

How the catchment-river-lake continuum shapes the downstream water quality

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ABSTRACT

Lakes play a crucial role in the nutrient cycling of Earth, despite covering only a small fraction of the planet's surface. Their interactions with their surrounding catchment areas significantly impact ecosystems and regulatory services. The connection between a lake and its catchment, especially the drainage ratio (catchment area to lake surface area), shapes the characteristics of lakes and their response to catchment processes. Within the catchment area, geological, land cover, and land use factors influence the composition of stream water that flows into the lake. These factors play a role in transporting various substances, both organic and inorganic, to the streams. Lakes act as dynamic filters, altering the chemical composition of water that flows through them. This study aims to investigate how a large, shallow lake impacts the quality of the river water as it passes through. It builds on an analysis of nutrient (carbon, nitrogen, phosphorus, silicon)

fluxes into Lake Võrtsjärv, using six years of monthly monitoring data from five main inflows and the outflow. The research explores how catchment characteristics and hydrology affect nutrient concentrations and loadings into the lake, as well as the retention or release of substances by the lake. Findings reveal that catchment characteristics, such as land use and forest cover, significantly influence water quality parameters. Different inflows showed variations in water quality, and annual variations were observed, largely correlated with precipitation and discharge. Võrtsjärv plays a critical role in retaining or releasing nutrients, with varying impacts depending on the water budget of the lake. In years with a positive water balance, the lake retains all nutrients, whereas in dry years only inflowing N and P loads exceed their outflow. Overall, this study underscores the importance of lakes as integral components of catchment ecosystems, shedding light on their complex interactions with the environment and the implications for water quality. It emphasizes the need for careful consideration of land use and hydrological factors in managing and preserving these vital aquatic systems.

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INTRODUCTION

Lakes belong to the accumulating part of the landscape partly retaining and transforming the matter flow from the catchment. Despite lakes make up only a small percentage (3-4%) of Earth's surface, they are highly important in global nutrient biogeochemical cycling (Einsele *et al.*, 2001; Cole *et al.*, 2007; Battin *et al.*, 2009; Tranvik *et al.*, 2009; Harrison *et al.*, 2012; Vachon *et al.*, 2021). Because of their huge role in the regulatory ecosystem services, lakes appear to be disproportionately important relative to their small areal extent. The key for understanding the character of any lake is its relationship with the catchment area *via* inflowing stream water. The larger is the drainage ratio (catchment area/lake surface area), the stronger is the impact of catchment processes on the lake ecosystem (Cremona *et al.*, 2019; Horppila *et al.*, 2019). The chemical composition of stream water is associated with the bedrock, land cover, and land use of the catchment area from which various organic and inorganic substances are carried to the streams by the surface or subsurface runoff waters. Concentrations of dissolved substances in stream water are related to discharge but

this relationship is commonly nonlinear (Volk *et al.*, 2002; Raymond *et al.*, 2016).

Identification of factors that affect the dissolved matter flow is essential for estimating the loading and accumulation of nutrients and other substances in lakes. The entry of phosphorus (P), carbon (C), nitrogen (N), and silicon (Si) into aquatic environments is complex, arising from a wide spectrum of origins like household, urban, and city wastewater, poorly treated sewage. Additionally, the bedrock, land cover, land use, and agricultural activities affect the presence of these elements through drainage and surface runoff into water bodies (Harrison *et al.*, 2009; Rothwell *et al.*, 2011; Baker *et al.*, 2014; Carey and Fulweiler, 2016; Carey *et al.*, 2019). Also atmospheric deposition of N can be an important source in some areas (Rogora *et al.*, 2006). A river mirrors its catchment area and hydrological conditions. Passing through lakes that retain certain substances and enrich the water with some others, has a specific impact on water parameters (Verburg *et al.*, 2013; Maranger *et al.*, 2018; Scibona *et al.*, 2022).

Lake Võrtsjärv, with a surface area of 270 km² and a terrestrial catchment of 3104 km², is situated in a flat lowland. The loadings of P and N into Võrtsjärv have been calculated earlier (Nõges and Järvet, 1998; Nõges *et al.*, 1998; Järvet, 2004; Nõges *et al.*, 2010; Pall *et al.*, 2011). There are also some attempts to estimate the Si fluxes into the lake (Nõges *et al.*, 2008; Pall *et al.*, 2011). Tamm *et al.* (2008) studied the import of dissolved organic carbon (DOC) into the lake. Piirsoo *et al.* (2012, 2018) characterised, respectively, DOC and particulate organic carbon (POC) in the inflows and in the outflow of Võrtsjärv. Toming *et al.* (2013) showed the importance of allochthonous C as the key to lake productivity. The C mass balance for Võrtsjärv was calculated by Cremona *et al.* (2014). This balance considered hydrological and biogeochemical processes affecting dissolved inorganic carbon (DIC), DOC and POC. Nõges *et al.* (2016) showed that most of the carbon species flow through the lake without changing their category.

In the present paper we explore in which direction and to what extent passing a large and shallow lake changes the river water

quality. By comparing the quality of water entering and exiting the lake, we analyse the lake's capacity to retain or release substances. This research builds upon a prior two-year analysis (2008–2009) by Pall *et al.* (2011) focusing on P, N, Si, and C fluxes into Võrtsjärv. By analysing monthly data over six years (2008–2013) from five main inflows and the outflow of the lake, alongside the specific characteristics of each sub-catchment, our aim was twofold: firstly, to understand how catchment features impact nutrients concentrations in inflowing streams and subsequently influence their loading into the lake, and secondly, to examine how hydrology contributes to these variations. Using this information, we developed a model to calculate nutrients loading into the lake.

Study area

Large but very shallow Võrtsjärv (mean depth 2.8 m) has the drainage ratio of 11.5. It is higher than that of other well-studied shallow lakes such as Peipsi (10.1) or Balaton (8.74) and much higher than the ratio of large and deep lakes such as Onega (5.21), Ontario (3.96), and Ladoga (3.86) (ILEC World Lake Database, accessed 3.03.2023, <http://wldb.ilec.or.jp>).

In the catchment area of Võrtsjärv, the deposits of the last glaciation predominate. The bedrock is poorly exposed while the Quaternary cover of unconsolidated deposits is considerably thick and consists of different tills and aqueoglacial deposits occurring above and beneath them. Carbonate rocks prevail in the land cover (50–60%, occasionally up to 76%; Miidel *et al.*, 2004). The climate is humid as the amount of precipitation exceeds the evaporation approximately two times (Järvet *et al.*, 2004). The lake is ice-covered on average for 131 days (Nõges and Nõges, 2014). Snow melt induces a seasonal high-water period in spring. The retention time of water in the lake is approximately one year (Järvet, 2004). The water level is unregulated and fluctuates naturally with annual amplitude of 1.4 m.

The study was carried out at five largest inflows (the rivers of Väike Emajõgi, Öhne, Tarvastu, Tännassilma, and Konguta) and outflow (the River Emajõgi) of Võrtsjärv (Fig. 1; Tab. 1).

Tab. 1. Morphometric, hydrological and land use characteristics of the sub-catchments of the five main inflows and the whole Võrtsjärv catchment.

