Cadmium Content in Sea Water, Bottom Sediment, Fish, Lichen and Elk in Finland

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The great toxicity of cadmium to all forms of life is well known. For most aquatic organisms, cadmium is the second in order of toxicity, of the heavy metals, mercury being first (for references see 1). The great toxicity of cadmium to laboratory animals and man has been known for many years.

In rats, cadmium, administered in doses capable of producing tissue concentrations comparable to those found in modern man, causes arterial hypertension, sclerosis of small arteries in kidneys, heart and other organs, proteinuria, testicular atrophy, and neoplasms (2-7). In man, cadmium is suspected of causing pulmonary emphysema, proteinuria and prostatic carcinoma (cf. 2). It is absent at birth, but accumulates, especially in the kidney, with increasing age (8). Perry et al. (9) found in the human kidney values (as ppm of ash) varying from 750 (Ruanda Urundi Africa) through 2250 (USA) to 5300 (Japan). Schroeder and Balassa (8) reported similar high values in Japanese samples. They calculated that the diet could contain 4 to 100 µg/day depending on whether sea food and kidneys were eaten. In Japan, rice could also contribute significantly to the total intake (8).

In Japan, cadmium has been recently identified by Kobayashi (10) as the main

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causative agent of a chronic disease which has afflicted the residents at Jintsu river, in Toyama prefecture, since the second world war. The patients have severe osteomalacia and suffer from intense pain in their bones. Kobayashi (10) reported the following values (ppm of ash) found in the organs of a patient who died: kidney 4 900, liver 7 050, rib 11 500. The disease was called "itai-itai- byo" (ouch- ouch- diseaes) because of the shrieks of the patients suffering from chronic pain. In February 1968 the death toll was 119 persons, mainly middle-aged women who had borne several children. Only 5 were men. In addition, 94 non-lethal typical cases and an estimated 1000 latent cases were reported (11). In the advanced stage of the sickness, the bones become brittle and fractures occur easily (10). A zinc mine at the upper course of the Jintsu River was identified as the origin of the cadmium. During the war, Production of zinc and lead was rapidly increased without proper treatment of the wastes, which were discharged into the river. Fine ore particles still containing heavy metals were deposited on rice fields downstream causing not only high cadmium levels in the rice, but also damage to the crop. In addition, many farmers used river water for drinking and food making, and river fish for food.

Kobayashi reports in the bone ashes of one patient 0.5-1.1 per cent cadmium, 0.02 per cent lead and 0.3 per cent zinc. Polished rice from the district contained 1.19 ppm of Cd in dry matter and 125 ppm in ash. Later the disease was identified on Tsushima Island outside a mine. The well water used by one patient on Tsushima contained 0.225 ppm of Cd, 13.37 ppm of Zn and 0.41 ppm of Pb (10). Kobayashi (10) confirmed, by feeding experiments with rats, that cadmium replaces calcium, a fact known for some time (12).

In the USA, Carroll (13) observed a positive correlation between the cadmium content of air and the incidence of hypertension and arteriosclerosis in 28 North- American cities.

In Scandinavia and Finland, a marked increase in the death rates caused by cardiovascular diseases has occurred in recent years. Between 1955-64 this increase was in Sweden 8, Finland 14, Denmark 17 and Norway 25 per cent, while the increase of deaths occuring from ischemic heart disease was even sharper: in Finland 33, Sweden 36, Denmark 41 and Norway 73 per cent (14). Masironi (15) speculates that increased industrialization in Norway has brought about higher pollution with cadmium which, being accumulated by shellfish and other marine animals, is eventually ingested by humans. This hypothesis is based on the facts that both the consumption of seafood, which is generally notoriously rich in cadmium (13), and the increase of cardiovascular diseases are exceptionally high in Norway. An increase of the cadmium level in fish and shellfish in Norway has not been reported, however. Masironi concludes that the experimental, clinical and statistical evidence indicates that cadmium may be an etiological factor in some forms of cardiovascular disease, but further investigations are needed to ascertain whether cadmium really plays a role and to establish what mechanism is involved (15).

