Zeitschrift:	Eclogae Geologicae Helvetiae
Herausgeber:	Schweizerische Geologische Gesellschaft
Band:	87 (1994)
Heft:	2: Pollution and pollutant transport in the geosphere, a major environmental issue : symposium held during the 173rd annual meeting of the Swiss Academy of Natural Sciences
Artikel:	Methodical approach for the detection of pesticides in groundwater : a Swiss example
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DOI:	https://doi.org/10.5169/seals-167462

Eclogae geol. Helv. 87/2:439–444 (1994)

0012-9402/94/020439-06 $1.50 + 0.20/0
Birkhäuser Verlag, Basel

Methodical approach for the detection of pesticides in groundwater: A Swiss example

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Key words: Groundwater, pollution, pesticides, methodology, detection of pollutants

ABSTRACT

A methodical approach for the detection of pesticides in porous aquifers is summarised and illustrated on the basis of a regional study. The process is mainly based on a sound knowledge of the three following elements: the hydrogeologic environment, data on the use of pesticide products and data on the behaviour of the pesticides in the soil and at deeper levels.

RESUME

Une méthodologie d'approche pour la détection de produits phytosanitaires dans les eaux souterraines d'aquifères meubles est résumée et illustrée à partir de l'exemple d'une étude régionale. Le procédé se base principalement sur une connaissance approfondie des trois éléments suivants: le milieu hydrogéologique, les données de l'utilisation des produits et, pour autant qu'elles soient disponibles, les données de comportement des substances phytosanitaires dans le sol et dans les niveaux plus profonds.

Introduction

In Switzerland an ever-growing number of pesticide residues are being detected in groundwaters. The latter constitute 80% of the drinking water supply (MICHEL & HARTMANN 1993), for the most part originating from porous aquifers. To date it has been possible to identify 22 pesticide substances and five decomposition products (KOZEL 1992).

A complete groundwater pollution monitoring on pesticide residues is extremely difficult, particularly for the following technical and financial reasons and due to the established regulations:

- the considerable number of pesticide substances used in various areas (in Switzerland approximately 300 substances) and the as yet unknown great number of decomposition products;
- the very heterogeneous chemical composition of the group of pesticides and their differing behaviour in the environment;
- the low concentration level accepted in drinking water (tolerated values in Switzerland: 0.1 μg/l per pesticide substance and 0.5 μg/l for the sum);
- the analytical difficulties of determining pesticide trace concentrations (μg/l to ng/l) and the high costs of these analyses;
- the lack of an appropriate method of detection and groundwater monitoring.

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Methods

To characterise the pesticide contamination status of an aquifer we have developed a hydrogeologic strategy based on our own field experiments, case studies and other bibliography (e.g. ARNETH et al. 1986; PARKER & FOSTER 1986; COHEN et al. 1987; LOCH & VERDAM 1989; PIONKE et al. 1988; EGGERS & WOLFF 1989). The approach, more widely covered in KOZEL (1992), is founded on a thorough study of the natural environment (aquifer), the anthropogeneous input (pesticide use) and the knowledge of the transport characteristics of these substances (pesticide behaviour).

We propose the following steps within the framework of our detection and monitoring strategy:

a. Collection of existing data about the study area (hydrology, hydrogeology, hydrochemistry, meteorology, etc.).
b. Evaluation of the aquifer vulnerability and risk assessment mapping (geometry and physiochemical characteristics of the soil, of the unsaturated zone and of the aquifer).
c. Installation of a groundwater observation network, adapted to the local hydrogeologic conditions.
d. Inventory of the pesticide use in agriculture (including crop rotation data) and if necessary in other domains (railways, roads, gardens, etc.) with the help of enquiries.
e. Determination of the hydrochemical composition of the groundwater (major parameters and indicators of inorganic and organic pollution).
f. Choice of pesticide substances to be considered for analysis (criteria: agricultural and other pesticide use; leaching properties, such as persistence and mobility; occurrence in other groundwaters; toxicity; availability of analytical techniques for the detection of trace residues, e.g. in ZULLEI-SEIBERT 1990).
g. Basic programme for pesticide analysis of groundwater (and soil) using analytical multiresidue techniques by high performance liquid chromatography (HPLC), gas chromatography (GC) and immunoassays.
h. Detailed programme for pesticide analysis and analysis of their most important decomposition products in groundwater, using all available analytical techniques (defined after the results of step g).
i. Appropriate interpretation and presentation of the results with respect to the detected pesticide trace concentrations.

