0.1 TRANSPORT OF PHOSPHORUS IN THE RIVER NETWORK OF A HIGHLAND BASIN WITH MIXED LANDUSE (THE MALŠE RIVER, CZECH REPUBLIC)

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Abstract: The aim of this study was the quantitative evaluation of phosphorus sources and in-stream retention in the Malše River Basin. We monitored the phosphorus export from the Malše River catchment at the hydrometric profile at Pořešín (upstream area of 436,7 km^2). Composite weekly water samples were analyzed for the main phosphorus forms, i.e., dissolved phosphorus (DP) and particulate phosphorus (PP) during the period from 1999 to 2003. In addition, 20 small subcatchments of various landuse type (forest to farmland area ratios from 1 to 0) and slope were monitored less intensively, but covering all hydrological and seasonal situations. Point sources, i.e., discharges of municipal waste water, were evaluated from the operation records of waste water treatment facilities. The streams with completely forested catchments showed the lowest concentrations of DP. (~0.015 mg l^{-l}). DP concentrations in farmland streams fluctuated in a wide range from <0.01 mg l^{-l} to 0.25 mg l^{-l}, with the highest values during the surface flow events. High PP concentrations (up to 0.6 mg l^{-l}) occurred during surface flow events in all streams across irrespective to landuse character. Waste water treatment plant effluents showed the highest DP and PP concentrations (up to 4 and 2 mg l^{-1}, respectively), which resulted in negative DP-concentration vs. flow relationships at the Pořešín river profile.

An analysis of phosphorus fluxes in the river network showed retention of DP (1,8–2,9 t per year) and PP (1,5–4,7 t per year). It can be concluded that the point sources in the Malše basin were a major factor of increased P river concentrations at low flow periods. However, they also significantly contributed at high flow conditions due to the flushing of temporarily stored pools in the river channel and the riverine and hyporheic zones.

Keywords: Phosphorus retention, communal sources, diffuse sources, Malše River, concentration discharge relation.

1. Introduction

Phosphorus input from a catchment is an important factor in the eutrophication and water quality in reservoirs. Phosphorus at the catchment outflow originates in different types of sources: (i) Natural background P concentration, linked with phosphorus content in rocks and soils, weathering intensity and the extent of water erosion, unaffected by anthropogenic impact (Ahl 1988). (ii) Diffuse sources, comprised of agricultural land use (fertilization, intensive pasture, presence of tile drain, stock raising), rain-wash and seepage from urban areas, and building or other human activities causing erosion processes (Ryding & Rast, 1989). (iii) Communal sewage water outlets, representing the most important point sources of P (Pitter 1999).

In the course of P transport within river network phosphorus goes through a number of processes, such as physical (sedimentation), physical-chemical (sorption), chemical (precipitation and solution) and biological (uptake, mineralization) (Newbold, 1992). The presence of any of these processes can result in temporal or permanent P retention in riverbed and in the surroundings (floodplain and hyporheal). The extent of P retention is dependent especially on total residence time of water in channels, in surrounding soil and rock horizons, and in reservoirs. The periods of retention and periods of increased P export alternate generally within years in relation to discharge and season (Svendsen et al., 1995).

Understanding the P retention along the river course prior to the monitored cross–section is of great importance for evaluation the significance of separate pollution sources in catchment.

This work presents the results of 5 years of detailed study of P export from an upland catchment in the Czech Massive (The Malše River Basin above Římov reservoir). The main aim of this study was (i) to determine the quantity and the relative weight of two major P sources in the catchment: communal waste water and diffuse sources and (ii) to evaluate the extent of P retention processes in the river network.

