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ENVIRONMENTAL IMPACT OF CLOSING OF OIL SHALE MINES ON RIVER WATER QUALITY IN NORTH-EASTERN ESTONIA

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Chemical and biological characteristics of the Pühajõgi and Kunda catchments were determined in 1995, 2000 and 2005. During last ten years the concentration of total nitrogen in the samples of the river water from the Pühajõgi catchment has decreased on the average almost 90% since four mines were closed. The concentrations of total nitrogen in the water samples of the Kunda catchment decreased on the average ca 20% during these ten years. The conductivity values of the river water samples of the Pühajõgi catchment between 800 and 1800 $\mu S\ cm^{-1}$ *indicated a significant amount of ionic species in the river water. The water was microbiologically unpolluted according to the results of the analysis in 2005.*

Introduction

Different parameters and their combinations are used to evaluate and characterize the quality of the surface water. Kowalkowski et al. [1] used chemometric techniques (cluster analysis, principal component analysis, discriminant analysis, and factor analysis) for the river water classification of the Brda River (Poland) and evaluation of pollution data. By applying factor analysis it was possible to identify main pollution sources in heavily polluted locations [1]. Neal et al. [2] studied the water quality of the River Dun (UK) and associated surface waters through weekly chemical analysis of a wide range of major, minor and trace elements. Their study showed short-term extremes in water quality, which were missed due to monitoring intervals of a week or more [2]. Cuffney et al. [3] studied site conditions in the Yakima River Basin (USA) based on multiple indicators of conditions: concentration of metals and pesticides, intensity of agriculture and relative abundance of

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fish, invertebrates and algae. Their results showed that the response of biological communities to land-use gradient can have dramatic and far-reaching consequences for managing water quality [3].

Association of agriculture and pollution of the surface water is widespread, but mining deteriorates the environment, too. Coal mining is one of the core industries in the world, because coal provides around 27% of global primary energy, and the environmental impact of coal mining on water regime was analyzed by Tiwary [4]. Acid mine drainage degraded the water quality in term of lowering the pH of the surrounding water resources and increasing the level of total suspended solids, total dissolved solids and heavy metals. Non-acidic mining water showed high hardness, total suspended solids and bacterial contaminants [4]. Beside coal, lignite, oil shale and peat are used for generating energy, but their mining has mainly local importance.

The northeastern part of Estonia is the region where the Estonia oil shale deposit is located and where oil shale underground mines and opencasts are concentrated. The impact of oil shale mining on water ecosystem depends on the location of the mine, the mining technology, the hydrology and climate of the area and the physical-chemical properties of the oil shale and by-products.

Due to mining technology, the level of subsoil water is lowered below the level of oil-shale stratum, and the water pumped out is directed through outlet ditches and rivers (Ojamaa, Rannapungerja, Pühajõgi, Mustajõgi Rivers, and Raudi Channel) mainly into the Gulf of Finland, but also into Lake Peipus [5].

Because of changing economical situation of Estonia in 1990, the oil shale mining decreased and four oil shale mines were closed in 1999–2002 [6]. The closed and exploited opencasts are located in the catchment’s area of the Purtse, Rannapungerja, Pühajõgi and Vasavere rivers. The wastewater of oil shale mining (so-called mine water) was continuously discharged into the catchment area of rivers mentioned above [6–8]. Presently the withdrawal of groundwater has decreased over three times as compared to the early 1990s and no deterioration of the groundwater quality can be observed, but it is necessary to continuously monitor the quality of groundwater [9].

The Purtse River is located in the centre of mining area and therefore it has been under serious anthropogenic stress. The water quality and hydrological conditions of the Purtse catchment are quite well studied [6–8] and these results are not included in the present study. The results of Rätsep et al. [10] showed that due to the closure of the mines, ecological situation of the Purtse River has improved and phytoplankton abundance has risen. The population of microorganisms reflects the condition of the water body, and the populations of river bacteria are controlled by a variety of abiotic and biotic forces. At the same time the degradation of contaminants in river water is catalyzed by microbes and it needs an active microbial community [11].

The water quality of the rivers of the Pühajõgi catchment is not so well studied in comparison to the Purtse catchment, but the Pühajõgi River is included into the complex hydrobiological field works in Estonia. The water samples of more than 200 rivers were studied during this field works at the end of June and in July every 5 years. The summary of the data collected in 1987–1997 was published in the monograph “Estonian Rivers” [12].

In the present paper the water quality of the Pühajõgi catchment is evaluated. In comparison the water quality of the Kunda catchment, located in the west of the oil shale mines, was studied. The impact of oil shale mining on chemical and microbiological characteristics of the Pühajõgi River was examined.

