Mobilization, transportation and sedimentation of weathering products from the abandoned brown-coal pits. (Iron pollution of the river Skjernå and Ringkøbing fjord, Western Jutland)

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Preliminary results concerning the effect of chemical weathering products from the abandoned brown-coal pits on the river system are presented. Two of these pits are especially contaminating. They include the Haunstrup pit with an outlet to Rimmerhusbæk-Vorgodå, and the Søby pit from where canals discharge into the river system Søbyå-Rindå. Concerning the soluble matter it must be concluded that the contamination from these two pits on the watercourses is intense, but subsides relatively quickly. The river transport of suspended iron is at present not known in detail due to lack of data. Therefore it cannot be excluded that suspended iron can contribute to the pollution of the river Skjernå, and especially Ringkøbing fjord.

During 1974 and 1975 a geochemical investigation of the river Skjernå was carried out by the Geochemical Department of the Geological Survey of Denmark. Preliminary results concerning the effect of chemical weathering products from the abandoned brown-coal pits on the river system are presented in this paper.

Analytical data
The description is based on chemical analyses of river water (table 1), lake water (table 2) and sediments (table 3). (In table 1 only a minor representative part of the analyses is presented).

Localization
An outline of the sampling localities is given in fig. 2 and pls. 1, 2 and 3.

Field procedures

The surface water was sampled in a plastic container just below the water surface. Subsamples were filtrated using 8 μ paper filter, and 0.45 μ membrane filter (N_2 pressure).

The pH value and the Fe^{2+} concentration were measured immediately after the sampling.

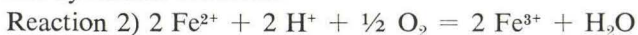The sediment was sampled at the sediment/water interface.

The abandoned brown-coal pits and their relative contribution to the pollution of the river system

Many abandoned brown-coal pits exist in the area surrounding the river Skjernå. The two largest pits are the Haunstrup pit, located about 10 km southwest of Herning, and the Søby pit situated about 15 km south-southeast of Herning (see pl. 1).

During the mining of brown coal, sediments rich in metal sulphides were exposed to the atmosphere (cf. Villumsen 1976). These layers are at present accessible to chemical weathering exemplified by the pyrite disintegration:

Reaction 1) $2\ FeS_2 + 7\ O_2 + 2\ H_2O = 2\ Fe^{2+} + 4\ H^+ + 4\ SO_4^{2-}$
and by further oxidation
Reaction 2) $2\ Fe^{2+} + 2\ H^+ + \frac{1}{2}\ O_2 = 2\ Fe^{3+} + H_2O$
It is seen from equation 1) and 2) that mobilization of metal ions (here Fe^{3+} and Fe^{2+}), SO_4^{2-} and H^+ occurs by the decomposition process.

As a result of the pH decrease a secondary decomposition may occur. Hereby Al, Si, Mn, Ca, Mg, etc. are mobilized from clay minerals, felspars, carbonates and similar potentially alkaline compounds.

Most of the brown-coal pits in the area are partially filled with water. These water reservoirs will henceforth be referred to as "brown-coal lakes". The hydrologic relationship of the "brown-coal lakes" to the adjacent surface-water system is not known in detail. At Haunstrup and Søby, however, direct outlets exist (see fig. 2 and pl. 2).

During August 1975 water samples were collected from 24 of the abandoned pits (see fig. 1). These lake-water analyses (see table 2) illustrate the variability of weathering intensity within the pits in the area. In some of them the chemical composition resembles the ground water in the area e.g. 95.33, whereas others contain extremely acidic water, e.g. 84.15 and 95.30.

Pls. 1, 2 and 3 show the seasonal variation of the concentrations of pollution indicators (Fe, SO_4 and pH) at selected river-water stations.

By comparing fig. 1 with pls. 1, 2 and 3 it is possible to estimate the present pollutive influence of the different "brown-coal lakes" on the river system. This comparison leads to the following conclusions:
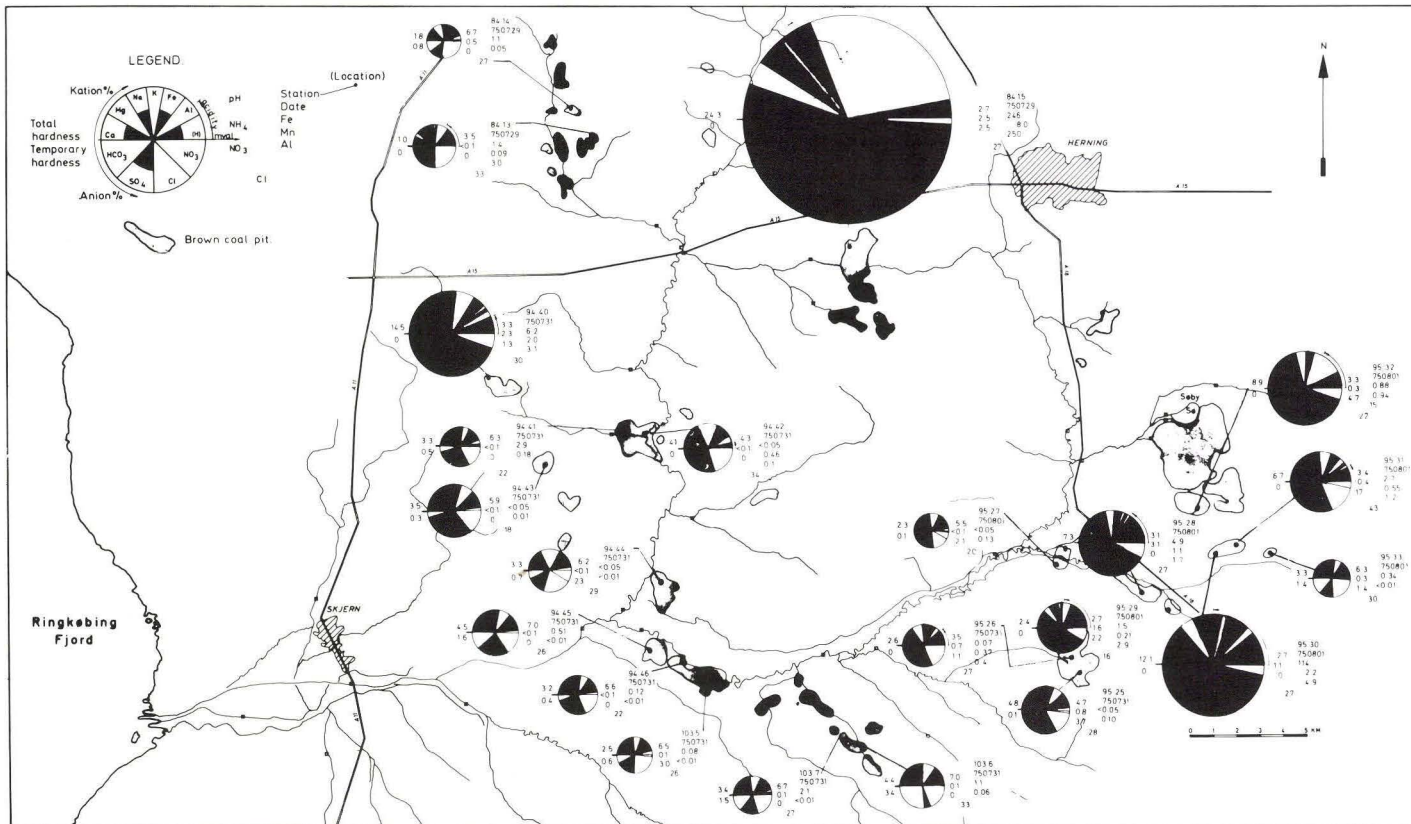
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Fig. 1. The water chemistry of the brown-coal lakes.

