NUCLEAR TECHNIQUES
IN GROUNDWATER POLLUTION RESEARCH
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NUCLEAR TECHNIQUES
IN GROUNDWATER
POLUTION RESEARCH

PROCEEDINGS OF AN ADVISORY GROUP MEETING
ORGANIZED BY THE
INTERNATIONAL ATOMIC ENERGY AGENCY

INTERNATIONAL ATOMIC ENERGY AGENCY
VIENNA, 1980
FOREWORD

The papers in this volume were prepared by participants in the Agency's Advisory Group Meeting on the Use of Nuclear Techniques in Water Pollution Studies, held in Cracow on 6—9 December 1976. The majority of the papers deal with problems of groundwater pollution that are encountered in the development of groundwater resources, in the siting of disposal grounds, and in the prediction and assessment of controlled and uncontrolled releases from industrial, urban, and agricultural pollution sources.

The principal aim of the meeting was to evaluate the advantages of nuclear methods in comparison with non-nuclear methods applied to studies of water pollution resulting from activities of man. This book is thus intended to serve as an introduction to groundwater pollution research and its methodology. Among the methods for the systematic investigation of the mechanism of groundwater pollution and its hydrogeological, hydromechanical and chemical parameters, nuclear techniques have proved to be an independent and in some ways unique tool of easy applicability in field research.
EDITORIAL NOTE

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INTRODUCTION

W. DROST
International Atomic Energy Agency, Vienna

The principal objectives of the Advisory Group Meeting on the Use of Nuclear Techniques in Water Pollution Studies were to discuss the current status and development of the application of nuclear techniques with special emphasis to groundwater pollution processes and prediction. Therefore, the title of these proceedings has been changed to “Nuclear Techniques in Groundwater Pollution Research”.

The terms “nuclear techniques” or “isotope techniques” refer to the utilization of natural or man-made isotopes in problems concerning the flux of water or pollutants within the hydrological system. Environmental isotopes are those which either exist naturally within the hydrological cycle, or are man-made but so widespread that they have become an integral part of the water environment. Their content in natural waters is subject to geographical and temporal variations which can be used as tracers of water movement and as indicators of processes affecting water in its cycle. The interpretation of artificially injected tracers demands the investigation of the evolution of their concentration either at the point of input (point dilution techniques, single borehole techniques) or during the passage in the aquifer (multi-well techniques). Further nuclear methods include the interaction of radiation and rocks (nuclear logging), and multi-element analysis by nuclear activation or X-ray fluorescence techniques (nuclear analytical methods).

The nineteen participants of the meeting were from nine countries and had expertise and experience in the application of nuclear techniques, as well as in practical problems of water pollution. Nineteen working papers were presented as a basis for the discussions, conclusions, and recommendations.

Papers

For publication, the papers representing the material presented during the meeting have been divided into three sections:

I. Problems and Case Studies Encountered in Groundwater Pollution
II. Analysis of Pollutants by Nuclear Techniques
III. Prediction and Analysis of the Movements of Groundwater Pollutants by Nuclear Tracer Techniques,

A certain number of presentations at the meeting were of uncompleted research and have not been included in the present volume.
INTRODUCTION

K.O. Münich's presentation introduced preliminary results gained from the study of infiltration in the zone of aeration, the problem of identifying fertilizers as a groundwater pollution source by measuring the natural uranium isotopic variations, and the problems of interpretation involved in the correlation of the content of uranium and bicarbonate in waters. L.J. Andersen raised the question whether environmental tritium can serve as an ideal tracer for identification of preferential paths for polluted groundwaters and for the determination of the velocity of the recharging water during the flow through the zone of aeration. H. Moser reported on the attempt to estimate river contribution to groundwater pollution by an approach combining conventional and environmental isotope techniques. Further, A. Zuber proposed the use of conservative and radioactive cobalt as an index tracer to measure the turnover time in reservoirs.

Conclusions and recommendations

The usefulness, reliability, and applicability of nuclear techniques in groundwater pollution problems were emphasized by all members of the Group. Considering that in many cases in the past, hydrological investigations based on the use of isotope data have suffered because of experimental design by hydrologists with an inadequate isotope analytical background or by nuclear experts with an inadequate hydrological background, the Group recommended the multidisciplinary approach. Research in the area of nuclear techniques in groundwater pollution should be encouraged and funded only with the assurance of intimate interdisciplinary support.

In evaluating current knowledge regarding groundwater pollution in summary, the evolution of groundwater pollution is influenced by:

- physical-mechanical factors: aquifer velocities, densities and viscosities of pollutants, pattern of waste disposal, duration and areas of contact between pollutant sources and water, mechanical filtration and dilution, pumping policies, and management of water resources;

- geological, structural, and geographical factors: geology of the sediments or rocks and pollutants, types of aquifers, climatic and hydrologic conditions varying in time and space; and

- chemical and biochemical factors: chemical properties of the sediments or rocks and of the pollutants, self-purification processes, such as microbial decay, chemical precipitation and co-precipitation, sorption, ion-exchange of gases.

The systematic study of these factors governing the movement and the spread of pollutants and contaminants in the underground requires the use of methods
combining experimental as well as mathematical tools converging in numerical, mathematical models which are the only effective and economical simulation instruments for prediction and control. The experimental tools comprise field methods for direct observations and measurements by short-term measuring campaigns and permanent networks and laboratory methods for the physical simulation of pollution phenomena by different techniques. It was stated that among these methods nuclear techniques are mostly independent additional tools and in some ways unique in their application. The significant advantage of nuclear methods is their applicability to all scales of pollution, the possibility of using the water molecule as a tracer, the offer of multitracer experiments, and the fact that, in general, isotope techniques permit the labelling of water without significant disturbance of the natural hydrological conditions and its detection in situ.

The Group concluded that isotopic approaches should be recommended in tackling the following problems of pollution:

- flow velocity vectors in an aquifer: by single- and multi-well tracer techniques and environmental isotope techniques;
- geometry of pollution sources: by nuclear logging and nuclear analytical methods;
- duration and areas of contact between pollutants and water: by nuclear logging, nuclear analytical methods, and environmental isotope techniques;
- dilution: by artificial and environmental tracer techniques, nuclear analytical methods;
- geology of the aquifer: by nuclear logging;
- stratification of the aquifer: by nuclear logging, single-and multi-well tracer techniques;
- types of aquifers: by environmental isotope techniques;
- climatic conditions: by environmental isotope techniques;
- determination of dispersion coefficients in the field: by single-and multi-well tracer techniques, environmental isotope technique models;
- downward movement of contaminants through the unsaturated zone: by environmental and artificial tracer techniques, nuclear logging;
- stream-aquifer exchanges: by environmental isotope techniques, single-and multi-well tracer techniques;
- identification of pollutant sources: by multi-element analyses using nuclear techniques; and
methodology for defining protection zones: by environmental tracer techniques, single- and multi-well tracer techniques.

Although nuclear techniques have been used in the past in hydrological investigations at quite a developed stage, the Group strongly recommended an improvement in experimental methods and interpretation techniques with particular reference to the following problems: the mechanisms of exchange in dead-end pores, the instability and fingering problems, biogeochemical factors, the geometry and pattern of pollution sources in the unsaturated zone. The complex nature of all pollution problems requires further development of tracers and their application at different stages of the evolution of groundwater pollution.

General research into new techniques and improvement of existing sampling and measurement techniques was strongly recommended in order to bring about simplification, faster results, and lower costs. Bearing in mind that, at present, only a few research centres have the potential to apply nuclear techniques, the commercial availability of all equipment, in particular that for field use, was considered to be of the utmost importance.

To overcome interdisciplinary communication problems, scientists confronted with actual groundwater pollution investigations at management level as well as at field level, but not in contact with nuclear scientists and unaware of their potential, should be encouraged to ask the Atomic Energy Authority or the National Committee for the IHP of each country, as well as the IAEA, for the provision of addresses of nuclear institutes which might be able to help solve hydrological pollution problems.
PROBLEMS AND CASE STUDIES
IN GROUNDWATER POLLUTION
PRESENT GROUNDWATER POLLUTION PROBLEMS

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Abstract

PRESENT GROUNDWATER POLLUTION PROBLEMS.

A general methodology of study of groundwater pollution exists now which shows that technical as well as fundamental problems have yet to be solved. Having summarized the mechanisms of groundwater pollution, mainly governed by miscibility and dispersion-convection theories in pore aquifers and by convection in other aquifers, the critical aspects of groundwater pollution are presented: the scale problem, linked to the heterogeneity of the aquifer and the instability of the miscible transport; the unsaturated flow and the influence of dead-end pores and the stream-aquifer exchanges; the physico-chemical exchanges and the self-purification processes; the establishment of protection zones. It is seen that various radioisotope techniques will be of help to approach the solution of these problems.

1. STATEMENT OF THE PROBLEMS

We wish here to emphasize the present aspects of groundwater pollution problems, how they arise, where they arise, what are their implications with respect to the use of nuclear techniques, pointing out their critical aspects where solutions are still needed.

During these last years, after some hesitations, a rather rigorous scientific approach of groundwater pollution problems has been used, based upon systematic methodologies. This approach briefly consists in the following steps: the investigations start in the field, yielding two sets of information, numerical and non-numerical data. These data are screened and used to identify the system, which is defined by its structure, the parameters of its elementary blocks and its behaviour under perturbations. These characteristics are also studied simultaneously in the laboratory on physical models to determine the elementary behaviour of the system under simplified conditions. All these experiments allow the derivation and calibration of models by using the consistency between model and information.
Once the model has been built, it may be necessary to go back to the field to collect various sets of parameters that have appeared in the modelling and also to gather lacking information. Then the model is used as a forecasting tool and must be checked by field control.

The critical problems occur at two levels: at the level of the field investigations and at the control level. In the first instance, they are mostly technical problems on the elaboration of experiments for determining the various model parameters such as dispersion coefficients. At the control level, it may happen that the models cannot be calibrated anymore; this means that the adopted modelling is not valid anymore and that new assumptions must be made to take physical phenomena into account that either had not been foreseen or newly occurred. We are facing here fundamental problems, as, for example, adsorption.

Of course these two types of critical problems are not rigidly separated, and fundamental and technical aspects are often mixed such as, for example, the determination of dispersion coefficients and scale changes.

We describe these critical problems after a brief recall of the mechanisms of groundwater pollution.

2. THE MECHANISMS OF GROUNDWATER POLLUTION

Groundwater is usually of very good quality, free of pathogenic germs and neither colored nor turbid; its temperature and chemical composition are generally constant. It flows in aquifers geologically classified as pore, fissured and karstic: pore aquifers, made up of small cavities of the size of the grains, display water velocities ranging from a few cm/d to a few m/d (usually less than 40 m/d); fissured aquifers, made up of fissures and faults, display water velocities varying from 1 m/d to 8 km/d; karstic aquifers, made up of fissures, faults and caves, show water velocities up to 30 km/d. Between the phreatic pore aquifers and the ground surface there exists a nonsaturated zone.

The quality of groundwater depends on the types and qualities of recharge waters, on the soil properties and the physico-chemical and biological processes in the ground. The movement of pollution can be split into three phases:
the washing of the pollutants either by precipitations or by the aquifer itself,
the flow of contaminated water or of the pollutant itself through the unsaturated zone to the aquifer,
the flow of pollution within the aquifer.

The movement of pollution is governed by the dispersion-convection scheme, whose characteristics depend on the miscibility of the pollutant with water and on the scale of the pollution: most frequent and dangerous pollutions either are miscible or are so light that they behave like miscible tracers and their evolutions in time and space are described by the theory of dispersion of miscible fluids in porous media. The mechanisms of dispersion have been analyzed in the laboratory; in the field, these mechanisms are complicated by heterogeneities and preferential paths and the validity of the description will depend on the scale of the phenomena: for long time periods and on long distances, the characteristic parameters have different orders of magnitude and, also, for instance, known miscible pollutions will be thoroughly described by convective models, neglecting the mixing aspects.

The evolution of pollution is not purely mechanical because the soil is not chemically inert and other mechanisms have to be taken into account: physico-chemical and biological mechanisms, characterized by exchanges between soil and water or between circulating water and water retained in the soil and by self purification processes.

In short, groundwater pollution is influenced by:

- mechanical factors: velocities in an aquifer, densities and viscosities of pollutants, geometry of the sources, duration and areas of contact between pollutant sources and water, mechanical filtration and dilution, pumping policies and management of water resources.

- geological, structural and geographical factors: geology of the aquifer material, stratification, types of aquifers, climatic and hydrologic conditions varying in time and space.

- chemical and biochemical factors: chemical properties of the soils and of the pollutants; self purification processes such as microbial decay, chemical precipitation, sorption, exchange of gases, effects of microorganisms.

The types of groundwater pollution are: mineral chemical pollution, hydrocarbons, biological pollution, detergents, pesticides, radioactive pollution, organic pollution. The origins of groundwater pollution are industrial, domestic, agricultural and environmental.
3. CRITICAL FUNDAMENTAL AND TECHNICAL PROBLEMS OF GROUNDWATER POLLUTION

3.1. The scale problem: it is one of the fundamental problems in physics, where the concept of equivalent continuum is the basis for many theories. Because of an abundance of local parameters, it is unpractical and even impossible to use the microscopic description of a porous medium for macroscopic studies. Thus scale levels are introduced which vary with the heterogeneity regimes, a level being obtained when, for the observed phenomena, the heterogeneous medium behaves as a homogeneous continuous equivalent medium. It is assumed and verified that pollution phenomena are of the same nature at each level, i.e. can be formally described by the same parameters; the values of these parameters vary considerably: in the laboratory, the dispersion coefficient ranges from a few millimeters to a few centimeters, whereas at the scale of a few meters (around a well for instance) it is of the order of a few decimeters and at a scale of several kilometers it can reach several tens of meters.

Dispersion results from the contrasts in the velocity distribution enhanced by the heterogeneities of the aquifer. The usual representation by means of the general diffusion equation and dispersion coefficients is valid only for the asymptotic regime, which depends on the heterogeneity distribution: when an asymptotic regime is reached, the heterogeneities are smoothed in some continuous homogeneous equivalent medium, defining a new level of homogeneity. The dispersion coefficients at the new level are regularizations of the more local parameters (including local dispersion and molecular diffusion coefficients). A good example has been provided by Marle for a horizontally stratified aquifer where the equivalent dispersion coefficient is an increasing function of the velocity contrasts and an inverse function of the local transverse dispersion coefficients, which explains the large values of the dispersion coefficients at large scales.

The validity of pollution modelling, absolutely necessary for description and prediction of pollution behaviour, is thus questioned, and basic as well as technical problems must be solved: the instability and fingering in miscible transport, the determination of the heterogeneities of an aquifer, the determination of the preferential paths, the measurements of dispersion coefficients in the field.

The miscible transport in porous media may be unstable: instead of a smooth dispersion profile, fingers will develop due to differences in densities, viscosities and velocities of the fluid phases. Fingering can be
explained by the fact that the regularizing effect of molecular diffusion and also of dispersion itself has had no time to play its part. A knowledge of its mechanisms is useful for refining the pollution models.

Linked in some way to fingering is the determination of the heterogeneities and of the preferential paths, the last being local heterogeneities influencing the local velocities. It is necessary to know the distribution of geological heterogeneities, such as clay lenses in an alluvial aquifer, and of permeability heterogeneities influencing the hydrodynamics at some scale. Detection and description of preferential paths is of great importance for modelling local situations such as local protection areas of pumping wells.

For several years now, some emphasis has been put on the field measurements of dispersion coefficients at given scale levels because of the impossibility of computing large-scale values from small-scale results. Research is still very active on that problem, especially focusing on least disturbing methods, which are more accurate and less expensive than others.

In some respect, fissured flow can be considered as a scale problem because an equivalent homogeneous medium can be introduced to describe very large scale pollutions. At lower scales, fissured flow will present analogies with flow through preferential paths with of course different velocity equations and distributions. A good example of mixed scale problems involving fissured and pore flow is the chalk in the United Kingdom presenting a porosity of fissures and a porosity of pores: infiltration and movement take place through the fissures and storage in the pores and the problem will be to determine the transfer of pollution from fissures to pores.

3.2. The unsaturated zone: it plays an important part in groundwater pollution as it is the required path for most pollutions infiltrating from the ground surface, and the location of various chemical reactions. All phenomena already described in the saturated flow exist here (dispersion, for instance), further complicated by their dependence on a varying water content.

The quality of water reaching the aquifer depends on its time of travel, which is related to the hydrodynamics of flow, to the dispersion and to the presence of dead-end pores: these are stagnant static fluid bodies, which are not part of the main flow but are hydraulically connected to it, and into and out of which pollution is moving by molecular diffusion. These mechanisms have a delaying effect on the pollution front with respect to the
HYDROGEOLOGY OF THE CHALK

The Chalk of southeast England is the major aquifer in the UK, providing over 40% of the total groundwater abstracted. Consisting generally of soft, white limestone, the Chalk extends from the east coast of England to the south coast, either at the surface or concealed beneath younger strata (Figure 1). Boulder clay and other superficial deposits obscure much of the outcrop. The thickness of chalk varies considerably from 100 m up to 500 m, but satisfactory well yields are only obtained at certain horizons where fissuring increases the bulk permeability of the rock. It has been common practice to sink large diameter wells into the Chalk and drive adits horizontally below the water table to intercept the maximum number of water bearing fissures. Yields of up to 15 ml/d have been obtained by this method. Lithological variations of the different layers of the Chalk have considerable influence on its transmissivity and porosity. The stratigraphical levels of hard bands are also responsible for the pronounced escarpments formed at outcrop.

The mass of Chalk as observed in quarry exposures is frequently traversed by horizontal and near-vertical joints and fissures. It is these
discontinuities which give rise to the locally high transmissivity values near to the water table, where solution of the calcium carbonate has been most rapid. The rock matrix is composed of fossil debris ranging in diameter from less than 1 μm up to 100 μm (Water Resources Board, 1972), and pore diameters are generally less than 1 μm. This gives rise to a very low intergranular permeability, but a very high porosity. Measurements on core samples of Chalk have yielded permeabilities of the order of $10^{-3}$ m/d, and porosities ranging from 0.3 to 0.4 (Young et al., 1976). The specific yield, however, is generally less than 0.02 and may be identified with the volume of draining fissures. The jointing pattern observed in quarry exposures is generally very irregular, with block sizes varying from a few centimetres to more than one metre. The size of joint openings is particularly difficult to estimate because of the effects of weathering on quarry faces. Horizontal discontinuities up to 10 mm in width have been reported by Ward et al. (1968), while Foster and Milton (1974) have noted tightly closed joints at relatively shallow depths. Examination of Chalk cores suggests that very
small or microscopic cracks are profuse throughout the rock mass so that no part of the pore space is remote from the fissure system.

A consequence of the unusually high specific retention of the Chalk matrix is that even above the water table the pore space is almost fully saturated. Figure 2 shows the water content profile for a cored, Chalk borehole near Winchester, Hampshire (Young et al., 1976). Water content was estimated by drying core samples in an oven. The profile shows no significant change at the water table; the variations with depth reflect, among other things, the presence of fissuring which will reduce the volumetric water content, and lithological features. The saturated zone is characterised by complete saturation of the fissure system, which will only be partially filled above the water table.

**MECHANISMS OF WATER AND SOLUTE MOVEMENT**

Given these characteristics there has been considerable speculation regarding the mechanisms of rainfall recharge, and of solute movement through the Chalk (Smith et al., 1970; Foster, 1975). In a fully saturated Chalk column with a vertical permeability of $10^{-3}$ m/d, and a porosity of 0.35, water would migrate downwards through the pore space at about 1 m/a. This is a similar rate to that reported by Smith et al. (1970) and by Young et al. (1976) for the movement of tritium through the unsaturated zone of the Chalk. Profiles have now been obtained from a number of sites located on the Chalk outcrop and the rates of movement of tritium inferred by correlation to the time variation of tritium in rainfall are all similar at between 0.8 m/a, and 1.05 m/a. Tritium is considered to be a particularly suitable tracer for water since it is part of the water molecule. It may therefore be inferred that if recharge is occurring through the pore space the water molecules themselves migrate downwards at about 1 m/a. This downward movement rate allows the storage in the pore space of the average annual infiltration to the Chalk of 350 mm, but it is not certain whether the maximum daily rates of infiltration could be as readily accommodated. It is also difficult to discount the multitude of fissures that are so evident in Chalk exposures as playing no role in the flow process.
It has been suggested (Foster, 1974; Young et al., 1976) that infiltration through the unsaturated zone may take place along the fissures, and that solutes may diffuse between this moving water and the relatively static water in the matrix. This could perhaps account for the observed slow downward movement of tritium and other solutes. Under natural rainfall conditions the fissures would be partially filled by slowly moving water. High infiltration rates resulting from intense rainfall could be accounted for by rapid flow down the fissure system resulting in some solutes being carried rapidly down to the water table.

THE RATE OF RAINFALL RECHARGE

An estimate of the rate of movement of water down the fissures to the water table has been obtained by considering the delay in water table response to infiltration. At two sites on the Chalk outcrop well levels were correlated to lagged distributions of calculated monthly infiltrations. The correlation equation postulated was

\[ h_i = \sum_{j=1}^{N} a_j p_{i-j+1} + b_1 + b_2 h_{i-1} \]  

(1)

where \( h_i \) = water level at end of month \( i \)

\( p_j \) = infiltration at the surface in month \( j \)

The last two terms on the right-hand side of equation 1 describe groundwater level recession, and the coefficients \( a_j \) apportion unit surface infiltration in some month to the consequent water level rises in the same month and in succeeding months. Thus, \( a_1 \) is the water level rise in the current month, \( a_2 \) the rise in the next month, and so on. It will be apparent that the sum of the coefficients \( a_j \) must equal the reciprocal of the specific yield. For each of the two sites four years of monthly data were available, and the coefficients were determined by least-squares fitting. The number of lags, \( N \), required in each case was determined as the maximum number which gave all positive coefficients \( a_j \), negative coefficients
having no physical meaning. Figure 3 shows the unit response function for each of the two sites, giving the distribution in time of water table infiltration resulting from unit input in one month at the surface. Median delay times between surface and water table infiltrations are shown on Figure 3, and the corresponding median vertical flow rates were calculated from the thickness of unsaturated chalk to be 0.6 m/d and 0.8 m/d respectively. The spreads of the unit response functions reflect the local heterogeneity of the Chalk and the range of fissure and joint sizes. It is interesting to note that both correlations indicate that 15% of the infiltration reaches the water table within about one month. This may be equated to a rapid fissure flow component arising from recharge through the larger fissures, and high intensity rainfall events.

THE RATE OF SOLUTE TRANSPORT

It is postulated that water and its solutes move slowly through the fissure system, and have a large area of contact with static water held in the Chalk matrix. If the mass transfer of solutes between the mobile and static water is assumed to be instantaneous, a simple solution to the equation of solute movement may be obtained. It is found that in the absence of mechanical dispersion solute pulses migrate downwards from the ground surface without change in shape at a velocity \( v \) given by

\[
v = u \frac{D_{m}}{D_{m} + D_{n}}
\]  

(2)
where \( u \) = velocity of flow in the fissure system
\( \theta_m \) = porosity of the mobile phase
and \( \theta_s \) = porosity of the static phase.
In reality, there will not be a unique flow velocity in the fissure system, and a range of velocities in inter-linked fissures will result in some dispersion of the solute profile.

If \( u \) and \( v \) of equation 2 are assigned average values of 0.7 m/d and 1.0 m/a respectively then we require

\[
\frac{0_m}{\theta_m + \theta_s} \approx 4.10^{-3}
\]

Total porosity averages about 0.35 so that for the assumed migration rates \( \theta_m \approx 1.4 \times 10^{-3} \) which indicates that the fissure space cannot be more than about 1/10th full during normal infiltration events.

The assumption of instantaneous equilibrium between the solute concentrations in the pores and in the fissures is, of course, very stringent. A rapid, but not infinite, rate of mass transfer would result in some dispersion of the input solute pulses. The movement of solutes in this case could be assessed with a numerical model and data is currently being collected at the Water Research Centre to facilitate this analysis. Some preliminary results from laboratory experiments are presented in the next section.

LABORATORY EXPERIMENTS

Unfortunately it is not possible to carry out comprehensive laboratory experiments on Chalk columns because of the difficulty in obtaining in a laboratory-scale sample a completely representative range of fissure sizes. However, experiments have been undertaken to measure the rate at which solutes will diffuse from fissures into the pore space. In these experiments Chalk cores approximately 100 mm diameter by 75 mm long were saturated with a NaCl solution and sealed in plasticine, leaving one face of the core
exposed. A small quantity of fresh water was placed in contact with the exposed face, and the rate of increase of NaCl concentration in the water was measured with a specific ion electrode. Within the Chalk block the concentration $c$ of the tracer obeys the diffusion equation:

$$\frac{\partial c}{\partial t} = D \nabla^2 c$$

where $D$ is the diffusion coefficient ($L^2 T^{-1}$) and is a property of the pore structure of the Chalk matrix and of the self-diffusion coefficient of NaCl. For the particular boundary conditions applied in this case there is an analytical solution to the change with time of concentration of tracer in the water in contact with the exposed face of the core (Carslaw and Jaeger, 1959, p.128). Figure 4 shows the measured concentration variation and the 'best-fit' analytical solution, obtained with a value of the diffusion coefficient $D = 1.3 \times 10^{-5}$ cm$^2$/s. This may be compared with a self-diffusion coefficient for chloride of $4.7 \times 10^{-5}$ cm$^2$/s. Further experiments are being planned using different tracers such as tritium and nitrate. The author is unaware of any experimentation on the relative mobility of various ions in the Chalk. However, in other media similar migration rates for nitrate and chloride have been reported from both field and laboratory studies (Kurtz and Melstead, 1973).
FIG. 5. Rate of approach to equilibrium concentration (see text).

The analytical solution may be used to estimate the effects of diffusion between fissures and blocks of varying sizes. The 2 graphs of Figure 5 were produced using the diffusion coefficient calculated from the chloride experiment. The graphs show the rate at which the concentration of some solute in the fissure water approaches the equilibrium concentration from an initial condition where all of the solute is in the pore water. The dimension of the Chalk block is assumed to be 0.2 m and the depth of water in the fissure in contact with the block is 1 mm in one case and 0.01 mm in the second case. It is seen that the concentration in the fissure water reaches 90% of its equilibrium value in approximately 0.5 d in the first case and 10 mins in the second case. The concentration in the fissure water reaches 98% of its equilibrium value after about 220 minutes in the second case. The physical dimensions used in these 2 examples were based on a rather superficial knowledge of the fissure geometry of the Chalk. Further research is required before a detailed analysis of the postulated diffusion process can be undertaken. However, the results illustrate that under certain circumstances the assumption of instantaneous equilibrium between pore and fissure concentrations may not be unrealistic.

SOLUTE TRANSPORT MODEL

It is apparent that in attempting to model the movement of solutes through the Chalk from the surface to the water table, the usual model of unsaturated flow (e.g. Brester, 1973) is inappropriate. However, both the
intergranular flow and fissure flow concepts indicate that a uniform-velocity, downward-flow model may be used to represent the movement of contaminants input at the ground surface. Such a model has been used to simulate the movement through the Chalk of tritium, and of nitrate resulting from agricultural activities. The surface inputs of tritium are known (Smith et al., 1970), and those for nitrate were based on control rules relating the mass of nitrogen released each year in the soil layers to antecedent land use and fertilizer applications (Young et al., 1976). The vertical flow rate in the model simulations was adjusted in each case to give the best match to field observations, but in all cases a constant value of dispersivity, equal to 0.2 m, was used to account for dispersion.
within the mobile and static phases and for non-equilibration of concentration between the two phases. It was also assumed in the simulations that 35% of the surface input of solutes travels rapidly to the water table and does not interact with the pore water. This fraction corresponds to that derived by correlating water table response to antecedent infiltration. The comparisons between the numerical model and field observations are shown in Figure 6.

The tritium profiles are particularly important as the surface inputs are accurately known. An excellent comparison between the computed and measured results for both peak position and peak size is obtained. The computed nitrate profiles do not match the measured profiles so well as those for tritium, but the peak positions are generally well predicted. Uncertainties concerning the quantities input could account for the discrepancies in peak magnitudes. The downward migration rates used in the model simulations all fall in the range 0.8 to 1.05 m/a and there appear to be no significant differences between the rates for tritium and nitrate.

The overall behaviour of the model in matching the nitrate and tritium profiles is generally good, and supports the hypothesis of a uniform downward migration rate. The results cannot, however, differentiate between the relative merits of the intergranular flow and fissure flow concepts.

CONCLUSIONS

Field investigations on the Chalk have indicated that solutes move through the unsaturated zone at a rate of about 1 m/a. Two distinct mechanisms of water and solute movement have been proposed to explain this phenomenon. One invokes flow of water and solutes through the Chalk matrix and largely ignores the presence of fissuring. The properties of the matrix are such that average annual rates of recharge could be transmitted through the pore space, but it is doubtful whether infiltration from high intensity rainfall events could be as readily accommodated. An alternative mechanism has been proposed which admits recharge via the fissure system and can, therefore, explain the rapid infiltration process which must occur after
high intensity rainfall. In this model water and its solutes move down through the unsaturated zone at markedly different rates. Water moves downwards through the fissures at about 0.7 m/d, and above the water table the fissures are, on average, about 1/10th full. Solutes diffuse between the water in the fissures, and the water in the pores under the action of concentration gradients. Instantaneous equilibration of concentrations in the fissures and pores results in surface inputs of solutes moving slowly down through the Chalk in an unaltered profile. A coefficient of diffusion of NaCl through the Chalk matrix, equal to about 1/3rd of the self-diffusion coefficient, has been estimated in laboratory experiments. Further research is needed to quantify the physical dimensions of fissures and blocks in the mass of the Chalk. It has been shown that in certain circumstances the mass transfer of solutes between fissure water and pore water may be extremely rapid compared with the rate of flow of water down the fissures.

The retardation of pollutant movement by diffusion between mobile and static water has been investigated by other workers (e.g. Gaudet et al.) particularly in unconsolidated media. The Chalk is probably exceptional, however, in its ability to retard the movement of solutes by a factor of about 250 relative to the rate of transmission of water. Retardation is also expected to occur in the saturated zone where it is generally recognized that the bulk of water movement in the Chalk occurs in the fissures. Flow velocities are much greater than in the unsaturated zone, however, and further research is needed to quantify the transport mechanisms. It is also expected that solute movement will be retarded in other cemented aquifers where both fissure flow and intergranular flow are operative. The implications for groundwater pollution are evidently very important, and model studies are now in hand to provide predictions of the rate at which nitrate now in the unsaturated zone will cause concentrations in pumped groundwater and in springs to rise.

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REFERENCES


   Study of water and dissolved substance transfers in non-saturated ground, considering a partly stagnant body of water. La Houille Blanche, 3/4, 243-252.

   Nitrates pollution of Chalk waters. Water Treatment and Examination, 19 (2), 169-182.

   Movement of chemicals in soil by water. Soil Science, 115 (3), 231-239.


   Water movement in the unsaturated zone of high and low permeability strata by measuring natural tritium. Proceedings of a symposium on isotope hydrology, IAEA, Vienna, 73-87.

    Geotechnical assessment of a site at Mundford, Norfolk, for a large proton accelerator. Geotechnique, 18, 339-431.


CONSIDERATIONS OF STATIONARY-PHASE INTERACTIONS IN GROUNDWATER POLLUTION STUDIES

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Abstract

CONSIDERATIONS OF STATIONARY-PHASE INTERACTIONS IN GROUNDWATER POLLUTION STUDIES.

Studies of groundwater pollution are complicated by retention of both pollutant and tracers as static phases associated with the rock matrix. Three types of static phase are considered: (1) immobile pore water, (2) equilibrium adsorbed layers and (3) bulk precipitates, including biological systems. A brief discussion of the systems is given with examples from the work of the Water Research Centre on the problems encountered in quantifying groundwater pollution where static contamination may occur.

1. INTRODUCTION

In the study of groundwater pollution, an incident that is perplexing interpretation is an obvious source of pollution that brings about little or no detectable contamination of sampled groundwater. Questions arise as to whether the contaminant, if organic, has undergone biological decay, has been physically or chemically retained in the aquifer, has been effectively diluted by moving groundwater or whether a hydrogeological error has allowed the pollution to flow away undetected in an unforeseen direction. Such uncertainty arises partly because little is known about the capacity of the rock matrix of an aquifer to contain or retain contamination by physical, chemical or biological means. This allows wide conjecture as what might have happened to a known input of potential groundwater pollutant and particularly whether it remains in the ground as a source of future pollution.

Doubts arise for similar reasons in the use of tracers for the study of groundwater pollution. Certain tracers, particularly dyestuffs, deservedly
fall under the suspicion of being retained by adsorption on internal surfaces of the aquifer rock. Where choice is made of a tracer that is certainly non-retentive, the relevance of its behaviour to that of retentive pollutants is then brought into question.

The study of groundwater pollution with regard to the interaction of the moving groundwater with the stationary matrix would be impracticable on both logistic and economic grounds except where the study establishes mechanisms that are widely applicable in groundwater pollution problems. Such studies are being carried out by the Water Research Centre in connection with pollution from landfills, surface spreading of sewage, nitrate from agricultural fertilisers and disturbances in groundwater composition as a result of artificial recharge (1, 2, 3,). Aspects of these problems that involve interactions between moving groundwater and the matrix are assisted by reference to several physico-chemical and biological principles that are well-known in disciplines apart from hydrogeology. This paper includes reference to these principles in the context of groundwater chemistry in order to distinguish systems of groundwater pollution that cannot properly be described by reference only to the water phase but require also consideration of the composition of the matrix.

2. TWO-PHASE DISTRIBUTION OF GROUNDWATER CONTAMINATION

The contribution of a contaminant to the pollution of groundwater depends upon the former's movement, which, in turn, is governed by its distribution between moving water and stationary phases, together with the rate of interchange between the two. Equilibration of a solute between static and moving phases is shown by chromatographic slowing of solute movement behind that of the water. This occurs by a factor equal to the distribution coefficient of the solute between the water phase and the portion of the stationary phase that is in exchange equilibrium with the water (4). Chromatographic separation of different solutes occurs where they have differing distribution coefficients. Sharpness of resolution in a chromatographic system requires a negligible equilibration time between the moving and static phases, and is favoured by the latter retaining the solute on its surface in contact with the moving phase. The sharpest resolution in laboratory systems occurs in chromatography.
between moving gas and the internal wall of narrow capillaries (0.2 mm diam). The longer the transfer time between moving and static phases or between the surface of the static phase and less accessible inner regions, the greater is the dispersion of the solute in the direction of flow.

For groundwater systems there is no reason to doubt that the chromatographic principle applies to the movement of solutes, but for even the most uniform of formations, the scale of distribution of flow paths and the dimensions of static phases, which will govern the resolution of solute distribution in the direction of water flow, is uncertain. A distinction may be drawn between the proportion of the porosity of the aquifer that is in exchange equilibrium with moving groundwater and the remainder being in varying degrees of non-equilibrium. A substantial proportion of accessible porosity being out of equilibrium with moving groundwater has the effect of smoothing out variations in input concentrations of a solute.

A similar effect is produced where non-equilibrium results from slow desorption of solute into the water stream. Saturation of the water phase by heavy contamination of the rock matrix or by deposits of low solubility generates a plume of contaminated water and a corresponding spreading of contamination on the rock surface diminishing in intensity downstream of the pollution source.

Contamination of the static phase of aquifers may be classified according to the following physical states.

1) Contaminated pore water contained in rock matrix that is capable of being displaced by or exchanging with moving groundwater.

2) Adsorbed contamination on rock surfaces that is capable of being moved by groundwater movement.

3) Bulk deposits of contamination that are liable to dissolve or ablate in moving groundwater during a prolonged period. These include geological deposits, organic and inorganic wastes and biological growths.

Whereas in a given groundwater system there is likely to be considerable interaction between the three groups, the classification is useful in separating fairly distinct methods of investigation of groundwater pollution problems. These
FIG. 1. (a) Nitrate and nitrite contents of Chalk from site C1e. (b) Nitrate, nitrite and chloride contents of Chalk from site C1g.
are considered more fully in the following sections, where reference is included
to relevant groundwater pollution studies being carried out by the Water Research
Centre.

3. CONTAMINATION OF PORE WATER

Pore water, mostly from the unsaturated zone of the chalk, but also from below
the water table and from the English Bunter Sandstone has been extensively
sampled in the course of investigations by the WRC into the nitrate contamination
of groundwater. The philosophy of studying nitrate in pore water in the Chalk
unsaturated zone followed from the earlier observations by Smith and others (5)
that most of the environmental tritium originating from the 1963 and 1964
peaks in thermonuclear testing appeared to be retained in the unsaturated zone
and moving downwards at approximately 1 m/year. From an estimate of
infiltration rate and with the assumption that all of the unsaturated zone is
accessible to moving tritium, it appears that most (ca. 85%) of the infiltration
moves through, or is in equilibrium with, the pore system of the unsaturated zone (2).

The many analyses that have now been made of the nitrate concentrations
occurring in extracted pore water from unsaturated zones have shown
concentrations ranging from almost zero to more than 160 mg N/litre, with the
highest concentrations occurring near the land surface. A selection from these
results is shown in Figures 1 (a) and (b). On the basis of the displacement
or rate of chromatographic movement of tritium, an interpretation of the
nitrate concentration profiles is that the peaks and troughs are a record of
former discrete highs and lows in input nitrate loads. A logical conclusion
from this model is that the concentrations are high near the surface because
of the intensified use of nitrogen fertilisers in recent years and that in a pro-
portionate number of years in the future, high nitrate peaks will enter the water
table.

However, this interpretation cannot be completely reconciled with other
observations, in particular, other aspects of pore water composition.
Measurements of carbon dioxide evolved from heating wet chalk to 200°C yield
amounts consistent with the atmospheres that occur sometimes in wells, but which
are some 5 to 10 times that occurring in normal Chalk groundwater. Measurements
of pore water ammonia concentrations have been found to be consistently about 0.3 - 0.6 mg N/litre rather than the more normal level for groundwater of less than about 0.1 mg N/litre. Concentrations of potassium in Bunter Sandstone pore water have been found up to 80 mg/l in comparison with local groundwater concentrations of about 1 mg/l. These observations indicate that much of the pore water content of the unsaturated zone is chemically quite different from groundwater and suggest that the predominant recharge route is through fissure type permeability, with little equilibration occurring with the pore water.

The downward progress of thermonuclear tritium would then have to be explained by its appearance only at certain points of intersection of the recharge route. Assuming that recharge water moves for most of the time horizontally, the shape of the vertical concentration profile is governed by the extent of dispersion from the flow path, and influenced by the distribution density of fissures and the occurrence of strata of low permeability.

From this viewpoint, a common feature of nitrate concentration profiles of there being high concentrations near the land surface may not represent a progressing sequence, but a system conforming over a broad time-scale to a steady state. The biological processes in soil giving rise to nitrate, ammonia and carbon dioxide occur more or less continuously and their concentrations carried downwards from the soil will vary approximately inversely with infiltration rate. Slow infiltration will acquire higher concentrations of biological products from the soil and will have greater opportunity for adsorption in the pore structure of the aquifer. Highest concentrations will occur in the pore system close to the land surface following drought, when accumulated products of biological processes in soil are dissolved in high concentration and retained totally by a moisture-deficient unsaturated zone. From this point of view, the input of environmental tritium to an aquifer is fundamentally different in that it occurs proportionally to infiltration, much of which occurs as a result of heavy precipitation following the satisfying of moisture deficit.

Accounting for the composition of pore water in the unsaturated zone has indicated several uncertainties about the mechanism of infiltration. Problems mostly concern defining the proportions of connected and unconnected porosity
and the extent of diffusional interchange between them under various conditions of moisture deficit. A particularly important question relating to the interpretation of nitrate profiles is whether the absence of high concentration in some samples is due to the nitrate having been washed away, having undergone removal by biological processes, or the sample having remained inaccessible to nitrate contamination because of hydrogeological factors.

4. CONTAMINATION BY ADSORPTION

Contaminating solutes that are not insoluble in groundwater will nevertheless be retained in some degree by adsorption at the rock surface. Adsorption is a phenomenon at or close to an interface whereby there is capacity for retention for a finite amount of solute. The capacity may result from a particular attraction of the solid surface for a solute (specific adsorption), from the attraction of ions having electrical charge of opposite sign to that of the surface (counter-ion adsorption) or through differential solubility of the solute between the bulk and interfacial region of the water (surface activity). Adsorption phenomena in aquifers may well be important in retarding the movement of some pollutants, but in the absence of dedicated experimentation, recourse has to be made to general principles of surface chemistry in assessing the probable behaviour of various pollutants (6).

4.1. Surface Activity

Surface activity is probably the most important mechanism of adsorption in groundwater systems in governing the behaviour of all uncharged organic substances and also some large ions. There is maximum thermodynamic advantage in adsorption at an interface that has maximum energy, i.e., at the electrocapillary maximum, which for equilibrium systems is the condition where the surface has zero charge (7). Most surfaces in contact with water near neutral pH are negatively charged, but the intensity of the negative charge and hence the adsorption of neutral molecules varies with the nature of the surface and the ionic composition of the water. Silica (quartz) approaches its zero point of charge (zpc) in pure water at about pH 2 (8), but this value moves closer to neutrality with increasing calcium ion concentration. Iron oxide has a zpc at pH 6.7 in pure water. Therefore it is anticipated that the adsorption of neutral molecules is insignificant on silica surfaces in soft water but possibly of importance in hard water and particularly where iron oxide occurs extensively.
Differences in the surface charge of oxides are related to small differences in their hydrophilic, or water attracting character. Increasingly hydrophobic character occurs where the negative charge of the surface of silica is reduced by acidity or the presence of multivalent cations or on surfaces which normally have a higher value of the spc. This charge is associated with increased capacity for the retention of low-solubility organic substances. Calcium carbonate is appreciably hydrophobic in pure water as shown by its capacity to prevent the coalescence of hydrocarbon droplets in water (6), which in the groundwater context would indicate a pronounced ability to retain oils by adsorption.

However, the adsorptive properties of surfaces may be totally changed by the presence of strongly surface-active ions which are adsorbed by a combination of electrical interaction and hydrophobic character. For example, small concentrations of long-chain amines and quaternary ammonium cations are attracted to the negatively charged hydrophilic surface of silica and confer hydrophobic character such that petroleum oils are strongly retained (9). The composition of an oil pollutant with respect to its content of organic cations would therefore greatly influence the mobility of pollution in sand formations, for example.

The opposite effect may occur in Chalk systems, where it has been suspected that natural carbohydrates (see section 5.1), having hydrophilic character, are precipitated as calcium salts on fissure walls, thereby conferring considerably less oil-retaining capacity, for example, than is shown by pure calcium carbonate.

4.2. Specific Adsorption
With the passage of inorganic salts through aquifers there may be some importance in the capacity of rock minerals to retain ions by their displacement of other ions in a crystal or ion-exchanging matrix. An example of the latter is the retention of calcium by natural zeolites and the retention of multivalent cations would be shown to a small extent by any siliceous surface in soft water. Exchanges also occur at the surface of calcite, but these appear to involve concentrations of foreign cations similar to that of the calcium, which would not allow for very thorough retention of the foreign cation. Furthermore, organic contamination of the kind found in Chalk may render natural calcium systems very insensitive to ion-exchange.
5. BULK CONTAMINATION

Forms of contamination that may occur in aquifers in amounts that saturate more than one displacement volume of groundwater include the following:
(i) Insoluble oils that have penetrated to the aquifer by seepage.
(ii) Heavy metal oxides and carbonates precipitated in basic rock formations as a result of discharge of effluents from metallurgical processes.
(iii) Heavy metal ores of geological origin which become leached by unnatural imposed groundwater flow regimes.
(iv) Microbial growths and waste products generated both at the land surface and within the aquifer.

Such deposits affect the composition by both direct solution and as a result of secondary microbial transformations. The first two categories of aquifer contamination are normally avoidable by the observance of reasonable pollution prevention measures and are not of serious occurrence in the United Kingdom. The latter two categories are natural phenomena, which, while not properly described as examples of pollution, are nevertheless involved in serious groundwater quality problems resulting from intensification of land and aquifer use. Both are currently being studied as part of the WRC programme of groundwater research and are summarised in the following sections.

5.1. Oxidation and Solution of Sulphides in an Aquifer

The Lower Tertiary of the London Basin in the region of the River Lea has been investigated by the drilling of 15 exploratory boreholes in connection with a prototype artificial recharge project to take place in 1977 (3, 10). A full-scale operation of this kind could be favourably economic provided that water injected into the Chalk be allowed to rise into the overlying sands of the Lower Tertiary. From the boreholes, within an area of some 90 km$^2$, samples of the sands were obtained and analysed for iron, manganese and oxidisable sulphur. In all samples except those close to outcrop, iron sulphide occurred in concentrations between 0.1 and 2% of both iron and sulphur. Abnormally high concentrations of iron were found to be accompanied by calcite and concentrations of up to 0.007% of manganese, which are interpreted as indicating sites of secondary ferrous and manganese carbonate precipitation. In occasional samples proportions of calcium sulphate (gypsum) of about 1% were detected.
FIG. 2. Four stages in the oxidative dissolution of iron/manganese sulphide and carbonates and the resultant sequence of iron, manganese and sulphate distributions.

Problems of groundwater quality that may occur due to the presence of this natural contamination in the Tertiary are as follows:

(a) Solution of calcium, ferrous and manganese sulphates giving undesirably high concentrations in abstracted groundwater.

(b) Bacterial oxidation of iron sulphide by the use of dissolved oxygen and nitrate, thereby releasing iron and sulphate to the groundwater.

(c) Solution of ferrous and manganese carbonates by sulphuric acid generated by sulphide oxidation.

These processes follow from geochemical conditions representing different stages in the oxidation of iron sulphide as a result of drainage due to water abstraction. This sequence is illustrated in Figure 2. The purpose of the investigation is to define the probable patterns of historical water movement from lithological and chemical examination and to extrapolate this information to the new regime caused by the injection of water containing dissolved oxygen and nitrate. An attempt is being made to formulate guidance as to how pumping programmes can be organised in order to avoid the worst problems of water quality and aquifer clogging.