In Sweden, occurence of cadmium in the environment has been studied recently by two groups of investigators: Rühling and Tyler in Lund (16-19) and Ljunggren et al. in Stockholm and Lysekil (20). The former authors analyzed several heavy metals in the moss Hylocomium splendens from northern and southern Scandinavia, finding, for cadmium, 0,18 ppm (in dry material) in northern and 0,99 ppm in southern samples (18). Tyler reports values for seven heavy metals in the cypress moss (Hypnum cupressiforme) in the neighbourhood of the industrial city of Norrköping in southern Sweden. In an area of a few square kilometers at the north-east corner of the city (the windward portion) values as high as 3 to 4 ppm were found, and in an area of about 100 km^2 values around 1 ppm were found. Ljunggren et al. (20) report the cadmium levels in plankton, plants, insects, crustaceans and fish from a fresh water system beginning at a non-polluted lake and running through urban and industrialized regions. The cadmium levels of those organisms increased in the respective order. Homogenized dried samples originated in the non-polluted lake had the lowest values, 0,6-1,5 ppm, while the highest values 0,6 -17 ppm, were found in samples from the polluted river. Pike from polluted fresh water gave 0,17 ppm of freshweight. Six pike from the Baltic outside the city of Oskarshamn, which is known to spread pollution, gave $\leq$ 0,020 ppm, but one pike gave $\leq$ 0,1 ppm. Cd per fresh weight.

Landner (21) in a preliminary experiment kept the aquarium fish guppy in water containing 0,1 ppm Cd. The cadmium level of the fish rose from 2 to 10 ppm in

7 weeks. When the fish were placed into clean water, their Cd level decreased with a half-time of about 18 days.

The purpose of the present study is two-fold: first, to get a broad picture of the cadmium levels in environmental samples in Finland, in comparison with other countries, both in coastal waters and inland, and second, to check the local environmental levels in the vicinity of the city of Kokkola, where a large zinc refinery with an annual capacity of 90 000 tons of zinc became operational at the end of 1969. The locations from which the first group of samples were taken are presented in Fig. 1; locations of the Kokkola samples are presented in Fig. 2. As hydrospheric samples, water, bottom sediments and organs of pike were analysed. The flesh of pike is probably representative of the sea food that man is likely to consume. As terrestrial sample, reindeer lichen (Cladonia alpestris) was chosen, because it grows very slowly (a 10-cm-high plant may be 50 years old) and retains all heavy metals very efficiently, as is well known from fallout studies. One analysis of elk kidney was also performed to have an idea of its importance as a dietary source of cadmium. About 8 000 elks are shot and consumed annually in Finland, which has about 4.7 million inhabitants.

Methods used

1. Collection of samples

Sea water samples were taken, from a boat, at a depth of about 0.5 m and placed into a 5-liter polyethylene container which had been rinsed 3 times with the local sea water before sampling. The samples had not been filtered but were homogenized by shaking before the aliquot for analysis was taken.

Bottom sediment samples were taken by a Birge-Ekman sampler accepting an area of 20 x 20 cms. Collection of about a 1 cm thick surface layer of the sediment was attempted.

The intact fish were sent fresh to the laboratory where the organs were separated, dried and homogenized.

Lichen samples consisted of the clean upper portion containing about half green "flower" and half grayish older cells.

2. Direct analysis of wet-ashed solution

The samples of bottom sediment, fish, lichen and tissues of elk and reindeer were dried overnight at 110°C. The bottom sediment samples were leached with 6 N HCl and the precipitate was removed by filtering. The dissolving of the fish, lichen, elk and reindeer samples was carried out by HNO_3 - $HClO_4$ wet-ashing. All sample solutions were diluted with water to a known volume.

The cadmium levels of these samples, with the exception of the fish flesh, were determined directly by atomic absorption spectrophotometry of the solutions obtained by wet-ashing. The atomic absorption spectrophotometer used was the Perkin-Elmer Model 303. The detection limit of this instrument for cadmium in water solution was 0.005 ppm. It was found that calcium concentrations higher than 500 ppm in sample solutions interferred with the determination of cadmium. This is due to the light scattering effect, which is especially potent at low wavelengths and when a high concentration of calcium is present (22). Also the total amount of solid material in the sample solution must be less than 1 %.

