Oil Shale, 2000, Vol. 17, No. 2
pp. 95-112
ISSN 0208-189X

TECHNOGENIC WATERFLOWS GENERATED BY OIL SHALE MINING: IMPACT ON PURTSE CATCHMENT RIVERS

A. RÄTSEP, V. LIBLIK*

Tallinn University of Educational Sciences,
Institute of Ecology
North-East Estonian Department
15 Pargi St., Jõhvi
41537 Estonia

The correlation between natural (meteorological, hydrological) and technogenic (mining-technological, hydrogeological, hydrochemical) factors caused by oil shale mining in the Purtse catchment region in northeastern Estonia during 1990–1998 has been studied. As a result of a complex effect of these factors (correlation coefficients r = 0.60–0.86), a so-called hydrogeological circulation of water has been formed in the catchment area. It totals 25–40 % from the whole amount of mine water pumped out at the present, but in the near future it will reach even up to 50–55 %. On the ground of average data, a conceptual balance scheme of water circulation (cycles) for the Purtse catchment landscape has been worked out. It shows that under the influence of technogenic waterflows a new, anthropogenic biogeochemical matter cycling from geological environment into hydrological one has been formed in this catchment area. Transition of the macro- and microelements existing in the composition of oil shale into the aqueous solution and their distribution in mine water are in a good harmony with the so-called arrangement of the elements by the electrode potentials. The technogenic hydrochemical conditions arising in the catchment rivers will not disappear even after finishing oil shale mining.

Introduction

One of the most important industries of Ida-Viru County (Estonia) is oil shale mining that has been developed quite intensively during several decades in the northern part of this county. A number of underground mines (*Kiviõli*, *Kohtla*, *Sompa*, *Viru*) and the *Aidu* openpit situate just on the territory of one of the more essential catchment areas of the county – the catchment of the Purtse River. The mining areas of the *Tammiku* and *Estonia* mines are also in

* E-mail: *valdo@ecoviro.johvi.ee*

contact with the latter. It means that water circulation in the Purtse catchment landscape and the outflow (runoff) structure of the rivers are increasingly under the influence of the complex of technogenic factors (besides the natural ones).

In the course of underground and opencast mining the Ordovician aquifer complex has been totally drained, and the large-scale water output from the mines to the catchment rivers has gone with it. Precipitation water intensively infiltrates the mines by different tectonic faults (and joints); water of the rivers and outflow ditches moves in turn through the geological environment back into the mines. It determines the genesis of water circulation with a new structure in the Purtse catchment area, which noticeably differs from the natural one. Because of the aeration of the mines and of the inflow of water enriched with oxygen and carbon dioxide into the ones, geochemical processes have intensified causing essential changes in the physical-and-chemical composition of mine water pumped out [1]. In the region of the Purtse catchment area there are also oil shale thermal processing enterprises (in Kohtla-Järve and Kiviõli) whose solid wastes and wastewaters have polluted the Purtse River with phenols and sulfides during decades [2].

It is clear that it is necessary to investigate the new situation in the outflow structure of the Purtse catchment rivers and also to asses the river water quality conditions in the situation of water circulation influenced technogenically. The aim of this paper is to analyse the correlations and co-effect of natural and technogenic factors on the water circulation of the Purtse catchment landscape, to work out a new conceptual water circulation balance scheme, and to indicate essential changes being taken and taking place in physical-and-chemical composition of river water, and to elucidate their causes. Potential hydrological and hydrochemical conditions of catchment rivers are also considered, and that in connexion with reduction (or even finishing) of oil shale mining. Such an investigation has been carried out for the first time.

Description of Study Area

The Purtse catchment area is located mainly in Ida-Viru County covering the territory with an area of about 816 km^2. It is about 24 % from the total territory (3364 km^2) of the county. The whole catchment area covers also the western part of Estonian oil shale mining area (Fig. 1, streaked areas). Total length of the Purtse River is 51 km, and it flows into the Gulf of Finland. Long-term means of the annual runoff for this river are following: total annual runoff – 210 million m^3, mean annual discharge – 6.7 m^3/s. Total slope of the river equals 77 m, slope per kilometre – 1.50 m [3]. The more important tributaries of the Purtse River are: Kohtla, Ojamaa, Hirmuse and Erra (Fig. 1). Many streams and ditches flow into them in their turn.

The landscape of the catchment area is plain, with prevailing arable lands, forests and embogged areas. Lands spoiled by quarrying and recultivated after quarrying remain on the territory of the *Aidu* openpit. To the left from the Purtse River, between the Erra and Hirmuse rivers, a large mining field of closed *Kiviõli* underground oil shale mine with an area of about 30 km^2 was formed. In the period of mine operations the pumped-out mine water was directed into the Hirmuse River.