The originality of the strategy is principally based on:

- the in-depth study of the hydrogeologic conditions (steps a and b). For example, the groundwater will only be analysed if major contact with an environment containing pesticides (e.g. high seepage rate, important river infiltration rate) is probable according to hydrogeologic information;
- the choice of pesticide substances to be analysed based on
  - agricultural and other pesticide using activities in the study area (step d);
  - the potential for leaching to groundwater at significant concentrations (estimation after list of risks in KOZEL 1992) (step f);
  - the analytical techniques available (step f).

Application of the method

A hydrogeologic project aimed at reviewing the wellhead protection zones of a pumping well supplying drinking water. Within this project it was possible to apply the proposed method. A detailed study of the consequences, particularly of agricultural activity on the groundwater quality could thus be carried out.

The pumping well, a collector well, with a maximum discharge of 12,000.00 l/min, is located in the quaternary sand an gravel aquifer of the 'Seeland' (40 km^2, North-West Switzerland). The study of existing data and recent hydrogeologic research (exploration drillings, tracer tests, pumping tests, etc.) indicate an average hydraulic conductivity of $3.0 \cdot 10^{-3}$ m/s with a considerable local heterogeneity ($1.1 \cdot 10^{-2}$ to $1.4 \cdot 10^{-5}$ m/s) and an aquifer thickness of 25 m. The recharge of the aquifer is of more than 75% due to the seepage of precipitation water (10 to 40% of 1,000 mm/year). The low permeability cover of the aquifer gravel is made up of silt and humus. This cover has an average thickness of 1.50 m, but is absent in some places. This characteristic, linked with a shallow grundwater table (~ 1 meter), makes the aquifer particularly vulnerable to any pollution from the surface.

An observation network for the groundwater (42 points) has been installed in the study area of 1.5 km^2 around the pumping well. This network consists of piezometers which are placed in the upper part of the saturated zone, with the addition of several double piezometers from which one is inserted at the top and one at the base of the groundwater.

The study area consists in its major part of land used for agriculture. The results of the enquiries carried out among the farmers, over a zone of some 290 ha, illustrate well the agricultural character of the region (Tab. 1). For each plot the following criteria were recorded: surface area, crop rotation, quantity of fertiliser used, pesticide substances and respective quantities used, plus dates of treatments.

Crops	Pasture	Nurseries, etc.	Non-agricultural	Total surface
149 ha	53 ha	18 ha	71 ha	291 ha
51.2%	18.2%	6.2%	24.4%	100%

Tab. 1. Land use in the study area.

Over two years no less than 88 pesticide products were used (42 herbicides, 30 fungicides and 16 insecticides) on the agricultural land of the study area to an extent of 2.5 kg/ha on average per year.

The high natural vulnerability of the aquifer, the hydrochemical data (spatial variations of the standard parameters such as nitrates, sulphates, etc.) and the agricultural data (massive use of pesticide products reaching 8 kg/ha/year) increased the likelihood of the presence of pesticides in the groundwater.

Results

A first programme for the simultaneous analysis of 17 active pesticide substances (comprising substances of different chemical groups as dithiocarbamates, phtalimides, organophosphors, pyrethrins, organochlorines and s-triazines) and of one decomposition product (ETU: ethylene-thio-urea, a direct decomposition product of dithiocarbamates) was established by using analytical multiresidue techniques (step g). The choice of the substances to be analysed, among the 300 pesticides admitted in Switzerland for agricultural use, was made by following step f mentioned above. The survey was in addition focused on substances used in a large area of nurseries, located in the contribution zone of the pumping well.

