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INVENTORY OF TRACE ELEMENTS IN GROUNDWATERS OF THE NETHERLANDS

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SUMMARY

An investigation of the Dutch groundwaters as for trace elements has been started.

A sampling method has been developed.

The results of the first measurements are given. They concern groundwaters from the East of the country as well as from the dune region.

The investigation is handicapped by the fact that observation pits may be contaminated by rests of drilling fluid.

Contrary to the first intention, production pits are also sampled now.

The measurements will be extended to a complete sampling network.

INTRODUCTION

After the drilling operations for a production or observation well, generally only analyses of the macroparameters are made.

These determinations may concern: conductivity, colour, pH, $KMnO_4$-consumption, Cl^-, NO_2^-, SO_4^{--}, HCO_3^-, CO_2, CO_3^{2-}, PO_4^{3-}, SiO_2, H_2S, NH_4^+, organic-bound NH_3, Fe, Mn, Ca^{2+}, Mg^{2+}, Na^+, K^+, $NaHCO_3$, total hardness and temporary hardness.

Subsequently the observation wells are only used for periodic determinations of the groundwater level, although incidental oxygen determinations may take place.

Production wells of water undertakings are subjected, to a six-montly control by the Government Institute for Public Health. This check is likewise confined to the raw water macro-parameters: conductivity, NH_4^+, Fe, Mn, $KMnO_4$ consumption, NO_2^-, NO_3^-, HCO_3^-, organic-bound NH_3, CO_2, O_2 and temperature. The indirect measurement in purified water involves a more comprehensive list.

In the case of private supplies, many analyses are of course also made by a variety of institutions.

Within the framework of an investigation into the influence of the purification process on the trace-element content in storage basin- or infiltration plants, the Government Institute for Public Health also analysed water from a few groundwater supplies. Table 1 summarizes the results.

The undertakings managing the dune infiltration in the West of The Netherlands have controlled the quality of infiltration and reproduced raw water for several years. Although this control does not concern undisturbed groundwater, the measured concentrations are at the same level as the above-mentioned groundwater supplies.

TABLE 1
Trace elements μg/l

	Cr	Pb	Cu	Zn	Hg	As	Se	Ni	Co
Groundwater supply in Gelderland 1971	1.0-2.0	<1-13	2-25	5-25	<0.1	<0.5-1.5	<0.1-0.4	–	–
Groundwater supply in Gelderland 1972	<1-1	1-9	<1-14	4-35	<0.1	<0.5-2.5	–	2-4	<1
Groundwater supply in Zuid-Holl. 1971	<0.5	<1-4	2-16	12-27	<0.1	<0.5-0.5	<0.1-0.5	–	–
Groundwater supply in Zuid-Holl. 1972	<1-1	1-5	2-12	4	<0.1	<0.5-2.0	–	<1-2	<1-2

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INVESTIGATIONS ABROAD

In the United States many measurements have been made in springwater. For instance, the arsenic determinations by Whitnack and Brophy (1969) are well-known. Hem refers to a number of zinc determinations (1972).

A national groundwater sampling network is operated in Sweden. This network consists of 50-60 stations, mostly natural springs. Each year they are sampled 2 to 4 times. Besides other parameters, Fe, Mn, Al, Zn, Cu, Pb, Mo, Ni, Cr and Co are determined.

Series of these determinations are available from 1968-1970. The measurements were initiated particularly to allow seasonal influences to be determined. The concentrations usually remain below 5 μg/l. Copper sometimes shows a slightly higher value, up to 20 μg/l. Occasionally the lead level may be considerably higher. Incidentally, concentrations of a few milligrammes per liter have been measured. For zinc and iron these concentrations invariably are considerably higher than the 5 μg/l range. The measurements have been made in loose sediments, not in rocky soil. In South Africa, measurements are made on samples actually drawn out of the subsoil. Spring water is struck at many places, and is also investigated for trace elements.

A review of the Chemical Abstracts, Volume 76, over the first six months of 1972, yielded only four abstracts about groundwater which are relevant, out of a total of 150.

These four concerned:

a. Determination of cobalt (2.9-8.6 μg/l) and copper (6-30 μg/l) in groundwater from Azerbeidshan. (C.A. 1972-1)
b. Determination of strontium, lithium, zinc, rubidium, caesium, aluminium, chromium, copper, iron, manganese, molybdenum, lead, nickel, titanium, bromine, iodine, arsenic, selenium and boron. in groundwater from Derbyshire, measured in 34 samples. (C.A. 1972-2)
c. Determinations in groundwater of the Samur region (U.S.S.R.) of titanium, chromium, manganese, copper, strontium, zirconium, molybdenum, silver, tin, barium and lead. (C.A. 1972-3)
d. Measurements of manganese, copper, zinc, strontium, lithium, rubidium, bromine, iodine and boron in 20 different groundwater samples from Missouri. (C.A. 1972-4)

For the second half of 1972 only three abstracts regarding trace elements in groundwater were included in a total of 110 about groundwater.

