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## **INFLUENCE OF OIL SHALE MINING ON STRONTIUM DISTRIBUTION IN STREAM SEDIMENTS, NORTH-EAST ESTONIA**

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*Oil shale mining in North-East Estonia results in extensive discharge of carbonate-rich mine water into the local river systems. The results of robust regression of strontium concentration on major element concentration in stream sediment samples, taken from two surveys in 1994 and 1998, suggests that naturally occurring Sr is associated with calcite and potassium-rich minerals. Carbonate-rich discharge appears to coincide with samples containing anomalous Sr concentrations and high CaO content. The spatial differences in Sr enrichment between the two surveys also reflect the reduction in the amount of mine water discharged into the local river systems between 1994 and 1998.*

### **Introduction**

The environment degradation caused by oil shale mining and the associated chemical industry in North-East Estonia has been subject to long and intensive study. One feature of mining is the discharge of alkaline, carbonate-rich mine water into the local river systems [1]. Although considerable attention has been paid to water quality studies (dealing largely with organic pollutants) in North-East Estonia, far less study has considered river sediment analysis, especially determination of heavy metals.

Anthropogenic inputs of heavy metals upon discharge into surface waters tend to be rapidly absorbed by sediments, particularly clay minerals and Fe-Mn (hydr)oxides, or incorporated into autochthonous minerals [2]. On a regional scale, these inputs represent secondary populations spatially mixed with the dominant population of naturally occurring heavy metals. A challenge in environmental geochemistry is to distinguish and evaluate anthropogenic populations from the natural background. Statistical procedures, such as regression analysis, have been used to determine anomalous populations in geosciences for decades.

However, the classical (parametric) methods are often unsuitable, because all the data is incorporated as a single population. In contrast, robust regression procedures, such as Least Median of Squares regression [3], tend to be outlier-resistant, resulting in enhanced anomaly recognition [4]. Application of LMS regression has been demonstrated in geochemical exploration [5] and environmental geochemistry [4].

The results of two stream sediment surveys in North-East Estonia, conducted in 1994 and 1998, provide insight on the distribution of Sr in river sediment. With the objective of determining the regional natural background and to distinguish any anomalous populations, Sr concentration in river sediment was regressed robustly against a suite of major element concentrations. The results indicate that anomalous Sr is associated with carbonate-rich mine drainage water.

## The Study Area

The exploited oil shale deposit in Estonia, distributed over 3000 km<sup>2</sup>, is located in the North-East corner of the country, extending 130–140 km east-west and 40–45 km north-south. Approximately fifty oil shale beds that constitute the deposit are Middle Ordovician in age and interbedded with limestones [6]. The deposit flanks the southern slope of the Fennoscandian Shield, with an outcrop to the north and a gradual dip to the south. As a result, opencast mining is common in the north of the area with underground operations dominating in the south (Fig. 1).

Pleistocene glacial and aqueoglacial deposits and Holocene terrigenous sediments overlie the bedrock. The relief in the area is generally low with a network of rivers that run northwards and discharge into the Gulf of Finland.

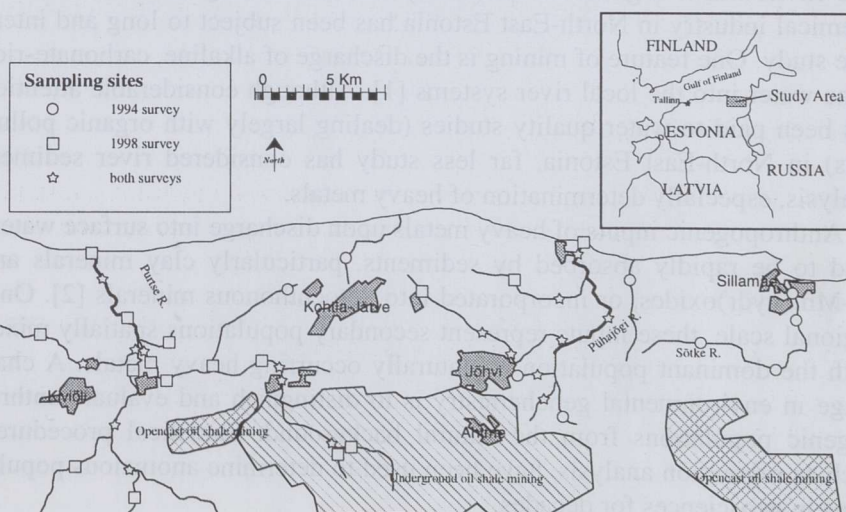


Fig. 1. Study area and stream sediment sampling locations

Although oil shale mining and associated industry has played a role in North-East Estonia since the beginning of the 1900s, the period following the World War II introduced intensive industrial development. Despite a marked reduction in production and some improvement in oil shale exploitation the recent years have seen, environment degradation persists. The effects of oil shale mining influence all facets of the surrounding environment, including the local river systems.