Study area, sampling and analysis

The water quality of Pühajõgi and Kunda rivers was examined during 1995–2005. The both rivers (Fig. 1) are located in the similar geological conditions having limestone ground as sedimentary rock, and the influence of carbonate weathering on the water quality is equal. The Pühajõgi catchment is located in the eastern part of Ida-Viru County between the oil shale mining area and Gulf of Finland. The Kunda catchment is located in the West-Viru County and it is not directly connected with the oil shale mines.

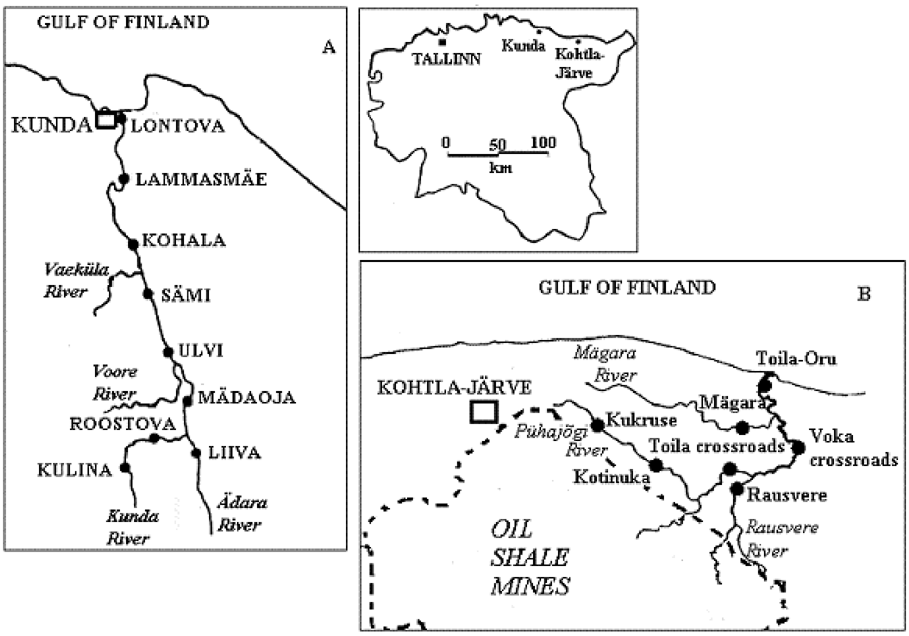

Fig. 1. Location of sampling points of the Kunda (A) and Pühajõgi (B) catchments and oil shale mines in Northern Estonia.

The water was sampled in different points of main rivers and streams in 1995, 2000 and 2005, and the sampling points were chosen to monitor evenly the main river and the larger tributaries. The distance between sampling points was ca 7 km, and access to sampling points was open in any case. The sampling was made in July when the water level is usually at the lowest, and water quality parameters are the most stable and well comparable. The mean discharges of rivers were calculated by average velocities and the cross-sectional area of the river. It was made for each sampling point and sometimes it was not determined due to variable water velocity in the river. Water pH and the concentration of dissolved oxygen were determined with the microsensor F/SET (WTW, Germany) in situ. Laboratory equipment was set up in the building near to the monitored river, and the analyses were made just after sampling or during the next day at least. Biochemical oxygen demand (BOD_7) was determined by the seeded dilution method. The samples of water were digested with potassium persulphate to determine total nitrogen (N_{tot}) and phosphorus (P_{tot}) [13]. The concentrations of total nitrogen, nitrite nitrogen (NO_2^--N) and nitrate nitrogen (NO_3^--N) were determined by the cadmium reduction method. They formed highly colored azo dye, its absorbance was measured by a spectrophotometer at 545 nm (Model 6300, Jenway, UK) [14]. The concentration of ammonia (sum of NH_3 and NH_4^+) was determined as ammoniac nitrogen by the indophenol blue method, and absorbance of the solution was measured by a spectrophotometer at 670 nm. The total phosphorus and phosphate phosphorus (PO_4^{3-}-P) concentrations were determined by the ascorbic acid method, and the absorbance of the solution was measured at 880 nm (Model 6300, Jenway, UK) [13]. The electrical conductance of water samples were measured by a conductivity meter (Model 4320, Jenway, UK) and the values have been corrected to a constant temperature of 25 °C [14]. Alkalinity of water samples was determined as a total alkalinity through titration with hydrogen chloride acid to the methyl orange endpoint by standard method [14].

The density of organisms of coliform group was determined by standard methods: membrane filters technique and M-Endo medium were used. Colonies with a metallic sheen within 24 h incubation at 35 °C were considered members of the coliform group [14].

Results and discussion

Concentration of the different forms of nitrogen

The concentrations of total nitrogen (N_{tot}) and nitrate nitrogen [NO_3^- -N] in the Pühajõgi and Kunda catchments are presented in Tables 1 and 2, respectively. The concentrations of different forms of nitrogen are calculated in millimoles per m^3 of water ($mmol\ m^{-3}$) for better comparison of the amounts of different ions in the water samples.

