

Urban Streamwater Contamination and Self-purification in a Central-Eastern European City. Part B

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Self-purification is a frequent phenomenon for Suceava River in the homonymous city. Self-purification is documented for $N - NH_4^+$, $N - NO_2^-$, $N - NO_3^-$, Total Nitrogen (TN), Total Phosphorus (TP) and SO_4^{2-} . During the 2006-2011 time interval, the monthly average self-purification percentages were: 18.7% $N - NH_4^+$, 36.3% $N - NO_2^-$, 14.4% $N - NO_3^-$, 12% TN, 35.4% TP, 11.96% SO_4^{2-} (2 sampling points: upstream and downstream the city). The main factors that contribute to the observed self-purification are: the iron-rich streamwater, the sedimentary and biological retention, the co-treatment of different contaminated waters and the hydraulic jumps. There are seasonal variations in average and maximum monthly self-purification percentages. When the water pollution is higher, the self-purification process is stronger.

Keywords: nutrient, self-purification, co-treatment, seasonal differences

There are numerous papers describing the water chemistry of Romanian surface waters [1-4]. However, the Romanian hydrological literature lacks papers describing self-purification events on the local streamwaters, even if, up to date, there are numerous papers documenting streamwater self-purification mechanisms in the international literature [5, 6]. Many of these studies focus on heavy metal [7] and nutrient [8, 9] removal by water self-purification.

Suceava River receives numerous polluted urban waters and, in Suceava city area, has a proper monitoring network that fulfills the international standards. The river divides the administrative area of the homonymous city and is a second order tributary of Danube. While Suceava River has a flow of at least 4 m³/s (17.47 m³/s average discharge during 1966-2011 at Itcani gauging station (Suceava city)), its urban tributaries collected within the city area have average discharge values ranging from 0.05 to 0.2 m³/s.

The objective of the present study is to prove the existence of a strong and persistent self-purification phenomenon on Suceava River and to propose the most appropriate hypotheses which could explain the observed streamwater self-purification.

Experimental part

We analysed the following parameters: Total Phosphorus (TP), Total Nitrogen (TN), nitrogen from azotate ($N - NO_3^-$), nitrogen from azotite ($N - NO_2^-$), nitrogen from ammonium ($N - NH_4^+$) and sulfate (SO_4^{2-}). These parameters were obtained from the *Romanian Waters* National Administration which provided data consisting of water quality analysis results for Suceava River, obtained in a laboratory meeting the SR EN I.S.O./CEI 17025:2005 requirements. The hydrological data for Suceava River were acquired from Itcani gauging station which is located

within the built-up area of Suceava city (for river discharge) and from Tisautii (T) and Mihoveni (M) sampling points (official sampling points for water quality analysis; M is located upstream the city, while T is downstream). The *Romanian Waters* National Administration also provided data regarding the discharge, TN and TP of the city's Wastewater Treatment Plant (WTP) effluent. The official data analysed in this study refers to the 2006-2011 time interval.

Results and discussions

We used data from the *Romanian Waters* National Agency in order to calculate the 2006-2011 monthly average concentrations of contaminants on Suceava River in M and T and for the partially treated wastewater (W) discharged into Suceava River by WTP.

The Total Phosphorus (TP) and the Total Nitrogen (TN) of M, T and W were converted from mg/L in g/s by using the river discharge values in M and T and the W discharge. Considering the fact that, between M and T, Suceava River collects several tributaries (Dragomirna River, Cetatii Creek, Scheia River and other minor urban tributaries), which are highly contaminated with nutrients (Part A), (M+W)/T must be <1 or almost equal to 1, if the tributaries have low contamination (albeit they never had concentrations below those of M). Table 1 shows that in some months the ratio is clearly above 1, therefore there is a lack of nutrients in T compared to the inputs from upstream. Consequently, we may assume that the cause for this is the self-purification phenomenon. Average monthly (M+W)/T for TP of the Suceava River in T is 1.42. The historical recorded minimum is 0.28, whereas the historical recorded maximum is 22.7. For TN, the values of (M+W)/T for monthly average, recorded minimum and recorded maximum are 0.85, 0.53 and 1.31, respectively. (M+W)/T is greater than 1 for TP in