After closing the mine the mine water outflow is directed into the Purtse River through a ditch system (in Fig. 1 marked with an arrow). To the right from the Purtse and Ojamaa rivers up to the Kohtla River and also over it, the *Aidu* openpit and *Kohtla*, *Sompa*, *Viru* and *Tammiku* underground mines are located. This whole mining territory within the boundaries of the catchment area has a total area about 160 km^2.

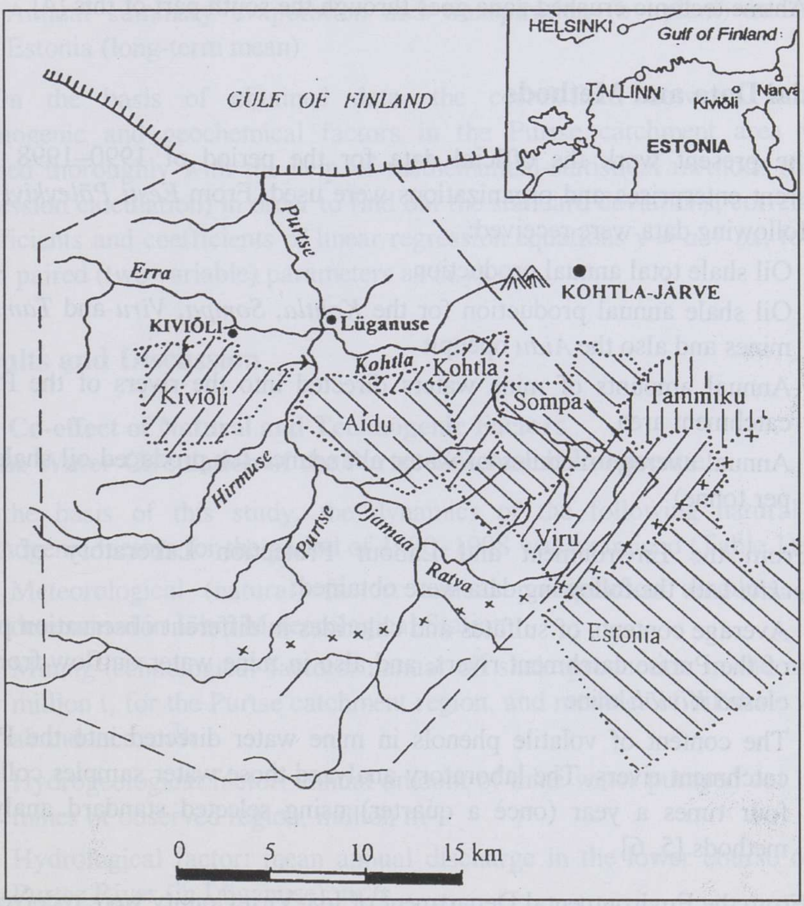

Fig. 1. Location of the Purtse catchment area: "– – –" – border of the catchment area; "......" – mines and openpit borders; "×××"– Ahtme tectonic crushed zone, [ash dump symbol] – ash dumps

For the present about 38 % from the total mined oil shale are excavated in named mines but about 43 % of the total mine water pumped out are directed into the Purtse catchment rivers. The mine water outputs to the rivers are as following: to the Ojamaa River – seven outputs from the *Aidu* openpit, the *Kohtla*, *Sompa* and *Viru* mines; to the Kohtla River – three outputs from the *Aidu* openpit, the *Kohtla* and *Tammiku* (only western part) mines. In addition to those, an output to the Kohtla River from the oil shale thermal processing plant of Kohtla-Järve (*Viru Keemia Grupp* Ltd.) in the form of ash-dump waters exists. Mine waters from the *Estonia* mine are not directed into the Purtse catchment rivers.

The mined-out areas of the former closed mines also remain in the north and north-east direction from the *Sompa* mine. In the Purtse catchment area oil shale lies in the depth of 20 m; the thickness of mined industrial layer reaches up to 2.5 m. The catchment area is rich in tectonic faults and karst; the Ahtme tectonic crushed zone goes through the south part of this [4].

Initial Data and Methods

In the present work the official data for the period of 1990–1998 from different enterprises and organizations were used. From *Eesti Põlevkivi* Ltd. the following data were received:

(1) Oil shale total annual production
(2) Oil shale annual production for the *Kohtla*, *Sompa*, *Viru* and *Tammiku* mines and also the *Aidu* openpit
(3) Annual amounts of mine waters directed into the rivers of the Purtse catchment area
(4) Annual average modules of water abundance for produced oil shale (m^3 per tonne)

From the Environment and Labour Protection Laboratory of *Eesti Põlevkivi* Ltd. the following data were obtained:

(1) Average contents of sulfates and chlorides in different observation points of the Purtse catchment rivers, and also in mine water outflow from the closed *Kiviõli* mine
(2) The content of volatile phenols in mine water directed into the Purtse catchment rivers. The laboratory analyzed those water samples collected four times a year (once a quarter) using selected standard analytical methods [5, 6]

From the Environmental Department of Ida-Viru County were received:

(1) Annual influxes of sulfates and chlorides with mine waters into the Purtse catchment rivers

(2) Annual amounts of ash-dump waters directed into the Kohtla River by *Viru Keemia Grupp* Ltd. in Kohtla-Järve, and the amounts of volatile phenols and sulfides discharged into the Kohtla River with ash-dump waters

(3) Monthly and annual average contents of volatile phenols in the water of the Purtse and Kohtla rivers. The Central Laboratory of *Viru Keemia Grupp* Ltd. analyzed water samples collected every month according to the time-table using selected standard analytical methods [5, 6]

From the Estonian Meteorological and Hydrological Institute were obtained:

(1) Annual precipitation amounts determined in Jõhvi Meteorological Station

(2) Mean annual discharges determined in Lüganuse, in the lower course of the Purtse River

(3) Annual summary evaporation and transpiration (by plant) in North Estonia (long-term mean)

On the basis of obtained data, the correlations between natural, technogenic and geochemical factors in the Purtse catchment area were studied thoroughly with the help of mathematical-statistical methods (linear regression calculation) in order to find out the standard deviations, correlation coefficients and coefficients of linear regression equations $y = a + bx$, for the main paired (two variable) parameters as (x,y).

Results and Discussion

The Co-effect of Natural and Technogenic Factors on the Water Circulation of the Purtse Catchment Landscape

As the basis of this study, the dynamics of the following natural and technogenic factors for the period of 1990–1998 was examined (Table 1):

- Meteorological (natural) factor: annual precipitation amounts, mm, determined in Jõhvi Meteorological Station
- Mining-technological factors: annual oil shale production in the mines, million t, for the Purtse catchment region, and modules of oil shale water abundance, m^3/t
- Hydrogeological factor: annual amount of mine water pumped out in the mines of observed region, million m^3
- Hydrological factor: mean annual discharge in the lower course of the Purtse River (in Lüganuse), m^3/s

From Table 1 it appears that the decrease in oil shale production inevitably follows the growth of the module of oil shale water abundance.

Table 1. **Dynamics of Technogenic, Natural and Geochemical Factors in the Oil Shale Mining in the Purtse Catchment Area for the Period of 1990–1998**

Factors	1990	1991	1992	1993	1994	1995	1996	1997	1998
Mining-technological factors									
Oil shale production, million t/yr:									
Total in the Ida-Viru County	21.2	18.3	17.0	14.3	14.0	13.3	13.1	12.9	10.9
Total in *Kohtla*, *Sompa*, *Viru* and *Tammiku* mines and *Aidu* openpit	7.6	6.6	6.1	5.1	5.0	4.8	4.7	4.5	4.0
Module of oil shale water abundance, m^3/t * (1)	15.5	16.5	16.4	16.6	16.7	17.6	11.3	17.2	20.8
Hydrogeological factors									
The amount of mine water directed into the catchment rivers million m^3/yr (2)	137.1	126.2	112.0	99.9	97.3	103.8	64.9	96.5	98.9
Ratio of the amount of mine water and module of water abundance (2) / (1)	8.85	7.65	6.83	6.02	5.83	5.90	5.74	5.61	4.75
Hydrological factors									
Mean annual discharge in the lower course of the Purtse River, m^3/s	10.3	8.7	7.2	6.3	6.2	7.8	3.6	6.6	9.6
Natural factors									
Annual precipitation amount, mm	786	835	600	692	659	775	587	724	841
Geochemical factors									
Input of the salts into the rivers, t/yr	–	–	–	–	–	40535	27299	35	26094
Including:									
Sulfates						37162	24948	32274	24165
Chlorides						3373	2351	2800	1929

* Calculated without mine water from the closed *Kiviõli* mine.

Table 2. **Results of Regression Analysis of Interdependence Between Natural and Technogenic Factors for the Purtse Catchment Area Affected by Oil Shale Mining**

Paired factors (x,y)	Standard deviation		Correlation coefficient $r(x,y)$	Coefficient of linear regression equation	
	$s(x)$	$s(y)$		a	b
Oil shale production – amount of mine water	1.0886	20.3876	0.8636	19.3686	15.5886
Annual precipitation amount – mean discharge of the Purtse River	94.7476	2.0267	0.8202	–5.3018	0.0175
Amount of mine water – mean discharge of the Purtse River	20.3876	2.0267	0.8443	–1.3681	0.0839
Amount of mine water – annual precipitation amount	20.3876	94.7476	0.6922	445.3893	2.6591
Module of oil shale water abundance – mean discharge of the Purtse River	2.0391	2.0267	0.6272	–2.7675	0.6234
Module of oil shale water abundance – annual precipitation amount	2.0391	94.7476	0.6034	266.3680	28.0361

The results of mathematical-statistical analysis (stat *xy*) of these factors are presented in Table 2. On the basis of data obtained by regression analysis we may conclude that the impact of natural and technogenic factors on the hydrological and hydrogeological regime and conditions of the Purtse catchment area has a complex character formed as a result of intensive oil shale mining, which unavoidably effects the outflow (runoff) structure of the Purtse catchment rivers and dynamical evolution of landscape water cycles. The correlation coefficients between the main factors lie within the range of 0.6034–0.8636.