Table 1. Selected analyses of river water.

Station	Date	pH field	Alk meq/l	Cl ppm	SO₄ ppm	HCO₃ ppm	PO₄ ppm	NO₃ ppm	NH₄ ppm	Na ppm	K ppm	Mg ppm	Ca ppm	Fe(<8μ) ppm	Mn ppm	SiO₂ ppm	KMnO₄- need	Al ppm
84.4	740520	6.3	0.60	25	25	37		7.4	<0.1	13	3.5	3.9	21	0.61	0.08	9	6	
84.4	740717	6.7	0.42	28	44	26	0.05	13	0.5	14	7.5	4.1	24	0.82	0.06	10	24	
84.4	740905	5.8	0.64	26	32	39	<0.02	6.2	0.4	13	4.3	3.5	21	0.87	0.08	12	10	
84.4	740929	6.6	0.48	30	47	29	0.03	18	<0.1	14	8.1	4.1	28	1.3	0.10	11	29	
84.4	741102	5.8	0.52	31	40	32	<0.02	12	0.3	14	4.9	4.1	25	0.81	0.10	13	9	
84.4	741126	6.4	0.50	30	42	31	0.06	23	<0.1	15	6.7	4.1	27	0.92	0.10	11	23	
84.4	750106	5.4	0.43	29	36	26	0.05	19	<0.1	16	6.2	3.6	24	0.99	0.10	9	24	
84.4	750207	6.2	0.36	27	34	22	0.05	14	<0.1	13	5.2	3.7	23	1.1	0.12	11	14	
84.4	750303	6.7	0.46	30	33	28	0.03	12	0.4	14	5.5	3.8	22	0.84	0.11	12	12	
84.4	750324	6.5	0.47	27	35	29	<0.02	11	0.3	13	3.9	3.9	21	1.0	0.09	13	7	
84.4	750429	6.8	0.54	26	35	33	<0.02	11	<0.1	14	4.1	3.8	21	0.82	0.09	13	7	
84.4	750522	6.9	0.51	27	28	31	0.02	7.4	0.4	13	3.5	3.9	20	0.81	0.08	11	7	
84.4	750624	6.8	0.67	25	30	41	0.07	6.8	<0.1	13	3.3	3.6	20	0.45	0.06	8	7	
84.4	750720	6.6	0.69	18	31	42	0.09	6.2	1.0	13	3.8	4.1	23	1.4	0.10	13	10	
84.4	751023	6.9	0.57	20	34	35	0.31	8.5	<0.1	15	3.9	4.0	22	0.51	0.10	14	7	
84.5	740520	4.5	−1.60	26	192	0	<0.02	6.2	1.2	22	3.2	7.5	31	4.2	0.69	17	5	14
84.5	740717	4.2	−1.35	24	168	0	0.10	8.1	0.4	13	4.2	5.9	30	11	0.57	17	4	11
84.5	740905	3.8	−1.75	26	197	0	0.26	7.4	1.0	16	4.2	7.3	32	15	0.68	18	4	14
84.5	740929	4.3	−1.67	25	200	0	<0.02	11	<0.1	14	4.7	7.4	33	11	0.66	19	4	14
84.5	741102	4.3	−1.30	25	177	0	<0.02	8.7	0.5	14	3.3	7.1	31	12	0.58	19	4	13
84.5	741126	3.3	−1.80	24	174	0	<0.02	14	0.4	15	4.5	7.0	32	16	0.57	17	5	13
84.5	750106	4.1	−1.65	26	168	0	<0.02	17	<0.1	14	4.8	6.8	32	8.8	0.60	15	4	13ₜ
84.5	750207	4.6	−1.60	32	180	0	0.49	14	<0.1	21	4.1	6.9	32	12	0.59	17	6	
84.5	750303	4.7	−1.77	57	201	0	<0.02	12	1.5	35	4.3	7.4	31	22	0.64	17	7	13
84.5	750324	4.8	−1.90	33	202	0	<0.02	8.7	0.8	24	3.4	7.2	30	13	0.62	17	5	17

84.5	750429	4.5	−1.95	31	203	0	<0.02	12	0.3	16	3.4	7.4	32	13	0.70	19	4	
84.5	750522	4.4	−1.87	32	212	0	<0.02	12	<0.1	19	3.3	7.5	31	12	0.80	18	4	18
84.5	750624	4.3	−1.80	59	224	0	<0.02	8.1	<0.1	44	3.5	7.4	31	8.1	0.70	18	6	15
84.5	750720	4.1	−2.05	28	214	0	0.02	8.7	0.6	12	3.0	8.1	37	7.2	0.86	20	5	17
84.8	751023	3.3	−6.62	29	669	0	<0.02	0	1.8	13	5.5	18	95	110	2.7	40	10	40
84.9	740524	2.9	−29.00	19	2051	0	<0.02	0	<0.1	14	7.5	40	118	248	7.2	38	14	190
84.9	740717	3.1	−19.00		1348	0	<0.02	0	1.8	14	6.4	27	89	200	4.6	31	16	108
84.9	740905	2.2	−21.00	21	1544	0	<0.02	3.9	2.5	13	6.5	30	90	232	5.0	42	26	135
84.9	740929	3.0	−21.00	18	1523	0	<0.02	0	2.5	14	6.2	30	91	233	4.9	32	12	129
84.9	741102	3.0	−21.00	23	1509	0	<0.02	0	2.2	14	6.3	30	93	226	4.6	38	14	130
84.9	741126	2.9	−18.50	20	1314	0	0.03	0	1.7	14	6.6	28	85	197	4.3	32	15	117
84.9	741129	4.5	−21.00	22	1329	0	0.03	3.5	1.8	13	6.4	27	82	200	4.3	31	14	116
84.9	750106	3.2	−21.00	22	1450	0	0.02	9.9	<0.1	16	6.3	27	88	208	4.6	31	14	129
84.9	750207	3.1	−21.15	18	1638	0	0.10	0	<0.1	14	6.5	31	96	234	5.1	33	17	156
84.9	750303	3.2	−25.00	21	1697	0	0.02	3.1	1.4	14	6.8	32	97	234	5.2	33	17	129
84.9	750324	3.1	−25.00	20	1634	0	0.03	2.4	1.8	14	6.7	31	95	199	4.1	32	15	166
84.9	750429	3.2	−23.00	20	1816	0	0.05	0	1.6	14	7.0	32	95	227	5.2	33	13	155
84.9	750522	3.1	−24.00	19	1763	0	<0.02	4.2	1.4	14	6.7	32	97	242	5.3	33	15	166
84.9	750624	3.0	−26.65	20	1922	0	0.03	3.0	2.2	14	7.3	34	95	252	6.6	36	13	178
84.9	750720	3.0	−25.50	24	1830	0	0.05	4.0	1.8	16	7.4	37	111	240	5.9	36	17	168
84.17	751023	5.1	0.12	280	286	7.3	<0.02	2.9	7.7	244	9.4	7.7	29	15	0.73	18	63	7.6
84.18	751023	5.5	0.03	30	47	1.8	0.07	3.8	<0.1	113	13.7	4.7	14	1.3	0.08	12	4	