Table 1. **Concentration of total nitrogen (N_{tot}) and nitrate nitrogen [NO_3^--N] in the water samples from the sampling points of the Pühajõgi catchment in July**

Sampling point	1995		2000		2005	
	N_{tot}, mmol m^{-3}	[NO_3^--N], mmol m^{-3}	N_{tot}, mmol m^{-3}	[NO_3^--N], mmol m^{-3}	N_{tot}, mmol m^{-3}	[NO_3^--N], mmol m^{-3}
Kukruse	345±20	3.5±0.2	139±8	45±2	173±10	9.7±0.5
Kotinuka	100±6	54±3	76±5	18±1	64±4	1.1±0.1
Toila crossroads	645±36	4.9±0.3	114±8	13±1	67±4	2.8±0.2
*Rausvere	186±7	138±5	192±13	46±3	77±5	27±2
Voka crossroads	327±15	180±12	165±11	53±3	100±7	24±2
*Mägara	31±2	2.1±0.2	31±2	0.36±0.02	57±4	15±1
Toila-Oru	327±16	252±17	137±9	75±5	70±5	19±2

* Sampling points of a tributary

Table 2. **Concentration of total nitrogen (N_{tot}) and nitrate nitrogen [NO_3^--N] in the water samples from sampling points of the Kunda catchment in July**

Sampling point	1995		2000		2005	
	N_{tot}, mmol m^{-3}	[NO_3^--N], mmol m^{-3}	N_{tot}, mmol m^{-3}	[NO_3^--N], mmol m^{-3}	N_{tot}, mmol m^{-3}	[NO_3^--N], mmol m^{-3}
Kulina	103±7	84±5	61±4	58±4	67±5	55±3
Roostova	131±7	121±8	132±9	131±8	105±7	99±6
*Liiva	174±10	152±10	128±8	76±5	101±6	82±6
Mädaoja	137±8	116±8	111±7	82±6	105±6	95±6
Ulvi	158±11	141±8	135±8	87±6	117±8	81±5
Sämi	150±10	138±11	134±7	86±7	121±7	90±6
Kohala	146±10	142±9	138±10	92±8	116±6	87±5
Lammasmäe	134±9	122±7	113±7	90±7	116±6	85±6
Lontova	127±9	110±7	153±11	77±5	135±9	89±6

*Sampling points of a tributary

The determined concentrations of total nitrogen and nitrate nitrogen in the water samples of the Pühajõgi catchment (Table 1) had quite different values, and the highest concentration of total nitrogen (645 mmol m^{-3}) was found in the sampling point of Toila crossroads in 1995. During the next ten years the concentration decreased on the average close to 90% since four mines were closed. The concentrations of nitrate nitrogen were very low which means that nitrogen occurred in other forms (ammonia and organic compounds) mainly. In the other sampling points (Table 1) the concentration of total nitrogen decreased by ca 40–80% during 1995–2005. The water samples from Mägara had different trend, and the concentration of total nitrogen increased 1.8 times during ten years and achieved almost the same value as in the water sampled at Toila crossroads (Table 1).

The concentration of total nitrogen of water samples from different sampling points of the Kunda River had quite similar values, and during ten years (1995–2005) the concentration decreased on the average only by ca 20% (Table 2). In the water samples of the Kunda catchment the concentration of nitrate nitrogen formed more than 70% of the total nitrogen concentration.

Nitrite nitrogen is generated through the oxidation of ammonia (NH_3) and nitrite anion is toxic to the living organisms in water. Beside the nitrite, high concentration of ammonia (NH_3) is an indicator for toxicity of river water. Ionization of ammonia depends on the pH of water mainly, and it is significant in the water with pH below 7. Beside pH, higher temperature decreases ionization of ammonia, but its influence is less than that of pH [15]. Ammonia (NH_3) is toxic to living organisms [16] and its importance increases at pH above 7.

Measured values pH and temperature of water as well as calculated mean discharges of both rivers are presented in Table 3. The fluxes of nitrogen calculated by concentrations of N_{tot} and mean discharges were decreased during ten years (1995–2005) in the water sampled from both rivers, but there was no clear trend as the mean discharges were significantly different. The values of mean discharges of rivers depend on the climate conditions, and their comparison can give inaccurate conclusions for different years.