The complex of regression equations enables to calculate and prognosticate the relative importance of ground water in the landscape water circulation, taking into account the data about the precipitation water infiltration into the mines through the overburden rocks and about the mine waters pumping out into the catchment rivers. As a result of intensification of these processes, the share of ground water in the catchment landscape water circulation is increased at least up to 50–60 %.

The connections derived between the factors give us a basis to conclude that in the catchment landscape total water circulation a so-called hydrogeological circulation must be formed, which essentially influences the share of mine water in the river flow of the Purtse River lower course. An extensive technogenic deformation of ground water flows in Keila-Kukruse aquifer has caused this new hydrogeological circulation.

A Conceptual Balance Scheme of the Catchment Landscape Water Circulation, and the Resultant Characteristics of the State of the Purtse River

For composing a conceptual water circulation balance scheme, the following data for the period of 1990–1998 were used:

- The area of the Purtse catchment region, km^2. 816
- Average amount of mine water directed into the catchment rivers, million m^3/yr 104
- Average annual amount of precipitation, mm/yr 722
- Annual mean discharge of the Purtse River, m^3/s. 7.4
- Total evaporation and transpiration by plant, mm/yr 400
- Precipitation water infiltrating the mines (by an assessment of the hydrogeologists), % from the pumped-out mine water . . . . 56 [7]
- Re-infiltration of waters from rivers and outflow canals into the mines (by an assessment of hydrogeologists), % from the pumped-out mine water . . . . 26 [8]

Marking the amounts of mine water pumped out, flowing out mine water and precipitation water infiltrating the mines with M_v, M and S, respectively, we can write that $M_v = 1.35M$ and $S = 0.75M$. A conceptual balance scheme of the catchment landscape water circulation composed is presented in Fig. 2.

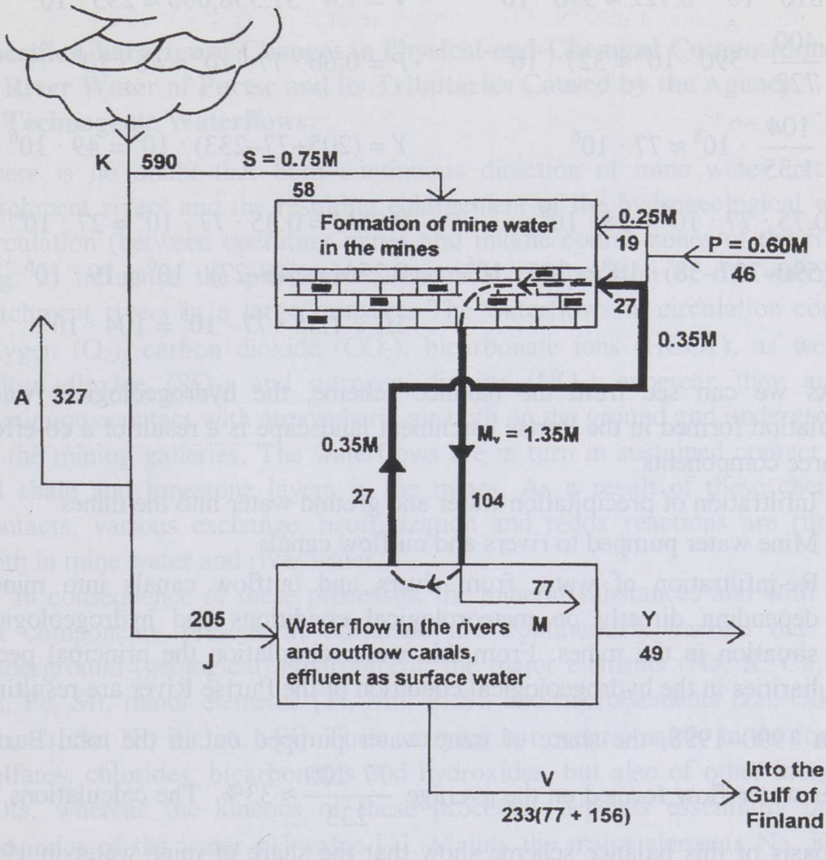

Fig. 2. A conceptual water circulation balance scheme of the Purtse catchment landscape (average for the years 1990–1998). Marking the waterflows: K – precipitation on the catchment area; A – evaporation and transpiration; S – infiltration of precipitation water into the mines; J – precipitation water into the rivers and flood flow; P – ground water flow into the mines; M_v – mine water pumped out, and the same flowing from the Kiviõli mine; M – mine water flow with river water; V – Purtse River flow into the Gulf of Finland; Y – water flow outwards the catchment area.

