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The Prediction of Waste Water Dilution by a Long-Term Tracer Experiment

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In general tracer experiments made for the evaluation of waste water dilution in recipients have been of short-term type, with the tracer having an injection time that is markedly less than the time scale of flowpattern changing. In typical Finnish lakes and coastal waters, with complicated topography and frequently varying winds, the results from short term experiments have proved to be of rather limited value. In view of this, a study has been made of the possibility of measuring the dilution under such circumstances, by means of a long-term experiment with a tracer injection time extending over several weeks. Indium was considered to be the most suitable tracer for such an experiment; the complex form of indium is preferable to ionic solution to ensure reliability in the results.

The applicability of the method in the fields is illustrated by an example of a waste-water dilution study made for a pulp mill under construction. Two subsequent long-term experiments were conducted for measurement of the dilution of waste water from two alternative discharge points. The results obtained gave a very clear illustration of the local average dilution ratios, and allowed a reliable comparison being made between the two alternative discharge points.

Introduction

In the prediction of the chemical and biological effects of a planned waste water discharge, it is neccessary to know the waste-water dilution in the recipient. Tracer techniques offer the most effective method for evaluation of this dilution.

In a tracer experiment, waste water is simulated by a tracer solution, which is injected into the planned discharge point. Estimation of the dilution of waste water can be made by the tracer concentrations measured in the recipient. Radioisotopes and dyes, both of which are detectable in very low concentrations, are the tracers most frequently used.

For the most part, the experiments have been of short-term type, with the injection time of the tracer being brief in comparison with the time scale of flow pattern changing. The results obtained in a short-term experiment indicate the dilution only in those circumstances prevailing during the experiment.

In typical Finnish lakes and coastal waters, the results arrived at in short-term experiments are of limited value, by reason of the flow patterns being usually very complicated, and rapidly changing. The shortcomings apparent in the short-term method led to a study being undertaken of the possibilities of a long-term experiment being made with tracer-injection extending over several weeks.

Long-Term Simulation of Waste Water Discharge

Basic Limitations of Tracer Techniques in the Prediction of Dilution Rates

When tracer techniques are applied for the prediction of waste-water transport and dilution, as a rule the simulation is to some extent incomplete, as the actual waste water flow is absent.

First, the effect of waste-water flow upon the flow patterns in the recipient is ignored. In reality, this is no serious shortcoming, as normally the momentum of waste-water flow is insufficient to change the flow pattern anywhere but in the close vicinity of the discharge point.

The second effect arises from the difference in density usually existent between the waste-water and the recipient water. For instance, it has been observed that in the case of pulp mill waste-waters the density difference is sufficiently large to exert a considerable effect upon the waste-water flow and the dilution in lakes and coastal areas during the ice-covered period. However, during the ice-free period so much mixing normally occurs as a consequence of wind that in the case mentioned above no effects attributable to density difference have been observed.

A Comparison between Short-Term and Long-Term Experiments

In most short-term experiments, injection has been made instantaneously. The temporal development of tracer concentration distribution is measured in the recipient area. Detailed information is obtained on the mechanisms of the phenomena of waste-water transport under the conditions prevailing during the experiment. If the flow pattern has remained essentially constant during the experiment, the waste-water dilution under these flow conditions can be evaluated at the points where the impulse response of the concentration has been totally obtained.

Instantaneous injection is of great practical value if only a few different types of simple flow patterns exist; for example, this is problably the case with an open coastal area. However, in the lakes and along the coasts of Finland, the numerous islands, the shallow waters, and the rapidly changing winds, create complicated flow patterns that exhibit quick variations. In these circumstances, the instantaneous injection method loses some of its attraction. A larger number of experiments would be called for to cover many different conditions of flow. The basic idea of computing the step response from the measured impulse response cannot be applied effectively, due to the changes in flow pattern, often significant, during the course of the experiments.

In a long-term experiment, the injection time of the tracer is long in comparison with the time scale of the flow pattern changes. The local dilutions desired are derived direct from concentration measurements. Basically, this provides the most natural and straightforward method for the measurement of dilution rates. Nevertheless, the labelling power of the tracer is exploited to a relatively poor extent; for this reason, great difficulty is experienced in finding a tracer which fulfils the high demands imposed by the method.