In studied rivers water was mostly weakly alkaline (pH 7.3-8.0). Considering measured pH and temperature of water and equilibrium calculations

Table 3. **Temperature, pH and mean discharge of water in the sampling points in July**

Sampling point	Temperature, °C			pH			Discharge, L s^{-1}	
	1995	2000	2005	1995	2000	2005	1995	2005
The Pühajõgi catchment								
Kukruse	12.5	12.3	18.7	7.2	7.0	7.3	8	20
Kotinuka	15.6	13.9	19.0	7.2	7.2	7.3	40	20
Toila crossroads	15.7	14.9	18.9	7.3	7.3	7.5	100	60
*Rausvere	14.6	14.2	12.8	8.0	7.5	7.3	500	400
Voka crossroads	15.4	15	17.3	7.6	7.6	7.6	870	450
*Mägara	11.0	14.9	20.2	7.6	7.7	8.0	30	60
Toila-Oru	15.7	16.3	19.2	8.0	7.8	7.9	900	1500
The Kunda catchment								
Kulina	10.6	12.9	14.5	7.6	7.2	7.2	ND	360
Roostova	11.7	12.4	14.2	8.1	7.4	7.3	650	540
*Liiva	12.6	12.4	14.0	7.7	7.2	7.7	600	700
Mädaoja	14.2	13.3	16.1	8.0	7.4	7.6	1200	1400
Ulvi	13.4	14.3	17.7	7.9	7.8	8.1	ND	ND
Sämi	13.3	13.8	16.3	7.9	7.8	7.9	2000	ND
Kohala	14.1	13.8	16.2	8.2	7.8	7.9	2000	ND
Lammasmäe	14.4	14.5	17.0	8.0	7.6	8.2	ND	7000
Lontova	15.0	15.4	15.9	8.1	8.1	7.8	2900	7000

*Sampling points of a tributary

ND – discharge was not calculated

of ammonia [15], the fraction of ammonia (NH_3) was up to 10% in the water samples of studied rivers.

The molar ratio of nitrate and ammonium ion can be used to characterize the quality of surface water, the low ratios indicating a higher concentration of ammonia and possible toxicity of water. The concentrations of nitrite nitrogen [NO_2^- -N] and the values of molar ratios of nitrate and ammonia of water samples are presented in Tables 4 and 5.

Concentration of nitrite nitrogen in the water samples from sampling points of the Pühajõgi River had different values, and the highest concentration of nitrite (7.8 mmol m^{-3}) was determined in the water sample from the sampling point of Kukruse in 2000 (Table 4). In the same year the

Table 4. **Concentrations of nitrite nitrogen [NO_2^--N] and the values of molar ratio of nitrate and ammonia in the water samples from the sampling points of the Pühajõgi catchment in July**

Sampling point	1995		2000		2005	
	[NO_2^--N], mmol m^{-3}	$\frac{[NO_3^-]}{[NH_4^+]}$	[NO_2^--N], mmol m^{-3}	$\frac{[NO_3^-]}{[NH_4^+]}$	[NO_2^--N], mmol m^{-3}	$\frac{[NO_3^-]}{[NH_4^+]}$
Kukruse	0.43±0.03	0.010	7.8±0.5	2.0	3.5±0.3	0.10
Kotinuka	0.79±0.05	20	1.9±0.1	15	0.29±0.02	0.43
Toila crossroads	0.14±0.01	0.011	1.4±0.1	0.88	0.36±0.03	0.63
*Rausvere	2.1±0.2	10	6.8±0.6	0.79	0.79±0.04	5.2
Voka crossroads	2.5±0.2	1.8	6.8±0.5	2.5	0.79±0.05	2.5
*Mägara	0.14±0.01	1.9	0.060±0.003	1.0	0.14±0.01	8.4
Toila-Oru	1.2±0.1	14	2.6	18	1.8±0.1	2.0

* Sampling points of a tributary

Table 5. **Concentrations of nitrite nitrogen [NO_2^--N] and the values of molar ratio of nitrate and ammonia in the water samples from the sampling points of the Kunda catchment in July**

Sampling point	1995		2000		2005	
	[NO_2^--N], mmol m^{-3}	$\frac{[NO_3^-]}{[NH_4^+]}$	[NO_2^--N], mmol m^{-3}	$\frac{[NO_3^-]}{[NH_4^+]}$	[NO_2^--N], mmol m^{-3}	$\frac{[NO_3^-]}{[NH_4^+]}$
Kulina	0.36±0.02	117	0.14±0.01	58	0.14±0.01	24
Roostova	0.29±0.02	154	0.21±0.02	184	0.21±0.02	138
*Liiva	0.50±0.03	424	0.43±0.08	59	0.36±0.02	76
Mädaoja	1.0±0.1	272	0.64±0.04	64	0.64±5	221
Ulvi	1.2±0.1	395	0.50±0.04	72	0.36±0.02	94
Sämi	0.44±0.03	323	0.57±0.04	67	0.29±0.02	314
Kohala	0.36±0.03	133	0.50±0.03	65	0.21±0.02	38
Lammasmäe	0.29±0.02	39	0.57±0.05	66	0.29±0.02	91
Lontova	0.29±0.02	119	0.71±0.05	45	0.14±0.01	89

* Sampling points of a tributary

concentration of nitrite was high in the sampling points of Rausvere and Voka crossroads (6.8 mmol m^{-3}).