These three abstracts comprise:

e. Arsenic and vanadium determination in the Buenos Aires region. (C.A. 1972-5)
f. Characterization of groundwater from the Central-Baraba region (U.S.S.R.), with reference to aluminium (< 22 mg/l), iron (< 33.6 mg/l), manganese (< 4 mg/l) and titanium (< 8 mg/l). (C.A. 1972-6)

In groundwater of the Massif Central in France a study of the occurrence of arsenic, boron, barium, cobalt, chromium, copper, gallium, nickel, lead, tin, strontium, vanadium and zinc was made. In groundwater of the Ivory Coast, a similar study was made, especially in connection with an investigation into the erosion of rocks. (C.A. 1972-7)

The subject is touched on by an article concerning the radiological stock taking of ^{53}Fe, ^{60}Co, ^{65}Zn, ^{90}Sr, ^{125}Sb, ^{137}Cs and ^{207}Bi in the Bikini Atoll, in the course of which measurements in groundwater were also performed. (C.A. 1972-8)

MOTIVE AND SET-UP OF A GROUNDWATER INVENTORY IN THE NETHERLANDS

The groundwater inventory in The Netherlands planned by the Government Institute for Water Supply is based on three considerations.

The first reason is that only little is known about the trace-element condition and balance of the groundwater.

The second motive is that if after say five or ten years pollution is to be determined, the present-day concentrations must be known.

The third reason is the possibility to obtain in this way data on groundwater currents. In the first instance it is the intention to select only a few pumping stations for every characteristic situation. For instance, a few locations with deep and well-protected groundwater are selected, some production wells with contamination risk are chosen, some locations with a proportion of bank infiltration will be sampled, two undisturbed dune-water production pits and a few dune-infiltration regions are chosen. Moreover, the selected sites are distributed throughout The Netherlands, thirty locations with 10 to 15 wells each.

Dependent on the results of this first set-up, the sampling network may be extended at a later stage.

SAMPLING AND THE APPARATUS

Because of the necessity to obtain undisturbed or at least only slightly disturbed samples, we decided to sample by means of observation or mark pits. The more recent risers are normally engineered in PVC, from which the release of trace elements is practically negligible. The same PVC pipes are applied in the neighbourhood of many pumping stations. Use of these observation pits makes the results at the different points directly comparable; in that case a separate description of each sample is not necessary.

The diameter of the observation pits is usually one inch, the deep wells often show a telescopic reduction from four inches to one. The groundwater is withdrawn at filter depth.

A grave complication is the fact that the modern deeper boreholes are engineered by the drilling fluid circulation system. Some of the drilling fluid is left in the annular space and may cause contamination. The drilling fluid is often a suspension of clay, and if required, bentonite, carboxymethylcelluse, sodiumhydroxide and quebracho may be added.

Two samples of drilling fluid have been investigated for the release of trace elements. The results are summarized in Table 2.

TABLE 2

	Treatment	Zn	Pb	Cu	Cr	Cd
I	28.929 g drilling fluid Dried 7.047 g subsequently suspended in 1 L aqua bidest.	110	10	12	28	1.3
II	9.816 g drilling fluid Dried 2.595 g subsequently suspended in 1 L aqua bidest.	10	<1	3	5	0.2

Release of trace elements in μg/l by drilling fluid consisting of: 750 kg Limb. clay, 125 kg bentonite, 15 kg C.M.C. and 15 kg NaOH to 3.75 m^3 water.

Conclusions based on the results of fluid-drilled wells will only be drawn with the necessary caution, even after clearing the well for a long time.

Pulsed wells may be contaminated in a mechanical way. This is the reason why the first rectilineair set-up could not be followed and production wells (preferably constructed of PVC but with metal pump components) are incorporated in the system. It also moved the investigation to the direct environment of the withdrawal points.

The maximum allowable diameter of the sampling apparatus is 2 cm, on account of the diameter of the pipes used for the observation pits. A submersible pump of this size is not available at this stage, and anyway it would contain metal parts.

An oxygen pipette modified by the Government Institute for Water Supply and suited for our sampling purposes, is represented in figure 1.

The brass parts seem to present no problem because of their relatively small surface, provided the contact time is short. From a 90 cm^2 plate of the same brass material, 310 μg Zn, 100 μg Pb and 400 μg Cu were leached in a contact time of 65 hours by 1 L aqua dest. After a contact of an hour these amounts were 30 and 3 to 4 μg respectively.