Demands Made upon the Tracer

The demands made upon the tracer are of the same type as those imposed in a short-term experiment, but are much more rigorous.

1. The tracer must follow the water flow for a sufficient length of time with negligible adsorption and precipitation for the indication of slow transport phenomena, and accumulation in areas with slow water exchange.

2. The sensitivity of tracer detection has to be extremely high, with a view to keeping the amount of tracer within sensible limits. This implies both very good analysis sensitivity and low background concentration at the same time. An example can provide some conception of the detection sensitivity required. The daily amount of waste water coming from a large pulp mill is of the order of $10^5 m^3$. If the requirement is that of predicting the dilution ratios down to 1:1000, during a long-term experiment an amount of tracer capable of labelling 10^8 m^3 of recipient water should be injected daily.

3. The use of tracer should not introduce any harmful effects into the environment. In any case, the total amount of tracer in a long-term experiment should be relatively large, and the potential risks attached to its release should be considered very carefully.

4. The costs of the tracer, its injection, and the concentration analysis, must be acceptable.

Choice of Tracer

Radioisotopes and the dyes used in short-term tests are not very suitable for large-scale, long-term experiments. The use of radio isotopes, even if this were licensed by the authorities, would become very impractical by reason of the difficulties and costs involved in the safe handling of the large amounts of radioactivity needed. As far as dyes are concerned, difficulties would be met in the handling of large volumes of dye, and the dye might result in some deleterious local effects.

To some extent, bacteriophages have also been utilised as tracers in natural waters (Niemelä, Kinnunen 1968). In principle, their detection sensitivity would be adequate, although the dependence of their lifetime upon environmental conditions might cause appreciable uncertainty in their use.

The rare elements, with high neutron activation analysis sensitivity, were considered to be the most promising canditates for tracers. Indium, europium and dysprosium were chosen for more detailed evaluation.

The analysis sensitivities for pure elements in the available neutron flux $1.8.10^{12}$ $1/s\ cm^2$ and the natural concentrations measured in lake waters (Lake Saimaa), and coastal waters (Gulf of Bothnia) for these elements, are listed in Table 1. Indications are also given of the prices, and for a practical comparison, the amounts needed to label 10^8 m^3 of water. It is observable from the table that it is not the analysis sensitivity, but the natural background, which limits the detection sensitivity of these elements.

In consequence of indium having the lowest background level, it is appreciably more advantageous than the two others, which are not economically acceptable in a large-scale study such as the example of the pulp mill.

Table 1 - Properties of some substances chosen for more detailed evaluation as tracers.

Substance	Background ng/dm^3	Sensitivity (1 dm^3 sample) ng/dm^3	Amount needed for 10^8 m^3	Price Fmk/kg
In	$<$ 0.3 (sea) $<$ 0.3 (lake)	$<$ 1	0.1 kg	1500
Eu	4 (sea)	0.1	0.4 kg	4000
Dy	30 (sea)	$<$ 1	3 kg	450
DTPA				125

Indium as a Tracer

Ionic solution constitutes the easiest form of indium to use. However, it has been observed that, in river water indium ions adsorb on to solid particles relatively quickly. The adsorption of indium can be greatly diminished if indium is complexed

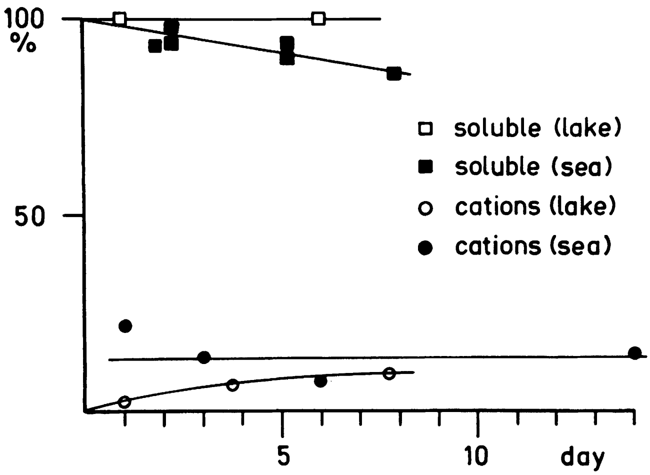


Fig. 1. Stability of In-DTPA complex in sea and lake water; a laboratory test.

with some aminocarboxylic acids. The best results have been obtained with DTPA (Hanson 1970, p. 36).