		V-Emajõgi	Öhne	River			Võrtsjärv 270 km ²
				Tarvastu	Tännassilma	Konguta	
Length, km (L)		91	103	27	36	17	-
Catchment area, km ² (C)		1 290	573	111	449	100	3104
C/L		14.2	5.6	4.1	12.5	5.9	-
Average stream gradient, m km ⁻¹		0.9	0.6	1.7	0.2	0.3	-
Average discharge, m ³ s ⁻¹	2008	14.09	7.31	1.40	6.56	1.65	36.4
	2009	12.71	6.52	1.25	5.27	1.55	31.9
	2010	14.16	7.56	1.40	4.95	1.45	34.6
	2011	10.51	6.06	1.06	4.42	1.30	27.1
	2012	11.71	6.59	1.12	4.86	1.43	29.9
	2013	9.27	4.69	0.88	3.55	1.04	22.8
CORINE land use, %	Arable land	33	30	51	38	60	36
	Pasture	13	9	6	5	12	10
	Mixed forests	34	40	37	46	18	37
	Coniferous forests	17	16	4	6	1	13
	Peat- and wetlands	1	4	>1	3	8	2
	Other	2	1	2	1	1	2

Sampling sites were positioned close to the lake. When direct sampling at the inflow was not possible, data was adjusted by comparing the entire inflow area to the sub-catchment upstream of the sampling point. The un-investigated area, not drained by the considered tributaries formed nearly a fifth (19%) of the lake's catchment area. For detailed descriptions of the rivers see Piirsoo *et al.* (2012).

METHODS

We used the hydrochemical database of inflows and outflow of Võrtsjärv (Vilbaste *et al.*, 2015) for the physico-chemical data. This database contains the hydrochemical data (different C, P, N, Si forms) that were collected from main inflows and outflow of Võrtsjärv. Samples were taken at least monthly. Additionally, it covers information on environmental parameters (Temp, pH, oxygen, conductivity) measured in the field when water samples were taken. Water pH, dissolved oxygen saturation (DO%), and electrical conductivity (EC) were measured with handheld multiparametric sonde (YSI ProPlus). Chemical analyses were done at Tartu Environmental Research Centre Ltd. Total nitrogen (TN) and phosphorus (TP) were measured in non-filtered water samples spectrophotometrically after oxidative and hydrolytic digestion in a UV- and a thermo-reactor following the standards ISO 29441 for TN and ISO 15681-2 for TP. Dissolved silica (DSi) was determined by a colorimetric method based on the ammonium molybdate reaction (EVS-EN ISO 11885). DIC was measured as HCO_3^- (EVS-EN ISO 9963-1,

1999) and DOC following the standard EVS-EN 1484, 1997.

To analyse the effect of passing the water through the lake on these variables, weighted average values were calculated for the inflows:

$$\text{Weighted Average} = \frac{\sum(\text{Weights} \times \text{Quantities})}{\sum \text{Weights}} \quad (\text{eq. 1})$$

The weight for inflow a (W_a) was calculated as the ratio of the catchment area of the particular inflow (CA_a) and the average catchment area of the 5 measured inflows (avg. $CA_{a\dots n}$):

$$W_a = CA_a / \text{Avg. } CA_{a\dots n} \quad (\text{eq. 2})$$

The percentages of the different land cover types within the river basins and the whole lake catchment area were calculated using CORINE land cover maps (see in more detail in Piirsoo *et al.*, 2012).

Data on precipitation, discharge, and ice-cover on the lake were obtained from the Estonian Weather Service. Monthly average amounts of precipitation were calculated by averaging the data from four meteorological stations (Viljandi 58°22'40"N, 25°36'01"E; Tõravere 58°15'50"N, 26°27'41"E; Valga 57°47'24"N, 26°02'16"E; Otepää 58°02'21"N, 26°30'24"E) representing different parts of the Võrtsjärv catchment area. ANOVA- analysis of variance was used to test the effect of stream and year on water quality variables. Tukey's method was used as a *post-hoc* test to calculate pairwise differences between five main inflows, consecutive years (2008-2013), and ice-free and ice-covered period. Pearson's Correlations between the vari-

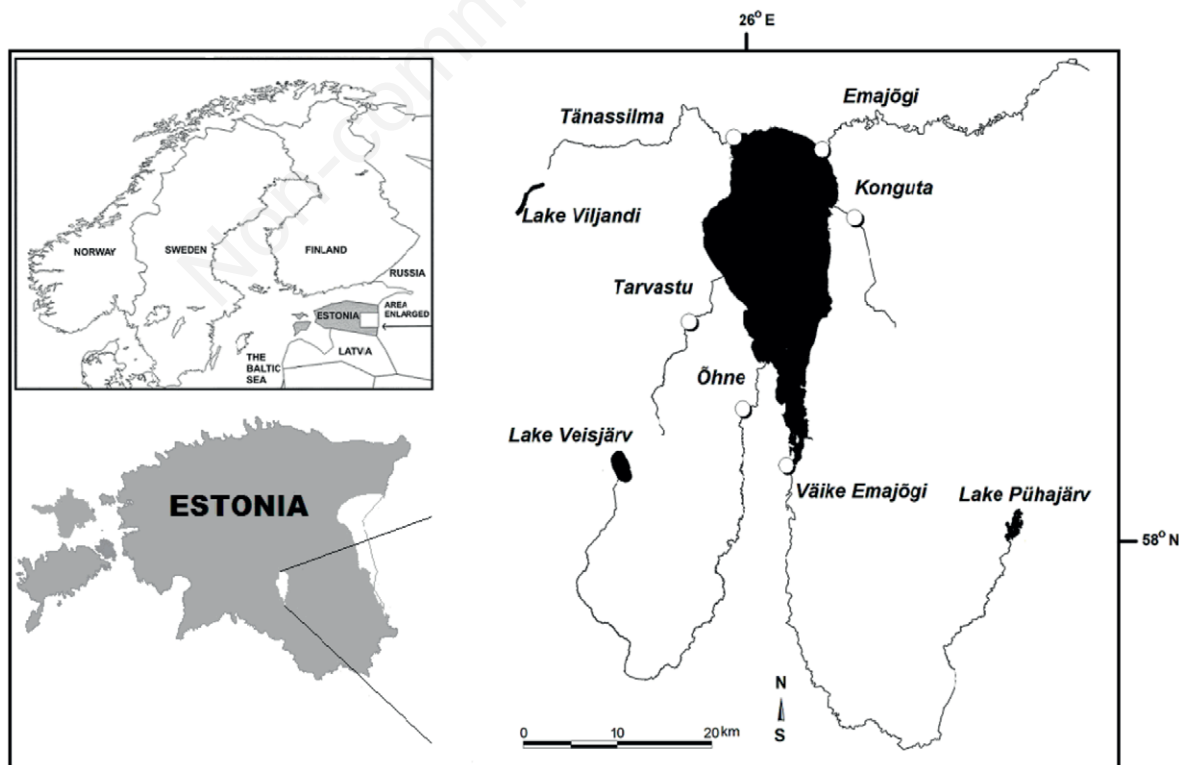


Fig. 1. Location of Lake Võrtsjärv and the sampling sites in the inflows and in the outflow (Emajõgi).

ables and Mann-Whitney U test to check the significance of differences between the variables of inflowing and outflowing waters were applied. Differences at $p < 0.05$ were accepted as significant. Calculations were carried out using the software STATISTICA 64 (version 13, TIBCO Software Inc. 2017).