In addition to the discharge of urban and industrial wastewater, the local rivers receive large quantities of carbonate-rich drainage water pumped from oil shale mines. This mine water also contains heavy metals and a variety of organic compounds, including phenol [1]. The amount of mine water discharged into the Purtse River system and the Pühajõgi River system has decreased by about 27 and 45 %, respectively, between 1994 and 1996 [1].

## Field Methods

In an initial survey in 1994 stream sediment samples were collected at 26 sites throughout the region. A second survey in 1998, which concentrated on the Pühajõgi and Purtse river systems, consisted of 34 sites with duplicate samples being taken from seven sites (see Fig. 1). Seventeen sites were common to both surveys. Both sets of samples were dried, disaggregated and sieved prior to analysis. The sieve size represents the only variation in analytical technique with the 1998 samples being finer (<100 µm) than the 1994 samples (<160 µm). Each sample was analysed for a suite of major and trace elements by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) after a hot aqua regia extraction. Aqua regia readily dissolves carbonates, sulphides, Fe/Mn (hydr)oxides and strips much of the absorbed cations from clay minerals, while more resistant silicates remain unaffected [7].

## Statistical Methods

Regression analysis is used to determine the relationship between a response variable  $y$  and a series of explanatory variables  $x_1, x_2, \dots, x_p$  in terms of the relation

$$y = b_0 + b_1x_1 + \dots + b_px_p$$

where  $b_0, b_1, \dots, b_p$  are the regression coefficients.

Classical (Ordinary Least Squares) regression calculates the coefficients to minimise the sum of squared deviations

$$\sum_i r_i^2 = \sum_i (y_i - \hat{y}_i)^2$$

where  $\hat{y}_i$  is the estimate of  $y_i$  [8].

Least Median of Squares (LMS) regression calculates the coefficients to minimise the median of  $r_i^2$  [3]. Therefore, the LMS estimator determines the best fit for half the data with the other half playing no role in the regression fit. As such, LMS regression can tolerate up to 50 % outlier data points. In this study, Sr concentration served as the response variable and  $\text{Al}_2\text{O}_3$ ,  $\text{K}_2\text{O}$ ,  $\text{Fe}_2\text{O}_3$ , and modified CaO and MgO (see Results and Discussion section for explanation) concentrations served as the explanatory variables.

Variables of chemical concentration represent compositional data. As such, they are constrained to the unit simplex

$$S^D = \{(x_1, \dots, x_D) : x_i > 0 (i = 1, \dots, D), x_1 + \dots + x_D = 1\}$$

where  $x_1, \dots, x_D$  are the components;  $D$  is the number of components [9].

This constraint (also known as the constant sum problem) renders statistical analysis of the raw components inappropriate [9, 10]. Logratio transformation, proposed by Aitchison [9], can overcome this constraint. The logratio transformation in this study was

$$\hat{g}_i = \log(x_i/x_D, \dots, x_{D-1}/x_D) (i = 1, \dots, D-1)$$

where  $x_1, \dots, x_{D-1}$  are the response and explanatory variables and  $x_D = 1 - (x_1 + \dots + x_{D-1})$ . After LMS regression, the variables were retransformed to compositional data with the inverse expressions

$$x_i = \exp(\hat{g}_i) / \{\exp(\hat{g}_i) + \dots + \exp(\hat{g}_{D-1}) + 1\} (i = 1, \dots, D-1);$$

$$x_D = 1 / \{\exp(\hat{g}_i) + \dots + \exp(\hat{g}_{D-1}) + 1\}$$

## Results and Discussion

The incomplete dissolution of minerals by aqua regia allows us to look upon each major element to represent a distinct mineralogical phase. Because the  $\text{Al}_2\text{O}_3$  concentration is much lower than the CaO, MgO and  $\text{Fe}_2\text{O}_3$  concentrations are (Table 1), dissolution of Al-silicate minerals contributes little to the total CaO, MgO and  $\text{Fe}_2\text{O}_3$  concentrations.

