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The biological effects of the titanium dioxide industry in Finland

by

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Finlands only titanium dioxide factory is located in the Borough of Pori. Production began in 1961, when the production capacity was only 20 % of the capacity in 1974. The amount of sewage at present is about 10 000 cu.m. per day. Sewage in 1974 contained about 4 % $FeSO_4$, 3 % H_2SO_4 , 0.3 % TiO_2 and smaller amounts of some other compounds, for example some heavy metals (Mn, Zn, V, Sb, Cr, Hg). The total amount of $FeSO_4$ is about 380 tons per day. The sewage is discharged into the sea through three pipes with an inner diameter of 315 mm to a distance of about 4.7 km from the shore to a depth of 17 m. The bottom of the sea is quite flat at this spot and the depth of the water increases very evenly on a gradual slope without large isolated basins. Only small, shallow basins have been found near the mouth of the effluent pipe.

The sewage containing $FeSO_4$ and H_2SO_4 has a direct effect on the sea water in the following way (WEICHART 1972, NESPITAL 1973, RACHOR & DETHLEFSEN 1974):

1. The pH value of the sea water decreases due to the sulfuric acid. The acid usually weakens very quicly. The concentrations of CO_2 and SO_4^{2-} increase in water.

2. The concentration of iron increases in the sea water. The Fe^{++} ions oxidize to Fe^{3+} ions and precipitate as finely divided hydroxide. This increases the turbidity of the sea water. In addition, the ferric hydroxide easily adsorbs colloids, oil, other particles , etc. The particles sink to the bottom, where they form sediments.

3. The concentration of oxygen in sea water decreases because of oxidation from $FeSO_4$ to $Fe(OH)_3$.
The effects of sewage have been studied in 1965 (Oy Keskuslaboratorio -Centrallaboratoriet Ab 1968), in 1971 (SEPPÄNEN & SHEMEIKKA) in 1972 (Merentutkimuslaitos 1973) and in 1973-1975 by the Finnish Game and Fisheries Research Institute, Fisheries Division. This study has contained e.g. an extensive test fishing and water quality control program, incubation of rainbow trout in net cages, studies on the contamination of fishing gear, fishery interviews, zooplankton studies, studies on bad taste and odor in fish and studies on the accumulation of some heavy metals in fish (Hg, Cd, Zn, Cr, Sb). This paper is a summary of the biological part of this study.

The weakening of sewage in sea water

Normally sewage weakens very quickly after it has been discharged into the sea. The density of sewage is about 1,1/cu.cm. and it is thus heavier than sea water (density about 1.004/cu. cm).. Consequently sewage stays on the bottom layer. Sometimes, however, quite undiluted sewage flows as a narrow current from the place of discharge. Such sewage can be found at a distance of at least 10-15 km from the place of discharge. The concentration of iron has been found to be over 100 mg/l and the pH value under 3 to a distance of over 5 km from the place of discharge. Jn such water the oxygen saturation percentage is almost 0 %. Usally the situation is better and the aforementioned condition occurs only very close to the mouth of the effluent pipe.
At the coastline the concentration of iron in water was found to have doubled from 1964-1965 to 1971-1972, with an average value of 0,8 mg/l in 1972. In summer the concentration has been clearly lower than in winter.
The precipitated iron deposits on the bottom sometimes rise to the surface water in connection with an upwelling of the sea, giving a russet color to the water. The iron concentration in such iron floats has been found to be 0,39-2,24 mg Fe/l and the pH value 6,9-7,9.

Effects on phytoplankton and primary production

SALONEN(1973) and Kokemäenjoki watercourse water pollution control association (1975) have found slightly smaller primary production values in the area of disharge than in the surrunding sea areas.

Effects on zooplankton

Harmful effects of acid-iron wastes have already been found for example by REDFIELD & WALFORD (1951) KETCHUM et al. (1958), VACCARO et al. (1972) and GRICE et al. (1973). The effects on the marine environment have, however been very slight. Sea currents transfer zooplankton rapidly from one place to another and the harwful effects are difficult to detect. In general the effects of sewage on zooplankton are slight.

