

**The Influence of Polluted Water Flows  
on Hydrological and Hydrochemical Conditions  
of Purtse Catchment Rivers, NE Estonia**

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The correlation between natural (meteorological, hydrological), mining-technological, hydrogeological and geochemical factors in the oil shale mining region in the Purtse catchment area for the period of 1990-1998 was studied. As a result of the interactions between these factors (correlation coefficients  $r=0.56-0.86$ ), a so-called hydrogeological circulation of water has formed in the catchment area. It was found that the circulation flow forms 25-40% of the total amount of mine water pumped out from the mines at present. On the basis of average data, a new balance scheme of water circulation (cycles) for the Purtse catchment was developed. Under the influence of different water flows a new, anthropogenic biogeochemical matter cycling from the geological environment into the aquatic environment of the rivers has formed in this catchment area. The pollution of the Purtse River from oil shale thermal processing is combined with the harmful impact of oil shale mining. The anthropogenic hydrochemical conditions arising in the rivers of this catchment will not disappear even after oil shale mining stops. A multiple regression formula was derived for prognosticating the flow regime (mean annual discharge) of the Purtse River using meteorological and mining-technological data.

## **Introduction**

Oil shale mining and processing in north-east Estonia were quite intensively developed throughout several decades. It is obvious that their impact on the water resources may range from minimal through to severe. The effects depend on the loca-

tion of the mines, mining and processing technologies, the hydrology and climate of specific areas, as well as the physical and chemical properties of the mined minerals (Clarke 1995).

A number of oil shale mines are located directly on the territory of one of the most important catchment areas in north-east Estonia – the catchment of the Purtse River – causing serious environmental problems. In the course of underground and open-cast mining, the Ordovician aquifer complex has been totally drained, and for draining a large network of the mine water outputs to the catchment rivers has constructed (Parakhonski 1983; Norvatov 1988). Water pumping from the mines is a technological inevitability of all operations. Therefore, water circulation with a new structure has developed in the Purtse catchment area, which noticeably differs from the natural one. The river water quality is under the influence of the various water flows of different pollution. It is necessary to investigate the new situation in the outflow (runoff) structure of the Purtse catchment rivers and to assess the river water quality in the situation where water circulation is influenced by oil shale mining and processing.

Systematic monitoring of the environmental situation in the Purtse catchment area is relevant for developing mitigation measures to improve the river water quality, and for establishing the major factors affecting the annual runoff of the Purtse River. Analysis of the situation is also necessary for the composition of water management plans for the Purtse catchment rivers, needed for achieving sustainability of the water resources.

The aim of this study was to analyse the interdependence between natural, mining and geotechnological factors and their effect on the water circulation in the Purtse catchment, to propose a new water circulation balance scheme, and to study the impact of polluted water flows on the chemical characteristics of the water of the catchment rivers. The purpose was also to estimate functional relationships between significant natural and mining-technological factors (as variables) for predicting the hydrological conditions of the Purtse River. Problems and perspectives of hydrological management of the Purtse catchment were also observed.

## **Study Area, Initial Data and Methods**

The Purtse catchment area is located mainly in Ida-Viru County. It covers an area of about 816 km<sup>2</sup> (~ 24% of the total territory of this county). The whole catchment area is located in the western part of the Estonian oil shale deposit. In the catchment area there are Kiviõli (now closed), Kohtla, Sompa and Viru mines, as well as Aidu opencast (Fig. 1, streaked areas). The mining areas of Tammiku and Estonia mines are also in contact with the catchment area. The whole mining territory within the boundaries of the catchment area covers about 200 km<sup>2</sup>. The total length of the Purtse River is 51 km, and it flows into the Gulf of Finland. Long-term mean total