Table 2. The water-chemistry of the brown coal lakes.

Station	Date	pH lab	Alk meq/l	Cl ppm	SO₄ ppm	HCO₃ ppm	PO₄ ppm	NO₃ ppm	NH₄ ppm	Na ppm	K ppm	Mg ppm	Ca ppm	Fe(<8 μ) ppm	Mn ppm	SiO₂ ppm	KMnO₄ need	Al ppm
84.13	750729	3.5	−0.70	33	45	0	<0.02	0	0.1	13	2.2	1.3	5	1.4	0.09	4.0	3	3.0
84.14	750729	6.7	0.30	27	18	18	0.47	0	0.5	15	3.2	3.1	8	1.1	0.05	1.6	14	
84.15	750729	2.7	−33.50	27	2331	0	<0.02	2.5	2.5	18	6.8	40	108	246	8.0	35	16	250
94.40	750731	3.3	−1.00	30	321	0	<0.02	1.3	2.3	16	4.8	13	82	6.2	2.0	17	4	3.1
94.41	750731	6.3	0.17	22	47	10	0.70	0	<0.1	11	3.3	2.0	20	2.9	0.18	9.8	17	
94.42	750731	4.3	−0.15	34	68	0	<0.02	0	<0.1	15	3.4	6.8	18	<0.05	0.45	9.4	3	0.1
94.43	750731	5.9	0.11	18	53	6.7	<0.02	0	<0.1	8.6	1.9	2.9	20	<0.05	0.01	1.9	3	
94.44	750731	6.2	0.26	29	27	16	<0.02	23	<0.1	13	2.5	6.5	13	<0.05	<0.01	6.1	13	
94.45	750731	7.0	0.55	26	51	34	<0.02	0	<0.1	13	2.7	4.3	25	0.51	<0.01	11	11	
94.46	750731	6.6	0.16	22	42	9.8	<0.02	0	<0.1	11	1.9	2.8	18	0.12	<0.01	13	7	
95.25	750731	4.7	0.03	28	78	1.8	<0.02	3.7	0.8	12	4.3	3.7	28	0.05	0.10	10	13	
95.26	750801	3.5	−0.45	27	63	0	<0.02	1.1	0.7	11	2.4	3.9	12	0.07	0.37	22	3	0.4
95.27	750801	5.5	0.05	20	31	3.1	<0.02	2.1	<0.1	10	2.2	2.6	12	0.05	0.13	11	4	
95.28	750801	3.1	−1.60	27	204	0	<0.02	0	3.1	9.5	5.0	4.7	44	4.9	1.1	32	4	1.7
95.29	750801	2.7	−1.30	16	108	0	<0.02	2.2	1.6	8.1	3.3	2.1	14	1.5	0.21	3.9	3	2.9
95.30	750801	2.7	−6.10	27	553	0	<0.02	0	11	12	7.0	12	67	114	2.2	59	26	4.9
95.31	750801	3.4	−0.68	43	123	0	<0.02	17	0.4	11	9.4	5.2	39	2.7	0.55	8.9	4	1.2
95.32	750801	3.3	−2.08	22	263	0	<0.02	4.7	0.3	11	3.0	7.0	52	0.88	0.94	31	4	1.5
95.33	750801	6.3	0.49	30	20	30	<0.02	1.4	0.3	11	2.6	2.6	19	0.34	<0.01	3.1	35	
103.5	750731	6.5	0.22	26	26	13	<0.02	3.0	0.1	11	3.4	2.3	14	0.08	<0.01	2.4	8	
103.6	750731	7.0	1.23	33	11	75	<0.02	0	0.1	14	9.9	5.0	23	1.1	0.05	3.9	51	
103.7	750731	6.7	0.52	27	26	32	<0.02	0	0.1	12	3.0	3.6	18	2.1	<0.01	7.2	40	
105.7	750801	6.0	0.18	29	35	11	<0.02	0	0.5	12	6.5	3.3	15	0.42	0.02	1.2	34	
105.8	750801	5.8	0.11	20	69	6.7	<0.02		<0.1	8.6	3.2	4.5	28	<0.05	0.26	1.6	13	

Table 3. Sediment analyses (aqua regia).

Station	S1	S2	S3	S4	S5	S6
(% of dry matter)						
Insoluble residue	26.1	14.9	12.9	21.4	23.7	96.7
Fe_2O_3	48.5	54.7	56.2	50.2	39.5	0.7
Al_2O_3	<0.5	4.5	4.7	4.7	5.2	2.2
TiO_2		0	0	0	0	<0.1
P_2O_5	<0.1	0	0	0	0	0
Mn_3O_4	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
CaO	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
MgO	<0.1	<0.1	<0.1	<0.1	0.1	0.1
Na_2O	0.1	0.2	0.2	0.2	0.2	0.1
K_2O	0.1	0.1	0.1	0.1	0.1	<0.1
Loss on ignition (1000° C)	24.3	24.9	25.2	22.2	28.2	2.0
Loss on ignition (500° C)	13.5	12.6	12.5	12.1	22.9	2.0
SO_4^{2-}	11.7	14.2	14.5	12.9	6.4	0
Fe^{2+}		0.9	0.9	1.2	3.8	0.2
NH_4^+	<0.1					

1. The pits of Haunstrup and Søby clearly reveal the highest level of pollution.
2. Some pits (e.g. 95.28 and 95.40) containing very contaminated water do not seem to affect the river system at present.

