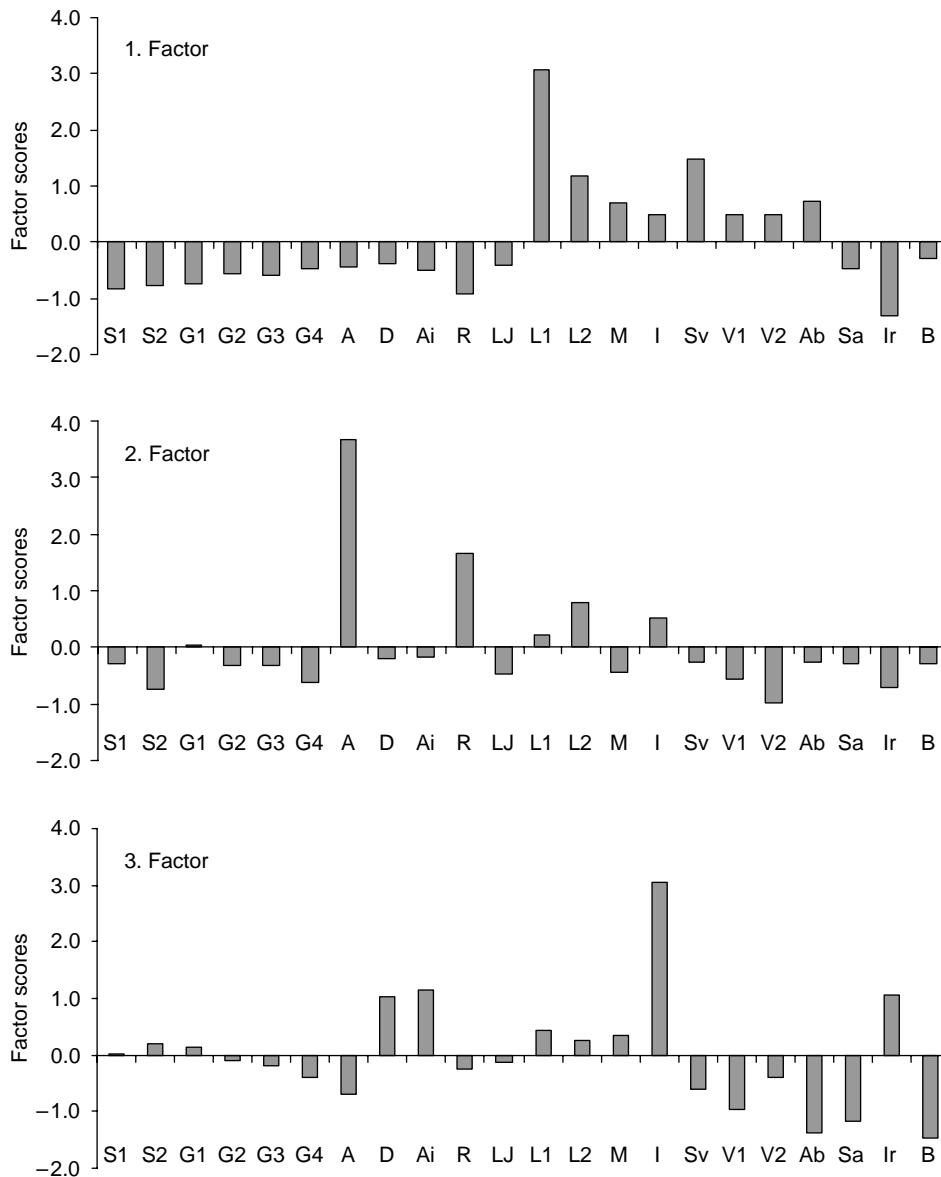


Figure 3 | Factor scores for 22 river water quality monitoring locations in Latvia (sub-basin codes as in Figure 1).

CONCLUSIONS

The analysis of factors influencing aquatic chemistry and the significance of these factors should be regarded as considerably different for river basins in Latvia. The total variability of changes of aquatic chemistry can be explained by three factors: (1) impacts associated with natural processes (mainly weathering of soils and bedrock); (2) human impacts (most strongly influencing concentrations of nutrients); and (3) proportion of wetlands and

bogs in basins, influencing the concentration of organic substances in waters. The impact of land use character on the aquatic chemistry therefore should be considered during the development of river basin management plans in Latvia according to the Water Framework Directive.

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