3. Concentrative extraction using the radioisotope ^{109}Cd for checking the yield

a) Sea water. The cadmium content of sea water samples is so low that it is necessary to concentrate the samples and to separate cadmium from the alkali metals and alkaline earths in order to allow atomic absorption analysis.

To determine the cadmium content of sea water samples, the following method was developed:

1. 1000 ml of sea water is poured into an evaporating dish. Radioactive carrier-free ^{109}Cd, in solution, is added to check the yield of the procedure. (The half-time of the ^{109}Cd isotope is 453 d; it decays completely by electron capture and γ-radiation of 88 KeV by the daughter ^{109}Ag is emitted). The sample is then evaporated to dryness.

2. The residue is soluted by 10 ml of concentrated HCl and 40 ml of distilled water is added. The sample is filtered. The solution is adjusted to pH 3 using NH_3.
3. The solution is then transferred to a separation funnel. 10 ml of 5 % aqueous solution of ammonium pyrrolidine dithiocarbamate (APDC) and 20 ml methyl-iso-butyl ketone (MIBK) are added (23, 24). The mixture is thoroughly shaken for five minutes and the layers are allowed to separate. The water phase is discarded.
4. The cadmium is transferred back into the water phase by shaking twice for five minutes, each time with 5 ml of 1N HCl. The combined water phase is transferred to a 10-ml centrifuge tube. The residues of MIBK are separated by centrifugation and discarded with the organic phase.
5. The solution is aspirated by the flame of the atomic absorption spectrophotometer. The cadmium content of the sample is determined using standard solutions of cadmium, which have been extracted in the same manner as the sample.
6. An aliquot of the 10 ml-water solution obtained in step 4 is taken for yield determination. The radioactivity of this aliquot is determined using a NaI(Tl)- detector and a multichannel analyzer. By comparing the radioactivity found with the amount added, the yield of the procedure can be calculated.

Using the method described, a hundred-fold concentration of sea water samples is obtained. The yield of the method was, on the average, 92 % (ranging from 79 % to 100 %). The precision of the method was good, according to the parallel determinations presented in Tables 1 and 3.

b. Fish flesh. To determine the cadmium level of fish flesh samples, the radioactive ^{109}Cd solution was added at the beginning of the wet-ashing. The solution obtained by wet-ashing was adjusted to pH 3 and the determination of cadmium proceeded as described in connection with the sea water samples (step 3).

Results

The results of w a t e r analyses are presented in Table 1. The samples can be divided into 3 groups: the non-polluted ones (Nos. 1 and 6) having 0.1 to 0.2 ppb of Cd, the heavily polluted ones from outside the zinc refinery (Nos. 8 and 12) having 5 to 10 ppb, and the less polluted ones having 0.4 to 0.7 ppb. Sample No. 4 was an exception, as it was very turbid and contained richly organic mud particles.

The results of the b o t t o m sediment analyses are presented in Table 2. All results are between 0.17 and 1.9 ppm Cd/dry weight. As the sediments varied greatly, from nearly pure sand (Nos. 7, 11, 12) to those rich in organic matter (Nos. 1 and 6), the cadmium level was also determined per unit weight of organic dry matter. The "nonpolluted" areas gave values between 4 and 10 ppm, the coastal area outside Kokkola gave 70 to 130 ppm and sediments taken about 2 kms. from the shore gave 15 to 30 ppm.

The results of the f i s h organ analyses are presented in Table 3. In most cases, the liver contains about 10 times more Cd than the muscle flesh of the same fish, and the kidney contains about 30 to 80 times more.

The muscle flesh and the liver of the older fish No. 16 contained 2 to 3 times more cadmium than the corresponding organs in the younger fish from the same area. There is no difference in the kidney values, however. The Kokkola values are roughly two times higher than the other ones showing the slight, initial effects of pollution.

The results of the l i c h e n analyses are presented in Table 4. They can be roughly divided into 3 categories. The samples from Lapland contained about 0.1 to 0.2 ppm of cadmium those taken near the zinc refinery in Kokkola contained about 1 ppm, and the reminder contained, for the most part, 0.3 to 0.4 ppm.