**Table 1. Statistics for North-East Estonia Stream Sediment Data (all units in % unless otherwise indicated)**

Variable	1994 survey		1998 survey	
	Mean	Median	Mean	Median
CaO	9.13	5.35	12.71	8.14
$\text{K}_2\text{O}$	0.13	0.12	0.20	0.18
CaO-MgO	2.59	2.30	2.96	1.99
$\text{Fe}_2\text{O}_3$	1.65	1.64	1.95	1.86
$\text{Al}_2\text{O}_3$	0.73	0.70	1.14	1.02
Sr, ppm	130	52	114	68

Therefore, the concentrations of these elements represent dissolution of non-silicate minerals. MgO was designated as a dolomitic phase ( $\text{CaMg}(\text{CO}_3)_2$ ), so the MgO concentration was modified to include an equal molar fraction of CaO with a corresponding reduction in the CaO concentration. The

remaining CaO was designated as calcite (and aragonite), with  $\text{Fe}_2\text{O}_3$  as Fe (hydr)oxides,  $\text{K}_2\text{O}$  as low-resistant potassium-rich minerals, such as biotite and chlorite, and Al as cation-deficient clay minerals.

This mineralogical designation is supported by the higher concentrations of almost all major elements in the 1998 survey (see Table 1). With respect to the 1994 survey, the finer mesh used to sieve the 1998 samples reduced the amount of coarser and more resistant minerals, chiefly quartz and Al-silicates, while increasing the concentration of less stable and finer-grained weathered material.

The difference in grain size had little effect on the LMS regression results (Table 2): CaO and  $\text{K}_2\text{O}$  were the only significant regressors ( $p$ -values < 0.10) in both surveys.

Table 2. Robust Regression Coefficients and Related Statistics for North-East Estonia Stream Sediment Data

Logratio variable	1994 survey*			1998 survey**		
	<i>b</i>	<i>t</i> -Value	<i>p</i> -Value	<i>b</i>	<i>t</i> -Value	<i>p</i> -Value
CaO	<b>0.555</b>	<b>13.152</b>	<b>0.000</b>	<b>0.634</b>	<b>10.824</b>	<b>0.000</b>
$\text{K}_2\text{O}$	<b>0.264</b>	<b>2.343</b>	<b>0.034</b>	<b>0.477</b>	<b>1.786</b>	<b>0.085</b>
CaO–MgO	0.141	1.702	0.111	–0.107	–1.302	0.203
$\text{Fe}_2\text{O}_3$	0.056	0.513	0.616	–0.138	–0.926	0.362
$\text{Al}_2\text{O}_3$	0.007	0.040	0.969	–0.308	–1.153	0.259
Intercept	<b>–5.765</b>	<b>–14.224</b>	<b>0.000</b>	<b>–7.247</b>	<b>–15.279</b>	<b>0.000</b>

\*  $R^2 = 0.972$ ;  $F$ -value = 97.122.

\*\*  $R^2 = 0.955$ ;  $F$ -value = 118.134.

*b* = regression coefficients; bold type denotes statistically significant variables and statistics.

Therefore, it appears that calcite and potassium-rich minerals control the natural Sr distribution. The large relative departures in magnitude and sign in the other variables are inconsequential, because these variables had little effect on the regression estimate ( $p$ -values > 0.10). In addition, the predicted Sr values  $\hat{y}$  compared to CaO concentration showed similar trends for both surveys (Fig. 2), suggesting that the different sieve sizes produced a similar Sr background.

The deviations of the predicted Sr values at concentrations < 11 ppm may be the result of lower analytical precision at lower concentrations. The actual Sr concentration  $y$  with respect to CaO depicted in Fig. 3 reveals several Sr-rich outliers. A plot of the LMS regression residuals  $r$  and CaO concentration shows that  $r$  varies  $\pm 1$  ppm/% CaO (Fig. 4). Furthermore, anomalous Sr residuals are associated with high CaO concentrations. This association suggests that Sr enrichment may reflect anthropogenic carbonate-rich discharge into the river systems.