Daily discharges of substances were calculated by multiplying the daily measured water discharges in the five inflows and the outflow with the measured concentrations of substances, which were linearly interpolated between the sampling dates. Loading from the un-investigated area was calculated based on the average runoff modulus ($L \text{ km}^{-2} \text{ h}^{-1}$) and average concentrations in the measured inflows. Further, monthly and annual loads were calculated as sums of daily discharges from the five inflows and the un-investigated part of the catchment (Pall *et al.*, 2011). However, the proportion of un-investigated area contributing to the total inflow discharge might be overestimated because there are only a few small streams with low discharge rates.

Stepwise multiple linear regression provided by SAS, Release 8.1 (SAS Institute Inc., 2008) was applied for the data over the five sub-catchments and six years ($n = 30$) to build the nutrient loading model of the lake. Each loading variable was separately subjected to stepwise regression analysis using hydrology parameters (precipitation and discharge) and different catchment characteristics including CORINE land use (Tab. 1). Statistically significant ($p < 0.05$) factors were used to estimate the annual mean loading of nutrients over the five main inflows. To calculate the total loading into the lake, these equations were used by applying the CORINE land use data of the whole lake catchment, the average amount of precipitation and the total discharge into the lake. The standard deviation of the annual total loading into the lake generated by bootstrapping (Bradley, 1979) our initial samples, was used to estimate its lower and upper limits.

RESULTS

Hydrology

The annual average amount of precipitation in the Vörtsjärv catchment area during the six research years was 741 mm. At that time, on average $691 \times 10^6 \text{ m}^3$ of water flowed into Vörtsjärv and $1001 \times 10^6 \text{ m}^3$ of water flowed out annually. There was a strong positive correlation between the amount of precipitation and water discharge into the lake ($r = 0.93$). The whole discharge into the lake differed between the years and had a downward trend, also the outflow discharge tended to decrease during the study. In 2008 and 2012 the lake gathered water. In 2009, the amounts of water flowing into and out of the lake were almost equal. In 2010, 2011, and 2013 the annual outflow exceeded the annual inflow from the catchment area. The years 2011 and 2013 had the smallest amount of precipitation (Tab. 1; Fig. 2).

Inflowing water quality

The inflowing water was alkaline, rich in oxygen, and with high electrical conductivity (Tab. 2; Fig. 3). The DO% was lowest in late winter under the ice and highest in autumn. The maximum and minimum concentrations of nutrients in various inflows exhibited approximately a 20-fold difference over several years, indicating significant fluctuations. However, the average values consistently indicated eutrophic conditions, with TP at $0.069 \pm 0.020 \text{ mg L}^{-1}$, TN at $2.0 \pm 0.8 \text{ mg L}^{-1}$, and DSi at

$3.1 \pm 1.0 \text{ mg L}^{-1}$, respectively (Tab. 2). The water flowing into Vörtsjärv was also rich in dissolved substances. The weighted average concentration of DIC ($51 \pm 10 \text{ mg L}^{-1}$) exceeded that of DOC ($15 \pm 5 \text{ mg L}^{-1}$) on average nearly three times (Tab. 2). Only in spring high water period, the concentration of DIC in the inflow dropped notably. Seasonal pattern of the changes was clearly expressed in case of DO%, EC, pH, TN, DSi, and DIC (Fig. 3). Oxygen saturation varied among the inflowing streams but was close to 100% in the outflow (Tab. 2), showing in both cases a seasonal increase from winter to autumn (Fig. 3a). The seasonal dynamics of the EC and DIC concentration were similar (Fig. 3 b,g) as there was a strong positive correlation between these two variables ($r = 0.80$). Both were more variable and showed higher values in the inflow compared to the outflow waters. In case of pH, the seasonality in the outflowing water was more expressed and the values higher compared to those in the catchment-size-weighted inflow water (Tab. 2; Fig. 3c). In the outflow, the pH was highest in summer and lowest in winter, being especially low (7.45) under the ice at the end of the long-lasting ice period in April 2011. The content of any nutrient was lower in the outflow than in the inflows (Tab. 2). Seasonally the DSi and TN concentrations declined from winter to summer/autumn in both inflowing and outflowing waters (Fig. 3 d,e). The outflowing TN concentration was less variable and almost permanently below 2 mg L^{-1} . In the dry year 2011, the concentration of DSi in the outflow rose to abnormal levels ($> 7 \text{ mg L}^{-1}$) for the autumn and winter, even exceeding the weighted average concentration in the inflow (*not shown*). The concentration of TP, on the contrary, had an increasing seasonal trend in the outflow and was rather constant in the inflows (Fig. 3f). Still the concentration in the outflow was constantly lower than the weighted average of the five inflows. DIC concentration was significantly lower in the outflow compared to the inflows and the discrepancy increased from winter to autumn (Fig. 3g). DOC concentrations were seasonally rather constant and did not differ significantly between in- and outflow (Fig. 3h).

Catchment effects

The studied hydrological and catchment characteristics had the smallest effect on pH and DSi concentration in inflowing water ($r < 0.30$) and the strongest on EC and TN ($r > 0.60$; Tab. 3). EC correlated negatively with average discharge, stream length, and % of coniferous forest in the catchment, and positively with % of cultivated land in the catchment. TN was positively correlated with % of arable land and peat- and wetlands

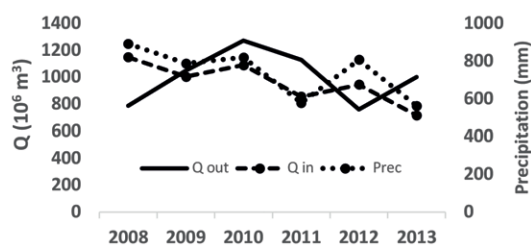


Fig. 2. Discharge into (Q in) and out (Q out) (10^6 m^3) of Vörtsjärv and annual precipitation (mm) in 2008-2013.

and negatively with % of forests land. The less forest there was in the catchment, the higher concentrations of DIC, DOC, TN and TP were (Tab. 3). According to ANOVA, there were no significant dissimilarities in any of water quality variables between the two largest inflows Väike Emajõgi and Öhne (Tab. 4). However, pairwise comparison revealed some differences in water quality parameters between other inflows, between the six years, and between the ice-free and ice-covered periods. The

smallest River Konguta differed significantly from all other rivers by higher EC and higher TP, TN, DOC and DIC concentrations. The second smallest River Tarvastu had somewhat higher pH, DO%, and EC, to the Väike Emajõgi and higher EC and DIC to River Öhne. The River Tännassilma showed lower DIC concentrations compared to the larger ones. The concentration of DSi was higher in Väike Emajõgi compared to Tännassilma (Tab. 4). There were no statistically significant

Tab. 2. Main statistics of water quality variables in five inflows and outflow of Võrtsjärv (n=76).