Since the pits at Haunstrup and Søby are causing the highest contamination to the river system, these were studied in closer detail (the contamination from the Søby pit is described briefly).

The pits at Haunstrup

The "brown-coal lakes" in the deposits of Haunstrup have two outlets towards the west, Haunstrupbæk and Nørrebæk. Both are tributaries of Rimmerhusbæk which is a tributary of the river Vorgodå (see fig. 2).

The lake system consists of a "central lake" close to the outlet to Haunstrupbæk, as well as several small lakes. Random analyses from the area suggest that the "central lake" is by far the most polluted lake. By comparing the water analyses from the "central lake" (84.15, fig. 1 and table 2) and "normal" river water (e.g. station 84.4, table 1) in the river Vorgodå the enormous differences in concentration show up (e.g. the iron content of 84.15 is 250 times higher than that of 84.4).

The progression of this acidic water through the river system will in the following be traced by the above-mentioned primary and secondary disintegration indicators (pH, Fe, SO_4^{2-}, Mn, Al etc.):
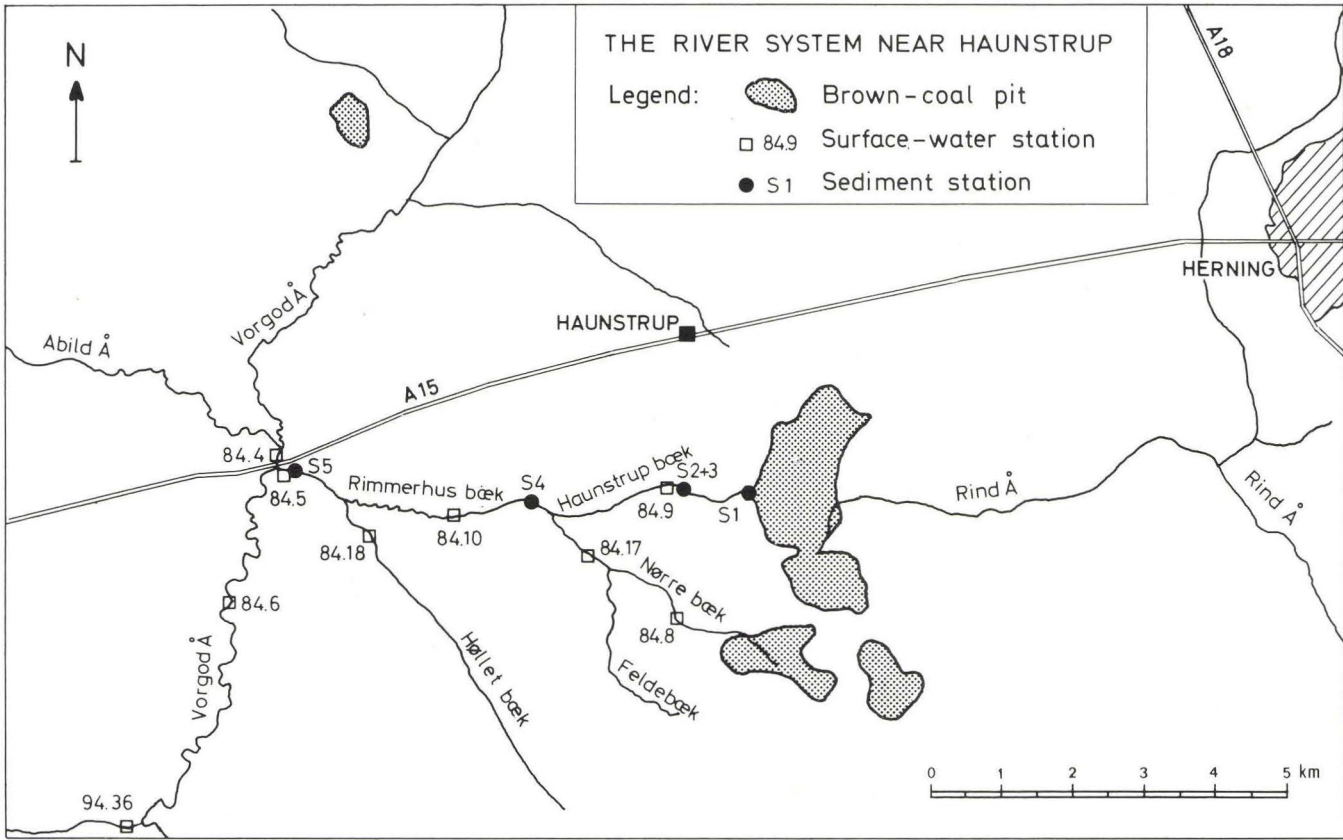
Fig. 2. The river system and sampling stations at Haunstrup.

S 1 (see fig. 2 and table 3)

The bottom of the upper part of Haunstrupbæk river (from the pit to station 84.9) is covered by an incrustation of a rather uniform yellow to brown colour. An analysis of a representative sample, S 1, showed that this crust consists predominantly of iron and sulphate, in all probability as alkaline iron sulphates and partly dehydrated iron hydroxides. The large amount of sulphate cannot be accounted for by known complex minerals (e.g. jarosit: $M^I Fe_3(SO_4)_2(OH)_6$, $M^I = K^+$, Na^+, NH_4^+, etc.) as the amount of univalent ions is too small. X-ray diffraction showed only reflections of quartz and felspar (arising from enclosed granules), which indicates that the iron and sulphate compounds are amorphous.

84.9 Haunstrupbæk river (see fig. 2, table 1 and 3)

Haunstrupbæk primarily drains the northern pits. A comparison of the analysis S 2 (sampled in rapid flow) and S 3 (sampled in a quiet environment) indicates that the precipitation of chemical material is independent of the river flow. The chemical composition of these samples compared to S 1 (1 km upstream) only significantly differs in the Al_2O_3 content, which indicates that a precipitation of aluminium has started somewhere between S 1 and 84.9, in accordance with the rise in pH at this stretch of the river.

Likewise, a comparison of 84.9 750720 (see table 1) and of 84.15 750729 (see table 2) shows that Haunstrupbæk river is somewhat less polluted than the "brown-coal lake", but it is obvious that the water type is the same. Considering the "central lake" as the principal source of pollution (as mentioned earlier), it must be concluded that sedimentation and dilution (drainage water and ground water) have only a slight effect on the concentration level of the decomposition products in the river system from 84.15 to 84.9.