Samples were taken from 5 soil profiles and from 30 groundwater observation wells evenly distributed over the surface area and at regular intervals (5 times per year). This allowed us to detect the following substances in the groundwater (detection limits varied from 1 to 100 ng/l):

- a zone of contamination by the s-triazine herbicide simazine (up to 2.6 µg/l) – see example in Figure 1;
- 2 areas of contamination by the s-triazine herbicide atrazine (up to 2.8 µg/l);
- the presence of ETU (up to 0.9 µg/l);
- a very slight but detectable s-triazine content (simazine, atrazine, terbuthylazine) over the entire area of the studied site (≤ 30 ng/l).

The inventory of the annual agricultural use of these substances had provided the following results: simazine 1.9 kg; atrazine 21.3 kg; dithiocarbamates 100 kg (total surface 210 ha).

No significant contamination has been detected in the soil profiles.

As early as step g and subsequently (step h) the analytical programme was modified to confirm the first results mentioned above and to locate the origin of the pollutions with more accuracy by using a larger range of analysis methods: HPLC coupled with diode array detector (HPLC-DAD); GC coupled with nitrogen-phosphor selective detector (NPD), with electron capture detector (ECD) and with mass spectrometry (MS); enzyme immunoassays. In this way it was also possible to reveal the presence of some decomposition products from triazines, such as desethyl-atrazine and desisopropyl-atrazine. A comparison of the results from HPLC, GC and immunoassays revealed a very good concordance of these three methods for triazine analyses.

Finally we were able to attribute the simazine contamination to a single leak in a nursery area. The atrazine contaminations were the result of the use of this weed killer along roadsides. The presence of the dithiocarbamate decomposition product ETU can be explained by the massive use of dithiocarbamate fungicides in market gardens (see also LOCH & VERDAM 1989). Low triazine residues detected in the whole study area appear to be the result of the use of these herbicides in maize growing and in the urban zone (here not taken into consideration).

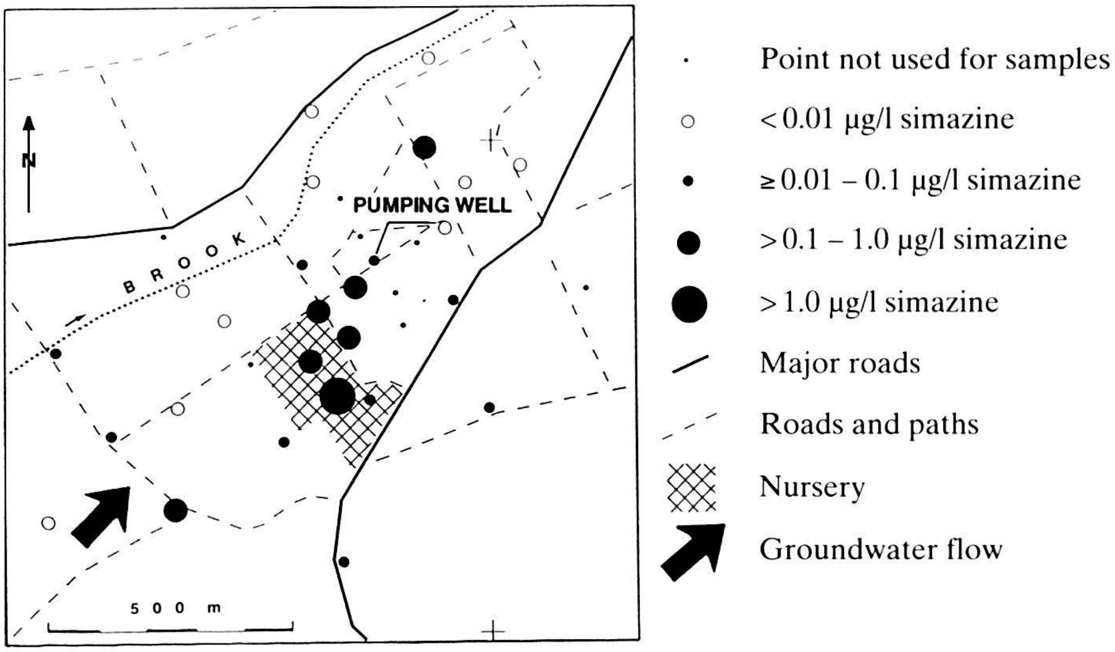

Fig. 1. Simazine content in the groundwater of the observed area in autumn 1987.