Effects on benthic fauna

The harmful effects are most clearly seen in benthic fauna. In the Pori sea area there is a clear correlation between the number and biomass and the distance from the place of discharge (SEPPÄNEN & SHEMEIKKA 1972). The dead area has a diameter of about 2 km. The mouth of the effluent pipe is in the middle of this area. Outside this district the bottom fauna is normal in the Gulf of Bothnia.

Effects on fish eggs and spawning grounds

The effects of sewage on fish eggs and spawning grounds were studied by incubating the eggs of pike (<u>Esox lucius</u>)and whitefish (<u>Coregonus lavaretus</u>) in cylindrical cages. The eggs turned brownish near the place of discharge. In labortory tests on herring eggs KINNE & ROSENTHAL (1967) found that the brownish layer prevents the gas exchange between the egg and the surrounding medium. They describe the effects of sewage in the following way: "Under conditions of maximum test medium effec iviness, percentages of successful fertilisation and of egg survival are considerably reduced, diameter of fertilized eggs remains smaller, embryonic growth rate is retarded while the heart frequency tends to increase, duration of incubation is shortened, percentage of successful hatching decrases and structural abnormalities of freshly hatched larvae increase."

In the Pori sea area the pike eggs developed to larvae at a spot about 1 km from the place of discharge, even if the eggs were a little browner before casting than the eggs in the control places. Unfortunately, it was not possible to grow the larvae to see if they were able to develope more fully. The eggs of whitefish turned brown at a distance of 3.5 km from the place of discharge. It can be estimated that eggs turn brownish to a distance of about 5 km from the mouth of the effluent pipe. This area has important spawning grounds of Baltic herring (Clupea harengus) and whitefish (Coregonus sp.).

Effects on adult fish

Laboratory test of the effecus of acid-iron wastes have been made for example by HALSBAND (1968), KINNE & SCHUMANN (1968) and SEPPÄNEN & SHEMEIKKA (1972). The toxic effects appeared in all these, tests but the lethal concentration depends on the concentrations of $FeSO_4$ and H_2SO_4 in the primary solution of sewage. According to SEPPÄNEN & SHEMEIKKA (1972) a mortality of fifty percent was found in perch (Perca fluviatilis) and young whitefish (Coregonus lavaretus) in concentrations more than 1:200 during an incubation period of 96 hours. Slight poisonous effects could still be found in a concentration of 1:500. The concentration of $FeSO_4$ and H_2SO_4 in sewage of the Finnish TiO_2 factory is about 3-4 times smaller than it is in most factories in the world. In 1974 rainbow trouts were incubated in net cages in the Pori sea area. The places where fish died because of acid-iron wastes are shown in fig. 1. This area is at least 5 km to the west of the place of discharge. Test fishing nets once contained one ruff (Acerina cernua) destroyed by acid-iron wastes at a distance of 12 km from the place of discharge. All fish killed by sewage were close to the bottom In surface water the fish were similar to boiled fish and decomposed easily when touched. WILSON & WHITE (1974) kept flounders (Platichthys flesus) in cages in the Humber estuary, where two major British TiO_2 factories are located.

The area where fish died in cages was smaller than that in Finland because of better current conditions.
The Pori sea area contains a distinct area around the effluent pipe, where fish catches are relatively small. The expelling effect reaches a distance of some kilometers from the place of discharge. In this area the catches of Baltic herring per effort are about fifty percent smaller than in the surroundings. The relative catch of bottom fish in the area of discharge is much smaller than that of pelagic fishes. This is why, for example, eelpout (Zoarces viviparus) and sculpins (Cottidae)are absent in this area. In addition to the stationary hazard area we must take into consideration, that the peculiar way in which sewage drifts from the effluent pipe affects a noticeably larger area than the stationary hazard area, in which tvansient local hazards appear. The location and width of this area depend on sea currents. Thus the hazard area changes its location continuously. According to water analysis, the effect in question reaches a distance of at least 10-25 kilometers depending on the direction from the effluent pipe. This phenomenon is closely connected with the ferric hydroxide floats in surface water. Precipitated iron has also been found to have a clear expelling effect on fish when it has risen to the surface as a result of strong winds and an upwelling of sea water.