The numbers mark the average waterflows (million m^3/yr).

Water hydrogeological circulation is indicated by continuous and dotted lines

Looking at the Fig. 2, it becomes evident that $K = A + J + S$, and $J + M = Y + V$, as well as $P = 0.25M + 0.35M$. The numerical values (million m^3/yr) of water flows are as follows:

$K = 816 \cdot 10^6 \cdot 0.722 \approx 590 \cdot 10^6$

$A = \frac{400}{722} \cdot 590 \cdot 10^6 \approx 327 \cdot 10^6$

$M = \frac{104}{1.35} \cdot 10^6 \approx 77 \cdot 10^6$

$S = 0.75 \cdot 77 \cdot 10^6 \approx 58 \cdot 10^6$

$J = (590–327–58) \cdot 10^6 = 205 \cdot 10^6$

$V = 7.4 \cdot 31{,}536{,}000 \approx 233 \cdot 10^6$

$P = 0.60 \cdot 77 \cdot 10^6 \approx 46 \cdot 10^6$

$Y = (205+77–233) \cdot 10^6 = 49 \cdot 10^6$

$0.35M = 0.35 \cdot 77 \cdot 10^6 \approx 27 \cdot 10^6$

$0.25M = (46–27) \cdot 10^6 = 19 \cdot 10^6$

$M_v = 1.35 \cdot 77 \cdot 10^6 = 104 \cdot 10^6$

As we can see from the balance scheme, the hydrogeological water circulation formed in the Purtse catchment landscape is a result of a co-effect of three components:

(1) Infiltration of precipitation water and ground water into the mines

(2) Mine water pumped to rivers and outflow canals

(3) Re-infiltration of water from rivers and outflow canals into mines, depending directly on meteorological conditions and hydrogeological situation in the mines. From this water circulation the principal peculiarities in the hydrogeological condition of the Purtse River are resulting

In 1990–1998, the share of mine water pumped out in the total Purtse River water flow formed on the average $\frac{77 \cdot 100}{233} \approx 33\%$. The calculations on the basis of this balance scheme show that the share of mine water in 1996 (poor in precipitation, annual precipitation amount 587 mm, annual mean discharge for the Purtse River 3.6 m^3/s) in the Purtse River water flow was even about 42 %. But in 1998 (rich in precipitation, annual precipitation amount 841 mm, annual mean discharge accordingly 9.6 m^3/s) it was only about 24 %. In 1998, the water hydrogeological circulation formed about 40 % from the amount of mine water pumped out. It led to a decrease in the share of mine water in the lower course of the Purtse River even up to 20 %. With regard to quality of river water it is useful, as the bigger dilution is formed.

A conceptual balance scheme of the water circulation worked out enables us to simulate the temporal-spatial dynamics of the hydrogeological water circulation components, proceeding from the geological specific character of oil shale mining taken and taking place in the catchment area (plenty of tectonic faults, nearness of the Ahtme tectonic crushed zone), and from deformation of ground water flow in the Keila-Kukruse aquifer, likewise from seasonal diversity of meteorological conditions. The hydrogeological circulation formed in the catchment area has created the basis for a new, anthropogenic biogeochemical matter cycling from geological environment into hydrological one.

Specific Character of Changes in Physical-and-Chemical Composition of River Water of Purtse and its Tributaries Caused by the Agency of Technogenic Waterflows

There is no doubt that both continuous direction of mine water into the catchment rivers and the resulting enlargement of the hydrogeological water circulation (between operating mines and middle course zones of the rivers, Fig. 2) influence the physical-and-chemical composition of the waters of catchment rivers in a large measure. The waterflows in circulation contain oxygen (O_2), carbon dioxide (CO_2), bicarbonate ions (HCO_3^-), as well as sulfur dioxide (SO_2) and nitrogen dioxide (NO_2), whereas they are in continuous contact with atmospheric air both on the ground and underground, in the mining galleries. The waterflows are in turn in sustained contact with oil shale and limestone layers in the mines. As a result of these chemical contacts, various exchange, neutralization and redox reactions are running both in mine water and river water.

In consequence of these processes, the mineral substances and with them all components present in oil shale are continuously carried out from underground (geological) environment: the major elements (Na, K, Ca, Mg, Al, Fe, Si), minor elements (Ti, Mn, P, S), and microelements (Zn, Cd, Pb, Cu, Cr, Se, Ni, Ba, etc.) [9]. Their carrying out occurs mainly in the form of sulfates, chlorides, bicarbonates and hydroxides, but also of other inorganic salts, whereas the kinetics of these processes depends essentially on the dynamics of the water pH value [1]. Mainly the major elements Na, K, Ca and Mg, as well as minor ones Ti and Mn form the above-mentioned salts.

