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Relationship Between Water Quality and Oil-Shale Mines in Northern Estonia

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1. Introduction

Different parameters and their combinations are used to evaluate and characterize the quality of the surface water: a) chemometric techniques (Brodnjak-Voncina et al., 2002; Kowalkowski et al. 2006); b) weekly chemical analysis of a wide range of major, minor and trace elements (Neal et al., 2006); c) multiple indicators of conditions (concentrations of compounds, intensity of agriculture and industry) (Cuffney et al. 2000); d) calculated water quality index (Pesce e al., 2000; Sanchez et al., 2007; Štambuk-Giljanovic, 1999).

The concentration of various constituents including different forms of nutrients (nitrogen and phosphorus) (Mainstone et al., 2002; Withers et al., 2002) and organic carbon is used to evaluate of surface water quality. Origin of organic matter in water is related to different sources (Peuravuori and Pihlaja, 2007; Zsolnay, 2003) and natural organic matter controls the geochemical processes in aqueous systems as a donor and acceptor of protons as a buffer solution (Aiken and Cotsaris, 1995) and it is known to play important role in the fate and transport of many toxic organic or inorganic chemicals and in nutrient cycling (Dawson et al., 2009; Steinberg, 2008). It is used for the classification of surface water bodies (streams, rivers and lakes). On the other hand the fluxes of nutrients (nitrogen, phosphorus and carbon) are used to evaluate the ecological quality of lakes. The fluxes of nutrients are important for the evaluation of risks of eutrophication of rivers and lakes, but the flux depends on the concentration of compounds and flow velocity of water (Dakova et al., 2000; Rätsep & Liblik, 2001; Tamm et al., 2008; Withers et al., 2002).

The objective of the present paper is to examine the chemical characteristics of the Purtse and Pühajõgi Rivers during the closing of oil shale mines and in comparison the water quality of the Kunda River was evaluated. The Purtse River is located in the centre of mining area and the Pühajõgi River is located between the oil shale mines and Gulf of Finland. The Kunda River is located in the similar geological conditions, but it is not directly connected with the oil shale mines.

2. Mining as one of the significant influence on water quality

The mining deteriorates directly the lithosphere, but the mining has significant influence on the atmosphere (generation of dust and gaseous emissions) and hydrosphere (discharge of

mine water) (Equeenuddin et al., 2010; Mighanetara et al., 2009; Tiwary, 2001). The underground mines have significant impact of hydrosphere as large amounts of groundwater is pumped out into the bodies of surface water generating changes in hydrological and hydrogeological conditions.

The environmental impact of mines can be evaluated by the analysis of water quality during mining in comparison of water quality before the mining started. It means that it is important to measure many values of different parameters before constructions of mines. It will be good to analyze quite well the surface water sampled in the different places and at different time for the better comparison (Finkelman et al., 1999; Kolker et al., 2009; Natarajan et al., 2006).

If we have already working mines then it is quite problematic to get additional information about the surface water bodies which are under the direct impact of mines. It is possible to analyze the water sampled from the water bodies which are located in the similar climatic and hydrogeological conditions, but this situation has some uncertainty due to the differences of water sources, composition of soil and bedrock and biological diversity of water bodies. On the other hand the closing of mines gives the alternative opportunity to evaluate the environmental impact of mining during the restoration of natural conditions in the mining area.

3. Specific influence of oil-shale mining on the water quality

In certain mines of base metals and iron where ores have high sulfur content, drainage from mine workings and waste heaps can become highly acidic and can contain high concentrations of dissolved heavy metals. The acid generation from the oxidation of sulfur-bearing minerals like pyrites in coal mines occurs only when the minerals react with water and oxygen in the presence of *Thiobacillus* bacteria to produce sulphuric acid and iron hydroxide or iron sulfate (Banks & Banks, 2001; Equeenuddin et al., 2010; Natarajan et al., 2006; Tiwary 2001).

Common characteristics of acid mine drainage include highly acid water with pH values as low as 2.0 and high sulfate concentration (up to 2 g L^{-1}) and the high metal loading typically including iron (up to 100 mg L^{-1}) and manganese (up to 5 mg L^{-1}) (Banks & Banks, 2001; Equeenuddin et al., 2010; Tiwary 2001). The high acidity results in further dissolution of minerals and the release of toxic metals and other constituents into waterways (Equeenuddin et al., 2010; Tiwary 2001).

The composition and properties of oil shale mine water is quite different in comparison with coal mines. The water quality in closed oil shale mines was studied by Rätsep (Rätsep & Liblik, 1998) and Reinsalu (Reinsalu et al., 2006) with coworkers. For the period of 2000-2004 Reinsalu et al. found the following mean values of characteristics for oil shale mine water: pH = 7.1, sulfate 342 mg L^{-1}, total iron 0.69 mg L^{-1}, calcium 174 mg L^{-1}, total hardness 13,7 mge L^{-1} and conductivity 1095 μS cm^{-1}. The mean values of concentrations of different forms of nitrogen are presented for the illustration: [NO_3^--N] = 11.7 mg L^{-1} (836 mmol m^{-3}), [NO_2^--N] = 0.015 mg L^{-1} (1.1 mmol m^{-3}), [NH_4^+-N] = 0.017 mg L^{-1} (1.2 mmol m^{-3}) (Reinsalu et al., 2006). In 1991-1992 the content of phosphates in mine water did not rise above 0.04 mg L^{-1} and during the following years (1993-1996) their content fell practically to zero level (below 0.001 mg L^{-1}) (Rätsep & Liblik, 1998).