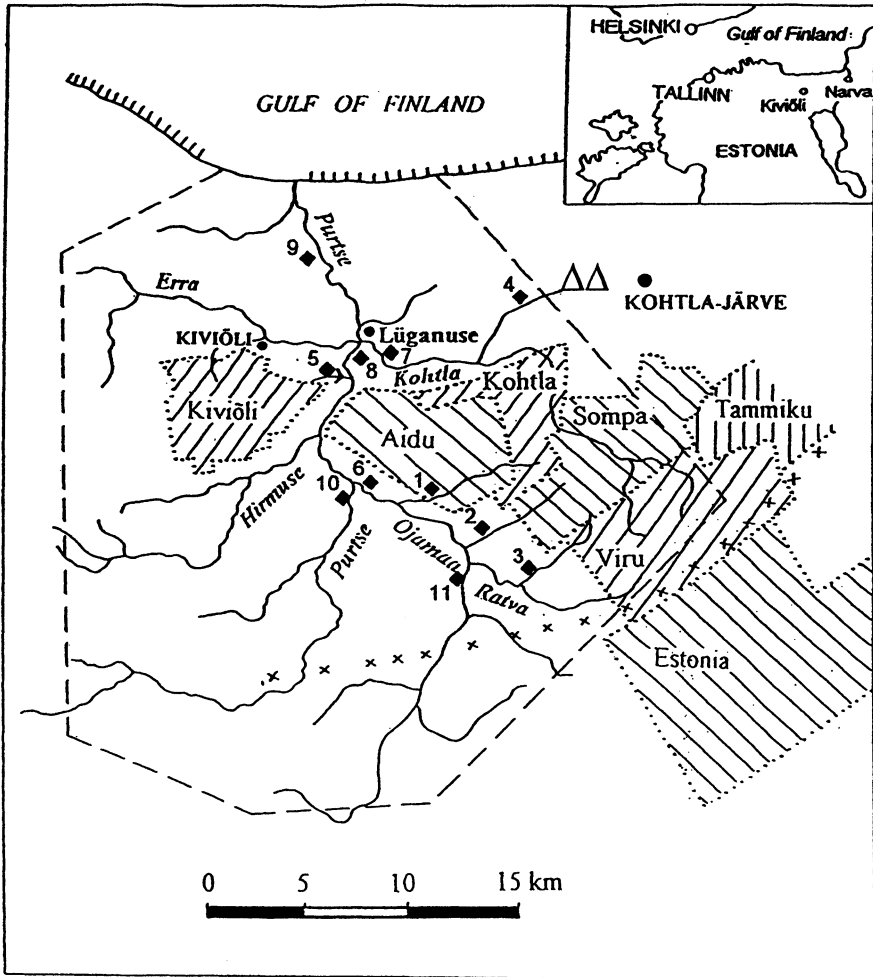


Fig. 1. Location of the Purtse catchment area: - - - - - border of the catchment area; ..... - borders of mines and opencast; × × × - Ahtme tectonic crushed zone; Δ Δ - ash-dumps; ♦ - observation and sampling points in the catchment area.

annual runoff of this river is 210 million  $m^3$ , and its long-term mean annual discharge is 6.7  $m^3/s$ . The most important tributaries of the Purtse River are the Kohtla, Ojamaa, Hirmuse and Erra (Fig. 1).

The mine water outputs to the rivers are as follows: 7 outputs to the Ojamaa River from Aidu opencast, Kohtla, Sompa and Viru mines; 3 outputs to the Kohtla River from Aidu opencast, Kohtla and Tammiku mines. In addition to those, an output to the Kohtla River exists in the form of ash-dump waters from the Kohtla-Järve oil shale thermal processing plant (Viru Keemia Grupp Ltd.). In the Purtse catchment

area oil shale lies at a depth of 20 m; the thickness of the 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 its southern part.

To characterize the factors of water circulation, we used the following initial data obtained from enterprises of the oil shale industry (mines, thermal processing plant) and the Estonian Meteorological and Hydrological Institute for the period of 1990-1998:

- meteorological (natural) factors: annual precipitation amounts, in mm, for the observed region (variable  $Y_1$ ), and annual evapotranspiration (long-term mean), mm;
- mining-technological factors: annual oil shale production in the mines, million t, for the Purtse catchment area, and modules of oil shale produced water abundance,  $m^3/t$  (variables  $Y_2$  and  $Y_3$ , respectively);
- hydrogeological factor: annual amounts of mine water pumped out from the mines of the observed region, million  $m^3$  (variable  $Y_4$ );
- hydrological factor: mean annual discharge in the lower course of the Purtse River (at Lügänuuse),  $m^3/s$  (variable  $Y_5$ );
- geochemical factor: annual input of salts (sulphates+chlorides) from the mines into the rivers (with mine waters), t (variable  $Y_6$ );
- composite hydrogeological factor: ratio of the amount of mine water and module of water abundance  $Y_4/Y_3$  (variable  $Y_7$ ). This factor was calculated by the authors of the paper.