In 2005 the concentration of nitrite was quite low (below 1.9 mmol m^{-3}) in the sampling points of the Pühajõgi River, except Kukruse (3.5 mmol m^{-3}). This showed that the closing of the mines reduced the concentration on nitrite anions in the Pühajõgi River.

The values of the molar ratio of nitrate and ammonia were mainly below 2 (Table 4), and this means that the concentration of ammonia was as high as half of the concentration of nitrate in the water samples of the Pühajõgi catchment. Only in the water samples from Kotinuka (1995, 2000), Rausvere (1995) and Toila-Oru (1995, 2000) concentration of ammonia was low and the value of molar ratio of nitrate and ammonia was higher than 10.

In 2005 the values of molar ratio of nitrate and ammonia were below 5, only in the sampling points of Mägara and Rausvere the value of molar ratio was between 5 and 10. It means that concentration of ammonia in the water of the Pühajõgi River was higher although the concentration of total nitrogen (Table 1) was reduced in comparison with the results in 1995 and 2000.

The water samples from the Kunda River were characterized by a quite steady concentration of nitrite nitrogen (below 0.64 mmol m^{-3}) over all the sampling area and period (Table 5). In 1995 higher concentration of nitrite nitrogen was determined in the water samples from sampling points Mädaoja (1.0 mmol m^{-3}) and Ulvi (1.2 mmol m^{-3}). These results characterized the influence of agriculture and settlement on the quality of surface water, because small farms, fields and villages are located near to the Kunda River catchment. In 1995 the values of molar ratio of nitrate and ammonia were higher than 100 (Table 5), and it means that the relative concentration of ammonia was very low. In 2000 and 2005 the analysis results showed higher relative content of ammonia in the water samples which may indicate the changes in the economical life (new summer houses and tourism farms near the river). In general, the quality of water in the Kunda catchment was much better in comparison with that of the Pühajõgi River.

Concentration of phosphorus fractions

The concentrations of total phosphorus (P_{tot}) and phosphate phosphorus [PO_4^{3-}-P] in the rivers of the Pühajõgi and Kunda catchments are presented in Tables 6 and 7, respectively.

The results of water analysis showed significantly different concentrations of total phosphorus and phosphate phosphorus in Pühajõgi and Kunda rivers (Tables 6 and 7). The concentrations of total phosphorus were high (up to 80 mmol m^{-3}) in the Pühajõgi River in 1995 (Table 6), but in 2000 and 2005 the concentration of phosphorus was even close to 100% less which was a good sign for the improvement of water quality in the Pühajõgi River. Low concentration of total phosphorus in the water samples from sampling point Mägara (below 1.8 mmol m^{-3}) shows the natural loading, and similar concentrations of phosphorus were determined in the water samples from the Kunda River (Table 7). It means that with mine water a lot of phosphorus was discharged into the Pühajõgi River.

The comparison of P_{tot} and [PO$_4^{3-}$-P] concentrations showed that the phosphorus occurred mainly as phosphate anion (up to 90%) in the samples of the Pühajõgi River. Water samples from sampling point Mägara (the tributary of the Pühajõgi River) and the Kunda catchment contained a lot of organic phosphorus compounds, and the content of phosphate phosphorus was less than 50% of that of total phosphorus.

During the 10-year monitoring period (1995–2005), the concentration of total phosphorus was decreased by 93 to 98% in the water samples of the Pühajõgi River and this is related to the closing of oil shale mines. For the water samples of the Kunda River the concentration of total phosphorus showed no clear decreasing trend, although in 2005 the concentrations of phosphorus were lower than in 1995 (Table 7).

Table 6. **Concentration of total phosphorus (P_{tot}) and phosphate phosphorus [PO$_4^{3-}$-P] in the water samples from the sampling points of the Pühajõgi catchment in July**

Sampling point	1995		2000		2005	
	P_{tot}, mmol m^{-3}	[PO$_4^{3-}$-P], mmol m^{-3}	P_{tot}, mmol m^{-3}	[PO$_4^{3-}$-P], mmol m^{-3}	P_{tot}, mmol m^{-3}	[PO$_4^{3-}$-P], mmol m^{-3}
Kukruse	50±3	45±3	4.5±0.3	3.3±0.2	9.1±0.7	8.0±0.6
Kotinuka	3.6±0.2	0.97±0.08	1.6±0.1	0.68±0.06	1.4±0.1	0.87±0.07
Toila crossroads	80±5	74±4	4.0±0.3	2.4±0.1	1.9±0.1	0.87±0.07
*Rausvere	15±1	14±1	9.6±0.8	8.8±0.6	1.1±0.1	0.61±0.05
Voka crossroads	27±2	24±2	8.0±0.6	5.9±0.4	1.0±0.1	0.39±0.03
*Mägara	1.8±0.2	0.97±0.08	0.61±0.05	0.0012 ±0.0002	1.0±0.1	0.32±0.02
Toila-Oru	30±2	25±2	7.7±0.5	6.1±0.5	2.3±0.2	1.7±0.1