Oil shale mining is accompanied by lowering of the water level and discharge of mine water into bodies of surface water (Rätsep & Liblik, 2000, 2001; Rätsep et al., 2002; Perens at al., 2006; Vaht & Rätsep 2009). For example, during the period of 1990-1998 the average amount of mine water directed into the Purtse catchment was 104 million m^3 per year (Rätsep & Liblik, 2000). An important problem is prognostication of hydrological processes after the shutting down of mines. The water in the mining area filtrates from one mine to another and feeds the waters of operating mines (Perens et al., 2006). There is also evidence that the decreasing amount of pumped-out mine water has a negative influence on the quality of the water of some rivers due to the decreasing amount of water in them (Punning et al., 1997).

4. Spatial changes in the water quality in the Kunda River, directly unconnected with oil-shale mines

The Kunda River is located in Lääne-Viru County in North-East Estonia (Figure1.). The length of the main river is 64 km, and the catchment covers an area of 530 km^2 [Järvekülg, 2001]. The Kunda River is located in similar geological conditions with oil shale mines having limestone ground as sedimentary rock, but the Kunda catchment is not directly connected with oil shale mines. Water was sampled in different points of the main river and streams in 1995, 2000 and 2005, and the sampling points were chosen to monitor the main river and the larger tributaries evenly (Fig. 1 A).

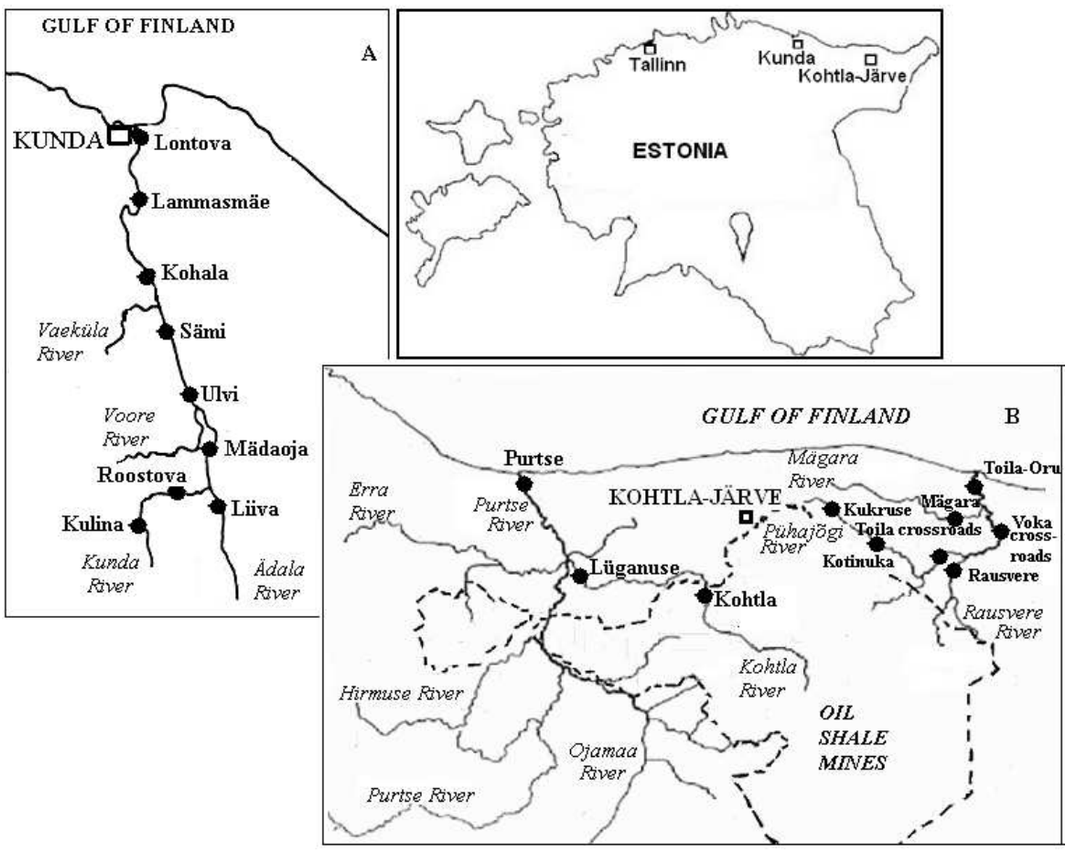


Fig. 1. Location of sampling points (●) of the Kunda (A), Purtse and Pühajõgi (B) catchments and oil shale mines in Northern Estonia.

Sampling was made in July when the water level is usually at the lowest; water quality parameters are the most stable and well comparable. The summaries of results of physico-chemical analysis are presented in Tables 1 and 2. The measurements of conductivity and alkalinity were included into the program of the complex hydrobiological field works after 2000, and because of that the values of conductivity and alkalinity of water samples are presented for 2005 only. Methodology of sampling and analysis was described in detail in our publication (Selberg et al., 2009) and it is not repeated here.

The Kunda catchment is 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 (Table 1). 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.