2. Methods & Material

2.1. Locality and site description

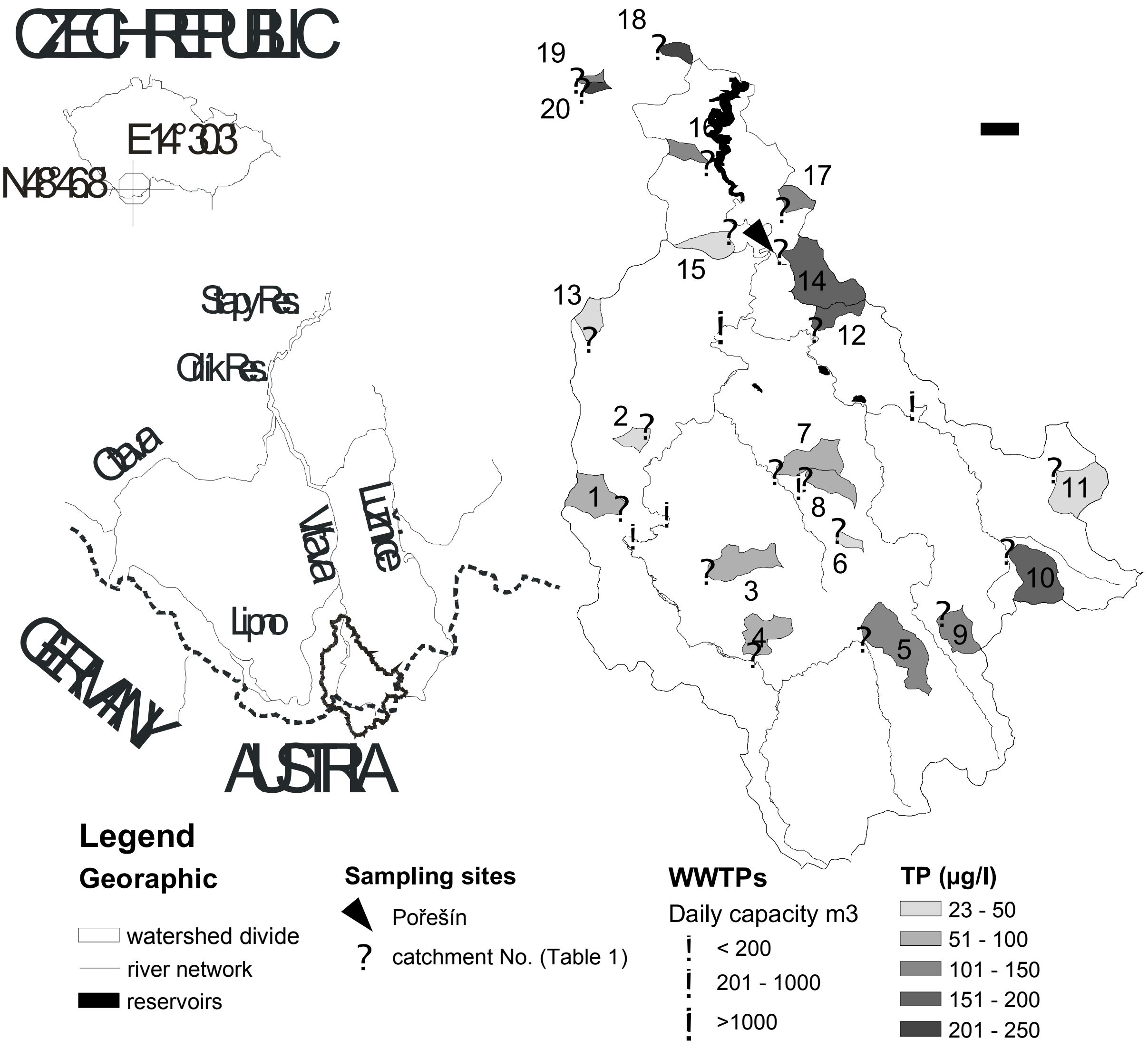

Figure 1. Map of the Malše Basin above Římov reservoir with sample sites, main communal sources (WWTPs), and mean TP concentrations of diffuse sources.

Phosphorus export from Malše Basin was measured at cross section Pořešín (492,9 m a.s.l, river log 40,1 km, ~7 km above the backwater end of Římov reservoir, mean annual discharge 4,05 $m^3.s^{-1}$) in the period from I.1999 to X.2003. The geographic position of all sampling sites is illustrated in Figure 1. The Malše catchment related to this point has an area of 436,9 km^2 with maximal altitude 1113,8 m a.s.l. and average annual precipitation amount 685 mm. It has about 16,7 thousands inhabitants, including ~4,7 thousands inhabitants in Austria. Further information about Pořešín is in Table 1.