The results of the e l k and r e i n d e e r analyses are presented in Table 5. The blood and meat of the elk contained about 2 ppm of Cd per unit of dry matter, while the kidney contained about 50 ppm.

Elk kidney is thus about 20 times more efficient as a source of cadmium than elk meat, and 200 times more efficient than pike flesh from the same region.

Discussion

Comparison of the cadmium levels in the coastal waters of Finland with the one value reported in well water in Tsushima (225 ppb) shows that even the highest value found in Finnish coastal sea water, 10 ppb in front of the sewer in Kokkola, falls far below the aforementioned Japanese well water value (which had been fatal). The present values found in pike muscle, mostly 0.002 to 0.004 ppm in fresh material, are lower than the one value given by Ljunggren et al.: $\leq$ 0.015 ppm. The present lichen values established for Lapland, 0.1 to 0.2 ppm, are the same as Rühling and Tyler found in the moss Hylocomium splendens: 0.18 ppm, and our highest overall lichen value, 1 ppm, was also the same as that found in southern Sweden: 0.99 ppm. Only 6 months of operation have increased the cadmium level five-fold at about 1 kilometers' distance from the zinc works (samples Nos. 22 and 24), but no increase is yet noticeable at a distance of about 4 kilometers (No. 23). On the whole, there does not seem to be an alarming level of cadmium in the neighborhood of the Kokkola zinc works. The situation must be followed carefully, however, as a several-fold increase in this level has already been found after only a few months operation.

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Table 1. Cadmium content of sea water samples in 1970. Nos 1-6, Gulf of Finland, Nos 7-12, Gulf of Bothnia. Sampling depth is in all cases 0.5 m.

No.	Region	Cordinates	Depth of sampling place [m]	Sampling date day & month	Cd content in ppb[1)]		
					1.	2	average
1_W	Kotka, Mussalo	60°25'N, 26°53'E	1	1.12.	0.2	-	0.2
2_W	Loviisa, Hamnholm	60°13'N, 26°14'E	40	2.8.	0.4	0.4	0.4
3_W	Porvoo, Pellinki	60°14'N, 25°51'E	10	2.8.	0.5	0.5	0.5
4_W	Porvoo, Wessö	60°17'N, 25°41'E	2 [2)]	5.6.	2.0	2.3	2.2
5_W	Helsinki, Tervasaari	60°11'N, 24°58'E	3	18.8.	1.0	0.4	0.7
6_W	Tvärminne, Lappohjan selkä	59°51'N, 23°16'	1	22.7.	0.1	0.1	0.1
7_W	Kokkola, Rikkihappo Oy [3)]	63°51'N, 23°02'E	1	3.8.	0.3	-	0.3
8_W	Kokkola, Outokumpu Oy [3)]	63°52'N, 23°03'E	1	3.8.	10.2	-	10.2
9_W	Kokkola, shipping channel	63°51'N, 23°00'E	10	3.11.	0.6	0.6	0.6
10_W	Kokkola, -"-	63°52'N, 23°00'E	14.5	3.11.	0.5	0.5	0.5
11_W	Kokkola, -"-	63°53'N, 23°02'E	13	3.11.	0.5	0.5	0.5
12_W	Kokkola, Outokumpu Oy [3)]	63°52'N, 23°03'E	1.5	3.11.	5.1	5.1	5.1

1) ppb = 10^{-6} g/l

2) High turbidity

3) Sample taken at about 40 m distance from the mouth of the sewer

Table 2. Cadmium content in bottom sediments (1970).
Nos 1-6, Gulf of Finland, Nos 7-12, Gulf of Bothnia.