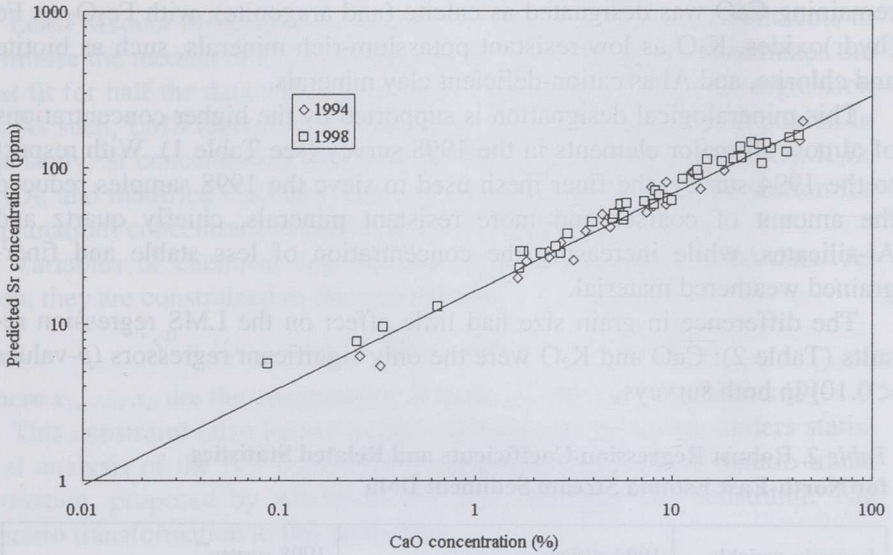


Fig. 2. Sr concentration as predicted by LMS regression  $\hat{y}$  vs. CaO concentration. Trendline depicts Reduced Major Axis regression

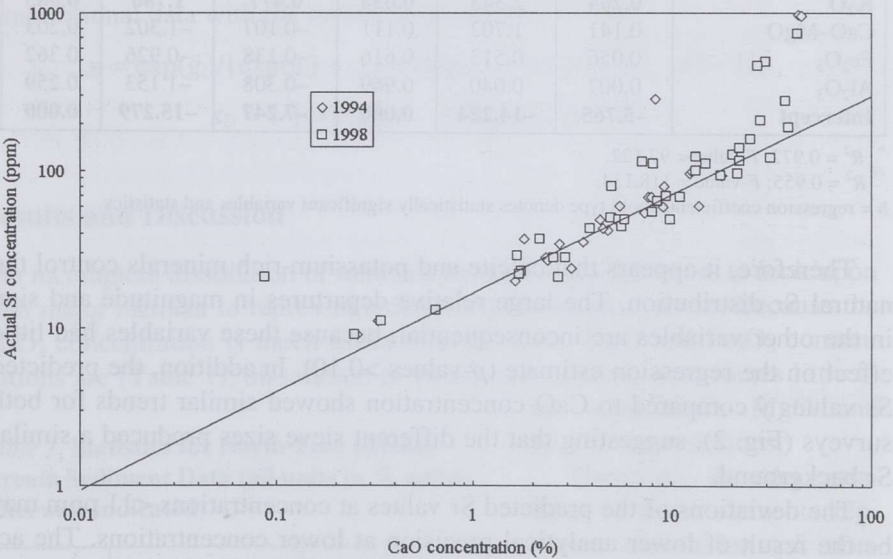


Fig. 3. Actual Sr concentration  $y$  vs. CaO concentration. Trendline reproduced from Fig. 2

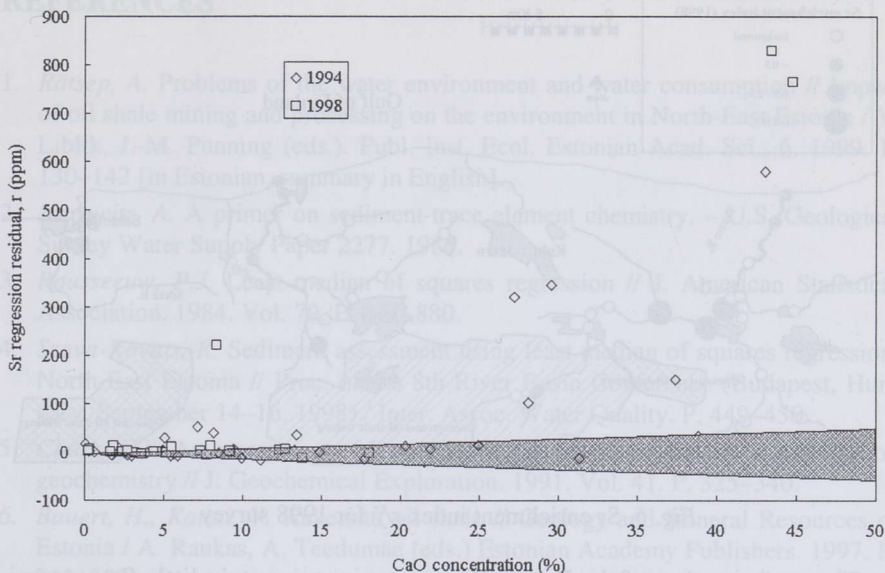


Fig. 4. Sr residuals  $r$  from LMS regression vs. CaO concentration. Shaded area depicts background variation as a function of CaO concentration

The Sr enrichment in the stream sediment was calculated as the ratio  $r/\hat{y}$ . Sr enrichment in the 1994 survey implies high discharge of carbonate-rich mine water into the Pühajõgi River system and the Purtse River system near Kohtla-Järve with a smaller degree of Sr contamination in the Sõtke River (Fig. 5).

