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Original Research

Changes in Stream Water Contamination in Select Slovakian Settlements

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Abstract

This article presents the results of concentrations of N-NO_2, N-NO_3, Cl^-, SO_4^{2-}, P-PO_4, N-NH_4, Fe, chemical oxygen demand with $KMnO_4$, HCO_3^-, P_{total}, acid neutralizing capacity between the pH range of 4.5 and 3.5 along with pH and electrolytic conductivity for Štiavnica Stream (in south-central Slovakia). These parameters were monitored at four monitoring places (Banská Štiavnica, Svätý Anton, Prenčov, and Hontianske Nemce) from 2006 to 2008. The rank order of soluble nitrogen forms on the basis of median values were in Banská Štiavnica N-NH_4>N-NO_2>N-NO_3, in Svätý Anton, Prenčov and Hontianske Nemce N-NO_3>N-NH_4>N-NO_2. The concentration of phosphates phosphor was high in all sampling places, with the highest in Banská Štiavnica (0.29 $mg \cdot L^{-1}$). Physico-chemical parameters such as pH were in the interval from 6.52 to 7.93, electrolytic conductivity and chemical oxygen demand were highest in Banská Štiavnica (EC = 51.51 $mS \cdot m^{-1}$, COD_{Mn} = 10.46 $mg \cdot L^{-1}$). The aim of our article is to prove, according to our analyses, that surface water quality has gotten worse and to point out the importance of monitoring smaller streams that are permanently contamined by local settlements.

Keywords: stream water, settlement, physical-chemical analysis, contamination

Introduction

There is a number of watercourses and lakes in the Banská Štiavnica area used mainly for watering purposes or by resorts [1]. The most important surface flowing water is Štiavnica Stream flowing into the Ipeľ River. Monitoring the water quality is Slovak Water Management Company (SWMC), while small watercourse monitoring is often underestimated. With continuous sustainable development it is inevitable that it is critical to monitor smaller watercourses [2], especially when they flow through rural settlements because they might be the greatest contributors of large watercourse pollution [3-5]. Anthropogenic processes (higher consumption of water resources, agricultural [6] and industrial activities) [7-10] influence river and stream water quality. Changes in the physical-chemical characterics of water quality are influenced not only by anthropogenic processes [6, 11], but also by natural processes such as hydrological conditions, topography and lithology, climate, precipitation inputs [12, 13], and catchment area [14], in combination with environmental influence.

The aim of the work is to evaluate, on the basis of our regular analysis, the quality of water [15], natural and anthropogenical sources of Štiavnica Stream contamination originating in rural settlements and to evaluate possibilities of natural self purification. The physical-chemical analysis [16] resulted in the water quality classification changing to group III-IV (Table 1).

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Table 1. Classification of surface water quality [17, 18].

STN 75 7221**							296/2005*
Indicators of water quality	Symbol	Unit	The Classification of surface water quality				Recommen. value
			I	II	III	IV	
Chemical Oxygen Demand with $KMnO_4$	CODMn	[$mg \cdot L^{-1}$]	<5	<10	<15	<25	15
Reaction pH	pH		6.5-8.0	8.0-8.5	6.0-6.5 8.5-9.0	5.5-6.0 9.0-9.5	6.5-8.0
Electrical Conductivity	EC	[$mS \cdot m^{-1}$]	<40	<70	<110	<160	-
Iron	Fe	[$mg \cdot L^{-1}$]	<0.5	<1.0	<2.0	<3.0	2
Chlorides	Cl^-	[$mg \cdot L^{-1}$]	<50	<200	<300	<400	200
Sulphates	SO_4^{2-}	[$mg \cdot L^{-1}$]	<80	<150	<250	<300	250
Ammonium nitrogen	$N\text{-}NH_4$	[$mg \cdot L^{-1}$]	<0.3	<0.5	<1.5	<5.0	1.0
Nitrate nitrogen	$N\text{-}NO_3$	[$mg \cdot L^{-1}$]	<1.0	<3.4	<7.0	<11.0	5.0
Nitrite nitrogen	$N\text{-}NO_2$	[$mg \cdot L^{-1}$]	<0.01	<0.03	<0.1	<0.3	0.02
Phosphates phosphor	$P\text{-}PO_4$	[$mg \cdot L^{-1}$]	<0.05	<0.1	<0.2	<0.5	-
Phosphor total	P_{total}	[$mg \cdot L^{-1}$]	<0.1	<0.2	<0.4	<1.0	0.4