No	Location	Sampling depth [m]	Sampling date	ppm Cd/ dry wt	Ash %	ppm Cd/ organic dry wt (calc.)
1_M	Kotka, Mussalo	1	1.12	0.47	86.0	3.4
6_{M_1}	Tvärminne, Byviken	5	23.7	1.88	80.3	9.6
6_{M_2}	-"- Lappohjan selkä	32	23.7	1.16	85.3	7.9
7_M	Kokkola, Rikkihappo Oy 1)	1	3.8	0.17	99.8	85.0
8_M	Kokkola, Outokumpu Oy 1)	1	3.8	1.37	98.0	69.0
9_M	Kokkola, shipping channel	10	3.11	0.92	93.7	15.0
10_M	Kokkola, -"-	14.5	3.11	1.23	93.8	20.0
11_M	Kokkola, -"-	13	3.11	0.29	99.0	29.0
12_M	Kokkola, Outokumpu Oy 1)	1.5	3.11	1.18	99.1	131.0

1) Sample taken at about 40 m distance from the mouth of the sewer.

Table 3. Cadmium content in organs of marine fish (pike, Esox lucius L.) at the shores of Finland.

No	Tissue	Weight of fish [kg]	Location	Sampling date	ppm Cd/ dry wt	ppm Cd/ fresh wt
6_{F_1}	flesh liver kidney	0.5	Gulf of Finland, Tammisaari	1.11.70	0.011 0.014 0.108 0.760	0.002 0.003 0.028 0.153
6_{F_2}	flesh liver kidney	≈0.5	Gulf of Finland Tvärminne	1.11.70	0.014 0.173 1.150	0.003 0.055 0.232
$13A_F$	flesh	0.55	Gulf of Finland Hiittinen	12.6.68	0.013 0.021	0.003 0.004
13_F	flesh	0.6	Gulf of Finland Porkkala	12.6.68	0.016 0.019	0.003 0.004
14_F	flesh liver kidney	0.9	Gulf of Bothnia Kokkola, Lång-holmen	6.8.70	0.018 0.148 1.519	0.004 0.034 0.169
15_{F_1}	flesh liver kidney	0.65	Gulf of Bothnia Kokkola	23.11.70	0.024 0.390 1.550	0.005 0.096 0.339
15_{F_2}	flesh liver kidney	0.64	Gulf of Bothnia Kokkola	23.11.70	0.018 0.280 1.520	0.004 0.070 0.308
16_F	flesh liver kidney	2.48	Gulf of Bothnia Kokkola	23.11.70	0.062 0.409 1.480	0.013 0.113 0.295

Table 4. Cadmium content in lichen (<u>Cladonia alpestris</u>) in Finland

No.	Location	Sampling date	Cd content ppm/dry wt.
6_{L_1}	Tammisaari, Koverhar	21.12.70	0.41
6_{L_2}	Tammisaari, Tvärminne	21.12.70	0.35
17_1	Virolahti, Klamila	30. 4.67	0.32
17_2	-"-	6.11.67	0.32
17_3	-"-	22. 6.68	0.29
18	Tuusula	2.10.64	{ 0.21 0.30
19_1	Helsinki, Kontula	22. 4.67	0.46
19_2	-"-	15.10.67	0.41
20_1	Loppi, Räyskälä	28.11.67	0.29
20_2	-"-	9.10.68	0.13
21	Asikkala, Salonsaari	20. 9.70	0.18
22	Kokkola, Ykspihlaja	3. 8.70	1.10
23	Kokkola, Kalvholm	23.11.70	{ 0.32 0.35
24	Kokkola, Sannanranta	23.11.70	{ 0.94 1.06
25_1	Lapland, Inari	26. 6.67	0.09
25_2	-"-	23. 7.67	0.10
25_3	Lapland, Kaamanen	3. 9.69	0.43
25_4	-"-	3. 9.70	0.17
25_5	-"-	4. 9.70	0.13
25_6	Lapland, Muddusjärvi	6. 9.70	0.13
26_1	Lapland, Hetta	22. 8.69	0.38
26_2	-"-	9. 9.70	0.05
26_3	-"-	9. 9.70	0.13

Table 5. Cadmium content in organs of elk and reindeer

No.	Sample	Animal age; sex	Location	Sampling date	Cd content		Dry wt./fresh wt. (%)
					ppm/dry wt	ppm/fresh wt.	
27	meat of elk	2-3 y, female	Porvoo	24.10.65	2.35	0.59	25,2
27	liver of elk	-"-	-"-	-"-	5.50	1,50	27.2
27	kidney of elk	-"-	-"-	-"-	51.9	8.05	15.5
28	blood of elk	1.5 y, male	Tuulos	28.11.65	2.35	0.51	21.5
25	backbone of reindeer	4.5 y, female	Lapland, Inari	11.12.65	6.90	5.10	73.8