5.2. Organic Matter in Chalk

As part of the groundwater nitrate investigation referred to in Section 3, samples of Chalk from the unsaturated zone from which pore water has been removed by centrifugation have been further analysed for organic content. This has involved the dissolving of the calcium carbonate component in hydrochloric acid and subjecting the residue to instrumental analysis for carbon and nitrogen and also by estimation of the total carbohydrate content in the whole chalk. A selection of value for two boreholes of the proportions of insoluble residue, nitrogen, carbon and nitrate-N in pore water are given in Tables I and II.
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<tr>
<th>Depth (m)</th>
<th>% insoluble residue</th>
<th>organic N (mg/kg)</th>
<th>organic C (mg/kg)</th>
<th>Nitrate-N (mg/kg)</th>
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* Correlation coefficient: organic N/residue = 0.86

The predominant land used at these sites was as follows:

C1g Fertilised grass, at least since 1949, except for Spring barley grown in 1970-1

C1e Mixed arable since 1949, with medium to high N-fertilisation rates

At site C1g, the proportions of acid-insoluble residue, organic-N and nitrate-N were significantly different from the corresponding values at the arable site.

An important observation appears to be that the low-nitrate site C1g contained the higher concentrations of organic-N at depth and also showed very high
values of both organic N and organic C near to the land surface, but which were not shown in the arable site. The chemical form of the organic-N has not yet been demonstrated, but a reasonable hypothesis is that the high organic status of the grassland soil has extended to affect also the composition of the aquifer at depth. Most of the variance in the organic-N values for the arable site is correlated with the variance in the insoluble residue content. This suggests that most of the organic content of Chalk under this site is either of geological origin or in some way closely combined with a mobile clay fraction. In contrast, at the grassland site no such correlation existed below 2m, indicating either a substantial contribution of organic matter not derived from geological sources or the presence of additional clay not containing organic nitrogen. Most of the prominent changes in Chalk composition are correlated with changes in pore water nitrate concentration, indicating that the latter is affected to some extent by rock composition.

It is recognised that in the development of the organic status of soils, available nitrogen is used together with carbonaceous substances derived from plants to build increasing populations of microfauna and concentrations of their waste products (11). The organic content remains high when the absence of aeration prevents active aerobic decay and occurs typically in undisturbed grassland and when drainage is poor. In extending biological development in soil to the notion of its spread downwards into the aquifer, it must be assumed that there is movement of both available nitrogen and carbonaceous matter and that penetration of biological activity is greatest when these components move alternately. Indeed this is the mode by which carbon and nitrogen are generated in soils according to season. Excess carbon production in soil occurs typically in summer by photosynthesis occurring with nitrogen shortage, leading to the production of extracellular carbohydrate. Some of this remains in the plant (e.g. beet and cane sugar) (12), some is used by symbiotic nitrogen-fixers (13) and some is liberated to attendant soil micro-organisms (14). On the other hand, nitrogen liberation in soil occurs predominantly when there is no plant growth and biological survival can occur only by cell decay.

As yet there is no unequivocal evidence for the movement of organic matter from the soil zone into the aquifer, but the occurrence of bacteria, including denitrifiers, on fissure faces and the presence of nitrite in pore water gives
support to there being a microbial food source available at depth. Conditions most favourable for the leaching of organic matter from soil are the absence of aeration accompanying winter infiltration so that carbohydrate generated through nitrogen-deficiency during the summer is not totally used up by soil micro-organisms.

Assuming that such a regime has prevailed during the history of agricultural soils, the advent of nitrogen-fertilisation and cultivation provides a source of nitrogen for conversion to organic form in the aquifer. In the evaluation of aquifers for nitrogen contamination, attention is therefore directed towards not only the concentration of nitrogen present in both soluble and insoluble forms, but also the concentration of extracellular carbohydrates that remain for further nitrogen assimilation. Interpretation of profiles of nitrate concentration in the light of possible biological influence then necessitates an allowance for in situ generation or consumption of nitrate by the same processes that occur in the soil layer. However, one essential parameter that poses great difficulties of measurement is the prevailing level of aeration at any given point in the aquifer profile. This will probably vary quite rapidly with the progress of infiltration pulses through the unsaturated zone.

Analyses of Chalk for total carbohydrate by both the phenol/sulphuric acid method and by gas chromatography (2) have shown concentrations between 30 - 800 mg/kg. A high mannose content in the carbohydrate hydrolysates indicated a material similar to bacterial and algal secretions (15). There was variance in the results of analysis of 1g samples that was removed only by taking 10g samples, which showed considerable small-scale inhomogeneity that may mark the scale of reticulation in a system of micro-fissures. Average concentrations in the Chalk for three boreholes are consistent with the inverse order of the average concentrations of nitrate in the respective pore waters, but not with the order of organic carbon values. The latter presumably include a large proportion of non-carbohydrate carbon in the form of humic substances. The highest values of carbohydrate, averaging 280 mg/kg down to 20 m depth, have been measured in Chalk freshly obtained from under an unfertilised grassland site where nitrate concentration was almost zero. Laboratory work is now in hand to determine whether the carbohydrate actively supports the growth of bacteria either by N-assimilation or denitrification and to date the material by
C-14 analysis in order to know whether it is of geological origin or more recent. The association of low nitrate values with carbohydrate of recent origin would suggest that there is a continuing recuperative influence that under suitable conditions of land use could ameliorate the groundwater nitrate problem.

6. CONCLUSIONS AND RECOMMENDATIONS

(i) The capacity of aquifer systems, particularly the unsaturated zone, to contain large quantities of potential groundwater contamination by pore water solution, adsorption and bulk precipitation introduces many problems in the study and interpretation of groundwater pollution. Analysis of moving groundwater for the presence of pollutants or added tracers may yield negative results because of their containment by adsorption or precipitation, besides the possibility of biological decay.

(ii) The removal of contamination by microbial degradation or assimilation cannot be proved without sampling of the rock matrix for actual evidence of the contamination and attendant microbial activity. Even then, there may be problems in distinguishing contamination in groundwater flow paths from contamination, which may be natural, occurring in regions of the aquifer that do not lie in significant flow paths. An example of this problem that concerns the WRC is the distinguishing of those regions of the unsaturated zone where insoluble organic matter and nitrate and other components in pore water contribute significantly to the quality of final groundwater. A particular problem in the study of biological products in the unsaturated zone is the difference in flow mechanisms between the slow leaching from biologically active soil to a moisture-deficient aquifer in autumn and the infiltration of heavy winter precipitation by which most of the thermonuclear tritium has been introduced. An additional problem in the interpretation of tritium movement is the extent to which chromatographic delay occurs because of the presence of bound water on silica surfaces or on the variable clay content of Chalk.

(iii) Characterisation of an aquifer for its ability to contain contamination appears to necessitate a measure of the volume accessible to the storage and release of contamination. This value is probably indicated by the specific yield plus a fraction of the pore storage that is within diffusional range of a flow path. Pumping test or laboratory test data, together with
values for diffusional resistance of the pore structure may provide an estimate of this, but evaluation of the latter component may depend critically in the English Chalk upon the allowance for the effect and distribution of microfissures. Another estimate of contamination capacity is by the chemical analysis of both liquid and solid phases of the pore system by reference to such parameters as total carbon dioxide content, dissolved oxygen concentration, pH, redox potential, etc., and comparison with the composition of moving groundwater. In the unsaturated zone moving water cannot be identified with certainty, but water perched above impervious bands may be representative of this.

(iv) The ability of accessible pore storage actually to retain a given contaminant will depend upon the surface chemistry of the rock and the water composition, particularly the water hardness. Calcitic or siliceous formations in hard water are likely to retain neutral and anionic organic substances. Retention of oils would be greatly enhanced by organic cations. Chalk may have variable retentivity, at least, in the unsaturated zone, according to its content of natural organic substances derived from the soil. Measurement of retentivity of an inert pollutant by small column simulation in the laboratory would appear to present no great experimental difficulty and could be performed where movement of a groundwater pollutant cannot be detected by water sampling.

(v) In the use of tracers for the study of groundwater movement it is self-evident that those having any surface affinity for the rock matrix are unsuitable and this can be established by observing for chromatographic delay in laboratory columns. A particular problem in the use of tracers in aquifers having high porosity but low specific yield is the exchange of the tracer between flow paths and pore storage at a rate which is uncertain and which probably depends critically upon groundwater velocity.

ACKNOWLEDGMENT

Acknowledgment is due to the Director of the Water Research Centre for permission to reproduce this paper.
REFERENCES


CHEMICAL PROFILES IN THE KARUP WATER-TABLE AQUIFER, DENMARK

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H. KRISTIANSEN
Geological Survey of Denmark,
Copenhagen,
Denmark

Abstract

CHEMICAL PROFILES IN THE KARUP WATER-TABLE AQUIFER, DENMARK.

Chemical profiles of groundwater and aquifer material from a water-table aquifer at Karup are analysed to examine the vertical distribution of nitrate and iron, among other constituents. The oxidation-reduction conditions are investigated at three sites by analysing the content of NO₃⁻, NH₄⁺, Fe(Fe²⁺ and Fe³⁺), SO₄²⁻, Cl⁻ and tritium in the groundwater and the content of Fe, Fe³⁺, total S and organic C in the aquifer material. The groundwater sampling technique is described. The division of the saturated zone into an upper oxidation zone and a lower reduction zone is described and discussed. Ferrous iron seems to be the most important reducing element in the aquifer.

1. INTRODUCTION

A great number of investigations, many of which are referred to by Young and Hall [1], deal with the distribution of nitrate in the unsaturated zone. Regarding the saturated zone, numerous groundwater analyses indicate an increasing nitrate content in groundwater all over the world, but apart from the fact that nitrate is normally absent from groundwater in confined aquifers, little is known about the vertical distribution of nitrate in the saturated zone. This paper deals with an investigation of the nitrate distribution in the saturated zone, using the concentration of environmental tritium in the interpretation of the data.

2. SCOPE AND PURPOSE OF INVESTIGATION

The investigation was carried out to gain information on the NO₃⁻-contamination of the groundwater and to test the hypothesis that the presence of Fe²⁺ ions in the groundwater zone causes rereduction of considerable amounts of nitrate to gaseous nitrogen [2]. Furthermore, the investigation was designed to add to knowledge of the groundwater flow pattern of the aquifer.
FIG. 1. Location of chemical profiles of groundwater.
3. AREA OF INVESTIGATION

The area selected for the investigation covers the Karup basin, within which comprehensive hydrological studies were carried out during the International Hydrological Decade from 1965 to 1974 [3].

The groundwater flow pattern is shown in Fig.1. The water-table aquifer is composed of outwash materials of sand and gravel underlain by a fine sand or silty deposit of mica sand and clay of Miocene age.

The map also shows the location of the testholes producing the chemical profiles of the groundwater. The saturated zone is not fully penetrated by the test holes that have been located in areas with arable land upstream. The saturated zone is about 25 to 30 metres from the main stream and about 30 to 40 metres from the groundwater divide of the area of investigation. The unsaturated zone increases in thickness to about 25 metres at the groundwater divide. The distance between the groundwater divide and the main stream, Skive-Karup Å, is 10 kilometres.

The mean annual precipitation over the area is 710 mm (or 816 mm when corrected for a 15% under-registration due to wind effects) and the recharge to the groundwater about 375 mm/year. The infiltration capacity of the surface layers is high, and overland flow is normally absent or very low.

4. VARIABLES ANALYSED

Groundwater samples collected at different depths down to about 10 m below the water-table at 3 sampling sites were analysed for NO$_3^-$, Fe, SO$_4^{2-}$, NH$_4$, Cl$^-$ and tritium. Two of the sampling sites are situated on the slope of the basin about midway between the groundwater divide and the main stream, and the third site is situated near the groundwater divide as shown in Fig.1. To minimize the depth of the test holes, the sampling sites were placed in areas of shallow depth to the groundwater. The results of the analyses are given in Tables I–III and Fig.2.

Aquifer material was sampled from a cable-tool test well, Test Well No.4, placed at Dybdal, at the same site as Test Hole No.1. The aquifer material from the saturated zone (sand and gravel) was analysed for total iron, manganese, ferrous iron, sulphur and carbon. Furthermore, analyses of total iron were made of aquifer material from two existing water wells at different localities of the same aquifer. As these samples were stored under oxidizing conditions, all iron was in the ferric state. The analyses of the aquifer material are shown in Tables IV and V.

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**TABLE II. CHEMICAL COMPOSITION OF GROUNDWATER**

Site: Karup, Test Hole No. 2
Sampling: 15th-16th June, 1976

DGU Well File no 76.1144
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FIG. 2. Results of analyses of groundwater samples.
TABLE IV. ANALYSES OF AQUIFER MATERIAL

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Sampling: 1st-2nd February, 1977  DGU Well File No. 76.1181

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<td>&lt;10</td>
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<tr>
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<td>180</td>
<td>17</td>
<td>2</td>
<td>&lt;10</td>
<td>20</td>
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</table>

( ) values slightly too high due to the higher amount of ferric iron.

TABLE V. ANALYSES OF AQUIFER MATERIAL WITHIN THE REDUCTION ZONE FROM WATER WELLS IN THE KARUP AQUIFER

<table>
<thead>
<tr>
<th>DGU File No.</th>
<th>Depth in m.b.s.</th>
<th>mg/Fe per 100 g dry sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>65.490</td>
<td>17</td>
<td>360</td>
</tr>
<tr>
<td>65.490</td>
<td>18</td>
<td>200</td>
</tr>
<tr>
<td>66.1087</td>
<td>27</td>
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<tr>
<td>66.1087</td>
<td>28</td>
<td>280</td>
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</tbody>
</table>
5. SAMPLING AND ANALYSIS

A schematic outline of the equipment for groundwater sampling is shown in Fig.3. A 2-inch galvanized pipe is hammered down to the depth at which the water sample has to be taken. A 10 cm perforated interval at the lower end of the pipe allows groundwater to enter the pipe. A check valve mounted just above the perforated part allows water to enter the closed pipe. A PVC tube is placed inside the pipe with the lower orifice near the valve and the upper end projecting through a cover at the top of the pipe.

The sampling procedure consists of blowing high-pressure nitrogen into the pipe in order to press out the water from the pipe. To prevent contamination from water above or below a given depth, the pipe is emptied of water once before each sampling. After sampling, the pipe is lowered (hammered) to a new depth, and the procedure is repeated.

The sampling method described above makes sampling of groundwater possible even at greater depths and at places where electric energy is not available for power supply of pumps. In sandy material, water samples may be taken down to about 20–25 m below the surface. At greater depths, the lowering of the pipe may be problematic and time-consuming.

Water samples were taken at intervals of 1 metre in the upper 5 metres of the saturated zone and at smaller intervals (25 cm) below this depth. In the field, the samples were analysed qualitatively for \( \text{NO}_3^- \) in order to determine the sampling frequency and the total depth of the profile. Samples for laboratory determination were stored in plastic bottles and transported to the laboratory. Small samples for determination of iron and manganese were filtrated in the field through filters with a pore size of 8 \( \mu \text{m} \).

The determination of total iron was made by atomic absorption. Before determination, an amount of 1 ml of concentrated hydrochloric acid per 100 ml of water sample was added.

Aquifer material from Test Hole No.4 was sampled at intervals of 0.5 m. The vessels containing the samples were closed watertight to prevent oxidation during transportation from the field to the laboratory (2 days). On their arrival, the samples were freeze-dried.

After homogenization of the dried samples the content of total iron and manganese soluble in hydrochloric acid (20% HCl) and the ferrous iron soluble in sulphuric acid (15% \( \text{H}_2\text{SO}_4 \)) were determined. The content of total sulphur and carbon was determined by combustion in an induction furnace.

The concentrations of the various elements are shown in Tables 1–V and the profiles of Test Hole Nos. 1–3 shown in Fig.2. Special attention should be paid to the \( \text{NO}_3^-\text{N} \) and Fe profiles. In all of them, the \( \text{NO}_3^-\text{N} \) contents are rather high and variable (typically 2–10 ppm \( \text{NO}_3^-\text{N} \)). However, at Test Hole Nos.1 and 2, the \( \text{NO}_3^-\text{N} \) content decreases to zero at depths greater than 7 to 8 m below the water table. In Test Hole No.3, \( \text{NO}_3^-\text{N} \) is present in the entire penetrated interval.
Generally, the Fe content is inversely proportional to the NO$_3$-N content. At the level where the NO$_3$-N content approaches zero, the Fe content increases abruptly. Part of the Fe content is assumed to be Fe$^{3+}$ suspended in the water (particle size smaller than 8 $\mu$m). The iron concentrations from the reduction zone (1–2 ppm) at levels 7 to 8 m below the water table indicate the amount of dissolved Fe$^{2+}$ in the non-oxidized ground water in this aquifer.
The Fe and NO$_3$-N profiles of the sampled part of the aquifer at Test Hole No. 3 near the groundwater divide deviate from the distribution pattern in Test Hole Nos. 1 and 2. As the Fe content is rather low and the NO$_3$-N content relatively high, except at about 10 m below the surface, the entire profile is supposed to be situated above the reduction zone. The high Fe content and the correspondingly low NO$_3$-N content at 10 m below the surface may be due to the presence of organic matter, i.e., lignite, in this interval of the aquifer.

The SO$_4^{2-}$ content increases with increasing depth in Test Hole Nos. 1 and 2, and decreases in Test Hole No. 3.

The Cl$^-$ content varies slightly, probably due to a variation in the input concentration.

The tritium content is different at the three sites. At Test Hole No. 1, the NO$_3$-N front coincides with the tritium front, contrary to the two other profiles, where tritium concentrations of about 100–200 TU have been found both above and below the NO$_3$-front.

The total iron content of the aquifer material is about 150 to 400 mg per 100 g of dry matter. The iron profile from Test Well No. 4 indicates that the iron content decreases downwards from more than 400 mg per 100 g of dry matter at 10 m below the surface to about 150–200 mg per 100 g below the zone of oxidation, approximately 13 m below the surface or 6 m below the water table.

6. DISCUSSION OF THE RESULTS

Denitrification by Fe$^{2+}$ is possible and experimentally proved in the laboratory [4, 5]. The observations concerning ferrous iron and nitrate in groundwater show that these two elements are normally not present at the same time.

If nitrate in the groundwater is reduced to gaseous nitrogen by ferrous iron in the aquifer, the amount of Fe$^{2+}$ required is given by the equation:

$$5 \text{Fe}^{2+} + \text{NO}_3^- \rightarrow \frac{1}{2} \text{N}_2 + 5 \text{Fe(OH)}_3$$

It appears from the equation that 5 Fe$^{2+}$ can reduce 1 NO$_3^-$, and 1 mg NO$_3$-N requires $(55.85 \times 5)/14 = 19.94$ mg Fe$^{2+}$ $\sim$ 20 mg Fe$^{2+}$.

From the above-mentioned ratio, knowledge of the NO$_3^-$ concentrations in the recharge water, the amount of recharge and the reduction capacity of the saturated zone, it is possible to calculate the thickness of the oxidation zone.
As the oxidation zone is equal to the part of the groundwater zone that may be contaminated with nitrate, a calculation or a qualified estimate of the thickness of this zone is important for prediction of the advance of the nitrate front.

Initially, the authors were of the opinion that the rather sharp nitrate front about 7–8 m below water table at Test Hole Nos. 1 and 2 could be explained as a reduction of nitrate by ferrous iron in the aquifer. Therefore, it seemed obvious to investigate if the amount of ferrous iron in the aquifer was sufficient to reduce the nitrate recharged during the past. The total amount of iron in the aquifer material from the existing water wells (Table V) is about 200–360 mg per 100 g of dry matter, and if this amount of Ferric iron was oxidized by nitrate, the above-mentioned process might explain the depth of the nitrate front.

However, the analyses do not indicate that the present iron content had originally been in the ferrous state. To gain new information about this problem, Test Well No.4 was drilled (Table IV). The analyses show that the total amount of iron in the aquifer material does not deviate much from the amounts previously found. However, only about 10% are in the ferrous state. Furthermore, there are only very small amounts of other reducing elements left in the aquifer material, which means that the reducing capacity of the aquifer at Test Well No.4 seems to be rather low even at depths below the nitrate front.

The present-day input of NO₃-N to the groundwater is about 5–20 mg NO₃-N, i.e. 10 to 20 times higher than it was prior to introduction of fertilizers in agriculture. With the above-mentioned ratio and an annual recharge of 375 mm, the advance of the NO₃⁻ front should be of the magnitude of 2 m per 100 years, compare with 1–2 m per 1000 years in the past. However, this implies that the recharge water moves vertically in the saturated zone, and that the rest of the ferrous iron is available for oxidation. None of these conditions seems to be fulfilled.

The low content of ferrous iron in the reduction zone of the aquifer seems to indicate that not all the iron was originally in the ferrous state. However, if this theory is correct, it is difficult to explain how the reduction of nitrate has been possible at all. The only possibility seems to be a reduction of nitrate outside the investigation area. Further investigations are needed to throw light on this question. The presence of tritium below the NO₃⁻ front at site 2 indicates that the NO₃⁻ front is governed by reduction at this site. Unlike this, the coincidence of the NO₃⁻ front and the tritium front at site 1 may be interpreted as a result of flow-governed distribution.

The future downward advance of the NO₃⁻ front, the input conditions being equal, is likely to decrease as the thickness of the oxidation zone increases. With increasing thickness of the oxidation zone, an increasing amount of the recharged water will flow within the oxidation zone, where the NO₃-content will remain high. Consequently, the discharge to the stream may be expected to increase in NO₃-N content.
7. CONCLUSION

The chemical profiles from the water-table aquifer at Karup, Denmark, demonstrate that the saturated zone may be divided into an upper zone of oxidation and a lower zone of reduction. The oxidation zone contains nitrate but no ferrous iron, the reduction zone the opposite. This seems to indicate that iron takes part in the reduction of nitrate to free N. Analyses of aquifer material demonstrate a decrease in total iron content with increasing depth. The content of ferrous iron is approximately 10% of the total iron content without marked differences between the two zones, which appears to be inexplicable. The decreasing iron content downward in the aquifer may be explained by a groundwater dissolution and transportation of iron. Analyses of environmental tritium show that the transition zone between the oxidation and reduction zones, coinciding with the NO₃⁻ front, is controlled mostly by chemical processes near the groundwater divide and on the slopes of the basin partly by chemical and partly by flow-dynamical processes.

As the content of reducing elements, such as sulphide and carbon, in the aquifer material is very low, the content of ferrous iron seems to be the most important source of reduction.

The rather low thickness of the oxidation zone is inexplicable in connection with the low content of ferrous iron in the upper part of the reduction zone. A possible explanation may be that the reduction of nitrate has taken place upstream of the investigated profiles. However, more profiles have to be examined to determine whether or not the results are representative for the aquifer, a section of which is shown in Fig.4.

REFERENCES

PREDICTION OF POLLUTANT MOVEMENT IN GROUNDWATERS

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Abstract

PREDICTION OF POLLUTANT MOVEMENT IN GROUNDWATERS.

The paper deals with problems related to predicting the movement of some chemical pollutants in the saturated zone. A case study of pollutant source extended in area and changing in time is presented as a basis for more general discussion. It is shown that groundwater velocity is the main governing parameter in the pollutant movement. In the case under study the differences between analytical models, with a different degree of approximation, and numerical models were negligible in comparison with differences caused by inaccurate estimates of groundwater velocity. Dispensivities needed for early predictions are known with a sufficient accuracy from cataloguing published data. Satisfactory accuracy of a pollutant movement prognosis can be achieved either by calibration, if the data on the pollutant movement are available, or by tracer methods. Column experiments were performed in order to establish relative suitability of some of the radioisotope activatable or fluorescent die tracers. Theoretical considerations as well as field and laboratory experiments showed that there is a possibility of an apparent movement faster than water velocity and that the concentration of a polluting cation may exceed the initial concentration. A simple model describes this phenomenon in the front part of a pollutant plume. Relative concentrations of ions may serve as an indicator of the movement phase of a pollutant or of a salt water intrusion.

1. INTRODUCTION

The methodology of predicting the pollutant movement has recently been described in detail by Fried [1], whereas Bredehoeft and Pinder [2], Pinder [3], and Robertson and Barraclough [4] gave examples based on numerical solutions of the water flow and dispersion equations. The advantages of the numerical solutions are unquestionable, as they allow for parameters variable in time and space. Their main drawback, however, is the time needed to learn and program them. Obviously, this is not an obstacle for centres which have numerical models at their disposal, but those who start work in this field and have to solve a given problem in a short time may have difficulties. On the other hand, according to Shen [5], "experience indicates that in many field problems there are not sufficient
data available for engineers to justify the use of spatially varied aquifer properties, such as permeability, dispersion coefficients, and adsorption constant. In such cases, the problem should be studied using an appropriate analytical model without going through the time-consuming procedures normally encountered with a numerical model". Analytical solutions also improve and facilitate the understanding of the interplay of parameters.

When choosing a model and when measuring or estimating its parameters, their relative importance has to be well understood. For instance, in the case of a point and instantaneous pollutant source, the longitudinal and transverse dispersivity will be as important as the velocity.

In the case of a line source parallel to streamlines, acting for a long time, the velocity and longitudinal velocities are needed to determine the appearance time of the pollutant front. However, the transverse dispersivity is the governing factor in estimating the concentration for a steady state. Slight fluctuations of streamline directions will be accounted for by the transverse dispersivity expressed on a large scale. Distinct and long-term changes in directions may require a numerical model.

A pollutant source of large lateral dimensions permits us to neglect or put less emphasis on the transverse dispersivity, as was the case in the present work. An exception may occur if a water well is situated at the side boundary of the expected pollutant plume. In such a case the transverse dispersivity may be a governing parameter.

If the aquifer thickness is small in comparison with the distance of the pollutant movement, the vertical transverse dispersion can be neglected, because in such a case, at a certain distance from the source, the pollutant will be dispersed in the whole water height. In other cases it may be necessary to consider the problem in two or even three dimensions. In the case of pollutant undergoing ionic exchange or adsorption, the distribution constant becomes one of the governing parameters.

The above examples show that the importance of different parameters as well as the choice of an analytical model should depend on the real situation. However, it has to be remembered that an analytical solution is exact when applied to simple, or imaginary cases for controlling numerical solutions. When an analytical solution is used as a model for pollutant movement in the field it becomes an approximation.

This paper will demonstrate that a numerical model is not necessarily required; even if the velocity is variable along streamlines, the pollutant source is variable in time and space, and the hydraulic head changes from one steady state to another. However, experience shows that once a numerical model is obtained its use is more convenient because it is more automatic.

Case study of this work concerns a pollutant source of extended lateral dimensions (with transverse dispersivity of little importance), and with the injection
variable in time and space, causing a distinct change in the hydraulic head. The problem could be treated in two dimensions only, because the aquifer is relatively thin.

Works of Bredhoefst and Pinder [2], Pinder [3], Robertson and Barracough [4], and Robertson [6] are classical examples of numerical solutions. In these works the flow velocity was determined by “adjustment of the hydraulic conductivity distribution until the simulated head pattern resembles the field pattern”. However, this method may yield the same head pattern for different distributions of the hydraulic conductivity, as indicated by Gillham and Farvolden [7]. In addition, if the aquifer thickness or porosity are not well known, a large error in velocity determination may occur. In the afore-cited works long records of both hydrological data and pollutant movement existed, permitting the calibration of the models. Thicknesses were well known, with the exception of Robertson and Barracough’s work [4, 6], where the thickness was assumed to be known. In the cited work excellent agreement of calculated and observed concentrations was obtained for the eastern part of the area, whereas in the western part a large discrepancy occurred.

In this work, because of the lack of reliable data on the aquifer thickness, a numerical or physical model could not be used for determining the flow velocity. In the early stage of the work the flow velocity was calculated along each chosen streamline from the observed hydraulic head and the hydraulic conductivity known from pumping tests. It appeared also that in this case the predicted velocities had to be corrected by a factor of 1 to 3 to fit the observed pollutant movement. The difficulties mentioned above do not mean that the numerical or analytical models are not satisfactory. On the contrary, they are so good that the only practical difficulty results from limited knowledge of the hydrologic parameters. However, a word of caution is necessary when multi-parameter models are applied. First of all, as mentioned above, different distributions of parameters may yield the same output of a model. Secondly, if numerical calculations are executed, it may be quite difficult to control their physical meaning without a careful comparison with simplified situations expressed by analytical solutions. As an example let us cite here an interesting work of Pickens and Lennox [8], in which for large values of longitudinal dispersivity the results obtained suggest that the pollutant moves upstream (see Figs 5, 6 and 7 in Ref. [8]).

Methods of conventional hydrogeology are satisfactory in many respects. However, their inadequacy in the prediction of pollutant movements results from the lack of a direct method for measuring the distance flow velocity and dispersivity. Those parameters are obtainable either by calibration of models on the basis of available data on the pollutant movement, or from tracer experiments. Thus, the aims of this work are:

(1) to demonstrate the applicability of analytical models, even in complicated situations,
FIG. 1. Investigated area with hydraulic field resulting from settling operations of the reservoir.
(2) to demonstrate that the potentialities of analytical and numerical models exceed limitations resulting from a limited knowledge of hydrologic parameters,
(3) to advocate the use of tracer methods for velocity and dispersivity determinations in an early stage of studies,
(4) to compare the applicability of various tracers and thus prove the need for further search for suitable tracers.

2. HYDROGEOLOGY AND THE POLLUTANT SOURCE

A settling reservoir in an ore-processing plant is the pollutant source. The 5 km² reservoir is situated on glacial outwash material of the Quaternary age with a saturated thickness of 25 to 35 metres, in some zones probably of up to 60 metres. This material is underlain by impermeable clays. The aquifer consists of beds and lenses of fine to coarse sand and gravel with thin silt and clay interbeddings locally separating permeable zones. The hydraulic conductivity was determined from pumping tests (20 wells giving values from 0.05 to 100 m/d, 13.7 m/d on the average). In spite of the high spread of the conductivity values, neither pumping tests nor core samples permitted distinction between larger zones of higher or lower conductivity. The average estimated porosity is 30%.

The investigated area of about 30 km² has boundaries defined by the reservoir, natural drains and external streamlines. In the initial stage there were 30 observation wells in the area, whereas at present their number approaches 60. The reservoir is formed by an embankment and natural relief. Settling operations in particular zones of the reservoir were started at different times, as shown in Fig.1. In each case, beginning these operations caused a fast increase of the hydraulic gradient by a factor of about two in a few months, with subsequent relatively low fluctuations. Thus, in all further considerations these changes are treated as instantaneous ones from one steady state to another. A similar fast change is expected at the end of reservoir utilization, which originally was supposed to take place in July 1976.

The pollutant water in the reservoir has mineralization of about 8g/l-chlorides and sulphates mainly. The input net concentration, \( C_0 \), can be calculated for each streamline from the known net concentration in the reservoir, \( C_1 \), and known hydraulic gradients by applying the mass balance principle

\[
q_0 C_0 = q_1 C_1 \tag{1}
\]

and

\[
q_0 = q_1 + q_n \tag{2}
\]
where $q_0$, $q_1$, and $q_n$ are the final, injected, and natural flow rates per unit width of the aquifer, respectively. Assuming, in approximation, that changes in hydraulic head do not change the flow height, the following final expression for $C_0$ is obtained

$$C_0 = \frac{C_1 (i_0 - i_n)}{i_0}$$ (3)

where $i_0$ and $i_n$ are the final and initial (natural) hydraulic gradients.

The settling operations commenced at the embankment and thus it can be assumed that the polluted water began infiltration just there. Later the infiltration area extended upstream. The actual pollutant distribution under the reservoir is unknown, but in the calculations it is assumed that the distribution is changing linearly for each streamline from $C_0$ at the embankment to zero at the farthest reach upstream.

Observed values of $C_0$ showed a pattern predicted by Eq.(3), though they were usually about 20% higher than expected. This discrepancy should be attributed to drawbacks of the sampling technique, which did not supply properly averaged samples over the whole aquifer thickness.

The first prognosis of the pollutant movement, made in 1971, was based on the average value of hydraulic conductivity over the effective porosity, $k/n = 47 \text{ m/d}$, whereas the second one, made in 1973, was based on a value of $138 \text{ m/d}$ found from the break-through curves of $\text{Cl}^-$ measured in observation wells in the central part of the area. However, field observations performed in 1973 and 1974 showed that in the eastern part the movement was slower, whereas there was no evidence of the pollutant movement in the western part. For final calculations the distribution of $k/n$ values shown in Fig.1 was accepted. As already mentioned, it was based on pollutant observations in several wells in the central and eastern part of the area. It is clear that the acceptance of constant $k/n$ values for the streamlines is an approximation. This approximation is partly justified by the general agreement of the direction of the streamlines with the direction of the sedimentation, which was from NE to SW. A constant $k/n$ value for a given streamline results in the velocity changing proportionally to the hydraulic gradient observed along this line.

A higher density of the polluting water acts as an additional factor to the vertical dispersivity. The distance at which good vertical mixing is achieved is unknown. Three concentration profiles were measured at three points close to wells 11, 12, and 13 (see Fig.1) at the time of pollutant front passage. They showed differences in concentration at different depths not larger than 20%. These differences had no regular pattern and probably resulted from a local fingering effect. Thus a two-dimensional treatment is justified. There is, however,
another density effect: the infiltrating water barely mixes with the polluted water. Thus, the greater the distance from the reservoir the thicker is the layer of fresh water observed at the water table. This water was not accounted for in the calculations, because its significance in the mean pollutant concentration is practically negligible.

Cations of heavy metals, such as Cu, Zn, Pb and Ni, were found in the reservoir in total concentrations varying between 50 to 850 mg/m$^3$ (280 mg/m$^3$ on the average) and under the reservoir in total concentrations of 100 to 250 mg/m$^3$, but up to 1974 they did not appear in the observation wells. Thus there is no doubt that their movement is considerably delayed. As there are no data available on their distribution constants no prognosis has been possible so far. Further field investigations into these cations will be performed.

Dispersivity is an additional parameter needed for a prognosis. From data compiled by Lenda and Zuber [9] a value between 5 to 10 metres was expected for the longitudinal dispersivity. Actually, from first field observations of Cl$^-$ movement a value of 8 metres was found (see Fig.2), which agrees well with other field observations performed in the area up to now. However, Pinder [3] reported 21.3 m for a similar geological formation, which on the other hand is not very different from the value given here.

**FIG.2.** An example of field data from two observation wells situated on the same streamline compared with analytical and numerical curves.
3. METHODS OF CALCULATION

Calculations were performed in four ways:

(1) The distance travelled by water along a given streamline is calculated for a
given time and then the pollutant spread is found from corresponding graphs
or numerical values of the known solution of Ogata and Banks [10]. Calcula-
tions for side streamlines are performed with the aid of the analytical
solution for a continuous injection on a line, allowing for the lateral disper-
sion. This analytical solution can easily be obtained by applying the
"Product law" [9, 11, 12]. Next, front concentration isopleths of a given
nonretarded ion can be easily drawn. When the settling operation ends it is
assumed that the hydrodynamic field returns to the initial steady state
(cf. Section 2) and the pollutant plume moves along new streamlines (natural
streamlines observed before the use of the reservoir). The front disperses
further, whereas the back of the plume is already so flat (cf. Section 2) that
it is assumed that a given concentration moves with a velocity equal to that
of the water. This method of calculation is called the rough approxima-
tion.

(2) Similarly, each streamline is divided into sections defined by equipotentials.
However, concentration given by the analytical solution at the end of a section
serves as an input function for the next section. This method requires
computer calculation. Calculations for side streamlines are performed with the
aid of an analytical solution allowing for the transverse dispersivity. This
method, further called the analytical approximation, is described in detail
by Małoszewski [12].

(3) The computer program of Małoszewski [12] for the analytical approximation
does not permit taking into account a change of the hydrodynamic field at
the end of settling operations. Thus, if a change takes place, a further pollutant
movement has to be calculated with the aid of the rough analytical approxi-
mation as described above.

(4) A two-dimensional numerical solution of the general dispersion equation given
in the tensor form by Bear [13] has been obtained by the finite difference
method. Components of the velocity vector and of the dispersivity tensor
were calculated in orthogonal co-ordinates just as in the works of Reddel
and Sunada [14], and Pickens and Lennox [8]. The Crank-Nicolson scheme
was used as described by Rosenberg [15]. In this scheme the space deriva-
tes are taken as arithmetic means of the centred-in-distance difference approxi-
mations calculated for two time levels. The time derivative is expressed as
the forward difference approximation. The whole area was covered with a
regular rectangular net of 2964 nodes. Details of this model are given
elsewhere [16].
4. RESULTS OF CALCULATIONS

An example of typical experimental and calculated breakthrough curves is given in Fig. 2. Concentration isopleths of 250 mg of Cl⁻ per litre were calculated in the whole area for each four years up to 1996, using all four methods described in Section 3. A simplified map for July 1976 and 1984, calculated under the assumption that the settling operation would end in 1976, is shown in Fig. 3. The water table of Fig. 1 was assumed up to July 1976, and thereafter that of Fig. 3 was taken for calculations. This field was observed before the settling operations and will presumably be observed again on their conclusion, as discussed in Section 2.

In general, an excellent agreement of all the calculating methods and experimental data was achieved. In particular, an astonishing agreement of the rough approximation with the numerical model is observable. It should be stressed that this rough approximation was obtained three years prior to the numerical results, in an early stage of the study. The differences between the particular calculating methods are smaller than differences between the calculated and observed values (Sept. 1976). These differences between the calculated and observed values mainly result from a limited knowledge of the input function at the side boundaries and from a large-scale fingering effect, as can be seen in Fig. 3 for the western and eastern parts of the area. In fact, the initial fingering in the western part was so strong that, accidentally, the pollutant plume omitted observation wells in the first line and as a result there was no experimental evidence to calibrate the models in this part up to 1975.

However, when comparing the calculated and the observed concentrations, it has to be remembered that the calculations shown in Fig. 3 were performed for calibrated models, i.e. the k/n values were fitted to the pollutant velocities observed in 1973 and 1974 in the central and eastern parts of the area, as described in Section 2. In other words an early prognosis based on uncalibrated models showed differences much larger than those seen in Fig. 3. Thus, a need for direct methods of flow velocity measurement becomes evident, as already mentioned in Section 1 and as discussed later in Section 6.

5. MOVEMENT OF EXCHANGEABLE IONS

Calcium, sodium and, to a certain degree, also potassium and magnesium are the main cationic constituents of the pollutant. It is well known (see Ref. [17]) that when a simple instantaneous equilibrium, linear adsorption model is used the movement of cations undergoing exchange is delayed by a factor
C(Cl) $\geq 250$ mg/l

YEAR 1976
- - - - ANALYTICAL APPROXIMATION
- - - - - - NUMERICAL
- - - - - - - - OBSERVED

YEAR 1984
- - - - - - - - ROUGH ANALYTICAL APPROXIMATION
- - - - - - - - - - NUMERICAL

FIG. 3. Isopleths of 250 mg of Cl$^-$ per l observed in 1976 and calculated from different models for 1976 and 1984.
FIG. 4. A field example of the movement of exchanging cations compared with the theoretical model.

\[ K_f = \left(1 + \frac{1-n}{n} \rho \right) K_d \]  \hspace{1cm} (4)

where

- \( K_f \) is the delay factor,
- \( n \) is the effective porosity,
- \( \rho \) is the solid matrix density,
- \( K_d \) is the distribution constant defined as the ratio of concentration in the solid phase expressed in g/g to concentration in the liquid phase expressed in g/cm\(^3\).

Field observations showed a delay of Na\(^+\) and K\(^+\) and an apparent faster movement of Ca\(^{++}\), as can be seen from a typical example given in Fig. 4. Assuming that the increase of Ca\(^{++}\) concentration is caused by the exchange of Na\(^+\) and K\(^+\) with Ca in the solid phase one can write

\[ C(Ca) - C_{ap}(Ca) = C_{ap}(Na + K) - C(Na + K) \]  \hspace{1cm} (5)
where all the concentrations are expressed in meq, and $C_{ap}$ means an apparent concentration which would be observed if there were no cationic exchange, i.e.

\[
C_{ap}(Ca) = C_0(Ca) \left( \frac{C}{C_0/Cl} \right)
\]

(6a)

and

\[
C_{ap}(Na + K) = C_0(\text{Na} + \text{K}) \left( \frac{C}{C_0/Cl} \right)
\]

(6b)

Putting Eqs (6) to Eq (5) and rearranging, one gets

\[
\left( \frac{C}{C_0/\text{Ca}} \right) = \left( \frac{C}{C_0/Cl} \right) + \frac{C_0(\text{Na} + \text{K})}{C_0(\text{Ca})} \left[ \left( \frac{C}{C_0/Cl} \right) - \left( \frac{C}{C_0/\text{Na} + \text{K}} \right) \right]
\]

(7)

milliequivalent.

In Fig. 4 the Na$^+$ + K$^+$ curve is obtained from the Cl$^-$ curve using Eq. (4), whereas the Ca$^{++}$ curve is calculated from the Na$^+$ + K$^+$ and Cl$^-$ curves using Eq. (7). The agreement between the theoretical curves and experimental data is within the
FIG. 6. Results of a laboratory experiment, confirming field results of Figs 4 and 5.

accuracy of the latter (cf. Section 3). In Fig. 5, a comparison of predicted curves with the experimental data for the observation well P12 is given. The theoretical model given by Eqs (4) and (7) was also confirmed in a column experiment, shown in Fig. 6, in which the accuracy of concentration determinations is better than that in the field. In this experiment a typical granular material from the observation field was used. Its chemical composition was as follows: SiO₂ = 98.14%, Fe₂O₃ = 0.42%, Al₂O₃ = 0.97%, CaO = 0.18%, MgO = 0.08%, burning loss = 0.64%. Its grain-size composition was: fraction below 0.05 mm = 1%, 0.05 to 0.25 mm = 15%, 0.25 to 0.5 mm = 25%, 0.5 to 2 mm = 42%, and 2 to 10 mm about 17%. The coefficient of uniformity U = d₆₀/d₄₀ = 4.5. The length of the column was 145 cm, porosity 30.7%, and water content 29.1%. The cation exchange capacity of this material was 1.6 meq/100 g. Other relevant data are given in Fig. 6, whereas total breakthrough curves can be seen in Fig. 7. As expected, the simple model of Eqs (4) and (7) does not describe the back part of the breakthrough curves (reverse exchange). The phenomenon is not symmetrical, as a fast decrease of concentration of Ca²⁺ and Na⁺ + K⁺ in the liquid phase cannot be compensated by a low concentration of Na and K in the solid phase. Na and K are slowly released from the solid phase at the expense of the background Ca²⁺ concentration showing a long, negative tailing effect.
FIG. 7. Complete breakthrough curves for the laboratory experiment. Note different behaviour of exchanging cations in front and back parts.

This whole exchange effect is interesting not only because of the previously unknown apparent faster movement of Ca\(^{2+}\) with the maximum concentration exceeding the initial concentration, but also because of its practical importance. Namely, when at chosen directions new wells were drilled or samples taken, the determination of the relative concentrations of Cl\(^-\), Ca\(^{2+}\) and Na\(^+\) from a single observation permitted a distinction to be made between the passage of the pollutant front from the saturation and from the retreat phase.

Similar phenomena should be observed in regions of salt water intrusions, especially if there are changes in the direction of their movement (forward or backward). In other words, the actual direction of their movement can be detected from a single chemical determination. First results of the observations performed by Kleczkowski and Nguyen-Manh-Ha [18] at the region of salt water intrusions from the Baltic Sea confirm this hypothesis.

In the experiment shown in Fig. 7 \(^{45}\)Ca\(^{2+}\) was used to trace the behaviour of calcium ions. The distribution constant calculated from Eq.(4) for this experiment is

\[
k_d(45\text{Ca}) = 0.17 \ \frac{\text{cm}^3}{\text{g}}
\]
and the concentration in the solid phase, involved in the exchange process

\[ k_d C_0 (Ca) = 1.2 \times 10^{-4} \frac{g}{g \text{ of soil}} \]

All this means that calcium ions undergo cationic exchange with calcium in the solid phase. As a result, the bulk movement of calcium is unretarded, but the movement of particular calcium ions is retarded and about 10% of calcium in the solid phase is involved in the exchange process. The distribution constant of sodium found from the field data (Figs 4 and 5) is

\[ k_d (Na + K) = 0.023 \frac{cm^3}{g} \]

which means that the increase of \( Na + K \) concentration in the solid phase during the passage of the pollutant plume is

\[ \Delta q (Na + K) = C_0 (Na + K) k_d = 3 \times 10^{-5} \frac{g}{g \text{ of soil}} \]

It may be interesting to note that \(^{40}\text{Ca}^+\) shows also a long tailing effect but its physical meaning differs from that of \( \text{Ca}^{++} \), as discussed earlier.

6. TRACERS

Considerations outlined in Sections 1 and 4 clearly show that a good prognosis can be achieved only if the model is properly calibrated. There is no problem with the calibration if there is experimental evidence concerning the movement of a pollutant in a given geological formation. Tracer methods may be advisable if the model cannot be calibrated directly because of the lack of data on the pollutant movement.

Recent development of single-well methods makes them promising for Darcy velocity measurements. The reader is referred to works of Halevy et al. [19], Drost and Neumaier [20], and Drost et al. [21]. In this section the discussion will be limited to tracers for the multi-well method, consisting in injecting a tracer in one or several wells, and observing its passing to other wells situated downstream. Before going to discussion on tracers an important fact has to be stressed. Namely, inspection of the transport equation shows that if the distance velocity is measured (the multi-well method) the porosity has to be known only for prediction of the pollutant concentration (see Kreft and Zuber [22]). However, if the Darcy velocity is measured, the porosity is also needed for a proper prediction of the pollutant spread for a given time.
FIG. 8. Laboratory experiment showing the behaviour of uranin in the polluted water. Dashed line denotes an ideal, undispersed tracer.