Although in all probability an indium atom would even after adsorption follow along the water flow for a considerable distance, the complexed form was preferred, for the sake of reliability in the results obtained. The stability of In-DPTA-complex was checked in lake and coastal waters by means of laboratory test. The results are illustrated in Fig. 1. After seven days in lake water, more than 90% of the indium was still to be found in anionic (complex) form. The corresponding percentage for coastal water was 80-90%. The conclusion drawn was that In-DTPA-complex well meets the demands imposed in the reliable tracing of water currents.

If the high analysis sensitivity needed is to be achieved, the indium from a water sample has to be first concentrated and then after neutron irradiation separated chemically from other disturbing elements present in the sample. Studies were made of two different analytical procedures. The first of these was based upon indium concentration by Fe $(OH)_3$ coprecipitation (Dahl, Haagensen, Thomasse and Tollan 1971) and the second was based upon concentration by ion exchange (Hanson 1970). The experience gained with concentration by $Fe(OH)_3$ was more favourable, and this method was chosen for the subsequent field experiment. The impurity of the chemicals used in coprecipitation limited the analysis sensitivity to 0.7 ng/1.

The selected size of the sample in practice was 0.8 1. Relatively speaking, the analysis was very time- and workconsuming. On the average, a laboratory assistant was able to perform 6 analyses a day.

To date, very few studies have been made in regard to the toxity of indium (Podosinovskii 1964, 1967; Yoshikava and Hasegawa 1971; Usher, Westerman, Ammerman and Sutherland 1970). They have indicated that indium is a heavy metal without particularly poisonous properties. As a rule, natural waters contain indium to an extent ranging from less than 1 ng/1 to a few ng/l (Matthews and Riley 1970; Chow and Snyder 1969) but in litosphere the amount is much higher, the average being 0.1 ppm (Lange 1961). During the injection period, a long-term experiment results in indium concentrations which exceed the background level by, say, two orders of magnitude, only within a limited area, close to the injection point. For instance, in the case study discussed below, the indium concentrations reached the background level everywhere within a week of the end of the injection. Even though the risk level seems fairly low, great care should be exercised in the utilisation of relatively large amounts of indium, and the total amount injected should be matched to the size of the water course in question.

Case Study

The Problem

Plans had been prepared for a new pulp mill, to be built on the coast of the Gulf of Bothnia near the town of Kaskinen. The mill's waste water, amounting to 49.000 m^3 daily, subsequent to mechanical and aeration treatment, was to be led into the sea. The relative importance of the coastal area for recreational and fishing purposes means that a great deal of emphasis had to be laid upon prior evaluation of the waste-water dilution in this area, and determination of a suitable point for discharge. Points P_1 and P_2, indicated in Figs. 2 and 3, were chosen as discharge points for which the dilution was to be evaluated. The method of evaluation chosen was that of a long-term tracer experiment.

Experimental Procedure

As only one suitable tracer was available, it was decided that the study should be divided into two successive parts; in one, the injection took place at P_1, and in the other at P_2. An injection period of 4 weeks was chosen for both experiments. The first experiment, with the injection at P_1, was made in the spring, and the second, with the injection at P_2, in the late summer of 1975.

In preparation of the In-DTPA-complex solution the molar ratio used was indium to DTPA 1:1.5. A check was made on the completeness of the chelate formation The total amount of indium used in each study was about 4 kg, and the amount injected daily was 143 g.