Sampling point	pH			Conductivity in 2005, μS cm^{-1}	Alkalinity [HCO_3^-] in 2005, mmol m^{-3}	Total dissolved solids (TDS) in 2005, mg L^{-1}
	1995	2000	2005			
Kulina	7.6	7.2	7.2	506	4899	339
Roostova	8.1	7.4	7.3	523	4999	350
*Liiva	7.7	7.2	7.7	474	4399	318
Mädaoja	8.0	7.4	7.6	497	4498	333
Ulvi	7.9	7.8	8.1	505	4398	338
Sämi	7.9	7.8	7.9	532	4599	356
Kohala	8.2	7.8	7.9	534	4598	358
Lammasmäe	8.0	7.6	8.2	530	4398	355
Lontova	8.1	8.1	7.8	542	4699	363

*-Sampling points of a tributary

Table 1. Values of pH, conductivity, alkalinity and concentration of total dissolved solid in the water samples from the sampling points of the Kunda catchment in July.

The values of pH of water samples from Kunda River (Table 1) were mainly around 8 as typical for the surface water in northern and western Estonia due to the limestone. 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. Conductivity of the water samples of the Kunda River was on the average 500 microsiemens per centimeter (μS cm^{-1}), practically independent of the sampling point.

The concentrations of total nitrogen and nitrate nitrogen of water samples from different sampling points of the Kunda River had quite similar values (Table 2), and during ten years (1995-2005) the concentration decreased on the average only ca 20%. In the water samples of the Kunda catchment the concentration of nitrate nitrogen formed more than 70% of the total nitrogen concentration (Selberg et al., 2009).

The water samples of Kunda catchment had quite steady concentration of nitrite (below 1.2 mmol m^{-3}) over all sampling area and period (1995-2005) (Table 2). The calculated mean values of concentration of NO_2^--N decreased during the ten years (1995-2005) as the mean values were 0.53±0.34, 0.48±0.18 and 0.29±0.1 mmol m^{-3}, respectively.

Sampling point	N_{tot}	$[NO_3^-$-N]	$[NO_2^-$-N]	$[NH_4^+$-N]
	Concentration in 1995,mmol m^{-3}			
Kulina	103	84	0.36	0.71
Roostova	131	121	0.29	0.79
*Liiva	174	152	0.50	0.36
Mädaoja	137	116	1.0	0.43
Ulvi	158	141	1.2	0.36
Sämi	150	138	0.44	0.43
Kohala	146	142	0.36	1.1
Lammasmäe	134	122	0.29	3.1
Lontova	127	110	0.29	0.93
Change of concentration in 2000,+/- %				
Kulina	-41	-31	-61	**41**
Roostova	**1**	**8**	-28	-10
*Liiva	-26	-50	-14	**261**
Mädaoja	-19	-29	-36	**202**
Ulvi	-15	-38	-58	**233**
Sämi	-11	-38	**30**	**179**
Kohala	-5	-35	**39**	**36**
Lammasmäe	-16	-26	**97**	-55
Lontova	**20**	-30	**145**	**83**
Change of concentration in 2005,+/- %				
Kulina	-35	-35	-61	**224**
Roostova	-20	-18	-28	-6
*Liiva	-42	-46	-28	**206**
Mädaoja	-23	-18	-36	0
Ulvi	-26	-43	-70	**139**
Sämi	-19	-35	-34	-33
Kohala	-21	-39	-42	**109**
Lammasmäe	-13	-30	0	-70
Lontova	**6**	-19	-52	**8**

*-Sampling points of a tributary

Table 2. Concentrations of different forms of nitrogen in the water samples from the sampling points of the Kunda catchment in July 1995 and their changes in July 2000 and 2005.

The concentrations of ammonia in water sampled from the Kunda catchment had also quite steady (Table 2). The highest concentration of NH_4^+-N up to 3.1 mmol m^{-3} was determined in water sampled from sampling point of Lammasmäe in 1995, but it was below 1 mmol m^{-3} in the other sampling points. In 2000 the concentrations of ammonia were below 1.7 mmol m^{-3}, while in 2005 the highest concentrations of ammonia up to 2.3 mmol m^{-3} were determined in water sampled from sampling points of Kulina and Kohala. The calculated variations of concentrations of different forms of nitrogen showed that concentrations of ammonia even were grown during the ten years and it can be connected with development in agriculture and settlement.

The fluxes of inorganic nitrogen formed more than 85% from the fluxes of total nitrogen in water of the Kunda River in 1995 and fluxes of toxic NO_2^--N and NH_4^+-N formed less than 1% of inorganic nitrogen (Table 3). In 2005 the fluxes of nitrogen were lower than in 1995, but the discharge of water was also lower in the upper reach of the Kunda River. The inorganic nitrogen formed more than 85% from the fluxes of total nitrogen in the upper reach, but it was below 75% in the lower reach of the Kunda River in 2005. The fluxes of toxic NO_2^--N and NH_4^+-N formed less than 2% of inorganic nitrogen. The fluxes of different forms of nitrogen increased further downstream of the Kunda River indicating the continuous infiltration of nitrogen from the untreated or purely treated wastewater of settlements and agricultural sources into the Kunda River in 1995 and 2005.