Variable	Statistic	Inflows					Outflow
		V-Emajõgi	Öhne	Tarvastu	Tännassilma	Konguta	
pH	Average	7.9	8.0	8.0	7.9	7.8	8.4
	StDev	0.2	0.2	0.2	0.2	0.2	0.3
	Median	7.9	8.0	8.0	7.9	7.9	8.4
	Min	7.5	7.6	7.7	7.3	7.2	7.5
	Max	8.8	8.6	8.8	8.4	8.4	8.9
	Weighted avg. inflow±StDev				7.9±0.2		
DO%	Average	76	84	91	68	79	98
	StDev	12	8	10	23	11	13
	Median	77	83	90	73	77	100
	Min	49	70	66	9	51	37
	Max	102	101	127	110	105	122
	Weighted avg. inflow±StDev			77±10			
EC, $\mu\text{S cm}^{-1}$	Average	420	389	502	481	621	357
	StDev	61	69	83	81	92	40
	Median	436	406	513	487	636	356
	Min	259	210	240	245	291	288
	Max	589	595	716	725	811	458
	Weighted avg. inflow±StDev			434±65			
TP, mg L^{-1}	Average	0.068	0.061	0.057	0.080	0.106	0.048
	StDev	0.026	0.017	0.021	0.036	0.042	0.024
	Median	0.063	0.058	0.052	0.074	0.096	0.040
	Min	0.034	0.031	0.028	0.025	0.038	0.016
	Max	0.180	0.109	0.133	0.230	0.272	0.177
	Weighted avg. inflow±StDev			0.069±0.020			
TN, mg L^{-1}	Average	1.7	1.9	2.6	2.3	5.6	1.6
	StDev	0.7	0.6	0.9	1.2	2.7	0.4
	Median	1.6	1.8	2.5	2.1	5.0	1.6
	Min	0.5	0.9	0.9	0.6	1.8	0.9
	Max	3.7	3.8	5.2	6.2	11.9	2.4
	Weighted avg. inflow±StDev			2.0±0.8			
DSi, mg L^{-1}	Average	3.4	2.9	2.9	2.6	3.0	2.7
	StDev	1.1	0.9	0.9	1.3	1.0	1.5
	Median	3.4	2.8	2.9	2.7	3.0	2.6
	Min	1.2	0.7	0.9	0.3	0.7	0.2
	Max	7.2	5.8	5.8	6.7	6.2	7.9
	Weighted avg. inflow±StDev			3.1±1.0			
DOC, mg L^{-1}	Average	15	16	12	17	20	16
	StDev	6	6	6	7	9	3
	Median	14	15	11	17	17	16
	Min	3	3	1	4	7	10
	Max	48	30	33	34	54	22
	Weighted avg. inflow±StDev			15±5			
DIC, mg L^{-1}	Average	50	47	57	57	64	40
	StDev	10	11	11	11	11	7
	Median	51	49	58	58	66	40
	Min	26	20	25	28	28	28
	Max	71	68	76	76	94	59
	Weighted avg. inflow±StDev			51±10			

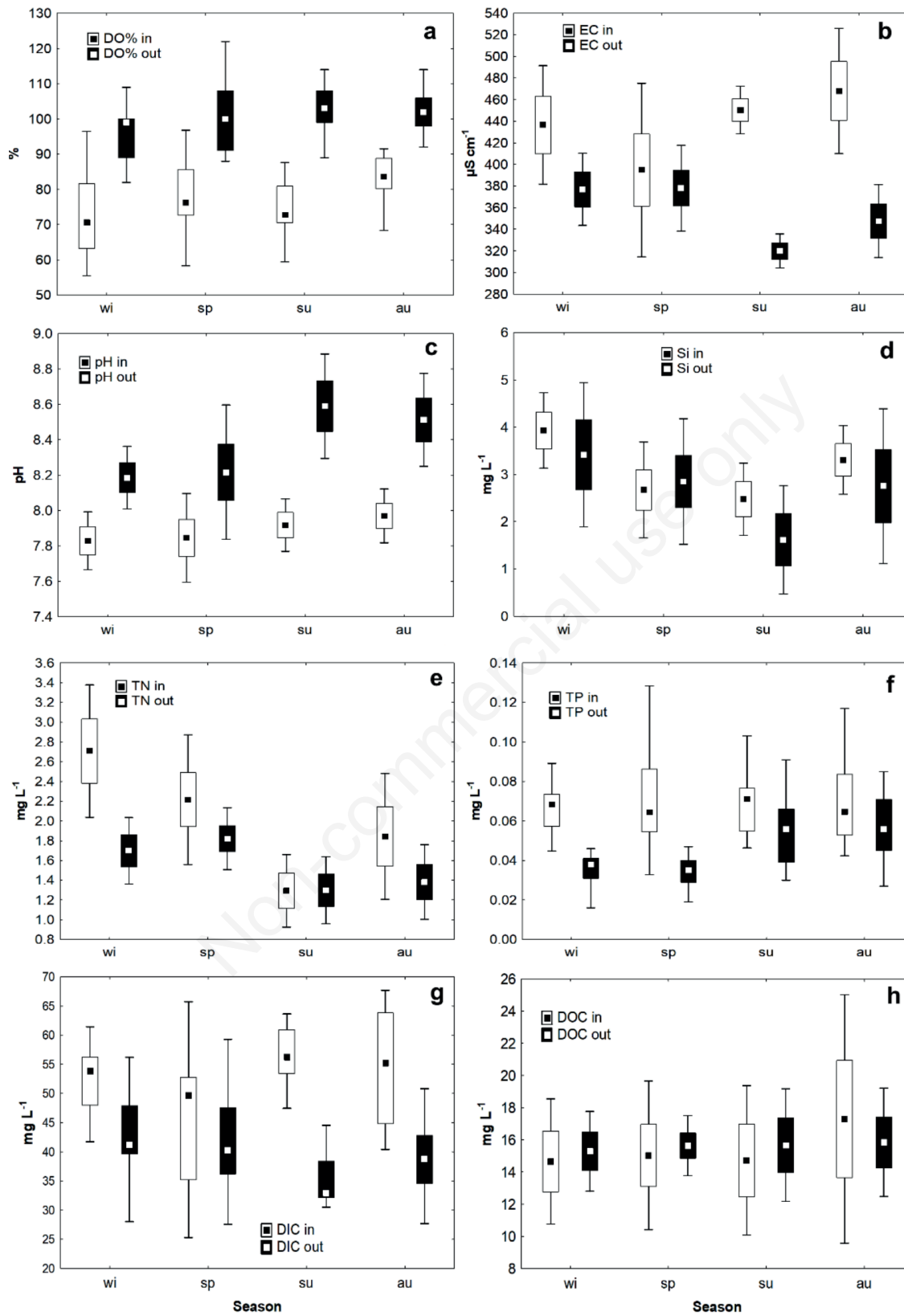


Fig. 3. Seasonal ranges of water quality variables in the inflows and outflow of Vörtsjärvi. Mean; Box: Mean \pm 2*SE; Whisker: Mean \pm SD. Inflow values are weighted with catchment size. n=17 for winter (wi: DJF), 23 for spring (sp: MAM), 17 for summer (su: JJA) and 18 for autumn (au: SON).

differences in the annual average Temp, DO%, TN, and DSi concentrations. However, in years with higher incoming discharges (2008, 2009, 2010), both TP and DIC exhibited lower average concentrations, while DOC levels were higher com-

pared to the years with smaller inflow (2011, 2013). The ice-free period differed from the ice-covered period by higher Temp, pH, DO%, concentration of DOC, and by lower concentrations of TN and DSi (Tab. 4).