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41.7% of months from 2006-2011 and in 27.1% cases for TN. The W discharge accounts for roughly 50% (approx. 0.3 m³/s) of the difference between the discharge values of Suceava River in T and M. The remaining 50% is represented by the input from urban and suburban tributaries and groundwater output. Data from other studies corroborate the occurrence of highly contaminated groundwater in Suceava city and its surrounding areas [10-12]. According to ACET, the company managing Suceava city wastewaters, in 2010 - 2011, some percentage of sewers and water supply pipes were as old as 100 years in some areas, whereas the majority were 50 years old. Groundwaters were heavily contaminated by leakages from the old sewage network, to such an extent that in some quarters the groundwater level has risen (combined with leakage from the water supply network), thus generating new springs in the respective areas. Within the study area, in the absence of rainfall, the groundwater recharges the rivers, therefore we may assume that the average TP and TN concentrations of Cetatii, Dragomirna and Scheia streams are representative for the remaining minor tributaries of Suceava River. If, for these tributaries, the measured PO₄³⁻, N - NO₃⁻ and N - NO₂⁻ (part A) are converted into mg/s (for TP and TN calculation), the following results are obtained: 81.4 mg/s N - NO₃⁻, 13 mg/s N - NO₂⁻ and 66 mg/s P - PO₄³⁻. TP measured from tributaries represents 8% of TP from wastewater (mg/s), while TN represents 2%. Because TN and TP are not composed only of N - NO₃⁻, N - NO₂⁻ and P - PO₄³⁻, the occurrence of self-purification is to be considered for ratio values slightly below 0.97 and 0.998: (M+W)/T < 1-0.03 for TP and < 1-0.002 for TN. Using the new values, the months with self-purification for TP represent slightly more than the previous 44.4% of the total number of months showed in table 1. Streamwater self-purification does not occur continuously, but is a discontinuous phenomenon in space and time [5].

Average self-purification percentages of TP based on $|T-(M+W)|/(M+W)$ are 35.4%; 12% for TN; 14.4% for N - NO₃⁻ and 36.3% for N - NO₂⁻ (fig. 1.a, b, c, d). N - NH₄⁺ was measured on a daily basis until December 2010 inclusively, and subsequently on a monthly basis, similar to the other analyzed parameters. The average N - NH₄⁺ self-purification is 18.7% in 2006-2011 (fig. 1.e) and 18.6% in 2006 - 2010. The minor difference between self-purification estimation based on monthly measurements and self-purification estimation based on daily measurements indicates that the monthly-based self-purification values for the other

analyzed parameters are representative. Maximum self-purification is 95.5% for TP, 32.3% for TN, 45.7% for N - NO₃⁻, 86.7% for N - NO₂⁻ and 68.7% for N - NH₄⁺ (for N - NH₄⁺, the maximum occurred during the 2006-2010 period). In some cases, streams with streambeds rich in sediments and algae are able to cause up to 99.5% N - NH₄⁺ and 97% P - PO₄³⁻ average self-purification [8] or 77% N - NO₃⁻ and 65% N - NO₂⁻ average self-purification, according to Schulz and Bischoff [13]. Suceava River has a natural riverbed composed of sand, pebbles and clay and the aquatic vegetal life is present, all of these supporting the enhanced self-purification capacity of the river.