Tracers for the multi-well method to be used on a large scale should be conservative (within the time scale of the experiment), cheap, easy to handle and easily detected in low concentrations (not necessarily in the field). The authors' experience obtained in other fieldwork shows that the choice of a tracer should permit easy sampling even by an unqualified person and the sample volume should not exceed a few tens of ml's. This remark concerns tracer experiments for a distance scale of a few hundred metres and for a time scale of a few months and more. The above requirement is met only by tritium and fluorescent dyes. Tritium is an ideal tracer for groundwaters, with some well known exceptions, e.g. see Ref.[23]. The use of artificial tritium may, however, be opposed by environmental isotope specialists. In cases similar to that presented in this paper, where deeper aquifers are well separated and the investigated aquifer discharges completely to surface waters at a short distance, the use of artificial tritium should be acceptable, if other tracers are not satisfactory.
Fluorescent dyes, especially uranin and eosin, have been successfully applied for many years in groundwater investigations in the Federal Republic of Germany (e.g. see Ref. [24]), and their detectability has recently been notably improved by Behrens [25]. However, laboratory experiments performed on the material described in Section 5 showed a considerable delay of both uranin and eosin, as can be seen in Figs 8 and 9, and Table I. Figure 8 shows the behaviour of the uranin when it is used to trace mineralized water from the settling reservoir (cf. Section 2). It is not known which constituent of the pollutant causes such a strong adsorption, but there is no doubt that in this case uranin cannot be used as a tracer for the polluted water. Other experiments shown in Fig.8 and Table I were performed with fresh water, and the delay observed for uranin may in some cases be acceptable, whereas the delay of eosin seems to be unacceptable. It has to be remembered that in materials finer than those used here the delay may be higher, whereas in coarser materials it may be lower.

The above considerations clearly show that both tritium and fluorescent dyes have their limitations. Thus, further search for suitable tracers is needed. Here some radioisotope and activatable tracers will be discussed. Hanson [26] considered a number of elements in EDTA and DDTA complexes.
### TABLE I. COMPARISON OF DIFFERENT TRACERS IN COLUMN EXPERIMENTS

<table>
<thead>
<tr>
<th>Meas. No.</th>
<th>Tracer&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Conc. (mg/m&lt;sup&gt;3&lt;/sup&gt;)</th>
<th>Delay&lt;sup&gt;b&lt;/sup&gt; factor</th>
<th>Recovery (%)</th>
<th>C&lt;sub&gt;max&lt;/sub&gt; C&lt;sub&gt;0&lt;/sub&gt;</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cl&lt;sup&gt;-&lt;/sup&gt;</td>
<td>2 X 10&lt;sup&gt;6&lt;/sup&gt;</td>
<td>1.00</td>
<td>100 ± 1</td>
<td>1.00</td>
<td>7.1</td>
</tr>
<tr>
<td>4</td>
<td>Cl&lt;sup&gt;-&lt;/sup&gt;</td>
<td>0.5 X 10&lt;sup&gt;6&lt;/sup&gt;</td>
<td>1.01</td>
<td>98 ± 2</td>
<td>1.00</td>
<td>about 7</td>
</tr>
<tr>
<td>2</td>
<td>K&lt;sub&gt;2&lt;/sub&gt;Co CN</td>
<td>4.0</td>
<td>1.03</td>
<td>97 ± 2</td>
<td>0.98</td>
<td>about 7</td>
</tr>
<tr>
<td>7</td>
<td>114mIn-EDTA</td>
<td>0.47 X 10&lt;sup&gt;3&lt;/sup&gt;</td>
<td>1.22</td>
<td>98 ± 2</td>
<td>0.98</td>
<td>6</td>
</tr>
<tr>
<td>8&lt;sup&gt;d&lt;/sup&gt;</td>
<td>114mIn-EDTA</td>
<td>0.47 X 10&lt;sup&gt;3&lt;/sup&gt;</td>
<td>1.27</td>
<td>85 ± 3</td>
<td>0.85</td>
<td>8</td>
</tr>
<tr>
<td>4</td>
<td>131I&lt;sup&gt;-&lt;/sup&gt;</td>
<td>1.6 X 10&lt;sup&gt;-5&lt;/sup&gt;</td>
<td>1.13; 1.04</td>
<td>82 ± 2</td>
<td>0.81</td>
<td>about 7</td>
</tr>
<tr>
<td>5</td>
<td>131I&lt;sup&gt;-&lt;/sup&gt;</td>
<td>10</td>
<td>1.12; 1.04</td>
<td>96 ± 2</td>
<td>0.98</td>
<td>about 7</td>
</tr>
<tr>
<td>3</td>
<td>60Sc-EDTA</td>
<td>0.5</td>
<td>1.33; 1.46</td>
<td>92 ± 2</td>
<td>0.83</td>
<td>about 7</td>
</tr>
<tr>
<td>6&lt;sup&gt;d&lt;/sup&gt;</td>
<td>60Sc-EDTA</td>
<td>8.0</td>
<td>1.18; 1.24</td>
<td>90 ± 2</td>
<td>0.90</td>
<td>about 6.5</td>
</tr>
<tr>
<td>1&lt;sup&gt;c,d&lt;/sup&gt;</td>
<td>Uranin</td>
<td>5.0</td>
<td>2.5 (front)</td>
<td>97 ± 10</td>
<td>1.83</td>
<td>7.1</td>
</tr>
<tr>
<td>2&lt;sup&gt;c,d&lt;/sup&gt;</td>
<td>Uranin</td>
<td>5.0</td>
<td>1.32; 1.47</td>
<td>87 ± 5</td>
<td>0.76</td>
<td>about 7</td>
</tr>
<tr>
<td>4&lt;sup&gt;d&lt;/sup&gt;</td>
<td>Uranin</td>
<td>10.0</td>
<td>1.36</td>
<td>99 ± 5</td>
<td>0.96</td>
<td>about 7</td>
</tr>
<tr>
<td>5&lt;sup&gt;d&lt;/sup&gt;</td>
<td>Uranin</td>
<td>10.0</td>
<td>1.46</td>
<td>98 ± 5</td>
<td>0.94</td>
<td>about 7</td>
</tr>
<tr>
<td>3&lt;sup&gt;c,d&lt;/sup&gt;</td>
<td>Eosin</td>
<td>100</td>
<td>2.0</td>
<td>90 ± 2</td>
<td>0.80</td>
<td>about 7</td>
</tr>
</tbody>
</table>

<sup>a</sup> Concentration of metal is given in the case of EDTA. Molar ratio of EDTA to metal was 10:1.

<sup>b</sup> In the case of different delays of front and back both values are given.

<sup>c</sup> In these experiments traces of organic matter in effluent were observed. In other experiments the column was washed with a solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O.

<sup>d</sup> Distinct tailing effect.

Radioisotopes of In and Sc shown in Table I seem to be acceptable for medium-scale experiments. These elements in the stable form seem to be adequate both for medium and large-scale experiments. If the activatable form is used, the background concentration can be reduced. However, as can be seen from Table I, the behaviour of these isotopes is not better than that of the dyes. It has to be mentioned here that in the course of the authors' experiments sporadic contamination of sampling vials was observed, which also shows a susceptibility of these tracers to adsorption. Cr-EDTA is known as a good tracer [23], but its activation parameters are not so good as those of In, Sc, Co or others.

Hexacyanocobaltate seems to be the best complex tracer both in the active and inactive form, though it also shows a slight delay in comparison with Cl<sup>-</sup>, which was used as a reference tracer.
Iodine as an activatable tracer is not very promising (cf. also Ref. [27]), but may be acceptable under favourable conditions. Bromine is well known for its good tracer characteristics. However, its use is limited by a high natural background. Commercially pure bromide is very cheap and its use as an activatable tracer may be acceptable in cases where large quantities of tracer can be injected without causing serious disturbances of the hydrodynamic field. However, it should be remembered that the use of activatable tracers usually requires a large sample volume (100 ml to 10 l), and enrichment procedure. Easy access to an activation analysis laboratory is indispensable.

7. CONCLUSIONS

The discussion in Section 1 and results given in Section 4 clearly show that the differences between analytical and numerical models are smaller than those resulting from an insufficient accuracy of the measurements or estimations of the relevant hydrological parameters. Thus, further progress of methods for determining these parameters seems to be essential in predicting pollutant movement in groundwaters. Tracer methods offer a unique opportunity in this respect. The main parameter to be measured is the distance velocity. Whenever possible the dispersionsities should be determined as by-products of tracer experiments. However, in many cases dispersionsities known from cataloguing the published data are sufficient, especially for a prognosis in an early stage. It is the authors' feeling that some investigators put too much emphasis on single-well tracer methods for determining dispersionsities.

In the study presented in this paper high accuracy of the models was achieved by calibration. Had the tracer experiments been performed in the late sixties, the same accuracy of prognosis would probably have been obtained much earlier. Unfortunately, there are two obstacles to the use of tracers for such purposes: One results from a general lack of understanding of tracer methods and their advantages, the other is related to the limited number of reliable tracers at the disposal of the experimenter, as discussed in Section 6. Further search for tracers which might be used for groundwater pollution studies, as well as further development of tracer methods, as proposed for instance by Hibsch and Kreft [28], should be recommended.

The ratio of the concentrations of exchangeable cations may serve as an indicator of the movement phase or, in the case of salt water intrusions, as indicator of the direction of the front movement.
ACKNOWLEDGEMENTS

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REFERENCES

[22] KREFT, A., ZUBER, A., "Remarks on the interpretation of tracer experiments in groundwaters", these Proceedings.
[28] HIBSCH, G., KREFT, A., "On the determination of aquifer characteristics by the multiwell method", these Proceedings.
GROUNDWATER POLLUTION CONSIDERED AS A CONTINUOUS INJECTION OF TRACERS

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Abstract

GROUNDWATER POLLUTION CONSIDERED AS A CONTINUOUS INJECTION OF TRACERS.

The Bavarian Geological Survey has been investigating for more than 10 years the extent and range of groundwater contaminants derived from a domestic and industrial refuse tip. The results of investigations have shown that contaminated groundwater traveled at least 5000 m. The investigation involved a general survey of electrical conductivity and groundwater temperature as well as supporting evidence of pollution by analysis for chloride, permanganate value and nitrate. A network of about 80 observation points had been installed. The sampling points were so placed that some gave slight and variable indications of possible contamination and others none at all. The frequency of observation of such a network over a long period must be chosen such that all variables, as well as overall trends, are known. As results showed, the chloride components increased sharply in groundwater passing under the tip. Chloride in the underflow cannot be removed and its concentration is reduced only by dilution. The investigations showed a relationship between electrical conductivity of groundwater and chloride concentration. On this basis, the chloride concentration, as indicated by electrical conductivity, allowed the path of the pollution to be traced throughout the zone in which the organic components and the nitrate were decaying or already decayed. A comparison of the direction of groundwater flow with the distribution of chloride and electrical conductivity shows very good agreement. Increased electrical conductivity could always be followed along a line of observation points. These bores mark the main path of the polluted groundwater and hence the direction of groundwater flow. Other bores, for example, stand on the edge of the polluted stream and therefore show great variations in conductivity. A comparison of electrical conductivity and its variation at different times shows the change of flow direction for a certain period. The investigation established that the direction of groundwater flow and its changes could certainly be traced over a distance of more than 5000 m. The hope of thus being able to follow certain maxima from bore to bore, and hence to obtain an indication of the flow velocity, was not fulfilled.

1. INTRODUCTION

The landfill site at Grosslappen lies to the north of Munich, where the effects of household refuse on the properties of groundwater have been investigated by the Bavarian Geological Survey since 1967 [1–3]. The aim of the investigation has been to investigate the spreading and range of contamination from the tip,
which was first started in 1954 on a porous groundwater aquifer without sealing the base. Moreover, the investigation had to be undertaken by means of existing hydrogeological profiles [3] (Figs 1 and 2) to calculate a materials balance in order to find out what quantities of Cl\(^-\), SO\(_4\)^{2-} and NO\(_3\)^- were evolved from the tip and how much is decomposed underground. To assist in this, the Institute for Radiohydrometry in Munich was commissioned to carry out measurements with radioactive isotopes using the single-borehole method [4, 5] in order to determine the Darcy velocity and the direction of flow at each observation point.

To arrive at a materials balance it is necessary to find out the quantity of water flowing in unit time through a particular cross-section of the flow path. Therefore the effective pore area of the section and the field velocity of the groundwater were required. A useful estimate of the average area of the effective pore cross-section can be made if reliable values of the Darcy velocity and the field velocity of the groundwater are known.

2. INVESTIGATION OF THE DARCY AND FIELD VELOCITY OF GROUNDWATER

The aquifer is composed of fluvioglacial, sandy gravels which in part have been redeposited many times by the Isar. For this reason, the permeability fluctuates greatly. This is true for the effective porosity and also for the groundwater flow velocity. Values for the permeability (k) that have found use in many cases lie between \(3.5 \times 10^{-3}\) and \(5 \times 10^{-3}\) m/s. The gradient lies between 2.5 and 4\%. From the Darcy equation,

\[
V = k \times 1 \times 86400
\]

where \(V\) is the Darcy velocity (m/d), \(k\) is the permeability (m/s) and \(l\) is the groundwater gradient (\%), values of \(V\) between 0.7 and 1.7 m/d are obtained, which can be regarded only as average values showing order of magnitude. Drost of the Institute of Radiohydrometry [4] has measured values of \(V \approx 0.6\) m/d close to the tip. Further afield, the values vary quite widely between about 0.2 and 5.5 m/d, depending upon whether the medium is sandy gravel, silt or coarse sand. With such a heterogeneous aquifer it was very difficult to estimate what represented a good mean value for the field velocity since a reliable value for the effective pore cross-section area was not available. Therefore, the Institute for Radiohydrometry was again commissioned to carry out test measurements to
FIG. 1. Distribution of sampling bores and location of cross-sections.
FIG. 2. Cross-section A: hydrogeology, chloride concentration and electrical conductivity. See also Table II.
TABLE I. FIELD VELOCITY OF GROUNDWATER

<table>
<thead>
<tr>
<th>Flow interval</th>
<th>Distance (m)</th>
<th>( V_{\text{max}} ) (m/d)</th>
<th>( V_{\text{mean}} / \text{m (d)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nos. 18-21</td>
<td>310</td>
<td>107</td>
<td>54</td>
</tr>
<tr>
<td>Nos. 18-36</td>
<td>1200</td>
<td>46</td>
<td>23</td>
</tr>
<tr>
<td>Nos. 18-40</td>
<td>1850</td>
<td>37</td>
<td>22</td>
</tr>
<tr>
<td>Nos. 18-53/54</td>
<td>2700</td>
<td>37</td>
<td>25</td>
</tr>
</tbody>
</table>

ascertain the field velocity. At the first attempt, since the flow path of the
groundwater was known, only 300 g of eosin in aqueous solution was introduced
at observation point No.18 and dispersed with 10 l of water. The results shown
in Table I were obtained by Behrens [6]:

In the second test by Behrens and Rauert the tracer was fed into the
upstream of the tip at observation point No.66. Since the groundwater had to
pass the reduction zone [7, 8, 9], it was considered that an organic dyestuff such
as eosin might undergo change or destruction by prevailing chemical or biological
processes. Therefore tritiated water containing 3.5 Ci of tritium was added to
5 kg of eosin in aqueous solution. The results were as expected, with the eosin
being markedly attenuated through the reduction zone so that only the tritium
measurements could be used for calculation. After a period of observation of
4.5 months, the tritium plume had travelled 3 km and stretched more than
2.5 km in the direction of flow, with a minimum width of 70 m. The maximum
tritium concentration of \( 2.5 \times 10^{-5} \) μCi/ml (ca. 8000 TU) was well below the
maximum permitted level for groundwater. The field velocity thereby obtained
was about 8 m/d at the tip and about 21 m/d downstream.

It was not surprising that relatively low values were obtained for Darcy and
field velocity on the northern edge of the tip and close downstream. In this region
both the reduction zone and intermediate oxidation zone of the groundwater are
strongly marked. In these zones the precipitation of iron sulphide and hydroxide
occur respectively and can eventually diminish the effective pore volume and
therefore also the permeability of the aquifer. An increase in field velocity does
not follow from this because the greater part of the groundwater follows the more
accessible route past the tip, without the gradient in the vicinity of the tip
noticeably changing. The quantity of water that flows under the tip, however,
is decreased.

The results given here show that not only radioactive tracers, but also organic
dyestuffs like eosin can be successfully used in the estimation of field velocity
under a waste disposal site. If the flow direction is known, only small amounts
need be used, although in the region of the reduction zone the usefulness of
organic dyestuffs has yet to be proved.
<table>
<thead>
<tr>
<th></th>
<th>Bore No.</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5a</td>
<td>13</td>
<td>9</td>
<td>14</td>
<td>Upstream mean values (Nos. 6, 10, 11, 12)</td>
<td>Date of measurement</td>
</tr>
<tr>
<td>1</td>
<td>Ground level</td>
<td>m AOD</td>
<td>490,64</td>
<td>488,43</td>
<td>488,29</td>
<td>488,60</td>
</tr>
<tr>
<td>2</td>
<td>Groundwater level</td>
<td>m AOD</td>
<td>486,67</td>
<td>486,56</td>
<td>486,38</td>
<td>486,32</td>
</tr>
<tr>
<td>3</td>
<td>Groundwater base</td>
<td>m AOD</td>
<td>485,84</td>
<td>484,68</td>
<td>484,49</td>
<td>484,30</td>
</tr>
<tr>
<td>4</td>
<td>Groundwater depth</td>
<td>m AOD</td>
<td>0,87</td>
<td>1,88</td>
<td>1,91</td>
<td>2,02</td>
</tr>
<tr>
<td>5</td>
<td>Groundwater temperature °C</td>
<td>at 20°C</td>
<td>8,0</td>
<td>11,5</td>
<td>17,5</td>
<td>15,0</td>
</tr>
<tr>
<td>6</td>
<td>Electrical conductivity</td>
<td>m S/cm</td>
<td>1,15</td>
<td>2,11</td>
<td>1,91</td>
<td>1,22</td>
</tr>
<tr>
<td>7</td>
<td>Cl⁻-concentration</td>
<td>mg/l</td>
<td>186,0</td>
<td>307,7</td>
<td>292,2</td>
<td>178,0</td>
</tr>
<tr>
<td>8</td>
<td>SO₄²⁻-concentration</td>
<td>mg/l</td>
<td>83,3</td>
<td>105,3</td>
<td>53,1</td>
<td>53,3</td>
</tr>
<tr>
<td>9</td>
<td>NO₃⁻-concentration</td>
<td>mg/l</td>
<td>93,0</td>
<td>3,0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>Distance</td>
<td>m</td>
<td>120</td>
<td>190</td>
<td>130</td>
<td>-</td>
</tr>
</tbody>
</table>
POLLUTION AS CONTINUOUS INJECTION

If the persistent pollutants evolved from a waste tip are regarded as tracers, not only the width and range [2, 3] of the polluted groundwater stream can be defined, but also its fluctuations in flow direction and lateral displacement. During the ten years of observation of the contaminated groundwater, two or three samples from each observation point have been chemically analysed each year. In order to monitor possible variations in groundwater properties, electrical conductivity and temperature were measured every 14 days at all observation points. An abundance of data was therefore available about changes in groundwater flow direction, which would not have been possible using conventional methods.

3. HYDROGEOLOGICAL AND CHEMICAL RESULTS FOR THE NORTH EDGE

Pollutants reaching an aquifer from a waste tip are diluted by the groundwater and transported in the direction of flow. How far a pollutant can be followed depends not only upon hydrogeological properties such as flow velocity and groundwater depth, but also upon chemical properties, i.e. whether the particular pollutant undergoes decomposition or adsorption besides losing concentration by dilution. Results for the north edge of the tip indicate the following:

The hydrogeological profile along the line of observation points 5a, 13, 9 and 14 (Fig.2) showed that there was comparatively little groundwater. The depth of the filled portion of the aquifer was between 0.8 m (No.5a) and 2.2 m (No.14). The total porosity was about 20%, with effective porosity in the range 10–15%.

Figure 2 compares chloride concentration with electrical conductivity for the particular hydrogeological profile. Mean upstream values are given by the broken horizontal baseline. The quantity of chloride acquired by the groundwater on passing beneath the tip is represented by the shaded area; similarly also for the electrical conductance and temperature of the groundwater (Fig.3). The similarity between the curves for conductivity and chloride shows that the latter was the principal dissolved ionic constituent. The conductivity can therefore be taken as a measure of the chloride component or, for that matter, as the general inorganic loading of inorganic pollution of the groundwater.

The spatial distribution of temperature increase (Fig.3) differs clearly from that of chloride content and electrical conductance in that the maximum is displaced from observation point No.13 in the direction of Nos 9 and 14. The different distributions show that the inorganic loading increases towards the centre of the tip, whereas the exothermic biological reactions occur most intensely in the NE part. That this was where there was most organic matter was indicated
FIG. 3. Cross-section A: temperature, nitrate and sulphate concentration in the reduction zone. See also Table II.
by the reduction of nitrate and partial reduction of sulphate in that region of the aquifer. The rise in nitrate value from 29 to 93 mg/l at point No. 5a was not due to effluent from the tip, but to intensive agriculture on directly adjoining land to the west.

At point No. 13 the nitrate concentration for 5th May 1971 was 3 mg/l, but the temperature curve suggests that the actual nitrate distribution between points 13, 9 and 14 might have been as shown by the dashed line rather than the continuous one. This would have meant that in the reduction zone between points 13, 9 and 14, all the nitrate present in the groundwater was moved a distance of about 310 m. Furthermore, from the run of the curves for temperature rise and nitrate concentration, it appears that the reduction zone did not end at point No. 14, but continued eastward. Likewise for the sulphate, the values for observation points 5a, 13, 9 and 14 are shown by the continuous line in comparison with the mean upstream value. The dotted line indicates the values of sulphate calculated on the basis of the chloride and conductance values without reduction occurring. As with nitrate, the actual concentration of sulphate between points 13 and 19 may have followed approximately the dashed line shown. This means that between points 5a and 13, a clear increase of sulphate concentration from the tip had occurred in the groundwater, while between points 13, 9 and 14 the concentration had been reduced by biological sulphate-reduction to less than the upstream value. The sulphate consumption is shown in this single section by the area lying between the dotted line and the lower of the estimated downstream values.

4. FLOW PATH OF GROUNDWATER

Direction of flow in groundwater is generally indicated from groundwater contours as the most direct path down the gradient, but the exactness with which this can be defined in local areas depends on the density of the observation grid. Figure 4 shows a good agreement between groundwater contours and the flow direction as indicated by the contour for electrical conductance.

Being largely unaffected by biological decomposition and sorption, chloride is the only major component draining from the waste tip that can be followed in the groundwater over large distances. However, a qualitative indicator for the path of significant concentrations of organic pollution is the absence of dissolved oxygen.

The two-weekly measurements of electrical conductivity provided an almost unbroken record of the spread and flow path of the contaminated groundwater. The significance of these data is considered from the following three aspects:
FIG. 5. Electrical conductivity maxima in groundwater.
FIG. 6. Lateral displacement of electrical conductivity maxima.
5.1. Displacement of maxima with time

Figure 5 shows the routes of conductivity maxima on various occasions during the investigation. Figure 6 shows the range of fluctuation for two periods, 1971–72 and 1971–75.

5.2. Distribution of electrical conductivity across flow path

Figure 7 shows the conductivity values measured across the W-E section through observation points 33 to 38. It can be clearly seen that the polluted stream shifted laterally in both directions during the observation period. Similar information is given in Fig.8 for the section through points 22 to 27. These W-E profiles show only point values and it would be only by chance if the actual maxima occurred precisely at an observation point.

5.3. Succession of conductivity

Figures 9 and 10 show the succession of conductivity values for several observation points during the hydrological year from 1 November to 31 October. An advantage of this representation is the ability to observe the rate of change of conductivity relative to a given observation point. For example, the two adjacent points Nos 24 and 39 showed only slight difference during August, which would be an indication that the maximum that lay between them was either very broad and of similar value to that measured, or sharply peaking to a much higher value, but with little lateral shifting.

The rapidity with which a maximum can shift from one position to another and immediately return is indicated by point 34 in Fig.9 for the first half of the time. This point showed a sharp rise in conductivity after the middle of April from 500 $\mu$S/cm to over 1500 $\mu$S/cm, falling to about 1000 $\mu$S/cm in mid-July and then increasing again for about 1.5 months to 1500 $\mu$S/cm. If it is assumed that the conductance varied more or less continuously between measurements, the following deductions may be made:

The polluted groundwater stream had drifted eastward from point No.34 after about mid-February and indeed so far that between 12–24 April 1972, it exerted no influence at all at that point of observation. The polluted stream then shifted back again westward and affected point No.34 ever more strongly until 5 June, when the maximum moved from point No.35 where it had been since December 1971. This state lasted about 10 days, after which the maximum moved to point No.35. Only between 8 August and 23 September was the maximum observed again at point No.34.

Text continued on p.101
<table>
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<tr>
<th>Bore No.</th>
<th>43</th>
<th>33</th>
<th>34</th>
<th>35</th>
<th>36</th>
<th>37</th>
<th>38</th>
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</tr>
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<tr>
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<td>73 220</td>
<td>73 590</td>
<td>73 680</td>
<td>73 760</td>
<td>73 820</td>
<td>73 870</td>
<td>73 960</td>
<td>74 340</td>
</tr>
<tr>
<td>Northing</td>
<td>44 580</td>
<td>44 400</td>
<td>44 360</td>
<td>44 320</td>
<td>44 300</td>
<td>44 260</td>
<td>44 260</td>
<td>44 390</td>
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<tr>
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<td>484,43</td>
<td>483,16</td>
<td>483,18</td>
<td>483,11</td>
<td>483,18</td>
<td>482,71</td>
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<tr>
<td></td>
<td>430</td>
<td>840</td>
<td>1 130</td>
<td>1 950</td>
<td>1 870</td>
<td>1 080</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>1 120</td>
<td>1 510</td>
<td>1 100</td>
<td>790</td>
<td>550</td>
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<tr>
<td></td>
<td>660</td>
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<td>1 420</td>
<td>830</td>
<td>550</td>
<td>720</td>
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<tr>
<td></td>
<td>440</td>
<td>480</td>
<td>1 500</td>
<td>1 130</td>
<td>1 070</td>
<td>470</td>
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<tr>
<td></td>
<td>480</td>
<td>1 220</td>
<td>1 760</td>
<td>1 670</td>
<td>1 320</td>
<td>890</td>
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</table>

+) between observation points
FIG. 7. Cross-section B: distribution of electrical conductivity across W-E section (bore Nos 33–38). See also Table III.
### TABLE IV. VALUES OF ELECTRICAL CONDUCTANCE FOR FIG.8

<table>
<thead>
<tr>
<th>Bore No.</th>
<th>22</th>
<th>23</th>
<th>29</th>
<th>24</th>
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<th>41</th>
<th>25</th>
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<td>Eastings</td>
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<td>74070</td>
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<td>74680</td>
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<td>481,86</td>
<td>481,32</td>
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<td>482,57</td>
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<td>14. 4.1975</td>
<td>920</td>
<td>900</td>
<td>960</td>
<td>1360</td>
<td>1600</td>
<td>1940</td>
<td>1250</td>
<td>650</td>
<td>450</td>
</tr>
<tr>
<td>4. 3.1974</td>
<td>650</td>
<td>1000</td>
<td>1210</td>
<td>1190</td>
<td>1710</td>
<td>1610</td>
<td>680</td>
<td>440</td>
<td>340</td>
</tr>
<tr>
<td>5. 6.1972</td>
<td>740</td>
<td>1020</td>
<td>1250</td>
<td>1120</td>
<td>740</td>
<td>520</td>
<td>480</td>
<td>470</td>
<td>590</td>
</tr>
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<td>17. 4.1972</td>
<td>740</td>
<td>880</td>
<td>1400</td>
<td>1540</td>
<td>1050</td>
<td>560</td>
<td>440</td>
<td>380</td>
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<td>16. 12.1971</td>
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<td>960</td>
<td>1630</td>
<td>1720</td>
<td>1540</td>
<td>840</td>
<td>640</td>
<td>520</td>
<td>430</td>
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<td>120</td>
<td>110</td>
<td>100</td>
<td>100</td>
<td>180</td>
<td>420</td>
<td></td>
</tr>
</tbody>
</table>

+ between observation points
FIG. 8. Cross-section C: distribution of electrical conductivity across W-E section (bore Nos 22–27). See also Table IV.

5. SIGNIFICANCE OF RESULTS

The variations, particularly the rapid variations in flow observed also by Behrens [6] in the movement of eosin, were caused by very small real variability of groundwater level. Since each element of water always follows gravity by the shortest route, it reacts to each change of gradient. The total course of movement of the groundwater is a composite of small-scale movements, much as the change in direction of a flock of birds is due to the change in direction of the individual. In this way, a polluted groundwater stream can shift laterally relatively quickly with change of gradient.

The origin of the change in gradient with groundwater level is the inhomogeneity of the aquifer with respect to porosity and permeability. These, in turn, depend upon the geological conditions occurring during sedimentation of the formation. When groundwater level changes, mostly the total permeability of single sections of the aquifer is affected to a varying degree. A consequence of this is a redistribution of the subterranean drainage which in turn causes an uneven change in the water table and hence in the gradient.

REFERENCES

METHODS FOR CASE STUDIES OF WASTE–BORNE POLLUTED GROUNDWATER ZONES

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Abstract

METHODS FOR CASE STUDIES OF WASTE-BORNE POLLUTED GROUNDWATER ZONES.
The processes of deterioration and self-purification in the ground can be evaluated by comparing the chemical, isotope-chemical, microbiological and hygienic properties of the groundwater upstream and downstream of the pollution source. During the investigations at three waste sites the necessary information was collected using the following procedures: (a) construction of a net of observation wells; (b) determination of groundwater direction and velocity using hydrologic and radiohydrometric methods (kr–determination by pumping-tests and single-well methods, construction of groundwater contours); (c) chemical and physical measurements of water samples from observation wells; (d) microbiological determinations in water and sediments of wells, ponds, creeks, or even of aquifer material itself; (e) evaluation of the data using feasible statistical and graphical tools (electronic data processing), and (f) study of the distribution of stable isotopes in leachates and groundwaters.

Introduction

The following information refers to the experience obtained during a 9 years' study on the effects of three waste deposits on the chemical, physical and hygienic properties of shallow groundwater in non-consolidated porous aquifers (Quaternary sand and gravel) underlain by impervious clays and marls of Tertiary age. The results are published together with numerous references in GOLWER et al. [1].
FIG. 1. Network of observation wells and sampling points at the waste site in the Frankfurt municipal forest [1].

The investigations focused on such hydrogeological conditions because in these porous media direction and velocity of groundwater flow can be determined more exactly than in fissured or karstified rocks. If comparable studies should be performed in such aquifers some changes of the research program will be necessary.

The observation network

The processes of deterioration and self-purification in the ground have been evaluated by comparing the chemical, microbiological and hygienic properties of the groundwater and surface water upstream and downstream of the source of pollution. Therefore an observation network was installed including newly constructed observation wells, old wells in the vicinity, ponds,
gravel excavations with open laid groundwater, creeks and - in one case - a river. The distribution of these observation points at the waste site in the Frankfurt municipal forest is shown in figure 1. The newly constructed observation wells were built with 4 or later on with 6 inch diameter, enabling the use of several types of pumps and measuring devices and the withdrawal of sludge and water samples. The screen of each well reaches from the bedrock upwards well above the groundwater table, in order to collect samples at any depth and to allow the groundwater to flow through the well over the whole water-filled profile (figure 2).
Determination of hydrologic conditions

During well construction ground samples were taken and the grain size distribution of the aquifer sands and gravels determined. Using the equation of HAZEN the hydraulic conductivity was calculated. Furthermore, each newly constructed well was developed and a 12 hours' pumping test was run. The results were evaluated using the formula for instationary and stationary flow conditions and gave additional information concerning the hydraulic conductivity at the respective well sites. The level of the groundwater surface was measured and groundwater contours for different hydrologic conditions (low and high water level) were constructed (figure 3), which show the general direction of the groundwater movement.

Furthermore, radiohydrometric methods were used to measure the Darcy-velocity $v_F$ and the effective porosity $P \geq 2$. The Darcy-
velocity was measured using the single-well method \( \mathcal{J} \). Using equation (1) the actual groundwater velocity \( v_a \) was calculated

\[
v_a = \frac{v_f}{P}
\]  

(1)

The effective porosity was determined using a combined pumping and tracer test. Two well-points were driven into different depth (3.7 m and 5.7 m below groundwater surface) at a distance of 3 m from an observation well. The tracer, Br-82 in a solution of \( \text{NH}_4 \)-Br, was injected into the well-points and the observation well was pumped with a constant rate of 10 m\(^3\)/h. The effective porosity \( P \) is calculated using equation (2)

\[
P = \frac{V}{\pi \cdot r^2 \cdot h} = \frac{Q \cdot t}{\pi \cdot r^2 \cdot h}
\]  

(2)

\( V \) = Volume pumped till tracer detection
\( Q \) = pumping rate
\( t \) = time interval between tracer-injection and detection = flow-time between injection and observation well
\( r \) = distance between injection and observation well
\( h \) = thickness of aquifer

The radiohydrometric data confirm the actual groundwater velocity of less than 1 m/day derived from pumping test data and groundwater contours \( \mathcal{J} \).

Chemical, microbiological and physical measurements of water samples from observation wells

As the experimental conditions of these field investigations cannot be repeated arbitrarily, an attempt was made from the beginning to consider all factors which may influence the contamination of the groundwater.

The scope of the analyses varied for different series of samples.
Usually groundwater samples were taken after half an hour's pumping for determination of the following characteristics: temperature, pH, Eh, specific electrical conductivity, total dissolved solids, content of dissolved oxygen, carbon dioxide, chloride, sulphate, nitrite, nitrate, hydrogen carbonate, sodium, potassium, ammonia, magnesium, calcium, manganese, iron, hardness, organic nitrogen, permanganate demand, chemical oxygen demand (COD), phenols, detergents (anion-active), and the sum of ether-soluble components L1J.

In connection with the pumping tests carried out after well construction, samples were taken and analysed not only for the components mentioned above but also for the following ones: total solids (by evaporation), solids after ignition, silica, fluoride, sulphide, hydrogen-phosphate, hydrogen-arsenate, total nitrogen, biochemical oxygen demand (BOD5), organic bound carbon, organic bound hydrogen, copper, zinc, molybdenum and lead L1J.

Only occasionally the contents of carcinogenic substances (3,4-benzopyrene), cyanide and of volatile tasting and smelling substances were determined.

Sludge samples were scraped out of the well sumps, from well walls, soil samples from the border of the ponds and even material from the aquifer itself. The sludge was analysed especially with respect to its heavy metal contents L1J. Pond water samples were taken from the border and using a boat. The measurements include temperature, pH, Eh and specific electrical conductivity L1J.

For the chemical and physical analyses the Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung L4,5J were used. As far as other methods were applied they are referred to in L6J.

Microbiological determinations of water and sediment

The samples for hygienic and microbiological observations are gained by pumping as described above, by drawing groundwater with a sampler as used in oceanography (RUTTNER-sampler), by
scraping out slimes from the well screen, from sludge from the bottom of the well and finally of soil from the border of the ponds.

The groundwater samples were drawn first of all directly beneath the groundwater table and secondly 25 cm above the bottom of the wells (figure 2). Another method used was to put small carriers into the wells for a time of about 2 or 6 months to act as platforms for the growth of less mobile or immobile microorganisms. Glass and synthetic rings, synthetic foils, asbestic ties and objective glasses were used as carriers. These were connected by synthetic strings at equal distances of about 25 cm. The identification of the different types of microorganisms in water, soil and sludge was made with the help of culture plates using selective media 7,8.

The total microbial count was determined by using a beef extract - yeast extract - glucose medium with the help of the most-probable-number method (tube-dilution method) and with the KOCH plate method. The nitrate reducing and denitrifying bacteria were identified with a glucose-maltose-medium (tube dilution method). Sodium lactate - iron sulphate-yeast extract medium under anaerobic conditions was used for the isolation of Desulfovibrio (tube dilution method) 7,7.

The germ carriers were treated in a specific way. One side of the microscopic slide was pressed on the surface of an agar plate with nutrient agar for the cultural analysis of the different types of microorganisms. These contact plates were incubated for 48 hours (bacteria) and 5 days for molds. The opposite side of the slides was colored and the total microbial population analysed.

All the cultures are incubated at 22-25°C.

Evaluation of data

The numerous chemical, physical and microbiological data of the water at the different sampling points were listed in tables (usually with their average values and their minima and maxima) and plotted in various graphs to visualise their distribution in space and in time.
Furthermore the chemical data were treated by means of electronic data-processing using 2 FORTRAN IV-programs; program HYDR gives column diagrams of the main constituents, program PIPDIA gives PIPER-diagrams. Both programs are advanced versions of programs originally published by MORGAN & McNELLISS (9) and McNELLISS & MORGAN (10). The programs were supplemented by a third FORTRAN IV-program PUWO, allowing the calculation of linear regressions and the statistical parameters necessary for their evaluation (11).

The statistical treatment showed the characteristic behaviour of the mean values of natural and polluted groundwater (figure 4).
Distribution of stable isotopes in leachates and groundwater

Measurements of deuterium and $^{18}O$ in leachates and groundwater showed that the polluted groundwater was enriched in $^{18}O$ with respect to the unpolluted groundwater nearby. This enrichment was in the range 1.5 to 2 %, compared to an experimental error of $\pm 0.1 \%$. Subsequently a similar enrichment was measured for deuterium. The mechanism for this isotopic enrichment is discussed in FRITZ et al. £12 J.

The principal advantage of studying isotope distribution is the possibility to distinguish between pollutant removal and dilution. This can be achieved by mixing diagrams involving $^{18}O$ and chemical concentration as has been shown by FRITZ et al. £12 J.

REFERENCES

CHEMICAL, MICROBIOLOGICAL AND PHYSICAL PROCESSES IN POLLUTED GROUNDWATER

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Abstract

CHEMICAL, MICROBIOLOGICAL AND PHYSICAL PROCESSES IN POLLUTED GROUNDWATER.

Inorganic and organic pollutants issuing from solid waste deposits cause a groundwater deterioration which depends in its nature and extent on the distance between the base of waste material and the groundwater surface, the quality and quantity of the leachates, the nature of groundwater and its flow velocity and the nature of the aquifer. The contaminants are diluted or decontaminated by biogeochemical, geochemical and physical effects as the groundwater flows downstream. The self-purification processes may be summarized by biogeochemical degradation, precipitation and co-precipitation, sorption at soil particles, at bacterial slimes and at colloidal hydroxides, ion exchange, mechanical filtration and gas exchange. The effect of dilution may be treated with help of the concept of hydrodynamic dispersion. A discussion of the relative importance of self-purification processes and dilution may use anomalous distribution of stable isotopes in the polluted groundwater.

Introduction

In 1964-1973 the effects of three waste deposits on the chemical, physical, microbial and hygienic properties of shallow groundwater were extensively studied. The three waste sites are situated in areas underlain by porous non-solidated aquifers, in which groundwater velocity was less than 1 m/day. The small distance of the groundwater table to the ground surface and air-permeable strata above the groundwater table favoured together with the low groundwater velocity an effective recovery of the groundwater quality by
self-purification processes and dilution. Under the given local condition the contaminated areas were confined to a few hundred metres of flow \( L_1 J \). The methods used for this study are described in a special paper of this panel meeting \( L_2 J \).

Extension of polluted zones at waste deposits

The processes of deterioration and self-purification in the ground can be visualised by comparing the chemical, microbial and hygienic properties of the groundwater upstream and downstream of the source of pollution.

At the disposal area in the Frankfurt municipal forest discussed here domestic refuse with smaller amounts of industrial wastes of a town of some 660,000 inhabitants has been piled up above groundwater table to a height of about 43 m, forming a dump whose volume is estimated at 18 million \( m^3 \), between the years 1924 and 1969. The dump covers an area of about 20 hectares. The aquifer below the site consists of Quaternary sands and gravels down to a depth at 8 to 11 m and is underlain by rather impervious clays and marls of Tertiary age.
The extent of the polluted groundwater zone may be assessed from the following illustrations. Figure 1 shows the distribution of the total dissolved solids as a measure of the gross pollution, and figure 2 represents the distribution of the permanganate demand as a measure of organic pollution. The figures illustrate that at this site, where the groundwater velocity is less than 1 m/day, the polluted zone is confined to some hundred metres. After a flow distance of 650 m, beginning at the margin of the waste site in the Frankfurt municipal forest, no deterioration was detectable in the groundwater. 

In fissured or karstified rocks much higher groundwater flow velocities up to 8 000 m/day and 26 000 m/day are observed respectively. It is obvious that under such conditions extent and shape of the polluted zone are different, e.g., in Munich, where groundwater flow velocities of >20 m are measured. The extent of the groundwater pollutions, both in space and time, is reduced by self-purification processes in the ground, including microbial decay, chemical precipitation and co-precipitation, sorption, ion exchange, mechanical filtration, exchange of gases and dilution.
FIG. 3. Distribution of dissolved free CO$_2$ in the groundwater at the waste site in the Frankfurt municipal forest.

FIG. 4. Distribution of ammonia in the groundwater at the waste site in the Frankfurt municipal forest.
FIG. 5. Biochemical zonation at waste sites above and dipping into the groundwater surface with the respective oxygen content, number of germs and groundwater temperature [1].

Microbial decay

Specialized microorganisms living in both aerobic and anaerobic environments are able to decompose organic substances in their metabolism to water and CO₂ nearly without exception /7,8,9,10,11,12, 13,14/ J. The contents of free dissolved CO₂ in the groundwater produced by the microbial activities are shown in figure 3. These processes may yield simpler organic compounds as by-products before final degradation.

In the zone of greatest pollution the dissolved free oxygen may be used up totally by the biochemical reactions. The microorganisms take up further oxygen by reducing nitrate and sulphate. In such a reducing environment high values of ferrous iron (up to 700 ppm) and ammonia (up to 1460 ppm) were found (figure 4). As the inorganic compounds are reduced and negative Eₚ values exist, this zone is called the "reduction zone" (figure 5).
Sulphates are reduced by specific bacteria, e.g. Desulfovibrio desulfuricans, to hydrogen sulphide and elemental sulphur. Hydrogen sulphide is produced also by decomposition of sulphur-bearing organic compounds. The hydrogen sulphide combines with heavy metals to form insoluble sulphides or may be used by other bacteria in their metabolism. Species of Beggiatoa and Thiothrix as found in this zone are able to oxidize hydrogen sulphide to elemental sulphur and to store it in their cells.

Nitrates may be reduced by several groups of nitrate-reducing and denitrifying bacteria. Their activities result in the production of nitrite, elemental nitrogen and ammonia. Ammonia is produced in addition by putrefying bacteria decaying organic nitrogen compounds, for instance proteins.

The total microbial count is raised considerably in the reduction zone. The biochemical process of degradation gives rise to much CO₂-gas and raises the temperature of the groundwater in the event of an excess of free energy.

Downstream of the reduction zone follows a zone where the intensity of the biochemical decomposition of organic matter decreases to such an extent that the oxygen brought in by diffusion from the soil air or dissolved in the seepage water is not used up any more. The surplus of oxygen oxidizes the inorganic substances and raises the E₅ₒ to positive values. The polluted groundwater zone with a permanent content of dissolved oxygen (≥ 0.7 mg O₂/l) and positive E₅ₒ-values is therefore called "the oxidation zone".

Between the reduction zone and the oxidation zone a transition zone is found where free dissolved oxygen is detected temporarily.

The boundary between oxidizing and reducing conditions is not sharp with respect to oxygen. The reduction processes of the different species of microorganisms begin at different oxygen contents between 0.7 and 0.01 mg O₂/l. The transition zone is characterized especially by the precipitation of dissolved ferrous iron. The oxidation of the ferrous to ferric iron is accomplished under participation of bacteria (Crenothrix spp., Leptothrix spp and Gallionella spp) which are typical for this zone.

The total microbial count is reduced markedly in the transition zone and reaches normal values in the oxidation zone. Here microorganisms decompose the remaining organic pollutants totally in practice.

The biochemical degradation of organic and inorganic pollutants is accomplished by autochthonous microorganisms living in small
FIG. 6. Distribution of microbial groups and species in the biochemical zones [15].

Quantities in the natural groundwater milieu, mostly forming a slimy microbial overgrowth on the surface of ground particles, and augmenting rapidly when the supply of nutrients is raised by pollution.

Microorganisms are adapted to the specific condition in the biochemical zone. Therefore, several typical populations can be found downstream of the source of pollution (figure 6). In the reduction zone Clostridium spp, denitrifying bacteria, Methanobacter spp and a remarkable abundance of Desulfovibrio desulfuricans are characteristic, whereas in this zone fungi are reduced. The typical microorganisms for the transition zone are iron bacteria (Leptothrix spp, Gallionella spp, Crenothrix spp) \( \{15,16\} \).

Bacterial pollutants entrained together with the other organic and inorganic contaminants are not likely to multiply or even survive in this milieu. Antagonistic microorganisms and disadvantageous environmental conditions usually confine the horizontal underground movement of bacterial pollutants in porous aquifers to
travel distances of a few metres or a few decametres \( L \). This may be confirmed by the fact that in the polluted groundwater near the waste sites investigated pathogenic intestinal bacteria (Salmonella sp., Shigella sp.) are not found in any sample \( L \).  

Chemical precipitation and co-precipitation

In the reduction zone iron sulphide is formed chiefly, but also other heavy-metal sulphides may occur. In the transition zone and in the oxidation zone hydroxides of ferric iron and manganese are precipitated. Other poorly soluble elements and compounds, as for instance copper, lead, zinc, arsenic, tungsten, vanadium, fluorides and phosphates, are co-precipitated and thus eliminated from the groundwater.

Co-precipitation is a fixation of a trace substance which otherwise would have remained in solution, to a precipitate. In the precipitate the trace substances are bound in different manner, e.g. substances co-precipitating together with iron- and manganese-hydroxides are fixed mainly on the surfaces of the hydroxide flakes and gels \( L \).  

Precipitation and co-precipitation effects may be the reason why the contents of heavy metal ions as copper, lead and zinc are not significantly raised in the polluted groundwaters (Tab. 1). The contents of lead, cadmium, chromium and zinc surpass the maximal permissible concentration in drinking water. The regional distribution of these heavy metals shows that they are eliminated after a flow distance of about 150-200 m beginning at the margin of the site \( L \).  