The contents of disintegration products at station 84.9 show only a slight seasonal variation i.e. the concentration levels reach a minimum during winter (markedly for SO_4, Mg, Fe, Ca and Mn) presumably corresponding to the added amount of precipitation in the wintertime.

The analyses of the different iron fractions, Fe_{tot} (unfiltrated sample), Fe ($< 8 \mu$) and Fe ($< 0.45 \mu$) show that $[Fe_{tot}] \simeq [Fe (< 8 \mu)]$ $\simeq [Fe (< 0.45 \mu)]$[1]. This indicates that if any particles are transported by the river, they must be of collodial size[2]. The lack of bigger iron particles

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1. 8μ and 0.45μ refer to filter size.
2. collodial particles = particles $< 0.5 \mu$

in the water indicates that the precipitation is insignificant compared to the total iron transport (ca. 1 kg/min.)[1] in the river. The type (a hard crust) and the thickness (only a few cm) of the sediment seem to support this statement. The high Fe^{2+} concentration in the river (see pl. 2) shows that reaction 2 (page xx) is only partly finished in this acidic medium (pH $\sim$ 3,0) in accordance with the fact that the rate of reaction 2) is given as:

$$- \frac{d[Fe^{2+}]}{dt} = k \ [Fe^{2+}] \ pO_2 \ [OH^-]^2 \quad (k = 1.5 \times 10^{13} \ l^2 \ mol^2 atm^{-1} \ min.^{-1})$$

(Lee and Stumm 1960), i.e. the oxidation rate decreases rapidly with the pH value.

In this connection it can be mentioned that conservation tests[2] have proved that the saturation of oxygen in the water is about 40–50 %.

This high amount is related to aeration caused by the several small waterfalls in Haunstrupbæk river at its beginning.

84.8 Nørrebæk river (see pls. 1–3 and table 1)

The Nørrebæk river functions as a direct outlet for the southern pits and has a chemical composition comparable to Haunstrupbæk river (84.9), although the river is less contaminated.

84.17 Feldebæk river (see fig. 2 and table 1)

The junction of Nørrebæk river with the more alkaline water in Feldebæk river can be seen in the analyses of the different iron fractions:

84.8: $[Fe_{tot}] \simeq [Fe(< 8 \ \mu)] \simeq [Fe \ (< 0.45 \ \mu)] \simeq 1.5 \ [Fe^{2+}]$
84.17: $[Fe_{tot}] \simeq 2 \ [Fe \ (< 8\mu)]$, and $[Fe \ (< 8 \ \mu)] \simeq [Fe \ (< 0.45 \ \mu)]$
$\simeq [Fe^{2+}]$

In Feldebæk river the iron content in the water can be classified into particles ($> 8 \ \mu$) and dissolved Fe^{2+}. This indicates that the precipitating of iron is oxidation controlled. That is; when Fe^{2+} is oxidized, the Fe^{3+} ions thus formed immediately precipitates according to the very low solubility of Fe^{3+} (pH $\sim$ 5); this precipitation results in a considerable suspension transport.

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1. the river discharge $\simeq$ 60 l/sec. (Jensen 1969)
   total iron transport = river discharge $\times$ $[Fe_{tot}]$.
2. $\frac{d[Fe^{2+}]}{dt}$ was followed in samples protected from the atmosphere.

84.18 Hølletbæk river (see fig. 2 and table 1)

The analysis gives an indication of the quality of surface water in a water course that drains the area surrounding the pits of Haunstrup. By comparing the "background" (i.e. the unpolluted part) of Vorgodå river (84.4) one can observe a much lower pH value in Hølletbæk river, but the concentrations of the other pollution indicators do not differ much from the values found at 84.4.

S 4 (see fig. 2 and table 3)

This sediment analysis indicates the same kind of the precipitation as at 84.9, 3 km upstream.

84.5 Rimmerhusbæk river (see pls. 1–3, fig. 2 and table 1)

At 84.5, 7 km from 84.9, there is still a distinct pollution (Fe, SO_4, Mn and Al), while the amounts of Ca, Si, and Mg are about to reach the level of the "background" (84.4). The analyses of the different iron fractions

$[Fe_{tot}] \simeq 2 [Fe (< 8 \mu)]$ and
$[Fe (< 8 \mu)] \simeq [Fe (< 0.45 \mu)] \simeq [Fe^{2+}]$

reveal an oxidation-controlled precipitation course similar to what was found at 84.17.

The sediment analysis S 5 (see table 3) shows almost the same content of iron and aluminium as further upstream (compensating for insoluble residue), while the amount of sulphate is distinctly smaller. Again no crystalline iron compounds were found by X-ray analyses. The seasonal variations at 84.5 (see table 1) are the same as at 84.8 and 84.9. It is obvious, however, that one of the characteristic features of the Skjernå system, the seasonal variation of NO_3^- concentration, is reestablished here (low during summer, high during winter). At 84.8 and 84.9 this variation was apparently choked by the reducing medium.

Evaluation of the transport of disintegration products of the Haunstrup pit

Previously, qualitative descriptions revealed how the concentrations of disintegration products decrease through the whole of Rimmerhusbæk river. By the use of river discharge measurements in a simplified model it can

now be estimated how large a decrease in concentration one can expect if it was only a question of dilution (the course is covered by stations 84.9, 84.8, and 84.5).

The model contains the following hypotheses:

1. The natural background in the area between the pits of Haunstrup and Vorgodå can be compared with the background of Vorgodå (see earlier); that is, if the concentrations of Fe, SO_4, Mn and Al at 84.4 are subtracted from the concurrent concentrations of the same parametres at 84.9, 84.8 and 84.5, a measurement of the real pollution can be obtained.

2. The relative river discharge at the different stations are expected to be constant in time.

Data and results

From Hedeselskabet the following river discharge measurements are available (Jensen 1969):

690909: 84.9: 58 1/sec.,

690910: 84.9: 46 1/sec., 84.8: 14 1/sec.

From Ringkøbing amts vandvæsen the following river discharge measurements are available:

741126: 84.9: 58 1/sec., 84.5: 532 1/sec.

Multiplication of these flows with the background-corrected concentrations of decomposition products gives an estimation of the flux through a cross section of the watercourse (gram/sec.).

Here the concentration data for 741126 are used.