The effects on bad taste and odor and on heavy metal concentrations in fish

Sewage evidently does not impart a bad taste or odor to fish. This is, however, difficult to observe in the Pori sea area because of the polluted Kokemäenjoki River, which imparts a very bad taste to all fishes. The river flows into the sea at Pori, close to the location of the effluent pipe of the TiO_2 factory. The concentrations of some heavy metals (Zn, Mn, Cr, Hg, Cd,Pb) are quite high in the water of the Kokemäenjoki River. In local fish it has been found, however, that at least the concentrations of chromium and zinc in fish depend to a noticeable degree on the sewage from the titanium dioxide factory.

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Figure 1.
The mortality of rainbow trout in net cages in 1974.

- ● All fish died and decomposed in at least one of the net cage experiments because of the sewage from the TiO_2 factory.
- ⊙ The mortality was bigger than usual, but no sign of sewage was observed in the fish.
- ○ no mortality.
- ▲ the location of the factory.
- - - - effluent pipe.

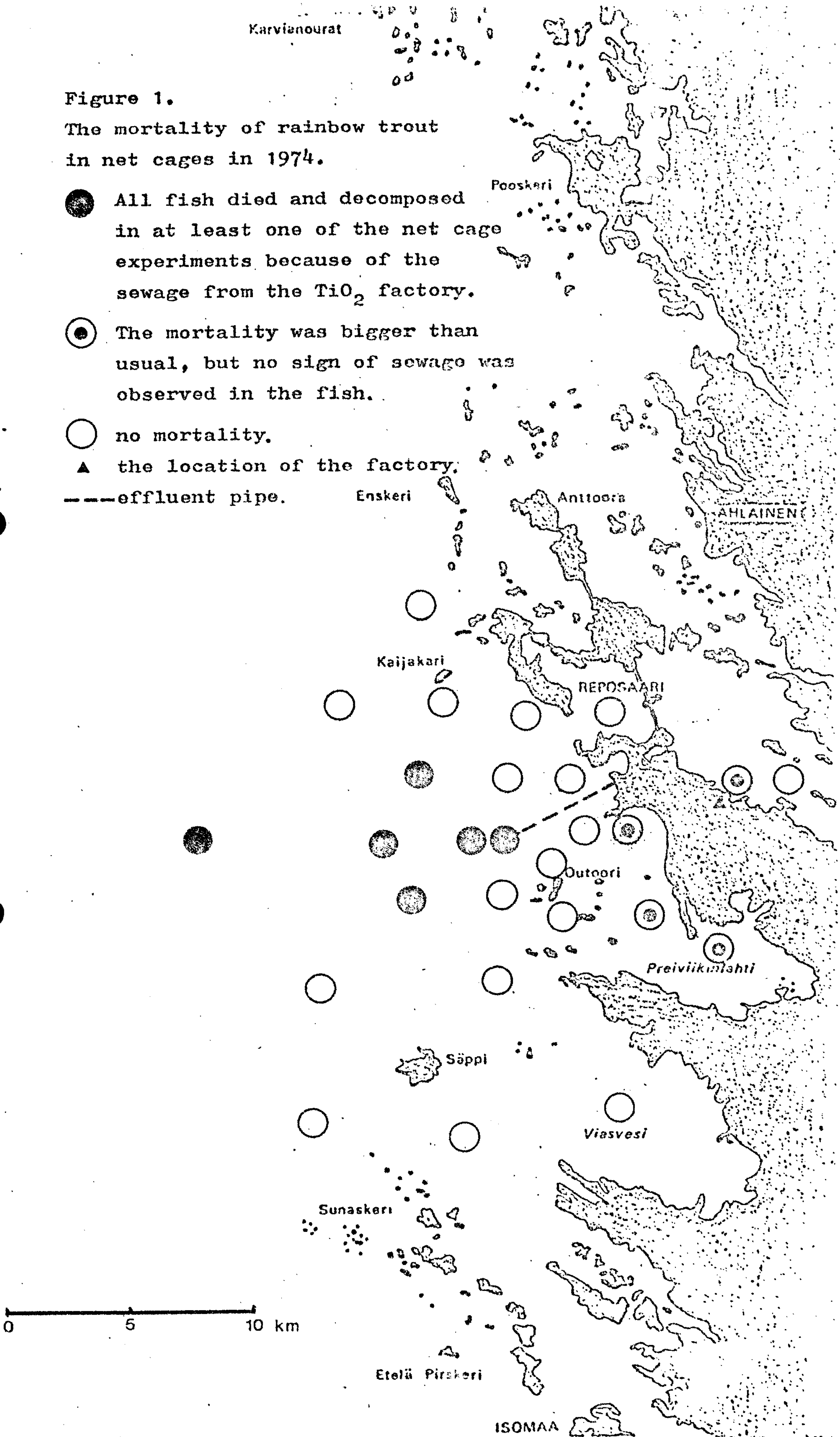


Figure 2.
The observed minimum pH values on the bottom layer in 1974.