* Sampling points of a tributary

Table 7. **Concentration of total phosphorus (P_{tot}) and phosphate phosphorus [PO$_4^{3-}$-P] in the water samples from the sampling points of the Kunda catchment in July**

Sampling point	1995		2000		2005	
	P_{tot}, mmol m^{-3}	[PO$_4^{3-}$-P], mmol m^{-3}	P_{tot}, mmol m^{-3}	[PO$_4^{3-}$-P], mmol m^{-3}	P_{tot}, mmol m^{-3}	[PO$_4^{3-}$-P], mmol m^{-3}
Kulina	0.35±0.03	0.16±0.01	0.48±0.03	0.26±0.02	0.23±0.02	0.13±0.01
Roostova	0.90±0.06	0.19±0.02	0.65±0.05	0.19±0.02	0.13±0.01	0.061±0.005
*Liiva	1.1±0.1	0.42±0.03	1.2±0.1	0.52±0.04	0.58±0.04	0.23±0.03
Mädaoja	0.84±0.07	0.55±0.03	1.5±0.1	0.74±0.05	0.74±0.05	0.19±0.02
Ulvi	0.84±0.07	0.32±0.02	1.4±0.1	0.42±0.03	0.52±0.03	0.033±0.002
Sämi	0.90±0.07	0.68±0.05	1.1±0.1	0.45±0.04	0.61±0.04	0.16±0.01
Kohala	0.97±0.07	0.74±0.06	4.3±0.3	4.0±0.3	0.74±0.05	0.29±0.02
Lammasmäe	1.3±0.1	0.90±0.07	1.0±0.1	0.61±0.04	0.74±0.06	0.26±0.02
Lontova	1.1±0.1	0.71±0.06	6.9±0.4	3.5±0.2	1.1±0.1	0.45±0.04

* Sampling points of a tributary

The fluxes of phosphorus calculated by concentrations of P_{tot} and mean discharges were decreased during ten years (1995–2005) in the water sampled from middle course and downstream of the Pühajõgi River, while it had similar values for water sampled from the Kunda River.

Conductivity and alkalinity of water samples

Specific conductance represents the ability of water to conduct electrical current and it is highly dependent on the amount of dissolved solids in water. Conductivity is a function of water temperature and the total number of dissolved ions in water. The measurements of conductivity were included into the program of the complex hydrobiological field works after 2000, and the conductivity of water samples was measured in 2005 only.

The capacity of water to accept protons (H^+ ions) is called alkalinity, and it serves as a pH buffer and reservoir for inorganic carbon. The basic species responsible for alkalinity in natural water are bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), and hydroxide ions (OH^-). The equilibrium between bicarbonate and carbonate ions in water depends upon pH, and bicarbonate ion is the predominant species in the pH range (pH = 7.5-9.5) found in most natural waters [17].

The Pühajõgi and Kunda catchments are located on the limestone base, and it means that the water samples are rather rich in carbonate ions ($HCO_3^- + CO_3^{2-}$) resulting in high alkalinity. In engineering terms, alkalinity is expressed in units of milligrams per liter (mg L^{-1}) of $CaCO_3$ [17], but in the present study alkalinity of water samples was calculated in millimoles of bicarbonate ions per m^3 of water (HCO_3^- mmol m^{-3}) for better comparison of the amounts of different ions in the water samples. The results of measured conductivity and determined alkalinity of water samples of the Pühajõgi and Kunda catchments are presented in Figures 2 and 3, respectively.

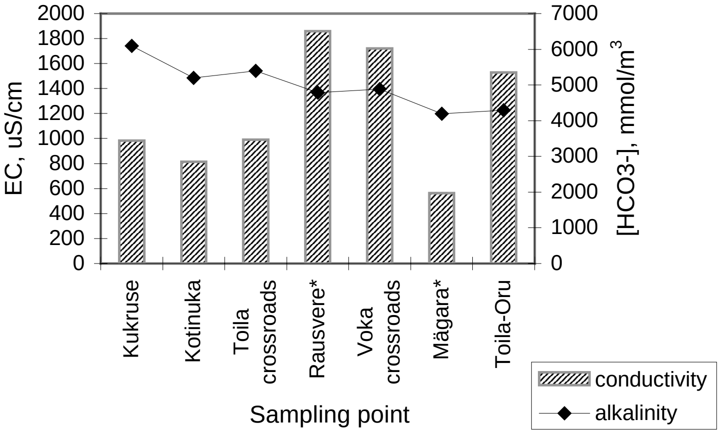

Fig. 2. Conductivity (EC) and alkalinity [HCO_3^-] of water in the sampling points of the Pühajõgi catchment in 2005 (* sampling points of a tributary).