Conclusions

The application of the proposed steps for detection of pesticide residues in groundwater can, compared to routine sampling and analysis of general priority pollutants in production wells only, contribute to improve the knowledge about a detailed pesticide contamination status of a porous aquifer. The status deals with spatial variability and temporal evolution of the most probable pesticide contaminants based on the specific local conditions (land use, hydrogeology) around a groundwater production well. This allows an improved prospect of the onset or worsening of pesticide concentrations in a pumping well and can provide early warning of pollution even at reasonable costs. Specific hydrogeologic information, the careful targetting of the substances to be analysed and the use of analytical multiresidue detection techniques are the major elements of this strategy. The results of the study showed the consequences of pesticide use for the groundwater quality, depending on land use, on hydrogeologic conditions and on product behaviour. It was shown once more that s-triazines, due to their high mobility and persistence, represent the group of pesticides with the highest contaminant potential in groundwater. The results of the study also served as a basis for regulating the use of these pesticide products within newly delimited wellhead protection zones.

Acknowledgements

This work was made possible thanks to the financial and logistical support from the Seeländische Wasserversorgung Gemeindeverband, Worben, and the Swiss National Science Foundation (Project No. 20.5612.88) and the scientific advice of Prof. Burger, Neuchâtel.

This paper has already been presented as a poster at the colloquium 'Phyt'eau': Eau – Produits phytosanitaires – Usages Agricoles et Connexes' (Eau – Produits Phytosanitaires – Usages Agricoles et Connexes) in October 1992 in Versailles, France.

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Manuscript received January 16, 1994
Revision accepted April 5, 1994

Eclogae geol. Helv. 87/2: 445–449 (1994)

0012-9402/94/020445-05 $1.50 + 0.20/0
Birkhäuser Verlag, Basel

Natural radionuclides in drinking water as pollutants and as useful tracers

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Key words: Natural radionuclide, radiotoxicity, radon, natural tracer

ZUSAMMENFASSUNG

Einige, der im Trinkwasser auftretenden natürlichen Radionuklide haben Radiotoxizitäten, die mit denen der gefährlichsten künstlichen Alpha-Strahler vergleichbar sind. Mineralwässer, die sich im Handel befinden, können natürliche Radionuklide in solchen Konzentrationen enthalten, dass der Vorteil der tiefen Nitratkonzentration fraglich wird. In Wasserwerken und in Thermalbädern kann Radon aus dem Wasser ausgasen und zu erheblicher beruflicher Strahlenexposition führen. In diesem Beitrag werden die allgemeinen Aspekte dieser Kontaminationsprobleme behandelt und die Situation in der Schweiz beurteilt.

Es gibt allerdings auch eine positive Seite der Allgegenwärtigkeit natürlicher Radionuklide in der Erdkruste. Sie können als natürliche Tracer in der Hydrogeologie benützt werden. Die diffuse Natur der Quellen und die komplexen Adsorptions- und Desorptionsprozesse, die in Gestein und Boden stattfinden, machen die Interpretation allerdings sehr schwierig. Ausserdem sind die traditionellen Radiochemiemethoden sehr zeitaufwendig und auf wenige spezialisierte Labors beschränkt. Vereinfachte radiochemische Methoden, ein in unserem Labor entwickelter kontinuierlicher «Radon-im-Wasser» Monitor und die volle Ausnützung der Analysen-Kapazität der Gammaspektrometrie könnten der Verwendung natürlicher Radionuklide als Tracer in der Hydrogeologie zum Durchbruch verhelfen.