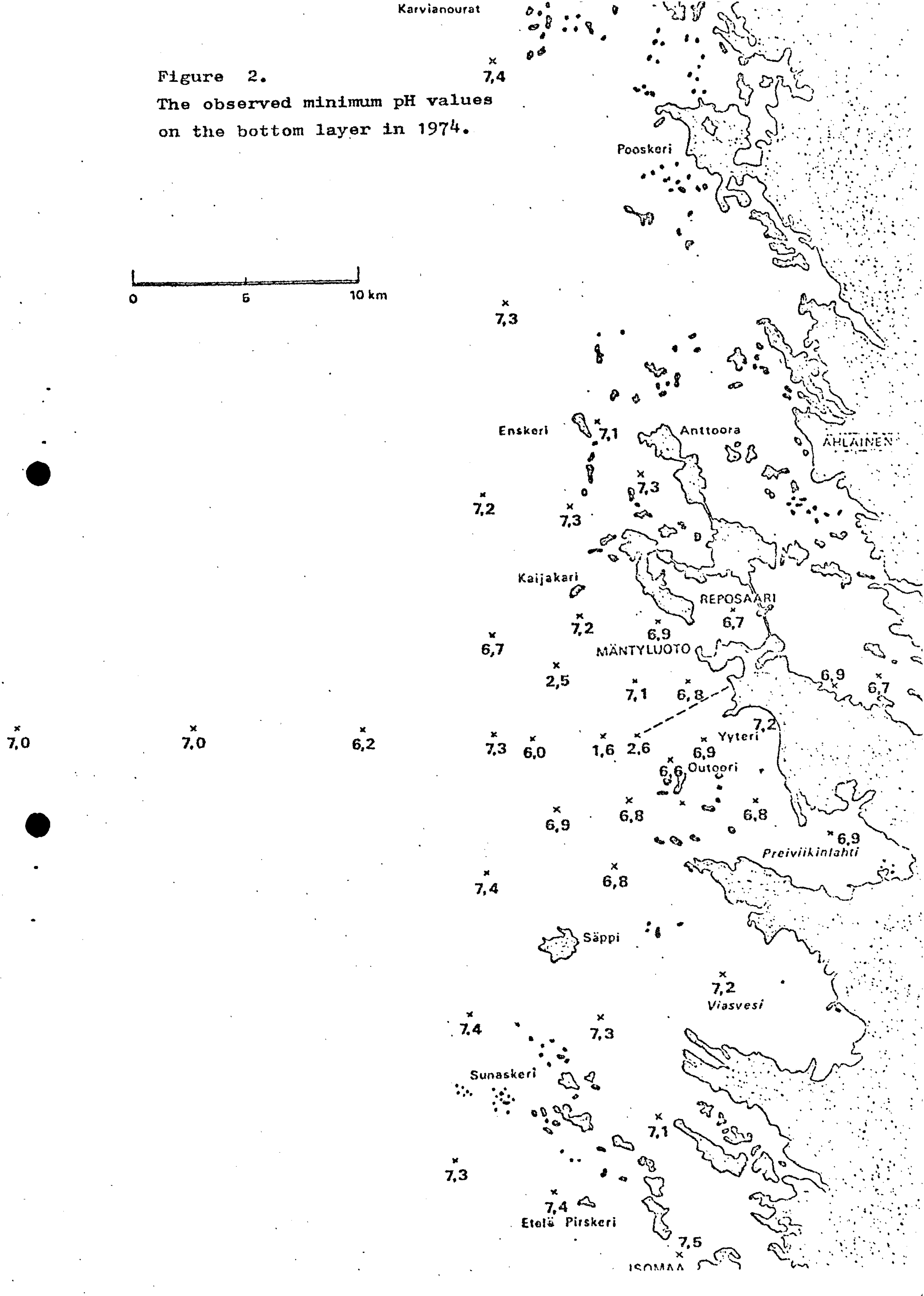
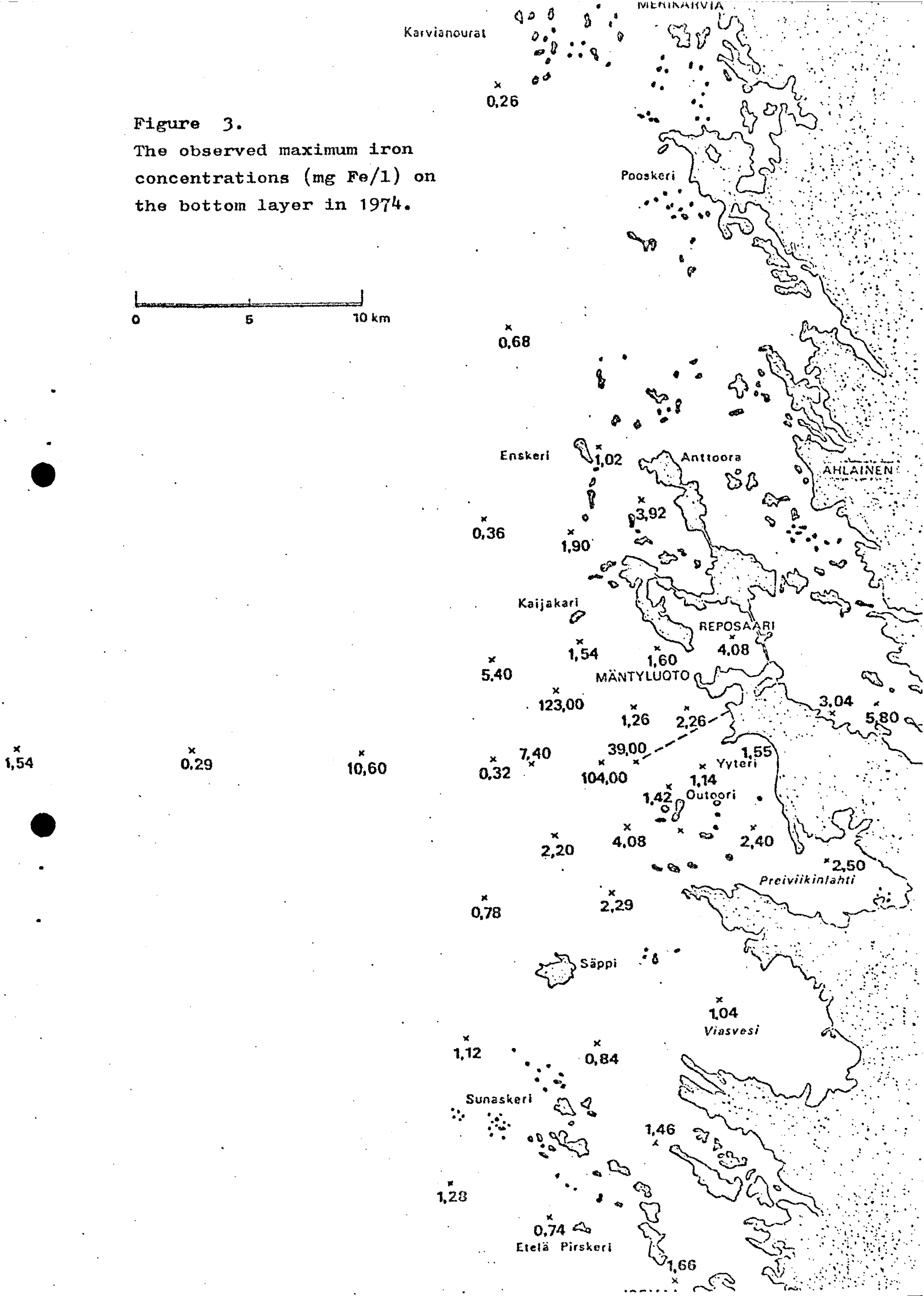


Figure 3.
The observed maximum iron concentrations (mg Fe/l) on the bottom layer in 1974.