Taking the years 1995–1998 as the study period (Table 1), the correlation between such technogenic and geochemical factors as annual oil shale production in the catchment region, amount of mine water directed into the rivers, the module of oil shale water abundance, and annual input of the salts (sulfates + chlorides) from the mines into the rivers (with mine water), was additionally investigated by means of regression analysis (stat *xy*) (Table 3). From Table 3 it appears that the correlation coefficients lie within the range of 0.5599–0.8003.

The correlation is satisfactory, and such a result is important as it proves interdependence between technogenic and geochemical factors, realized in the actual conditions of the water hydrogeological circulation formed in the catchment area.

Table 3. **Results of Regression Analysis in Study of Correlations Between Technogenic and Geochemical Factors for the Purtse Catchment Area Affected by Oil Shale Mining**

Paired factors (x,y)	Standard deviation		Correlation coefficient $r(x,y)$	Coefficients of linear regression equation	
	$s(x)$	$s(y)$		a	b
Oil shale production – input of salts	0.3559	6807.4698	0.6292	– 21907.0000	12035.0000
Amount of mine water – input of salts	17.6796	6807.4698	0.5599	12625.6155	215.5988
Module of oil shale water abundance – input of salts	2.8941	6807.4698	0.8003	3588.9944	1882.5291
The ratio of the amount of mine water and module of water abundance – input of salts	0.5139	6807.4698	0.6721	–16719.0784	8903.5597

Taking the average input of sulfates and chlorides in 1995–1998 into the Purtse River for 29 640 t/yr and 2610 t/yr, respectively, at least 740 000 t of sulfates and 65 000 t of chlorides have been discharged into the Purtse River during the last 25 years, and finally they have reached the Gulf of Finland.

In Table 4 the concentrations of sulfates and chlorides in different observation points of the Purtse catchment rivers for the period of 1995–1998 are shown. From those data it becomes evident that mainly the lower course of the Ojamaa River, and the middle and lower courses of the Purtse and Kohtla rivers are under the pollution load of sulfates and chlorides carried out with mine water. Besides the mine water, the Kohtla River is also polluted with ash-dump waters of *Viru Keemia Grupp* Ltd., which contain, in addition to sulfates and chlorides, organic pollutants (phenols, oil products) and sulfides as well.

Table 4. **Average Concentration of Sulfates and Chlorides in Different Observation Poins of the Purtse Catchment Rivers for the Period of 1995–1998, mg/l**

Observation point	Parameter	Year			
		1995	1996	1997	1998
In the Ojamaa River before flowing into the Purtse River	Sulfates Chlorides	573 29.3	555 32.6	609 21.9	563 24.2
In the Purtse River before falling of the Kohtla River	Sulfates Chlorides	322 35.9	404 38.7	233 24.3	274 19.8
In the Kohtla River before flowing into the Purtse River	Sulfates Chlorides	337 40.3	395 37.2	414 35.8	362 29.1
In mine water outflowing from the *Kiviõli* mine into the Purtse River	Sulfates Chlorides	296 33.2	285 30.3	236 33.2	239 25.3
In the Ojamaa River before falling of the Ratva stream	Sulfates Chlorides	45.4 13.6	40.5 11.1	34.0 16.0	24.7 9.1

In 1995–1998, 600–800 thousand m^3/yr of ash-dump waters were directed into the Kohtla River which makes 20–30 t/yr of volatile phenols and 120-150 t/yr of sulfides thrown into the river. As a result of this, water of the Kohtla River, before flowing into the Purtse River, contained at the most 3–8 mg/l of volatile phenols, and in the Purtse River, after falling of the Kohtla River (5 km downstream), the phenol content was up to 0.6 mg/l. Depending on seasons, the content of volatile phenols in the river water fluctuated noticeably: the minimum concentrations in the Kohtla River lay within the range of 0.01–0.2 mg/l, in the Purtse River 0.002–0.02 mg/l, respectively. Thus, the phenolic pollution of the Kohtla River carries a very fluctuating character. In the observation period the content of sulfides in the Kohtla River was 0.8–3.5 mg/l. These circumstances cause also a large fluctuating in the river water oxygen regime, whereas the oxygen concentration does not achieve the saturation degree (not above 60–70 %).

Dispersion aureole of pollutants generated by ash-dump waters and located in Kohtla-Järve produces the pollution spreading in many ways:

(1) The pollutants flow from the Kohtla River into the Purtse River

(2) The soil and ground water in surroundings of the ash-dumps are polluted

(3) The pollutants appear in the mine water pumped out by the action of water hydrogeological circulation

Therefore, the pollution of the environment in surroundings of the Kohtla River resulting from oil shale thermal processing combines with harmful impact of oil shale mining. That is why in the mine water the concentration of volatile phenols up to 0.003–0.004 mg/l have been determined.

For the sectors of rivers not polluted by technogenic waterflows (for example, in the Purtse River before falling the Ojamaa River, and in the Ojamaa River before falling the Ratva stream), the concentrations of sulfates and chlorides in water in the same period did not exceed 45 mg/l and 20 mg/l, respectively (Table 4).