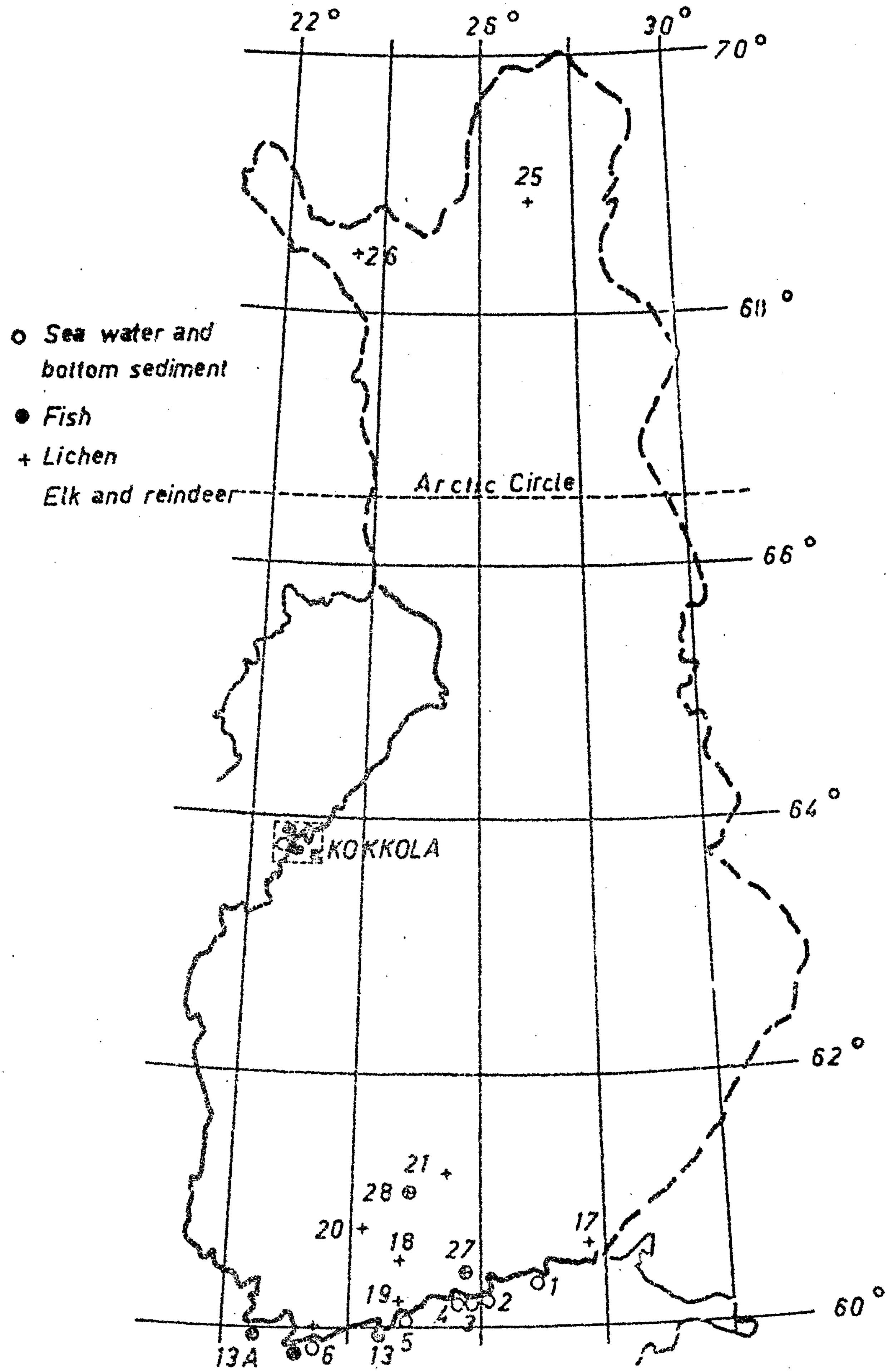

Fig. 1. Map of Finland showing the locations where samples were collected for cadmium analyses.