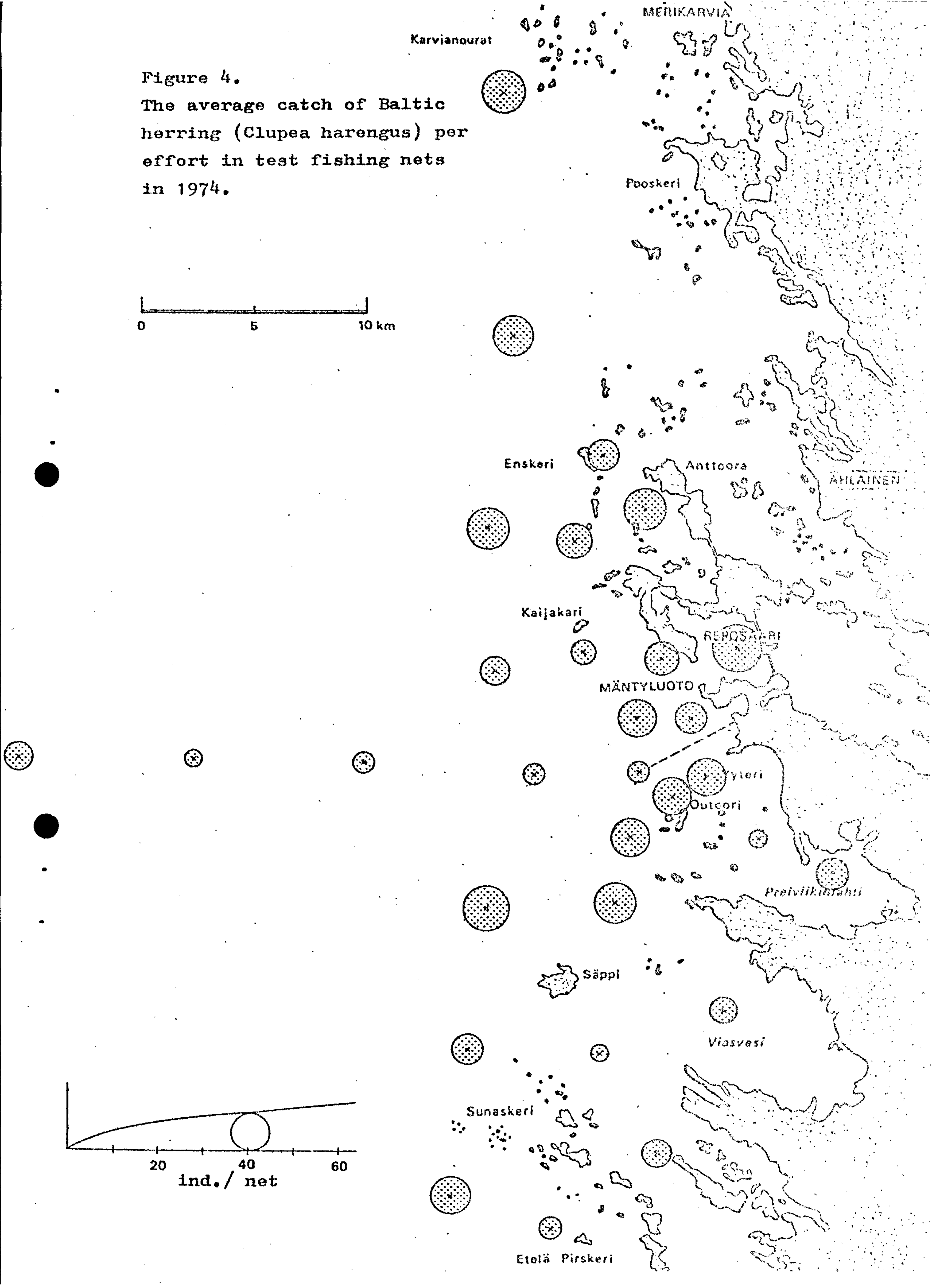


Figure 4.
The average catch of Baltic herring (Clupea harengus) per effort in test fishing nets in 1974.