The maximum WTP discharge occurs at 8 a.m., when the discharge is double than the average; the sudden increase in the morning is an effect of the initiation of human activities and is followed by a slow decrease during the following hours. The measurements made in Tisauti by the *Romanian Waters* National Agency took place in various time frames from 9 to 11 a.m. Suceava River average stream velocity is 0.5 m/s at low discharge (~4 m³/s), thus the maximum time for the WTP peak discharge to arrive in Tisauti is approximately 1.5 h. Thus, all measurements in Tisauti were performed during the passing discharge peak of the WTP or on the descending slope of the same peak. Therefore, the self-purification values calculated previously are a minimal assumption.

TP retention is caused by macrophytes [13], microphytobenthos [14] and wood debris [15]. Burkholder [16] states that suspended sediments readily adsorb phosphate. Suspended solids provide nuclei for the formation of iron flocs - when iron oxy-hydroxides (ochre) precipitate, phosphorus is removed from water via sorption onto iron precipitates [17-19]. By observing the co-treatment of 2 different contaminated waters, Johnson and Younger [20] observed that phosphorus removal mirrors iron removal - this explains why measurements on Fe showed a strong and continuous decrease of iron concentrations from point A to point C (part A). The high concentrations of Fe in Suceava River are constant and have natural causes [21], i.e. the upstream and local catchment geology. The abundance in iron indicates higher self-purification capacity of the streamwater. Moreover, ochreous deposits are ideal site for the attachment of denitrifying bacteria [20, 22]. On Suceava River, iron-rich waters also imply the existence of TN self-purification, as previously calculated. In some instances, mixing waters with different contamination sources can result in self-purification of the combined volume; it is the case of

a.	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
2006	1.49	2.66	1.24	0.92	0.40	0.78	1.00	0.80	0.71	3.21	0.88	22.70
2007	2.47	1.33	0.87	0.55	1.19	1.74	2.02	0.58	1.87	0.90	0.69	0.93
2008	0.95	1.17	0.28	0.67	0.45	0.59	1.61	1.12	1.08	1.49	0.97	3.59
2009	0.69	0.33	1.36	0.79	1.23	0.65	1.49	3.39	0.97	0.92	1.06	0.60
2010	0.95	0.36	1.31	0.40	0.90	0.54	0.90	1.24	0.56	0.51	1.01	0.80
2011	0.67	1.20	0.59	0.53	1.77	0.32	0.38	3.39	2.66	0.64	0.65	0.56
avg	1.20	1.18	0.94	0.64	0.99	0.77	1.23	1.75	1.31	1.28	0.88	4.86
min	0.67	0.33	0.28	0.40	0.40	0.32	0.38	0.58	0.56	0.51	0.65	0.56
max	2.47	2.66	1.36	0.92	1.77	1.74	2.02	3.39	2.66	3.21	1.06	22.70
b.	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
2008	0.74	0.87	0.92	1.05	0.87	0.76	0.98	1.17	0.96	0.97	0.61	0.75
2009	1.03	0.89	0.73	0.96	0.76	0.44	0.65	1.02	1.13	0.68	0.90	0.92
2010	0.86	0.67	1.10	0.43	0.43	0.52	0.88	1.02	0.49	0.79	1.04	1.08
2011	0.96	0.78	0.79	1.07	1.13	0.78	0.61	1.01	0.87	1.31	0.73	0.72
avg	0.90	0.80	0.89	0.88	0.80	0.63	0.78	1.05	0.86	0.94	0.82	0.87
min	0.74	0.67	0.73	0.43	0.43	0.44	0.61	1.01	0.49	0.68	0.61	0.72
max	1.03	0.89	1.10	1.07	1.13	0.78	0.98	1.17	1.13	1.31	1.04	1.08

Table 1
MONTHLY (M+W)/T RATIO AT T FOR
TP (a) AND TN (b)