Beside the macroelements (major and minor elements), a number of the microelements as Ba, Se, Cr, Zn, Cd, Ni, Pb, Cu, etc. in mine water have been determined [10, 11]. A more thorough analysis showed that the appearance of both the macro- and microelements in mine water, and their distribution in the latter as well as in river water is in a good harmony with the so-called arrangement of the elements by the electrode potentials (in the interval of –3 V … +3 V) [12]. The location of an element in the arrangement shows how easily it ionizes in water solution, and, therefore, characterizes its chemical activity. The electrode potentials of the macroelements K, Na, Mg and Ca lie in the interval of –2.92 … –2.36 V, but the potentials for the microelements Se, Cr, Zn, Cd, Ni, Pb and Cu remain in the interval of –0.92 … +0.52 V, only for Ba the electrode potential is more negative (–2.91 V).

In mine water, in certain conditions (especially, in the presence of bicarbonates and carbon dioxide) the metal ions can be activated, and a complex of running exchange reactions takes place, in the course of which the mutual extrusion of the metal ions from originated compounds proceeds in keeping with their electrode potentials. In addition to the macroelements just the microelements with negative or close to nought electrode potential are the first to enter the water solution. In mine water the above-mentioned microelements in the limits of 0.2–10 μg/l have been found [10]. The amount of the microelements existing in mine water increases on the account of the microelements from the atmospheric air. They get mixed in river water. The microelements Se, Zn, Cd, Ni, Pb and Cu as sulfophilic ones occur in pyrite (FeS_2) in isomorphic modes or as micro-additions [9] what promotes their transition into the mine water during transformation and geochemical reactions of pyrite as a component of oil shale. The geochemical and hydrochemical processes in mine water concerning the microelements still demand quite radical investigations to obtain a more complete review about their migration in the hydrological environment and their participation in the biogeochemical matter cycling.

About the Future Condition of Catchment Rivers, Potential Changes in the Balance Scheme

Today the whole mined-out area in the Purtse catchment region constitutes about 200 km^2 that is roughly 25 % from the total catchment area. Taking into account the continual increase in the mined-out area and its perimeter, we can clearly suppose that as a result of the co-effect of natural and technogenic factors, a permanent tendency for essentially changing the physical-and-chemical composition of the Purtse River's water in its middle and lower course has formed. The following changes in the balance scheme (Fig. 2) may have been occurred:

- The amount of precipitation waters infiltrating the mining galleries will increase slowly but continuously. When during the last 10 years it formed, on average, about 56 % from the amount of mine water pumped out, the waterflows infiltrating from above (through the overburden rocks) may increase up to 65–75 % from yearly average dewatering the mines, respectively
- The waterflow being in continuous hydrogeological circulation will also increase up to 50–55 % from the total amount of mine water pumped out

It means that the amount of water flowing into the Purtse River from underground (geological) environment (in Fig. 2, marked with *M*) decreases to a certain extent, stabilizing at about 20 % from the total waterflow in the lower course of the Purtse River. Therefore, the share of ground water in the catchment landscape water circulation will increase surely, but this share of water as a whole did not always reach the lower course of the Purtse River (and the Gulf of Finland), due to hydrogeological circulation. It is one of the most essential features of the Purtse catchment landscape water circulation.

The tendency of the quality change of the Purtse River water will not disappear even after finishing the active production processes, i.e. after the final closing of mines. In the period just after closing the mines, the hydrogeochemical factor will acquire an essential importance, which affects the input of sulfates, chlorides, bicarbonates and hydroxides into the rivers [13]. The changes in the physical-and-chemical composition of mine water flowing into the Purtse River after closing the *Kiviõli* mine showed it expressively [1]. The content of sulfates in water flowing from the mine decreases indeed, but in any case exceeds the natural background 4–5 times (Table 4).

It can be said on the ground of the results that the situation formed for the present time for drainage of mine waters into the catchment rivers cannot be considered useful for the river water ecological condition. The Ojamaa and Kohtla rivers have been under a particularly great and long-time technogenic load. The polluted water of those rivers damages in turn the water quality in the middle and lower course of the Purtse River: for the present it is damaged irreparably. River's flora and fauna have been impoverished by the agency of both the mine waters and ash-dump phenolic waters of *Viru Keemia Grupp* Ltd., essentially worsening the use of the catchment rivers in the region hydrological management system (fishing, catching of crayfish, water supply, recreation).

For drainage of mine waters the new hydrological scheme must be worked out in the Purtse catchment landscape area. However, outflow of the ash-dump waters into the Kohtla River must be fully stopped, thereby considering the large quantitative seasonal fluctuation of all technogenic waterflows during the year. The best solution would be to direct the mine drainage waters straight into the Gulf of Finland partially.