* Regulation of Government SR No. 296/2005 Coll. [17].
** Slovak National Standard STN 75 7221 "Surface water quality". According to STN 75 7221 surface waters are classified into five quality grades: I. – very clean water, II. – pure water, III. – polluted water, IV. – heavily polluted water, V. – strongly polluted water [18].

Methods

Samples of the water were taken from four locations – where the stream leaves the territories of Banská Štiavnica, Svätý Anton, Prenčov and Hontianske Nemce. Sampling was performed in one-week intervals below the surface in the middle of the stream; 62 samples were taken from each monitored place during the period from 2006 to 2008 (Fig. 1).

Analyses of the samples were performed within 24 hours after sampling.

Hydrogencarbonates were determined by calculation from the values of acid-neutralizing capacity up to pH 4.5. Acid neutralizing capacity ($ANC_{4.5}$) is determined by titration of the sample by HCl standard solution (0.1 $mol \cdot L^{-1}$). Chlorides were determined by the method of flow injection analysis, using a wavelength of 480 nm. Indicators of sulfates and nitrates nitrogen were determined isotachophoretically, nitrites nitrogen were determined spectrophotometrically using a wavelength of 520 nm. Ammonium nitrogen was determined photometrically, using wavelength of 425 nm. Iron was determined photometrically, with thiocyanate and wavelength of 500 nm. A MultiLine P4 device was used for pH values and specific conductivity measurements. Kubel´s titration method was used to determine potassium permanganate's oxygen consumption. The values of phosphates phosphor and of total phosphor were determined photometrically using a wavelength of 690 nm.

Processing the digital map in GIS [19] was performed using basic software: IDRISI, GEOMEDIA, MICROSTATION, and IRASB. Digital model of the terrain, maps of

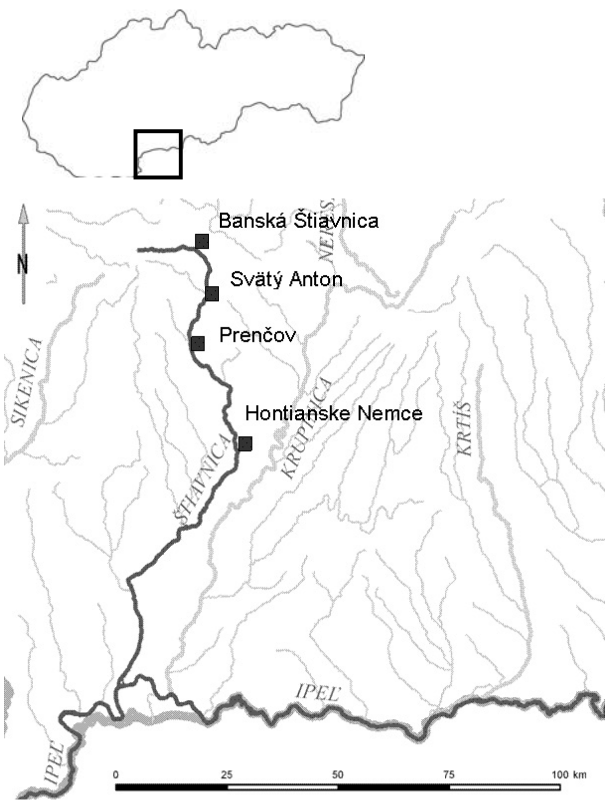

Fig. 1. Location of the Štiavnica Stream catchment and monitored places.

orientations and slopes, maps of hypsometry (Fig. 2), sun power and of derivative countryside structure were designed.