Figure 5.
The average catch of four-horned sculpin (Myoxocephalus quadricornis) per effort in test fishing nets in 1974.

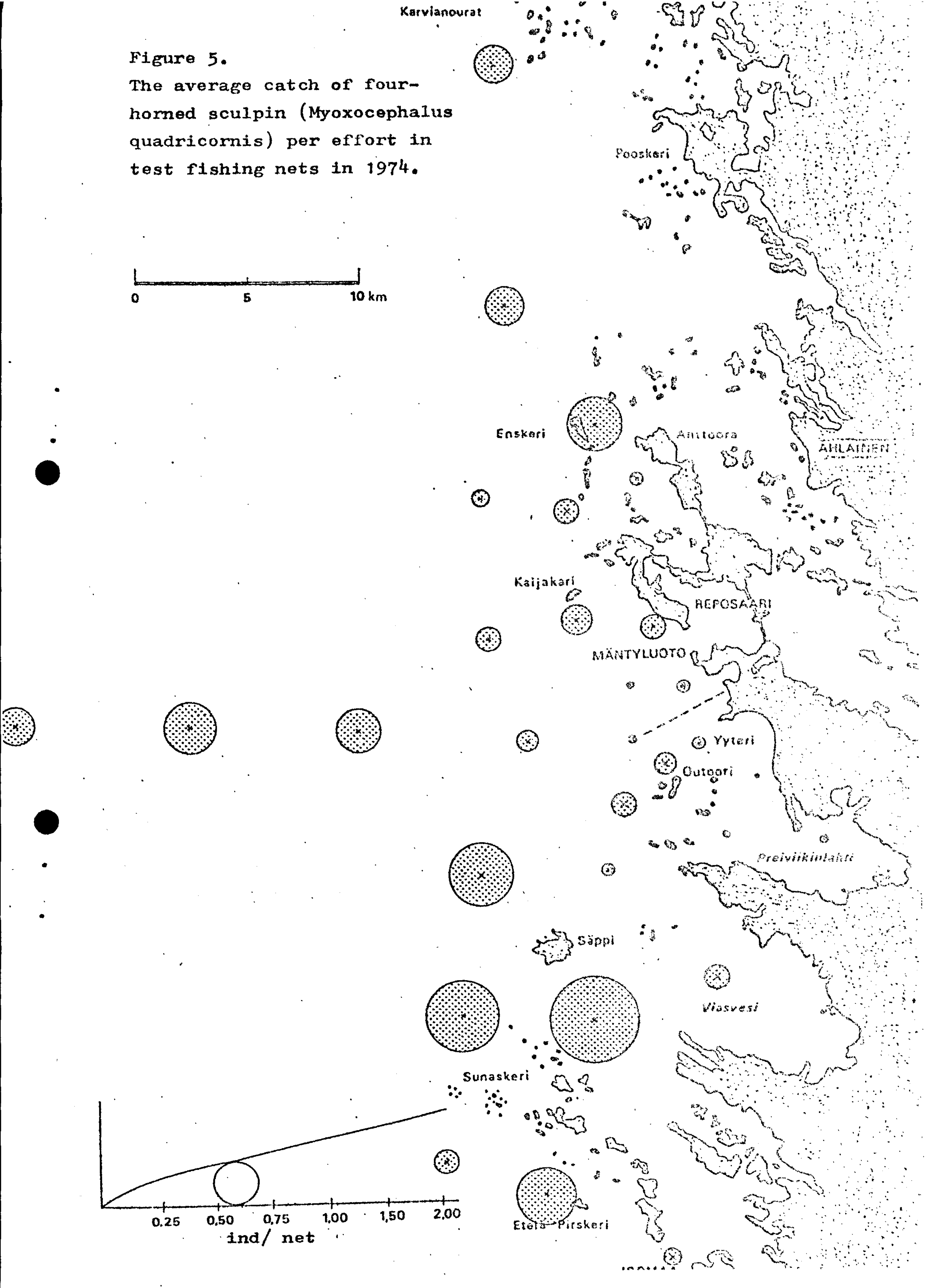


Figure 6.
The average catch of eelpout (Zoarces viviparus) per effort in test fishing nets in 1974.