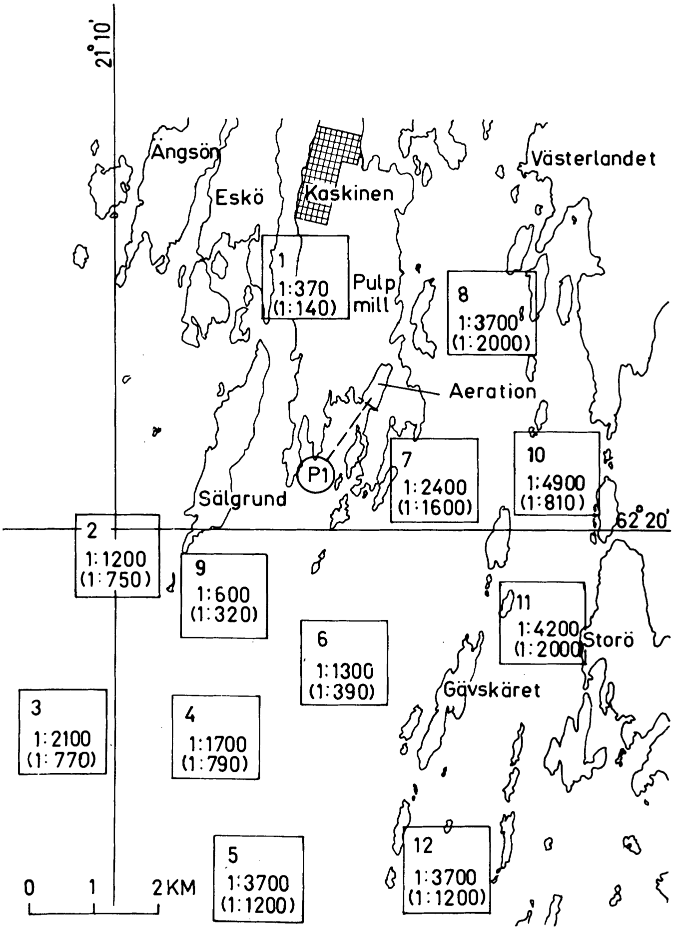


Fig. 2. Area of the first experiment: injection point *P*1, sampling points 1...12, mean dilution ratios, and below them, in parentheses, the »worst« dilution ratios.

For practical reasons, continuous tracer injection was replaced by the pouring of tracer solution into the water at the injection point twice a day. Experience gained in short-term tracer experiments along Finnish coasts had indicated that the pulsed injection would not exessively increase the concentration variation even at the nearest sample points. The pulsed injection had very little effect upon the local mean dilution ratios, which represented the main practical result of the study.

The cost of indium analysis was relatively high, and for this reason the total number of the analyses was to be reduced as much as possible. The sampling points are indicated in Figs. 2 and 3. With the exception of point 9, they were the same in