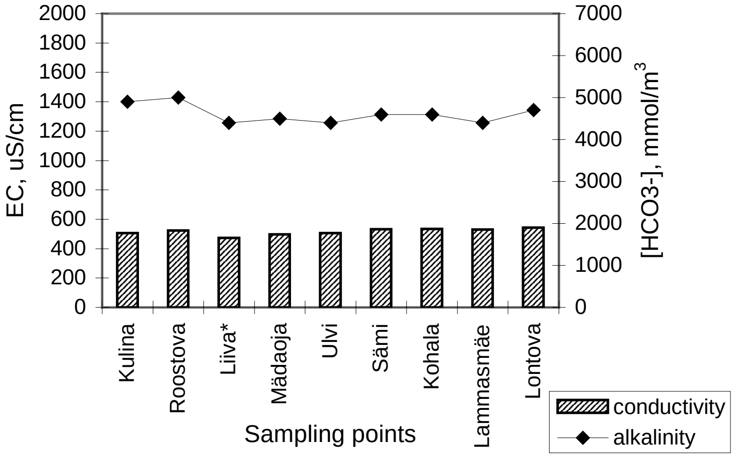

Fig. 3. Conductivity (EC) and alkalinity [HCO_3^-] of water in the sampling points of the Kunda catchment in 2005 (* sampling points of a tributary).

When comparing alkalinity (Figures 2 and 3) with concentrations of total nitrogen (Tables 1 and 2) and phosphorus (Tables 6 and 7) it can be seen that the concentration of bicarbonate ions was up to an order of magnitude higher. It means that the dissolved nitrogen and phosphorus compounds had minor influence on the conductivity of water samples.

The results show that the alkalinity of river water samples decreased on the average to 66% of that of sampling point of Kukruse (6000 mmol m^{-3}) to Toila-Oru (4200 mmol m^{-3}) in the Pühajõgi catchment (Fig. 2). At the same time the alkalinity of water samples from the sampling points of the Kunda catchment was on an average 4700 mmol m^{-3}, independent of sampling points (Fig. 3).

Although the concentration of carbonate and bicarbonate anions was quite similar in the water samples of both catchments, the measurement of conductivity showed a significant difference. Conductivity of water samples of the Pühajõgi River was between 800 and 1800 microsiemens per centimeter (μS cm^{-1}) which was 1.5–3 times higher than the conductivity of water sample from Mägara sampling point (tributary of the Pühajõgi River) (Fig. 2). Conductivity of the water samples of the Kunda River was on the average 500 μS cm^{-1}, practically independent of the sampling point (Fig. 3). This situation was similar to the results of phosphorus (Table 6 and 7), showing environmental impact of mine water on the quality of river water.

High values of conductivity of the water samples from the Pühajõgi River showed that the water of Pühajõgi contained significant amounts of ions generating quite a high specific conductance. Although the oil shale mines were closed and concentrations of nitrogen and phosphorus were reduced, the water quality of the Pühajõgi River became worse. The reason can be the leaching of dissolved salts from sediments in the mining area.

Biochemical and biological characteristics of the water samples

Beside the chemical analysis the biochemical and biological characteristics can be used to evaluate the water quality of rivers.

Concentration of dissolved oxygen was calculated as an oxygen saturation value at measured temperature and air pressure. Oxygen saturation value shows the content of oxygen in the water and allows calculation of oxygen needed for respiration of living organisms and oxidation of pollutants. Biochemical oxygen demand (BOD) shows the amount of oxygen needed for the biochemical degradation of pollutants, and it is often used to evaluate the amount of biodegradable pollutants in water. The density of organisms of coliform group (BC) indicates faecal pollution, which usually originates from untreated or purely treated wastewater of towns, settlements and agricultural sources. The results of analysis in 2005 of oxygen saturation values, values of BOD and densities of BC are presented in Table 8.