Study Area

River network development was influenced by the overall nature of the Štiavnica Mountains as an oval polymorphic elevation. All the watercourses located in the Štiavnica Mountains are relatively short, showing very low average annual flow-rates. According to their hydrological regime they belong to the hilly type, reaching maximal flow-rates in March and April.

The Štiavnica Mountains Channel network is part of the Hron River basin. Watercourses bringing water into the Hron are relatively short and create a fan-shaped river network (e.g. Teplá, Jasenica). Watercourses flowing on southern slopes, having relatively low gradients as well as larger distances between their sources and confluence with the Ipeľ, might have created a more complex fan-shaped channel network due to erosion effects. For example Krupinica Stream, Klastavský Stream, and Štiavnica Stream. They are mainly supplied by rainfall and snowfall, with the largest flow in the spring because of snow melting and the smallest at the end of summer because of the little rainfall and great evaporation. The watercourses do not reach highest flow rates in the rainiest periods because air temperatures are the highest in those months, causing evaporation or consumption by vegetation.

Generally speaking, the Štiavnica Mountains are created by calorific rocks containing little water and by relatively warm climate have little surface water. About one third of annual rainfall flows away, thus specific outflow of the watercourses of the Štiavnica mountains is low.

The riverbed of Štiavnica Stream is relatively narrow and canalized at the beginning of the flow (the area of Štiavnické Bane, Štefultov, and Banská Štiavnica) but in the further part of the stream the riverbed gradually widens (Svätý Anton, Hontianske Nemce). The stream bottom has a natural character. The impact of human activity is evident on the stream, e.g.: riverbanks were fixated, bridges were built, flow regulation was done. Štiavnica Stream has a lot of tributaries all over its length.

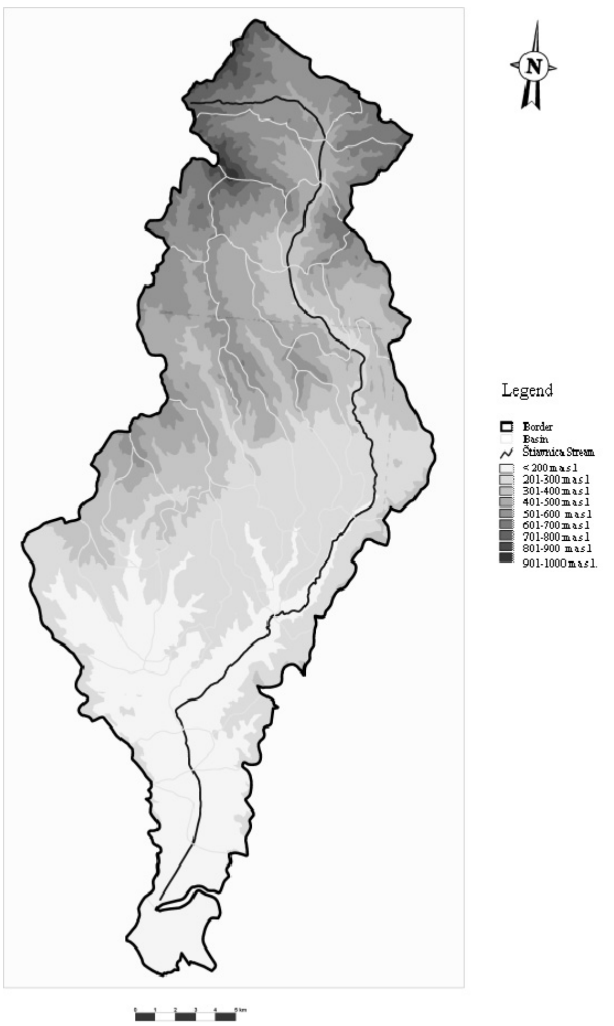

Fig. 2. A hypsometric map of the Štiavnica Stream.

Sources of Contaminants in the Area

Anthropogenic pollution of the stream was monitored 20 km from the source down to Hontianske Nemce. The stream itself has a large number of tributaries that impact water quality, because part of the tributaries are located in the Štiavnica Mountains Protected Landscape Area, therefore water is influenced by geological subsoils in this area.