Mobilized material from 84.9 and 84.8					Retrieved at 84.5 (%)	
Fe_{total}:	11.6	+ 1.7	= 13.3	g/sec.	12.2	g/sec. (92 %)
Fe ($< 8\ \mu$):	11.4	+ 1.6	= 13.0	g/sec.	8.0	g/sec. (62 %)
SO_4:	73.8	+ 9.5	= 83.3	g/sec.	70.2	g/sec. (85 %)
Mn:		0.244 + 0.44	= 0.288	g/sec.	0.250	g/sec. (87 %)
Al:	6.73	+ 0.63	= 7.36	g/sec.	6.91	g/sec. (94 %)

In comparing "% retrieved material" for the 5 parametres it is characteristic how identical these figures are for SO_4, Mn, Al and Fe_{tot}, whereas the figure for Fe ($< 8\ \mu$) are distinctly lower (the figures are to be seen in connection with the analytical uncertainty as well as with the more significant uncertainty (5–10 %) on the measurements of the discharge). Chemically one should not expect any particular precipitation of SO_4, Mn, and Al in this acidious water medium. The amount and composition of the sediment also give this indication.

In natural watercourses, Mn (II) is thermodynamically unstable as far as oxidation is concerned (Morgan 1967). The transformation in an acid medium is slow unless it is catalysed. The fact that the loss of Mn cannot be traced in the sediment samples may partly be explained like this: The amount is relatively small (in comparison with Fe, SO_4 and Al), and the special chemistry of Mn may cause locally catalysed precipitations within small areas. This is supported by findings of Pyrolysite (MnO_2) concretions, at stone salients, for example.

According to the quantitative ratio (% retrieved material), the drop in concentration down to watercourse for SO_4, Al and Mn is primarily due to a dilution effect.

Concerning Fe, however, flocculation (formation of particles) and suspension transport are important. Only 62 % of the particles < 8 μ ($\sim$ dissolved iron at 84.8 and 84.9, see earlier) is retrieved at 84.5. This indicates that flocculation will occur.

Judging from the values of Fe_{tot}, however, the main part of the particles formed is lead downstream, as only 8 % of the mobilized iron seem to precipitate. This is supported by the previously mentioned phenomenon that the relative quantity of iron particles $= Fe_{tot} \div Fe$ (< 8 μ) increase greatly downstream. This conclusion, however, is only to be perceived as a description of a tendency connected with the precipitation of iron as it is difficult to select a representative sample for Fe_{tot} determination in this heterogenous system of river water and iron particles, whereby Fe_{tot} is subject to some uncertainty.

The pollution of Vorgodå river

84.4 Vorgodå river at mainroad A 15 (see table 1 and pls. 1–3)

The water quality of Vorgodå river is described just before the outlet of Rimmerhusbæk river through analyses from 84.4. The low alkalinity and considerable amounts of iron and manganese found are typical for watercourses in the western part of Jutland. The seasonal variations show the same pattern as at 84.5.

84.6 Vorgodå river, Vorgod, and 94.35 Vorgodå river, Nr. Vium (see pl. 1)

These stations describe Vorgodå after the outlet of Rimmerhusbæk river. In comparing 84.6 with 84.4 and 94.35 it is possible to estimate the pollution of the river about 2 and 8 km downstream.

Table 4.

Average 74/75	pH	Alk.	SO₄	Mg	Ca	Mn	SiO₂	Fe_tot	Fe (< 8 μ)
84.4	6.7	0.52	35	3.9	23	0.09	11	2.4	0.91
84.6	6.1	0.28	60	4.6	26	0.20	12	5.0	1.60
94.35	6.5	0.43	48	4.3	24	0.17	12	3.9	0.68

It appears from the table 4 that Vorgodå river is markedly contaminated: The pH decreases about half a unit, the alkalinity is halved, and the concentration of primary decomposition products is nearly doubled.

The water chemistry of the most important tributaries to Vorgodå river is described in the following:

94.36 Herborgbæk river by Egeris (see pls. 1–3)

The water quality at this station corresponds to the background quality of Vorgodå (84.4).

94.34 Viumbæk river before the brown-coal pits of Nr. Vium (see pls. 1–3)

This station was for practical reasons established just before the brown-coal pits of Nr. Vium. The type of water is characteristic for the area and corresponds to 84.4.

The analyses from some of the brown-coal lakes at Nr. Vium 94.41 and 94.42 (see fig. 1 and table 2) seem to show that the weathering activity is very moderate: The water quality at 94.41 is comparable to that of Vorgodå river (84.4), and the brown-coal lake 94.42 shows only signs of moderate decomposition in the acidity and in the content of SO_4, while the content of iron is too low to be determined. It is therefore not very likely that Vorgodå river is polluted by these pits.

94.6 Vondå river at Troldhede (see pls. 1–3)

Vondå is the last great outlet to Vorgodå river. The water quality is normal for the area (the same as 84.4). Only the pH is relatively high on the average.

Summing up, it can be concluded that the tributaries to Vorgodå river do not pollute the river significantly.

94.2 Vorgodå at the outlet to Skjernå (see pls. 1–3)

The chemical data from this station are very similar to those of 84.4 (about 20 km towards the North). Divergence from the average values (they are reasonable to use as there is only a slight seasonal variation) is of the same size as the analytical accuracy for most of the parametres. Even though the river is heavily charged by brown-coal contaminants the effect of this source is quickly drowned by the main contribution to the water-course: seeping of ground water, drainage water and precipitation.

The mouth of Vorgodå river in Skjernå river at Borris

A comparison between stations 94.3 (the background of Skjernå), 94.2 (the background of Vorgodå) and 94.4 (Skjernå after the outlet) shows that the water quality at the three stations is almost similar. If the average values of possible "pollution indicators" (see the chapter about Vorgodå) are compared, one obtains the following:

	pH	Alk	SO_4	Mn
94.3	6.9	0.57	42	0.10
94.2	6.6	0.39	43	0.12
94.4	6.8	0.52	42	0.14

The background levels of SO_4 and Mn in Vorgodå and Skjernå river are similar. Vorgodå river is slightly less alkaline than Skjernå, but the difference between stations 94.4 and 94.3 is extremely small. The contamination with iron from Vorgodå river on Skjernå river is not significant as far as Fe^{2+}, Fe ($< 0.45 \; \mu$) and Fe ($< 8 \; \mu$) are concerned. However, it looks as if the particle transport of iron is somewhat larger at 94.2 (see figs. 3 and 4). This particle transport measured as $Fe_{tot} \div$ Fe ($< 0.45 \; \mu$) is a temporary measure and should not be considered as representing an exact value for the following reasons:

1. The large and irregular variations of the analytical values give an indication of a poor coverage of the real conditions outside the heavily acid watercourses. The reason for this may be that it is difficult to collect a sample that is representative, and/or that more frequent observations are needed.
2. It has not yet been determined what will further happen to the already precipitated iron compounds (cf. Villumsen 1976), but it is obvious that the soluble matters arising from the deposit do not directly pollute Skjernå river and Ringkøbing fjord.

The brown-coal pits at Søby

The river system at Søby is mapped in pl. 1. The stations 95.23 and 95.7 are located at canals, which drain different "brown-coal lakes". Thus several direct outlets to the Søbyå-Rindå river system exist.