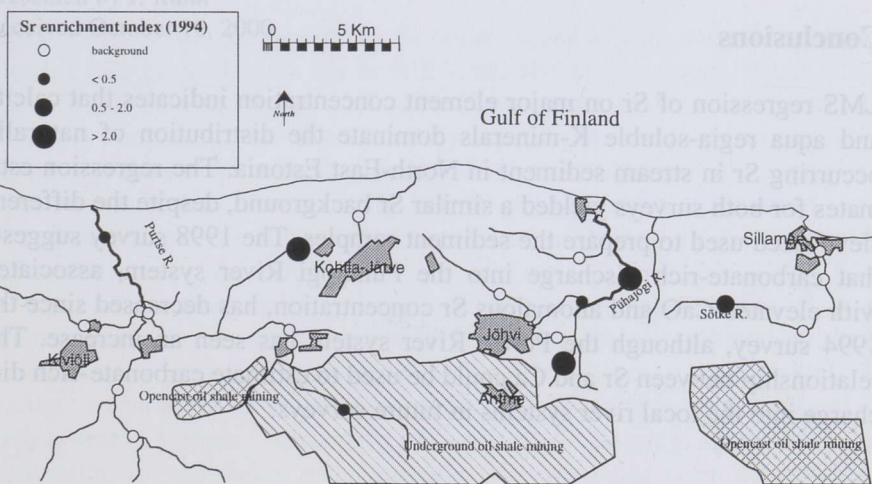


Fig. 5. Sr enrichment index  $r/\hat{y}$  for 1994 survey

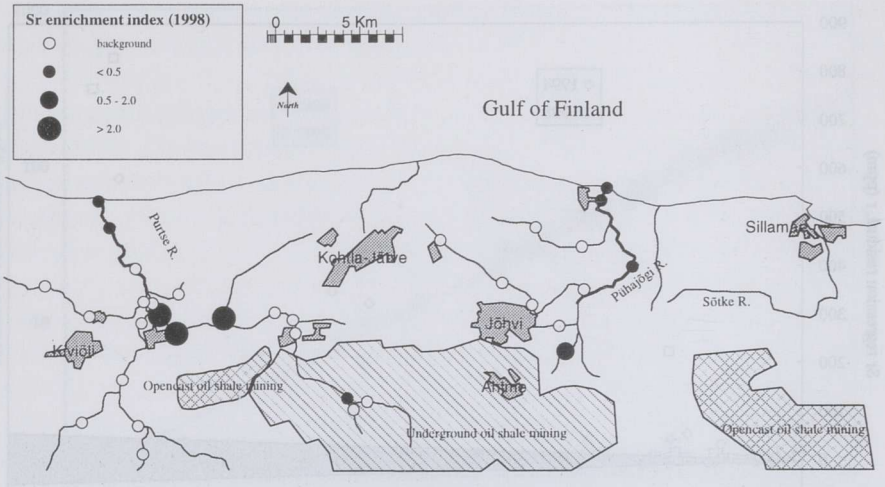


Fig. 6. Sr enrichment index  $r/\bar{y}$  for 1998 survey

The main portion of the Purtsi River appears to contain little Sr contamination. Results of the 1998 survey indicate reduced Sr contamination in the Pühajõgi River system with anomalous Sr in the Purtsi River system (Fig. 6). This change suggests that carbonate discharge into the Pühajõgi River system has decreased during the four-year interval between the surveys, while the Purtsi River has seen an increase during the same period. Published data on mine water discharge into the local river systems [1] affirms this decrease and attests to the use of Sr and Ca as a tracer of carbonate-rich wastewater.

## Conclusions

LMS regression of Sr on major element concentration indicates that calcite and aqua regia-soluble K-minerals dominate the distribution of naturally occurring Sr in stream sediment in North-East Estonia. The regression estimates for both surveys yielded a similar Sr background, despite the different sieve sized used to prepare the sediment samples. The 1998 survey suggests that carbonate-rich discharge into the Pühajõgi River system, associated with elevated CaO and anomalous Sr concentration, has decreased since the 1994 survey, although the Purtsi River system has seen an increase. The relationship between Sr and Ca could be used to estimate carbonate-rich discharge into the local river systems in future surveys.



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