Sampling point	N_{tot}, mg s^{-1}	$[NO_3^-$-N], mg s^{-1}	$[NO_2^-$-N], mg s^{-1}	$[NH_4^+$-N], mg s^{-1}
	1995			
Kulina	nd	nd	nd	nd
Roostova	1190	1099	3	7
*Liiva	1458	1273	4	3
Mädaoja	2293	1956	17	7
Ulvi	nd	nd	nd	nd
Sämi	4204	3874	12	12
Kohala	4112	3980	10	30
Lammasmäe	nd	nd	nd	nd
Lontova	5174	4481	12	38
2005				
Kulina	337	278	0.7	12
Roostova	797	747	2	5
*Liiva	990	799	4	11
Mädaoja	2059	1856	13	8
Ulvi	nd	nd	nd	nd
Sämi	nd	nd	nd	nd
Kohala	nd	nd	nd	nd
Lammasmäe	11410	8288	28	91
Lontova	13230	8757	14	98

*-Sampling points of a tributary
nd – not determined

Table 3. The fluxes of dissolved nitrogen in the sampling points of the Kunda River

The concentrations of total phosphorus (P_{tot}) and phosphate phosphorus $[PO_4^{3-}$-P] in the water of the Kunda River were quite low in 1995 (Table 4) and the concentrations of phosphorus were increased in the most sampling points in 2000.

Sampling point	Concentration in 1995, mmol m^{-3}		Change in concentration in 2000, +/- %		Change in concentration in 2005, +/- %	
	P_{tot}	$[PO_4^{3-}$-P]	P_{tot}	$[PO_4^{3-}$-P]	P_{tot}	$[PO_4^{3-}$-P]
Kulina	0.35	0.16	**37**	**63**	-34	-19
Roostova	0.90	0.19	-28	0	-86	-68
*Liiva	1.1	0.42	**9**	**24**	-47	-45
Mädaoja	0.84	0.55	**79**	**35**	-12	-65
Ulvi	0.84	0.32	**67**	**31**	-38	-90
Sämi	0.90	0.68	**22**	-34	-32	-76
Kohala	0.97	0.74	**343**	**441**	-24	-61
Lammasmäe	1.3	0.90	-23	-32	-43	-71
Lontova	1.1	0.71	**527**	**393**	0	-37

*-Sampling points of a tributary

Table 4. Concentrations of different forms of phosphorus in the water samples from the sampling points of the Kunda catchment in July 1995 and their changes in July 2000 and 2005.

In 2005 the concentrations of phosphorus were reduced in all sampling points of the Kunda River. The variations of phosphorus concentrations can be connected with weather condition of sampling time, because rain water can lower the concentration due to dilution. The calculated fluxes of phosphorus were quite similar in the water of the Kunda River in 1995 and 2005 and fluxes of PO_4^{3-}-P formed about 50% of the flux of total phosphorus (Table 5).

Sampling point	1995		2005	
	P_{tot}, mg s^{-1}	$[PO_4^{3-}$-P], mg s^{-1}	P_{tot}, mg s^{-1}	$[PO_4^{3-}$-P], mg s^{-1}
Kulina	nd	nd	3	2
Roostova	18	4	2	1
*Liiva	22	8	13	5
Mädaoja	31	20	32	8
Ulvi	nd	nd	nd	nd
Sämi	56	42	nd	nd
Kohala	60	46	nd	nd
Lammasmäe	nd	nd	161	56
Lontova	107	64	238	98

*-Sampling points of a tributary

Table 5. Fluxes of dissolved phosphorus in the sampling points of Kunda River

5. Changes in the water quality in the Pühajõgi and Purtse Rivers, directly connected with oil-shale mines

5.1 The Purtse River

The Purtse River is located mainly in Ida-Viru County in North-East Estonia (Fig. 1). The total length of the Purtse River is 51 km and the catchment covers an area about 816 km^2. The whole catchment area is located in the western part of the Estonian oil shale deposit and the catchment area is rich in tectonic faults and karst (Rätsep & Liblik, 2001).

The Purtse River is located in the center of mining area and therefore the water quality and hydrological conditions of the Purtse catchment are quite well studied (Kaasik & Sõukand, 2000; Karhu & Põllumaa, 2006; Rätsep& Liblik, 1998, 2000, 2001, 2004; Rätsep et., 2002). Besides the mine water, the Kohtla River (tributary of the Purtse River, Fig. 1) is also polluted with toxic ash-dump waters of the Kohtla-Järve oil shale processing plant, which contain in addition to sulfates (above 600 mg L^{-1}) and chlorides (up to 500 mg L^{-1}) also phenols (above 50 mg L^{-1}) and sulfides (above 200 mg L^{-1}) (Rätsep & Liblik, 2001). In 1990 the amount of mine water directed into the Purtse River catchment was about 137 million m^3 per year (Rätsep & Liblik, 2000), while the amount of mine water going into the Purtse River decreased to 26 million m^3 per year in 2001 as the Kohtla mine was closed (Rätsep et al., 2002).

Water samples of the Purtse River were sampled and analyzed by different scientists and because there are some problems in comparing different results. The sampling points of the Purtse River are presented in Fig. 1A and results are presented in Tables 6 and 7.