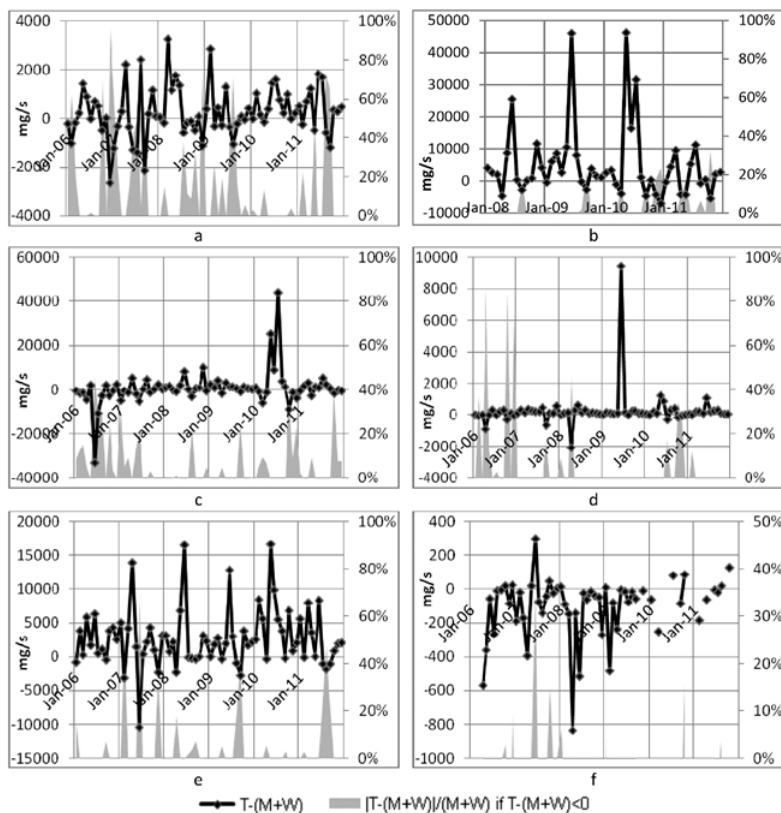


Fig. 1. Self-purification evolution of TP (a), TN (b), $N - NO_3^-$ (c), $N - NO_2^-$ (d), $N - NH_4^+$ (e), SO_4^{2-} (f)

wastewaters rich in suspended particles which meet wastewaters rich in iron, causing iron flocculation, with phosphate removal [20]. Wastewater from WTP and Cetatiu Creek are rich in suspended particles (40.5 mg/L in T); suspended solids from WTP certainly create numerous nuclei for the formation of iron flocs.

By analyzing the months with contamination values above the multiannual mean of each month (55.6% cases), we observed that self-purification occurs in 57.5% of over-contamination cases for TP; 71.9% self-purification cases occurs during over-contamination. For TN, over-contamination occurs in 52.1% of months and self-purification occurs in 36% cases of over-contamination; 69.2% self-purification occurs during over-contamination. During over-contamination, contaminants' concentration in T is often significantly higher than in M; however, the values are not the ones we would expect when calculating just the contaminant input into the river. Higher contaminant input means higher self-purification ratio (more chemical and biological processes) because the over-contamination does not reach the upper self-purification limit.

Most frequently, self-purification occurs in February, July, August and September (50% altogether, equally distributed) for TP and in August (30.77%) and April (15.38%) for TN. The highest degree of self-purification occurred in December for TP, whereas for TN it is highest and more frequent in August. Wagenschein and Rode [23] observed that denitrification depends on the temperature, as denitrifying bacteria have lower activity in the cold season. The analysis of the average self-purification ratio (2006 - 2011) showed that the cold season has a higher (M+W)/T ratio (1.72 TP, 0.87 TN) than the warm season (1.12 TP, 0.83 TN). The average ratio of the maximum monthly ratio (for each month of the year) has the same behavior (TP: 5.58 = cold season, 2.08 = warm season, TN: 1.07 = cold season, 1.04 - warm season). The amplitude of ratio values and self-purification are higher for TP. Klotz [24] also observed that the concentration of phosphate changes

seasonally due to various factors, such as the decomposition rates or the temperature, and that phosphate concentration is higher in summer (implying lower TP self-purification).