Tab. 3. Pearson's correlations of water quality variables with hydrological and morphometric characteristics, and CORINE land use data of the sub-catchments of the five main inflows of Vörtsjärvi; $n=360$; $p<0.05$; $r>0.50$ are in bold.

	pH	DO%	EC	DIC	DOC	TN	TP	DSi
Average discharge	ns	0.20	-0.51	-0.38	ns	-0.44	-0.20	0.12
Precipitation	0.12	ns	ns	-0.29	0.41	ns	-0.32	-0.11
Length (L)	ns	ns	-0.63	-0.45	ns	-0.48	-0.27	0.11
Catchment area (C)	ns	-0.18	0.48	-0.30	ns	-0.44	-0.15	0.16
C/L	-0.15	-0.40	-0.21	ns	ns	-0.28	ns	ns
Average stream gradient	0.27	0.39	-0.13	ns	-0.28	-0.21	-0.34	ns
Arable land	ns	0.14	0.67	0.42	0.11	0.62	0.31	ns
Pasture	-0.15	ns	0.10	ns	0.14	0.25	0.21	0.18
Mixed forests	0.13	-0.10	-0.51	-0.26	-0.80	-0.60	-0.35	ns
Coniferous forests	ns	ns	-0.63	-0.43	ns	-0.52	-0.27	0.13
Peat- and wetlands	-0.21	ns	-0.46	-0.25	0.30	0.59	0.43	ns
Other	0.24	0.32	-0.24	-0.18	-0.28	-0.3	-0.35	0.14

ns, non-significant.

Tab. 4. Differences in mean water variables according to ANOVA between five main inflows of Vörtsjärvi, between years (2008-2013), and between ice-free and ice-covered period; $p<0.001$; for units see Tab. 2.

	Temp	pH	DO%	EC	Variables				
					TP	TN	DSi	DOC	DIC
Between streams									
Väike Emajõgi and Õhne	ns	ns	ns	ns	ns	ns	ns	ns	ns
Väike Emajõgi and Tarvastu	ns	-0.13	-14.8	-81.4	ns	ns	ns	ns	ns
Väike Emajõgi and Tännassilma	ns	ns	ns	-61.0	ns	ns	0.78	ns	-6.90
Väike Emajõgi and Konguta	ns	ns	ns	-200	-0.039	-3.86	ns	-4.82	-13.6
Õhne and Tarvastu	ns	ns	ns	-112	ns	ns	ns	ns	-9.85
Õhne and Tännassilma	ns	ns	15.9	-91.9	-0.019	ns	ns	ns	-10.7
Õhne and Konguta	ns	0.13	ns	-230	-0.046	-3.71	ns	-4.02	-17.4
Tarvastu and Tännassilma	ns	0.17	23.1	ns	-0.023	ns	ns	-4.43	ns
Tarvastu and Konguta	ns	0.20	12.4	-118	-0.049	-2.98	ns	-7.25	-7.58
Tännassilma and Konguta	ns	ns	-10.7	-139	-0.027	-3.28	ns	ns	-6.72
Between years									
2008 and 2009	ns	ns	ns	ns	ns	ns	ns	ns	ns
2008 and 2010	ns	ns	ns	ns	ns	ns	ns	7.79	ns
2008 and 2011	ns	ns	ns	ns	-0.040	ns	ns	10.66	-9.62
2008 and 2012	ns	-0.18	ns	ns	ns	ns	ns	8.13	-11.5
2008 and 2013	ns	ns	ns	ns	-0.023	ns	ns	10.04	-10.7
2009 and 2010	ns	ns	ns	ns	ns	ns	ns	4.15	ns
2009 and 2011	ns	ns	ns	ns	-0.032	ns	ns	7.01	-8.69
2009 and 2012	ns	-0.17	ns	ns	ns	ns	ns	ns	-10.5
2009 and 2013	ns	ns	ns	ns	ns	ns	ns	6.40	-9.81
2010 and 2011	ns	ns	ns	ns	-0.023	ns	ns	ns	-7.30
2010 and 2012	ns	-0.28	ns	ns	ns	ns	ns	ns	-9.13
2010 and 2013	ns	ns	ns	ns	ns	ns	ns	ns	-8.42
2011 and 2012	ns	-0.24	ns	ns	ns	ns	ns	ns	ns
2011 and 2013	ns	ns	ns	-61.3	ns	ns	ns	ns	ns
2012 and 2013	ns	0.21	ns	ns	ns	ns	ns	ns	ns
Between ice-free and ice-covered period									
	10.8	0.15	9.92	ns	ns	-1.02	-1.12	5.87	ns

ns, non-significant.

Loadings

On average, Vörtsjärv received yearly 63 t of TP, 2330 t of TN, 2937 t of DSi (1370 t of Si), 15900 t of DOC, and 45284 t of DIC (Tab. 5) from the catchment. The exact values for each inflow depended on the discharge and the catchment characteristics of the inflow. The ability of sub-catchments to release nutrients differed by years. The yield of DSi (approximately $1 \text{ g m}^{-2} \text{ y}^{-1}$) was rather uniform over the five sub-catchments and years. Only in the driest years of 2011 and 2013, it was somewhat lower ($0.81\text{--}0.75 \text{ g m}^{-2} \text{ y}^{-1}$). At the same time, the respective value for DIC varied between sub-catchments and years around two times (average $14.6 \text{ g m}^{-2} \text{ y}^{-1}$), for TP and DOC 2–3 times (averages $20.4 \text{ mg m}^{-2} \text{ y}^{-1}$ and $5.12 \text{ g m}^{-2} \text{ y}^{-1}$, respectively),

and for TN even 3–5 times (average $0.74 \text{ g m}^{-2} \text{ y}^{-1}$; Tab. 5). During the six years study, there was a downward trend in the loadings of DOC and DIC into the lake. In total, the DOC loading was nearly three times higher in 2008 compared to 2013 (Tab. 5). The DIC loadings did not differ so much between the years. It was the highest in 2012 and the lowest in 2013 when it set up 74% of the loading of former year. Strong downward trend in DOC loadings caused a similar trend also in the DOC/DIC ratio (Tab. 5). The variation in loadings was explained at high level ($R^2 = 0.76\text{--}0.90$) in the regression equations by hydrology and the proportion of arable land in the catchment. The loadings of all studied five substances were controlled by discharge and/or precipitation. Discharge was the only variable explaining

Tab. 5. Annual loadings in tons (t) and annual yields per catchment m^2 of TP, TN, DSi, DOC, and DIC of the five inflows and total to the lake (sum of five inflows plus loadings from uninvestigated area) in 2008–2013.