The annual values of these factors were found by summarising the monthly values.

On the basis of the obtained data (Table 1), the correlation coefficients  $r_{jk}$  were computed for the proper set of paired values of  $Y_j$  and  $Y_k$  (the indexes  $j \dots k$  indicate the numbers of the variables). By simple and multiple linear regression analyses the linear regression equations in the form of  $Y=a+bX$  and  $Y=a+b_1X_1+b_2X_2$ , and the coefficients of determination  $r^2$  were calculated to explain some of the variation of  $Y$  by  $X$ , using the latter variable as a statistical control (Sokal and Rohlf 1998). Differences were considered significant at the 95% confidence level ( $p \leq 0.05$ ).

Initial data on the chemical composition of polluted water flows (mine waters, ash-dump waters) and river water in different observation and sampling points (Fig. 1) were received from environmental laboratories of the enterprises. During the period 1995-1998 these laboratories collected 12 water samples from each point yearly (22 samples in each sampling campaign, in all 264 samples) and analysed them using selected standard analytical methods (Lurje and Rybnikova 1984; Semjonov 1977). The concentrations of sulphate, chloride, sulphide, and the values of pH and chemical oxygen demand ( $COD_{Cr}$ ) were determined. The content of volatile phenols in water samples was determined by HPLC (method SFS3011, detection limit 0.002 mg/l). The authors of the paper calculated average values and standard deviations of chemical parameters.

## On the Influence of Polluted Water Flows

Table 1 – Dynamics of Mining-technological, Hydrological, Natural and Geochemical Factors in the Oil Shale Mining in the Purtse Catchment Area for the Period 1990-1998

| Factor  | 1990  | 1991           | 1992  | 1993                   | 1994 | 1995  | 1996  | 1997  | 1998  | Average |     |
|---|-------|----------------|-------|------------------------|------|-------|-------|-------|-------|---------|-----|
| <b>Mining-technological</b>   |       |                |       |                        |      |       |       |       |       |         |     |
| • Oil shale production, million t/yr  |       |                |       |                        |      |       |       |       |       |         |     |
| – total in Ida-Viru County  | 21.2  | 18.3           | 17.0  | 14.3                   | 14.0 | 13.3  | 13.1  | 12.9  | 10.9  | 15.0    |     |
| – total in Kohtla, Sompä, Viru and Tammiku mines and Aidu opencast                        | 7.6   | 6.6            | 6.1   | 5.1                    | 5.0  | 4.8   | 4.7   | 4.5   | 4.0   | 5.4     |     |
| • Module of oil shale water abundance, m <sup>3</sup> /t * (1)                            | 15.5  | 16.5           | 16.4  | 16.6                   | 16.7 | 17.6  | 11.3  | 17.2  | 20.8  | 16.5    |     |
| <b>Hydrogeological</b>  |       |                |       |                        |      |       |       |       |       |         |     |
| • Amount of mine water directed into the catchment rivers, million m <sup>3</sup> /yr (2) | 137.1 | 126.2          | 112.0 | 99.9                   | 97.3 | 103.8 | 64.9  | 96.5  | 98.9  | 104.0   |     |
| • 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  | 6.35    |     |
| <b>Hydrological</b>   |       |                |       |                        |      |       |       |       |       |         |     |
| • Mean annual discharge in the lower course of the Purtse River, m <sup>3</sup> /s        | 10.3  | 8.7            | 7.2   | 6.3                    | 6.2  | 7.8   | 3.6   | 6.6   | 9.6   | 7.4     |     |
| <b>Natural</b>  |       |                |       |                        |      |       |       |       |       |         |     |
| • Annual precipitation, mm  | 786   | 835            | 600   | 692                    | 659  | 775   | 587   | 724   | 841   | 722     |     |
| • Annual evapotranspiration, mm   |       |                |       | long-term mean is used |      |       |       |       |       |         | 400 |
| <b>Geochemical</b>  |       |                |       |                        |      |       |       |       |       |         |     |
| • Input of salts into the rivers, t/yr including sulphates chlorides                      |       | not determined |       |                        |      | 40535 | 27299 | 35074 | 26094 | 32250   |     |
|   |       |                |       |                        |      | 37162 | 24948 | 32274 | 24165 | 29637   |     |
|   |       |                |       |                        |      | 3373  | 2351  | 2800  | 1929  | 2613    |     |

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

## Results and Discussion

### Interaction Between the Effect of Natural, Mining and Geotechnological Factors on the Catchment Water Circulation

From Table 1 it appears that decreasing oil shale production is followed by a growth of the module of oil shale water abundance.