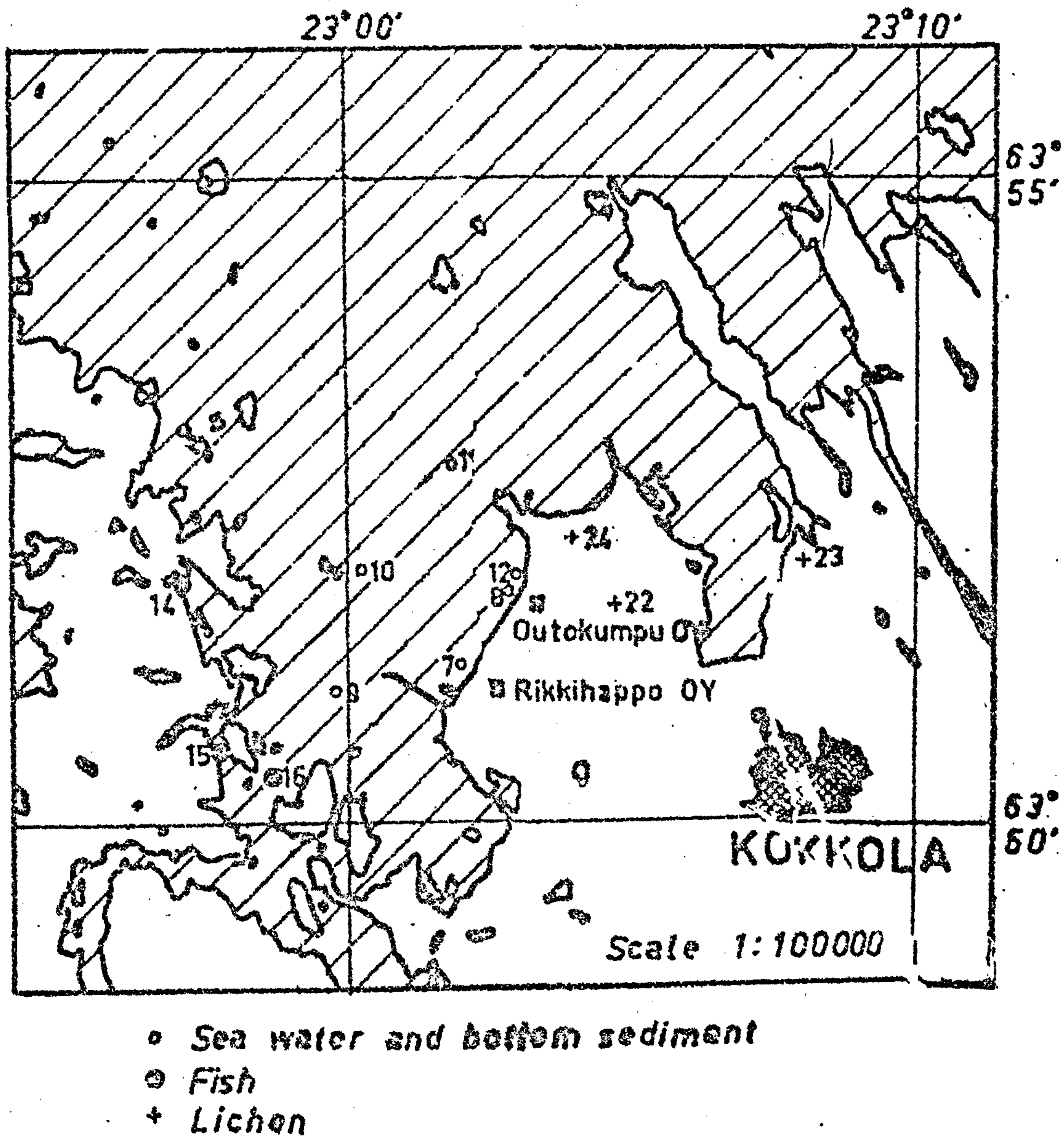

Fig. 2. Map of sampling locations in the vicinity of Kokkola.
For location of this area see Fig. 1.