2.2. Cross-section Pořešín

The water stage at Pořešín was recorded by the Czech Hydrometeorological Institute (CHMI). The water temperature was registered by thermistors TidbiT TBI32-5+37 (Onset, USA) and automatic weather station MS4016 (Fiedler–Mágr, CR). Water samples from the Malše River for P determination were collected at daily intervals (more frequently during high flow periods) and then combined proportionally to discharge into cca weekly samples for chemical analysis. Composite samples were filtered trough nylon sieve (200 µm mesh size) and analyzed for phosphorus species, including total P (TP, Kopáček & Hejzlar, 1993), dissolved phosphorus (DP) and dissolved reactive phosphorus (DRP; Murphy & Riley, 1962).

Particulate P was calculated (PP; 0.45–200 µm) as the difference between TP and DP, and dissolved non-reactive P (DNP) as difference between DP and DRP. Mass fluxes of P were calculated as a product of the daily discharge and of the concentration which represented the whole period of ~1 week and were then summarized for intervals of one month, half year, and year.

2.3. Diffuse sources

20 streams (1st–2nd order according to Strahler) in the region of Římov without any communal source of pollution were sampled to assess the natural concentration background of P (Figure 1). Catchments of the selected streams varied foremost in land use and slope circumstances (Table 1). Samples were taken 3-4 times a year 2002, with a view to recording various seasonal and flow situations (from discharge Q with probability of exceedance p>0.65 (i.e. 240 days in year; Q_{240d}) to 5-years flood exceedance probability; $Q_{5\text{-}year}$). Catchment characteristics noted in Table 1 were compiled using a digital terrain model (DTM), satellite photographs from Landsat 1995 recording, and topographical digital maps (DMÚ) with a uniform scale of 1:25000. These datasets were processed by the application of GIS tools in the following software packages: (ArcView 8.2, ESRI, USA; ANUDEM and Geomatica, PCI, Canada).

2.4. Communal sources

Communal inputs of P (point sources) into the river network were determined from available data covering P concentrations in and amounts of sewage effluents of the largest wastewater treatment plants (WWTPs) (operation evidence of sewage works facility Voodovody a Kanalizace Jižní Čechy a.s. for WWTPs in Kaplice, Dolní Dvořiště, Rychnov nad Malší, Malonty and Benešov nad Černou). The P export from inhabitants without connection to monitored WWTPs (P_{com}) was calculated according to the Equation 1.

$$P_{com} = P_{spec} \times E \times I \tag{1}$$

P_{spec} – specific human P production (2,3 $g.day^{-1}$ per capita, in Austria 1,6 $g.day^{-1}$ per capita, due to common usage of phosphate-free washing powders); E – coefficient of P transport efficiency into surface waters (a value 0,5 is assigned to dispersed build-up, 0,6 to small WWTPs with biological ponds, and 0,8 to septic tanks); I – the population number. Numbers of inhabitants and their connectivity to sewerage in the region were based on the census from 1991 of Czech statistical office. In Austria the population number was estimated according to the number of buildings as depicted in a map (1:25000).

Table 1. Catchment characteristics: A – catchment Area; J_{avg} – mean slope; H_{avg} – mean altitude; TP and DP – mean Phosphorus concentrations ($\mu g.l^{-1}$).