ABSTRACT

Some radionuclides naturally present in drinking water have radiotoxicities well comparable to those of the most toxic artificial alpha emitters. Commercially available mineral waters may contain natural radionuclides in concentrations that make questionable the benefits from their low nitrate levels. Outgassing of radon at water treatment plants and spas can lead to considerable occupational radiation doses. This paper presents general aspects of these pollution problems and assesses the situation in Switzerland.

There is, however, also a positive side of the omnipresence of natural radionuclides in the earth's crust. They can be used as tracers in hydrogeology. But the diffuse nature of the sources and the complex adsorption and desorption processes taking place in rocks and soils make data interpretation very difficult. In addition, traditional radiochemical methods are time-consuming and limited to few specialized laboratories. Simplified radiochemical methods, a continuous radon-in-water monitor developed at our laboratory and the full use of the gamma spectrometry's analytical power may boost the use of natural radionuclides as tracers in hydrogeology.

Natural radionuclides as pollutants

Natural radionuclides are seen by the general public as harmless for they are "natural", but also many scientists still have not realized that our body makes no difference between natural and artificial sources.

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The ^{238}U, ^{232}Th and ^{235}U series present naturally in the earth's crust and therefore also present in our drinking water may be divided into groups each with a long lived main nuclide and its short lived daughters. In the context of drinking water "short lived" are those radionuclides that develop during underground transport or during processing and storage prior to consumption. "Long lived" are those radionuclides that went into solution at the rock-water interface and are still detectable at the point of sampling (well, spring or drain output).

Of these main nuclides thorium isotopes have such a low water solubility that they are hardly present in drinking water. Members from the ^{235}U series can be neglected with respect to the ^{238}U series, the natural $^{235}U/^{238}U$ activity ratio being only 0.046.

The main isotopes thus remaining are ^{238}U, ^{234}U, ^{226}Ra, ^{222}Rn, ^{210}Pb, ^{210}Po, ^{228}Ra and ^{224}Ra. Except for ^{222}Rn their radiotoxicities when ingested, are quite high, ^{210}Pb and ^{210}Po are even in the range of the worst artificial isotopes like ^{239}Pu or ^{241}Am (Fig. 1). According to current models, ^{222}Rn (a noble gas) is not absorbed when ingested, thus does not contribute considerably to the radiation dose from drinking water. However, radon can escape from the water to the indoor air in water treatment plants and in spas. Workers there may receive considerable radiation doses due to the inhalation of radon daughters. Data for Switzerland are lacking.