On the basis of the data obtained by correlation analysis (Fig. 2) we may conclude that the impact of natural, mining-technological, hydrogeological and geochemical factors on the hydrological and hydrogeological regimes of the Purtse catchment area has attained an integrated character. Intensive oil shale mining (up to 7.6 million t/yr) has affected the outflow (runoff) structure of the rivers in the Purtse catchment and dynamical evolution of water cycles. The correlation coefficients between the main factors lie within the range of 0.56-0.86. There are significant correlations between the pairs of variables ( $Y_4, Y_5$ ) and ( $Y_1, Y_5$ ) (Fig. 2). The mean discharge of the Purtse River (variable  $Y_5$ ) correlates significantly and simultaneously with the amount of mine water discharged into the rivers and the annual precipitation amount (random variables  $Y_1$  and  $Y_4$ , respectively). This correlation is very useful for the composition of the model relationships. The pairs of variables ( $Y_2, Y_4$ ) and ( $Y_3, Y_6$ ) also showed a good correlation (Fig. 2). Other pairs of variables had weaker effects of a common cause but we could not eliminate these from system analysis.

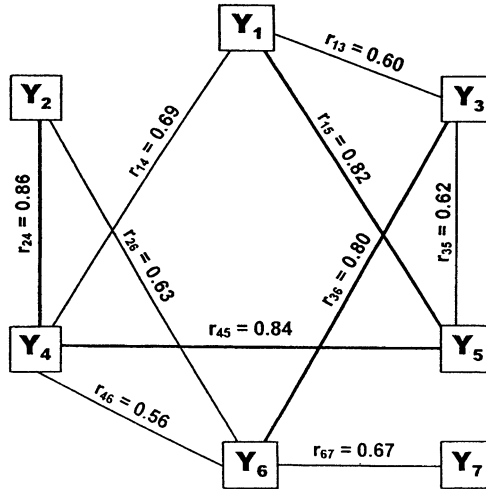


Fig. 2. Correlation graph showing the interdependence between natural, mining-technological, hydrogeological, hydrological and geochemical factors (at the 95% confidence limits around  $r$ ). Variables:  $Y_1$  – annual precipitation amount, mm;  $Y_2$  – oil shale production, million t/yr;  $Y_3$  – module of oil shale water abundance (1),  $\text{m}^3/\text{t}$ ;  $Y_4$  – amount of mine water pumped into the rivers (2), million  $\text{m}^3/\text{yr}$ ;  $Y_5$  – mean annual discharge of the Purtse River,  $\text{m}^3/\text{s}$ ;  $Y_6$  – input of salts into the rivers, t/yr;  $Y_7$  – ratio (2) / (1).

Taking into account the data on the amounts of mine water pumped out (on the average 104 million  $\text{m}^3/\text{yr}$ ), and of precipitation water infiltration into the mines through the overburden rocks (on the average 56% of the mine water pumped out), as well as that of precipitation water flowing into the rivers (on the average 205 million  $\text{m}^3/\text{yr}$ ), our results indicate that the share of groundwater in the water circulation of the catchment has increased at least up to 50-60%.

The relations between the factors suggest that in the total water circulation of the catchment a so-called hydrogeological circulation must have formed, which essentially influences the proportion of mine water in the flow of the lower course of the Purtse River. The water circulation balance-scheme (Fig. 3) shows that it forms as a result of an interaction of three components: infiltration of precipitation water and groundwater into the mines, mine water pumped out into the rivers and outflow canals, and re-infiltration of water from rivers and outflow canals into the mines, which depends directly on the meteorological conditions and hydrogeological situation in the mines. In 1990-1998, the hydrogeological circulation of water formed about 25-40% of the amount of mine water pumped out, and the share of the mine water pumped out formed on the average 33% of the total Purtse River water flow (Fig. 3). This hydrogeological circulation has created the basis for a new, anthropogenic biogeochemical matter cycling from the geological into the hydrological environment.