River Year	TP		TN		DSi		DOC		DIC		DOC/DIC
	t	$\text{mg m}^{-2} \text{ y}^{-1}$	t	$\text{g m}^{-2} \text{ y}^{-1}$	t	$\text{g m}^{-2} \text{ y}^{-1}$	t	$\text{g m}^{-2} \text{ y}^{-1}$	t	$\text{g m}^{-2} \text{ y}^{-1}$	
V-Emajõgi											
2008	23.56	18.3	944	0.73	1301	1.01	8859	6.87	18722	14.5	0.47
2009	21.63	16.8	657	0.51	1302	1.01	7432	5.76	17378	13.5	0.43
2010	29.82	23.1	814	0.63	1456	1.13	7046	5.46	18665	14.5	0.38
2011	29.26	22.7	727	0.56	1052	0.82	4049	3.14	15240	11.8	0.27
2012	24.64	19.1	789	0.61	1409	1.09	5232	4.06	20616	16.0	0.25
2013	24.04	18.6	623	0.48	1011	0.78	3498	2.71	15571	12.1	0.22
Õhne											
2008	11.61	20.2	534	0.93	574	1.00	5153	8.99	9117	15.9	0.57
2009	10.38	18.1	343	0.60	562	0.98	3937	6.87	7836	13.7	0.50
2010	11.75	20.5	407	0.71	687	1.20	3943	6.88	8794	15.3	0.45
2011	12.76	22.2	399	0.41	529	0.92	2417	4.22	8202	14.3	0.29
2012	13.37	23.3	459	0.80	626	1.09	3516	6.14	9958	17.4	0.35
2013	10.04	17.6	319	0.56	439	0.77	1893	3.30	7570	13.2	0.25
Tarvastu											
2008	2.13	19.1	156	1.40	122	1.09	896	8.04	2131	19.1	0.42
2009	1.97	17.7	100	0.89	106	0.95	658	5.90	1924	17.3	0.34
2010	2.25	20.2	111	1.00	131	1.17	493	4.43	2055	18.4	0.24
2011	2.46	22.1	105	0.95	92	0.83	323	2.90	1628	14.6	0.20
2012	2.23	20.1	118	1.06	108	0.97	390	3.51	2031	18.3	0.19
2013	2.00	18.0	87	0.78	85	0.77	354	3.18	1510	13.6	0.23
Tänassilma											
2008	10.55	23.5	632	1.41	536	1.19	4996	11.1	10369	23.1	0.48
2009	9.92	22.1	383	0.65	432	0.96	3195	7.12	8119	18.1	0.39
2010	8.55	19.1	410	0.58	428	0.95	2626	5.85	7235	16.1	0.36
2011	10.66	23.8	440	0.98	353	0.79	1992	4.44	7191	16.0	0.28
2012	9.36	20.8	449	1.00	457	1.02	2533	5.64	8994	20.0	0.28
2013	10.54	23.5	348	0.78	324	0.72	1383	3.08	6555	14.6	0.21
Konguta											
2008	4.69	46.9	417	4.17	188	1.88	1507	15.1	3786	37.9	0.40
2009	4.14	41.4	343	3.43	137	1.37	1289	12.9	2775	27.8	0.46
2010	5.27	52.7	308	3.08	135	1.35	845	8.45	2513	25.1	0.34
2011	5.26	52.6	316	3.16	107	1.07	676	6.76	2274	22.7	0.30
2012	4.34	43.4	358	3.58	131	1.31	698	6.98	2977	29.8	0.23
2013	5.43	54.3	249	2.49	90	0.90	565	5.65	1743	17.4	0.32
Total inflows											
2008	61.03	19.7	3022	0.97	3189	1.03	24601	7.93	50864	16.4	0.48
2009	55.82	18.0	2061	0.66	3008	0.97	19185	6.18	44288	14.3	0.43
2010	68.37	22.0	2343	0.75	3361	1.08	17491	5.63	45981	14.8	0.38
2011	70.94	22.9	2248	0.72	2512	0.81	10915	3.52	40021	12.9	0.27
2012	62.80	20.2	2457	0.79	3237	1.04	14253	4.59	51997	16.8	0.27
2013	60.80	19.6	1850	0.60	2313	0.75	8952	2.88	38555	12.4	0.23

the DSi and DIC loadings in regression equations. For TP and DOC loadings it was the second strongest factor while precipitation was the first. TN loadings were determined by discharge and the proportion of arable land in the catchment whereas for TP loading, the proportion of arable land was the third important factor (Tab. 6). Although the stepwise linear regression model tended to underestimate the measured values, they were still within the margin of limits (Fig. 4). In 2008, 2011, and 2013 all the measured values were higher and for TP DSi and DIC the measured values were all the years higher than the model predicted. In some years the measured values were even above the upper limits of the model (Fig. 4 a,c,e). The model predicted quite adequately TN for 2009 and 2010 and DOC for 2010 and 2012 (Fig. 4 b,d).

Differences in water quality between the inflows and the outflow

In-lake processes elevated considerably the pH and DO% of the water flowing through the lake, while the EC of water and the concentrations of TP, TN, DSi, and DIC decreased noticeably (Tab. 2). According to Mann-Whitney U test, all differences between the inflow and outflow parameters, except DOC, were statistically significant (*not shown*). In the years with a positive water budget (2008, 2012), the lake retained all the substances under observation (Fig. 5). Less DIC, DOC, TN, TP, and DSi flowed out than into the lake. TN and TP were retained by the lake every year, with an average annual retention of 918 t and 24 t, respectively. The average annual retention rates were 37% for TN and 38% for TP (*not shown*). The dynamics of DIC and

Tab. 6. Stepwise multiple linear regression model of nutrient loading into Vörtsjärv.

	Intercept	Var 1		Var 2		Var 3	Sum R ²
TP	0.441	-0.0009	Prec	0.0001	Q	0.0060 Arab	0.76
TN	-49.11	0.0031	Q	1.1039	Arab		0.78
DSi	3.026	0.0025	Q				0.88
DOC	-193.3	0.2780	Prec	0.0166	Q		0.89
DIC	120.6	0.0370	Q				0.90

Prec, precipitation; Q, discharges; Arab, arable land (%); $p < 0.05$.