Conclusions

Oil shale production in the Purtse catchment region (about 816 km^2) seriously influences the hydrological, hydrogeological and hydrochemical regime and conditions of the catchment rivers. Under the complex co-effect of natural and mining technogenic factors in the catchment area the so-called hydrogeological water circulation has formed which constitutes 25–40 % from the amount of mine water pumped out. This circulation has made a basis for the new, anthropogenic biogeochemical matter cycling from geological environment into the hydrological one of the rivers.

A conceptual balance scheme of water circulation for the Purtse catchment landscape was worked out which enables to simulate the temporal-spatial dynamics of hydrogeological circulation components. An annual input of sulfates and chlorides with mine water into the catchment rivers is in satisfactory correlation (r = 0.60–0.80) with technogenic factors of oil shale mining. Transition of the macro- and microelements existing in the composition of oil shale into the aqueous solution and their distribution both in mine water and river water are in a good harmony with the so-called arrangement of the elements by their electrode potentials.

Preferably the elements and heavy metals with negative electrode potentials, as Ba, Se, Cr, Zn, Cd, Ni, Pb, etc. enter the mine water. In geochemical reactions the pyrite (FeS_2) as a chemically active oil shale component has the key role, creating the basis for the complete cycle of chemical reactions.

Due to the co-effect of natural and technogenic factors, a strong tendency for transformation of physical-and-chemical composition of the Purtse River water has formed (heightened content of sulfates and chlorides). That tendency will not disappear even after finishing the active production processes and closing the mines. The waste products (leachates from the ash-dumps) of oil shale thermal processing cause a pollution, which will be combined with that caused by oil shale mining.

Restoration of the water quality of the whole Purtse catchment area rivers to the natural level demands a thorough alteration of the present mine water drainage hydrological scheme.

Acknowledgements

The authors are grateful to Estonian Ministry of Education for the financial support of this investigation (theme No. 0280340s98). We acknowledge the technical personnel and Environment and Labour Protection Laboratory of *Eesti Põlevkivi* Ltd., Environmental Department of Ida-Viru County Government, as well as Estonian Meteorological and Hydrological Institute for their data which enabled us to carry out the present work.

REFERENCES

1. *Rätsep, A., Liblik, V.* Changes in physico-chemical composition of mine water in closed *Kiviõli* oil shale mine // Oil Shale. 1998. Vol. 15, No. 4. P. 341–352.
2. *Rätsep, A.* Problems of water environment and water consumption // Impact of Oil Shale Mining and Processing on the Environment in North-East Estonia / V. Liblik and J.-M. Punning (Eds.). Publ. Inst. Ecol. Vol. 6. Tallinn, 1999. P. 130–142 [in Estonian].
3. Estonia - Nature / A. Raukas (Ed.). – Tallinn, 1995 [in Estonian].
4. *Gazizov, M. S.* Geological conditions of mining Baltic oil shale deposits // Proceedings of the 1st United Nations Symposium on the Development and Utilization of Oil Shale Resources / E. Petukhov (Ed.). Tallinn, 1970. P. 99–117 [in Russian].
5. *Lurje, J. J., Rybnikova, A. M.* Chemical Analysis of Industrial Wastewater. – Moscow, 1984 [in Russian].
6. *Semjonov, A. D.* Handbook of Chemical Analysis of Surface Water. – Leningrad, 1977 [in Russian].
7. *Parakhonski, E. V.* Conditions of Formation and Outflowing Wastewaters of Oil Shale Mines and Open Pits. – Tallinn, 1983 [in Russian].
8. *Norvatov, J. A.* Investigation and Prognosis of Technogenic Regime of Underground Water (in Operating Mineral Wealth Deposits). – Leningrad, 1988 [in Russian].

9. *Pets, L.* Probable modes of occurrence of elements in kukersite mineral matter // Oil Shale. 1998. Vol. 15, No. 3. P. 268–276 [in Russian with English summary].
10. *Rätsep, A., Toomik, A.* Hydrotechnogenic influxes into the Purtse Basin rivers in North-East Estonia // Energy, Environment and Natural Resources Management in the Baltic Sea Region – 4th International Conference on System Analysis / Ü. Mander et al. (Eds.). The Nordic Council of Ministers, Copenhagen, 1993. P. 459–462.
11. *Liblik, V., Rätsep, A.* Pollution sources and the distribution of pollutants // The Influence of Natural and Anthropogenic Factors on the Development of Landscapes – the Results of a Comprehensive Study in NE Estonia / J.-M. Punning (ed.). Publ. Inst. Ecol. Vol. 2. Tallinn, 1994. P. 70–93.
12. *Rabinovich, V. A., Havin, Z. J.* Short Chemical Handbook. – Leningrad, 1977 [in Russian].
13. *Clarke, L. B.* Coal mining and water quality // IEA Coal Research Publications, 1995. P. 1–99.

Presented by J. Kann
Received January 31, 2000