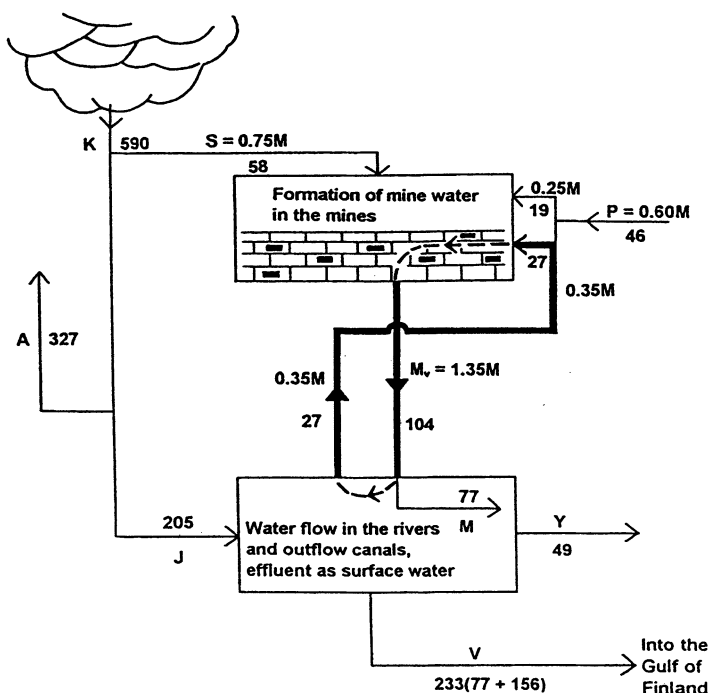


Fig. 3. Water circulation balance scheme of the Purtse catchment area (average for the years 1990–1998). Designation of the waterflows:  $K$  – precipitation on the catchment area;  $A$  – evaporation and transpiration;  $S$  – infiltration of precipitation water into the mines;  $J$  – precipitation water flow into the rivers and flood flow;  $P$  – groundwater flow into the mines;  $M_v$  – mine water pumped out and flowing out from the Kiviõli mine;  $M$  – mine water flow with river water;  $V$  – Purtsse River flow into the Gulf of Finland;  $Y$  – water flow outwards from the catchment area.

The numbers show the average water flows (million  $m^3/yr$ ). Hydrogeological water circulation is indicated by continuous thick and dotted lines.

### Changes in Hydrological Conditions of the Purtse River, Application of the Proposed Model System

At the beginning of 2000 Sompa and Tammiku mines were partially closed. Because of the changed technologies of mining operations in 2000, the amount of mine water going into the Purtse River decreased to 61.3 million  $m^3/yr$ . In 2000, the annual precipitation amount was 834 mm, and the mean annual discharge in the lower course of the Purtse River was 6.34  $m^3/s$ .

It is interesting to verify the applicability of the developed regression equations for determining the mean annual discharge of the Purtse River (for the year 2000) on the basis of these data.

Table 2 – The Linear Regressions Showing the Dependence of the Variable  $Y_5$  on the Independent Variables  $X_1$  and  $X_4$

| Regression equation                   | Coefficient of determination, $r^2$ | $p$ -value |
|---------------------------------------|-------------------------------------|------------|
| Simple linear regressions:            |                                     |            |
| $Y_5 = -1.368 + 0.0839X_4$            | 0.71                                | <0.05      |
| $Y_5 = -5.302 + 0.0175X_1$            | 0.67                                | <0.05      |
| Multiple linear regression:           |                                     |            |
| $Y_5 = -3.335 + 0.042X_4 + 0.0088X_1$ | 0.83                                | <0.05      |

$Y_5$  – mean annual discharge of the Purtse River,  $m^3/s$ ;

$X_1$  – annual precipitation amount, mm;

$X_4$  – amount of mine water discharged into the rivers, million  $m^3/yr$ .

For this purpose, the pairs of variables ( $Y_4, Y_5$ ) and ( $Y_1, Y_5$ ) were used to describe functional relationships between the variable  $Y_5$  as a dependent variable and the variables ( $X_1, X_4$ ) as the independent ones, to predict  $Y_5$  in terms of  $X_1$  and/or  $X_4$  (Table 2).