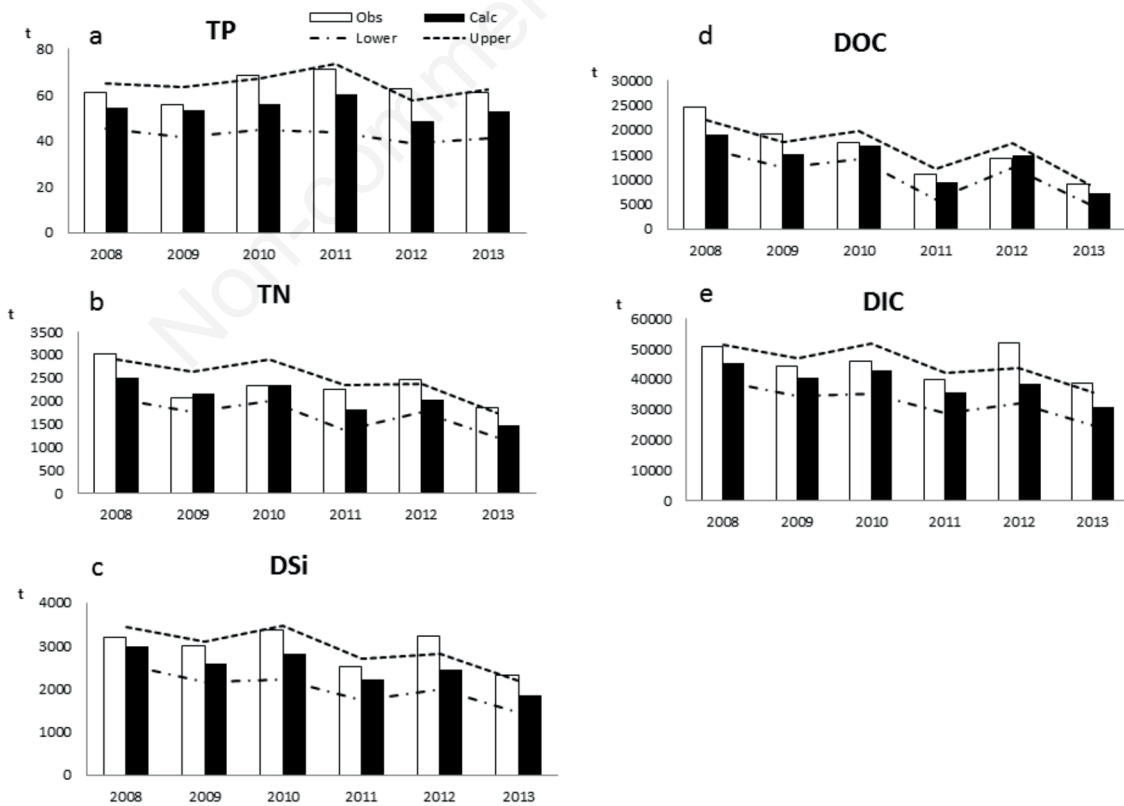


Fig. 4. Observed (Obs) and calculated according to stepwise multiple linear regression model (Calc) loadings of substances into Vörtsjärv; lower and upper limits of the calculated values show the standard deviation of the bootstrapped results.

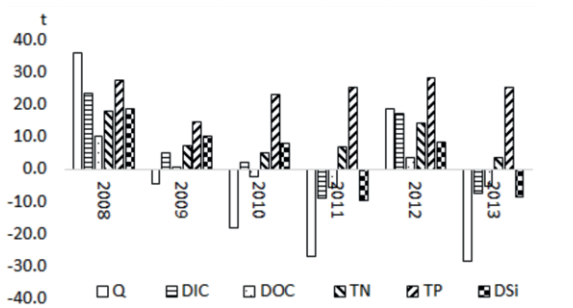


Fig. 5. Difference between inflows and outflows of Vörtsjärvi in discharges ($Q \times 10^4 \text{ m}^3$), and loadings of DIC ($\times 10^3 \text{ t}$), DOC ($\times 10^3 \text{ t}$), TN ($\times 10^2 \text{ t}$), TP (t), and DSi ($\times 10^2 \text{ t}$) in 2008-2013.

DSi was similar evidenced by a strong positive correlation between them ($r = 0.90$). In dry years with little precipitation (2011, 2013), more DIC and DSi flowed out than into the lake. However, the average annual retention rate for them was around 10%. The behaviour of DOC showed no consistent pattern (Fig. 5) and the retention varied significantly between years, ranging from 41% in 2008 to -60% in 2013.

DISCUSSION

Impact of catchment on water quality

At European scale, water bodies with a long-term average alkalinity $>1.0 \text{ meq L}^{-1}$ are considered highly alkaline (European Commission, 2000). In our study, high alkalinity of the inflowing water was evidenced by weighted average pH of 7.90, EC of $434 \mu\text{S cm}^{-1}$, and DIC of 51 mg L^{-1} that roughly correspond to the long-term average alkalinity of $3.3 \pm 0.6 \text{ meq L}^{-1}$ measured in Vörtsjärvi (Nöges and Nöges, 2012). Unusual for the boreal region with peat- and wetlands, the waters of studied rivers were highly alkaline and with high concentration of DOC. The reason is the geology: although silicate bedrock prevails in the study area the post Ice age glacial carbonate moraine (till) dominates in the land cover all over the area.

Chaplot and Mutema (2021) showed differences in DOC and DIC concentrations depending on geographic region. In humid boreal and tropical lakes, DOC is the dominant form of C inputs to the lakes (Sobek *et al.*, 2007; Einola *et al.*, 2011) whereas in temperate regions DIC dominates (Stets *et al.*, 2009; Khan *et al.*, 2020). In our study, DIC concentrations exceeded DOC concentrations nearly 3-fold. Comparing DOC concentrations in our study ($16 \pm 3 \text{ mg L}^{-1}$ in the inflow; Tab. 2) with the global average estimate for lakes of 3.88 mg L^{-1} (Toming *et al.*, 2020), our values are rather high and scale with those reported from Finland (Kortelainen *et al.*, 2006; Sarkkola *et al.*, 2009), Scotland (Dawson *et al.*, 2004); England (Clark *et al.*, 2005; Baker *et al.*, 2008); Czechia (Hruška *et al.*, 2009), Canada (Roulet *et al.*, 2007; Finlay *et al.*, 2009), and Australia (Westhorpe and Mitrovic, 2012). In our study, there was a negative correlation between DIC and DOC concentrations similarly to some British rivers where the concentration of DIC was higher than that of DOC (Baker *et al.*, 2008). Peatlands and wetlands are a major source of DOC entering inland waters in boreal catchments (Ågren *et al.*, 2010; Asmala *et al.*, 2019). DIC has

been shown to be linked to local geologic features, weathering, and pH-related variables (Giesler *et al.*, 2014; Jantze *et al.*, 2015; Magin *et al.*, 2017).

We also observed an impact of land use on the levels of TP and TN concentration in the inflow. Within the River Konguta sub-catchment, the highest proportion of arable land coupled with the lowest share of forest (Tab. 1). Notably, the highest average and maximum concentrations were detected in this area: TP 0.106 mg L^{-1} and 0.272 mg L^{-1} , TN 5.6 mg L^{-1} and 11.9 mg L^{-1} , respectively (Tab. 2). These findings align with Kupiec *et al.* (2021), demonstrating positive correlation ($R = 0.59$) between TP and the arable land area, and negative ($R = -0.62$) between TP and forested land area. Similarly, Abell *et al.* (2011) found in New Zealand lakes a negative relationship of TP and TN concentrations with the percentage of native forests in the catchment. Conversely, they observed a positive correlation of TP and TN with the proportion of high-producing grasslands, particularly intensive pastures. This factor emerged as a significant predictor, explaining 38.6% and 41.0% of the variation in TN and TP concentrations, respectively. Duan *et al.* (2021) emphasized that N concentration is predominantly influenced by extent of agriculture, whereas P concentrations are chiefly driven by population density (Hu *et al.*, 2019) and precipitation intensity (Ockenden *et al.*, 2016). P concentrations tend to elevate during dry periods and diminish during wet seasons due to dilution effects. Our study also revealed higher TP concentrations during drier years (2011, 2013) and lower concentrations during wetter years (2008, 2010; Tab. 4).

Loadings

Our results, that hydrological factors, precipitation and discharge, are mostly responsible for nutrient loading into the lake (Tab. 6) are consistent with the results of EUROHARP project (Bouraoui *et al.*, 2009) where climatic variables and in particular the total rainfall also explained most of the variance found in the nutrient load measured at the catchments outlet. Like in our study, water discharge and Si load were strongly linked also in the study of Nöges *et al.* (2008) in different catchments in countries surrounding the Baltic Sea.