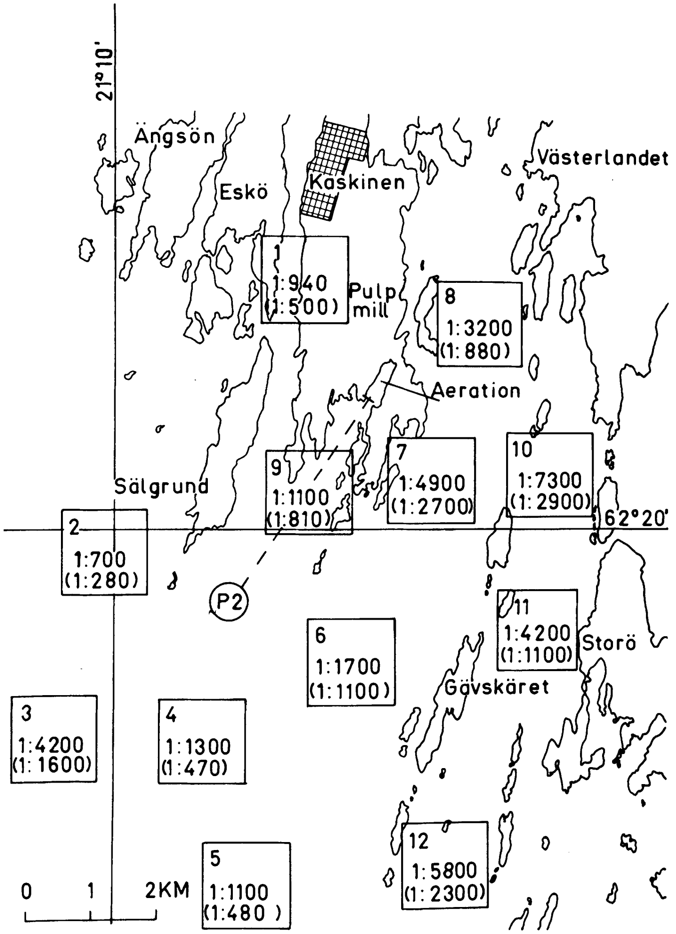


Fig. 3. Area of the second experiment: injection point *P*2, sampling points 1...12, mean dilution ratios, and below them the »worst« dilution ratios.

both experiments. The samples were taken at these points, from several depths, twice a week. All of the samples taken from surface water were analysed, as they usually contained the highest concentrations of indium. No more than an adequate number of samples were analysed from other depths, with a view to checking the vertical distribution of indium. About 150 samples were analysed in both experiments.

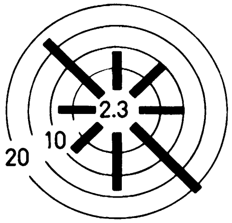
For practical reasons, the work on the site, that is to say the injection and the sampling, was left to local people. The obvious risk of sample contamination made it necessary to keep the injection and sampling completely separate from each other.

Flow Conditions during Experiments

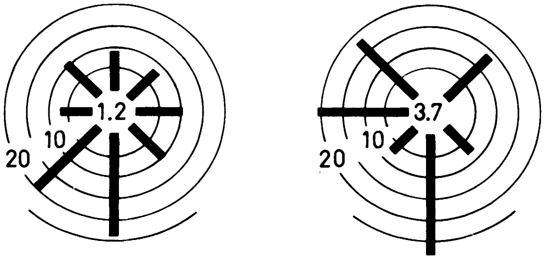
On comparison of the discharge points, and evaluation of the general validity of the results, account must be taken of the differences between the flow conditions which existed during the two experiments, and their deviations from the long-term average distribution.

The wind represents the most important component of flow conditions. Fig. 4 illustrates the percentage wind distributions during both expriments, and the long-term average distribution. During both experiments the wind varied very frequently. The longest period with moderately constant wind conditions was 2-3 days. The average wind speed was about the same during both experiments, but was less than the long-term average.

The water-body was practically nonstratified during experiments.



years 1951-1960
mean velocity 4.0 m/s



first experiment
mean velocity 2.75 m/s

second experiment
mean velocity 2.95 m/s

Fig. 4. Percentage distributions of winds from different directions in the experimental area.

Results and Discussion

Dilution ratio D is obtained from the measured indium concentration C of the sample, by application of the following formula

$$D = \frac{C}{C_0}$$

C_0 is the conceptual initial tracer concentration, equal to the injection rate of the tracer divided by the assumed discharge rate of waste water.

The local mean dilution ratios in the surface water during the experiments are illustrated in Figs. 2 and 3. The mean values should possess a relatively high level of reliability, as the flow conditions which existed during the two experiments quite well represented the long-term average distribution.

The most unsatisfactory dilution ratios which correspond to the maximum local tracer concentrations observed are indicated in parentheses below the mean value.