The oxygen saturation values and BODs showed a similar trend. Water quality of the Pühajõgi and Kunda rivers was rather similar, and the values of analyzed parameters were quite similar (Table 8). Only the water sample from Kukruse sampling point (the Pühajõgi River) gave different results: the oxygen saturation value was 66% and that of BOD (12.6 $mgO_2\ L^{-1}$) was two- to threefold as compared to the others. It showed that the impact of oil

Table 8. **Oxygen saturation value, biochemical oxygen demand (BOD) and density of organisms of coliform group (BC) in the river water samples in July 2005**

Sampling point	Oxygen saturation value, %	BOD_7, $mgO_2\ L^{-1}$	BC, cells $(100ml)^{-1}$
The Pühajõgi catchment			
Kukruse	66	12.6±1.3	27000
Kotinuka	87	3.1±0.3	290
Toila crossroads	74	6.6±0.6	450
*Rausvere	105	3.7±0.3	90
Voka crossroads	112	4.3±0.4	360
*Mägara	116	3.6±0.3	140
Toila-Oru	108	4.9±0.5	300
The Kunda catchment			
Kulina	84	1.9±0.2	5
Roostova	101	2.4±0.2	55
*Liiva	78	3.0±0.2	120
Mädaoja	110	3.8±0.3	155
Ulvi	103	2.9±0.3	260
Sämi	97	2.8±0.3	210
Kohala	93	3.1±0.3	300
Lammasmäe	94	2.7±0.3	350
Lontova	91	3.6±0.4	480

*Sampling points of a tributary

shale mining was not significant on the water quality, as to the biochemical and biological analysis.

Results of the analysis of coliform group indicated severe faecal pollution at the upper course of the Pühajõgi River. The reason of this pollution is poorly treated wastewater of the Kukruse settlement. Low oxygen saturation value and relatively high oxygen demand at this sampling site confirm the results (Table 8). As the Pühajõgi River has low discharge and thus it is quite small at the upper course, it can be affected easily. Further downstream the situation improves as the river gets additional water from springs and from mines. The mining water seems to be microbiologically unpolluted as shown by the analysis in 2005.

Conclusion

The water qualities of the Pühajõgi and Kunda catchments were evaluated because the mining water from oil shale mines were discharged into the Pühajõgi River, but the Kunda catchment is not connected with oil shale mines.

The highest concentration of total nitrogen in the water samples of the Pühajõgi catchment, 645 mmol m^{-3}, was determined in 1995, and during the next ten years it was lowered on the average by ca 90% since within this time four mines were closed. The concentrations of nitrate and nitrite were quite low, and nitrogen was mainly in the form of ammoniacal nitrogen in the water samples of the Pühajõgi catchment. In the downstream points the concentration of ammonia decreased and concentration of nitrate increased due to the oxidation of ammonia. The highest concentrations of nitrite up to 7.8 mmol m^{-3} in the water samples of the Pühajõgi catchment were determined in 2000, but in 2005 the concentrations of nitrite were below 1.9 mmol m^{-3} indicating the positive effect of closing of mines.

The concentrations of total nitrogen in the water samples of the Kunda catchment were on the average 130 mmol m^{-3} in 1995, and during the next ten years the concentration of total nitrogen decreased by 20–40%, mainly due to reduced use of fertilizers in agriculture. The concentration of nitrate formed more than 70% of the concentration of total nitrogen and the concentration of ammonia formed less than 1% of the concentration of nitrate. In 2000 and 2005 the values of molar ratio of nitrate to ammonia were mainly lower than 100, showing an increase in the concentration of ammonia. The water samples of the Kunda catchment were characterized by quite steady concentration of nitrite (below 0.64 mmol m^{-3}) over all sampling area and period (1995–2005).

The concentration of total phosphorus was up to 80 mmol m^{-3} in the Pühajõgi River in 1995, but it has lowered by more than 90% in 2000 and 2005. Low concentrations of total phosphorus (below 1.8 mmol m^{-3}) in the water samples from tributary of the Pühajõgi River and from the Kunda catchment indicated significant discharge of phosphorus through mining water into the Pühajõgi River.

The comparison of concentrations P_{tot} and $[PO_4^{3-}\text{-P}]$ showed that the phosphorus occurred mainly as phosphate anion (up to 90%) in the water samples of the Pühajõgi River, while water samples from the Kunda catchment contained a lot of organic compounds of phosphorus and the content of phosphate phosphorus was less than 50% of the concentration of total phosphorus.

The alkalinity of water samples was calculated as concentration of bicarbonate ions, and its values decreased from 6000 mmol m^{-3} to 4200 mmol m^{-3} further downstream of the Pühajõgi River, but the alkalinity of water samples of the Kunda River was on an average 4700 mmol m^{-3}, irrespective of the sampling point.

The conductivity of the water samples of the Pühajõgi catchment was between 800 and 1800 µS cm^{-1} which exceeded 1.5–3 times the values of water samples of the Kunda catchment (on an average 500 µS cm^{-1}), indicating a significant amount of the ions in the water of the Pühajõgi River.

Results of the analysis of coliform group indicated severe faecal pollution at the upper course of the Pühajõgi River. This is evidently caused by poorly treated wastewater of the Kukruse settlement. The mining water seems to be microbiologically unpolluted according to the results of the analysis in 2005.

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