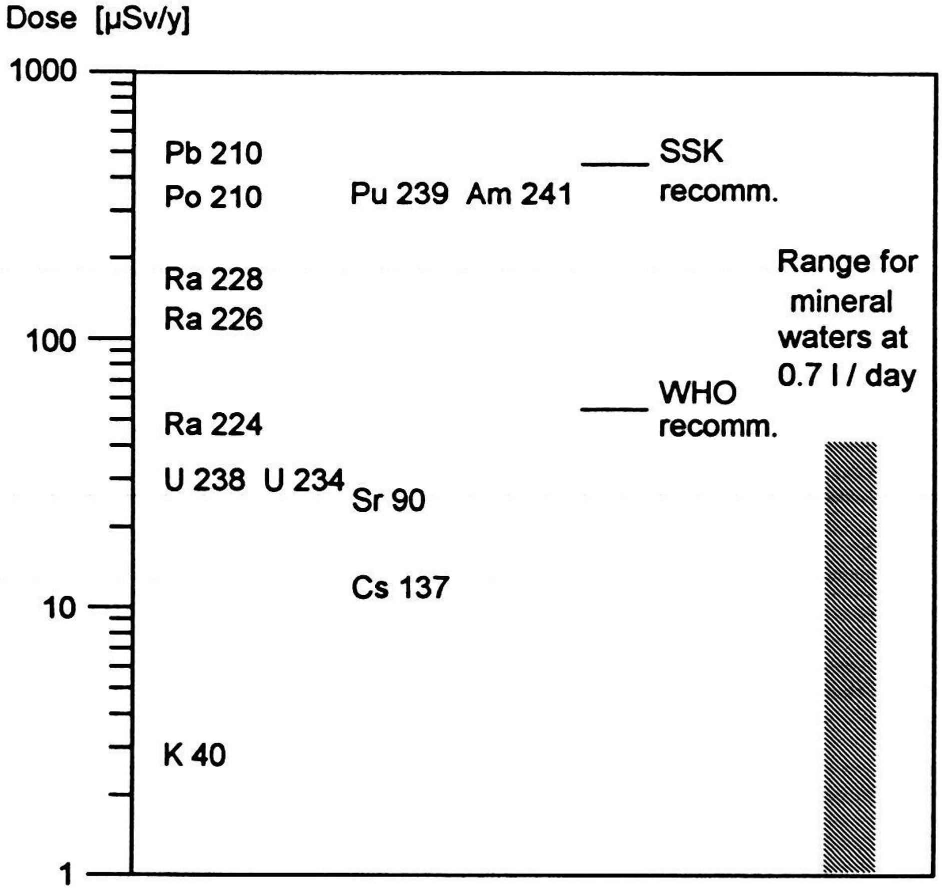

Fig. 1. Annual radiation dose by ingestion of various radionuclides in drinking water. Daily consumption: 1.7 liter. Radionuclide concentration: 1 Bq/liter. SSK: German Radiation Protection Commission. WHO: World Health Organization.

Despite of the high radiotoxicity natural radionuclides are not routinely determined in drinking water. Some 30 brands of commercially available mineral waters have been analyzed some years ago at the Paul Scherrer Institute (PSI) at Villigen. Unfortunately only a very brief summary, where brand names have been omitted, has been published (BAG 1992). The radiation dose range for these mineral waters is shown in Figure 1. Except for total uranium, there are nearly no data for Swiss drinking waters (Baertschi & Keil 1991). Total uranium is not a useful measure for the dose by ingestion, for uranium