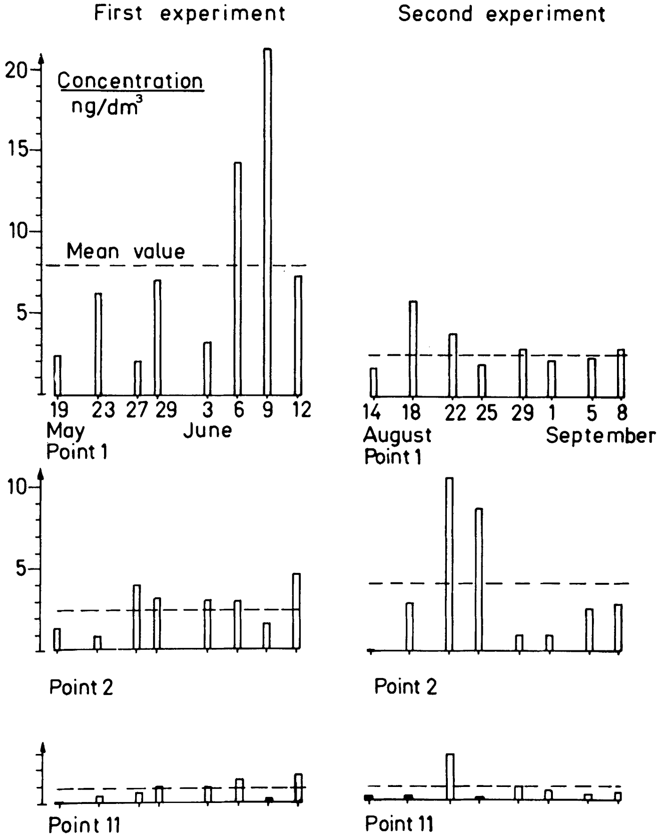


Fig. 5. Temporal variation in tracer concentrations.

These worst ratios are not local extreme values that are created under long-lasting conditions of constant flow. The worst values indicated provide an approximate measure of the variation of the local dilution ratio around its mean.

The temporal variation of local dilution ratios is illustrated for some points in Fig. 5. The variation is after all surprisingly small which indicates that the water exchange in the area is a relatively slow process as compared to the time scale of wind variation.

Some typical vertical distributions of indium are shown in Fig. 6. Since the major proportion of the indium was transported in the surface layers of water, dilution ratios of the same order would probably also be obtained under stratified conditions.

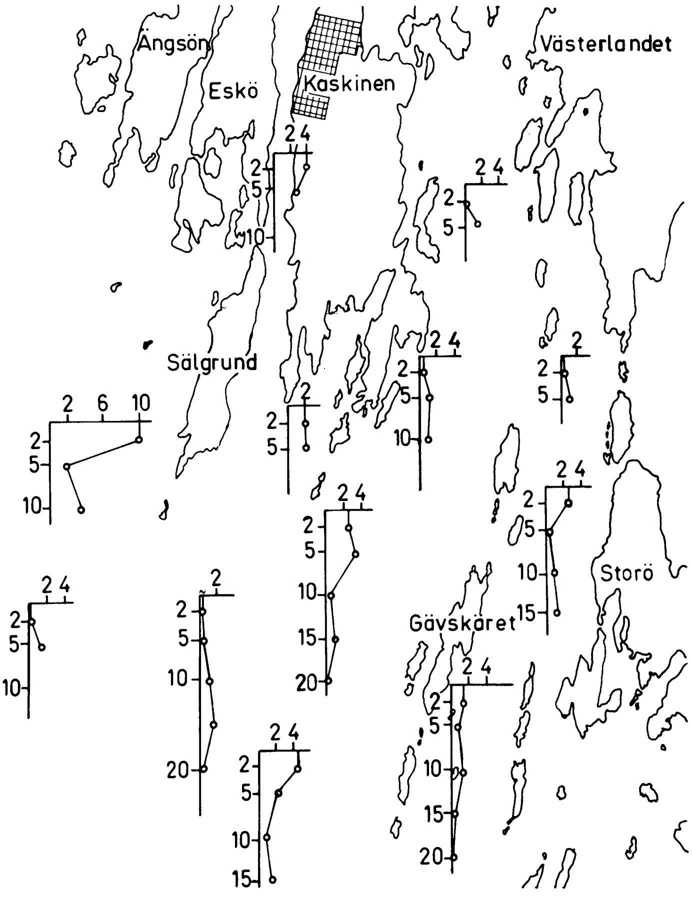


Fig. 6. An example of vertical distribution of the tracer. Concentration given as ng/dm^3, depth in metres.

When the results arrived at are employed for comparison of the discharge points, the accuracy of the comparison is diminished by the differences in flow condition distributions. To some extent, the effects of these differences can be evaluated qualitatively by study of the momentary tracer distributions during the experiments.