Adsorption, ion exchange and mechanical filtration

Adsorption may be defined as a fixation of organic or inorganic substances at the surface of any solids out of solution by intermolecular effects ranging from VAN DER WAAL's forces to valence bondage. Adsorption is controlled by an equilibrium which may be described by FREUNDLICH's isothermal equation (1)

\[
C_s = k C_w^n
\]

which combines the concentration of the adsorbed substances at the sorbent \( C_s \) with the concentration of the substances in the water \( C_w \). \( k \) and \( n \) are constants specific for the substance.
Table 1: Maximal permissible concentration according to Trinkwasserverordnung of 31.1.1975 and maximal observed contents of heavy metals in groundwater at the waste site in the Frankfurt municipal forest [17].

<table>
<thead>
<tr>
<th>Heavy metal</th>
<th>Maximal permissible concentration mg/l</th>
<th>Maximal observed concentration mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>0.04</td>
<td>0.032</td>
</tr>
<tr>
<td>Pb</td>
<td>0.04</td>
<td>0.19</td>
</tr>
<tr>
<td>Cd</td>
<td>0.006</td>
<td>0.013</td>
</tr>
<tr>
<td>Cr</td>
<td>0.05</td>
<td>0.056</td>
</tr>
<tr>
<td>Cu</td>
<td>-</td>
<td>0.18</td>
</tr>
<tr>
<td>Ni</td>
<td>-</td>
<td>0.15</td>
</tr>
<tr>
<td>Hg</td>
<td>0.004</td>
<td>0.0008</td>
</tr>
<tr>
<td>Ag</td>
<td>-</td>
<td>0.001</td>
</tr>
<tr>
<td>Zn</td>
<td>2.0</td>
<td>4.0</td>
</tr>
</tbody>
</table>

Equation (1) shows that decreasing contents of dissolved substances will cause a desorption and vice versa. An exchange of bound ions against dissolved ions is defined as ion exchange.

The aquifers with the best sorptive effects and exchange capacity are permeable sediments containing small quantities of clay or humic substances. Fissured and karstified rocks have low sorption capacity. In contrast to the sands, gravels, clays and humic substances whose sorption capacity is exhausted after some time, the precipitating hydroxides and the bacterial slimes, which are regenerated continuously by the decomposition of the organic matter, offer perpendicularly new active surfaces. Suspended matter may be transported many kilometers in the flow channels of fissured or karstic rocks, depending on the widths of the interstices. But in porous media they are removed by filtration after a short flow distance. For that reason no suspended matter was found in the porous aquifers investigated.
Exchange of gases

Volatile breakdown products such as methane, carbon dioxide and nitrogen escape into the ground air and atmosphere, thus finally removing considerable amounts of carbon dioxide and nitrogen from the polluted zone. Polluted groundwater zones are characterized by high CO₂-contents in the ground air (up to 25 Vol. %, natural background 0.1 Vol. %) \( \leq 20 \text{ J} \).

The oxygen of the groundair, which is in exchange with the atmosphere, dissolves in percolating water and groundwater. Since the rate of oxygen supply determines the velocity of decomposition of organic pollutants, the relation between oxygen supply by gas exchange and oxygen consumption by biodegradation in the polluted water determines whether there are oxidizing or reducing conditions.

The gas exchange in the shallow groundwater may be described with help of the diffusion equation \( \leq 20 \text{ J} \).

The importance of the gas exchange for the self-purification can be shown by the favourable effects of any open-laid groundwater-table downstream from a waste site which give rise to a high supply of atmospheric oxygen in direct contact \( \leq 1 \text{ J} \). Poorly permeable strata above the groundwater, e.g. clays and silts, reduce the oxygen supply and the escape of volatile decomposition products, thus slowing down the biochemical processes.

Dilution

Downstream from the waste site polluted groundwater may be diluted by admixture of pure groundwater or seepage water. The effect of this dilution depends on the quantity of admixing water and its chemical and physical properties. The rate of groundwater recharge is one of the most important factors influencing the dilution. The effect of dilution may be treated with help of the concept of hydrodynamic dispersion.

The discussion of the importance of dilution is restricted by the lack of a feasible measure of comparison. The chloride ion commonly used as a measure for dilution is influenced by physicochemical processes in the ground. McMAHON & THOMAS \( \leq 21 \text{ J} \) and MATTSON \( \leq 22 \text{ J} \) report a sorption of chloride ions by positively
charged sesqui-oxides of low sorption capacity. For the evaluation of the dilution effect the stable isotopes Deuterium and \(^{18}O\) may be used, which are ideal tracers \(^2\)J. Polluted groundwater at waste sites proved to be enriched in deuterium and \(^{18}O\) in comparison to natural groundwater.

The good correlation between \(Cl^-\) and \(^{18}O\) content is an argument for dilution of \(Cl^-\)-content in downstream groundwater. The different behaviour of \(K_2Cr_2O_7\)-demand and \(^{18}O\)-content is due to microbial degradation processes, which are obvious in the comparisons of the behaviour of \(NH_4^+\) and \(SO_4^{2-}\) to \(^{18}O\) \(^2\)J.

Conclusion

The biochemical, chemical and physical processes in a polluted groundwater zone change the water quality in such an extent that for identification of a waterbody moving through such a zone conservative tracers are necessary, which can be provided by isotope techniques. Combined use of chemical and isotope technique will allow evaluation of the quantitative relations between the different mechanisms of the elimination of pollutants.

REFERENCES


ANALYSIS OF POLLUTANTS
BY NUCLEAR TECHNIQUES
NUCLEAR TECHNIQUES APPLICABLE TO STUDIES OF POLLUTANTS IN GROUNDWATER

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Richland, Washington,
United States of America

Abstract

NUCLEAR TECHNIQUES APPLICABLE TO STUDIES OF POLLUTANTS IN GROUNDWATER.

This paper summarizes the current nuclear methods which can be used for the analysis of inorganic pollutants or tracers, including radioactive species in sediments and in their associated atmospheric and aqueous media. Nuclear techniques allow many trace elements to be analysed in the parts per $10^6$ to parts per $10^9$ range in both field and laboratory experiments. For direct in situ field measurements, techniques of X-ray fluorescence and neutron activation analysis are discussed. Direct instrumental techniques, as well as chemical procedures enhancing their effectiveness, are discussed as they are applied in laboratory analysis. Radioactive pollutants or tracers can be measured through radiative emissions under laboratory and field conditions. In the laboratory, a few disintegrations per minute can be measured in thousand-U.S. gallon water volumes through the use of pre-analysis concentration methods. Laboratory instrumentation discussed includes X-ray fluorescence analysers, total absorption gamma-ray spectrometry, multidimensional coincidence gamma-ray spectrometry, multidimensional gamma-ray spectrometry with beta coincidence, dual Ge(Li) anticoincidence shielded systems, as well as single Ge(Li) and NaI(Tl)-Ge(Li) coincidence gamma-ray spectrometers. Detection sensitivities for radioisotopes from fallout and those produced by neutron activation analysis methods are presented.

INTRODUCTION

In the past, man's concern about his environment was primarily esthetic--its visible appearance, taste of water and foods, and odors. At the present time, a much deeper concern exists which is centered on acute or potentially chronic effects of all forms of pollution as they affect man and his environment. These pollutants are found in all phases of man's environment--in the atmosphere, the oceans, fresh water, land areas, and in the associated flora and fauna. For this reason, there is a continuing need for analytical methods to measure environmental levels of pollutants and to utilize tracers to determine the flow of these pollutants from their source to man. During the past few years, the use of nuclear techniques has come to the forefront for the analysis of pollution in waters, sediments, and gaseous media. Various nuclear techniques allow many pollutants to be analyzed at environmental levels under field and laboratory conditions.

The purpose of this paper is to present some nuclear techniques which can be applied to studies of pollution in sediments and their associated conditions.
ground waters. These nuclear techniques include X-ray fluorescence analysis and neutron activation analysis. Special gamma-ray spectrometric methods included are: total absorption gamma-ray spectrometry, multidimensional coincidence gamma-ray spectrometry with dual beta coincidence, and a variety of Ge(Li) noncoincidence and coincidence gamma-ray spectrometry. The special adaptation of chemical procedures enhancing the use of these instrumental methods in the laboratory is also presented.

METHODS

The nuclear analytical methods which are discussed in this paper are based on the detection of X-rays or photons emitted from the subject element. These emissions may be associated with primordial, cosmogenic, or man-made radioactive species, or may arise from decay of radionuclides following neutron activation, and from excitation of an element with energy such as in X-ray fluorescence analysis. These procedures allow ppm to ppb elemental concentrations to be measured in environmental matrices in the field and in the laboratory. The decision to use field or laboratory instruments must be based on the requirements of the experiment. If sensitivity is the prime requirement, then the experiment must be planned with laboratory analysis techniques. Often the hydrologist can add sufficient tracer, or sufficient natural tracer is present in the environmental system under study to allow the criteria of real-time measurement to be the prime experimental consideration. This latter condition requires the use of field instrumentation.

FIELD INSTRUMENTATION

X-ray Fluorescence

At Battelle-Northwest in Richland, Washington, USA, many techniques for the in situ analysis of tracers and environmental pollutants are being investigated. One of these techniques uses energy dispersive X-ray fluorescence. Its applicability for determining the elemental content of materials has been well established. The normal procedure is to induce characteristic X-ray emissions from elements in samples by irradiating those samples with a beam of low-energy photons or charged particles. The X-rays are analyzed by a Si(Li), or intrinsic Ge detector, yielding pulses which are proportional to the energy deposited. This procedure allows a very rapid and inexpensive multielement analysis in the ppm range. Part-per-billion sensitivities are accomplished in the laboratory through chemical procedures that concentrate the elements of interest from a bulk matrix.

A field X-ray fluorescence analyzer has been developed as shown in Fig. 1 which allows in situ elemental measurements of sedimentary material or elements of interest in a water column at the ppm level. This in situ X-ray fluorescence analyzer uses a solid cryogen (Freon-22) cooled Si(Li) detector. It uses approximately 100 uCi of 133Ba, 241Am, or 60Co as its excitation source. The system as shown can be operated to 100 m water depths. The detector vacuum is protected from external pressure with a 0.1 mm Be window. An additional external Be pressure window serves as protection against the pressures developed in underwater conditions. This latter window can be varied in thickness from 0.2 to 1 mm to allow minimum window desorption for the X-rays at a given depth. This window can also be made of Ti, which allows greater

* Parts per U.S. billion (= 10^9).
FIG. 2. In-situ X-ray fluorescence spectra of Puget Sound, Washington sediments.

pressure depths to be investigated. However, operating at greater depths causes a loss in sensitivity for low Z elements. The system as shown has been operated from a surface vessel and from a submarine for the analysis of pollutants in the water column and sedimentary material in Long Island Sound, New York; Puget Sound, Washington; and Lake Washington, Washington, in the United States. The prominent X-ray energies used for elemental analysis are the K-shell X-rays in the range from 5 to 20 keV, which encompass the transition elements. L-shell X-rays are often used with $^{197}$Cd excitation for analysis of heavier elements. This $^{197}$Cd excitation allows 15 to 20 elements to be identified simultaneously. When specific heavy elements such as Pb or Hg are being investigated, a $^{57}$Co source (122 keV) is used for K X-ray excitation. Sensitivities for the system range from a few ppm to 50 ppm depending on the element. It should be remembered that this is a direct infield application of X-ray fluorescence and, thus, sensitivities will be worse than those obtainable in the laboratory with preconcentration schemes. Figure 2 shows a typical spectrum taken in the field in Puget Sound, Washington sedimentary material.
Table I shows the elemental concentrations obtainable from this type of spectrum taken in a 5-min analysis period. It should be noted that the column designated "water" in this table is an analysis of water containing colloidal or particulate material. This sample is sea water which should contain on the order of 60 ppm Br, yet Br is on the order of 280 ppm. Many of the elemental concentrations in this sample are higher than that for natural sea water. These elements can thus be used to identify material which is not typical of marine waters. The use of Fe, Ni, and Zn allows a study of the amount of particulate material in the water column. The ratio of the coherent and incoherent scatter peak provides a measure of the amount of low Z material seen by the analyzer system. The Puget Sound study was primarily concerned with the concentrations of the pollutants Hg, Pb, and As in the water column and associated sedimentary material. The elemental concentrations measured in situ agreed to within 20% of those obtained from grab samples which were subsequently analyzed in the laboratory with X-ray fluorescence techniques. As shown in Table I, some 11 elements were identified directly.

The feasibility and practicality of using in situ X-ray fluorescence systems have been proven with these types of studies. The system can measure major pollutant elements at concentrations down to a few ppm in the top few mm of undisturbed surface sediment. This allows real-time measurements within a marine or freshwater system. With this system, at least 10 samples/hour can be analyzed for from 10 to 40 elements depending on the matrix.

<table>
<thead>
<tr>
<th>WATER DEPTH TO SHORE (m)</th>
<th>ELEMENT ppm (UNLESS NOTED OTHERWISE)*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
</tr>
<tr>
<td>PUGET SOUND WATER</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.06</td>
</tr>
<tr>
<td>EAST (PT. DEFIANCE)</td>
<td>7</td>
</tr>
<tr>
<td>&quot;&quot;</td>
<td>7</td>
</tr>
<tr>
<td>LAUNCH (PT. DEFIANCE)</td>
<td>3</td>
</tr>
<tr>
<td>&quot;&quot;</td>
<td>3</td>
</tr>
<tr>
<td>SLAG PILE (PT. DEFIANCE)</td>
<td>12</td>
</tr>
<tr>
<td>&quot;&quot;</td>
<td>13</td>
</tr>
</tbody>
</table>

* The elements Ti, V, Cr, Ba, Cu, Ga, Se, AND U were below 0.01%, 0.02%, 30 ppm, 1%, 30 ppm, 20 ppm, 10 ppm AND 10 ppm respectively.
X-ray tube secondary target excitation systems are also being considered for this type of analysis. In the analysis of Au, for example, one could use specific excitation energies from an X-ray tube with the subsequent measurement of the 68.8 keV Au X-ray. High energy (50-100 keV) X-rays are analyzed using intrinsic Ge detectors since their efficiency is greater than the Si(Li) detector normally used.

The X-ray fluorescence technique can also be used in the field by pumping the water or associated sedimentary material from depth to a sampling chamber on board a boat or vehicle. With this technique, a German government laboratory team identified elements of economic interest in near-shore sands. The sensitivity for detection by this technique ranges from per cent to ppm levels, depending on the element and, of course, its atomic characteristics.

**Neutron Activation Analysis**

A second technique which has been developed for use on land surfaces and in freshwater and marine environments is neutron activation analysis. This method requires that a neutron be captured by the element of interest to produce a radioactive specie. Photons are emitted at the time the neutron is absorbed (prompt gamma) and from the decay of the radioactive specie (delayed gamma). With the advent of the man-made isotope $^{252}$Cf, which decays by spontaneous fission with associated neutron emission, a portable neutron source was available for terrestrial, saline, and freshwater elemental analysis. In general, this technique is more applicable to the analysis of sedimentary materials than to aqueous analysis. However, selected trace elements can be analyzed in a water column with this technique.

Two possible applications for $^{252}$Cf elemental analysis from an infield survey vessel have been investigated. The first involves the use of a shipboard laboratory in which the $^{252}$Cf source and its associated Ge(Li) detector system are employed for the analysis of dredged or cored specimens, or chemically prepared water specimens to determine the elemental composition. The second method involves the placement of the neutron source and detector system on the ocean floor or in the water column for the rapid in situ analysis of the material. Both techniques have been used. The measurement sensitivity of the elements depends on their nuclear parameters--how well they capture neutrons and how efficiently they decay through a given photon energy which can be detected for element identification.

Figure 3 shows the construction of an underwater Ge(Li) or intrinsic Ge detector system. This system is similar in nature to that shown for the X-ray fluorescence technique. The solid-state detector is cooled electronically or with a solid cryogen—either Freon-22 or a Freon-22/propane mixture. The electronics are housed underwater, including the preamp, amplifier, and high-voltage power supplies. The detector is protected from pressure with a 0.5 mm-thick stainless steel honeycomb window. This window can withstand pressures of 500 psi, allowing application to water depths of 300 m. With this technique, the area is first irradiated with the $^{252}$Cf neutron source, followed by detection of the induced radioactive species with photon analysis using the Ge(Li) diode (delayed gamma). "Prompt gamma detection" is another method which can be used, although the technique requires a smaller $^{252}$Cf source and its use is limited in a marine environment. The prompt gamma emission technique fails to measure many trace elements in a marine environment due to the high concentration of photons from the induced activity.

* 1 psi = 1 lbf/in$^2$ = 6.895 X 10$^5$ Pa.
of Na and Cl. For specific elements at per cent concentration levels, the technique provides good data. This technique has been employed in an instrument by which manganese nodules are analyzed to depths of 6000 m on the seafloor of the Pacific Ocean. Both delayed gamma and prompt gamma techniques can be used in freshwater or for the analysis of land surfaces. Table 2 provides a comparison of in situ X-ray fluorescence and neutron activation analysis sensitivities. They, in general, range from ppm to per cent levels for some 40 elements.

Elemental tracers can be used with this technique to determine water flow and sand movement—two of the many applications possible. One potential tracer which could be used is the element Dy. Dysprosium could be added to a sand or aqueous media and the nuclear probe used to activate and follow its movement in tidelands or deeper ocean areas. For example, if 100 kg of Dy were distributed over 1 sq. km of ocean floor to a depth of 1 cm, it could be measured at 2 kg/km², a three-fold concentration above the normal Dy content of the sea sands. For water flow determinations, one needs an element which is characteristic of the water and not perturbed from its injection point to its measurement point. These elements must be specific to a site. In general, through the use of this activation analysis technique, some 20 elements can be measured simultaneously at the per cent to ppb levels, depending on the nuclear characteristics of the element being measured. The multielement capability allows the ratio of elements to indicate tracer action under field conditions.
<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>DETECTABLE CONCENTRATION</th>
<th>DETECTABLE CONCENTRATION</th>
<th>DETECTABLE CONCENTRATION</th>
<th>DETECTABLE CONCENTRATION</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X-RAY FLUORESCENCE² (ppm)</td>
<td>X-RAY FLUORESCENCE¹ (ppm)</td>
<td>BY NEUTRON ACTIVATION¹</td>
<td>BY NEUTRON ACTIVATION¹</td>
</tr>
<tr>
<td>Al</td>
<td>--</td>
<td>0.1 %</td>
<td>Nb</td>
<td>5</td>
</tr>
<tr>
<td>Sb</td>
<td>10</td>
<td>1 %</td>
<td>Sc</td>
<td>--</td>
</tr>
<tr>
<td>As</td>
<td>5</td>
<td>0.1 %</td>
<td>Se</td>
<td>5</td>
</tr>
<tr>
<td>Ba</td>
<td>20</td>
<td>0.1 %</td>
<td>Ag</td>
<td>10</td>
</tr>
<tr>
<td>Cd</td>
<td>10</td>
<td>1 %</td>
<td>Sr</td>
<td>5</td>
</tr>
<tr>
<td>Cr</td>
<td>5</td>
<td>4 %</td>
<td>Sn</td>
<td>10</td>
</tr>
<tr>
<td>Co</td>
<td>5</td>
<td>0.1 %</td>
<td>Ti</td>
<td>10</td>
</tr>
<tr>
<td>Cu</td>
<td>5</td>
<td>0.1 %</td>
<td>W</td>
<td>10</td>
</tr>
<tr>
<td>Dy</td>
<td>10</td>
<td>10 ppm</td>
<td>V</td>
<td>10</td>
</tr>
<tr>
<td>F</td>
<td>--</td>
<td>0.01 %</td>
<td>Zn</td>
<td>5</td>
</tr>
<tr>
<td>Au</td>
<td>5</td>
<td>30 ppm</td>
<td>Ga</td>
<td>5</td>
</tr>
<tr>
<td>Hf</td>
<td>10</td>
<td>1 ppm</td>
<td>Ge</td>
<td>5</td>
</tr>
<tr>
<td>In</td>
<td>10</td>
<td>1 ppm</td>
<td>Br</td>
<td>5</td>
</tr>
<tr>
<td>Fe</td>
<td>5</td>
<td>50 %</td>
<td>Rb</td>
<td>5</td>
</tr>
<tr>
<td>La</td>
<td>20</td>
<td>0.01 %</td>
<td>Y</td>
<td>5</td>
</tr>
<tr>
<td>Mg</td>
<td>--</td>
<td>0.01 %</td>
<td>Er</td>
<td>5</td>
</tr>
<tr>
<td>Mn</td>
<td>5</td>
<td>0.01 %</td>
<td>Ce</td>
<td>20</td>
</tr>
<tr>
<td>Hg</td>
<td>10</td>
<td>1 %</td>
<td>Pb</td>
<td>5</td>
</tr>
<tr>
<td>Mo</td>
<td>5</td>
<td>0.01 %</td>
<td>Hg</td>
<td>5</td>
</tr>
<tr>
<td>Ni</td>
<td>5</td>
<td>1 %</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* NOT EVALUATED TO DATE

¹ BASED ON 2 min. IRRADIATION WITH 1 mg $^{252}$Cf, 40 s DECAY, AND 2 min GAMMA-RAY ANALYSIS WITH 15% Ge(Li) DIODE

² BASED ON 50 mc $^{109}$Cd EXCITATION (OR $^{241}$Am WHERE NECESSARY) SOURCE AND 80 mm² Si(Li) DETECTOR
Radionuclide Detection

In addition to the field use of X-ray fluorescence and neutron activation analysis, radiation detectors can be used to detect radioactive pollutants or tracers in waters and their associated sediments. Typical photon detectors consist of NaI(Tl) crystals, intrinsic Ge, Ge(Li), and Si(Li) diodes. These systems can be designed to operate at underwater depths of thousands of meters. Through these direct measurement techniques, one can easily measure a few hundred dpm of fission products from fallout or species accruing in the sediments and water from waste pond or reactor operation effluents\textsuperscript{12}. As will be discussed later, a 1000-fold lower detection limit for water analysis can be obtained through preconcentration methods and the use of laboratory instrumentation.

A typical system\textsuperscript{13} designed for borehole identification of gamma ray emitters is shown in Fig. 4. This system consists of a Ge, Ge(Li) or Si(Li) solid-state diode with associated liquid N\textsubscript{2} cooling dewar. Simpler systems using NaI(Tl) require only a pressure housing to protect the crystal itself. The major difference between systems, as will be discussed later in the laboratory section of this paper, is the resolution with which the detector can identify specific gamma-ray emitters.
<table>
<thead>
<tr>
<th>SINGLE $\gamma$-RAY</th>
<th>MULTIPLE $\gamma$-RAYS</th>
<th>COINCIDENCE $\gamma$-RAYS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{7}$Be</td>
<td>$^{57}$Co</td>
<td>$^{22}$Na</td>
</tr>
<tr>
<td>$^{40}$K</td>
<td>$^{58}$Co</td>
<td>$^{46}$Sc</td>
</tr>
<tr>
<td>$^{51}$Cr</td>
<td>$^{59}$Fe</td>
<td>$^{60}$Co</td>
</tr>
<tr>
<td>$^{54}$Mn</td>
<td>$^{65}$Zn</td>
<td>$^{88}$Y</td>
</tr>
<tr>
<td>$^{99}$Nb</td>
<td>$^{95}$Zr</td>
<td>$^{110m}$Ag</td>
</tr>
<tr>
<td>$^{103}$Ru</td>
<td>$^{106}$Rh</td>
<td>$^{124}$Sb</td>
</tr>
<tr>
<td>$^{137}$Cs</td>
<td>$^{125}$Sb</td>
<td>$^{134}$Cs</td>
</tr>
<tr>
<td>$^{141}$Ce</td>
<td>$^{131}$I</td>
<td>$^{140}$La</td>
</tr>
<tr>
<td>$^{144}$Ce</td>
<td>$^{140}$Ba</td>
<td>$^{152}$Eu</td>
</tr>
<tr>
<td></td>
<td>$^{144}$Pr</td>
<td>$^{207}$Bi</td>
</tr>
<tr>
<td></td>
<td>$^{155}$Eu</td>
<td></td>
</tr>
</tbody>
</table>

LABORATORY INSTRUMENTATION

NaI(Tl) Spectrometers

In the laboratory, aqueous or sedimentary radioactive pollution is normally analyzed with NaI(Tl) or Ge(Li) spectrometers. Some environmental radioactive species which can be used as tracers in aqueous systems are shown in Table 3. Some of these radionuclides emit a single photon; others emit multiple photons which are not in coincidence; and still a third group emit multiple photons which are in a time coincidence. Each of these groups (based on their photon emission characteristics) can be more easily identified with a different nuclear detection technique. In the detection techniques discussed below, the radiation produces interactions in the detector which are converted to current or voltage pulses proportional to the energy of the radiation.

One of the most sensitive instruments for detection of coincidence gamma-ray emitters is shown in Fig. 5. This system consists of large 23-cm diameter x 20-cm thick NaI(Tl) primary crystals which are encased in 30-cm x 20-cm long NaI(Tl) cylinders. Each primary crystal is shielded from its respective phototubes with a 7.6-cm thick NaI light pipe. Cladding around the crystals has been kept to a minimum to reduce photon scatter. In many cases, the outer annulus which serves as an anticoincidence detector is made from plastic phosfor. When phosfor are used, the standard 10-cm lead shield which surrounds the crystal system has a 10-cm (5% by weight) paraffin liner. This paraffin liner serves to reduce background photons by thermalization and capture of neutrons produced in the lead shield by cosmic rays. This is necessary in the case of a plastic phosphor annulus since neutron reactions would occur with $H$ in the phosphor, creating a background photon at 2.225 MeV. The sample to be analyzed is placed between the primary crystals.
FIG. 5. Schematic of an all NaI anticoincidence shielded multidimensional gamma-ray spectrometer.

TABLE 4. MINIMUM DETECTION LEVEL FOR REACTOR EFFLUENT RADIONUCLIDES

<table>
<thead>
<tr>
<th>ISOTOPE</th>
<th>ENERGY (keV)</th>
<th>7.5 x 7.5 cm NaI</th>
<th>65 cc Ge(Li)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{24}$Na</td>
<td>1369</td>
<td>6.6</td>
<td>7.0</td>
</tr>
<tr>
<td>$^{51}$Cr</td>
<td>320</td>
<td>64.0</td>
<td>42.0</td>
</tr>
<tr>
<td>$^{54}$Mn</td>
<td>834</td>
<td>5.2</td>
<td>5.4</td>
</tr>
<tr>
<td>$^{56}$Mn</td>
<td>847</td>
<td>5.4</td>
<td>5.6</td>
</tr>
<tr>
<td>$^{59}$Fe</td>
<td>1095</td>
<td>6.6</td>
<td>9.6</td>
</tr>
<tr>
<td>$^{58}$Co</td>
<td>810</td>
<td>5.6</td>
<td>5.2</td>
</tr>
<tr>
<td>$^{60}$Co</td>
<td>1332</td>
<td>5.6</td>
<td>7.0</td>
</tr>
<tr>
<td>$^{64}$Cu</td>
<td>511</td>
<td>13.0</td>
<td>12.0</td>
</tr>
<tr>
<td>$^{65}$Zn</td>
<td>1115</td>
<td>11.0</td>
<td>14.0</td>
</tr>
<tr>
<td>$^{103}$Ru</td>
<td>497</td>
<td>5.5</td>
<td>4.8</td>
</tr>
<tr>
<td>$^{106}$Ru</td>
<td>512</td>
<td>23.0</td>
<td>21.0</td>
</tr>
<tr>
<td>$^{137}$Cs</td>
<td>622</td>
<td>4.7</td>
<td>37.0</td>
</tr>
<tr>
<td>$^{140}$Ba</td>
<td>537</td>
<td>14.0</td>
<td>13.0</td>
</tr>
</tbody>
</table>

1 Interference free basis using 5 cm Marinelli breakers and 30 minutes counting time.
5 cm THICK WWII Fe PLATE LINER
40 x 40 x 50 cm ID

10 cm PRE WWII Fe PLATE

15 cm LEAD

10 cm LEAD SHADOW SHIELD

TOTAL SHIELD = 80 x 80 x 100 cm
L - W - H

FIG. 6. High-efficiency/low-background Ge(Li) gamma-ray detector system.
System operation is enhanced by absorbing radiation produced by the scatter of photons from one detector to the second. This is accomplished by placing Pb or Au absorbers between the two primary crystals to cover the area not occupied by the sample. In this fashion, scattered radiation is kept to a minimum. Beta detectors can also be placed between the 2 primary NaI(Tl) crystals to enhance system sensitivity. A beta or electron signal is then required in coincidence with the gamma emission. In this operational mode, a NaI(Tl) spectrometer achieves backgrounds in the range of 1 count in 20,000 min, yet gamma ray efficiencies are maintained in the 1 to 10% range for most coincidence photon emitters.

**Ge(Li) Spectrometers**

The most useful photon detector system for single gamma ray emitters and multiple gamma ray emitters is one constructed from a Ge(Li) diode. This type of radiation detector system has a better resolution than that of the NaI(Tl) crystal systems just discussed; however, its efficiency is lower.

For comparison, the minimum detection level of reactor effluent radionuclides is shown in Table 4 as determined with a 7.6 x 7.6 cm NaI(Tl) crystal and a 65 cc Ge(Li) detector. As one can see, the minimum detection level with these two systems is in general identical for each radioisotope measured separately.

One of the best construction methods for providing a low background, yet high efficiency Ge(Li) system is shown in Fig. 6 wherein a 90° angle is maintained between the liquid N₂ cryostat and detector head. In this fashion the inherent radioactivity of the molecular sieve is placed in the N₂ dewar and can be shielded from the detector. The use of pre-World War II Fe plates minimizes the background by eliminating materials contaminated from fallout while providing a low background shield for the detector head. Lead is used to provide shielding against cosmic rays, as well as K, U, and Th photons from the surfaces of the analyzer room.

As shown in Fig. 7, the resolution of the Ge(Li) diode is such that many photons, and thus radioactive species, can be measured simultaneously. Often this is not possible with a NaI(Tl) detector.

The Ge(Li) diodes can also be placed inside a detector which is used to detect photons in coincidence. As shown in Fig. 8, two Ge(Li) detectors are surrounded by a plastic phosphor in a large cave system. This is equivalent to the NaI(Tl) gamma-ray spectrometer previously discussed. Since each Ge(Li) detector requires at least 1000 channels for storage of its spectra, a Ge(Li)-Ge(Li) coincidence system requires 1 million channels of memory and thus a main computer. This system is very selective but it has low efficiency and is of limited value. A more useful system is constructed from one primary Ge(Li) diode surrounded by a detector (shield) which serves to detect coincidence pulses. In this system operation, two operational modes are possible. In the first mode, all pulses received by the primary detector are thrown out if a pulse is recorded by the shield. In the second mode, Ge(Li) events which are recorded in time sequence with a pulse in the shield are stored in 1/2 of a pulse-height analyzer memory; events not in time coincidence with the shield are routed to the second half of the memory. Both operational modes are used by various laboratories, although more information is gained by the nuclear scientist in the second mode of operation.
As shown in Fig. 9, this second mode of operation of the shield allows data to be obtained which would normally be unavailable from conventional Ge(Li) analysis. The spectrum shown in the upper curve is from a sample analyzed for $^{54}$Fe, $^{137}$Cs, $^{55}$Mn, and $^{65}$Zn by a 12% efficient 3 keV resolution Ge(Li) diode. The four lower spectra were taken with the same diode operated in a noncoincidence mode using the routing operation. Whereas only $^{137}$Cs can be analyzed in the upper curves, all four isotopes can be identified in the lower set of curves. Increased sensitivity has thus been achieved with this type of detector system.
FIG. 8. Schematic of an anticoincidence shielded dual Ge(Li) gamma-ray spectrometer.

FIG. 9. Gamma-ray spectra of Bikini tuna.

The detector systems just discussed have detection limits based upon their background counting rates and efficiencies. In general, they will detect a few dpm of the radioactive specie. Both Ge(Li) and NaI(Tl) systems can simultaneously identify 20 to 25 radionuclides from fallout with their coincidence or routing techniques.

For large environmental samples and the analysis of coincidence gamma-ray emitters, the large NaI(Tl) multidimensional gamma-ray spectrometer would be the detector of choice. The detector of choice for a point source of single gamma ray-emitting radionuclides would be a simple Ge(Li) detector with an efficiency of about 25%. If either of these systems has a considerable amount of interfering radionuclide activity, an analytical radiochemical approach is required to determine which system will yield the most data. In practice both systems should be used if an entire series of 25 radionuclides are to be analyzed in environmental materials. However, in general, more information will be obtained with the Ge(Li) detector for multiple radionuclide analysis per dollars spent than with the NaI(Tl) systems.
The techniques used for sample collection of radioactive materials are varied and are dictated by the concentration of the particular radionuclide and sensitivity of the instrument available for its measurement. For those radionuclides that are present in sufficiently high concentration, a 10-100 liter sample of water is collected and the material is isolated and concentrated by coprecipitation and radiochemical separation. Several concentration methods have also been developed in which the material of interest is collected on a matrix that is exposed to water. Ferrocyanides of Co or Cu have been used\textsuperscript{17} which are specific for Cs collection to measure the concentration of \textsuperscript{137}Cs. The amount of water contacted is determined by measuring the quantity of inert Cs, a conservative element retained in the collector. Jute fiber or sponges impregnated with hydrous ferric oxide have been used\textsuperscript{18} to extract Si and \textsuperscript{28}Si from tens of tons of sea water. In yet another application, acrylic fibers impregnated with Mn oxides have been used\textsuperscript{19} to extract Ra isotopes from several thousand liters of sea water.

In a more general case, concentration of \textsuperscript{7}Be and the gamma-emitting fission products in sea water have been collected\textsuperscript{20,21} from a 4000 liter sample. The collection system consists of 8 parallel filters to remove particulate material greater than 0.3 \( \mu \) in diameter. Sample flow is then directed through a 0.64-cm thick bed of neutral alumina which retains a determinable fraction of the radionuclides of interest. The alkali metals and alkaline earths which are present in rather high concentrations in marine waters are not absorbed and pass through the alumina bed. Cesium-137 can be absorbed by a second bed of ammonium phosphomolybdate. In this fashion, 0.001 dpm/liter quantities of gamma-ray emitting pollutant species produced in fallout or reactor operations can be used as a tracer of the water mass.

NEUTRON ACTIVATION ANALYSIS

The instruments just discussed have also been used extensively in the United States and Europe for the analysis of trace elements by neutron activation. These techniques use either direct instrumental analysis\textsuperscript{22} or radiochemical separation\textsuperscript{23} of the elements following irradiation to provide a pre-concentration or purification of the radioactive specie prior to its measurement. Since the latter technique requires many man-hours for the isolation and identification of each specie, the most extensive work has been accomplished with the direct instrumental analysis approach. In this technique, normally short, medium, and long neutron irradiation times are used; followed by long, medium, and short count times to identify some 60 pollutants or tracer elements in a single sample. Recently the use of cyclic neutron activation\textsuperscript{4} and counting has also been used. In this procedure, the sample is irradiated for a few seconds. It is then pneumatically transferred in hundreds of milliseconds to a Ge(Li) detector, and the resultant radioactivity analyzed for periods of a few seconds. The sample is then pneumatically transferred back into the source of neutrons. This cycle of irradiation and counting is normally accomplished a few hundred times to complete the analysis. This technique allows the identification of many elements through their short half-life radioactive species without allowing the build-up of long half-life radioactivity. This is especially critical in the analysis of saline media. Of course, group separation of the elements may also be used to enhance neutron activation analysis, selectivity, and sensitivity. These separation techniques may involve evaporation of the sample, precipitation with ferric hydroxide, solvent extraction, precipitation with APDC, and other procedures. Analytical techniques have also been developed for specific pollutants. For example, identification of U is accomplished by cyclic neutron activation followed by detection of the delayed neutrons emitted by fission products of U \textsuperscript{9}. This technique measures ppb quantities of U in a 10 ml aqueous solution.
In activation analysis, the use of $^{252}$Cf in subcritical multiplications systems has been applied to the measurements of aqueous and sedimentary elements. In this technique (Fig. 10), fissionable material such as enriched U rods is assembled in a configuration which approaches but does not reach criticality. The uranium system serves as a multiplying agent for any source of neutrons. Californium-252 is normally used to supply the neutrons. In this fashion, thermal neutron fluxes approaching $10^{11}$ neutrons/cm$^2$·s$^1$·s$^1$ have been achieved for laboratory cyclic activation analysis and standard activation analysis of bulk materials with a 100 mg $^{252}$Cf source.

As shown in Fig. 11, this multiplication effect of neutrons can decisively increase the activation of elements. In the spectra, a Mo concentrate used to trace a water column was irradiated first with a small $^{252}$Cf source, then with the same source inside a small subcritical multiplier. The data graphically demonstrate the increased activation through the increased flux from the subcritically multiplied $^{252}$Cf neutrons. Shown in Fig. 12 is a standard National Bureau of Standards orchard leaf spectra. This spectra has been obtained from irradiation of the sample with a fluence of $1 \times 10^{17}$ neutrons.
FIG. 11. Gamma-ray spectra of neutron-activated molybdenum concentrate.
FIG. 12. Lithium-drifted spectra of NBS orchard leaf following neutron activation.
TABLE 5. APPROXIMATE LIMITS OF DETECTION OF VARIOUS TRACE METALS IN RIVER WATER BY NEUTRON ACTIVATION AND GROUP SEPARATIONS

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>APPROXIMATE ESTIMATE OF CONCENTRATION IN RIVER WATERS (µg/l)</th>
<th>DETECTION LIMITS BY NAA AFTER GROUP SEPARATION (µg/l)</th>
<th>ALLOWABLE LIMITS (µg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag*</td>
<td>0.3</td>
<td>0.01</td>
<td>50</td>
</tr>
<tr>
<td>As</td>
<td>2</td>
<td>0.1</td>
<td>50</td>
</tr>
<tr>
<td>Ba</td>
<td>10</td>
<td>5</td>
<td>1000</td>
</tr>
<tr>
<td>Br*</td>
<td>20</td>
<td>0.01</td>
<td>10</td>
</tr>
<tr>
<td>Cd</td>
<td>--</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Cl*</td>
<td>7800</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Co*</td>
<td>0.2</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>Cr*</td>
<td>1</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Cs*</td>
<td>0.02</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>7</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Fe*</td>
<td>--</td>
<td>300</td>
<td></td>
</tr>
<tr>
<td>Hg</td>
<td>0.07</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>K*</td>
<td>2300</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Mn*</td>
<td>7</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>Na*</td>
<td>6300</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Nb*</td>
<td>1</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Sn*</td>
<td>0.3</td>
<td>0.001</td>
<td></td>
</tr>
<tr>
<td>Sc*</td>
<td>0.004</td>
<td>0.001</td>
<td></td>
</tr>
<tr>
<td>Se*</td>
<td>0.2</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Zn*</td>
<td>20</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

*ELEMENTS NORMALLY DETECTED AND MEASURED BY INAA
**30 TO 80 ml WATER SAMPLES; INTEGRATED THERMAL NEUTRON EXPOSURE 2 x 10^16 n/cm²; COUNT FOR 10 min, 60 min, AND 1000 min AFTER DECAY TIMES OF 3 h, 24 h, AND 25 d, RESPECTIVELY; 20 cc Ge(Li) DETECTOR

This technique can also be used in a mobile laboratory situation allowing neutron irradiations with relatively high fluxes.

In Table 5 the approximate limits of detection for various trace metals in river waters are shown for instrumental neutron activation analysis and group separation neutron activation analysis. The data are compared to the allowable limits being set for pollutants in the United States. In general, values are on the order of µg/l with neutron activation analysis following group separation. In some select cases, the limit is as low as 0.001 µg/l.

The detection limit for instrumental neutron activation analysis in saline waters is shown in Table 6 for a select series of elements\(^{24}\). Detection limits vary from 10\(^{-4}\) to 100 µg/l based on a 25 ml sample of sea water, a 24-h irradiation at 10\(^3\) neutrons per cm\(^2\)/s, 40 days of decay, and a 1000 min count on a small 20 cc diode. Detectable concentrations\(^{24}\) for the heavy metals measured in saline waters by instrumental neutron activation analysis and by activation analysis with group separations are shown in Table 7. The separations process normally allows 0.001 µg/l, or below, to be measured, whereas values from 100 to many 1000-fold greater concentrations of elements can be measured by instrumental neutron activation analysis. This difference is created by the elimination of interferences such as photons from Na, Cl, or in some cases, elements with photon energies close to those being used to identify the element of interest.
**NUCLEAR TECHNIQUES**

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>TYPICAL SEAWATER CONCENTRATION (µg/L)</th>
<th>DETECTION LIMIT (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr</td>
<td>8000</td>
<td>100</td>
</tr>
<tr>
<td>Rb</td>
<td>120</td>
<td>5</td>
</tr>
<tr>
<td>Fe</td>
<td>1-20</td>
<td>1</td>
</tr>
<tr>
<td>Zn</td>
<td>0.5-10</td>
<td>0.2</td>
</tr>
<tr>
<td>U</td>
<td>3.3</td>
<td>0.1</td>
</tr>
<tr>
<td>Cs</td>
<td>0.3</td>
<td>0.003</td>
</tr>
<tr>
<td>Sb</td>
<td>0.2</td>
<td>0.005</td>
</tr>
<tr>
<td>Hg</td>
<td>0.01-0.3</td>
<td>0.05</td>
</tr>
<tr>
<td>Co</td>
<td>0.001-0.1</td>
<td>0.001</td>
</tr>
<tr>
<td>Sc</td>
<td>1-20 x 10^-4</td>
<td>1 x 10^-4</td>
</tr>
</tbody>
</table>

* 25 ml SEAWATER; 24 h IRRADIATION AT 10^{13} n/cm²/s; 40 d DECAY; 1000 min COUNT ON 20 cc Ge(Li) DIODE DETECTOR

**TABLE 7. ESTIMATED MINIMUM DETECTABLE CONCENTRATIONS OF HEAVY METALS IN SALINE WATERS BY INAA AND BY NAA WITH SEPARATIONS**

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>TYPICAL REPORTED CONCENTRATIONS IN SEAWATER (µg/L)</th>
<th>MINIMUM DETECTABLE CONCENTRATIONS (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg</td>
<td>0.01-0.3</td>
<td>0.05</td>
</tr>
<tr>
<td>Cd</td>
<td>0.06-0.7</td>
<td>0.001</td>
</tr>
<tr>
<td>Ag</td>
<td>0.002-0.05</td>
<td>0.001</td>
</tr>
<tr>
<td>As</td>
<td>2-3</td>
<td>NOT POSSIBLE</td>
</tr>
<tr>
<td>Cu</td>
<td>0.5-2</td>
<td>NOT POSSIBLE</td>
</tr>
<tr>
<td>Cr</td>
<td>0.02-0.6</td>
<td>0.3</td>
</tr>
<tr>
<td>Zn</td>
<td>0.5-10</td>
<td>0.2</td>
</tr>
<tr>
<td>Sn</td>
<td>0.02</td>
<td>NOT POSSIBLE</td>
</tr>
<tr>
<td>Se</td>
<td>0.08</td>
<td>0.2</td>
</tr>
<tr>
<td>Sb</td>
<td>0.2</td>
<td>0.005</td>
</tr>
</tbody>
</table>

* 25 ml SEAWATER; 24 h IRRADIATION AT 10^{13} n/cm²/s; 40 d DECAY; 1000 min COUNT ON 20 cc Ge(Li) DIODE DETECTOR

** 500 ml SEAWATER; ELEMENTS CHEMICALLY SEPARATED; 24 h IRRADIATION AT 10^{13} n/cm²/s; 3 d DECAY; 500 min COUNT ON A 20 cc Ge(Li) DIODE DETECTOR; BASED ON TWICE Bg CONTRIBUTION IN PEAK AREAS
TABLE 8. LIMITS OF DETECTION OF VARIOUS ELEMENTS IN TAP WATER. SENSITIVITIES IN PART-PER-BILLION

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>WITH SEPARATIONS</th>
<th>WITHOUT SEPARATIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>0.01</td>
<td>0.3</td>
</tr>
<tr>
<td>Br</td>
<td>0.01</td>
<td>100</td>
</tr>
<tr>
<td>Ce</td>
<td>1</td>
<td>200</td>
</tr>
<tr>
<td>Co</td>
<td>0.01</td>
<td>20</td>
</tr>
<tr>
<td>Cs</td>
<td>0.01</td>
<td>40</td>
</tr>
<tr>
<td>Eu</td>
<td>0.2</td>
<td>400</td>
</tr>
<tr>
<td>Ga</td>
<td>5</td>
<td>6000</td>
</tr>
<tr>
<td>In</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>Ir</td>
<td>0.005</td>
<td>0.8</td>
</tr>
<tr>
<td>K</td>
<td>50</td>
<td>50,000</td>
</tr>
<tr>
<td>La</td>
<td>1</td>
<td>40</td>
</tr>
<tr>
<td>Mo</td>
<td>1000</td>
<td>300</td>
</tr>
<tr>
<td>Na</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>5000</td>
<td>400,000</td>
</tr>
<tr>
<td>Pr</td>
<td>25</td>
<td>3000</td>
</tr>
<tr>
<td>Rb</td>
<td>0.1</td>
<td>500</td>
</tr>
<tr>
<td>Sb</td>
<td>0.01</td>
<td>1</td>
</tr>
<tr>
<td>Sc</td>
<td>0.001</td>
<td>5</td>
</tr>
<tr>
<td>Sm</td>
<td>0.1</td>
<td>5</td>
</tr>
<tr>
<td>Sn</td>
<td>100</td>
<td>20,000</td>
</tr>
<tr>
<td>Sr</td>
<td>1000</td>
<td>3000</td>
</tr>
<tr>
<td>Ta</td>
<td>0.1</td>
<td>9</td>
</tr>
<tr>
<td>Te</td>
<td>200</td>
<td>5000</td>
</tr>
<tr>
<td>W</td>
<td>1</td>
<td>200</td>
</tr>
</tbody>
</table>

It should be remembered that the detectable concentrations shown in the various tables are achieved by using the NaI(Tl) multidimensional gamma ray and Ge(Li) detector systems previously discussed.

Limits of detection of various elements in tap water are shown in Table 8 with sensitivities in ppb. The neutron activation analysis sensitivities with chemical separations range from 0.005 to 5000 ppb, depending on the nuclear characteristics of the element. The instrumental neutron activation analysis sensitivities are, of course, higher. In some cases, as is shown in Table 9, specific elements can be measured through chemical procedures designed for a unique series of elements. In this case, the ppb sensitivity for measurements of rare earths, Ba, Sr, and U is shown. The concentrations in reactor process water are shown and compared to the sensitivity achieved in neutron activation analysis measurement with chemical separation and a shielded Ge(Li) diode measurement. Sensitivities range from 0.05 to 50 ppb for this series of rare earth or rare-earth-like elements.