Although the river Rindå rises in the Haunstrup area, the data at 95.19 (see pls. 1, 2 and 3) seem to indicate that the pollution of Rindå from the Haunstrup pits can be disregarded at this location (ca. 30 km downstream), consequently the contamination of the river Rindå south of the mouth of Søbyå river must come from the Søby area.

As the main features of the pollution from the Søby pits are the same as found at Haunstrup, only some important differences are stated here:

1. The concentrations of decomposition products in the outlet water from Søby are significantly smaller (it is impossible to compare the flux as river discharge measurements in this area are lacking).
2. Ferrous ions represent only a minor part of the Fe ($< 0.45 \mu$) content in the outlet water. Consequently the precipitation downstream is pH controlled, as the Fe^{3+} ion is extremely insoluble at higher pH values (Hem 1970).
3. The sediment analysis S 6 at 95.23 (see table 3) show that practically no iron compounds are found in the sediment in the upper part of the canal. This is in accordance with the visible impression i.e. no red-brown colour appears in the sediment.

The effect of the Søby pits on the river system

To get an impression of the effect of the Søby pits on Rindå average values (74/75) of the weathering indicators are compared:

	pH	SO₄	Mn	Alk	Fe ($< 8 \mu$)
95.19	6.7	43	0.21	0.60	0.73
95.20	6.6	71	0.40	0.35	0.53

The pollution is obvious as regards SO_4^{2-}, Mn and alkalinity. It is, however, evident that the iron has dropped out of solution in accordance with the high pH value found at 95.20.

A similar comparison of 95.19 and 95.10 shows that the contamination is negligible as far as soluble compounds are concerned. However, the effect of the suspension transport on the final recipient, Ringkøbing fjord, must still remain an open question for reasons quoted earlier (see page 71).

Dansk sammendrag

I Skjernåens opland findes adskillige nedlagte brunkulsgrave. Under brydningen af brunkul blottedes lag, som indeholdt metalsulfider (fortrinsvis svovlkis, FeS_2). Disse lag, der nu ligger som tipper, er tilgængelige for forvitring, hvorved jern og sulfat mobiliseres og pH sænkes. Denne pH-sænkning kan give anledning til en sekundær forvitring af potentielt basiske stoffer (kalk, feldspat, lermineraler m. m.), hvorved f. eks. Ca, Al, Mn og Mg mobiliseres.

Ved hjælp af kemiske analyser på overfladevands- og sedimentprøver undersøgtes brunkulslejernes påvirkning af å-systemet og Ringkøbing fjord, idet de tidligere omtalte forvitringsprodukter brugtes som belastningsindikatorer.

En sammenligning af forvitringsniveauet i og ved de respektive brunkulsgrave (pl. 1–3) viste, at kun Haunstruplejet og Søby-lejet belaster å-systemet i nævneværdig grad på nuværende tidspunkt. Forureningen fra disse lejer undersøgtes derpå nærmere.

»Brunkulsøerne« i *Haunstrup* har direkte afløb til Haunstrup bæk og Nørrebæk og via Rimmerhus bæk til Vorgod å (fig. 2). Haunstrup bæk og Nørrebæk er præget af ekstremt høje indhold af primære og sekundære forvitringsprodukter og en lav pH-værdi ($\sim$ 3.0). Trods gode iltningsbetingelser er Fe^{2+}-indholdet i forhold til Fe_{tot} (se pl. 3) temmelig højt. Dette vanskeliggør udfældningen af jern, idet Fe^{2+} er opløselig selv ved ret høje pH-værdier, Fe^{2+} må derfor først ved iltning omdannes til det tungere opløselige Fe^{3+}, hvis udfældningen skal foregå i det sure vand; udfældningen er således oxidationskontrolleret.

Suspensionstransporten af jern er negligibel i de sure vandløb, men tiltager efterhånden som pH stiger ned igennem bæk-systemet før udløbet til Vorgod å (station 84.5). Den kemiske sammensætning af sedimentet ændres ikke væsentligt på denne strækning, men koncentrationen af forvitringsindikatorer falder betydeligt.

Dette koncentrationsfald skyldes for SO_4, Mn og Al primært en fortynding med ubelastet åvand. For jern derimod iagttages en flokkulation, og hovedparten af de dannede partikler føres videre med strømmen.

I Vorgod å kan belastningen fra Haunstrup-lejet kun spores få km nedstrøms. Dette gælder dog kun for det opløste stof, idet effekten af suspensionstransporten ikke kan bedømmes med tilstrækkelig sikkerhed på nuværende tidspunkt. Afløbskanalerne ved *Søby-lejet* er mindre belastede med forvitringsprodukter end afløbene ved Haunstrup-lejet (se pl. 1–3), men vandtyperne er ens.

Jern mobiliseres overvejende som Fe^{3+}, og som følge deraf bliver udfældningen pH-kontrolleret.

Dette indebærer, at der udfældes jern når forvitringsvandet møder mere basisk å-vand (udløbet i Rind å). Belastningen med forvitringsprodukter kan for det opløste stof ikke spores efter Rind å's sammenløb med Skjern å.

Det må konkluderes, at brunkulslejernes belastning, hvad angår opløst stof, er intens, men så hurtigt afklingende, at indflydelsen på Skjern å og Ringkøbing fjord er negligibel. Suspensionstransporten af jern kan have betydning for forureningen, selv om det ikke fremgår af disse foreløbige data.