Point Contaminants

Waste – to a large extent the water in Štiavnica Stream is polluted and contaminated by the effect of illegal waste dumps. Unpolluted parts of the stream can only be found closest to the headwaters. As Štiavnica Stream gradually flows through villages and inhabited parts, its water gets polluted by home waste (e.g. glass and plastic bottles, papers, covering material from milk and other foods) and by other waste such as various plastic materials, tyres, metal pipes, clothing, shoes, not excluding dead animals. In addition to the impact of climatic conditions together with raising water surface and faster water flowing, the waste is gradually extended along the whole length of the stream. All waste dumps in Štiavnica Stream are illegal. The area is used as a holiday resort with plenty of houses pouring sewage straight into the stream.

Industry – not located in the surroundings.

Agriculture – there are a number of cooperative farms and smaller family farms keeping animals or growing forage plants that contaminate the water illegally.

Line Contaminants

Transport – nearly all of Štiavnica basin spreads along a second-class road – II/525. The stream is mainly threatened by fuel or oil leakage and by air pollutants from fumes. In the winter it is threatened by chemicals spread on

Table 2. Arithmetic average (x), standard deviation (SD), min. and max. values of physico-chemical indicators from sampling places (2006-08).

Monitor locations	Banská Štiavnica				Svätý Anton			
Indicator places	x	SD	Min	Max	x	SD	Min	Max
pH	6.80	0.1993	6.52	7.86	6.78	0.0774	6.62	6.98
*EC	51.51	8.0063	40.50	75.50	17.34	0.4927	16.20	18.30
** $ANC_{4.5}$	3.90	0.5868	2.25	4.33	2.83	0.3103	2.10	3.50
***$N\text{-}NO_2$	0.12	0.0267	0.06	0.19	2.00	0.1184	1.67	2.18
***$N\text{-}NO_3$	2.77	1.555	1.16	6.45	7.08	0.4197	5.80	8.26
***Cl^-	35.95	8.3886	20.00	47.20	21.55	1.9568	17.30	24.80
***SO_4^{2-}	116.78	15.8467	84.00	141.00	123.79	6.2962	110.00	136.00
*** $P\text{-}PO_4$	0.29	0.0762	0.14	0.41	0.26	0.0091	0.23	0.27
***$N\text{-}NH_4$	5.50	3.0752	0.02	9.46	3.91	0.8637	2.54	5.23
***COD_{Mn}	10.46	1.8802	6.45	12.50	6.23	0.4511	5.20	8.84
***Fe	0.81	0.2799	0.21	1.06	0.93	0.1557	0.59	1.85
***HCO_3^-	238.04	35.7361	137.20	264.10	172.38	18.9625	128.10	214.00
**P_{total}	0.30	0.0676	0.15	0.38	0.25	0.0213	0.20	0.29
****A-254	0.34	0.0087	0.33	0.35	0.16	0.0023	0.15	0.16

* Electrical Conductivity (EC) results presented in $mS \cdot m^{-1}$;
** results presented in $mmol \cdot L^{-1}$;
*** results presented in $mg \cdot L^{-1}$;
**** results presented in nm;
$ANC_{4.5}$ = Acid Neutralizing capacity between the pH range of 4.5 and 3.5;
COD_{Mn} = Chemical Oxygen Demand with $KMnO_4$.

the roads. The average values of vehicle frequency monitored showed the majority were private cars and lorries.

Results and Discussion

Water quality was monitored in 2006 to 2008. Water quality in Štiavnica Stream was evaluated on the basis of regular analysis of chosen indicators. Results of determined indicators from individual samplings are included in the following tables (Tables 2-3), for each place of sampling, respectively.

It can be inferred from the abovementioned results that chosen indicators did not exceed the limit of the standard, except for the following groups:

There is an increased amount of nitrites nitrogen, nitrates nitrogen, ammonium nitrogen and phosphates phosphor in the Štiavnica. Concentrations of most contaminants exceed limited value of I and II class, determined pursuant to standard according to Government Regulation of the Slovak Republic No. 296/2005 Coll. (Fig. 3).