Using the multiple linear regression equation (Table 2) we calculated the mean annual discharge of the Purtse River in 2000 as  $6.58 m^3/s$ . This computational outcome differed from the measured parameter ( $6.34 m^3/s$ ) only by 0.24 units (3.8%), which is a good final result. For the period 1990-1998, the proposed model system showed a perfect fit between observed and modelled annual mean discharge (runoff) of the Purtse River. Application of the proposed multiple linear regression equation is rational for composing projects to improve the hydrological conditions of the rivers in the Purtse catchment using meteorological and mining-technological data.

### Physico-chemical Composition of Polluted Water Flows and River Water in the Catchment Area

There is no doubt that both the constant discharge of mine waters into the rivers of the catchment and the resulting increase in the hydrogeological circulation of water (between the operating mines and the middle courses of the rivers, Fig. 3) influence markedly the chemical composition of the river water. As a consequence of these processes, the mineral substances and with them all other constituents of oil shale are continuously carried out from the underground (geological) environment (Pets 1998). This occurs mainly in the form of magnesium, calcium and sodium sulphates, chlorides, bicarbonates and hydroxides, but also other inorganic salts, whereas the kinetics of their formation in the mine water essentially depends on the water pH value (Rätsep and Liblik 1998).

In 1995-1998, the years of our study period (Table 1), the correlation between mining-technological and geochemical factors was quite strong: the correlation coefficients lie within the range of 0.56-0.80 (Fig. 2). As in 1995-1998 the average input of sulphates and chlorides into the Purtse River was 29,640 t/yr and 2,610 t/yr,



*On the Influence of Polluted Water Flows*

Table 3 – Average Values and Standard Deviations of Chemical Parameters for Technological Water Flows and River Water from Different Observation Points (Fig. 1) During the Period 1995-1998

| Parameter                               | Water flows 1) |           |         | River water 2) |         |         |         |
|---|----------------|-----------|---------|----------------|---------|---------|---------|
|   | 1-3            | 4         | 5       | 6              | 7       | 8       | 9       |
| pH                                      | 8.0±0.5        | 9.5±0.8   | 8.0±0.4 | 7.8±0.6        | 7.9±0.7 | 7.6±0.5 | 8.0±0.2 |
| Sulphate, mg/l                          | 610±130        | 640±90    | 264±31  | 575±24         | 377±34  | 308±73  | 340±28  |
| Chloride, mg/l                          | 53±8.0         | 490±85    | 31±3.7  | 27±4.8         | 36±4.7  | 30±9.0  | 33±5.5  |
| COD <sub>Cr</sub> , mgO <sub>2</sub> /l | 20±11          | 4150±1300 | –       | –              | –       | –       | –       |
| Volatile phenols, mg/l                  | ≤0.004         | 55±30     | ≤0.002  | ≤0.002         | 3.4±2.9 | ≤0.002  | ≤0.6    |
| Sulphide, mg/l                          | –              | 235±30    | –       | –              | 2.1±1.2 | –       | ≤0.02   |

- 1) Points 1-3 – mine waters (into the Ojamaa River);  
 Point 4 – ash-dump waters (into the Kohtla River);  
 Point 5 – from closed Kiviõli mine (into the Purtse River).
- 2) Point 6 – Ojamaa River (before flowing into the Purtse River);  
 Point 7 – Kohtla River (before flowing into the Purtse River);  
 Point 8 – Purtse River (before the Kohtla River falls into it);  
 Point 9 – Purtse River (after the Kohtla River falls into it).

respectively, then during the last 25 years at least 740,000 t of sulphates and 65,000 t of chlorides have been discharged into the Purtse River. Ultimately these substances reach the Gulf of Finland. Table 3 presents the concentrations of sulphates and chlorides in mine waters and in different observation points on the rivers of the Purtse catchment for the period of 1995-1998. The figures show that under the pollution load of mine waters with sulphates and chlorides are mainly the lower course of the Ojamaa River and the middle and lower courses of the Purtse and Kohtla rivers. Besides the mine water, the Kohtla River is also polluted with toxic (with respect to water biota) ash-dump waters of the Kohtla-Järve oil shale processing plant (600-800 thousand m<sup>3</sup>/yr), which contain in addition to sulphates and chlorides also phenols and sulphides (Table 3). In 1995-1998, 20-30 t/yr of volatile phenols and 120-150 t/yr of sulphides were thrown into the Kohtla River. As a result, the water of the Kohtla River, before it flows into the Purtse River, contained 6-8 mg/l of volatile phenols, and in the Purtse River 5 km downstream, from where the Kohtla River falls into it, the content of phenols was up to 0.6 mg/l. Depending on the season, the content of volatile phenols and sulphides in the river water fluctuated noticeably. This fact causes also a large fluctuation in the river water oxygen regime, whereas the oxygen concentration does not achieve the saturation degree (not above 60-70%).