Sampling point	N_{tot}	$[NO_3^-$-N]	$[NO_2^-$-N]	$[NH_4^+$-N]
	Concentration in 1995, mmol m^{-3}			
Kohtla	22	12	0.14	0.71
Lüganuse	67	2.8	0.93	43
Purtse	121	107	0.71	5.7
Change of concentration in 2000, +/- %				
Kohtla	-72	-65	-67	**300**
Lüganuse	-76	-78	-69	-92
Purtse	**42**	**32**	**150**	-38
Change of concentration in 2005 (or 2011),+/- %				
Kohtla	**300**^{x}	**371**^{x}	nd	-83^x
Lüganuse	**39**^{x}	**700**^{x}	nd	**12**^{x}
Purtse	-18	-33	-70	-62

nd – not determined
^{x}-Samples from Kohtla and Lüganuse were analyzed in 2011.

Table 6. Concentrations of different forms of nitrogen in the water samples from the sampling points of the Purtse catchment in July 1995 and their changes in July 2000 and 2005(or 2011).

In 1995 the concentrations of total, nitrate and nitrite nitrogen (Table 6) in water sampled from the Purtse River were lower than concentrations of respective fractions of nitrogen of water sampled from the Kunda River (Table 2) which can be connected with huge amounts

of discharged mine water. In 2000 their concentrations were lowered more than 60%, but in sampling point of Purtse the concentrations were increased more than 30%. Only the concentrations of ammonia were higher in water sampled from the Purtse River in comparison with the results of Kunda River. In 2000 the concentration of ammonia was increased in sampling point of Kohtla (Table 6) and it was lowered in the other sampling points in comparison with results in 1995. In 2005 the concentrations of different forms of nitrogen were significantly increased in water sampled from the Kohtla River. It can be connected with leachate from the ash-dumping heaps.

The concentrations of different forms of phosphorus are presented in Table 7 and in 1995 their values were quite similar to results for the Kunda River (Table 4). There is no the clear trend for the concentrations of phosphorus in the water samples of the Purtse River in 2000 and 2005. In the downstream of the Purtse River (sampling point Purtse) the concentration of phosphorus was increased, but it was lowered in 2011.

Sampling point	Concentration in 1995, mmol m^{-3}		Change of concentration in 2000, +/- %		Change of concentration in 2005 (or 2011),+/- %	
	P_{tot}	$[PO_4^{3-}$-P]	P_{tot}	$[PO_4^{3-}$-P]	P_{tot}	$[PO_4^{3-}$-P]
Kohtla	0.32	0.32	0	0	**370**[x]	nd
Lüganuse	1.3	1.3	**84**	-50	**27**[x]	nd
Purtse	0.77	0.45	**25**	**86**	-17	-23

nd – not determined
[x]-Samples from Kohtla and Lüganuse were analyzed in 2011.

Table 7. Concentrations of different forms of phosphorus in the water samples from the sampling points of the Purtse catchment in July 1995 and their changes in July 2000 and 2005 (or 2011).

5.2 The Pühajõgi River

The Pühajõgi River is located in Ida-Viru County in North-East Estonia (Figure 1B). The length of the main river is 28 km, and the catchment covers an area of 196 km^2 (Järvekülg, 2001). The whole catchment is located in the western part of the Estonian oil shale deposit area and large volumes of mine water were discharged into the upper reach of the Pühajõgi River (Vaht & Rätsep, 2009). The Pühajõgi River is not so well studied (Selberg et al., 2009, Vaht & Rätsep, 2009), but it was included into the hydrological field works. Water was sampled in different points of the main river and streams in 1995, 2000 and 2005, and the sampling was made in July. Summary of results is presented in Tables 8-12 (Selberg et al., 2009, Selberg, 2010).

The analyzed water samples were mostly weakly alkaline (pH 7.3-8.0) and they had quite high alkalinity (Table 8). 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. 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 (Table 1).

Sampling point	pH			Conductivity in 2005, μS cm^{-1}	Alkalinity [HCO_3^-] in 2005, mmol m^{-3}	Total dissolved solids (TDS) in 2005, mg L^{-1}
	1995	2000	2005			
Kukruse	7.2	7.0	7.3	984	6097	659
Kotinuka	7.2	7.2	7.3	814	5195	545
Toila crossroads	7.3	7.3	7.5	991	5392	664
*Rausvere	8.0	7.5	7.3	1860	4786	1246
Voka crossroads	7.6	7.6	7.6	1720	4884	1152
*Mägara	7.6	7.7	8.0	564	4196	378
Toila-Oru	8.0	7.8	7.9	1528	4294	1024

*-Sampling points of a tributary

Table 8. pH, conductivity, alkalinity and concentration of total dissolved solid in the water samples from the sampling points of the Pühajõgi catchment in July.

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 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.1). Conductivity of the water samples of the Kunda River was on the average 500 μS cm^{-1}, practically independent of the sampling point (Table 1).

The determined concentrations of nitrate nitrogen in water samples of the Pühajõgi catchment (Table 9) had quite different values (variation up to 10 times), and the highest concentration of nitrate nitrogen (252 mmol m^{-3}) was determined in the sampling point of Toila-Oru in 1995. The concentrations of nitrate nitrogen were very low (up to 1% from the concentration of total nitrogen) in the sampling points of Kukruse and Toila crossroads which means that nitrogen occurred in other forms (ammonia and organic compounds). The concentrations of total nitrogen and nitrate nitrogen were lowered in 2000 and 2005 mainly in the downstream of the Pühajõgi River.