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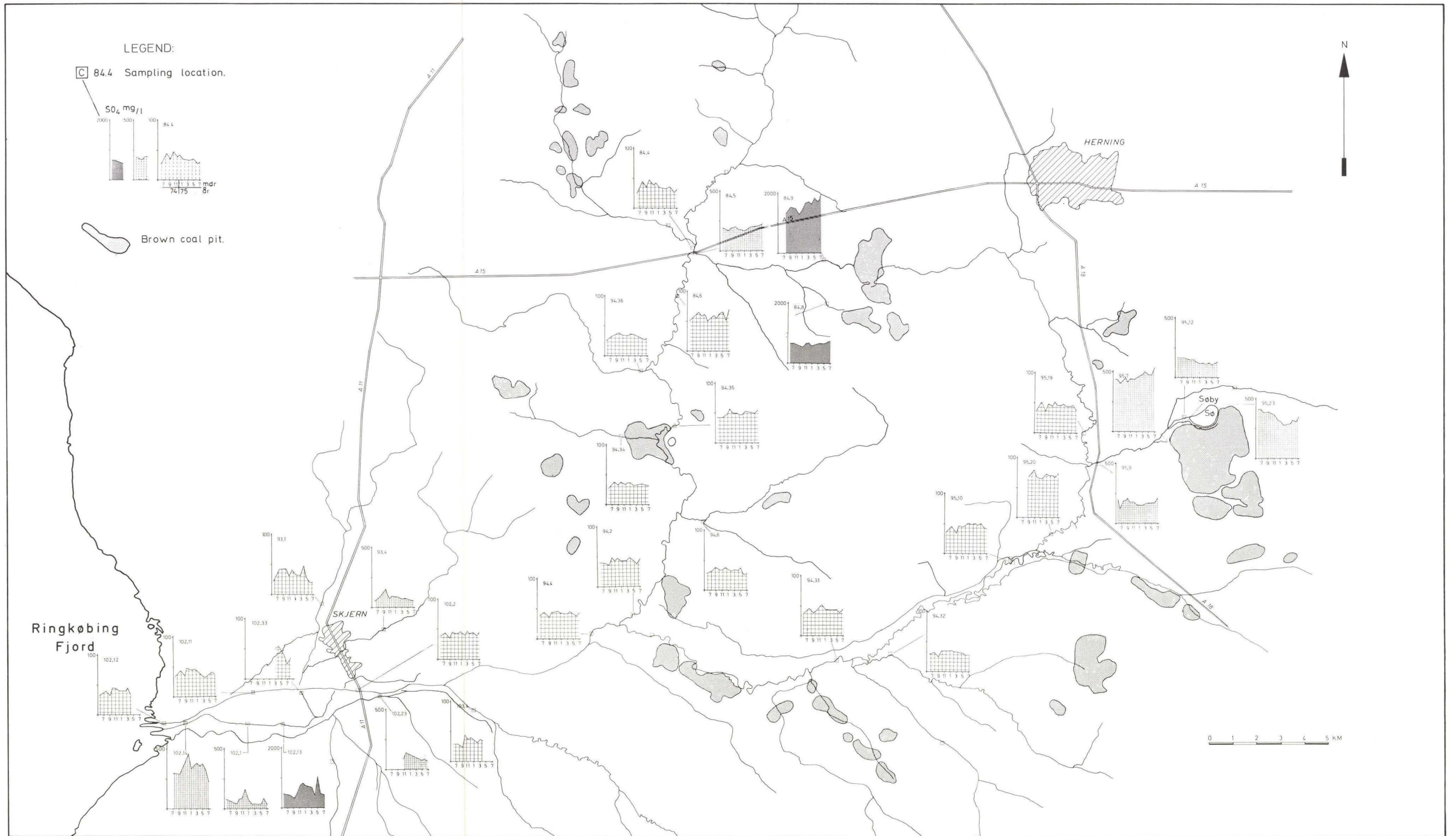
Plate 1. The sulphate content in the Skjernå river system.

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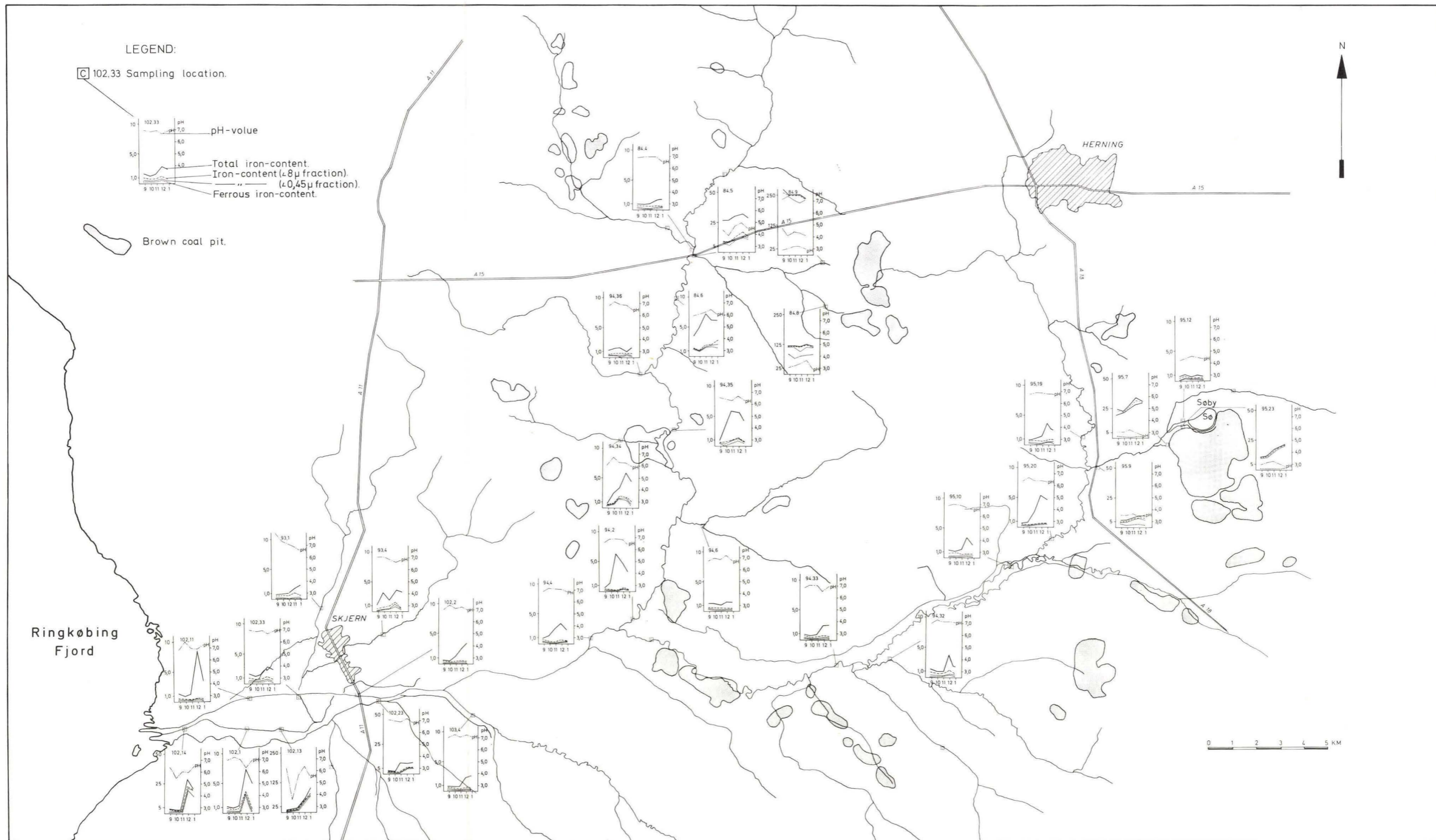Plate 2. The iron content in the Skjernå river system.

Tegn. nr 1974-250

Plate 3. The iron content and pH in the Skjernå river system.