Therefore, in the surroundings of the Kohtla River, the pollution of the environment from oil shale thermal processing is combined with the harmful impact of oil shale mining. The pollutants appear in the pumped out mine water due to the hydro-

geological circulation of water. Because of that, in the mine waters the concentration of volatile phenols reaches up to 0.003-0.004 mg/l. The ash-dumps are located not far from the mined area.

In the same period, for the sectors of rivers not affected by polluted water flows (in the Purtse River before the Ojamaa River falls into it, and in the Ojamaa River before the Ratva stream joins the river, Fig. 1, observation points 10 and 11), the concentrations of sulphate and chloride in water did not exceed 45 mg/l and 20 mg/l, respectively.

### **Problems and Perspectives of Hydrological Management of the Catchment**

Today the whole mined area in the Purtse catchment constitutes about 200 km<sup>2</sup>, *i.e.* roughly 25% of the total catchment area. Taking into account the continuous increase in the mined area and its perimeter, it is obvious that a permanent tendency towards essential changes in the chemical composition of the water in the middle and lower courses of the Purtse River will persist. Both the amounts of precipitation water infiltrating into the mining galleries and of the water flow that is in continuous hydrogeological circulation will increase slowly but continuously. Therefore, the proportion of groundwater in the water circulation of the catchment will undoubtedly increase, but because of hydrogeological circulation it will not always reach the lower course of the Purtse River (and the Gulf of Finland).

The tendency towards qualitative changes in the Purtse River water will not disappear even after the final closing of the underground mines. In the period after closing the mines, the hydrogeochemical factor will attain an essential importance, which will affect the input of sulphates, chlorides, bicarbonates and hydroxides into the rivers (Rätsep and Liblik 1998). The polluted water of the Ojamaa and Kohtla rivers will damage in turn the water quality in the middle and lower courses of the Purtse River, which is already severely damaged. By the agency of both the mine waters and ash-dump phenols containing waters, the river flora and fauna have been impoverished, which has essentially hampered the use of the catchment rivers in the region's hydrological management system (fishing, catching of crayfish, water supply, recreation, farming) (Liblik and Rätsep 1994; Gravenfors *et al.* 1994).

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 (The REDOS project 1996). The new scheme must enable to regulate the mine water outputs to the catchment rivers. However, the inlet of the ash-dump waters into the Kohtla River must be fully stopped. The ash-dump waters need an individual chemical-biological treatment (Rahe 1997).

## **Conclusions**

Oil shale production in the Purtse catchment area (816 km<sup>2</sup>) seriously influences the hydrological, hydrogeological and hydrochemical regime and conditions of the catchment rivers. Under the interactions of natural and mining-technological factors, the so-called hydrogeological water circulation has formed in the catchment area, which constitutes 25-40% of the amount of mine water pumped out. This circulation has created a basis for a new, anthropogenic biogeochemical matter cycling from the geological environment into the hydrological one of the rivers. In this area, some irreversible qualitative and quantitative transformations in the composition of underground water will unavoidably occur. All this has resulted in the formation of a new situation that can be described as a hydrogeochemical anomaly: increased concentrations of sulphate and chloride. The waste products (leachates from the ash-dumps) of oil shale thermal processing cause a pollution, which is combined with that caused by oil shale mining.

To convert the quality of river water in the Purtse catchment area closer to natural, a thorough alteration of the present hydrological scheme of mine water drainage is needed. The inlet of ash-dump waters into the Kohtla River must be finished.

A multiple regression formula for calculating the mean annual discharge of the Purtse River is suggested. The model is suitable to provide near real-time analysis for the planning of the Purtse River water resources.

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