	Name of stream–profile	A,	J_{avg},	H_{avg},	Land use, %				TP,	DP,
		Km^2	°	m a.s.l.	forest	Meadow	Arable	other*	$\mu g.l^{-1}$	$\mu g.l^{-1}$
	Malše-Pořešín	436,9	6,3	708	55	24	18	2,1	91	53
1	Trojanský p.	3,48	3,4	691	75	8	16	0,9	83	26
2	Zdíkovský p.	1,08	2,2	639	81	2	17	-	45	20
3	Obecní p.	3,46	5,8	685	57	34	9	-	85	21
4	Cetvinský p.	2,88	4,7	689	52	48	-	-	97	55
5	Kabelský p.	6,00	6,8	848	93	7	-	-	112	14
6	Bělský p.	0,58	5,9	742	100	-	-	-	33	17
7	Jaroměřský p.	3,17	2,5	643	56	8	36	0,7	71	21
8	Malontský p.	1,96	3,7	672	8	6	85	1,4	72	23
9	Uhlišťský p.	2,56	7,5	869	100	-	-	-	117	13
10	Tisový p.	4,74	6,9	809	99	1	-	0,2	186	20
11	Mlýnský p.	4,44	6,2	878	97	3	-	0,1	23	13
12	Kohoutský p.	1,64	7,7	646	80	17	3	-	184	21
13	Krakovický p.	1,58	8,3	836	99	1	-	0,0	46	18
14	Budský p.	6,47	5,7	616	45	9	45	1,3	155	37
15	p. u Výhně-J	2,01	4,7	595	49	7	43	0,2	34	7
16	Chodečský p.	1,11	3,4	553	13	26	59	2,1	147	33
17	Chlumský p.	1,33	4,5	545	36	1	63	0,1	134	50
18	Dolnosvinenský	0,92	2,4	534	8	21	71	0,1	237	106
19	Černický p.	0,38	1,2	549	-	7	93	-	102	73
20	p. u Mojného	0,46	0,8	549	-	-	100	-	227	84

**urban, water courses and reservoirs*

3. Results and Discussion

3.1. Concentration and Mass fluxes at Pořešín Profile

Monthly average concentrations of TP varied to a great extent (24–260 $\mu g.l^{-1}$) within the detailed monitoring period. Increased concentrations were observed both in low discharge conditions, probably due to insufficient dilution of communal waste water (with consequent increase of DP concentration, Figure 1c) and during high discharges, when most of the TP was formed by high PP concentrations (for example during the flood in August 2002). Despite great fluctuations in monthly TP and DP concentrations the mean yearly values showed almost no variability with the exception of 2002, the year of extreme flooding (Table 2).

Figure 2. TP, DP Fluxes and concentrations at profile Pořešín–Malše: a, b – calculated mass fluxes gathered from diffuse and point sources; c, d – Volume weighted TP and DP concentrations measured at Pořešín against concentrations calculated from sum of modeled sources (TP.src, DP.src).