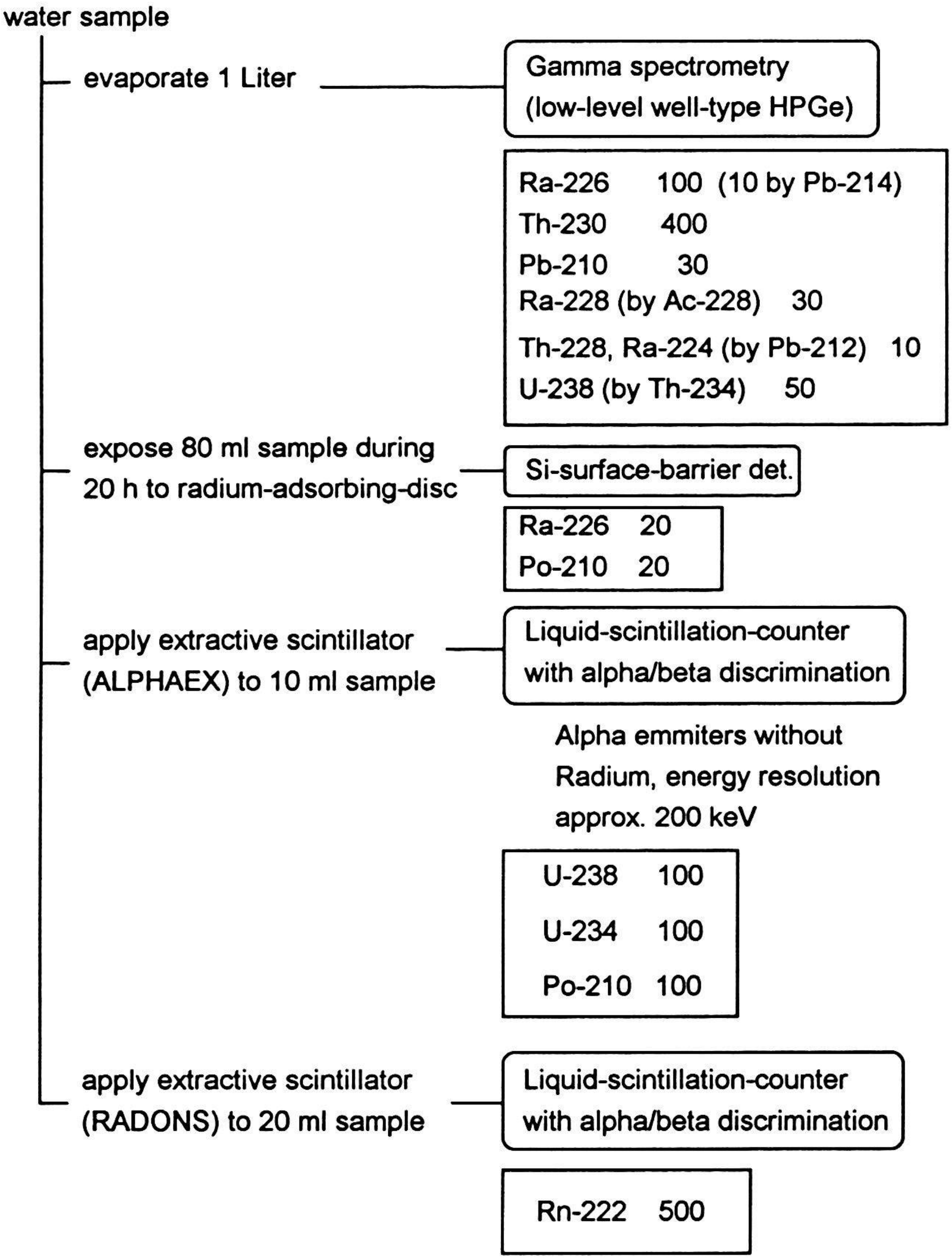

Fig. 2. Procedure for the analysis of natural radionuclides in drinking water. Numbers after nuclide names are typical detection limits in mBq/liter.

itself has a low radiotoxicity and its more problematic daughters are as a rule not in equilibrium with the uranium.

Because of this lack of information on the concentration of natural radionuclides in Swiss drinking waters we started an extensive study in 1993. In the near future Swiss consumers will be able to make their own choice between low nitrate and low radionuclide concentration.

One of the reasons that there are so few data is that the traditional preparation methods for alpha spectrometry are very time consuming; most of the natural radionuclides of interest in drinking waters are alpha emitters. We therefore developed easier methods like our radium-adsorbing-discs (Surbeck et al. 1989). We also make full use of the analytical power of low-level gamma spectrometry and of state-of-the art liquid scintillation counting. Most of the alpha emitters of interest can be determined by their gamma emitting daughter products. The measurement procedure currently in use at our laboratory is shown in Figure 2. An important point of our study is that we do not need record-low detection limits, the methods have been chosen according to the real needs of radioprotection. The detection limits achievable with the procedure in Figure 2 guarantee that no individual nuclide will contribute more than 50 μSv to the annual radiation dose. This is just the limit recommended by the World Health Organization (WHO). The German Radiation Protection Commission (SSK) recommends 500 μSv/year. In Switzerland there are currently no official recommendations for natural radionuclides in drinking water.