The chemical procedures used throughout the neutron activation analysis scheme are detailed in a large volume of literature and thus will not be discussed in detail. The procedures use evaporation techniques, coprecipitation or direct precipitation techniques, solvent extraction, and in many cases, ion exchange procedures.
At the sub-ppm levels at which many trace elements are present in the oceans or fresh waters one of the most formidable tasks in their measurement is the collection of representative, uncontaminated samples. The collection of uncontaminated subsurface samples is particularly difficult because one is frequently faced with using metal hydro wire and some sort of sampling bottle which has not been designed for collecting water for trace metal analyses. Thus unreliable metal data have been obtained. Techniques using all plastic hydro wire, all PVC nylon-teflon construction sampling bottles, and plastic filtration systems have allowed these sub-ppm concentrations of metals in sea water and fresh water to be obtained.

X-RAY FLUORESCENCE

In addition to the use of neutron activation analysis, X-ray fluorescence techniques can also be used in the laboratory to measure elemental concentration---the ppm to ppb range, depending on the preconcentration methods used for sample preparation. The rapid multielement analysis capability of energy dispersive X-ray fluorescence has been applied in Europe and the United States to the analysis of natural water samples, as well as other types of terrestrial material. In general, the X-ray fluorescence method can detect nanograms/cm² for many elements on some type of mounting matrix. Techniques are used which prepare water samples as a thin layer on some substrate. Various techniques can be used to prepare the sample in this method, such as the use of thionylid and ammonium-pyrollidine dithiocarbamate (APDC).
These organic compounds allow the recovery of tracer elements from aqueous samples by coprecipitation. For example, through the use of thionald, Cr(III) in sea water has been concentrated allowing its measurement by X-ray fluorescence at the 1 to 5 ppb level with a 3σ detection limit of 0.17 ppb. APDC has been used to precipitate Ni, Cr, Cu, Pb, Fe, Zn, and Hg in the concentration ranges of 1 to 100 ppb from both sea and fresh waters. More than 30 transition metals form insoluble precipitates with APDC and thus this method is extremely useful for multielement X-ray fluorescence analysis preparation.

Additional techniques such as ion exchange and liquid-liquid extractions are also useful. Specific discussion of the variety of preconcentration steps which can be used for the X-ray fluorescence analysis in the laboratory will be omitted in this discussion since this is being presented as an entire paper in this proceedings by another author.

It should be noted here that one additional technique utilizing atomic analysis is in a developing stage. This is the measurement of select elements through the use of laser fluorescence and ionization25,26. This technique should provide a sensitive method to measure from thousands of atoms to ppb concentrations of specific gaseous elements extracted from water media.

SUMMARY

This paper has discussed some of the most useful nuclear techniques that have been developed for use in the laboratory for studies of pollution in ground water. The techniques were divided into two parts—field and laboratory, with the predominant field techniques being the direct analysis of photons with sensitive detection equipment such as NaI(Tl) or Ge(LI) detectors. The in-field measurement of elemental components was accomplished through the use of X-ray fluorescence and neutron activation techniques. In the laboratory, these same techniques were also discussed and shown to be about 1000-fold more sensitive than in the field. Presently these field and laboratory techniques are being applied in the United States and Europe for the measurement of inorganic and radioactive pollutants in aqueous and sedimentary samples at a variety of locations.

REFERENCES


TRACE ELEMENT COMPOSITION OF GROUND WATER BY INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

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Chalk River Nuclear Laboratories,
Chalk River, Ontario, Canada

Abstract

TRACE ELEMENT COMPOSITION OF GROUND WATER BY INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS.

Ground water from the Perch Lake basin has been analysed by instrumental thermal neutron activation analysis. The concentrations of about forty elements are reported. The composition of samples from various locations in the basin is compared with that of the surface water in the basin. A general description is given of sampling techniques, methods used in preparing and analysing the samples and data reduction.

INTRODUCTION

The Perch Lake basin is the site of the Chalk River Nuclear Laboratories Waste Management Area, and studies of the geology and hydrology of the basin have been carried on for the past 30 years. Most of the earlier work was concerned with the movement of radionuclides in the Waste Management Areas and classic work in this field was carried out by Parsons. However, when the Perch Lake evaporation project was set up in 1965 as part of Canada’s program for the International Hydrological Decade, hydrological research in the basin was greatly expanded. Two sophisticated meteorological stations were installed, the surface water entering the lake was controlled and measured with a series of dikes and weirs, and an extensive program of research into ground water movement in the basin was initiated. The results of the Perch Lake project have been edited by Barry and published as an Atomic Energy of Canada Limited document [1].

Years of experience have now given us confidence in our ability to predict the movement of various radionuclides in the basin. However, we are still generally ignorant as to the complex hydrogeochemistry that governs this movement.
For this reason, it was decided it would be of interest to determine the elemental composition of the ground water and to determine the change in composition as it moves through the basin. In addition, as part of a feasibility study on the possibility of carrying out a trace element budget of the basin, it was necessary to know the composition of the ground water, which contributes about 14% of the water entering the lake.

Instrumental thermal neutron activation was selected as the method of analysis. It is probably unparalleled in its ability to combine great sensitivity with the identification and measurement of a large number of elements. Irradiation, counting and computing facilities were available and experience in the technique for the analysis of water samples had been gained in other projects [2].

SAMPLING

Because of the very low concentrations of many of the elements being measured, special sampling techniques were employed. All wells sampled had 10 cm PVC well screens. New polyethylene bottles were treated with dilute redistilled nitric acid, thoroughly rinsed with redistilled water and stored full of redistilled water until required. The wells were pumped at about 5 L/min for 1 h before and during the sampling. Small-bore polyethylene tubing which had been thoroughly cleansed with redistilled water was lowered down into the well screen. The sample was pulled up into the sample bottle with a vacuum pump, and taken to the laboratory immediately for preparation.

One hundred millilitres of the sample was evaporated to dryness on 0.01 mm polyethylene film supported in a fluorocarbon cup under an infrared lamp in a laminar flow clean hood. Drying time was about 30 h. The films were folded and inserted into clean polyethylene capsules for irradiation. Blanks were prepared similarly.

The samples were irradiated in the NRX reactor at a flux of $7 \times 10^{13}$ neutrons cm$^{-2}$ s$^{-1}$ for 5 s and counted a few minutes after irradiation and 24 h later. The samples were then irradiated in the NRU reactor at a flux of $2 \times 10^{14}$ n/cm$^2$ s for 4 h and counted 7 and 14 h after irradiation. Counting was carried out on a 125 cm$^3$ Ge(Li) detector connected to a 4096 channel analyzer. Resolution was 2.3 keV at 1.33 MeV and peak-to-Compton ratio was 42:1. Neutron fluxes were measured with cobalt monitors irradiated with the samples. Counter efficiencies for the various peaks were taken from a curve prepared by counting a series of standard sources.
The peaks in the spectra were located and their energies and areas determined using the PEKIN and JAGSPOT programs at the CRNL Computing Centre [3]. The energies and areas of the peaks, along with data on neutron flux, length of irradiation, counting-time, elapsed time between irradiation and counting and the counter efficiency curve are used as input to a computer routine for determining the amount of each element detected. A library of nuclear data is stored in the computer memory. The routine matches energies of peaks in the spectra.
TABLE I. INCREASING CONCENTRATION THROUGH THE BASIN

<table>
<thead>
<tr>
<th>Element</th>
<th>GWO</th>
<th>GW-DT</th>
<th>GWK</th>
<th>PLW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>147</td>
<td>1.8</td>
<td>8.3 x 10^3</td>
<td>3.3 x 10^3</td>
</tr>
<tr>
<td>Al</td>
<td>0.47</td>
<td>1.2</td>
<td>2.4</td>
<td>0.61</td>
</tr>
<tr>
<td>Fe</td>
<td>1.7 x 10^5</td>
<td>3.2 x 10^4</td>
<td>2.8 x 10^4</td>
<td>840</td>
</tr>
<tr>
<td>Cr</td>
<td>1.3</td>
<td>9.4</td>
<td>17</td>
<td>0.075</td>
</tr>
<tr>
<td>Sc</td>
<td>0.20</td>
<td>1.73</td>
<td>1.19</td>
<td>0.10</td>
</tr>
<tr>
<td>Hf</td>
<td>0.072</td>
<td>0.064</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>La</td>
<td>0.42</td>
<td>3.3</td>
<td>2.3</td>
<td>0.90</td>
</tr>
<tr>
<td>Ce</td>
<td>4.3</td>
<td>35</td>
<td>25</td>
<td>0.012</td>
</tr>
<tr>
<td>Sn</td>
<td>0.053</td>
<td>0.42</td>
<td>0.33</td>
<td>0.020</td>
</tr>
<tr>
<td>Eu</td>
<td>0.084</td>
<td>0.67</td>
<td>0.53</td>
<td>0.51</td>
</tr>
<tr>
<td>Nd</td>
<td>3.0</td>
<td>21</td>
<td>0.29</td>
<td>0.013</td>
</tr>
<tr>
<td>Tb</td>
<td>0.056</td>
<td>0.35</td>
<td>0.29</td>
<td>0.0089</td>
</tr>
<tr>
<td>Yb</td>
<td>0.083</td>
<td>0.28</td>
<td>0.65</td>
<td>0.014</td>
</tr>
<tr>
<td>Lu</td>
<td>0.081</td>
<td>0.23</td>
<td>0.21</td>
<td></td>
</tr>
</tbody>
</table>

Concentrations are quoted in µg/l or parts per billion. Since a 100 ml sample was used for analysis, less than 1 picogram was measured for several elements.

with those in the library and then proceeds to reject unlikely candidates on the basis of half-life, gamma ray intensity, absence of other peaks for that element, target isotope abundance and thermal neutron capture cross-section. The mass of the target isotope is then calculated for each selected nuclide. Where two or more elements are selected for a peak, the experimenter must exercise his judgement as to the most appropriate or as to whether or not both are present. The procedures may be carried out sequentially on a mini-computer using overlay programs, but at CRNL, with a large computer available, the whole procedure takes only a few seconds.

RESULTS

The samples were taken from the wells shown in Figure 1 and from Perch Lake. In general, the lake water has the lowest concentration of most elements. The elements may be divided into groups according to their behaviour as they move down the basin. The largest group is that with the highest concentration in the wells adjacent to the lake (Table I).
### TABLE II. DECREASING CONCENTRATION THROUGH THE BASIN

<table>
<thead>
<tr>
<th>Element</th>
<th>GWO</th>
<th>GW-DT</th>
<th>GWK</th>
<th>PLW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>$1.34 \times 10^8$</td>
<td>$2.9 \times 10^5$</td>
<td>$1.21 \times 10^5$</td>
<td>$3.6 \times 10^3$</td>
</tr>
<tr>
<td>K</td>
<td>$3.9 \times 10^5$</td>
<td>$1.02 \times 10^3$</td>
<td>270</td>
<td>$1.23 \times 10^5$</td>
</tr>
<tr>
<td>Cl</td>
<td>152</td>
<td>16</td>
<td>13</td>
<td>19</td>
</tr>
<tr>
<td>Cu</td>
<td>610</td>
<td>126</td>
<td>147</td>
<td>163</td>
</tr>
<tr>
<td>Sr</td>
<td>117</td>
<td>66</td>
<td>68</td>
<td>42</td>
</tr>
<tr>
<td>Co</td>
<td>19</td>
<td>0.68</td>
<td>0.25</td>
<td>0.105</td>
</tr>
</tbody>
</table>

### TABLE III. STABLE CONCENTRATION THROUGH THE BASIN

<table>
<thead>
<tr>
<th>Element</th>
<th>GWD</th>
<th>GW-DT</th>
<th>GWK</th>
<th>PLW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>1.76</td>
<td>2.4</td>
<td>2.5</td>
<td>0.72</td>
</tr>
<tr>
<td>Ca</td>
<td>$3.6 \times 10^3$</td>
<td>$3.7 \times 10^3$</td>
<td>$3.3 \times 10^3$</td>
<td>$1.60 \times 10^3$</td>
</tr>
<tr>
<td>Ba</td>
<td>76</td>
<td>72</td>
<td>71</td>
<td>16</td>
</tr>
<tr>
<td>Br</td>
<td>2.6</td>
<td>2.3</td>
<td>1.8</td>
<td>2.1</td>
</tr>
<tr>
<td>Au</td>
<td>$1.34 \times 10^{-4}$</td>
<td>$1.87 \times 10^{-4}$</td>
<td>$2.1 \times 10^{-4}$</td>
<td></td>
</tr>
</tbody>
</table>

### TABLE IV. VARIABLE CONCENTRATION THROUGH THE BASIN

<table>
<thead>
<tr>
<th>Element</th>
<th>GWD</th>
<th>GW-DT</th>
<th>GWK</th>
<th>PLW</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>21</td>
<td>18</td>
<td>18</td>
<td>0.20</td>
</tr>
<tr>
<td>Zr</td>
<td>12</td>
<td>9.4</td>
<td>9.4</td>
<td>2.6</td>
</tr>
<tr>
<td>Zn</td>
<td>8.8</td>
<td>7.0</td>
<td>7.0</td>
<td>7.0</td>
</tr>
<tr>
<td>Cs</td>
<td>0.035</td>
<td>0.087</td>
<td>0.087</td>
<td>0.016</td>
</tr>
<tr>
<td>Sb</td>
<td>0.031</td>
<td>0.14</td>
<td>0.14</td>
<td>0.14</td>
</tr>
</tbody>
</table>

The next group are those that have a decreasing concentration as they move down the basin (Table II). Table III shows those elements whose concentrations remain relatively constant throughout the basin. Table IV includes those elements that were detected but do not fit into the other categories. Zinc could not be measured in the wells near to the lake because
its peak was buried in the large scandium peak which is only 5 kev different in energy. A few elements detected in Perch Lake water, but not in the ground water, include Se, Hg and Ag. These probably enter the lake directly in precipitation or surface water.

DISCUSSION

At the recharge area at the head of the basin there is dissolved oxygen in the ground water. However, as the water moves through the basin the oxygen is depleted and conditions become more and more reducing. The multi-valent elements that comprise the first group change to their lower valence states which are more soluble than the higher state and the concentration in the ground water increases. Iron is a good example; increasing from about 2 to 28 mg/l.

The second group shows a decrease in concentration and are probably added to the basin from the waste management area. They are diluted with normal ground water as they move down the basin. Elements that are unchanged are those at their natural levels in the ground water and are not affected by redox conditions.

These results are preliminary. The samples analyzed were all taken in the winter months. The program will be continued, with samples taken at different times of the year, to look for seasonal effects. Also, it is hoped to be able to move further up the basin, into the recharge area, and to add more wells to the sampling program.

REFERENCES


TRACE ELEMENT POLLUTION IN GROUNDWATER USING NUCLEAR ANALYTICAL METHODS

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Abstract

TRACE ELEMENT POLLUTION IN GROUNDWATER USING NUCLEAR ANALYTICAL METHODS.

Neutron activation and X-ray fluorescence methods were used in trace level analysis of groundwater. The results of the determination of indigenous elements as well as those deriving from pollution in urban, industrial and agricultural regions are presented. The concentration distribution of different elements in groundwater, metallic and non-metallic, were obtained. Investigating the relationship of water quality and trace element concentration, a linear correlation was found. Case studies demonstrate that the data collected on trace element occurrences in groundwater enable the localization of pollutant sources and can be very useful in predicting the movement of pollutants.

1. INTRODUCTION

Growing pollution of the natural environment changes the trace element composition of groundwaters. Some trace elements are known or thought to be essential for life, or health, whilst others are toxic, or cause diseases if present in excess. Thus it is essential to know the background environmental levels and the changes occurring.

Such information is of benefit to biologists and hydrochemists, and also to hydrogeologists when the concentrations exceed the maximum permissible levels in groundwater. Other benefits from trace element studies arise from the use of these elements as naturally existing tracers in pollution movement. Our present approach to the problem is a detailed study of trace element composition in pollution sources, the natural background level in groundwater, and the distribution in groundwaters of trace elements deriving from pollution.

The investigations presented in this paper are restricted mainly to Quaternary sand aquifers. The number and composition of observed trace elements were determined by analytical methods, X-ray fluorescence and neutron activation.
2. INPUT MODEL

A simplified trace element input model is shown in Fig.1. Direct high-concentration input sources can be represented by waste disposal reservoirs and sewage channels, from which leakage occurs. A large volume of polluted water passes directly to the aquifer, being mixed with groundwater.

Infiltration input is represented by solid waste materials deposited on the surface of the earth, and pollutants distributed into the atmosphere, washed out by the rain waters infiltrating the soil-aerated zone. The industrial and municipal subsurface wastewaters contribute usually to the aerated zone below the soil zone. It can be presumed that the dissolved ions of trace elements will undergo processes similar to those determining the basic chemical composition of groundwater. However, other processes enabling a selective movement of trace elements may occur.

3. ANALYTICAL TECHNIQUES

Reactor neutron activation and X-ray fluorescence have been used to identify the elemental components in water.

Neutron activation analysis was based on the following procedure and equipment:

Neutron flux: \( n \times 10^{13} \, n \cdot cm^{-2} \cdot s^{-1} \)

Irradiation time: 4 days
Decay time: 8 days to 60 days

Gamma spectrometer Ge(Li) with energy resolution of 1.6 keV (FWHM) for 320 keV. Volume: 36 cm$^3$

Computer spectra processing

Sample: 100 mg of dry residue after ashing at a temperature below 80°C.

Standards, internal standards, and additional control standards. The reference standards were prepared as single element standards, and natural water standards.

The minimum detection limits are sufficient for determination of about 20 elements at their natural background level. Average precision of measurements (2S) was within about 6%. The major ion composition of the water sample has practically no influence on the detection limits, however the minor and trace elements, when in excess, can considerably reduce the detection limits of other elements contained in the sample. The high concentrations of zinc, iron, and scandium particularly distort the measurements.

X-ray fluorescence analysis has been used with a radioisotope excitation source, and Si(Li) spectrometer, having energy resolution of 180 eV (FWHM). Analyses were made of dry residue specimens, (thick source) giving minimum detection limits higher than with neutron activation. X-ray fluorescence was used mainly as a control method for rapid determination of some elements in excess.

4. TRACE ELEMENTS IN GROUNDWATER

Water sampling for trace element investigation was carried out during 1975 and 1976 in the area, which extends from central region of Poland to the Baltic, including some eastern regions.

4.1. Unpolluted groundwaters

Two groups of watersheds have been sampled. In the first group, the samples were taken from the wells representing large Cretaceous and Tertiary aquifers. The tritium content in all the samples was below a measurable value (5 TU), giving proof that no direct contact with the surface exists.

Text continued on p. 166
<table>
<thead>
<tr>
<th>Element</th>
<th>Natural environment</th>
<th>Urban-industrial areas</th>
<th>Agricultural areas</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No. of sampled wells</td>
<td>Range</td>
<td>Average</td>
</tr>
<tr>
<td>Scandium</td>
<td>38</td>
<td>0.01 - 0.35</td>
<td>0.07</td>
</tr>
<tr>
<td>Chromium</td>
<td>42</td>
<td>0.07 - 2.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Cobalt</td>
<td>42</td>
<td>0.01 - 0.13</td>
<td>0.03</td>
</tr>
<tr>
<td>Zinc</td>
<td>26</td>
<td>1.5 - 80</td>
<td>15</td>
</tr>
<tr>
<td>Selenium</td>
<td>38</td>
<td>0.01 - 0.08</td>
<td>0.05</td>
</tr>
<tr>
<td>Bromine</td>
<td>26</td>
<td>12 - 150</td>
<td>30</td>
</tr>
<tr>
<td>Ruthenium</td>
<td></td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>Rubidium</td>
<td>18</td>
<td>0.05 - 2.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Strontium</td>
<td>26</td>
<td>10 - 1240</td>
<td>100</td>
</tr>
<tr>
<td>Antimony</td>
<td>26</td>
<td>0.13 - 1.0</td>
<td>0.3</td>
</tr>
<tr>
<td>Caesium</td>
<td>28</td>
<td>0.003 - 0.027</td>
<td>0.01</td>
</tr>
<tr>
<td>Barium</td>
<td>28</td>
<td>3 - 60</td>
<td>15</td>
</tr>
<tr>
<td>Lanthanum</td>
<td>24</td>
<td>0.02 - 0.47</td>
<td>0.12</td>
</tr>
<tr>
<td>Cerium</td>
<td>32</td>
<td>0.04 - 3.2</td>
<td>1.0</td>
</tr>
<tr>
<td>Terbium</td>
<td></td>
<td>76</td>
<td></td>
</tr>
<tr>
<td>Ytterbium</td>
<td>34</td>
<td>0.001 - 0.2</td>
<td>0.04</td>
</tr>
<tr>
<td>Hafnium</td>
<td>16</td>
<td>0.003 - 0.4</td>
<td>0.12</td>
</tr>
<tr>
<td>Europium</td>
<td></td>
<td>81</td>
<td></td>
</tr>
<tr>
<td>Mercury</td>
<td></td>
<td>4</td>
<td>0.04 - 1.0</td>
</tr>
</tbody>
</table>
FIG. 2. The frequency distribution of Zn, Co, Cr, Sb, Vb, in groundwater, sampled in urban-industrial areas. Dashed line indicates the maximum concentration observed in unpolluted water. Range "A" corresponds to natural occurring concentrations. Range "B" results from movement of pollutants to groundwater.
FIG. 3. Trace elements deriving from industrial effluents. The concentrations are shown with respect to unpolluted groundwater.
<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (ppb)</th>
<th>Concentration (ppb)</th>
<th>Concentration (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rivers</td>
<td>Waste-disposal</td>
<td>Industrial effluents</td>
</tr>
<tr>
<td></td>
<td>No.of samples</td>
<td>Range</td>
<td>Average</td>
</tr>
<tr>
<td>Scandium</td>
<td>18</td>
<td>0.005 - 0.165</td>
<td>0.11</td>
</tr>
<tr>
<td>Chromium</td>
<td>17</td>
<td>0.5 - 22.9</td>
<td>1.9</td>
</tr>
<tr>
<td>Cobalt</td>
<td>19</td>
<td>0.03 - 0.71</td>
<td>0.2</td>
</tr>
<tr>
<td>Zinc</td>
<td>30</td>
<td>3.0 - 57</td>
<td>16</td>
</tr>
<tr>
<td>Selenium</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bromine</td>
<td>28</td>
<td>0.4 - 5.5</td>
<td>1.1</td>
</tr>
<tr>
<td>Rubidium</td>
<td>15</td>
<td>0.9 - 394</td>
<td>131</td>
</tr>
<tr>
<td>Strontium</td>
<td>16</td>
<td>0.11 - 1.4</td>
<td>0.5</td>
</tr>
<tr>
<td>Antimony</td>
<td>20</td>
<td>0.001 - 0.26</td>
<td>0.03</td>
</tr>
<tr>
<td>Caesium</td>
<td>15</td>
<td>0.13 - 9.5</td>
<td>2.6</td>
</tr>
<tr>
<td>Lanthanum</td>
<td>12</td>
<td>0.01 - 0.41</td>
<td>0.6</td>
</tr>
<tr>
<td>Cerium</td>
<td>32</td>
<td>0.7 - 2.5</td>
<td>1.2</td>
</tr>
<tr>
<td>Ytterbium</td>
<td>16</td>
<td>0.001 - 0.014</td>
<td></td>
</tr>
</tbody>
</table>
The second group included the samples taken from Quaternary waters of the areas free of contamination. The following criteria were adopted for sample selection:

Absence of any evident pollution sources in the sample area
Non-agricultural area
Results of chemical analysis giving no evidence of pollution.
The sampling depth extended from 5 metres to 40 metres.

4.2. Polluted areas

The polluted waters were selected according to the results of the chemical analysis, in which the changes of water quality were reflected. Urban areas with population of about 30,000–60,000 were sampled, and industrial areas as well. About 120 wells were investigated. In agricultural areas samples were taken from 22 wells. The sampling depth extended from 10 metres to 40 metres in sand aquifers, partially isolated from the surface.

4.3. Analytical results

The measured values for 19 trace elements are summarized in Table I. The range and average concentrations in the waters free of pollution present the natural background data, which can be used for estimating the pollutant movement. However, the data obtained should be considered as preliminary, because we can expect to encounter the aquifers with higher concentrations originating from interaction with host rocks enormously rich in elements.

The elemental data obtained from groundwater sampling of industrial urban and agricultural areas show a much broader range of concentration and higher average values. For several elements such as zinc, selenium, cobalt and barium, the observed concentrations are from ten to a hundred times higher than in unpolluted waters. The analytical results make evident the movement of trace element pollution into groundwater. This may be seen in detail on the frequency distribution diagram shown in Fig.2. The dashed lines representing maximum observable values in unpolluted waters divide the distribution into regions of naturally occurring elements, and of pollution elements.

5. SOURCES OF POLLUTANTS

The samples were taken from industrial sewage systems, effluents and waste storage reservoirs, which potentially create the main risk of groundwater pollution.
However, one should keep in mind that solid wastes can also make a considerable contribution.

We have examined the content and composition of trace elements in pollutants from several industrial plants including chemical, textile, pharmaceutic, sugar, rubber, leather, cellulose, soda, food, metallurgical, and alcohol distillation plants.

A visual impression of the composition and concentration levels with respect to the natural water background can be seen in Fig. 3.

The rivers were sampled downstream from the industrial and municipal sewage outlets at a distance ensuring mixing had occurred.

The results obtained for industrial pollution sources and rivers are presented in Table II. A visual comparison of pollution levels in rivers and groundwaters with respect to unpolluted waters and concentrations of sources is presented in Fig. 4. It may be noted that the concentrations in pollution sources are up to a thousand times higher than in unpolluted waters. It is also interesting to add that the concentration levels in river waters are lower than in polluted groundwaters. Of course, we have excluded from our observations some small rivers in industrial regions, which are sometimes used as open sewage channels.

6. CORRELATION BETWEEN POLLUTANTS AND TRACE ELEMENTS

Knowing that the excess concentrations of trace elements observed in groundwaters originate from pollution, one should search for a correlation between
FIG. 5. Cross-section through an industrial-urban area, giving a visual impression of the physical and chemical properties and trace element compositions of sampled wells. Fairly good correlation is evident. The location of pollution sources is reflected selectively in high trace element concentrations in wells.
FIG. 6. Relationship between water pollution indicators (WPI) reflected in the dry weight, Cl⁻, SO₄²⁻, NO₃⁻ data and trace element concentration of Co, Cr, Se, Ce, in groundwaters. 

a – urban area; b – industrial area.

FIG. 7. Diagram showing the average level of chemical pollution indicators and of trace elements, measured in industrial, urban and agricultural regions.
FIG. 8. Concentration diagram showing the salinisation of wells in a Cretaceous aquifer. The sampled wells show various degrees of salinity. The deep saline waters mix with fresh waters. The Ca content reflects the host rock interaction.

FIG. 9. Concentration diagram of some major components and trace elements showing the mixing of sea-water with fresh water. The measured values are related to sea-water concentration. Well No. 4 presents the composition of fresh water.
pollutants and trace elements distributed in groundwaters. For this purpose the following physical and chemical pollution indicators were adopted: colour, hardness, Na, Cl, Fe, NO₃⁻, SO₄⁻, O₂ contents and dry weight. Trace elements were represented by Cr, Co, Se, Cr, Cs, Sr.

The investigations were carried out on industrial-urban and agricultural areas. The wells were simultaneously sampled for chemical and trace element analysis.

Analytical results obtained from the investigation carried out on an industrial-urban area are presented in cross-section in Fig.5. A good agreement between chemical and trace element data may be noticed. However, the appearance of single indicators is selective and one may observe several differences which would require additional detailed examination. It may also be noted that the high concentrations of trace elements reflect the industrial pollution inputs. This cannot always be stated regarding chemical indicators.

This can be seen from well No.33, which shows a very high concentration of chromium, the pollution coming from a metallurgical plant in this area.

Figure 6 presents the correlation diagrams constructed for wells representing: (a) an industrial region, (b) an urban region. The pollution indicators are reflected in dry weight, Cl⁻, SO₄⁻, and NO₃⁻ data. Trace elements included Co, Cr, Se, Ce. The values were obtained by dividing the measured values by locally occurring background level. A linear correlation was obtained for the industrial area:

\[ y = 4.7x - 9.8 \]

A similar procedure was used to investigate the urban area. A linear correlation was also obtained, but with a much lower slope:

\[ y = 0.29x - 0.54 \]

The results obtained imply that in industrial areas trace elements move much more intensively into groundwaters, and then changes of water quality occur.

A similar picture is seen in Fig.7, constructed on the basis of a large number of samples. The diagram shows the average levels of chemical indicators and trace elements in industrial and in urban areas, and in an agricultural area. The agricultural area also shows a faster increase of trace elements. However, because of the small number of samples (12 samples), reservations must be entertained regarding this finding.

Text continued on p. 176
FIG. 10. The leakage from a flotation reservoir. The cross-section shows schematically the location of the sampled wells. The diagram shows the trace element composition related to reservoir water. Sr, Rb, Br, Co, are in excess in reservoir water. Zn, Sb predominate in groundwater.
FIG. 11. Groundwater pollution caused by leakage from a waste storage reservoir. Sampling points are shown in cross-section. The diagram shows the groundwater composition with respect to reservoir water.
FIG. 12. Trace element composition diagram showing movement of pollutants in a sand aquifer in Kazubskaja Valley. The lines diverge, indicating the selective movement of pollutants. Wells Nos 1, 2, 3 and 4 are polluted. The map shows schematically the location of the sampled wells.
FIG. 3. Trace element composition of well located in an industrial and an agricultural area. Concentrations are related to maximum levels occurring in unpolluted waters. Selective movement of cobalt in industrial and selenium in agricultural areas can be observed.
7. PATTERN OF MOVEMENT

Data have been collected of several case studies and presented in the form of diagrams to illustrate trace element movement to groundwaters according to the previously described pattern.

7.1. Direct input

A direct input of polluted waters to an aquifer can be demonstrated by leakage from a storage reservoir. A similar effect will be obtained as in the case of the familiar intermixing of saline and fresh waters. Figure 8 presents a diagram showing mixing of deep saline waters with fresh waters, in a Cretaceous aquifer. The sampling depth extended from 120 metres to 240 metres. No sign of bomb tritium was found. The diagram was constructed for some major ions, Cl⁻, Mg²⁺, Ca²⁺, and some minor ions, Br⁻, Fe⁺⁺. The results are shown with respect to sample No.1, representing the most saline water. (Dry weight: 5150 mg/l. Cl 3800 mg/l). Sample 4 represents fresh water, with dry weight of 278 mg/l, and Cl content of 22 mg/l.

An ideal mixing should occur in concentration lines parallel to a reference line, slightly modified by the background level contribution. The observed concentration line plot shows a mixing of saline and fresh waters followed by some host rock interaction processes.

A similar mixing pattern can be observed in Fig.9, showing mixing of Baltic sea water with fresh water. The diagram has been constructed for some major ions and trace elements. Similar movement patterns are evident as in the previous example.

Industrial pollution input to groundwaters is presented in Fig.10. The polluted waters from a post-flotation reservoir leak directly to groundwater, reaching well No.5 at a distance of 1000 metres. The area investigated and the sampled wells are shown in cross-section in Fig.10a. The diagram in Fig.10b, indicates dilution of polluted water in groundwaters. The concentration plots are similar to those presented previously but are more evident because of the different composition of water. Strontium, rubidium and cobalt dominate in reservoir water. Zinc and antimony are in excess in groundwater. The crossing point shows the same concentration of caesium.

A similar case can be observed in Fig.11. The area investigated and sampling points are shown in Fig.11a. The water seepage through an earth-filled dam is contributing to adjacent groundwater. The concentration diagram presents a relative decrease of trace element concentration as distance from the dam increases. This case shows, in addition to the dilution process, selective movement of elements.
7.2. Infiltration input

This is a most common trace element pollution input in urban and industrial areas. The pollution moves with rainwater to soil, the aerated zone and then to the saturated zone. Leakages from urban and industrial sewage systems contribute directly to the aerated zone, omitting the soil.

Selective movement of trace elements to groundwater can be seen on the concentration diagram (Fig. 12) obtained for a sand aquifer in Kaszubsksa Valley, North Poland. The aquifer is about 50 metres in depth, and is recharged from high land (Fig. 12a). Point 7 represents several wells simultaneously pumped for water supply. The water was of good quality and no sign of pollution trace elements has been found. However, in the vicinity several pollution sources have been determined. In the area of wells Nos 1, 2, 3, and 4 an agricultural enterprise was located. The western part of the valley was cut by a municipal sewage channel. Observation of the diagram makes it evident that the concentration lines have different plots, as in the previously presented diagrams. The lines diverge, showing a selective movement of trace elements to groundwaters. The observed concentrations in wells Nos 1, 2 and 3 are higher than in well No.7, reflecting pollution movement from an agricultural enterprise. Also, well No.8 shows a high concentration of chromium, due to a local contamination source. On the other hand, no pollution was observed from sewage.

Selective movement of trace elements in urban and agricultural areas can be well observed in concentration diagrams presented in Fig. 13. As a baseline, the natural concentration level in unpolluted waters was chosen. The points lying above this line indicate movement of pollutants into groundwater. It can be noted that in the industrial area cobalt moves very selectively to groundwater, and also selenium in the agricultural region.

8. CONCLUSIONS

The survey of trace elements carried out in groundwaters has given a picture of the present state of water pollution in urban and industrial areas.

The knowledge gained from the occurrence of trace elements in groundwaters, both polluted and unpolluted, and also from the concentrations deriving from pollution sources, facilitates a look into the physical and chemical models of pollutants movement. Observations made with regard to selective movement of some trace elements raise the question of their chemical form and transport mechanism.

The trace element study also has some practical application in regard to the identification of pollution sources.
It should be stressed that such a large-scale trace element survey in groundwaters was possible only because of the use of neutron activation, which offers very good minimum detection limits and which can determine simultaneously more than 20 elements.
ENERGY DISPERSION X-RAY FLUORESCENCE TECHNIQUES IN WATER POLLUTION ANALYSES

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Abstract

ENERGY DISPERSION X-RAY FLUORESCENCE TECHNIQUES IN WATER POLLUTION ANALYSES.

Advantages and limitations of energy dispersion X-ray fluorescence methods for analysis of pollutants in water are discussed. The necessary equipment for X-ray measurement of insoluble and dissolved trace metals in water is described. Different techniques of enrichment of trace metals are presented: ion exchange on selective Chelex-100 exchanger, precipitation with chelating agents DDTc and APDC, and adsorption on activated carbon. Some results obtained using different preconcentration methods for trace metals determination in different waters are presented.

1. INTRODUCTION

The present need for monitoring water quality has resulted in determination of trace elements in water becoming increasingly necessary. The energy-dispersion X-ray fluorescence [EDXRF] method of analysis offers an easy and sensitive way of detecting many pollutants in water and waste effluents. It has been shown [1–5] that many analytical problems connected with environmental pollution can be solved using this technique. Its advantages are that

1. only simple sample preparation is required;
2. many elements can be determined simultaneously; and
3. the accuracy of determination for most elements is better than 10 per cent (relative to the standard deviation).

The limitation is that energy-dispersion X-ray analysis systems are not usually designed to measure the low-energy X-ray line characteristic for elements with low atomic number. Therefore only elements of atomic number Z larger than about 20 can be quantitatively determined by means of the EDXRF method.

Direct XRF analysis of aqueous samples is only feasible for parts per million concentrations of higher atomic number elements [6]. The detection limits are
approximately about 1—5 ppm for such elements as Cu, Zn and Pb. This rather poor detection limit is due to the backscatter background and X-ray absorption effects. To reach a detection limit in the pp10⁶ range a preliminary chemical enrichment must be undertaken before attempting X-ray analysis. The methods of isolating trace elements will be discussed in subsequent sections.

Trace elements may be found in water in different chemical forms:

(1) insoluble particulates, e.g. colloidal particulates (particle size 0.001—0.1 μm), aggregates of hydrous metal oxides and suspended particles (particle diameter > 0.1 μm);
(2) soluble species — metal ions and metal complexes with inorganic and organic ligands.

Very often the subdivision of a water sample into a soluble and insoluble fraction is necessary in order to analyse both fractions separately. When the X-ray fluorescence method is used, the most convenient method of separating...
TABLE I. EDXRF detection limits\textsuperscript{a,\textb{b}}

<table>
<thead>
<tr>
<th>Element</th>
<th>Radioisotope source \textsuperscript{238}Pu (100 mCi) [9]</th>
<th>Low-power X-ray tube (Ag) [9]</th>
<th>High-power X-ray tube with second. target [11]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\mu g \cdot cm^{-2})</td>
<td>(\mu g \cdot cm^{-2})</td>
<td>(\mu g \cdot cm^{-2})</td>
</tr>
<tr>
<td>Cr-K(_{\alpha})</td>
<td>0.24</td>
<td>0.064</td>
<td>0.019</td>
</tr>
<tr>
<td>Mn-K(_{\alpha})</td>
<td>0.127</td>
<td>0.056</td>
<td>0.016</td>
</tr>
<tr>
<td>Fe-K(_{\alpha})</td>
<td>0.175</td>
<td>0.064</td>
<td>0.017</td>
</tr>
<tr>
<td>Ni-K(_{\alpha})</td>
<td>0.080</td>
<td>0.020</td>
<td>0.010</td>
</tr>
<tr>
<td>Cu-K(_{\alpha})</td>
<td>0.103</td>
<td>0.029</td>
<td>0.012</td>
</tr>
<tr>
<td>Zn-K(_{\alpha})</td>
<td>0.072</td>
<td>0.033</td>
<td>0.009</td>
</tr>
<tr>
<td>Pb-L(_{\alpha})</td>
<td>0.103</td>
<td>0.033</td>
<td>0.040</td>
</tr>
<tr>
<td>Se-K(_{\alpha})</td>
<td>0.095</td>
<td>0.021</td>
<td>–</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Detection limit is expressed as equal to

\[
\frac{3}{m} \sqrt{\frac{I_b}{t}}
\]

where

- \(I_b\) is background count rate, \(\text{counts} \cdot \text{s}^{-1}\)
- \(m\) is slope of the straight calibration line
- \(t\) is counting time.

\textsuperscript{b} The values of detection limits for 2000 s counting time refer to pollutant material collected on a surface of a membrane filter.

suspended matter is filtration of water samples through membrane filters (pole diameter 0.45 \(\mu\)m). In such a case the soluble and colloidal fractions are taken together and regarded as a "soluble" fraction.

2. INSTRUMENTATION

Since analysis of environmental samples is multi-element, measurement equipment of high resolution has to be used. It consists of a Si/Li semiconductor detector having an energy resolution of at least 200 eV at MnK\(_{\alpha}\) (5.9 keV), a source of exciting radiation and a sample holder. The sample holder is sometimes
located in a vacuum chamber to eliminate air scattering of the primary beam and absorption of characteristic X-rays in the sample-detector pathway. The counting electronics include a multi-channel analyser with a printer for recording and digitizing the X-ray spectrum. Very often a mini-computer is on-line linked with XRF equipment. Two kinds of primary radiation sources can be used in energy dispersion XRF systems: low-energy radioisotope gamma or X-ray sources ($^{55}$Fe, $^{238}$Pu, $^{109}$Cd, $^{241}$Am) and low- or high-power X-ray tubes with or without secondary fluorescers [7, 8]. Measurement geometries for both kinds of excitation sources are shown in Fig. 1. The main advantage of using a radioisotope source is its small dimensions, compact measurement geometry and low cost, compared with an X-ray tube. On the other hand the quanta output from a radioisotope source (namely $^{239}$Pu — 100 mCi) is smaller than from an X-ray tube, which results in a poorer detection limit. Especially X-ray tubes with secondary targets are superior to radioisotope excitation.

The values of detection limits for various elements in water are listed in Table I for a radioisotope source, a low-power "transmission" X-ray tube with Ag target and a high-power X-ray tube.

3. SAMPLING AND SAMPLES PRESERVATION

In chemical trace analysis particular attention has to be paid to proper water sampling and storage because these procedures greatly influence the accuracy of any method for the determination of trace elements.

The sample must not be contaminated with the elements to be determined and cannot undergo physicochemical changes which result in loss of trace elements by adsorption or volatilization during transportation and storage. For analysis for most metals, water samples should be acidified by glacial acetic acid (or nitric acid) to about pH 2–3. Acidification tends to minimize precipitation and sorption on the wall of the sample container. Also, freezing of water samples is helpful in minimizing changes due to biological activity, e.g. redox processes. The best way of avoiding the analysis errors due to contamination or losses is to filter the water sample and perform some simple preconcentration at the sampling-site.

4. ANALYSIS OF INSOLUBLE MATTER

The EDXRF method is particularly suitable for analysis of suspended matter. The sample can be collected easily on a membrane filter and after drying, directly examined using the X-ray system. Practically no sample preparation is required. An additional advantage is that a layer of a deposit on
### TABLE II. MEMBRANE FILTERS USED FOR PARTICULATES SELECTION

<table>
<thead>
<tr>
<th>Filter Type</th>
<th>Diameter (μm)</th>
<th>Mass per unit area (mg·cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Millipore HAWP</td>
<td>0.45</td>
<td>5.5</td>
</tr>
<tr>
<td>Millipore THWP</td>
<td>0.45</td>
<td>1.4</td>
</tr>
<tr>
<td>Sartorius SM 111</td>
<td>0.45</td>
<td>4.5</td>
</tr>
<tr>
<td>Synpor</td>
<td>0.60</td>
<td>3.8–5.2</td>
</tr>
<tr>
<td>Nuclepore</td>
<td>0.40</td>
<td>1.15</td>
</tr>
</tbody>
</table>

### TABLE III. RESULTS OF ANALYSIS OF WATER PARTICULATE MATERIAL

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>0.84</td>
<td>11</td>
<td>62</td>
<td>5.6</td>
</tr>
<tr>
<td>Cr</td>
<td></td>
<td></td>
<td>12</td>
<td>15.0</td>
</tr>
<tr>
<td>Mn</td>
<td>0.056</td>
<td>58</td>
<td>28</td>
<td>7.3</td>
</tr>
<tr>
<td>Fe</td>
<td>7.5</td>
<td>1.3</td>
<td>600</td>
<td>0.6</td>
</tr>
<tr>
<td>Ni</td>
<td>0.48</td>
<td>5.8</td>
<td>n.d.¹⁰</td>
<td>0.6</td>
</tr>
<tr>
<td>Cu</td>
<td>0.045</td>
<td>100</td>
<td>n.d.¹⁰</td>
<td>0.6</td>
</tr>
<tr>
<td>Zn</td>
<td>0.30</td>
<td>9</td>
<td>22</td>
<td>3.0</td>
</tr>
<tr>
<td>As</td>
<td>0.104</td>
<td>15</td>
<td>66</td>
<td>2.1</td>
</tr>
<tr>
<td>Br</td>
<td>0.68</td>
<td>3.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rb</td>
<td>0.11</td>
<td>16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sr</td>
<td>0.19</td>
<td>10</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

¹ Results obtained for energy dispersion XRF system with X-ray tube.
² Not detectable.
a filter surface can be regarded as a "thin sample" [9–11] provided that the filter load is limited to only 1–2 mg·cm\(^{-2}\) for X-ray energies higher than about 5 keV. In such a case linear relations between signals measured and mass per unit area of elements determined are obtained and matrix effects may be usually neglected.

Various kinds of membrane filters are now commercially available (Table II). Usually filters of pore diameters of 0.40 to 0.60 \(\mu\)m are used for insoluble matter selection.

Since spectrum background depends on filter mass per unit area and metal impurities in filter material, the thinner and cleaner the filter, the better are the detection limits that can be achieved [12]. Metal impurities in filter material (mainly Al, Fe, Zn, Cu, Cr) can be minimized by washing the filter with dilute nitric acid followed by bidistilled water before use [13].

Usually river and sea water fine suspensions give satisfactorily uniform distribution of the particulate matter on the filter material. The standard deviation calculated from scatter of the analysis results from the different parts of the filter is about 4% according to van Grieken [12] and our results [9]. A significant error can occur when particles are coarse and their size distribution is variable. If calibration samples are homogeneous, having been obtained by a method of spotting of standard solutions [2] or by depositing powdered metal oxides or other compounds [14] on the filter's surface and if analysed samples are non-homogeneous, the error due to grain size effects can exceed 100% (relative to the standard deviation). There exist however some methods of eliminating this effect.

If particle size distribution of particulate material is known (e.g. from sedimentation or microscopic measurements) the calculated correction factor can be used in order to minimize particle size effects. Our results show that the values of correction factors for Fe determination in rainfall particulates are 1.6 and 3.1 for particle size fractions of Fe\(_2\)O\(_4\) 25–35 \(\mu\)m and 88–102 \(\mu\)m respectively [15]. As one can see, the values of correction factors are large and the influence of particle size effect cannot be neglected.

Some authors apply preliminary particle size differentiation and separate measurement of different grain size fractions [12]. The particle size effect can also be eliminated by using two different energies of primary radiation for exciting characteristic X-rays of the elements to be determined. Two radio-isotope sources, e.g. \(^{55}\)Fe–\(^{109}\)Cd and \(^{238}\)Pu–\(^{241}\)Am, or two different targets, e.g. Ti–Cu and Cu–Ag, can be used in the X-ray tube system. Taking the ratio of the signals obtained with two measurements, one can calculate the correction factor for particle size effect [15, 16].

To the author's knowledge, only a few applications of EDXRF to water particulate analysis have been reported to date [2, 9, 10, 12]. Some results are shown in Table III. Since this method is simple, rapid and sensitive enough, it
seems to be competitive with flameless atomic absorption, which is a sequential method and requires particulate material to be dissolved. Energy-dispersion X-ray spectrometry seems to be particularly applicable to analysis of particulate material in polluted rivers, waste effluents and rain and/or snowfalls.