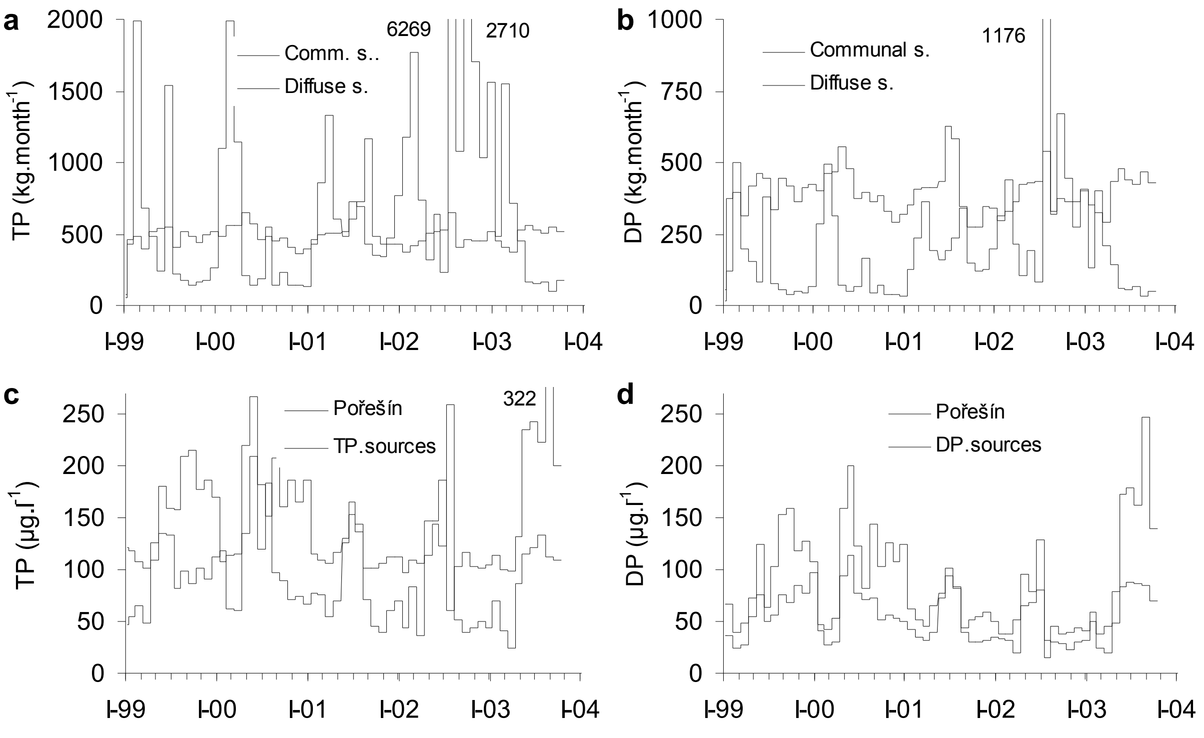

Table 2. Water temperature, P mass fluxes at Malše–Pořešín and export of P from sources in catchment. Average values and sums for half-year periods (vegetation and no vegetation season of each water year): T_w – water temperature, Q – discharge, Pořešín – measured P fluxes at hydrometric profile, Sources – computed export from both point and diffuse sources, Retention – difference between Sources and Pořešín, Diffuse s. – (percentage) portion of diffuse sources on total modeled export.

Period	T_w	Q	Pořešín, t		Sources, t		Retention, t		Diffuse s., %	
	°C	$m.s^{-1}$	VP	RP	VP	RP	VP	RP	VP	RP
I.99-IV.99	4,0	5,2	2,5	1,1	4,6	2,0	2,1	0,8	69	42
V.99-X.99	14,0	2,2	4,1	2,1	5,8	3,3	1,7	1,2	48	24
XI.99-IV.00	3,0	4,0	5,2	2,7	7,9	3,8	2,7	1,1	61	33
V.00-X.00	14,7	1,5	3,4	1,9	4,5	3,0	1,1	1,2	32	16
XI.00-IV.01	3,1	3,0	3,1	1,8	5,7	3,0	2,6	1,2	54	28
V.01-X.01	13,8	3,7	5,7	3,4	7,3	3,9	1,6	0,6	56	32
XI.01-IV.02	3,3	4,7	4,3	2,3	7,8	3,4	3,5	1,1	69	42
V.02-X.02	14,3	11,0	34,0	6,1	14,2*	4,9*	-19,8*	-1,2*	86*	55*
XI.02-IV.03	2,9	6,0	4,2	2,6	9,7	4,0	5,5	1,3	73	47
V.03-X.03	14,8	1,4	2,3	1,5	4,4	3,1	2,1	1,6	28	13

**Influence of flood in August 2002, values may be distorted as water samples were not taken in satisfactory frequency after the first culmination of the flood (device failiture), the regression models could not be verified for such extreme discharge situation.*

3.2. Diffuse sources:

TP and DP concentration in small streams without communal pollution ranged from 9,3 to 671 µg.l^{-1} and 4,4 to 281 µg.l^{-1} respectively (Figures 3-4, Table 1). High concentrations of TP were determined in particularly on the date of 7.8.2004 with a discharge of $\sim Q_{5\text{-year}}$ even in the catchments with a majority of forested area, where evidently both surface erosion processes on the steepest slopes, and bank erosion during rapid run-off had developed. Since steep agriculture catchments and flat forested catchment were not represented in the sample and this situation may be reflected in the TP relation to agriculture land ratio (Figure 3).