Nitrites nitrogen enter the waters as the products of ammonium biochemical oxidation, or as products of reduction of nitrates. The waste waters and sewage originating from homes are mainly the source of nitrites nitrogen. The recommended values of nitrites nitrogen concentration in water were exceeded on each sampling place. The increase of concentration is apparent on the sampling place where the flow leaves Svätý Anton with a concentration almost 10 times higher than values detected in other sampling places of the Štiavnica.

Nitrates nitrogen concentration in the water in the sampling places in Banská Štiavnica does not exceed the recommended limit, but it gradually increases in the sampling place Svätý Anton, where it exceeded the standard in the

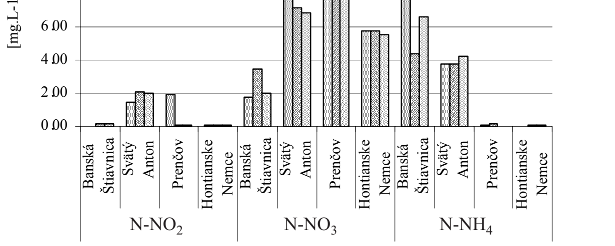

Fig. 3. The values of concentrations in water samples from monitored places.

Table 3. Arithmetic average (x), standard deviation (SD), min. and max. values of physico-chemical indicators from sampling places (2006-08).

Monitor locations	Prenčov				Hontianske Nemce			
Indicator places	x	SD	Min	Max	x	SD	Min	Max
pH	6.73	0.0899	6.52	6.95	7.02	0.1959	6.75	7.93
*EC	49.69	1.3979	47.70	53.20	42.65	1.8393	39.60	47.60
**$ANC_{4.5}$	2.51	0.1734	2.11	2.96	0.31	0.6761	0.05	2.80
***N- NO_2	0.09	0.0196	0.03	0.12	5.22	1.5808	0.05	6.45
***N-NO_3	9.71	1.2433	7.45	11.60	20.84	4.7134	5.12	26.60
***Cl^-	23.50	1.7836	19.60	27.50	86.20	19.4593	20.10	101.00
***SO_4^{2-}	98.17	3.6717	90.80	115.00	7.77	25.6771	0.14	96.40
*** P-PO_4	0.22	0.0334	0.15	0.26	0.17	0.0374	0.02	0.26
**N-NH_4	0.10	0.0614	0.02	0.26	6.34	1.8853	0.02	7.29
***COD_{Mn}	3.63	0.2328	3.10	4.02	0.85	1.8538	0.21	7.23
**HCO_3^-	0.41	0.0642	0.27	0.69	164.77	53.9415	0.22	223.80
***Fe	153.12	10.5750	129.00	180.50	12.84	42.9122	0.11	170.80
***P_{total}	0.24	0.0223	0.20	0.29	0.17	0.0218	0.11	0.22
A-254nm	0.12	0.0013	0.12	0.12	2.70	0.8419	0.16	3.67

* Electrical Conductivity (EC) results presented in $mS \cdot m^{-1}$;
** results presented in $mmol \cdot L^{-1}$;
*** results presented in $mg \cdot L^{-1}$;
**** results presented in nm;
$ANC_{4.5}$ = Acid Neutralizing capacity between the pH range of 4.5 and 3.5;
COD_{Mn} = Chemical Oxygen Demand with $KMnO_4$.

Regulation of the Government SR No. 296/2005 Coll. and in Prenčov the value was double the limit. Nitrates nitrogen in waters are mainly of anthropogenic origin and enter the waters in fertilizers or in human and animal excrements. Larger amounts of nitrates nitrogen in the water can indicate faecal pollution.

Fig. 3 proves that average values of ammonium nitrogen concentration determined by analysis of the water in all monitored sampling places have unequal ammonium nitrogen representation. Increased concentrations, greatly exceeding the limits in the Regulation of the Government SR No. 296/2005 Coll., were detected in sampling places Banská Štiavnica and Svätý Anton.