The analysis of water samples showed that variations of concentrations of ammoniacal nitrogen were significant (between 1.1 and 520 mmol m^{-3}) and the higher concentrations of NH_4^+-N up to 340 mmol m^{-3} (up to 99% from N_{tot}) and 520 mmol m^{-3} (up to 81% from N_{tot}) were determined in the water sampled from Kukruse and Toila crossroads in 1995, respectively. It confirmed that nitrogen occurred in form of ammonia. The concentration of ammonia decreased significantly during the next ten years indicating the reduction of pollution of the Pühajõgi River.

Concentrations of nitrite were quite low (up to 7.8 mmol m^{-3}) in the water samples from the catchment of the Pühajõgi, whereas variations of concentrations of ammoniacal nitrogen

were significant and the highest concentration of NH_4^+-N up to 520 mmol m^{-3} was determined in 1995. The concentration of nitrite nitrogen was increased almost in all the sampling points of the Pühajõgi River in 2000, but it decreased during the next five years (Table 9).

Sampling point	N_{tot}	$[NO_3^-$-N]	$[NO_2^-$-N]	$[NH_4^+$-N]
	Concentration in 1995,mmol m^{-3}			
Kukruse	345	3.5	0.43	340
Kotinuka	100	54	0.79	2.6
Toila crossroads	645	4.9	0.14	520
*Rausvere	186	186	2.1	14
Voka crossroads	327	180	2.5	98
*Mägara	31	2.1	0.14	1.1
Toila-Oru	327	252	1.2	18
Change of concentration in 2000,+/- %				
Kukruse	-60	**1186**	**1714**	-94
Kotinuka	-24	-67	**141**	-58
Toila crossroads	-82	**165**	**900**	-97
*Rausvere	**3**	-67	**224**	**321**
Voka crossroads	-50	-71	**172**	-79
*Mägara	0	-83	-57	-67
Toila-Oru	-58	-70	**42**	-77
Change of concentration in 2005,+/- %				
Kukruse	-50	**177**	**714**	-72
Kotinuka	-36	-98	-63	-4
Toila crossroads	-90	-43	**157**	-99
*Rausvere	-59	-80	-62	-63
Voka crossroads	-69	-87	-68	-90
*Mägara	**84**	**614**	0	**64**
Toila-Oru	-79	-92	**50**	-48

*-Sampling points of a tributary

Table 9. Concentrations of different forms of nitrogen in the water samples from the sampling points of the Pühajõgi catchment in July 1995 and their changes in July 2000 and 2005.

Calculated fluxes of nitrogen showed that 80% of nitrogen had infiltrated into the Pühajõgi River as NH_4^+-N in 1995. The fluxes of NO_2^--N and NH_4^+-N were reduced in further downstream of the Pühajõgi due to oxidation as the fluxes of nitrate increased (Table 10). In 2005, the fluxes of nitrogen had reduced 3-5 times in comparison with 1995 and the fluxes of organic nitrogen constituted more than 50% of the fluxes of total nitrogen in the Pühajõgi River.

Sampling point	N_{tot}, mg s^{-1}	$[NO_3^-$-N], mg s^{-1}	$[NO_2^-$-N], mg s^{-1}	$[NH_4^+$-N], mg s^{-1}
	1995			
Kukruse	39	0.4	0.05	38
Kotinuka	56	30	0.4	1
Toila crossroads	903	7	0.2	728
*Rausvere	1304	969	15	95
Voka crossroads	3993	2186	31	1188
*Mägara	13	0.9	0.06	0.5
Toila-Oru	4131	3177	15	225
2005				
Kukruse	48	3	1	26
Kotinuka	18	0.3	0.08	0.7
Toila crossroads	57	2	0.3	4
*Rausvere	431	152	4	29
Voka crossroads	630	153	5	59
*Mägara	48	13	0.1	2
Toila-Oru	1460	390	39	195

*-Sampling points of a tributary

Table 10. The fluxes of dissolved nitrogen in the sampling points of Pühajõgi River

The results of water analysis showed significantly different concentrations of total phosphorus and phosphate phosphorus in Pühajõgi and Kunda rivers (Tables 4 and 11). The concentrations of total phosphorus were even close to 100% lower during the ten years (1995-2005) which was a good sign for the improvement of water quality in 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.

In 2005 the situation of the fluxes of phosphorus was much better and PO_4^{3-}-P formed about 50% from the fluxes of total phosphorus as it was in sampling point of Mägara (the tributary

is not directly connected with oil shale mines) in 1995. The fluxes of phosphorus increased further downstream of Pühajõgi River indicating the continuous infiltration of phosphorus into the Pühajõgi River in 1995 and 2005.

The fluxes of PO_4^{3-}-P formed about 50% from the flux of total phosphorus in water of the Kunda River (Table 12) and similar situation was observed for Pühajõgi River in 2005. It means that the Pühajõgi River can achieve the natural conditions after the closing of oil shale mines.

Sampling point	Concentration in 1995, mmol m^{-3}		Change in concentration in 2000, %		Change in concentration in 2005, %	
	P_{tot}	$[PO_4^{3-}$-P]	P_{tot}	$[PO_4^{3-}$-P]	P_{tot}	$[PO_4^{3-}$-P]
Kukruse	50	45	-91	-93	-82	-82
Kotinuka	3.6	0.97	-56	-30	-61	-10
Toila crossroads	80	74	-95	-97	-98	-99
*Rausvere	15	14	-36	-37	-93	-96
Voka crossroads	27	24	-70	-75	-96	-98
*Mägara	1.8	0.97	-66	-99	-44	-67
Toila-Oru	30	25	-74	-76	-92	-93

*-Sampling points of a tributary

Table 11. Concentrations of different forms of phosphorus in the water samples from the sampling points of the Pühajõgi catchment in July 1995 and their changes in July 2000 and 2005.