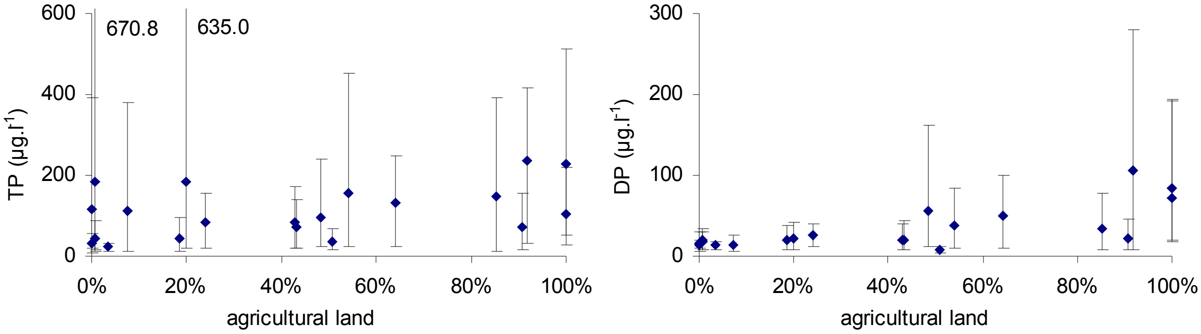

Figure 3. The relationship of TP and DP concentrations to the portion of agricultural land (arable land and pastures together; Table 1) in the catchment area, Points represent mean values and abscissae mark concentration range)

Simple regression models for individual P species (DRP, DNP, and PP) concentrations were generated on the basis of the above mentioned values. Constants, best predictors and model formulas with parameters of the fit between modeled and measured concentrations (Figure 4) are presented in Table 3. The DRP concentration model was based on the observed fact that during low flows (with base flow forming the major part) DRP concentrations did not changed with land use and showed only a limited oscillation around ~8 µg.l^{-1}, in contrast to high flows, when the increase in concentration was exponentially dependent on agricultural vs. forested land ratio.

DNP concentrations were strongly and positively correlated to DOM concentrations, that again fit tightly with temperature and discharge in the case of the Malše River (Hejzlar et al, 2003). The temperature term $\left(\frac{T_w+273}{273}\right)$ in the base number of the DNP model formula can characterize the extent of biomass production and in the exponent it can characterize the decay rate and P leaching potential.

The PP regression model seems to be less realistic due to its tendency to gross averaging in different situations of PP export, especially during low and high flows (Figure 4). Although more combinations of basic functions were tested, none had showed better results (Table 3).

We assume that the main reason for the fidelity lack of this model was the omission of the hysteresis effect the on P concentration–discharge relationship. Although several situations with clear hysteresis were observed at Pořešín, we lack the information about maxima and timing of peaks in small streams which would make reasonable modeling of PP diffuse sources and erosion processes possible.

Figure 4: Modelled versus measured Phosphorus concentrations (µg.l^{-1}). Various log scales

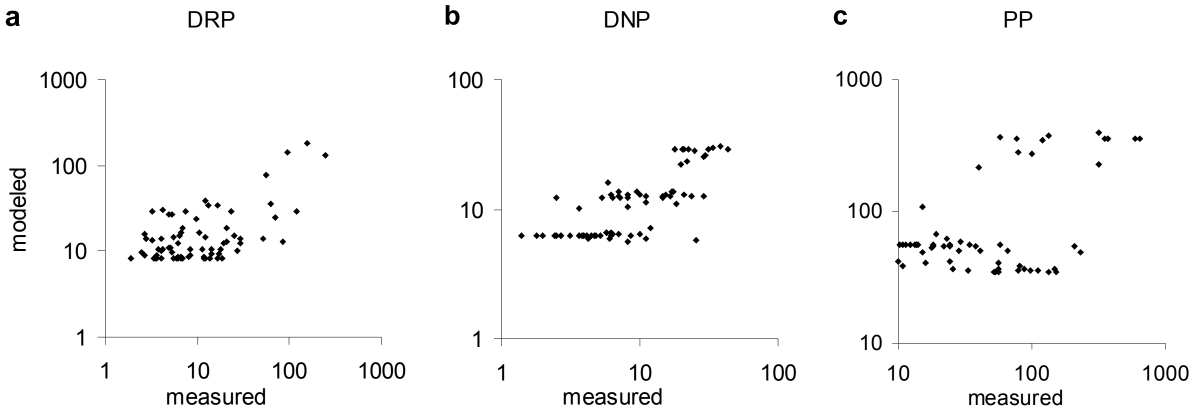

Table 3: The formulas of P concentration regression models (µg.l^{-1}), their coefficients and predictors: Q_s–specific discharge (l.km^{-2}.s^{-1}); Z- agriculture land ratio; T_w – water temperature at Pořešín; a,b,c – model coefficients; r^2 – coefficient of determination: AME – absolute mean error of the model.