5. ANALYSIS OF SOLUBLE SPECIES

It has already been mentioned that natural water cannot be accurately analysed by EDXRF at the pp10^5 level without a preconcentration step. For routine use, a preconcentration procedure should be simple, relatively rapid,
accurate and not very expensive. Besides, a "thin sample" should easily be obtained. Enrichment of trace elements can be carried out in two ways:

1. water is removed by evaporation or lyophilization;
2. trace elements are separated from water.

Evaporation of water samples (e.g. 250 ml volume) is time-consuming and can lead to losses of trace elements by adsorption on walls of the container as well as contamination by elements leaching from the beaker material. An additional disadvantage of this method is the difficulty of preparing a "thin sample" from dry residue with satisfactory reproducibility. Lyophilization is also time-consuming and rather expensive. Some chemical methods of separation of trace metals are rapid and give good results. In connection with X-ray fluorescence and neutron activation analysis several preconcentration procedures have been proposed in the literature. They are:

1. ion exchange on ordinary (e.g. strong acid IR-120) and chelating exchangers [17–21];
2. precipitation with organic reagents such as sodium-diethylidithiocarbamate (DDTC) [14, 22, 23], ammonium-pyrrolidine-dithiocarbamate (APDC) [24, 25] and 1-(2-pyridylazo) – 2-naphtal (PAN) [23];
3. collection of trace elements on activated carbon [13, 26, 27].
5.1. Ion exchange

The use of granulated ion exchange resin for resin-loaded filters has certain limitations. One of them is the lack of specificity. For this reason such filters cannot be used for separation of metal cations from natural waters mainly because of their saturation by alkaline earth ions.

Selective ion-exchanger Chelex-100 seems to have much wider application, because of the high affinity of resin to transition metals.

Chelex-100-loaded filters (e.g. Acropor Chelex, Gelman Instr. Comp.) which incorporate chelating resin in a cellulose matrix are very thin (5.0 mg cm\(^{-2}\)) and can be directly presented for X-ray analysis after the exchange reaction has been completed. Their use, however, is limited to the analysis of drinking water, rain and "snow-water" because they have very low capacity, about 0.035 meq per filter. Better results have been obtained with granulated Chelex-100 resin. Several parameters of exchange reaction have been studied [19], for example, kinetics and yield of ion exchange, influence of pH and the presence of Na and Ca ions in aqueous solution on the degree of exchange. Some of our results are shown in Figs 2 and 3. The enrichment procedure was as follows. Usually 0.1 g of dry resin (capacity of about 4 meq/g) of particle size below 60 \(\mu\)m was put into a beaker together with a measured volume (100 to 500 ml) of aqueous solution. A magnetic stirrer was used to facilitate an exchange reaction. After equilibrium had been reached (1 to 2 hours), the resin was filtered through a membrane filter (0.45 \(\mu\)m porosity), air-dried and then analysed by XRF. Standard samples prepared by dissolving high purity salts in \(10^{-4}\) N HCl were measured in the same way. The method described has been used for the determination of Mn, Fe, Ni, Zn, Cu and Pb in ground and rain water. Although the capacity of 100 mg of Chelex-100 resin is ten times greater than that of Chelex-100 filter, the presence of Na and Ca ions at concentrations higher than 0.9% and 0.02%, respectively, influences the recovery of metal ions under investigation.

5.2. The precipitation method

Precipitation is a classical method of separation and preconcentration in analytical chemistry. In particular, chelating agents [24, 28] are used extensively for precipitation of trace elements. Dithiocarbamates have been used by Luke [22] for trace metals separation prior to wavelength-dispersion X-ray measurements. These reagents have a very high affinity for transition metals while that for alkaline and alkaline earth metal ions is very low. The advantage of the precipitation method is that precipitate collected on a membrane filter can be directly examined by X-ray spectrometry. The deposit forms a satisfactorily uniform layer on a filter, which can be regarded as a "thin sample".
The enrichment procedures for the precipitation methods with DDTC and APDC are described in detail in Refs [14, 23—25]. The sample volume taken for analysis is usually from 100 to 500 ml, depending on the trace element concentrations. The pH value of the water sample is adjusted to 4.0 or 6.0 for APDC and DDTC reagent respectively. After the addition of 10 to 20 ml of 2% carbamate solution the precipitate formed is allowed to stand for about 30 min. It is then filtered through the membrane filter. The deposit on the filter is air-dried and analysed by the XRF method. The time required to prepare the sample for measurement, including enrichment procedure, does not exceed one hour. If concentrations of metal ions in water are very low (a few ppb $10^9$ only) Fe$^{3+}$ or Ni$^{2+}$ can be added as a carrier. On the other hand when concentrations of some elements are much higher than of others (e.g. iron, zinc or manganese), a complexing agent can be used to prevent precipitation of the
FIG. 5. X-ray spectrum of mineral water sample [metal concentrations in ppb are given in brackets].

unwanted element [14]. Trivalent iron, which is often present in water and waste effluents in higher concentration than the trace metals, can be effectively complexed by EDTA and partially by citrates [22].

The advantage of the method described is that the presence of high concentrations of alkaline and alkaline earth elements does not influence the results. This method, therefore, can be used for trace metal determination in seawater, saline and mineral water. Typical spectra of DDTC precipitates for rain water and mineral water obtained by us are shown in Figs 4 and 5.

Detection limits expressed as the amount of element which gives a signal above background equal to three times the standard deviation of the background are shown in Table IV. The detection limits were determined from multi-element samples and therefore their values are higher than those obtained by other authors [2, 25] for single element standard samples.

Table V shows the precision of our results obtained with the DDTC method. The precision was determined from multiple precipitations (usually 10) of elements under investigations.

The described precipitation method is simple, rapid and accurate enough for most applications. It was used for determining mercury in the saturated sodium
### TABLE IV. DETECTION LIMITS FOR DDTC METHOD [9]a

<table>
<thead>
<tr>
<th>Element</th>
<th>Radioisotope source</th>
<th>X-ray tubeb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$^{239}$Pu/100 mCi/ (pp10^9)</td>
<td>(pp10^9)</td>
</tr>
<tr>
<td>Cr Kα</td>
<td>6.0</td>
<td>1.6</td>
</tr>
<tr>
<td>Mn Kα</td>
<td>3.2</td>
<td>1.4</td>
</tr>
<tr>
<td>Fe Kα</td>
<td>4.4</td>
<td>1.6</td>
</tr>
<tr>
<td>Ni Kα</td>
<td>2.0</td>
<td>0.5</td>
</tr>
<tr>
<td>Cu Kα</td>
<td>2.6</td>
<td>0.7</td>
</tr>
<tr>
<td>Zn Kα</td>
<td>1.8</td>
<td>0.8</td>
</tr>
<tr>
<td>Pb Lα</td>
<td>2.6</td>
<td>0.8</td>
</tr>
</tbody>
</table>

a Results for 500 ml water sample and 2000 s counting time.
b Measured with low-power X-ray tube with Ag target operated at 30 kV and 150 μA.

### TABLE V. PRECISION OF THE DDTC METHOD [9]a

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (pp10^9)</th>
<th>Precision % (1 st. dev.)</th>
<th>Statistical error % (1 st. dev.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>5.0</td>
<td>51.0</td>
<td>28.0</td>
</tr>
<tr>
<td>Mn</td>
<td>25.0</td>
<td>5.4</td>
<td>4.0</td>
</tr>
<tr>
<td>Fe</td>
<td>50.0</td>
<td>5.4</td>
<td>3.0</td>
</tr>
<tr>
<td>Ni</td>
<td>2.5</td>
<td>23.0</td>
<td>15.0</td>
</tr>
<tr>
<td>Cu</td>
<td>40.0</td>
<td>5.0</td>
<td>1.8</td>
</tr>
<tr>
<td>Zn</td>
<td>250.0</td>
<td>3.8</td>
<td>0.45</td>
</tr>
<tr>
<td>Pb</td>
<td>25.0</td>
<td>9.8</td>
<td>3.1</td>
</tr>
</tbody>
</table>

a Results for 500 ml water sample and 2000 s counting time; measured with low-power X-ray tube with Ag target operated at 30 kV and 150 μA.
chloride solutions used for electrolytic production of chlorine and the sewage discharge from a plant (at ppm and pp10^9 levels respectively). The method was also used for analysis of metal pollutants in rainwater and snow-water collected in an urban area (Cracow) [3, 9].

5.3. Adsorption on activated carbon

Both the described methods of preconcentration using ion-exchange with Chelex-100 and precipitation techniques permit only metal ions to be determined. Since strong organic complexes of metals can also occur in natural waters, the use of these methods can sometimes lead to uncertain results. This can happen when the contribution of complex forms of trace metal is large.

Another enrichment technique using adsorption of trace metals on activated carbon has been recently reported by Van der Sioot [13] and Vanderborght and Van Grieken [27]. A comprehensive discussion of the use of activated carbon for preconcentration of a number of elements is given in the papers. Adsorption of free metal ions on activated carbon is very weak. On the other hand, organic compounds are generally adsorbed more effectively. For this reason the water sample is treated by chelating complexing agents as 8-hydroxyquinoline [27] or APDC [13] before activated carbon is added. The quantity of activated carbon which is needed for quantitative adsorption of trace metals depends on the kind of water. For tap and ground water 100 mg/l is recommended by Vanderborght while for sea water Van der Sioot used 20 mg of activated carbon per 100 ml water sample. Since the adsorption of elements on activated carbon depends on a number of parameters such as: acidity, amount of complexing agent, salinity,
Ca, Mg ion content, the optimized conditions for adsorption have to be worked out for different kinds of water. The above-mentioned adsorption method seems to be promising for natural waters since it permits naturally occurring organic complexes of trace metals to be collected. An additional advantage of this preconcentration method is that it can be easily used at the sampling-site. The method has been used in combination with neutron activation for analysis of sea and surface water [26]. According to the author's knowledge no practical applications with EDXRF analysis have been reported so far.

To summarize the described techniques of enrichment of trace elements from water samples, a scheme of soluble analysis is presented in Fig. 6.

6. CONCLUSIONS

A suitable analytical procedure for trace metals monitoring in an aquatic environment should have

(a) high sensitivity and a low detection limit;
(b) high selectivity and minimum interference with water chemistry (e.g. salinity, Ca, Mg ions);
(c) ability to distinguish free and complex metallic species.

Besides, it should be relatively rapid, not expensive and simultaneous determinations of several trace elements should be possible. Unfortunately, such an analytical procedure is not currently available. There however exists a number of analytical techniques which fulfil some of these demands.

A very low detection limit can be attained by neutron activation analysis (NAA). The use of this method is limited by the availability of reactor facilities. Furthermore, direct irradiation of water samples is usually avoided due to water radiolysis. Therefore isolation of trace elements from an aqueous matrix is usually necessary. In addition, this method is time-consuming.

Flameless atomic absorption spectrometry is frequently used for trace metal analysis in natural and waste waters. A number of elements without sample pretreatment can be determined at the pp 10⁶ level. This technique, however, is not suitable for multi-element analysis. In addition insoluble material has to be dissolved prior to analysis.

Energy dispersive X-ray spectrometry is a multi-element method, having the advantage of consuming little time. In addition, insoluble particulates collected on a filter surface can be directly analysed. On the other hand, even with preliminary enrichment energy dispersion, XRF does not permit as low detection limits as does the atomic absorption method.
It is concluded that the EDXRF method is a very useful analytical tool for water pollution and waste effluent monitoring, if concentrations of trace elements are at a few ppb level. For lower concentrations flameless atomic absorption is preferable.

REFERENCES


PREDICTION AND ANALYSIS OF
THE MOVEMENT OF
GROUNDWATER POLLUTANTS
BY NUCLEAR TRACER TECHNIQUES
INTERPRETATION OF TRACER EXPERIMENTS IN GROUNDWATERS

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Abstract

INTERPRETATION OF TRACER EXPERIMENTS IN GROUNDWATERS.

The paper deals with some controversial problems arising in the interpretation of tracer experiments and pollutant movements in groundwaters. Differences in the properties of the two most common solutions of the dispersion equation are discussed. These solutions are obtained either for injection given by the Dirac δ(x) or δ(t) function. It is pointed out that neither the arithmetic mean (M₁/M₀) nor the harmonic mean (M₂/M₁) of the tracer curve provides a general formula for finding the mean velocity of water. The applicability of a particular model or formula depends on the injection/detection mode which has to be formulated in the initial conditions. It is also pointed out that the dead-end pore model is a useful tool for a better understanding of tracer movement in an unsaturated zone, though its original formulation was not entirely correct.

A quantitative interpretation of tracer experiments requires the use of mathematical models. For instance, the determination of the mean transit time of water from the maximum of the concentration curve, as the arithmetic mean (centre of gravity), or in any other way, requires certain assumptions which are not necessarily understood by the experimenter. Considerable development of mathematical models is observed in chemical engineering, where a quantitative interpretation is a must, and where input-output relations are usually sought. When these relations are the subject of an experiment, any model can be used, even a polynomial. In hydrology the situation is usually different in that from the measured input-output relations we want to find some physical parameters of the investigated system (for other possible applications of the models see Ref. [1]).
So, firstly we should use models which have a physical meaning, and secondly we should avoid models with too many parameters. Such an example is the dead-end pore model (discussed later), which has a physical meaning, but the number of its parameters is too large for solving the inverse problem. Another example is the multi-cell model which has little physical meaning, and the number of its parameters is often chosen in an arbitrary way (e.g., see discussion on Ref. [2]).

Confining our discussion to items pertinent to pollution problems, we shall concentrate on the dispersion equation, which is the best model available, though not uncriticized. Here (because of space limitations) we shall discuss solutions to this equation only for unidimensional dispersion and instantaneous injections. For other solutions see Refs [3–8].

The following well-known solution is most frequently used

$$c(x,t) = \frac{M}{nS} \cdot \frac{1}{\sqrt{4\pi Dt}} \exp \left[ -\frac{(x-vt)^2}{4Dt} \right]$$  \hspace{1cm} (1)

which is valid for infinite media and was obtained for the boundary and initial conditions

$$c(x,0) = \frac{M}{Sn} \delta(x)$$

and

$$c(\infty, t) = 0$$

where

- \(c\) is the concentration of the tracer in water,
- \(M\) is the injected mass or activity of the tracer,
- \(S\) is the area of the cross-section of the medium normal to the flow lines,
- \(n\) is the effective porosity,
- \(D\) is the dispersion coefficient,
- \(v\) is the mean interstitial velocity of water,
- \(\delta(x)\) is the Dirac delta function defined in space,
- \(x\) and \(t\) are the space and time variables.

Lenda and Zuber [9] obtained another solution

$$c(x,t) = \frac{M}{S n v} \cdot \frac{x}{\sqrt{4\pi Dt^3}} \exp \left[ -\frac{(x-vt)^2}{4Dt} \right]$$  \hspace{1cm} (2)
for the boundary and initial conditions given by Hubert et al. [10]:

\[ c(0,t) = \frac{M}{nS_v} \delta(t) \]

\[ c(x,0) = 0 \]

and

\[ c(\infty, t) = 0 \]

which mean that the tracer is injected in the flux (velocity proportional injection). Equation 2 is valid for a semi-infinite medium \( x > 0 \), regardless of the existence or non-existence of the medium in \( x < 0 \).

Another solution is given by de Vries [11] and Siegenthaler (see Martinec et al. [12]). All the solutions, their properties, and some new solutions are discussed elsewhere. Here we shall concentrate on the most important properties of Eqs 1 and 2.

Equation 1 gives concentration in water present at the moment \( t \) at distance from the injection point. In the initial conditions it is assumed that the tracer is homogeneously distributed over the whole cross-section area. Equation 1 gives the mean transit time of tracer, \( \bar{t} \) (calculated as the ratio of the first to zero-th moment), different from that of water, \( t_0 = x/v \).

\[
\bar{t} = \frac{M_1}{M_0} = \frac{\int_0^\infty c(x,t) \, dt}{\int_0^\infty \delta \cdot c(x,t) \, dt} = t_0 \left(1 + 2 \frac{D}{v^2 x}\right)
\]  

(3)

It means that in this case the movement of tracer does not represent directly the movement of water (the residence-time distribution of tracer differs from that of water).

In the case of Eq.2 it is assumed that both the injection and the detection are performed in the flux (injection and detection proportional to the flow velocity). Consequently, Eq.2 gives the mean transit time of tracer calculated as the ratio of \( M_1 \) to \( M_0 \) equal to \( t_0 \).

The above considerations show that a tracer experiment has to be interpreted taking into account the mode of the injection and detection. It is inconsistent to stick to the model given by Eq.1 and determine the mean velocity of water from the first moment of the concentration curve. Equations 1, 2, or any other, cannot be used as a residence-time distribution without first knowing if they describe the
initial and boundary conditions of our experiment. Unfortunately, many theoreticians treat Eq. 1 as a general dispersion model, though it is one of the solutions to the dispersion equation obtained for initial and boundary conditions that are difficult to realize in the experiment. Its applicability will also be discussed later.

Some investigators advocate the following formula for determining the mean flow velocity

\[
v = \frac{x \int_0^\infty \frac{1}{t} c(t) \, dt}{\int_0^\infty c(t) \, dt}
\]

which means that \( v \) is calculated as a quotient \( x/\bar{t}_h \), where \( \bar{t}_h \) is the harmonic mean,

\[
\bar{t}_h = \frac{M_0}{M_1} = \frac{\int_0^\infty c(t) \, dt}{\int_0^\infty \frac{1}{t} c(t) \, dt}
\]  

(4a)

Here, by applying the same departure formulas as Fried [8] did, we shall demonstrate that Eq. 4 is not applicable if the concentration curve represents the residence time distribution of the water flux, namely

\[
E(t) = \frac{c(t)}{\int_0^\infty c(t) \, dt}
\]

(5)

Mean velocity is defined as [8]

\[
\bar{v} = \frac{\int_0^\infty v \phi(v) \, dv}{\int_0^\infty \phi(v) \, dv}
\]

(6)

where \( \phi(v) \) is the velocity distribution of the water and tracer. \( \phi(v) \) may be expressed by \( E(t) \), calculating the volume of water in the system which has the residence time from \( t \) to \( t + \Delta t \). From the velocity distribution we have:

\[
dV = V \phi(v) \, dv = -V \phi(t) \frac{x}{t^2} \, dt
\]

(7)
and on the other hand from the residence time distribution

\[ dV = tQ E(t) \, dt \]  

(8)

where

- \( q \) is the total flow rate through the system,
- \( V \) is the total volume.

According to Nir and Lewis [1] the physical significance of Eq. 8 is that the parts of the flow having longer residence times occupy the system in direct proportion to these times.

Comparing Eqs (7) and (8) and using Eq. (6) we get:

\[ \bar{v} = \frac{\int_0^x \frac{x}{t} q(t) E(t) \, dt}{\int_0^x q(t) E(t) \, dt} = x \frac{\int_0^x c(t) \, dt}{\int_0^x t \, dt} = \frac{x}{\bar{v}} \]  

(9)

which shows the applicability of the arithmetic mean if the residence-time distribution of tracer corresponds to that of water.

These considerations do not imply that the velocity of water cannot be found from Eq. 4. It only means that Eq. 4 is inconsistent with the assumption of the concentration curve representing the residence-time distribution of water in the system. However, it can easily be shown that Eq. 4 (harmonic mean) is consistent with the model represented by Eq. 1, but is inconsistent with Eq. 2 or with the model given by de Vries [11] and Martinec et al. [12], and with the binomial model sometimes applied in the interpretation of environmental tritium data (e.g. see Ref. [13]). One should not claim general applicability of the arithmetic or harmonic mean, and use models inconsistent with that claim.

A better understanding of the role of the injection/detection mode in tracer experiments can be achieved by considering a laminar flow in a capillary. The reader is directed to a classic work of Taylor [14], and others (given by Sheppard [15]). Earlier works in this field have been summarized and extended recently by Gardner et al. [16]. In Table IV of the work cited the authors present different cases for an instantaneous injection and collimated detection (\( X \to 0, L_m \to 0 \)). When both the injection and detection are uniform (proportional to the cross-section) neither Eq. 3 nor Eq. 4 applies. When either the injection or the detection is velocity-proportional, we may easily find that Eq. 4 applies. If both injection and detection are velocity-proportional (tracer injected and measured in the flow) the arithmetic mean (defined by Eq. 3) applies.

Layered systems require a separate discussion beyond the scope of this work. However, because of their importance we would like to make some comments
here. Assuming that there is no mixing of the tracer between the layers we can find the rules for averaging by analogy to the previously discussed laminar flow in a capillary. Zuber [17] considered an injection proportional to the thicknesses of the layers (the injection is uniform in the sense of the terminology used for capillaries) and the detection in outflow (velocity-proportional) finding that neither the harmonic nor arithmetic mean give the mean flow rate. In the case of the injection proportional to the transmissivities and the detection in the outflowing water, we have again Eq. 3 for finding the mean velocity [17, 18]. The authors do not know how to realize uniform injection in the field, whereas proportional injection and detection are often easy to achieve [17, 18]. The multi-level injection and detection method developed by Pickens et al. [19] gives details of the water movement but cannot be used directly for determining the mean flow velocity.

All this clearly shows that the model used for the interpretation also depends on the initial conditions (i.e. injection and detection modes). It does not matter if the model is used directly for the interpretation of tracer experiments or as a residence distribution function in the general tracer theory [1]. Those who state that either the arithmetic mean or the harmonic mean is a general formula for the mean velocity of water in artificial tracer experiments are mistaken.

However, an important property of the dispersion model is that the differences between the solutions become negligible for high Peclet numbers (vx/D), or in other words for the cases of low dispersion. Thus, in such a case, the experimenter may use any method for finding the mean velocity of water (harmonic mean, arithmetic mean, maximum value, middle of the half-width, and so on). This explains the wide, successful use of Eq. 1 in spite of its theoretical limitations. However, when the mean value of flow rate or velocity in a layered system is needed, or when a high dispersion is encountered, a proper model is essential. In such cases, if a wrong model is chosen, the estimates of the hydrologic parameters may be incorrect by a factor of 2 or more. Models are also very useful in planning the experiments [9] and indispensable in more sophisticated tracer methods, as for instance the method proposed by Hibsch and Kreft [20].

In the work of Alquier et al. [21] there is an important proof showing that a good mixing means that the lateral distribution of the tracer flux is proportional to the velocity. In other words, all the homogeneous systems or systems with a good lateral mixing (even a capillary for a sufficiently large distance — see Ref. [14]) have a tendency to achieve the velocity-proportional distribution of the tracer. This means that after travelling the distance of "good mixing" the tracer starts to behave as if it was velocity-proportional injected. However, in the cited work the acceptance of Eq. 4 led the authors to conclude that the tracer in principle moves with a velocity different from that of the traced material. If this were true, the tracer would not satisfy its definition.
There is another important point relevant to tracer experiments and prediction of pollutant concentrations. In a proper formulation of initial conditions the porosity of the medium has to appear, if the concentration is defined in units of mass (or activity, or any other) per unit volume of water. The proper formulation can be found in the works of Bear et al. [22] and Bear [7], and its physical meaning was discussed by Lenda and Zuber [9]. A number of papers may be cited here, in which the porosity is properly accounted for. Unfortunately, there are also important theoretical works in which this factor is omitted.

When discussing porosity, we are concerned with the effective porosity, defined as the fraction of the volume occupied by the mobile water. The effective porosity is not equal to the specific yield as cited by several authors (e.g. as in Ref. [8] or [23]). Usually it is closer to the total porosity, especially in well permeable media. The definition of the specific yield and its relation to the total porosity for granular media can be found in Davies and de Wiest [24].

For the sake of simplicity we have discussed unidimensional dispersion. However, very often one has to deal with two-dimensional or three-dimensional dispersion. Whichever solution to the dispersion equation is chosen as a model, it can easily be seen that if we detect the tracer at a point, neither Eq.3 nor Eq.4 applies. In such a case there is no problem with high Peclet numbers, but with low Peclet numbers the models are indispensable.

We should add here that the moments calculated for two- or three-dimensional solutions are equal to the unidimensional moments if the whole tracer cloud is integrated over the transversal co-ordinates. However, such moments are not measurable in groundwater experiments because of the inaccessibility of the investigated system.

A brief discussion should also be dedicated to the movement in the unsaturated zone. There are a number of works presenting experimental evidence which shows beyond any doubt that the movement of a tracer or a pollutant front is in such a case highly dispersed and delayed in respect to the water movement, exhibiting a strong tailing effect. The reader is referred in this respect to a review paper by Nielsen and Biggar [25], to other original works of these authors, and to neat experiments of Gaudet (in discussion to Ref. [26]). In spite of some criticism the authors consider the dead-end pore model of Coats and Smith [5] a very good one for understanding the main mechanism of the tracer movement in unsaturated medium. Inoue and Kaufman [27] were probably the first to realize that the concentrations in the dispersion equation are defined as quantity of mass per unit volume of space. Therefore if there is an exchange of mass between the liquid and solid phase (Inoue and Kaufman) or between the mobile and stagnant water (the dead-end pore model of Coats and Smith) we have to use proper coefficients linking concentrations in units of space with concentrations expressed in common measurable units (mass per unit volume of water for the liquid phase and mass per unit mass of the solid phase). Unfortunately, the model
of Coats and Smith [5], cited also by Fried and Combarous [28] is not correctly formulated in this respect. The dead-end pore model properly written is a set of two equations

$$nD \frac{\partial^2 C_m}{\partial x^2} - n\nu \frac{\partial C_m}{\partial x} = n \frac{\partial C_m}{\partial t} + n_r \frac{\partial C_r}{\partial t}$$  \hspace{1cm} (10)$$

and

$$\frac{\partial C_r}{\partial t} = K(C_m - C_r)$$  \hspace{1cm} (11)$$

where $C_m$ and $C_r$ are concentrations (in unit volume of water) in mobile and stagnant water respectively, $n_r$ is the stagnant-water porosity (fraction of space occupied by stagnant water), and $K$ is the rate constant. Obviously $n_r + n = n_t$, where $n_t$ is the total porosity, excluding incommunicable pores.

This model for $K = 0$ reduces to the normal dispersion equation. For $K = \infty$, $C_m = C_r$, Eq.10 reduces again to the dispersion equation, but with the velocity of tracer divided by $n_t/n$, or the time variable multiplied by this factor. This means that the distribution of tracer in pores is homogeneous in the whole liquid phase. It can easily be checked that the original dead-end pore model for the extreme two cases reduces to other, unjustified equations, though Coats and Smith [5] in the text of their paper describe properly how the model should behave. Molinari et al. [29] consider a more general model in which an additional term appears in Eq.10, namely

$$n_r D_r \frac{\partial^2 C_r}{\partial x^2}$$

where $D_r$ is the dispersion coefficient in the stagnant-water pores ($D_r$ should be equal to the coefficient of molecular diffusion divided by the tortuosity factor of these pores). However, this term may appear only if the stagnant-water pores are interconnected. Otherwise there is no transport of solute in the stagnant water, though the transport is affected by this water according to Eqs 10 and 11.

The dead-end model cannot be used for solving the inverse problems in tracer experiments because of an excessive number of parameters, unless these parameters are independently determined. However, as mentioned earlier, this model is a very good tool for understanding the movement of an ideal tracer or a non-adsorbed pollutant in the unsaturated zone. If the movement of water is very slow, as a result an instantaneous equilibrium can, in approximation, be assumed ($K = \infty$) and the final result is that the movement of the tracer or pollutant is delayed in
respect to the movement of water. Intermediate cases are analytically complicated [5, 10]. However, we would expect for an instantaneous injection the rising part of the concentration/time curve to be delayed in respect to the ideal movement in the effective volume, but to be exaggerated with respect to the ideal movement in the whole volume. The descending part of the concentration/time curve should exhibit a tailing effect. For a continuous injection we shall observe a fast increase of the initial part of the curve and a slow approach to the injected concentration (e.g. see Ref. [25] and Gaudet in Ref. [26]). A tracer experiment interpreted in such a case by the normal dispersion model will exhibit a false water velocity and a high apparent dispersion coefficient.

Finally, for a very fast movement of water it may, in approximation, be assumed that $K = 0$. The movement of tracer is then in the effective volume only and should give the right velocity of water, though the unit volumetric flow rate will remain unknown because of the unknown value of the effective porosity. Results of Smith et al. [30] seem to suggest that in the case of a fast movement in unsaturated chalk formation there was no exchange with stagnant water. Whichever case we face, a properly chosen tracer should identify the velocity and provide data for the prediction of the pollutant movement, though the infiltration velocity of water may remain unknown.

In general, the proper use of a model with a number of parameters depends on the purpose which the model is supposed to serve. For instance it can be either a quantitative description of the physical phenomena, or a prediction of the pollutant movement, or determination of hydrologic parameters from a tracer experiment. The last case is a typical inverse problem, which requires careful consideration as to whether it can be solved at all, and if so, what is the accuracy of the solution. Otherwise the mere fitting of a multiparameter model to experimental data may be worthless.

Finally, we would like to discuss some basic problems related to the tracer methods. Nir and Lewis [1] define an ideal tracer as having an identical response (residence-time distribution) to the traced material. Nir's and Lewis's definition is logical as used by them in the general tracer theory applied to unknown systems. However, as we saw earlier, depending on the injection detection mode this definition is seldom satisfied (e.g. neither Eq.1, nor some cases of flow in a capillary discussed earlier satisfy this definition). In the authors' opinion the general definition of an ideal tracer should not include the experimental procedure as it tacitly arose in the cited work.

Consider, for instance, two identical systems having volumes $V_{ef}$ and with flow rates $Q$. Let us assume that the second system has a connection with an additional volume occupied by stagnant water, $V_r$.

In the first case a properly injected and detected tracer (proportionally to flow as discussed earlier) will render the mean residence time of water, $t_0$. Namely

$$\bar{t} = \frac{M_1}{M_0} = t_0, \text{ where } t_0 = \frac{V_{ef}}{Q}$$

(12)
In the second case, if the flow through the system is fast enough to prevent the tracer from diffusing into the stagnant volume, we have again Eq. 12, where $V_{ef} \neq V_{total} = V_{ef} + V_T$. However, if the movement of the water through the system is slow enough for the tracer to diffuse into the stagnant water then

$$t = \frac{M_1}{M_0} \# t_0$$  \hspace{1cm} (13)

This case corresponds to the dead-end pore model discussed earlier. In other words, in both systems we have the same velocity of water in bulk but the mean velocities of water molecules differ. In the later case the movement of the tracer is delayed with respect to the bulk movement.

In the authors' opinion, an ideal tracer of water should be defined as a material moving exactly in the same way as water molecules move. However, as we have seen, this does not mean that an ideal tracer represents the bulk movement of water under any circumstances. An ideal tracer of a pollutant is defined as a material which moves in exactly the same way as the molecules (or ions) of the pollutant.

It has to be remembered that the tracer which undergoes exchange with the same kind of ions or molecules in the solid phase does not represent the velocity of the traced material. This is the case with tritium when bound water or hydrogen exists in the solid material of the porous medium (see, for example, Ref. [31]). Then the exchange between two phases causes delay of molecules of the tracer and a decrease of its concentration in the liquid phase, whereas the total number of molecules of the water in the mobile part of the system does not change and its bulk movement is unaffected. Another example is given by Matoszewski et al.[32] where because of the exchange of calcium from the liquid phase with calcium in the solid phase, $^{40}$Ca$^{++}$ moves in a way completely different from that of the bulk movement of Ca cations. In this case the concentration of the tracer is affected by the exchange, whereas the concentration of the traced material is not necessarily affected. In the cases cited the radioisotope supplies information on the behaviour of ions of the traced element but cannot serve as a tracer for its bulk movement.

In general tracers are available at the molecular or ionic level. When the bulk movement of a given substance is of interest, even an ideal tracer of this substance may satisfy the requirements of a given experiment only under favourable circumstances. An ideal tracer of a given ion or compound is not necessarily a proper tracer for the observation of mass transport of the traced material. In each situation we have to consider if we really traced what we wanted to trace.

In conclusion, it is hoped that this work will stimulate a discussion on the behaviour of tracer under different conditions, and on the applicability of the discussed theoretical models. Some of the problems considered may be controver-
sial. However, experiments in hydrological systems are neither completely controlled nor easily reproducible in a laboratory and that is why very often there is no other possibility for an independent determination of parameters sought. On the other hand, the limited accuracy of the measurements does not allow a direct judgement of multiparameter models. Thus, careful theoretical consideration may be helpful, and use should also be made of analogies with the behaviour of tracers in other well known and simpler systems, e.g. capillaries. The further theoretical and experimental research is undoubtedly called for as regards models in tracer hydrology.

Avoidance of the controversial problems may lead to stagnancy, whereas their discussion should stimulate further progress.

REFERENCES


THE DISTRIBUTION COEFFICIENT AS A GEOCHEMICAL MEASURE OF THE MOBILITY OF CONTAMINANTS IN A GROUND WATER FLOW SYSTEM

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Abstract

THE DISTRIBUTION COEFFICIENT AS A GEOCHEMICAL MEASURE OF THE MOBILITY OF CONTAMINANTS IN A GROUND WATER FLOW SYSTEM.

The distribution coefficient ($K_d$) has been used in radioactive waste management studies to describe the partitioning of a radioactive contaminant between solid (rock or sediment) and aqueous solution (ground water) phases. It offers the hydrogeologist a parameter with which to describe either the relative affinity of the aquifer matrix for a particular contaminant or the mobility of the contaminant in the aquifer or ground water flow system. At the Chalk River Nuclear Laboratories studies are under way to determine the geochemical controls on the mobility of $^{90}$Sr and $^{137}$Cs in a shallow, sandy aquifer, and their bearing on the distribution coefficient for these two contaminants. Finally, the applicability of this parameter to non-radioactive waste management is considered.

INTRODUCTION

For a substance to be an environmental hazard it must be both potentially toxic at some threshold concentration and environmentally mobile. Life on this planet has developed in the presence of large masses of toxic heavy metals. However, because most of these heavy metals are only sparingly soluble and are generally immobile in typical aqueous environments, their toxicity has not prevented the development of complex organisms such as Man. It is apparent that a geochemical measure of the mobility of
potential contaminants is a vital prerequisite in the management of the quality of natural waters. An example of such a measure is the distribution coefficient.

The purposes of this paper are (1) to review the concept of the distribution coefficient, (2) to examine the geochemical controls on the distribution coefficient in a particular aquifer at the Chalk River Nuclear Laboratories, Ontario, Canada and (3) to consider the wider use of the parameter in groundwater quality management.

THE NATURE OF THE DISTRIBUTION COEFFICIENT

The distribution coefficient, $K_d$, has been defined as "the number of milliequivalents of an ion adsorbed per gram of exchanger divided by the number of milliequivalents of that ion per millilitre remaining in solution at equilibrium" [1]. In the hydrogeological context the exchanger is the grains of the aquifer and the solution is the ground water. It should be noted that reactions other than ion exchange may affect the $K_d$.

For the simple chemical equilibrium representing an ion exchange process [1]:

$$A^+ + B^+R^- \leftrightarrow A^+R^- + B^+$$

where $A^+$ and $B^+$ are the competing cations for $R^-$ the cation exchanger (e.g. aquifer material such as a clay particle), a selectivity quotient may be written:

$$K_B = \frac{(A^+R^-)(B^+)}{(A^+)(B^+R^-)} = \frac{(A^+R^-)(A^+)}{(B^+R^-)(B^+)}$$

where $(A^+)$ and $(B^+)$ are the concentrations of these ions in solution and $(A^+R^-)$ and $(B^+R^-)$ are their concentrations in the adsorbed phase. Jenne and Wahlberg [2] have pointed out that the selectivity quotient may only be considered as a mass action equilibrium constant if (1) the activities of all four forms may be calculated, (2) the adsorption reaction is reversible and (3) secondary reactions which are not readily reversible, such as ion fixation due to lattice collapse, do not occur and so prevent the attainment of true equilibrium. The estimation of the activities of the adsorbed phases, $A^+R^-$ and $B^+R^-$, has been discussed by Truesdell [3].

The selectivity quotient can be related to the distribution coefficient if the cation exchange capacity, $Q$, of the exchanger, $R^-$, and the total competing cation concentration in solution, $C$, are known [1]. By definition:

$$C = (A^+) + (B^+) = Q$$

$$C = (A^+R^-) + (B^+R^-) = Q$$
When the system under consideration (equation 1) is at equilibrium, then by definition

$$K_d^A = \frac{(A^+R^-)/(A^+)}{Q}$$

(6)

and the selectivity quotient may be rewritten, using equations (3) and (4), as

$$K_d^A = \frac{K_d^A [C - (A^+) - (A^+R^-)]}{[Q - (A^+R^-)]}$$

(6)

For the case in which the contaminant, $A^+$, is present in amounts much less than $B^+$, $(A^+)^0 < C$ and $(A^+R^-)^0 << Q$, the distribution coefficient may be rewritten as

$$K_d^A = \frac{K_d^A Q}{C}$$

(7)

Therefore the distribution coefficient is directly proportional to the cation exchange capacity and the selectivity quotient, and inversely proportional to the total competing cation concentration. For the above case in which $(A^+)^0$ and $(A^+R^-)^0$ are assumed to be very small, $(B^+)^0 = C$ and therefore $K_d^A$ is proportional to $(B^+)^{-1}$. More complex cases, for example involving monovalent-divalent exchange, may be developed using similar reasoning.

Since $Q$ is usually expressed in milliequivalents (meq) of cations per gram of exchanger and $C$ in terms of meq/ml, the units of the distribution coefficient are ml/g. Those working in the field of radioactive waste management have tended to measure $K_d$ by radiochemical analysis such that the distribution coefficient is determined as the ratio:

$$K_d = \frac{dps/g}{dps/ml}$$

(8)

where dps stands for disintegrations per second.

The distribution coefficient measures the affinity of the aquifer materials for a specific contaminant. Therefore it must also imply something about the mobility of that contaminant in that aquifer system. Hydrogeologists involved in radioactive waste management have expressed this mobility in terms of what we shall call the (one-dimensional) retardation equation [4]:

$$V_A = \frac{V_{GW}}{1 + \frac{\rho_b}{\rho_n} K_d}$$

(9)
in which \( V_A \) is the mean velocity of contaminant ion \( A^+ \), \( V_{GW} \) is the mean velocity of ground water, \( \rho_B \) and \( n \) are the bulk density and porosity of the aquifer material respectively, and \( K_d \) is as defined. We have called this expression the retardation equation since nonzero values of \( K_d \) dictate that \( V_A < V_{GW} \), and hence the contaminant ion is retarded in its flow through the aquifer. If \( V_A \), \( V_{GW} \), \( \rho_B \) and \( n \) are known for a particular aquifer system contaminated by ionic species \( A^+ \), then \( K_d \) may be determined. We shall refer to this method of solution as field mapping since \( V_A \) can then obviously be determined from field mapping contaminant migration over time.

An interesting derivation of an expression similar to equation (9) has been given by Lai and Jurinak based on the convective-dispersion equation [5]. Their expression is essentially identical to equation (9) for the case in which \( K_d \) is constant (i.e. linear exchange isotherm), provided that the geochemical reactions which occur (i.e. ion exchange or precipitation) do not affect the ratio \( \rho_B/n \). This proviso may reasonably be assumed to be a necessary condition for equation (9) as well.

GEOCHEMICAL CONSIDERATIONS

The simple ion exchange equilibria which we have discussed so far do not suffice in describing the more complex geochemical realities which determine ground water quality. In his recent review of ground water geochemistry Edmunds [6] has described the roles of various processes such as precipitation, redox, complex-ion formation and acid-base buffering in governing the quality of ground water. These processes affect the mobility of contaminants and therefore their distribution coefficients.

In addition to their adsorption from solution, contaminants may be removed from solution either by direct precipitation or by isomorphous substitution with an ion of similar size in a crystal that is forming (coprecipitation) or that has formed (replacement). It is possible to deduce from a chemical analysis of a ground water sample whether precipitation or dissolution of particular mineral species is likely to be occurring. This is accomplished by comparing the actual ion activity product of the dissolved constituents of a mineral species with its solubility product, yielding the saturation index, \( S I \),

\[
S I = \log_{10} \left( \frac{IAP}{K_{SP}} \right)
\]

where IAP is the ion activity product \( (A)^+ (B)^- \) and \( K_{SP} \) is the solubility product of the mineral \( [A_B] \). If \( S I < 0 \) the ground water is undersaturated with respect to \( [A_B] \) and a net dissolution of the mineral should occur; at \( S I = 0 \) the ground water is at equilibrium with the mineral; when \( S I > 0 \) the ground water is supersaturated with the mineral's constituent ions and net precipitation should occur. It is quite conceivable that kinetic delays may prevent the precipitation from solution of a mineral which is supersaturated in solution [6].

The replacement of one element in a crystal lattice by another is common in the creation of distinct minerals. It has been pointed out by Krauskopf [7] that those elements which replace one another tend to be of similar ionic radii, covalent character and valence. The significant feature of replacement and coprecipitation processes is that the new solid phase is more stable in the final solution than the original solid phase.
**DISTRIBUTION COEFFICIENT**

This implies that the new solid phase is more insoluble than the original solid phase, and that the propensity of a contaminant ion to be absorbed into a mineral lattice can be expressed by solubility arguments.

A theory of such reactions has been proposed by Stumm and Morgan [8] such that for the solid solution of B in A

\[ A(s) + B(aq) = B(s) + A(aq) \]  \hspace{1cm} (11)

where \( s \) denotes the solid phase and \( q \) the aqueous one, a coprecipitation index can be calculated from the quotient of the solubility products of the two mineral species:

\[ CI = \frac{K_{SP}(A)}{K_{SP}(B)} \]  \hspace{1cm} (12)

Consequently in a solution of radium ions \( B(aq) \) undersaturated with respect to \( RaSO_{4} \) \( (-log K_{SP} = 10.4) \) but saturated with respect to \( BaSO_{4} \) \( (-log K_{SP} = 9.5) \), it is not unreasonable to expect the coprecipitation of \( (Ba, Ra)SO_{4} \) \( (CI < 1) \). Like the saturation index, this coprecipitation index merely indicates the likelihood of a reaction occurring \( (CI > 1) \) but does not guarantee that such will be the case.

Two important features characterize the aqueous geochemistry of the transition metals (e.g. Fe, Mn, Co, Zn, Pb, Cu, Ni, Cr) and consequently determine their mobility in hydrogeochemical environments. Firstly, most have variable oxidation states or valences and, secondly, they form inorganic and organic complex ions in solution. These two features complicate the adsorption or precipitation reactions of these metals.

Considering oxidation-reduction (redox) processes first, we [9] have developed from the work of Stumm and Morgan [8] a thermodynamic model of the sequential utilization of oxidized species (e.g. \( O_{2}, NO_{3}^{-} \)) in aquifers which have an excess of reduced dissolved organic carbon (DOC) rather than dissolved oxygen. This sequence is illustrated in Table I; the individual redox reactions are listed in the order of their increasingly negative values of the free energy change at pH7, \( \Delta G^{o}(W) \). Consequently we postulate, that in a confined aquifer containing excess DOC and solid phase Mn(IV) and Fe(III) minerals, the oxidized species are reduced in the following order: dissolved oxygen, nitrate, (solid) manganese oxide, (solid) ferric hydroxide, sulfate, dissolved \( CO_{2} \) (i.e. \( HCO_{3}^{-} \)) and dissolved nitrogen. Occurrences of such a sequence have been observed in ground water flow systems by both ourselves [9] and Edmunds [6].

The significance of this model with respect to the mobility of the transition metals in ground water flow systems is at present largely speculative. However we propose that in recharge areas \( (O_{2} \) present) iron (III) and manganese (IV) oxyhydroxides may be important transition metal scavengers. In discharge areas \( (HgS \) present) the solubility of the transition metals may be controlled by sulfide equilibria.

The hydrogeochemical implications of the complexing of contaminants by inorganic or organic ligands are largely unknown. What is known is that these ligands may complex the transition metal ions and therefore alter their adsorption or precipitation from solution. Duursma [10] has shown that the adsorption of radioactive cobalt and zinc is significantly
**TABLE I. REDOX PROCESSES IN A CLOSED SYSTEM**

Conditions: Excess organic material (DOC), water initially contains $O_2$, $NO_3^-$, $SO_4^{2-}$ and $HCO_3^-$

Example: Recharge of natural waters through a reactive soil zone into a confined aquifer system containing $MnO_2$, $Fe(OH)_3$ and excess DOC.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equation</th>
<th>($\Delta G^\circ , (W)$)* (kcaIs at pH = 7.0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerobic Respiration</td>
<td>$CH_4 + O_2 \rightarrow CO_2 + H_2O$</td>
<td>-120.0</td>
</tr>
<tr>
<td>Denitrification</td>
<td>$CH_4 + 4/5 NO_3^- + 4/5 H^+ \rightarrow CO_2 + 2/5 N_2 + 7/5 H_2O$</td>
<td>-113.9</td>
</tr>
<tr>
<td>Mn (IV) Reduction</td>
<td>$CH_4 + 2 MnO_2(s) + 4H^+ \rightarrow 2 Mn^{2+} + 3 H_2O + CO_2$</td>
<td>-81.3</td>
</tr>
<tr>
<td>Fe (III) Reduction</td>
<td>$CH_4 + 8 H^+ + 4 Fe(OH)_3 \rightarrow 4 Fe^{2+} + 11 H_2O + CO_2$</td>
<td>-27.7</td>
</tr>
<tr>
<td>Sulphate Reduction</td>
<td>$CH_4 + 1/2 SO_4^{2-} + 1/2 H^+ \rightarrow 1/2 HS^- + H_2O + CO_2$</td>
<td>-25.0</td>
</tr>
<tr>
<td>Methane Fermentation</td>
<td>$CH_4 + 1/2 CO_2 \rightarrow 1/2 CH_4 + CO_2$</td>
<td>-22.2</td>
</tr>
<tr>
<td>Nitrogen Fixation</td>
<td>$CH_4 + H_2O + 2/3 N_2 \rightarrow 4/3 H^+ + 4/3 NH_4^+ + CO_2$</td>
<td>-19.2</td>
</tr>
</tbody>
</table>

(g) = gas, (s) = solid

* $\Delta G^\circ \, (W) = \Delta G^\circ - RT \ln ([H^+]_P)$, ([H$^+$]) = 1.0 x $10^{-7}$ M, $p$ = stoichiometric coefficient for H$^+$, $\Delta G^\circ$ is the standard free energy change of the reaction, $R$ is the gas constant, $T$ is the absolute temperature, $e$ is the number of electrons involved in the reaction and $F$ is the Faraday constant.