Sampling point	1995		2005	
	P_{tot}, mg s^{-1}	$[PO_4^{3-}$-P], mg s^{-1}	P_{tot}, mg s^{-1}	$[PO_4^{3-}$-P], mg s^{-1}
Kukruse	12	11	6	5
Kotinuka	5	2	0.9	0.5
Toila crossroads	247	228	4	2
*Rausvere	240	210	14	8
Voka crossroads	720	635	14	5
*Mägara	2	0.9	2	0.6
Toila-Oru	846	693	108	81

*-Sampling points of a tributary

Table 12. Fluxes of dissolved phosphorus in the sampling points of Pühajõgi River

6. Conclusion: Environmental impact of closing of oil-shale mines on the surface water quality

Four oil shale mines were closed in 1999-2002 and the discharge of mine water into the rivers was reduced. The results of water analysis give information about the restoration of natural conditions in the rivers. The chemical status of the Purtse River is moderate on the basis of data obtained from the supplementary monitoring of 2003 and the national monitoring. For the drainage of mine waters in the Purtse catchment area, a new hydrological scheme is needed to restore gradually the natural hydrochemical conditions of the Purtse River water. However, the inlet of the ash-dump waters into the Kohtla River must be fully stopped. In connection with the closing of mines the impact of mine water on the hydrologic state of the rivers in the Purtse catchment area decreased significantly, whereas its changed balance has set more favorable conditions for development of phytoplankton.

The determined concentrations of nitrate nitrogen in water samples of the Pühajõgi catchment had quite different values (variation up to 10 times), and the highest concentration of nitrate nitrogen (252 mmol m^{-3}) was determined in 1995. The concentrations of total nitrogen and nitrate nitrogen were lowered in 2000 and 2005 mainly in the downstream of the Pühajõgi River. The analysis of water samples showed that variations of concentrations of ammoniacal nitrogen were significant (between 1.1 and 520 mmol m^{-3}) and the higher concentrations of NH_4^+-N were determined in 1995. The concentration of ammonia decreased significantly during the next ten years (1995-2005) indicating the reduction of pollution of the Pühajõgi River. 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.

The analysis of water quality showed that the Pühajõgi River could achieve natural conditions after closing oil shale mines, but it needs longer time as additional pollutants can be dissolved from the sediments of rivers.

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8. References

Aiken, G.., Cotsaris, E. (1995) Soil and hydrology: their effect on NOM. *J. AWWA*, 87, 36–45.

Banks, S.B., Banks, D. (2001) Abandoned mines drainage: impact assessment and mitigation of discharges from coal mines in the UK. *Engineering Geology*, 60, 31-37.

Brodnjak-Voncina, D., Dobcnik, D., Novic, M., Zpan, J. (2002) Chemometric characterization of the quality of river water. *Analytica Chimica Acta*, 462, 87-100.

Cuffney, T. F., Meador, M. R., Porter, S. D., Gurtz, M. E. (2000) Responses of physical, chemical, and biological indicators of water quality to a gradient of agricultural land use in the Yakima River Basin, Washington,. *Environmental Monitoring and Assessment*, 64, 259–270.

Dakova, Sn., Uzunov, Y., Mandadjiev, D. (2000) Low flow – the river's ecosystem limiting factor. *Ecological Engineering*, 16, 167-174.

Dawson, J.J.C., Malcolm, I.A., Middlemas, S.J., Tetzlaff, D., Soulsby, C. (2009) Is the composition of dissolved organic carbon changing in upland acidic streams? *Environmental Science and Technology*, 43, 7748–7753.

Equeenuddin, Sk.Md., Tripathy, S., Sahoo, P.K., Panigrahi, M.K. (2010) Hydrogeochemical characteristics of acid mine drainage and water pollution at Makum Coalfield, India. *Journal of Geochemical Exploration*, 105, 75-82.

Finkelman, R.B., Gross, P.M.K. (1999) The types of data needed for assessing the environmental and human health impacts of coal. *International Journal of Coal Geology*, 40, 91-101.

Järvekülg, A. (Ed.) (2001) *Estonian Rivers*. Estonian Agricultural University, Institute of Zoology and Botany. Tartu [in Estonian].

Kaasik, M., Sõukand, Ü. (2000) Balance of alkaline and acidic pollution loads in the area affected by oil shale combustion. *Oil Shale*, 17(2), 113-128.

Karhu, A., Põllumaa, L. (2006) Environmental hazard of the waste streams of Estonian oil shale industry: an ecotoxicological review. *Oil Shale*, 23(1), 53-93.

Kolker, A., Panov, B.S., Panov, Y.B., Landa, E.R., Conko, K.M., Korchemagin, V.A., Shendrik, T., McCord, J.D. (2009) Mercury and trace element contents of Donbas coals and associated mine water in the vicinity of Donetsk, Ukraine. *International Journal of Coal Geology*, 79, 83-91.