The self-purification cases occur preferentially during the warm season for TN (61.5%), while TP has a balanced ratio (50%). The cause for the greater number of TN self-purification instances during the warm season is the favourable temperature, which enhances the activity of denitrifying bacteria. August is the month with the highest water temperature (21.05°C) of Suceava River in Tisauti, followed by July (19.97°C), June (16.97°C) and September (16.42°C). P uptake by plants is also greater in the warm season. The water temperature also results in different dissolved oxygen concentrations, i.e. 11.1 mg/L in the cold season and 8.6 mg/L in the warm season in Tisauti. Low oxygenation causes a decrease in the aerobic processes which remove P and N from the water. Moreover, in Suceava city there are hydraulic jumps of Suceava River caused by the structures built to protect Itcani and Burdujeni bridges. Along with the hydraulic jump of Mihoveni Dam, the former create local high water aeration resulting in water self-purification. The hydraulic jump of Mihoveni Dam is created by 3 consecutive man-made waterfalls; the main one is 4 m high, whereas the next two ones amount to 1.5 m together. Itcani hydraulic jump is created by the protective structures of Itcani Bridge and represents a 4 m-high man-made waterfall. Burdujeni Bridge has some of its protective structures against river regressive erosion 1 km downstream. The hydraulic jump is created by a main 2 m waterfall and three consecutive waterfalls adding up 2 m together. The higher water oxygenation during the cold season, combined with the existence of the hydraulic jumps, generates higher P and N removal during the cold season.

Just 0.1 km downstream of the Burdujeni Bridge hydraulic jumps there is the outlet of the partially treated wastewater from AMBRO, the largest Romanian manufacturer of paper for corrugated cardboard. Pulp and paper mills introduce high bacterial abundance and

biomass concentration into a river, leading to microbial self-purification of TN and TP [6]. AMBRO certainly has a contribution to the P and N removal from Suceava River. Also, the wastewater from paper mills increases the amount of solids in rivers [25]; the additional solids from AMBRO also provide nuclei for the formation of iron flocs, removing P from water.

Sulfate reduction modifies the streamwater nutrient load indirectly because sulfide, produced by sulfate reduction, interferes with iron-phosphate from sediments, releasing phosphate in freshwater and forming iron sulfides [26-28]. The sulfate (M+W)/T ratio between 2006-2011 is 0.93 in the cold season and 0.92 in the warm season. Ratio values above 1 occur in 66.7% of cases during the cold season. Sulfate self-purification is less visible and has an average value of 11.96% average and 40.19% maximum (fig. 1.f). The anaerobic biological processes of sulfate reducing bacteria that produce biogenic sulfides (very insoluble precipitates) do not occupy important sectors alongside Suceava River as a result of the existence of hydraulic jumps. However, an increased supply of sulfate may lead to sulfide toxicity to the roots of aquatic plants [29], explaining why P self-purification is often present in the warm season, but not as efficient as in cold season. If sulfide can significantly affect P and N uptake by plants, it does not have the same effect on the sediment capacity to purify water in an iron-rich environment. This is also the conclusion of Zak et al. [30] after studying River Spree, Germany, where they observed that there is no significant increase of P through formation of metal sulfides in streamwater because there is enough ferrous iron at the interface between water and sediment to effectively retain P through iron precipitates.

Conclusions

The self-purification capacity of Suceava River is very high, as proved by the monthly maximum self-purification percentages: 68.7% N - NH₄⁺, 86.7% N - NO₂⁻, 45.7% N - NO₃⁻, 32.3% TN, 95.5% TP, 40.19% SO₄²⁻. There are seasonal variations in the self-purification occurrence and intensity. The iron-rich streamwater has probably the most important impact on the self-purification process. Higher contaminant input implies higher self-purification ratio, suggesting that contamination did not reach the upper self-purification limit.

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