Model	a	b	c	r^2	AME
$RRP = a + bQ_s^{(cZ/100)}$	3,86	4,42	0,98	0,61	14,02
$RNP = \left(\frac{T_w+273}{273}\right)^a + Q_s^{\,b\frac{T_w+273}{273}}$	33,02	0,56	-	0,63	4,5
$PP = a + bQ_s$	30	1,53	-	0,39	67,57

Volume weighted monthly concentrations of P export from diffuse sources ranged between 48–119 µg.l^{-1}, with an average of 66 µg.l^{-1} for TP, and 10-29 µg.l^{-1}, with an average of 19 µg.l^{-1} for DP respectively. These values were very low in comparison to concentrations at the Porešín profile, which demonstrates the limited influence of agriculture on increase of natural background concentrations (Figure 3).

3.3. Communal sources

The DP load from WWTPs oscillated between 3,3–15 kg.d^{-1}, with an average of ~7,7 kg.d^{-1} (i.e. ~2,8 t.y^{-1}). The mean DP export from the population without access to the WWTP under evidence (48% of inhabitants in the Malše Basin) was determined as 8,0 kg.d^{-1} (i.e. 2,9 t.y^{-1}), and the relative contribution of Austria was ~3,5 kg.d^{-1}. The relative contribution of communal sources to the total sources in the Malše Basin increased rapidly in the months with low flow conditions, when it reached up to 85%. On the other hand the percentage of communal sources dropped to less than 10% at high flow events (Table 2).

3.4. Retention processes

Calculated TP retention in the river network ranged from 20 to 2110 kg per month during the whole monitoring period. However, in three cases the export of TP exceeded the sources in the catchment (II.2000, VIII.2000 a VIII.2002 – Figure. 2). DP and PP showed different behavior during the season. Mean annual retention of DP was relatively stable with the exception of the year 2002 (table 2). A negative correlation between DP retention and discharge was found for the months of vegetation season (V-X) and for monthly discharges $Q_m<10$. The observed relationship was significant both for absolute retained DP mass ($r^2=0,33$; $p<0,001$), when the retention extent dropped from 270 kg per month at mean discharge ~1 m^3.s^{-1} to values below ~1 kg at discharge 5–10 m^3.s^{-1}), and for the relative portion of retention on total sources of DP ($r^2=0,49$; $p<0,001$), when the values decreased from 50% to below 1% of DP sources, with the same change of mean discharge as mentioned above. In non-vegetation months no correlation between discharge and retention was observed and the retention values oscillated slightly around 250 kg (i.e. 36 % of DP sources) during whole time.

We suppose that sorption in stream beds and banks and the uptake of riparian cover are the main retention processes. Retention of PP was strongly and positively correlated to discharge and its values ranged from export of 290 kg.month^{-1} to retention of ~1,8 t.month^{-1}. Most of the erosion particles were exported certainly during high flow. These suspended particles were usually transported until the flux velocity decreased in the accumulation parts, or until the river overflowed. However, the highest calculated export rates of PP from sources (and thus its higher retention) were also influenced by the nonrealistic behavior of PP model (Figure 4).

4. Conclusions

Malše Basin's natural background concentration was very low especially for dissolved phosphorus forms (DRP ~8 μg.l^{-1}, DP 14 μg.l^{-1}), but the PP concentrations values increased rapidly with discharge to hundreds of μg l^{-1} as a consequence of erosion events on the steepest slopes of the mountainous part of catchment. Diffuse sources contributed significantly to the total exported mass of TP (PP), but their influence on increasing the DRP and DP background concentration values was almost neglible. The contribution of the communal sources to the river network load was 40% and 65% for TP and DP respectively. The Percentage of communal sources displayed of distinct seasonality and reached 85% of TP and 94 % DP in dry periods. The comparison of P export from sources with P mass fluxes at Pořešin profile demonstrated the great retention extent of TP and especially DP in the river network. About one third of P released from sources in the catchment was retained in the river network in periods, whose discharge was close to long-term average values.

5. Acknowledgments

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