In Fig. 7 the difference between the discharge points is illustrated in a way which corresponds to the accuracy of the comparison although it well matches the needs of practical decision making. The recipient area is divided into five subareas, for which there are predicted the ratios of the mean waste-water concentrations induced from P_1 and P_2. In the sound of Kaskinen (sub-area I), the discharge at P_1 induces about 2.5 times as great, and on the eastern shore (sub-area II) about 1.5 times as great a

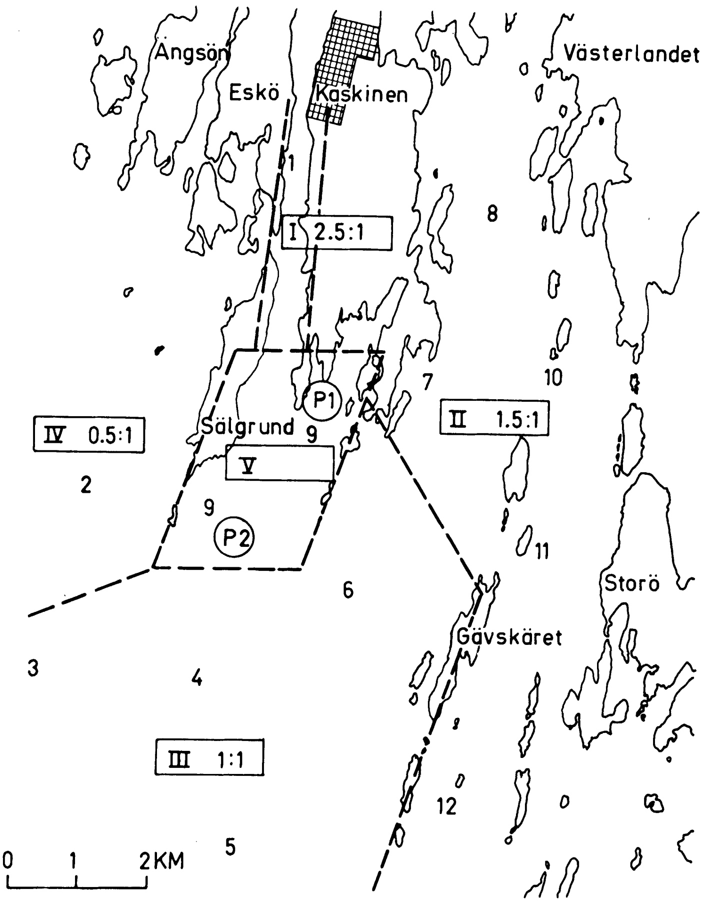


Fig. 7. Assumed waste-water ratios C_1:C_2 induced by discharge points P_1 and P_2 in different subareas.

mean concentration as the discharge at P_2. In sub-area III, to the south of P_1 and P_2, the ratio is about 1. In western sub-area IV, the average concentration ratio is about 0.5. In the proximity of the discharge points, sub-area V, the local temporal variations are large, and are dependent upon the direction of water currents. Naturally, both discharge points have the effect of inducing high mean concentrations in their close vicinity.

The results obtained indicate that waste water should have approximately the same rates of dilution from both P_1 and P_2. This implies that the mixing processes around P_2 are not significantly more marked, even though this point is situated much nearer to the open sea. Extension of the outlet from P_1 to P_2 does no more than change the place of the concentration distribution in a corrsponding way.

Evaluation of the Method

The long-term simulation of waste-water discharge provides a reliable prediction of waste-water dilution in the recipient, as the method simulates the actual situation in a very natural way. The desired local dilution ratios are derived direct from measured tracer concentrations. The method is of particular advantage in cases where flow conditions are changing rapidly, and the topography is complicated, as in typical Finnish lakes and coast.

The costs of a long-term experiment are substantially higher than those of a short-term experiment. In the case mentioned above, the costs of analysis represented the main part of the total expenditure on the study. The number of analyses, and correspondingly the cost involved can be greatly diminished if the prediction of only the local mean dilution ratios is sufficient.

In the case of two alternative discharge points it would be very desirable that in addition to indium another tracer with comparable characteristics would be available. With the simultaneous use of these two tracers, one for each discharge point, comparison would be more accurate and the costs of field operations would be reduced to one half.

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