Kowalkowski, T., Zbutniewski, R., Szpejna, J., Buszewski, B. (2006) Application of chemometrics in water river classification. *Water Research*, 40, 744–752.

Mainstone, C.P., Parr, W. (2002) Phosphorus in rivers – ecology and management. *The Science of the Total Environment*, 282-283, 25-47.

Mighanetara, K., Braungardt, C.B., Rieuwerts, J.S., Azizi, F. (2009) Contaminant fluxes from point and diffuse sources from abandoned mines in the River Tamar catchment, UK. *Journal of Geochemical Exploration*, 100, 116-124.

Natarajan, K.A., Subramanian, S., Braun, J.-J. (2006) Environmental impact of metal mining – biotechnological aspects of water pollution and remediation – an Indian experience. *Journal of Geochemical Exploration*, 88, 45-48.

Neal, C., House, W. A., Jarvie, H. P., Neal, M., Hill, L., Wickham, H. (2006) The water quality of the River Dun and the Kennet and Avon Canal. *Journal of Hydrology*, 330, 155–170.

Perens, R., Punning, J.-M., Reinsalu, E. (2006) Water problems connected with oil shale mining in North-East Estonia. *Oil Shale*, 23, 228-235.

Pesce, S.F., Wunderlin, D.A. (2000) Use of water quality indices to verify the impact of Cordoba City (Argentina) on Suquia River. *Water Research*, 34, 291-2926.

Peuravuori, J., Pihlaja, K. (2007). Characterization of freshwater humic matter. In: Nollet, L.M.L. (Ed.), *Handbook of Water Analysis*. CRC Press, pp. 435–448.

Punning, J.-M., Boyle, J.F., Alliksaar, T., Tann, R., Varvas, M. (1997) Human impact on the history of Lake Nõmmejärv, NE Estonia: geochemical and palaeobotanical study. *The Holocene*, 7, 91-99 [in Estonian, summary in English].

Reinsalu, E., Valgma, I., Lind, H., Sokman, K. (2006) Technogenic water in closed oil shale mines. *Oil Shale*, 23, 15-28

Rätsep, A., Liblik, V. (1998) Changes in physico-chemical composition of mine water in closed Kiviõli oil shale mine. *Oil Shale*, 15(4), 341-352.

Rätsep, A., Liblik, V. (2000) Technogenic waterflows generated by oil shale mining: impact on Purtse catchment rivers. *Oil Shale*, 17(2), 95-112.

Rätsep, A., Liblik, V. (2001) The influence of polluted water flows on hydrological and hydrochemical conditions of Purtse catchment rivers, NE Estonia. *Nordic Hydrology*, 32(3), 215-226.

Rätsep, A., Rull, E., Liblik, V. (2002) Impact of oil shale mine water discharges on phytoplankton community of Purtse catchment rivers. *Oil Shale*, 19(3), 297-306.

Rätsep, A., Liblik, V. (2004) Impact of oil shale mining and mine closures on hydrological conditions of north-east Estonian Rivers. *Oil Shale*, 21(2), 137-148.

Sanchez, E., Colmenarejo, M.F., Vicente, J., Rubio, A., Garcia, M.G., Travieso, L., Borja, R. (2007) Use of the water quality index and dissolved oxygen deficit as simple indicators of watersheds pollution. *Ecological Indicators*, 7, 31-328.

Selberg, A., Viik, M., Pall, P., Tenno, T. (2009) Environmental impact of closing of oil shale mines on river water quality in north-eastern Estonia. *Oil shale*, 26(2), 169-183.

Selberg, A. (2010) *Evaluation of environmental quality in Northern Estonia by analysis of leachate*. PhD Thesis, University of Tartu.

Steinberg, C.E.W. (2008) *Ecology of Humic Substances in Freshwater*. Springer.

Štambuk-Giljanovic, N. (1999) Water quality evaluation by index in Dalmatia. *Water Research*, 33, 3423-3440.

Tamm, T., Nõges, T., Järvet, A., Bouraoui, F. (2008) Contributions of DOC from surface and groundflow into Lake Võrtsjärv (Estonia). *Hydrobiologia*, 599, 213-220.

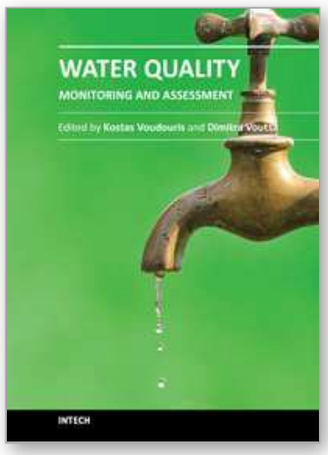
Tiwary, R. K. (2001) Environmental impact of coal mining on water regime and its management. *Water, Air, Soil Pollution*, 132(1–2), 85–199.

Vaht, R., Rätsep, A. (2009) Impact of oil shale mine water on hydrology and runoff of a small river. The Pühajõgi River case study. *Oil Shale*, 26(1), 84-93.

Withers, P.J.A., Lord, E.I. (2002) Agricultural nutrient inputs to rivers and groundwaters in the UK: policy, environmental management and research needs. *The Science of the Total Environment*, 282-283, 9-24.

Zsolnay, A. (2003) Dissolved organic matter: artifacts, definitions, and functions. *Geoderma*, 113, 187-209.

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