We compared annual TN and DSi yields from our catchments ($0.74 \text{ g m}^{-2} \text{ y}^{-1}$ and $0.95 \text{ g m}^{-2} \text{ y}^{-1}$, respectively) with the data from the Grand-Duchy Luxembourg river basins from the study of Onderka *et al.* (2012), $1.18 \text{ g m}^{-2} \text{ y}^{-1}$ TN and $2.45 \text{ g m}^{-2} \text{ y}^{-1}$ DSi, respectively. It appears that the leakage of these substances from our catchments was lower assumingly due to the smaller slopes of our rivers in the rather flat catchment. Also, the Japanese study by Kikuchi *et al.* (2023) demonstrated that the slope had a strong positive correlation with DSi concentration. Our correlation analysis showed that DIC concentration was negatively correlated with precipitation and water runoff and positively with percentage of cultivated land in the catchment (Tab. 3). Rehn *et al.* (2023) highlighted the sensitivity of DIC concentrations to runoff as most studied streams had decreasing DIC concentrations during spring flood over, and about half showed declines during summer in boreal landscapes. However, we did not observe such a decrease in summer (Fig. 3g). Still, the DIC loading depended almost completely ($R^2 = 0.90$) on the flow rate (Tab. 6). The regression models developed by Tye *et al.* (2022) demonstrated that river DIC loading was largely explained by the geology of the landmass, along with a

negative correlation to annual precipitation. It has been demonstrated that there is positive correlation between DOC concentration and discharge (river flow) and negative correlation between DIC concentration and discharge (Baker *et al.*, 2008). Raymond and Oh (2007) stated that precipitation had the strongest correlation with annual carbon export for all carbon pools as DOC loadings generally increased with increasing discharge. Clark *et al.* (2005) have reported lower DOC concentrations in streams during drought years and have attributed this to low flows. Stepwise multiple linear regression model tended to underestimate almost all loadings (Fig. 4). The problem is that we considered only hydrology (flow and precipitation) and land use when creating the model. Nutrient loading from the catchment is strongly related to catchment land use (Suresh *et al.*, 2023, and references therein) and the water protection measures in place (Garnier *et al.*, 2021). However, there are still several geologic and topographic conditions affecting the loadings of substances into a lake (Jabbar and Grote, 2019). Differences in the soil characteristics can also affect the leaching and loadings of substances (Röman *et al.*, 2018). Soil type and water network connectivity and drainage features are important predictors of TN and TP concentrations as well (Rinaldi, 2013).

Despite the fact that only a few significant explanatory variables were identified, the models explained the TN and TP loadings by up to 78% and 76%, respectively. But for DSi, DOC and DIC, the model explains even 88-90% of the variation (Tab. 6).

Lake shapes the downstream water quality

Lakes can significantly impact downstream water quality. They act as natural filters, trapping pollutants and sediments, thereby improving water quality by reducing sediment transport and nutrient loads in the downstream areas. Although there were significant differences between the water characteristics of the inflows (Tabs. 2 and 4), Vörtsjärv had a double effect: it levelled them as a mixed reactor, but the in-lake processes modified the water characteristics in a specific way. When comparing the means of lake outflow water quality variables with those of the inflows, only pH and DO% were higher in the outflow, while EC, TP, TN, DSi, and DIC were lower. The average concentration of DOC did not change much (Tab. 2; Fig. 3). However, the incoming loadings of nutrients were constantly higher than the outgoing fluxes. The lake accumulated nutrients (N and P) regardless of the lake's water balance (gaining or losing water), but the balance between DIC, DOC, and DSi accumulation and release depended on the lake water budget. When the lake accumulated water, it also accumulated these compounds; however, when it released more water, it could also leak them (Fig. 5).

Mattsson *et al.* (2005) confirmed that lakes in the boreal region retained dissolved TOC, TN, and TP. Verburg *et al.* (2013) investigated TP and TN retention in the deep oligotrophic Lake Brunner, revealing retention rates 47% for TP and 21% for TN respectively. Kuriata-Potasznik *et al.* (2020) demonstrated that various lakes in Poland were capable of retaining 8.8-56% of incoming TN and 7.7-42% of TP. The examination of a 17-year dataset and the nutrient budget for two interconnected semi-arid lakes in R. Murray, Australia, discovered that these lakes served as significant sink for TP and Si, yet, the retention of TN was comparatively limited, accounting for 55, 39 and 7%, respectively (Cook *et al.*, 2010). For Lake Vörtsjärv, these averages figures were 38, 11 and 37%, respectively, for TP, DSi, and TN.

That means the lake retained more than a third of the incoming TP and TN from its inflows, but when it came to Si, this capability was lower.

The retention of P and N in the lake is linked to the lake's hydrodynamics – the longer the residence time, the more effective the retention (Wang *et al.*, 2020). Additionally, lake morphometry plays a significant role – lower lakes exhibit a denser association with sediments, aiding in the binding of these nutrients. Tammearg *et al.* (2022a) demonstrated that Vörtsjärv retained P well, which settled to the bottom, and high amounts of DOC (humic substance) prevented P from leaching back into the water. Also, the presence of aquatic plants, algae, and microorganisms influences nutrient uptake and cycling in a lake. Biological processes like photosynthesis and microbial activity can enhance or reduce nutrient retention and whole lake primary production should be considered in lake studies (Cremona *et al.*, 2016).

Vörtsjärv eutrophied rapidly in the 1980s while in the early 1990s the declining agricultural land use intensity in Estonia reduced eutrophication of lakes (Nöges and Nöges, 2012). In the lake, regardless of the declined external nutrient loading, no improvement in phytoplankton indicators has been observed so far (Janatian *et al.*, 2021). It is assumingly due to the internal P loading (Tammearg *et al.*, 2022b) and also increased N loadings in the 2000s (Nöges *et al.*, 2020). Tammets and Jaagus (2013) supposed that in our region, the frequency and intensity of heavy rainfall increase due to climate warming. According to our data, the years with the highest precipitation (2008 and 2012) coincided with the highest TN and DIC loads into the lake (Tab. 5). Ockenden *et al.* (2016) highlighted that P load may increase by up to a tenth in cases of intense rainfall. Furthermore, as climate warming reinforces eutrophication (Moss *et al.*, 2011), the stronger limitation of nutrient loading is needed to reduce eutrophication of Vörtsjärv.

CONCLUSIONS

The water balance of the large, shallow and unregulated Vörtsjärv depends largely on the variable amount of precipitation: it collects water in some years and releases it in other years. Nutrient concentrations in various inflows exhibited substantial differences across years, yet average values consistently indicated eutrophic conditions. The lake acts as both a mixer and a modifier of incoming water. It evens out differences between the inflows but also changes the water in its own way. In positive water balance years, the lake retains all nutrients, whereas in dry years with minimal precipitation, incoming loads exceed outgoing loads only for N and P. Annual retention rates averaged at 37% for TN and 38% for TP. In dry years with minimal precipitation (*e.g.*, 2011, 2013), outflow of DIC and DSi was greater than inflow, but their average annual retention remained close to 10%. DOC retention lacked consistency, varying widely between 41% in 2008 and -60% in 2013. Regression analysis highlighted hydrology and catchment arable land proportion as major contributors to nutrient loading variability. This understanding aids in explaining the diverse nutrient load variations impacting the lake. As the increasing frequency of heavy rainfall due to climate warming intensifies eutrophication, stricter control of nutrient input is needed to diminish eutrophication in Vörtsjärv.

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