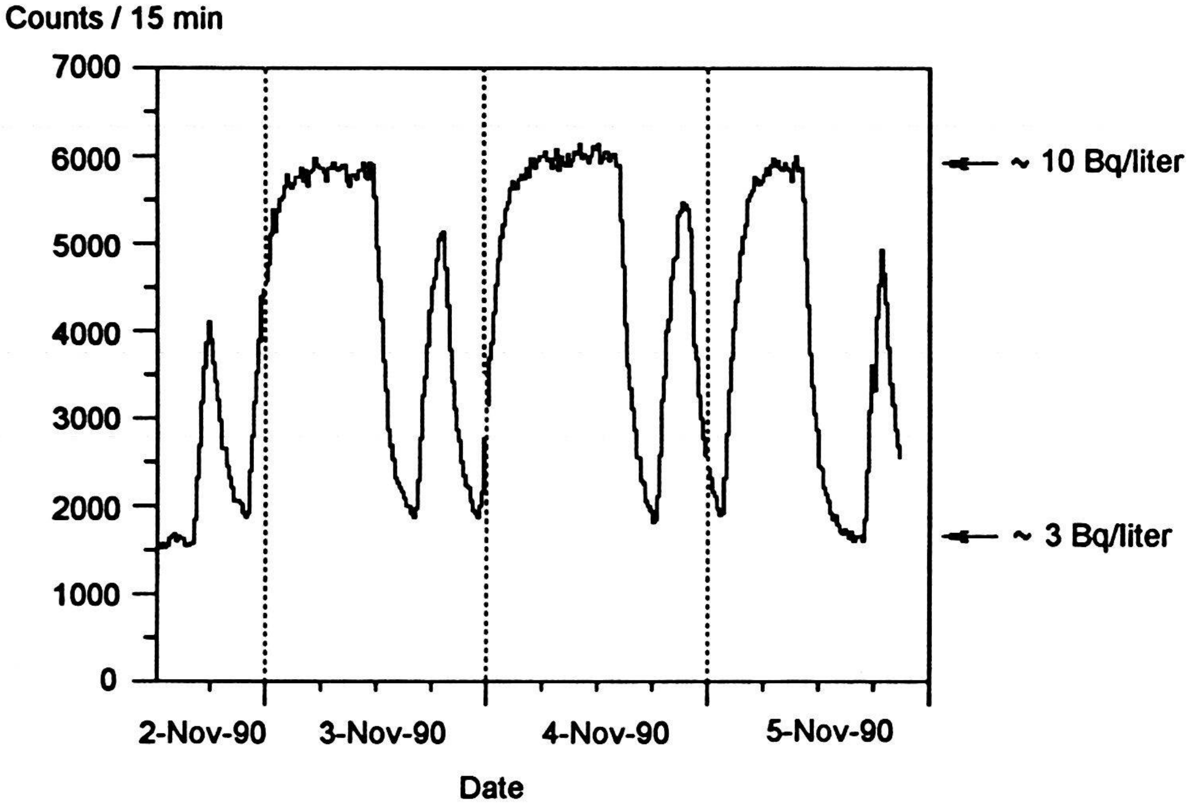

Fig. 3. Radon-222 concentration as a function of time for tap water at Fribourg, Switzerland.

Natural radionuclides as tracers

The presence of natural radionuclides in groundwater may be a pollution problem, but there is also a positive aspect. Numerous studies have shown that e.g. the disequilibrium in the uranium series can give information about geochemical processes (Ivanovich & Harmon 1992). A still rarely used member of the ^{238}U series, ^{222}Rn, has the potential to become a useful tracer in hydrogeology (Höhn & von Gunten 1989; Höhn et al. 1991; Surbeck & Eisenlohr 1993). It is present in easily measured concentrations in most aquifers. It can even be measured directly in the field and a continuous monitoring is possible with the apparatus developed at our laboratory (Surbeck 1992). The high temporal resolution achievable (app ... 15 min.) is ideal to study fast mixing processes. An example may illustrate this. Figure 3 shows variations of radon activity observed in tap water in the city of Fribourg.

The variations are due to the mixing of waters from two different locations. During low consumption periods (night) the quantity supplied by the high-radon drain east of Fribourg (Hofmatt) is sufficient. When consumption increases, water from wells south of Fribourg (Tuffiere) is added. This water has a far lower radon concentration.

Radon is still far from being a routine tracer, but this paper may motivate some of you to enter this rapidly growing field.

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Manuscript received October 11, 1993
Revision accepted March 16, 1994