Modified after Stumm and Morgan [8].
FIG. 1. The effect of increasing the concentration of an organic ligand (leucine) on the distribution coefficient of $^{60}$Co and $^{65}$Zn in fresh water sediments. Data from Duursma [10] in molar (M) concentrations.

decreased in the presence of dissolved organic carbon (DOC) compounds, which are to be found in all natural ground waters [11]. This decrease is due to the formation of organo-cobalt and organo-zinc complexes whose $K_d$ may differ from that of the hydrated metal ions. Figure 1 shows the effect of increasing the DOC concentration on the adsorption of $^{60}$Co and $^{65}$Zn by clayey, alluvial sediments. It should also be noted that organic complexing of cobalt and zinc will increase their solubility in solution therefore reducing the effectiveness of precipitation as a retarding mechanism.

The geochemical controls on the mobility of radiocontaminants in a shallow ground water flow system in central Canada have been studied with such processes in mind. While we are not yet able to account for all the effects of these processes, the following represents a summary of our present understanding of the geochemical factors affecting the magnitude of the distribution coefficient for two radiocontaminants - $^{85}$Sr and $^{137}$Cs.
FIG. 2. Cross-section of the Lower Perch Lake Basin along the profile YY’ (see Fig. 4) with the positions of piezometer HAl, NA2 and NA3 superimposed.

THE HYDROGEOLOGICAL ENVIRONMENT OF THE STUDY AREA

The Lower Perch Lake Basin at the Chalk River Nuclear Laboratories, 200 kilometres northwest of Ottawa, is the southern part of an hourglass-shaped watershed, the constriction of which is formed by bedrock ridges. The sides of the basin, also bedrock ridges, rise approximately thirty metres above the swamp land which forms the flood plain of the main stream draining the upper basin. The ridges are covered with aspen, birch, maple, jack pine and oak. The low lying bogs are populated predominantly by ash, alder, balsam and spruce. The climate of the Chalk River area is that of a cold snow forest (Koppens’s classification) with a warm summer and no distinct dry season. The mean air temperature ranges from a January low of -12°C to a July high of +19°C. Annual precipitation is of the order of 84 cm [12].

The bedrock in the basin is mainly pink and grey granitic gneiss and is overlain by a sequence of sandy glacial and glaciofluvial sediments [13]. Immediately overlying the Precambrian gneiss is a sandy grey till which was laid down between approximately 12 000 and 60 000 years b.p. (N.R. Gadd, Geological Survey of Canada, Ottawa, Ontario, Canada, pers. comm.). Following the retreat of the continental ice sheet about 10 000 years b.p., large volumes of deltaic sediments were deposited in the Chalk River area, some of which were reworked into aeolian deposits. The deltaic sediments are composed predominantly of fine- and medium-grained sands which today form an aquifer system in the valley bottom of the basin, and dispersed in which are thin beds of silts and clays (Figure 2).
FIG. 3. X-ray diffractogram of the <2μm fraction of the silt and clay unit at 0 piezometer nest (depth of sample = 12 metres).

The hydraulic conductivity of the sand has been estimated by a variety of methods including pumping test analysis, falling head and constant head tests of piezometers and by field permeameter tests; if all methods of analysis are considered a hydraulic conductivity value of the order of 1 x 10^{-3} to 5 x 10^{-3} cm/s is indicated [14]. Porosity measurements on over 100 samples yielded a mean value of 0.38 [15]. When this value is used together with a specific gravity of 2.73 g/cm^3 for the sands one obtains a bulk density value of 1.69 g/cm^3.

Mineralogical examinations of the sand and clay fractions of the sands have been conducted. Approximately 60% of the 80-200 μm fraction of the sands is quartz, the majority of the remainder being mica and feldspar. Some weathering of the feldspar grains is evident. Cation exchange capacities for the sands (as 1% clay sized particles) by the ammonium acetate method are of the order of 1 meq/100 grams. Figure 3 is an X-ray diffractogram of the < 2 μm fraction of the silt and clay unit at 0 piezometer nest. A semiquantitative analysis of the peak height ratios suggests the following quantities of minerals: 35% mica, 27% chlorite-vermiculite, 14% hornblende, 14% quartz and 10% plagioclase. The presence of the hornblende and the sharpness of the 10 Å and 14 Å peaks suggest that little geochemical weathering has occurred. X-ray analyses of the clay-sized fraction dispersed within the sands suggest that plagioclase and quartz are the predominant minerals present and that minor to moderate amounts of mica and interstratified mica-vermiculite are present (N. Miles, Soil Research Institute, Ottawa, Ontario, Canada, pers. comm.).
FIG. A. Plan view of the radioactive waste contaminant migration paths over time. Approximate depth of the front near QB piezometer nest is 5 metres. Approximate depth of the front near NA piezometer is 11 metres. Parameter $V_A$ in Eq. (9) is estimated from the field mapping of the path front over time.
TABLE II. VALUES OF $K_d$ BY FIELD MAPPING AND RADIOCHEMICAL ANALYSIS

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Retardation equation</th>
<th>Radiochemical analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{90}\text{Sr}$</td>
<td>7</td>
<td>15</td>
</tr>
<tr>
<td>$^{137}\text{Cs}$</td>
<td>80</td>
<td>500</td>
</tr>
</tbody>
</table>

The ground water flow pattern is shown in cross section in Figure 2. Ground water flow direction arrows have been drawn crossing the silt and clay unit since field mapping of the radioactive waste migration patterns indicates that the silt and clay unit contains permeable windows. The upland area near A Disposal Area forms the recharge area of the Basin, while the swamp near Perch Lake and the Lake itself form the ground water discharge area.

THE GROUND WATER GEOCHEMISTRY OF THE SANDY AQUIFER

In 1954 about 70 m$^3$ of medium-level, liquid radioactive waste containing about 60 curies (Ci) of $^{90}\text{Sr}$ and 70 Ci of $^{137}\text{Cs}$ were released into a pit at A Disposal Area lined with lime and dolomite. An experimental disposal in 1955 contained 300 Ci of $^{90}\text{Sr}$ and 250 Ci of $^{137}\text{Cs}$, however no attempt was made to neutralize it with lime or dolomite as in the previous disposal.

Since that time these wastes have chromatographically separated into $^{90}\text{Sr}$ and $^{137}\text{Cs}$ plumes (Figure 4) which are migrating through the sandy aquifer at characteristic velocities much less than the velocity of the transporting ground water ($v_{gw} = 2 \times 10^{-6}$ m/s). For $^{90}\text{Sr}$ this characteristic velocity is approximately 3% of that of the ground water; for $^{137}\text{Cs}$ it is about 0.3%. Table II shows the estimates of $K_d$ by both field mapping and radiochemical analysis methods. The field mapping estimates are lower than the radiochemical estimates because only the fronts of the radioactive waste plumes have been mapped which therefore yields an estimate of the fastest radionuclides, whereas the ground water velocity is a mean value. Consequently this method of front-to-front field mapping can only give an accurate estimate of $K_d$ if the front of a conservative tracer is also mapped. Therefore the radiochemical analyses are more reliable in this case.

We attribute the retardation of the radiocontaminants to either their adsorption or precipitation from solution. To gain some understanding of which of the processes might be operating we must consider the nature of the ground water. Table III lists the measured values for various ions and aqueous parameters which are of interest in this study. The methods of chemical analysis of these ground waters have been described elsewhere [16].
TABLE III. GROUND WATER GEOCHEMICAL DATA

<table>
<thead>
<tr>
<th>PIEZOMETER</th>
<th>pH</th>
<th>Eh</th>
<th>O₂</th>
<th>Total Fe</th>
<th>Total Mn</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>Sr²⁺</th>
<th>K⁺</th>
<th>Na⁺</th>
<th>SO₄²⁻</th>
<th>Total S²⁻</th>
<th>Cl⁻</th>
<th>NO₃⁻</th>
<th>HCO₃⁻</th>
<th>DIC</th>
<th>DOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA1</td>
<td>5.4</td>
<td>596</td>
<td>2.4</td>
<td>n.d.</td>
<td>0.03</td>
<td>5.2</td>
<td>2.0</td>
<td>-</td>
<td>1.8</td>
<td>91.3</td>
<td>15.1</td>
<td>n.d.</td>
<td>170</td>
<td>3.5</td>
<td>9.3</td>
<td>-</td>
<td>2.0</td>
</tr>
<tr>
<td>M2</td>
<td>6.0</td>
<td>434</td>
<td>-0.1</td>
<td>0.1</td>
<td>0.04</td>
<td>12.8</td>
<td>1.3</td>
<td>0.05</td>
<td>1.9</td>
<td>4.2</td>
<td>15.2</td>
<td>-</td>
<td>11</td>
<td>-</td>
<td>27.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>M3</td>
<td>6.2</td>
<td>217</td>
<td>-n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>20.5</td>
<td>12.5</td>
<td>0.14</td>
<td>3.3</td>
<td>34.1</td>
<td>19.4</td>
<td>n.d.</td>
<td>-</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NA2</td>
<td>6.4</td>
<td>196</td>
<td>&lt;0.2</td>
<td>4.3</td>
<td>0.10</td>
<td>3.7</td>
<td>5.3</td>
<td>-</td>
<td>1.8</td>
<td>21.5</td>
<td>12.8</td>
<td>0.04</td>
<td>31</td>
<td>1.5</td>
<td>52.0</td>
<td>10.2</td>
<td>4.2</td>
</tr>
<tr>
<td>NA3</td>
<td>8.0</td>
<td>50</td>
<td>&lt;0.2</td>
<td>0.8</td>
<td>0.13</td>
<td>23.3</td>
<td>8.2</td>
<td>-</td>
<td>3.2</td>
<td>13.6</td>
<td>12.8</td>
<td>0.01</td>
<td>37</td>
<td>1.7</td>
<td>122.0</td>
<td>23.2</td>
<td>2.4</td>
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<tr>
<td>O10</td>
<td>6.8</td>
<td>141</td>
<td>-2.8</td>
<td></td>
<td>0.13</td>
<td>13.9</td>
<td>4.0</td>
<td>0.11</td>
<td>2.0</td>
<td>11.2</td>
<td>9.6</td>
<td>-</td>
<td>24</td>
<td>-</td>
<td>66.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>O7</td>
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<td>167</td>
<td>-1.1</td>
<td></td>
<td>0.14</td>
<td>14.4</td>
<td>8.9</td>
<td>0.10</td>
<td>3.0</td>
<td>11.8</td>
<td>18.0</td>
<td>-</td>
<td>28</td>
<td>-</td>
<td>62.8</td>
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<tr>
<td>O8</td>
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<td>142</td>
<td>&lt;0.2</td>
<td>5.0</td>
<td>0.05</td>
<td>10.1</td>
<td>5.8</td>
<td>0.05</td>
<td>2.6</td>
<td>11.9</td>
<td>15.6</td>
<td>0.02</td>
<td>20</td>
<td>0.4</td>
<td>51.5</td>
<td>11.2</td>
<td>0.8</td>
</tr>
</tbody>
</table>

a All data in mg/litre unless otherwise specified, ground water temperatures 7-10°C.

b Dissolved inorganic carbon

c Dissolved organic carbon.

d Not detectable.

e Bicarbonate computed from alkalinity titration.
<table>
<thead>
<tr>
<th>PIEZOMETER</th>
<th>CaCO$_3$ (calcite)</th>
<th>SrCO$_3$ (strontianite)</th>
<th>Fe (OH)$_3$ (amorphous)</th>
<th>FeOOH (goethite)</th>
<th>Mn (OH)$_2$ (pyrochroite)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA1</td>
<td>-4.7</td>
<td>-</td>
<td>+0.3</td>
<td>+3.7</td>
<td>-11.8</td>
</tr>
<tr>
<td>M2</td>
<td>-3.1</td>
<td>-2.7</td>
<td>+1.3</td>
<td>+4.8</td>
<td>-10.2</td>
</tr>
<tr>
<td>M3</td>
<td>-2.7</td>
<td>-2.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NA2</td>
<td>-3.0</td>
<td>-1.5$^b$</td>
<td>+0.2</td>
<td>+3.6</td>
<td>-9.2</td>
</tr>
<tr>
<td>NA3</td>
<td>-0.3</td>
<td>+0.3$^c$</td>
<td>+1.5</td>
<td>+4.9</td>
<td>-6.0</td>
</tr>
<tr>
<td>010</td>
<td>-2.0</td>
<td>-1.2</td>
<td>+0.2</td>
<td>+3.6</td>
<td>-8.2</td>
</tr>
<tr>
<td>07</td>
<td>-1.9</td>
<td>-1.2</td>
<td>+0.5</td>
<td>+3.9</td>
<td>-8.1</td>
</tr>
<tr>
<td>08</td>
<td>-2.1</td>
<td>-1.5</td>
<td>+0.8</td>
<td>+4.3</td>
<td>-8.4</td>
</tr>
</tbody>
</table>

$^a$ All data are converted to log$_{10}$ S I where S I = IAP/K$_{sp}$.

$^b$ Sr$^{2+} = 0.17$ mg/l, HCO$_3^-$ = 29.4 mg/l (chemical analysis other than reported in Table III).

$^c$ Sr$^{2+} = 0.13$ mg/l, HCO$_3^-$ = 116.5 mg/l (chemical analysis other than reported in Table III).
Because of the high solubility of the alkali metals, $^{137}\text{Cs}$ cannot be precipitated from solution in such a dilute geochemical environment as the Lower Perch Lake Basin, therefore its retardation must be due to adsorption from solution. However, it is conceivable that $^{88}\text{Sr}$ might be precipitated from solution either directly as $\text{SrCO}_3$ or indirectly by isomorphous substitution or coprecipitation with $\text{CaCO}_3$. Thus a saturation index for each mineral was computed. The values in Table IV demonstrate that equilibrium between aqueous and solid carbonate species is approached (i.e. $S I = 0.0$) only in parts of the deeper ground waters, in which calcite or strontianite may be present, and that precipitation of either carbonate may be occurring near only one of the piezometers (NA3). Consequently the precipitation of carbonate species does not seem to be an effective control on the migration of $^{88}\text{Sr}$, at least in the upper sands.

It has been demonstrated by Kurbatov et al. [17] that identical quantities of $^{88}\text{Sr}$ can be removed from aqueous solution by either coprecipitation with or adsorption by amorphous ferric oxyhydroxides; this is probably also true for manganese oxyhydroxides. Consequently saturation indices for some Fe and Mn oxyhydroxide species have been calculated and are shown in Table IV. An examination of this table shows that it is conceivable that ferric oxyhydroxides may be acting as a sink for $^{88}\text{Sr}$ and, possibly, $^{137}\text{Cs}$. Following the methods of Whittemore and Langmuir [18] we note that the Chalk River groundwaters are saturated with amorphous ferric oxyhydroxides ($pQ = -\log [\text{Fe}^{3+}][OH^-]^3 - 38$) which may be undergoing slow diagenesis to a more crystalline phase.

Furthermore it is conceivable that $^{88}\text{Sr}$ and $^{137}\text{Cs}$ are being retarded in their migration through the aquifer by adsorption from solution by either clay minerals or other inorganic or organic colloids. It is very probable that the great affinity of micaceous minerals for cesium is the cause of the relatively slow migration rate vis-à-vis. Tamarua [19] has ascribed this affinity to the preferential adsorption of $\text{Cs}^+$ into interlayer positions near the edges of crystallites with 10 Å d spacings. Second, there exist in the Chalk River sands significant amounts of sedimentary organic matter (1% by weight, loss on ignition) which may have significant cation exchange capacities. The results of Oppel et al. [20] suggest a direct correlation exists between the exchangeable $^{88}\text{Sr}$ adsorbed to the sandy bottom sediments of Perch Lake and the amount of sedimentary organic matter.

We have presented a variety of possible geochemical mechanisms for the observed retardation of $^{88}\text{Sr}$ and $^{137}\text{Cs}$. However the relative importance of clay minerals, organic matter and amorphous iron precipitates to the mechanism of retardation is as yet unknown and is the subject of our present research. Nevertheless the distribution coefficient offers the hydrogeologist a convenient integrated measure of all the geochemical reactions affecting specific contaminants present in the aquifer.

**DISCUSSION**

The problems of applying the distribution coefficient concept beyond its present context of radioactive waste management to ground water quality management in general have been addressed by hydrogeologists at the University of Waterloo [21]. They have pointed out that improved laboratory and field techniques are needed for its estimation. At present in their laboratory work they are investigating the effect on contaminant uptake when a sample of aquifer material or soil is disturbed during laboratory analysis. They have suggested two types of field methods might
be considered - multiple well tracer studies using the contaminant of interest and the chemical analysis of aquifer materials and ground waters from a contaminant plume. These two field methods are somewhat akin to the field mapping and radiochemical analysis methods discussed in this paper.

A further problem, that of predicting the distribution coefficient of fractured rock, is being studied by G.E. Grisak (Alberta Environment, Lethbridge, Alberta, Canada) using tracers and a 1000 kg sample of fractured till in a laboratory press by which the in situ lateral stresses are simulated. Grisak's conceptual model of flow through a fractured media results in a retardation equation similar to equation (9) except that, by taking into account adsorption from solution along a fracture surface, it includes a distribution coefficient with units of ml/fracture surface area.

The wider use of the distribution coefficient concept in ground water quality management will probably occur when regulatory agencies concerned with the quality of ground waters demand hydrogeological impact statements of the results of toxic waste disposal. It will therefore be necessary to measure a parameter similar or identical to \( K_d \), and the hydrogeologist or geochemist responsible for such a measurement will have the choice of either laboratory or field estimation. As has been noted laboratory estimation of \( K_d \) involves problems such as sample disturbance and that of reproducing the geochemical environment in the contaminated aquifer. Field tests, such as those mentioned, are costly and time-consuming, however they offer results that to our mind are the most reliable, provided the waste solution used will accurately reflect that to be disposed.

Consequently either method of estimating distribution coefficients would involve reproducing the geochemical environment within the contaminated aquifer. In radioactive waste management studies this reproduction has generally involved only alkali and alkaline earth metals and reference clays or local sediments; however future work must consider the simulation of the redox, complex-forming and acid-base buffering environments relevant to the transition metals. While conceptual models of these processes (e.g. Table 1) do seem to explain various features of the ground water geochemistry of aquifers, our knowledge of the mechanisms of the processes themselves is primitive.

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REFERENCES


DETERMINATION OF AQUIFER CHARACTERISTICS BY THE MULTI-WELL METHOD

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Abstract

DETERMINATION OF AQUIFER CHARACTERISTICS BY THE MULTI-WELL METHOD.

The paper deals with the determination of some aquifer characteristics required for prediction of pollutant movement. A new method of interpretation of multi-well experiments is proposed. This method provides a possibility of determining in a single experiment the flow velocity, flow direction, longitudinal and transverse dispersion coefficients. Geometric conditions for the performance of the experiment in the field are given.

1. INTRODUCTION

With the increasing concern for groundwater protection, the problem of predicting the movement of pollutants has gained greater attention. Recently a number of numerical models based on the finite element method have been developed. Work of Pinder [1], Rubin and James [2] and Smith et al. [3] provides examples of this trend. The current status of numerical computation is that the differential equation governing dispersion superposed with adsorption can be handled efficiently. The numerical methods enable modelling problems with complicated boundary conditions and spatially varied flow parameters such as the flow velocity vector, dispersion coefficients and adsorption constant. With today's numerical techniques and digital computers, the mathematical simulation of pollution transport for any given groundwater field is possible, provided the parameters are known. However, in many field problems the advantages of the

* Work performed while holding an IAEA fellowship at the Institut für Radiohydrometrie, Neuherberg, Federal Republic of Germany.
numerical methods can be used only to a very limited extent, because appropriate data are lacking. Usually, "modellers" try to overcome these difficulties by fitting their very sophisticated models with spatially varied parameters to observational data. Such a procedure (justified by necessity) has the weaknesses that fitting multiparameter non-linear models can frequently lead to wrong estimation, and that extremely long computing time is required. On the other hand, when using constant parameters (instead of spatially varied ones) the advantages of the numerical approach over the analytical one become questionable.

In view of the increasing demand for knowledge of aquifer characteristics more effort should be spent on their determination directly in the field. Knowledge of the actual values of the flow velocity and dispersion coefficients would improve the effectiveness of the numerical approach and make the prediction of pollutant movement more precise. As is well known, tracer methods can be used to determine almost all properties of the aquifer required for pollutant movement simulation. To date comparatively little attention has been paid to the determination of the transverse dispersion coefficient. Laboratory methods [4, 5, 6] can be hardly applied in the field. Geoelectric methods [7] can be used only for shallow aquifers.

The present paper deals with the interpretation of multi-well tracer experiments. The authors propose a modification of the experimental procedure and suggest a method of interpretation which enables the simultaneous determination of the flow velocity vector and two dispersion coefficients. For parameter estimation the method of fitting the analytical model to the experimental data is applied. For the sake of brevity, most of the mathematical problems encountered in this work are only briefly mentioned here and will be discussed elsewhere.

2. INTERPRETATION OF MULTI-WELL EXPERIMENTS

2.1. Mathematical model

The experimental setting of the multi-well experiment (cf. [7]) involves two-dimensional treatment of the problem. For the two-dimensional case, the differential equation of dispersion in homogeneous media reads:

\[
\frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial x^2} + D_T \frac{\partial^2 c}{\partial y^2} - V \frac{\partial c}{\partial x}
\]

(1)

where \( c \) is the concentration of the tracer in water, \( x \) and \( y \) are the Cartesian coordinates (the \( x \)-axis is taken along the flow direction), \( t \) is the time variable, \( v \) is the mean distance velocity, \( D_L \) is the longitudinal dispersion coefficient, \( D_T \) is the transverse dispersion coefficient.
The experimental procedure mainly consists in an instantaneous injection of the tracer in a well fully penetrating the aquifer (line injection) followed by measurements of the tracer concentration in boreholes situated downstream. The mode of the injection can be mathematically described using the following initial and boundary conditions:

\[ c(0,0,t) = \frac{M}{nhv} \delta(t) \]  
\[ c(\infty,y,t) = 0 \]  
\[ c(x,\infty,t) = 0 \]  
\[ c(x,y,0) = 0 \]  

where \( M \) is the mass of the tracer, \( \delta(t) \) is the Dirac delta function, \( n \) is the effective porosity, \( h \) is the thickness of the aquifer.

The solution to Eq.(1) for conditions (2) given by Lenda and Zuber [8] reads:

\[ c(x,y,t) = \frac{\rho x}{4\pi v t^2 \sqrt{D_L D_T}} \exp \left[ \frac{(x-vt)^2}{4D_L t} - \frac{y^2}{4D_T t} \right] \]  

where \( \rho = \frac{M}{nh} \).

Solution (3) describes the breakthrough curve (concentration distribution) versus time resulting from an appropriate experiment in the homogeneous aquifer. Real aquifers cannot be considered as homogeneous media. However, any real groundwater field can be locally approximated by the model assuming homogeneity of the material and uniformity of flow. The only question is how large parts of the aquifer can be described by this simplified model.

Solution (3) has been selected for application in this work also for some mathematical reasons. Namely, Eq.(3) can be transformed to the linear form with respect to the parameters. In the case of the linear model, the fitting procedure is reduced to solving an overdetermined linear system. It has great advantages: the problem of the initial values of the parameters does not arise and the computation time is relatively short. Equation (3) can be considered as a function of one variable \( t \) and four parameters: \( v, D_L, D_T \) and \( \rho \) (\( x \) and \( y \) are assumed to be known constants). By substituting

\[ Q_1 = \ln \left( \frac{\rho x}{4\pi v \sqrt{D_L D_T}} \right) + \frac{xv}{2D_L} \]
\[ Q_2 = \frac{x^2}{4D_L} + \frac{y^2}{4D_T} \]
\[ Q_3 = \frac{v^2}{4D_L} \]  

(4)
FIG. 1. Arbitrary co-ordinates \((p,q)\) and co-ordinates \((x,y)\) defined by the flow direction \(v\). 
IW - injection well, OW1, OW2 - observational wells, \(Q_i\), \(\bar{Q}_i\) \((i = 1,2,3)\) - intermediate parameters.

and taking logarithms of both sides of Eq.(3) one obtains:

\[
\ln c = -2\ln t + Q_1 - Q_2 t^{-1} - Q_3 t
\]  

(5)

Transformation (4) decreases the number of the parameters, which means that in the initial model (3) parameters interact. The inverse transformation to (4) does not exist. It follows that parameters \(v\), \(D_L\), \(D_T\) and \(p\) cannot be determined using only one breakthrough curve. The information obtained from one measuring point is obviously not sufficient.

2.2. Determination of flow parameters

Because of the interaction of the parameters of Eq.(3), the solution of the inverse problem (i.e. determination of their values) is not trivial. Three intermediate parameters, \(Q_1\), \(Q_2\) and \(Q_3\), obtained by fitting formula (5) to any observed curve, do not determine the four initial parameters. Besides, in practice, \(x\) and \(y\), co-ordinates of the measuring point in the system with the \(x\)-axis taken along the flow direction, cannot be treated as known values (on the contrary, the experiment is expected to improve the preliminary flow direction estimation). Therefore, the experiment should yield more than one breakthrough curve. It will be shown that the observations from two suitably chosen boreholes are sufficient for solving the inverse problem.

Let us introduce any arbitrary co-ordinate system where positions of the observation wells can be simply measured. Figure 1 shows the relationship between this arbitrary system \((p,q)\) and the co-ordinate system defined by the
actual flow direction \((x, y)\). The angle \(\alpha\) between \(p\) and \(x\) axes is an additional unknown parameter. Using the well-known transformation:

\[
\begin{align*}
    x &= p \cos \alpha + q \sin \alpha \\
    y &= -p \sin \alpha + q \cos \alpha
\end{align*}
\]  \hspace{1cm} (6)

one can express Eq.(3) in the arbitrary system.

Let us assume that the tracer is observed in two wells and that sets of intermediate parameters, \((Q_1, Q_2, Q_3)\) for OW1 and \((\overline{Q}_1, \overline{Q}_2, \overline{Q}_3)\) for OW2 can be determined. Expressing the intermediate parameters (see formulas (4)) in an arbitrary co-ordinate system one obtains the following set of five equations with respect to \(v, D_L, D_T, \rho\) and \(\alpha\):

\[
\begin{align*}
    Q_1 &= \ln \left( \frac{\rho}{4 \pi v \sqrt{D_L D_T}} \right) + \ln(p_1 \cos \alpha + q_1 \sin \alpha) + \frac{v}{2 D_L} (p_1 \cos \alpha + q_1 \sin \alpha) \\
    \overline{Q}_1 &= \ln \left( \frac{\rho}{4 \pi v \sqrt{D_L D_T}} \right) + \ln(p_2 \cos \alpha + q_2 \sin \alpha) + \frac{v}{2 D_L} (p_2 \cos \alpha + q_2 \sin \alpha) \\
    Q_2 &= \frac{(p_1 \cos \alpha + q_1 \sin \alpha)^2}{4 D_L} + \frac{(q_1 \cos \alpha - p_1 \sin \alpha)^2}{4 D_T} \\
    \overline{Q}_2 &= \frac{(p_2 \cos \alpha + q_2 \sin \alpha)^2}{4 D_L} + \frac{(q_2 \cos \alpha - p_2 \sin \alpha)^2}{4 D_T} \\
    Q_3 &= \overline{Q}_3 = \frac{v^2}{4 D_L}
\end{align*}
\]  \hspace{1cm} (7)

A procedure used for solving the equation system (7) consists of the following steps:

1. by means of elementary operations the equation system (7) is reduced to one equation with respect to \(\alpha\)

\[
\begin{align*}
    (p_1 q_2 - p_2 q_1)(p_1 q_2 + p_2 q_1) \cos 2\alpha + (q_1 q_2 - p_1 p_2) \sin 2\alpha
    \\
    4 \left[ Q_2 (q_2 \cos \alpha - p_2 \sin \alpha)^2 - \overline{Q}_2 (q_1 \cos \alpha - p_1 \sin \alpha)^2 \right]
    \\
    = \left[ \frac{(p_1 - p_2) \cos \alpha + (q_1 - q_2) \sin \alpha}{(Q_1 - \overline{Q}_1) - \ln \left( \frac{p_1 \cos \alpha + q_1 \sin \alpha}{p_2 \cos \alpha + q_2 \sin \alpha} \right)} \right]^2 Q_3
\end{align*}
\]  \hspace{1cm} (8)
(2) Eq.(8) is solved numerically using the bisection method [9]. 
(3) for each \( \alpha \) value being the solution of Eq.(8) the other parameters are computed according to the following formulas:

\[
D_L = \frac{(p_1 q_2 - p_2 q_1) [(p_1 q_2 + p_2 q_1) \cos 2\alpha + (q_1 q_2 - p_1 p_2) \sin 2\alpha]}{4 [Q_2 (q_2 \cos \alpha - p_2 \sin \alpha)^2 - Q_2 (q_1 \cos \alpha - p_1 \sin \alpha)^2]}
\]

\[
D_T = \frac{(p_2 q_1 - p_1 q_2) [(p_1 q_2 + p_2 q_1) \cos 2\alpha + (q_1 q_2 - p_1 p_2) \sin 2\alpha]}{4 [Q_2 (p_2 \cos \alpha + q_2 \sin \alpha)^2 - Q_2 (p_1 \cos \alpha + q_1 \sin \alpha)^2]}
\]

\[
v = 2 \sqrt{Q_3 D_L}
\]

\[
\rho = 4 \pi v \sqrt{D_L D_T} \exp[Q_1 - \ln(p_1 \cos \alpha + q_1 \sin \alpha) - \frac{v}{2 D_L} (p_1 \cos \alpha + q_1 \sin \alpha)]
\]

It may happen that Eq.(8) and in consequence the whole system (7) has more than one, one or no solution. It depends mostly on the positions of the observational points. By means of an elementary analysis of Eq.(8) the following configurations excluding the existence of the solution have been identified:

(1) all three wells, IW, OW1, OW2 lie on a straight line;
(2) OW1 and OW2 are situated symmetrically with respect to the flow direction \((x_1 = x_2 \text{ and } y_1 = -y_2)\).

The geometry of the experiment should differ as much as possible from these two situations. It is much more difficult to point out the geometric conditions which lead to unambiguous interpretation and the most precise estimation of the parameters. In order to investigate this problem, breakthrough curves for various configurations and various aquifer characteristics have been simulated and then interpreted. On the basis of these simulations the conditions given in Fig.2 have been found favourable. They are formulated in some respects arbitrarily and should not be understood rigorously. If the transverse dispersion is very high, the distance \(l_2\) can be greater than 0.2 \(l_1\) (see Fig.2) and for the very small transverse dispersion \(l_2\) should be smaller than 0.05 \(l_1\).

To realize the proper experimental setting in the field some preliminary knowledge of the flow direction and the transverse dispersion coefficient is desired. The estimation of the flow direction based on the general recognition of the hydropotential field seems to be sufficient for this purpose. In most cases also the transverse dispersion coefficient can be roughly estimated from the fact
that it depends on the lithology and structure of the aquifer, which is usually investigated before starting with the tracer experiment (this preliminary information is essential only for performing the experiment; it is not used for the interpretation of the results). No doubt the choice of the geometry in the field is a critical point of the method. However, this is a general disadvantage of the multiwell method.

Solving the equation system (7) ends only the mathematical treatment of the problem. Even under favourable geometric conditions more than one solution may be obtained. Then the interpreter should analyse the results from a physical point of view and reject those solutions which have no sense or contradict the experimental evidence. The solution can be considered as non-physical if:

1. any of the parameters \( V, D_L, D_T, \rho \) is negative in its whole confidence interval;
2. a value of any parameter is evidently incompatible with results of other independent investigations of the given aquifer.

The second criterion concerns mainly the ratio \( D_L/D_T \). For large velocities of flow in isotropic media this ratio should not be outside the range 5–25 (cf. Ref.[10]). For very slow flow, where molecular diffusion is predominant, this ratio should be about 1. The other values of \( D_L/D_T \) can be met in the case of an anisotropic permeability.

3. VERIFICATION OF THE METHOD

3.1. Simulated experiments

For the preliminary test of the method derived in this work the technique of simulated experiments was used. At this level of verification the analytical
model (3) is identified with a real object. The aim of these tests was to examine the precision and the reliability of the parameter determination for various geometries, various flow parameters and varying mass (or sensitivity of the detection system). The analysis of results obtained leads to the following conclusions.

1. The reliability and the precision of the parameter determination depend on the geometry of the experiment. However, for a wide range of configurations (described in Fig.2) this dependence is not essential.

2. The particular parameters are determined with differing precision; the best for $v$ (then $D_L, \alpha, D_T$) and the worst for $\rho$. Due to the low precision for the estimation of $\rho$, the proposed method cannot be considered as a method for determining the effective porosity ($n = M/\rho \cdot h$, assuming $M$ to be a known value).

3. The precision of the parameter estimation increases considerably with the precision of measurements (depending on the sensitivity of the detection system and the mass of the tracer). If the measurements are performed in a discrete way, a number of samples is also of importance.

3.2. Laboratory experiments

The experiments were conducted in a steel box with a length of 120 cm, a width of 120 cm and a height of 40 cm. The unconfined porous bed was formed of a quartz sand with a mean grain size, $d_{50} = 0.75$ mm, a uniformity coefficient, $d_{60}/d_{10} = 1.85$ and a total porosity, $n_t = 0.35$. The flow was governed by two constant head tanks and the slope of the box. They were adjusted so that the water table was parallel to the bottom of the box. The thickness of the water body was 35 cm. A filtration velocity measured with the aid of the volumetric method was 0.37 cm/min and a distance velocity (calculated assuming the effective porosity equal to the total one) was 1.06 cm/min.

The injection well and two observational wells penetrated the whole porous bed perpendicularly to the water table. All the wells were formed of perforated plexiglas tubes with an inner diameter of 6 mm and a wall thickness of 1 mm.

The tracer was 2% water solution of disodium fluorescein (density compensated with the aid of alcohol). The tracer was injected as uniformly as possible along the whole filter tube and then immediately mixed. In two experiments which were conducted the injected volume of the tracer was about 0.5 cm$^3$.

Observations were made by taking samples of 100 $\mu l$ from the observational wells. Then the samples were diluted by factor of 100. Analyses of the diluted
samples were performed using a spectrofluorimeter. The configurations of the wells, measured concentrations and results of the interpretation are given in the Appendix.

The results of these tests seem to be reasonable. In both cases the controlled flow parameters, v and α, were estimated quite well. The dispersion coefficients were estimated with poor precision. However, the information that the dispersion coefficients are smaller than given values is also of importance. The goodness of fit of the model (5) to the experimental data was unsatisfactory. However, one cannot conclude that the analytical model is not applicable. The experimental setting described above was far from being ideal from the point of view of the method; the injection of the tracer was not really instantaneous; the observational wells and the sampling procedure itself disturbed the flow conditions. It seems that in the field the experimental setting can much better fulfil the prerequisites of the method than these laboratory experiments.

4. CONCLUSIONS

(1) It seems necessary to distinguish two kinds of applications of mathematical models in groundwater pollution problems.

(a) A model used as a tool for predicting the movement of pollutants (provided the parameters are known). It should be capable of describing the whole variety of the system.

(b) A model used as a computational tool for determining the aquifer characteristics (being parameters of the model) from the tracer experiments. In this case the model should enable the solution of the inverse problem (i.e. its parameters cannot interact).

(2) Four flow parameters: flow velocity, flow direction and two dispersion coefficients can be determined simultaneously in a multi-well experiment involving only two observational wells. This possibility has been shown theoretically and proved by the simulated experiments. Results of the first laboratory experiments are encouraging and further experiments in the laboratory as well as in the field are planned at the Institute of Radiohydrometry in Neuherberg.

(3) The mathematical models appear to be very useful not only for interpreting the tracer experiments but also for optimizing their setting.
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REFERENCES


Appendix

RESULTS OF THE LABORATORY EXPERIMENTS

Positions of the observational wells are given in the co-ordinate system with the x-axis taken along the flow direction and the origin at the injection well. Values of concentrations given in Tables I and II refer to samples taken from the porous bed. In reality, 100 μl samples were diluted in 9.9 ml of pure water and then analysed. Errors of instrumental analyses are negligible in comparison with errors caused by the sampling procedure. The resulting relative standard deviation does not depend practically on measured concentration and is equal to 0.10.
TABLE I. BREAKTHROUGH CURVES MEASURED IN EXPERIMENT 1

<table>
<thead>
<tr>
<th>time (min)</th>
<th>c (10^{-9} g/cm^3)</th>
<th>time (min)</th>
<th>c (10^{-9} g/cm^3)</th>
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<tr>
<td></td>
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</tr>
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</table>

Experiment 1

Geometry: 0W1 (p_1 = 0.650 m, q_1 = -0.013 m)
0W2 (p_2 = 0.915 m, q_2 = 0.025 m)

Results of the interpretation:

\[ \alpha = (4.6 \pm 2.8) \times 10^{-2} \text{ rad} \]
\[ D_L = (2.6 \pm 3.5) \times 10^{-5} \text{ m}^2/\text{min} \]
\[ D_T = (-0.36 \pm 1.28) \times 10^{-7} \text{ m}^2/\text{min} \]
\[ v = (9.7 \pm 6.7) \times 10^{-3} \text{ m/min} \]
\[ \rho \] undetermined due to negative \( D_T \) value.
### Table II. Breakthrough Curves Measured in Experiment 2

<table>
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<tr>
<th></th>
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<th>OW2</th>
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<td>c ( \times 10^{-9} ) g/cm²</td>
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</table>

**Experiment 2**

Geometry:  
- OW1 \( p_1 = 0.812 \text{ m}, q_1 = -0.033 \text{ m} \)  
- OW2 \( p_2 = 0.980 \text{ m}, q_2 = 0.029 \text{ m} \)

Results of the interpretation:

- \( \alpha = (-1.2 \pm 2.0) \times 10^{-2} \text{ rad} \)
- \( D_L = (2.6 \pm 2.4) \times 10^{-6} \text{ m}^2/\text{min} \)
- \( D_T = (-1.1 \pm 3.2) \times 10^{-7} \text{ m}^2/\text{m} \)
- \( v = (1.27 \pm 0.57) \times 10^{-2} \text{ m/min} \)
- \( \rho \) undetermined due to negative \( D_T \) value.
FIELD DETERMINATION OF THE PHYSICAL CONTAMINANT TRANSPORT PARAMETERS IN A SANDY AQUIFER

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Abstract

FIELD DETERMINATION OF THE PHYSICAL CONTAMINANT TRANSPORT PARAMETERS IN A SANDY AQUIFER.

The physical transport parameters necessary for the prediction of contaminant migration in subsurface flow systems are groundwater velocity and dispersivity. Detailed field determination of these parameters has been performed in a sandy aquifer near one of the waste management areas of the Chalk River Nuclear Laboratories (CRNL). Groundwater velocities in the aquifer were (1) estimated using the Darcy equation with a knowledge of the distribution of hydraulic head, hydraulic conductivity and porosity and (2) measured directly using point dilution tests. Values of hydraulic conductivity were determined using four independent methods including a pumping test, single-piezometer response tests, point dilution tests and a tracer test. The point dilution tests proved to be advantageous in indicating directly the zones of highest velocities in the aquifer. The dispersion studies undertaken have involved laboratory column and sandbox experiments, and a field tracer test using the two-well recirculating withdrawal-injection method. The dispersivity values obtained range from 1 cm for the column experiments to 10 cm and 50 cm for the field tracer test. The 50 cm value of dispersivity, obtained from analysis of the breakthrough curve at the withdrawal well, is probably an apparent dispersivity resulting from the water samples taken from the well being an integrated mixture of the water flowing into the well over the entire aquifer thickness. This points out the need in dispersion studies for obtaining point samples rather than mixed samples from wells slotted over large intervals. For this purpose, the multilevel point sampler described in this study was shown to be very useful.

1. INTRODUCTION

The physical processes that cause transport of contaminants in groundwater flow systems are convection (i.e. the flux due to the mean velocity) and dispersion. The parameters required to describe these processes are groundwater velocity and dispersivity. For the prediction of contaminant migration from existing or proposed waste management sites it is necessary to determine the distribution of the values of these parameters.
or early Holocene time. The sand is fine-to medium-grained and well sorted. It appears unstratified when viewed in the form of relatively undisturbed core samples. At outcrops elsewhere in the vicinity of the watershed, sands of this type have minor laminations and small-scale cross bedding. It is believed that the aquifer also has these features but that they are not evident from core samples in a wet state. At the study site, the aquifer is confined below by a silty clay bed that is about 1 m in thickness. It is confined above by a much thinner bed or thin zone of bedded silt and clay. The aquifer is the main zone through which contaminants from the waste disposal area in the uplands north of the site are migrating.

3. INSTRUMENTATION

There is an extensive piezometer and well network between the waste management area and Perch Lake (Fig. 1). The physical hydrogeology of this area is described by Cherry et al. [14]. The groundwater velocity and dispersion studies that will be described were carried out in the middle sand aquifer at the location designated with a heavy arrow in Figure 1.
During the summer of 1976, the field site was instrumented with 32 piezometers, 2 wells and 13 multi-level samplers. The layout of the instrumentation for the field tests is shown in Figure 2.

The piezometers were used for testing of the hydraulic conductivity of the geologic materials around their tips, monitoring of the natural piezometric levels in the groundwater flow system, and monitoring of the piezometric levels during the pumping test and the two-well withdrawal-injection tracer test. The piezometers were installed through a steel casing that was driven through the combined effect of mechanical vibration and jetting with a water hose extending to the bottom of the casing. After installation of the piezometer pipe to the desired depth, the casing was removed by jacks, resulting in immediate caving of the sediments into the hole around the piezometer. Since the sands of these deposits caved readily,
it was not necessary to grout the hole above the piezometer tip as the casing was removed. The piezometers are constructed from 2.5 cm diameter PVC pipe. The intake portion at the bottom of the piezometer is about 50 cm in length and was constructed by slotting with saw cuts and wrapping with fiberglass cloth tape to prevent fine-grained material from entering. This type of piezometer is inexpensive and provides reliable data. The piezometers were installed to various depths in order to monitor the hydraulic head in the different stratigraphic units.

The two wells were used in the pumping test for hydraulic conductivity determination and in the withdrawal-injection tracer test. They were constructed of PVC pipe with ABS plastic-wrapped screens having slot openings of about 0.1 mm (0.004 in). They were screened from 3 m to 10 m below ground surface which is approximately the extent of the middle sand aquifer and were located 8 m apart. The wells were installed through a steel casing driven by a cable-tool drilling rig. The casing was then removed using jacks. The borehole was grouted as the casing was removed in the upper 2.5 m to prevent hydraulic connection of the upper and middle sand aquifers.

During the driving of the steel casing for the wells, continuous sampling of the borehole materials was accomplished using a cohesionless soil sampler [15] to obtain relatively undisturbed samples. These samples were obtained in 5 cm diameter by 61 cm long methyl methacrylate tubing. These transparent tubes allow visual inspection of the samples without removal and are easily adapted for column tracer experiments.

The network of multi-level samplers permitted the monitoring, in three dimensions, of the movement of tracer during the two-well withdrawal-injection tracer test. The 13 samplers contained a total of 160 sampling points. The details of the construction of a multi-level sampler are discussed elsewhere [16]. A schematic diagram, depicting a field installation of the sampler and a cross-section of an individual sampling point on the sampler, is shown in Figure 3. Each sampler consists of a PVC pipe with a number of sampling points positioned at predetermined stratigraphic levels along its length. The sampler is inexpensive and it can be easily constructed in the field. Samples were collected by connecting the polypropylene tubing which extends to above ground surface to a vacuum flask and applying suction. The samplers were installed by the washboring method as described for the piezometer installations.
4. GROUNDWATER VELOCITY MEASUREMENTS

4.1 Darcy Equation

One of the most common methods for estimating the distribution of groundwater velocities through a flow system is by the use of the Darcy equation. In its simplest form, the Darcy equation is written:

\[ u = K \nabla h \]  \hspace{1cm} (1)

where \( u \) is the Darcy velocity or specific discharge, \( K \) is the hydraulic conductivity and \( \nabla h \) is the hydraulic head gradient.
<table>
<thead>
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in the direction of flow. The average linear porewater velocity, referred to as the groundwater velocity, is related to the Darcy velocity by the relation:

$$V = \frac{u}{n}$$  \hspace{1cm} (2)

where $V$ is the groundwater velocity and $n$ is the porosity.

To use this approach for estimating groundwater velocity requires a knowledge of the distribution of hydraulic head, hydraulic conductivity and porosity. Of these three parameters, hydraulic conductivity is the one which often exhibits the largest degree of variability in space throughout a flow system and also exhibits the greatest uncertainty in the values that are obtained. For this reason, a comparative study of hydraulic conductivity was conducted at the field site. The field methods employed include a pumping test, single-piezometer response tests, point dilution tests and a two-well tracer test.

The pumping test involved pumping one of the wells and recording the response, with time, in piezometers slotted in the same aquifer [17]. The data was analyzed using the methods of Theis, Jacob, Chow and Thiem described by Kruseman and De Ridder [17]. The hydraulic conductivities obtained from the pumping tests are bulk hydraulic conductivities of the full aquifer.

The single-piezometer water-level response tests were conducted on all piezometers slotted at 3.4 m and 8.8 m depths in the middle aquifer. The tests were performed by dropping an aluminum rod of known dimensions into the water in the piezometer causing a sudden rise in the water level in the piezometer. The water-level response with time was then measured. The data was analyzed using the methods of Hvorslev [18], Cooper et al. [19] and Bouwer and Rice [20]. Single-piezometer response tests yield estimates of the hydraulic conductivity of the geologic materials surrounding the slotted portion of the piezometer or well.

Hydraulic conductivities at depths of 3.4 m and 8.8 m were also determined using point dilution tests and using a two-well injection-extraction tracer test. These are further described in the following section and their results along with the results of the pumping test and single-piezometer response tests are shown in Table I.
The values of hydraulic conductivity obtained by the four different test methods, some of which utilized several procedures of data analysis, are in close agreement. The values obtained vary over a factor of about 5. Uncertainty of this magnitude or larger is typical of hydraulic conductivity determinations. This fact must be considered when predicting contaminant migration in groundwater flow systems.