Its presence might have been caused either by animal and vegetable organic nitrogenous compound decomposition or sewage originating in homes. The concentration of amonnium nitrate decreased further downstream because of dilution caused by inflow from the tributaries [20]. In Prenčov the ammonium nitrogen concentration apparently decreased to levels below the limit value. Its decrease can be explained by the self-cleaning capability of the water and by the fact that the flow is not polluted by anthropogenic activity.

Concentration of phosphates phosphor was high in all sampling places (Fig. 4). The phosphorus compounds are regarded as the most important parameter affecting the trophic condition of water bodies [21, 22]. They mainly originate from washing liquids and powders, whose presence was obvious. Phosphates phosphor might also originate from fertilizers.

The concentrations of sulphates and chlorides in the water samples do not exceed the limited value (Table 1: sulphates = 250 $mg \cdot L^{-1}$, chlorides = 200 $mg \cdot L^{-1}$) determined by standard Regulation of the Government SR No. 296/2005 Coll. (Fig. 5).

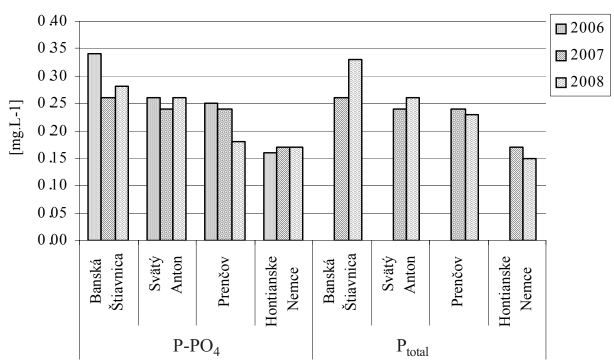

Fig. 4. The concentration of phosphates phospor a total phospor in samples from monitored places.

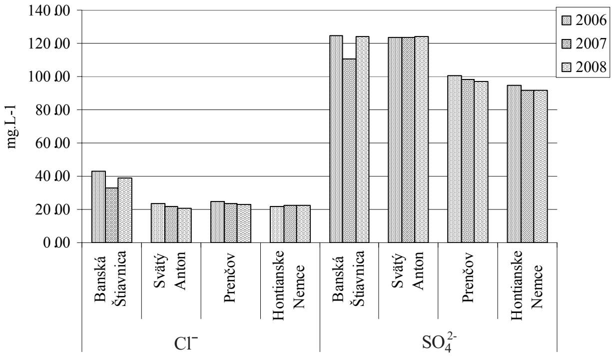

Fig. 5. The concentration of sulphates and chlorides in samples from monitored places.

From line contaminants the concentration of lead in the water is relatively balanced in all monitored sampling places (Banská Štiavnica, Svätý Anton, Hontianske Nemce = 1 μg·L^{-1}, Prenčov = 1 μg·L^{-1}). Its concentrations do not exceed the limited value (20 μg·L^{-1}) determined by standard Regulation of the Government SR No. 296/2005 Coll.

The differences among particular monitored places along Štiavnica Stream in the concentration of contaminants are influenced by natural purification of water as well as decreased water pollution due to antrophogenic capacity. The self-cleaning effect has its own dynamics depending on biological balance, including natural physical, chemical and biological processes. The process can decrease water pollution to a certain concentration with the presense of the organisms that are able to decompose the substances. The very important factor in self cleaning is oxygen, its transmission from the air to the water and making good conditions for chemical and biological processes. It is hard to specify general rules for self cleaning because of various channel shapes, different water flow speed, the deepness of the channels different physical and biological factors and more.

Conclusion

According to our analyses, surface water contamination occurs regularly because of the rural settlements' culture. Despite convenient natural conditions and long distances between villages, the self-cleaning process is insufficient. It is necessary for local authorities to be strict both in the formal and practical control and thus to improve water quality. The pressure canalization that is being built in the lower part of Terany is only designed to collect sewage originating in homes. However, leakage from stables, dry toilets, cowsheds and dunghills, which are concentrated in the vicinity of the riverside, will continue to contribute excessive nutrients that will cause more unwanted eutrophication. On the basis of valid legislation, it is essential to take actions to stop continuous polluting without any delay.

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