The hydraulic conductivities obtained from the pumping test are bulk hydraulic conductivities of the full aquifer rather than being point or localized estimates as are determined by using single-piezometer response tests or point dilution tests. In contaminant migration studies, these average or bulk hydraulic conductivities are only marginally useful because the critical hydraulic conductivities are those of the geologic layers or lenses in which the most rapid contaminant movement occurs.

### 4.2 Tracers

#### 4.2.1 Point dilution tests

A comprehensive review of the uses and limitations of the single-well point or borehole dilution technique for groundwater velocity measurements has been given by Halevy et al. [21]. Essentially, the technique consists of labelling the water in a section of the well screen with a tracer and observing the rate of dilution. The rate of dilution is related to the velocity of the groundwater through the equation [21, 22]:

\[
V = -\frac{U}{\theta Ft} \ln \frac{C}{C_0}
\]  

where \( U \) is the dilution volume, \( F \) is the cross-sectional area of the well, \( t \) is the time since the beginning of measurement, \( C_0 \) is the original concentration of the tracer in the volume \( U \), \( C \) is the observed concentration at time \( t \), and \( \theta \) is a correction factor which accounts for the distortion of the flow pattern caused by the presence of the well. Other corrections may be required as a result of well construction, the presence of vertical currents in the well, density and temperature effects, diffusion of the tracer, and effects of the apparatus used. Of these, the one that is commonly of greatest significance is the presence of vertical currents.

The apparatus used in this study was designed to fit inside a 10 cm plastic well screen. It uses inflatable packers
to seal off a section 41 cm in length in the well. An oscillator pump sealed in a waterproof case is positioned just above the top packer and is used to keep the dilution volume between the packers well mixed. The effect of vertical currents is minimized by using a pressure-equalizing tube across the packers. Rhodamine WT was used as the tracer. Water from the dilution volume was recirculated to above ground surface and passed through a fluorometer to record changes in the tracer concentration. The value of δ had been previously evaluated [22] to be 0.5.

The velocity distribution under natural gradients was determined throughout the depth of the aquifer using point dilution tests. The results are shown in Figure 4; the solid
bars indicate the packed-off interval in the well for each test. The corresponding hydraulic conductivities were calculated using these velocities, the hydraulic head gradient determined from the piezometer network (Fig. 2) and a porosity of 0.38 [15] for the sand. The hydraulic conductivity values for depths of 3.4 m and 8.8 m are included in Table I for comparison with the other methods.

The results shown in Figure 4 demonstrate the detailed velocity profiling of a groundwater flow system that is possible using the point dilution technique. Zones of high transport rates can be delineated using this method. With this technique, it is possible during site surveys to locate waste management sites in areas that minimize their hydraulic connection to high transport zones.

4.2.2 Multiple-well tracer tests

The multiple-well tracer test usually involves introduction of a tracer at one or more wells with subsequent monitoring in other wells located along the direction of expected tracer movement. This method permits the determination of the groundwater velocity under natural gradients and also the direction of movement. This type of tracer study can be quite expensive and time-consuming because numerous monitoring points are required to map the migration patterns and because groundwater velocities are commonly very low. A tracer study of this type is currently in progress at the field site.

A two-well recirculating withdrawal-injection tracer test was conducted. This test is described in more detail in the next section. The tracer movement was monitored using the multi-level samplers in the flow regime induced by the withdrawal and injection system. An analysis of the movement of the tracer at different levels using a computer simulation model permitted an evaluation of the hydraulic conductivity with depth. The results at depths of 3.4 m and 8.8 m have been included in Table I for comparison.

5. DISPERSION MEASUREMENTS

5.1 Laboratory Experiments

Studies of dispersion were carried out in the laboratory using both column and sandbox experiments. The sand sample for the column experiment was obtained from a depth of 2.6 m at the field site using the cohesionless soil sampler. The sample had a length of 30.5 cm and a diameter of 4.5 cm and was relatively undisturbed.
Both tritium and the tracer used in the field two-well tracer test, $^{51}$Cr-EDTA, were used as tracers in the column test to assess the suitability of $^{51}$Cr-EDTA as a groundwater tracer by comparing its transport with that of tritium. A detailed evaluation of $^{51}$Cr-EDTA as a tracer for groundwater flow is reported by Knutsson and Forsberg [23]. For a wide range of soil types and using tritium as a reference tracer they found $^{51}$Cr-EDTA at concentrations down to 0.001 ppm to be neither adsorbed nor considerably retarded by primary minerals such as quartz, feldspars, some micas and calcite; but some ferro-magnesium silicates, other iron-bearing minerals, and clays had a considerable effect upon $^{51}$Cr-EDTA. For our column test, the flow rate was chosen to give an average porewater velocity of 2 cm/h which is of the same order of magnitude as the groundwater velocities expected in the two-well field tracer test. Groundwater taken from a piezometer at the field site was passed through the soil column for several hours prior to introducing the tracer solution. Hourly samples were taken during the column tracer test using a fraction collector. The activity of $^{51}$Cr was measured using a well-type NaI scintillation counter and the tritium activity by using a liquid scintillation counter. The results of the column test are given in Figure 5. The breakthrough curves for the two tracers were essentially identical, indicating that $^{51}$Cr-EDTA was an acceptable tracer in the geologic and groundwater environment chosen for the two-well tracer test.
The breakthrough curves for the tracers in the column experiment were analyzed to obtain estimates of dispersivity for the sand sample according to the procedure described by Lai and Jurinak [4]. The relation used for estimating dispersivity is:

$$\alpha = \frac{L}{4\pi \frac{V_o}{S_o} d^2}$$  \hspace{1cm} (4)

where $\alpha$ is the dispersivity, $L$ is the length of the column, $V_o$ is the effluent volume at the relative concentration of $C/C_o = 0.5$ ($C_o$ is the input concentration) and $S_o$ is the slope of the breakthrough curve at $C/C_o = 0.5$. The value of dispersivity obtained was approximately 1 cm, which is near the upper limit of the range normally reported for column tests on homogeneous granular materials.

Sandbox experiments were carried out to illustrate qualitatively the movement of a tracer during a two-well withdrawal-injection tracer test. The sandbox was constructed of methyl methacrylate plastic and had dimensions 90 cm x 30 cm x 6 cm deep. Small wells were located in the box with injection ports for introducing the tracer. Sandbox experiments were useful both for illustrative purposes and for aiding in the design of field experiments. Further sandbox experiments are being conducted to determine quantitatively the effect of geologic heterogeneities on dispersion.

5.2 Field Tracer Test

5.2.1 Field procedure

A two-well withdrawal-injection tracer test was conducted using the instrumentation shown in Figure 2. Water was withdrawn from one well and recharged in the other well at a rate of 27 l/min. The withdrawal and injection system was in operation for several days prior to introducing the tracer to produce a steady-state flow field. The piezometer network was monitored daily to establish the hydraulic head distribution during the test. Approximately 100 mCi (3.7 GBq) of the tracer, $^{51}$Cr-EDTA, were added to the injection water at a continuous rate over a period of 3.2 days. The concentration input history of $^{51}$Cr-EDTA from samples taken from the injection well is shown in Figure 6. The input concentration was maintained at about 57 cpm/µl during the 3.2 days of tracer addition.
Recirculation of tracer in the pumping water occurred after about 3 days. The tracer test was continued for 15 days with monitoring of the $^{51}$Cr-EDTA concentration in the injection well, withdrawal well and multi-level sampler sampling tubes. All sample activities were corrected for radioactive decay to the time at which the tracer test was started.

The concentration profiles for the multi-level sampler midway between the two wells are illustrated in Figure 7. The stratigraphy at the site is shown on the left, the hatched area indicates the screened interval of the wells and the x's indicate the depths of the sampling points in the multi-level sampler. The profiles were generated by plotting the counting rate of the water taken from the sampling points versus their depth below ground surface. The tracer moved most rapidly at the 7.5 m depth and slowest at the 3.5 m depth. This figure illustrates the great detail possible in monitoring the movement of a tracer using this sampler. This type of monitoring device has great potential for tracing contaminant movement in groundwater flow systems.

The relative velocity distribution throughout the depth of the aquifer was determined by analyzing the concentrations profiles from the five multi-level samplers located directly between the two wells. The results (Fig. 8) show reasonable agreement with the results obtained using the point dilution technique (Fig. 4). This confirms the validity of the point dilution results and indicates the potential of the point dilution technique in identifying zones of high transport in a groundwater flow system.
FIG. 8. Relative velocity distribution in the aquifer determined from network of multi-level samplers.

5.2.2 Analysis using two-well model

Field dispersivity values were obtained from the results of the two-well withdrawal-injection tracer test using the method described by Grove and Beech [24]. The assumptions for the method include the following:

1. the aquifer is horizontal and confined,
2. the flow field from the withdrawal-injection scheme is in steady-state,
3. the natural areal groundwater velocity is small compared to the velocities induced by the withdrawal-injection system,
(4) the tracer is added to the injection well as a square-wave pulse,

(5) the tracer travels evenly over the entire vertical thickness of the aquifer, and

(6) the flow regime is sufficiently simple so that the flow field can be divided into a series of crescentic flow tubes that approximate dispersion columns of known length from the injection to the withdrawal well along which the tracer is assumed to pass.

The breakthrough curve concentration profiles, generated using an analytical solution for the convective-dispersive transport of the tracer with an assumed value of dispersivity, from each arc or flow column are summed to produce a composite breakthrough curve at the withdrawal well for the entire flow field. Various values for dispersivity are used as input in the computer model until the calculated composite breakthrough curve closely matches the experimental one measured in the field. Tracer material passing through the withdrawal well and continuously returned to the injection well is accounted for in the calculation procedure. The computer model is listed in the report by Grove [25].

In the two-well tracer test conducted in this study the following assumptions have been satisfied: the aquifer is horizontal and confined; a constant withdrawal-injection rate was used; the natural areal groundwater velocity is low; and the tracer was added continuously for a set time period. Results from the network of multi-level point samplers showed that the tracer movement was uniform at any particular depth and hence that the aquifer was homogeneous areally. The concentration profiles for the multi-level sampler midway between the two wells (Fig. 7) indicate that even though the aquifer appears to be homogeneous vertically on the basis of visual inspection of core samples, the tracer did not travel evenly throughout the vertical thickness of the aquifer. It is well known that satisfying the assumption of aquifer homogeneity is impossible in any natural geologic environment. The data from this test enabled the effect of minor stratigraphic heterogeneities to be evaluated in terms of their influence on the dispersivity determinations.

The initial breakthrough of the $^{51}$Cr-EDTA in the withdrawal well occurred about 3 days after the start of introduction of the tracer. The peak concentration was reached at about 7 days. The results of the two-well model analysis are given in Figure 9. This compares the $^{51}$Cr-EDTA breakthrough curve obtained by measuring samples from the withdrawal well
FIG. 9. $^{81}$Cr-EDTA breakthrough curve at withdrawal well for field measurements and two-well model.

to the breakthrough curve generated by the computer model using a dispersivity of 50 cm. This dispersivity produced a breakthrough curve that most closely matched the field data.

5.2.3 Analysis using finite-element model

A computer model based on the finite-element method was used to simulate in a horizontal plane the movement of the tracer in the two-well tracer test. The model used is a modified version of that described by Pickens and Lennox [26] for computer simulation of solute transport in cross-section, through a steady-state saturated groundwater flow systems.

In this analysis, a horizontal slice at any specified depth in the aquifer was assumed to be homogeneous and isotropic. The differential equation describing the areal steady-state distribution of hydraulic head in this case is Laplace's equation written:

$$\frac{\partial^2 h}{\partial x^2} + \frac{\partial^2 h}{\partial y^2} = 0$$  \hspace{1cm} (5)

where $h$ is hydraulic head, and $x$ and $y$ are the Cartesian directions in the horizontal plane. The groundwater velocities were calculated using Equations (1) and (2).
The two-dimensional form of the differential equation describing the convection and dispersion of a conservative solute in a steady-state saturated flow regime is written:

\[
\frac{\partial}{\partial x} \left( \frac{D_{xx}}{\partial x} \frac{\partial C}{\partial x} + \frac{D_{xy}}{\partial y} \frac{\partial C}{\partial y} \right) + \frac{\partial}{\partial y} \left( \frac{D_{yx}}{\partial x} \frac{\partial C}{\partial x} + \frac{D_{yy}}{\partial y} \frac{\partial C}{\partial y} \right) \\
- V_x \frac{\partial C}{\partial x} - V_y \frac{\partial C}{\partial y} = \frac{\partial C}{\partial t}
\]  

(6)

where \(V_x\) and \(V_y\) are the groundwater velocities in the \(x\) and \(y\) directions; \(D_{xx}, D_{xy}, D_{yx}\) and \(D_{yy}\) are the coefficients of hydrodynamic dispersion; \(C\) is the concentration of material in solution; and \(t\) is time. The coefficients of hydrodynamic dispersion are defined [27] by:

\[
D_{xx} = D_L \frac{V_x}{V} + D_T \frac{V_y}{V} + D_d T
\]  

(7a)

\[
D_{yy} = D_T \frac{V_x}{V} + D_L \frac{V_y}{V} + D_d T
\]  

(7b)

\[
D_{xy} = D_{yx} = \left( \frac{D_L}{D_T} - D_L \right) \frac{V_x}{V} \frac{V_y}{V}
\]  

(7c)

\[
D_L = \alpha_L V
\]  

(7d)

\[
D_T = \alpha_T V
\]  

(7e)

where \(D_L\) and \(\alpha_L\) are the longitudinal dispersion coefficient and longitudinal dispersivity respectively in the direction of flow, \(D_T\) and \(\alpha_T\) are the lateral dispersion coefficient and transverse dispersivity respectively normal to the direction of flow, \(V\) is the resultant groundwater velocity, \(D_d\) is the molecular diffusion coefficient in a water solution, and \(T\) is the tortuosity of the porous media. In this study, the contribution of molecular diffusion to the hydrodynamic dispersion coefficients has been neglected because it is insignificant relative to the convection-dependent component of dispersion.
FIG. 10. Finite element discretization used to analyze tracer movement in the horizontal plane.

FIG. 11. Equipotential and flow lines for withdrawal-injection flow field from finite element model.

The finite element method using a Galerkin technique [26] was used to formulate the preceding equations and solve for the hydraulic head distribution, groundwater velocities and transient concentration distribution during the two-well test. Figure 10 shows the finite element grid that was used in the horizontal-plane analysis. P and I denote the location of the withdrawal and injection wells respectively. Because the flow field is a mirror image about a line drawn through the two wells, only half of the system was considered in the analysis. The equipotential and flow lines for the two-well system as determined by the model are shown in Figure 11. The calculated hydraulic head distribution was consistent with the measured values from the piezometer network.
FIG. 12. Concentration profiles between the two wells at 8.1 m depth showing field and model results.

FIG. 13. Concentration distribution at 8.1 m depth showing field and model results.
The concentration data from the network of multi-level samplers indicated that the tracer movement was essentially horizontal at all levels in the aquifer. For simulation of the movement of the $^{60}$Cr-EDTA, a horizontal slice at depth 8.1 m was chosen. This slice is representative of the zone of most rapid tracer movement. Figure 12 shows the concentration profiles directly between the two wells at this depth. Using a longitudinal dispersivity of 10 cm in the finite element model yields a closer agreement of model concentration values to the field values than using 50 cm, which was the value obtained with the two-well model. Further simulations are being conducted using other dispersivity values. It is expected that closer agreement between model and field results will be obtained using a dispersivity somewhat lower than 10 cm. In Figure 13, areal concentration contours from values calculated using the finite element model are compared with the field values for a time of 4 days from the beginning of the tracer test. Moderately good agreement was obtained by using a longitudinal dispersivity of 10 cm.

5.3 Discussion of Dispersivity Results

The dispersivity value computed by a one-dimensional analysis of data from the laboratory column test on an undisturbed sample from the aquifer is 1 cm. The horizontal plane analysis of the concentration variations using the finite element transport model produced a value of approximately 10 cm. The dispersivity analysis using only concentration data from the withdrawal well in conjunction with the analysis procedure developed by Grove and Beetem [24] gave a dispersivity value of 50 cm. The range in dispersivities obtained from these three methods is therefore one and a half orders of magnitude. All of the values are below the range normally reported for field-scale dispersion in granular aquifers.

The two-well dispersivity value is much larger than the values from the other two methods because it includes the effects of concentration dilution produced by sampling the withdrawal well. The well concentrations represent mixtures from the various transport zones within the aquifer. The point dilution tests and concentration profiles from the multi-level point samplers indicate that the tracer was transported at significantly different rates at different depths as a result of minor geologic stratification. This occurred, even though the aquifer appeared on the basis of drill logs to be relatively homogeneous both vertically and areally. The dispersivity obtained from the withdrawal well analysis should be regarded as representing only an apparent dispersivity that is dependent primarily on the sampling device (i.e. well screen interval). It is not unreasonable to expect that many of the
large values of dispersivity from two-well tests reported in the literature represent an apparent dispersivity.

The dispersivity value obtained from horizontal-plane analysis of data from the multi-level point samplers in the zone of most rapid transport indicates that this transport zone in the aquifer is only weakly dispersive. The most important effect of heterogeneities in the aquifer, which apparently occur in the form of slight stratification or lensing, is to cause channeling of the tracer through the most permeable zones at velocities that exceed the average velocity in the aquifer by a factor of 2 and exceed the minimum velocity in the aquifer by a factor of 5. In terms of the two physical transport parameters, groundwater velocity and dispersivity, the velocity is the one of major importance in this aquifer system at the time and space scales used in these studies.

6. CONCLUSIONS

The following conclusions have been developed from the results obtained from the laboratory and field investigations:

(1) Hydraulic conductivity values obtained from single-piezometer response tests, a pumping test, point dilution tests, and a two-well withdrawal-injection tracer test were all within a factor of 5 of one another. Uncertainty of this magnitude or larger is typical of sandy deposits and must be considered when predicting contaminant migration in groundwater flow systems.

(2) The detailed field tracer experiment indicates that the multi-level point sampling device used in this investigation is an efficient and relatively inexpensive means of monitoring the migration of tracers or contaminants in shallow granular aquifers.

(3) The point dilution technique is an efficient and reliable method for identifying high transport zones within the aquifer.

(4) The horizontal-plane analysis of the two-well withdrawal-injection tracer test using tracer concentration data from the multi-level point sampler network indicates that the aquifer zone studied here has a relatively small dispersivity of 10 cm. In this aquifer, at the time and space scales considered, dispersion is not a major transport process.
(5) A dispersivity of 50 cm was obtained using the usual method for field determination of dispersivity from analysis of the breakthrough curve for the withdrawal well in the two-well withdrawal-injection test. This value of dispersivity is likely an apparent dispersivity obtained as a result of the water samples taken from the extraction well being an integrated mixture of the water flowing into the well over the entire aquifer thickness.

ACKNOWLEDGEMENTS

The results presented in this paper represent a joint research project involving Environmental Research Branch of Chalk River Nuclear Laboratories, Hydrology Research Division of Environment Canada and Department of Earth Sciences at the University of Waterloo. The authors appreciate the assistance of B.A. Risto, K.J. Inch, R.E. Jackson, G.E. Grisak, R.W. Gillham and E.A. Sudicky in various aspects of the experiments and the analysis. Financial support has been provided through Atomic Energy of Canada Limited, Environment Canada and National Research Council of Canada Grant No. A8184.

REFERENCES


APPLICATION OF SINGLE BOREHOLE TECHNIQUES

A study of groundwater flow in the vicinity of a water works drawing bank filtrate on the Lower Rhine

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Abstract

APPLICATION OF SINGLE BOREHOLE TECHNIQUES: A STUDY OF GROUNDWATER FLOW IN THE VICINITY OF A WATER WORKS DRAWING BANK FILTRATE ON THE LOWER RHINE.

For the last decade, single borehole techniques have been extensively and reliably used for various groundwater investigations. The present study demonstrates their applicability and usefulness. By a combined approach using single borehole and environmental isotope techniques, the flow pattern at the site of a group of wells tapping bank filtrate from the Rhine has been investigated. It was possible to gather data on the residence time of the pumped water in the underground as well as in its pathways under different boundary conditions.

1. Introduction

For the last decade, single borehole techniques using radioactive tracers to measure the filtration velocity and flow direction, as well as the vertical flow distribution in a boring, have been used increasingly for successful investigations into groundwater problems. The results provided a valuable insight into potential groundwater yield, the origin of the groundwater, its flow pattern, groundwater pollution risks, and the establishment of protection zones for groundwater production installations. The application of these techniques has shown that in many cases they not only confirm the results obtained by classical hydrological methods, but they provide additional information which often demands a change in the original conception and design of a project.

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The problems of the protection of the groundwater environment are essentially problems of prediction. In their solution, single borehole techniques have been proved quite reliable for the evaluation of the groundwater regime under natural conditions. By direct measurements during short-term campaigns, they have provided indispensable experimental data which are of vital importance for the approach of the system by numerical mathematical models.

Investigations of this kind have been performed before the establishment of potential waste disposal facilities so that through an assessment of the groundwater flow pattern the potential extent of pollutants released in spite of all safeguards to the underground could be determined. For example, at the site of a nuclear power plant, it could be shown that contrary to the findings of drilling two groundwater storeys of different permeability exist in an approximately 10 m thick gravel aquifer of which only the upper one will drain pollutants [1].

At the downstream site of landfills, single borehole investigations have been promising in in situ determinations of groundwater flow vectors, the changes of natural flow patterns at various scales in a given aquifer for better understanding of the processes of deterioration and recovery of groundwater quality. They have been proved of useful value in calibrating the extent of leachate dilution by unpolluted groundwater [1, 2, 3].

Groundwater protection zones are established to prevent pollution reaching drinking water supply wells in harmful concentrations. Their proper evaluation was, in the past, frequently the aim of the application of single borehole techniques. In particular, the investigation of a vertical flow profile in a well during pumping has called for reconsiderations of the protection zone estimated by means of drilling results [1].

The increasing trend in the pollution of surface water has consequently affected well galleries which tap bank filtrate. Single borehole techniques have been applied to investigate the residence time in the underground as well as to determine the proportion of bank filtrate in addition to locally recharged groundwater. The results have been quite valuable in particular if a combined approach by environmental isotope techniques was undertaken [1, 2, 4].

The present paper demonstrates the use of single borehole techniques as well as the determination of isotopes of water molecules to investigate problems of bank filtrate at a well gallery at the Lower Rhine near Cologne (P.R.G.). At a loop of the Rhine there is located a group of twelve pumped wells, which curve in a westerly/south-easterly direction at a distance of 600 m from the bank of the river (Fig. 1). These wells have now been used for about ten years to draw water from the approximately 20 m thick low-terrace gravels in order to provide a drinking water supply. The effects of the organic and inorganic loading of the Rhine on the quality of the drawn water have been studied by Eussenaur [5]. An attempt made successfully at other water works drawing bank filtrate to reach conclusions regarding the pathways and residence time in the subsoil on the basis of the variation over time in the quality of the water in the river and in the pumped wells failed in the given case because the wells were too far away from the bank of the river. Accordingly, the problem faced was to determine the groundwater flow
conditions by isotope techniques, using the existing network of gauges in the area under study, and to derive therefrom data on the contribution made by the bank filtrate to the pumped water and on the residence time of groundwater from the Rhine to the wells.

2. Measuring techniques

In the studies, use was made of single-well methods as well as of deuterium and tritium analyses of water samples.

The single-well techniques are used to determine the filtration velocity \( v_f \) (Darcy's velocity, specific discharge), the flow direction \( \theta_f \), and the vertical movement of the groundwater [see, for example, 2, 6]. The filtration velocity is equal to the groundwater discharge \( Q \) moving through the cross-sectional area \( F \) in the aquifer.

\[
Q = v_f \cdot F
\]
Further it is proportional to the distance velocity $v$

$$v_f = v \cdot n_e$$  \hspace{1cm} (2)

where $n_e$ is the effective porosity. For the calculation use was made, in addition, of Darcy's law:

$$v_f = k \cdot J$$  \hspace{1cm} (3)

which relates the filtration velocity to the hydraulic gradient $J$ and the permeability coefficient $k$.

The deuterium and tritium contents were measured in the normal manner and are given in the internationally accepted units ($^\delta$D-value, referred to the SNOW Standard, and tritium unit (T.U.), corresponding to 3.2 pCi/litre (see [6]). To take water samples from the observation wells use was made of devices permitting sampling at set levels.

3. **Measurements**

Five series of measurements were made at different river water levels and at varying pumping rates, in gauges 484, 485, 486, 437, 435, 483 and 471 (Fig. 1):

- First series of measurements \hspace{1cm} 13 - 21 June 1973
- Second " " \hspace{1cm} 7 - 15 November 1973
- Third " " \hspace{1cm} 19 - 29 November 1973
- Fourth " " \hspace{1cm} 9 - 17 July 1974
- Fifth " " \hspace{1cm} 25 Nov. - 2 Dec. 1974

The single-well measurements were carried out at vertical distances of between 2 and 4 m in gauges developed all the way down with filter tubes and filter packs, and passing right through the approximately 20 m thick gravel and sand of the low terrace. To check the environmental isotope contents, three water samples were taken during each series of measurements, in each gauge below groundwater table, midway between groundwater table and bed, and just above the confined bed. Although the pumping rate was kept generally constant during each series of measurements, fluctuations in the water level of the Rhine during individual series could not be ruled out. More especially, measurements of the third and fifth series were adversely affected by transient highwater conditions.

4. **Measurement results and discussions**

4.1 **Presentation of results**

The results of the measurements made in the isotope hydrology studies are shown in Tables I - III and in Figs 2 - 6.
TABLE I(a). SUMMARY OF THE RESULTS OF FIVE SERIES OF MEASUREMENTS TO DETERMINE THE FILTRATION VELOCITY \( v_f \) OF GROUNDWATER IN A WATER CATCHMENT AREA DRAWING BANK FILTRATE IN THE LOWER RHINE (see Fig.1)

<table>
<thead>
<tr>
<th>Measurement series No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean pumping rate</td>
<td>-35</td>
<td>-27</td>
<td>-53</td>
<td>-49</td>
<td>-49</td>
</tr>
<tr>
<td>during measurement</td>
<td>(10^{-3}) m(^2)/d</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean river water</td>
<td>-37.5</td>
<td>-37</td>
<td>-37.5</td>
<td>-38.5</td>
<td>-39.5</td>
</tr>
<tr>
<td>level in m a.s.l.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Cologne gauge)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>during measurements</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Gauge No.</th>
<th>Mean ( \bar{v}_f ) (m/d) of values determined in each gauge</th>
</tr>
</thead>
<tbody>
<tr>
<td>484</td>
<td>3.1 3.8 7.1 3.7 3.8</td>
</tr>
<tr>
<td>485</td>
<td>1.5 1.4 3.0 1.9 1.9</td>
</tr>
<tr>
<td>486</td>
<td>0.3 0.5 0.8 0.2 0.4</td>
</tr>
<tr>
<td>437</td>
<td>5.5 2.7 7.6 10.8 3.5</td>
</tr>
<tr>
<td>435</td>
<td>1.9 2.6 6.4 4.8 5.4</td>
</tr>
<tr>
<td>483</td>
<td>2.2 0.8 6.8 1.9 1.9</td>
</tr>
<tr>
<td>471</td>
<td>1.6 1.7 4.4 2.5 2.2</td>
</tr>
</tbody>
</table>

Fig. 2 shows, as an illustration, the filtration velocity vectors obtained from two measurement series in relation to the general layout of the gauges.

Table I(a) summarises the mean values \( \bar{v}_f \) of the filtration velocities obtained per gauge and measurement series.
TABLE I(b). SUMMARY OF THE RESULTS OF FIVE SERIES OF MEASUREMENTS TO DETERMINE THE GROUNDWATER FILTRATION VELOCITY $v_f$ AND DIRECTION OF FLOW OF RI IN GAUGES 484, 485, 486, 437, 435, 483 AND 471 (see Fig. 1).

The mean $v_f$ (m/d) of the individual filtration velocity values $v_i$ in the vicinity $h$ (m) of the gauge (N...E) with approximately the same direction of groundwater flow Ri, and the derived products $v_f \cdot h$ (m$^2$/d).

<table>
<thead>
<tr>
<th>Measurement series No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>Direction towards wells (N...E)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R$_i$ (N...E) (m/d) (m$^2$/d)</td>
<td>$v_f$ (N...E) (m/d) (m$^2$/d)</td>
<td>$v_f \cdot h$ (N...E) (m/d) (m$^2$/d)</td>
<td>$v_f$ (N...E) (m/d) (m$^2$/d)</td>
<td>$v_f \cdot h$ (N...E) (m/d) (m$^2$/d)</td>
<td></td>
</tr>
<tr>
<td>484</td>
<td>340, 3.1</td>
<td>62</td>
<td>340, 3.1</td>
<td>350</td>
<td>3.8</td>
<td>76</td>
</tr>
<tr>
<td>485</td>
<td>340, 1.5</td>
<td>30</td>
<td>340, 1.5</td>
<td>30</td>
<td>1.4</td>
<td>28</td>
</tr>
<tr>
<td>486</td>
<td>340, 0.3</td>
<td>54</td>
<td>340, 0.3</td>
<td>300</td>
<td>0.5</td>
<td>5</td>
</tr>
<tr>
<td>437</td>
<td>60, 5.4</td>
<td>100</td>
<td>60, 5.4</td>
<td>340</td>
<td>2.4</td>
<td>31</td>
</tr>
<tr>
<td>435</td>
<td>40, 1.9</td>
<td>35</td>
<td>40, 1.9</td>
<td>300</td>
<td>1.9</td>
<td>8</td>
</tr>
<tr>
<td>483</td>
<td>160, 0.7</td>
<td>2</td>
<td>160, 0.7</td>
<td>270</td>
<td>0.4</td>
<td>2.6</td>
</tr>
<tr>
<td>471</td>
<td>30, 1.6</td>
<td>23</td>
<td>30, 1.6</td>
<td>270</td>
<td>1.6</td>
<td>11</td>
</tr>
</tbody>
</table>
TABLE II. RESULTS OF FIVE SERIES OF MEASUREMENTS TO DETERMINE THE DEUTERIUM CONTENT $\delta^D$ IN GROUNDWATER SAMPLES FROM GAUGES 484, 485, 486, 437, 435, 483 AND 471 AND IN THE RHINE

The $\delta^D$ values refer to the given sampling depths in the gauges; $\delta^D$ is the mean of the individual measurements. The samples for the additional measurements 1(a) were pumped out on 4 October 1973.

<table>
<thead>
<tr>
<th>Measurement series No.</th>
<th>1</th>
<th>1a</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gauge No.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sampling depth (m)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>435</td>
<td>-66.0 &amp; -66.6</td>
<td>-72.2 &amp; -74.6</td>
<td>-73.1 &amp; -73.2</td>
<td>-66.9 &amp; -70.5</td>
<td>-69.8 &amp; -70.2</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>-66.3 &amp; -67.2</td>
<td>-73.9 &amp; -73.9</td>
<td>-73.3 &amp; -73.2</td>
<td>-71.8 &amp; -71.8</td>
<td>-67.4 &amp; -67.3</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>-70.9 &amp; -72.2</td>
<td>-72.6 &amp; -72.6</td>
<td>-72.0 &amp; -72.0</td>
<td>-71.8 &amp; -71.7</td>
<td>-71.8 &amp; -71.7</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>-65.1 &amp; -65.1</td>
<td>-64.3 &amp; -64.3</td>
<td>-64.0 &amp; -64.0</td>
<td>-64.6 &amp; -64.6</td>
<td>-64.4 &amp; -64.4</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>-65.9 &amp; -65.9</td>
<td>-64.7 &amp; -64.7</td>
<td>-64.6 &amp; -64.6</td>
<td>-66.4 &amp; -66.4</td>
<td>-67.2 &amp; -67.2</td>
<td></td>
</tr>
<tr>
<td>471</td>
<td>-64.1 &amp; -64.1</td>
<td>-66.8 &amp; -66.8</td>
<td>-66.9 &amp; -66.9</td>
<td>-70.0 &amp; -70.0</td>
<td>-69.7 &amp; -69.7</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>-64.6 &amp; -64.6</td>
<td>-64.7 &amp; -64.7</td>
<td>-64.6 &amp; -64.6</td>
<td>-69.7 &amp; -69.7</td>
<td>-69.7 &amp; -69.7</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>-66.9 &amp; -66.9</td>
<td>-66.8 &amp; -66.8</td>
<td>-66.9 &amp; -66.9</td>
<td>-70.0 &amp; -70.0</td>
<td>-69.7 &amp; -69.7</td>
<td></td>
</tr>
<tr>
<td>484</td>
<td>-63.0 &amp; -63.0</td>
<td>-66.6 &amp; -66.6</td>
<td>-67.0 &amp; -67.0</td>
<td>-67.9 &amp; -67.9</td>
<td>-68.2 &amp; -68.2</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>-63.1 &amp; -63.1</td>
<td>-66.0 &amp; -66.0</td>
<td>-65.7 &amp; -65.7</td>
<td>-67.5 &amp; -67.5</td>
<td>-68.0 &amp; -68.0</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>-63.2 &amp; -63.2</td>
<td>-66.0 &amp; -66.0</td>
<td>-65.7 &amp; -65.7</td>
<td>-67.5 &amp; -67.5</td>
<td>-68.0 &amp; -68.0</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>-63.2 &amp; -63.2</td>
<td>-66.0 &amp; -66.0</td>
<td>-65.7 &amp; -65.7</td>
<td>-67.5 &amp; -67.5</td>
<td>-68.0 &amp; -68.0</td>
<td></td>
</tr>
<tr>
<td>485</td>
<td>-65.3 &amp; -65.3</td>
<td>-66.5 &amp; -66.5</td>
<td>-65.5 &amp; -65.5</td>
<td>-65.1 &amp; -65.1</td>
<td>-65.0 &amp; -65.0</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>-65.4 &amp; -65.4</td>
<td>-66.0 &amp; -66.0</td>
<td>-65.4 &amp; -65.4</td>
<td>-65.1 &amp; -65.1</td>
<td>-65.0 &amp; -65.0</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>-65.7 &amp; -65.7</td>
<td>-69.9 &amp; -69.9</td>
<td>-70.6 &amp; -70.6</td>
<td>-69.8 &amp; -69.8</td>
<td>-68.0 &amp; -68.0</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>-65.7 &amp; -65.7</td>
<td>-69.9 &amp; -69.9</td>
<td>-70.6 &amp; -70.6</td>
<td>-69.8 &amp; -69.8</td>
<td>-68.0 &amp; -68.0</td>
<td></td>
</tr>
<tr>
<td>Rhine</td>
<td>-67.1 &amp; -67.1</td>
<td>-72.3 &amp; -72.3</td>
<td>-70.8 &amp; -70.8</td>
<td>-75.7 &amp; -75.7</td>
<td>-66.8 &amp; -66.8</td>
<td></td>
</tr>
</tbody>
</table>
TABLE III. RESULTS OF MEASUREMENT OF TRITIUM CONCENTRATION IN THE RHINE AND IN GROUNDWATER SAMPLES FROM PUMPED WELLS 2, 6 AND 8 (first series of measurement).

<table>
<thead>
<tr>
<th>Sampling point</th>
<th>Tritium concentration (T.U.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Well 2</td>
<td>142 ± 12</td>
</tr>
<tr>
<td>Well 6</td>
<td>136 ± 12</td>
</tr>
<tr>
<td>Well 8</td>
<td>145 ± 12</td>
</tr>
<tr>
<td>Rhine</td>
<td>175 ± 12</td>
</tr>
</tbody>
</table>

Table I (b) gives the mean filtration velocities \( v \), for the depths \( h \) of the gauges with approximately equal direction of groundwater flow, and the product \( v_p \cdot h \). This product \( v_p \cdot h \) is a measure of the groundwater discharge in the given direction of flow \( R_i \).

Figs 1–4 are plots showing the filtration velocities obtained for each measurement series as a vertical profile for most of the gauges. An attempt was also made in the case of some of the gauges to indicate the dependence of the mean filtration velocities \( v_p \) or flow contribution \( v_p \cdot h \) in the direction of the wells on the water level of the Rhine and the pumping rate.

Table II as well as Figs 5 and 6 summarise the results of the deuterium measurements in the five series, together with those of an additional sampling made on 4 October 1973 [Series 1(a)]. Table III gives the tritium concentrations in samples of water from the first series of measurements.

### 4.2 Results of single-well measurements

(a) Southern gauges 484, 485, 486 (Figs 2 and 3)

In the vicinity of gauges 484 and 485, the groundwater flows over its entire thickness towards the wells during all five series of measurements. The value \( v_p \) obtained from the two gauges increases with the pumping rate, and decreases as the level of the river rises. In gauge 484, about 300 m from the pumped wells, the mean filtration velocity is generally twice as
FIG. 2. Filtration velocity vectors determined during measurement series No. 2 (above) and No. 5 (below) as illustrations of the single-well method of measurement in a drinking water supply area on the Lower Rhine. (For pumping rate and river water level, see Table I(a).)
FIG. 3. Results of five series of single-well measurements in gauges 484, 485 and 486 (Fig. 1). Gwsp = groundwater table;
(a) Filtration velocities $v_1$ for the individual measurements series at various depths;
(b) Dependence of the mean filtration velocity $\bar{v}_1$, calculated for each series of measurements from the individual $v_1$ values, on the pumping rate $Q$ of pumped wells at different river water levels (gauge 484);
(c) Dependence of $\bar{v}_1$ (see (b)) on the river water level for two different pumping rates (gauge 484).
high as in gauge 485, which lies about 700 m away from them. The filtration velocity profile in gauge 484 has a maximum at about 30 m a.s.l., given a water level in the Rhine of 38 m a.s.l., the former figure moving up to about 35 m a.s.l. as the level of the river rises. The filtration velocity profile in gauge 485 normally shows the highest $v_f$ above the confined bed between 20 and 26 m a.s.l. This maximum moves up to 30 m a.s.l. during the fifth series of measurements (at the higher Rhine level of about 40.5 m a.s.l.).

At gauge 486, the most southerly of the group at a distance of about 1000 m from the battery, the $v_f$ profile shows a maximum (at about 35 m a.s.l.) that does not shift in the course of the five series of measurements. The low filtration velocities may be due to anomalies in the hydraulic gradient; the measurements of the direction of groundwater flow show, in any case, that in the vicinity of this gauge the groundwater does not flow towards the wells in a uniform manner and that it even turns westwards over the entire groundwater thickness during the third measurement series (Table 1(b)).

(b) Eastern gauges 435 and 437 (Fig. 2)

In these gauges lying close to the river the flowlines formed, probably as a function of the gradient down to the river, are directed partly towards the Rhine and partly inland, and are also non-uniform in the vertical borehole profile (see Table 1(b) and Fig. 2). As compared to the individual measurements, there is here no reproducibility. Even the $v_f$ profiles for these gauges differ greatly in time, the $v_f$ maxima and minima shifting, as a result, from one series of measurements to another.

(c) Northern gauges 471 and 483 (Figs 2 and 4)

These two gauges appear to lie downstream from the cone of depression, since most of the flow direction measurements during low and medium Rhine levels show groundwater flow westwards or northwards in the natural direction of flow. It is only when the water level in the Rhine rises higher that the groundwater flows southwards towards the well battery with a maximum $v_f$ at 25-30 m a.s.l.

In the vicinity of gauge 483, the flow towards the wells, initiated when the river water level is > 38 m a.s.l., takes place only in the lower half of the aquifer. In the case of both gauges the groundwater flow towards the wells appears to decrease, irrespective of the well yield, when the river water level rises sharply (5th series).

4.3 Results of environmental isotope measurements

The environmental isotope measurements centred on $^6$D determinations as being more easy to execute than tritium measurements, which were abandoned after they showed only slight tritium differences in pumped water and Rhine
FIG. 4. Results of the five series of single-well measurements in gauges 483 and 471; Gwap = groundwater table;  
(a) Filtration velocity $v_t$ for the individual series of measurements at different depths;  
(b) Dependence of the filtration velocity $v_t$ averaged from the individual values in the direction of wells for each series of measurements,  
and the product $v_t \cdot h$ on the pumping rate $Q$ of the wells; $h$ is the vicinity of the gauge in which the groundwater flow is towards the wells;  
(c) Dependence of $v_t$ on the water level of the Rhine.
water during the first series of measurements. The value of the $\delta^D$ readings is limited, partly on account of the very long sampling intervals and the small number of samples. In addition, samples from the wells were in general not available due to lack of access to each single well. Furthermore, some $\delta^D$ values of about $-62\%$ below the water table of gauges 483 and 471 were apparently enriched by direct precipitation infiltration and therefore not utilizable. However, the results still make it possible to observe the following facts:

(a) The $\delta^D$ value increases when moving inland from the river, converging at about $-67\%$ near to the wells (Fig. 5). This may be explained by mixing of the river bank filtrate and natural groundwater while on the way towards the pumped wells. Considering that the $\delta^D$ value of natural groundwater is $-52\%$, it follows there is about $70\%$ of bank filtrate recharge.

(b) The amplitudes of the seasonal pattern in the $\delta^D$ values for the Rhine appear to be phase shifted by about half a year, as compared to those for groundwater in gauges 437 and 435 near the river bank, and also in gauge 486 (Fig. 6). This phase shift appears to increase in gauges 471, 483 and 485 lying nearer the wells. Gauge 484 shows no periodicity.

(c) The tritium values obtained for the three pumped wells 2, 6 and 8 are virtually the same (see Table III). This means that well 2 on the west side draws the same mixture of bank filtrate and natural groundwater as wells 6 and 8 lying in the centre.

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1 The hydrograph for $\delta^D$ values in the Rhine largely tallies with that for $\delta^{18}O$ measured by Mook [7] for the year 1968 in the Rhine at Mookingen (Netherlands).
4.4 Conclusions

In considering the results of both single well and environmental isotope measurements, the following conclusions can be drawn:

(a) From the south the wells receive an inflow of river bank filtrate in the direction of the undisturbed groundwater flow. The bank filtrate mixes with groundwater on its way to the wells. This inflow from the south increases with the pumping rate and decreases as the water level of the river rises (>38 m a.s.l.). As the river rises, the flow shifts towards the upper horizon of the aquifer.

In the vicinity of gauge 485, which lies at a mid-point between the wells and the river, the measured mean and maximum filtration velocities $v_f$ and $v_{f \text{ max}}$, together with an assumed porosity $n$, of 15%, gave the following distance velocities $v$ and flow times $t$ between the river and wells for the following three different boundary conditions:

1) $Q = 30 \cdot 10^3$ m$^3$/d, river water level < 38 m a.s.l.
   
   $v_f = 1.5$ m/d, $v = 10$ m/d, $t = 140$ d
   
   $v_{f \text{ max}} = 2.2$ m/d, $v_{\text{ max}} = 14.5$ m/d, $t_{\text{ min}} = 97$ d
\[ Q = 50 \cdot 10^3 \text{ m}^3/\text{d}, \text{ river water level } < 38 \text{ m a.s.l.} \]
\[ \bar{v}_f = 3 \text{ m/d}, \quad v = 20 \text{ m/d}, \quad t = 70 \text{ d} \]
\[ \bar{v}_f_{\text{max}} = 5 \text{ m/d}, \quad v_{\text{max}} = 33 \text{ m/d}, \quad t_{\text{min}} = 42 \text{ d} \]

\[ Q = 50 \cdot 10^3 \text{ m}^3/\text{d}, \text{ river water level } > 38 \text{ m a.s.l.} \]
\[ \bar{v}_f = 1.9 \text{ m/d}, \quad v = 13 \text{ m/d}, \quad t = 108 \text{ d} \]
\[ \bar{v}_f_{\text{max}} = 3.8 \text{ m/d}, \quad v_{\text{max}} = 25 \text{ m/d}, \quad t_{\text{min}} = 56 \text{ d} \]

It follows from the above that, given a normal pumping rate \((Q = 30 \cdot 10^3 \text{ m}^3/\text{d})\), a flow time of 50 d ("50-day limit") is considerably exceeded.

(b) To the north of the wells, a mixture of river bank filtrate and groundwater was likewise found in the vicinity of gauges 483 and 471. However, the bank filtrate flows towards the wells against the direction of the natural groundwater flow, only when the river water level is > 38 m a.s.l. This only happens, moreover, in the lower horizon of the aquifer and to an equal extent both for normal and high pumping rates. In the vicinity of gauge 483, which lies at a mid-point between the wells and the river, the filtration velocities measured give us the following distance velocities, \(v\), and flow times \(t\) between the river and the wells for \(Q = 50 \cdot 10^3 \text{ m}^3/\text{d}\) and a river water level > 38 m a.s.l.
\[ \bar{v}_f = 2.2 \text{ m/d}, \quad v = 15 \text{ m/d}, \quad t = 41 \text{ d} \]
\[ \bar{v}_f_{\text{max}} = 4.5 \text{ m/d}, \quad v_{\text{max}} = 30 \text{ m/d}, \quad t_{\text{min}} = 20 \text{ d} \]

These flow times lie partly below the "50-day limit", but are valid only for highwater conditions in the Rhine (>38 m a.s.l.) and high pumping rates. When the river level was less than 38 m a.s.l., no flow from the north towards the wells was found, even at a high well yield (50 \(\cdot\) 10^3 m^3/d).

(c) In the east of the area studied, in the vicinity of gauges 437 and 435, annual variations of the deuterium content of the groundwater, as compared to that of the river, indicate a travel time of about six months. Since, however, on the basis of the measured filtration velocities the distance velocities in the vicinity of these gauges are considerably greater than would correspond to this travel time and to the shortest distance to the river, it must be assumed that the catchment area for this groundwater lies likewise in the south of the area investigated. This indicates a high bank filtration for the southern area, that may be due to the fact that here the "impacted" bank (Praufer) is on the left; in the course of the loop in the river it changes over, opposite gauges 437 and 435, to the right-hand side.

The summary of the results indicates that the pumped wells draw to the major part Rhine bank filtrate basically from the south. The residence times between the river and the wells, given a normal well yield, generally lie above the "50-day limit". As the water level of the Rhine rises, the wells
also receive an inflow from the north, primarily in the lower layers of the aquifer, the flow of groundwater towards the wells in the south of the area studied shifting upwards at the same time. The velocity distribution in the vertical aquifer profile is not uniform. Hence to some extent the groundwater in the vicinity of the wells would seem not yet replaced by bank filtrate.

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