In the meantime a pipette constructed entirely of PVC and polyethylene has come into use (fig. 2). As the investigations do not concern oxygen determinations the design of the pipette could be more simple. A ballast is necessary because of the slight weight of the pipette. Every trace element content is determined by the atomic absorption technique, partly with the aid of the graphite furnace, partly by the flame method.

RESULTS

The groundwater has been investigated at four localities. Fifteen filter samples have been taken from the Crown estates (location 1 in fig. 3). In addition, measurements have been carried out in the region of a groundwater plant (2), in the ground of a real dune-water undertaking (3) and in the vicinity of a pumping station where infiltration is already employed (4 , fig. 3).

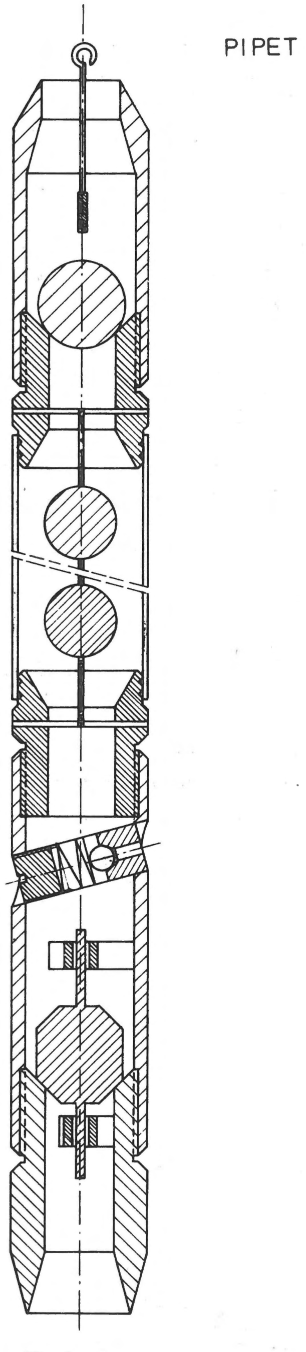

Fig. 1

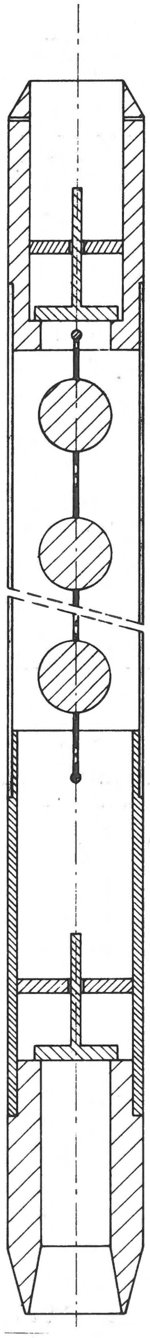

Fig. 2

Especially for Zn and Cr the results from the Crown estates require supplementary data about water from the producing pumping stations in the neighbourhood.

As regards the other three locations, we must confine ourselves to a few general remarks at this stage.

TABLE 3

Well	Date	Depth of the filter below surface	µg/l									
			Cr	Cu	V	Pb	Be	Zn	Li	Co	Cd	Ni
1	Sept. 24	75.50- 77.50 m	7	210	1	41	0.1	740	3.0	11	0.6	15
		261 -263 m	16	360	4	36	0.2	680	2.2	3	0.5	8
2	Sept. 24	from jetty in Uddel lake	3	8	1	5	0.1	50	1.1	1	0.4	7
		23.50- 25.50 m	3	48	2	5	0.2	160	2.6	2	0.6	22
		40 - 42 m	6	102	6	18	0.2	120	2.6	3	0.3	9
3	Sept. 24	52 - 56 m	4	35	<1	15	0.2	170	1.6	1	0.4	10
		65 - 69 m	9	60	1	16	0.2	140	1.6	1	0.2	9
		85 - 89 m	4	35	5	12	0.3	90	2.3	1	0.4	10
		120 -123.50 m	20	126	1	24	0.2	340	1.7	1	0.3	16
		136 -140 m	9	204	<1	17	0.6	230	1.2	2	0.4	20
		180 -184 m	6	470	<1	18	0.1	400	1.4	1	0.5	9
		190 m	3	138	<1	12	0.1	240	1.1	6	0.4	8
4	Sept. 24	28 - 30 m	10	32	1	10	0.3	220	1.6	2	1.0	19
		45.50- 47.50 m	4	76	1	28	0.1	120	2.0	1	0.7	11
5	Sept. 24	25 - 27 m	13	196	2	124	0.4	190	4.0	3	0.6	13
		40 - 42 m	5	106	2	47	0.1	190	1.6	1	0.2	10
1	Nov. 20	75.50- 77.50 m	0.5	30				200				

Before discussing the results, we should examine the geological situation near the wells. A jump in the groundwater level is found for the wells *1* (from 1969), *2* (from 1971) and *5* (from 1972).

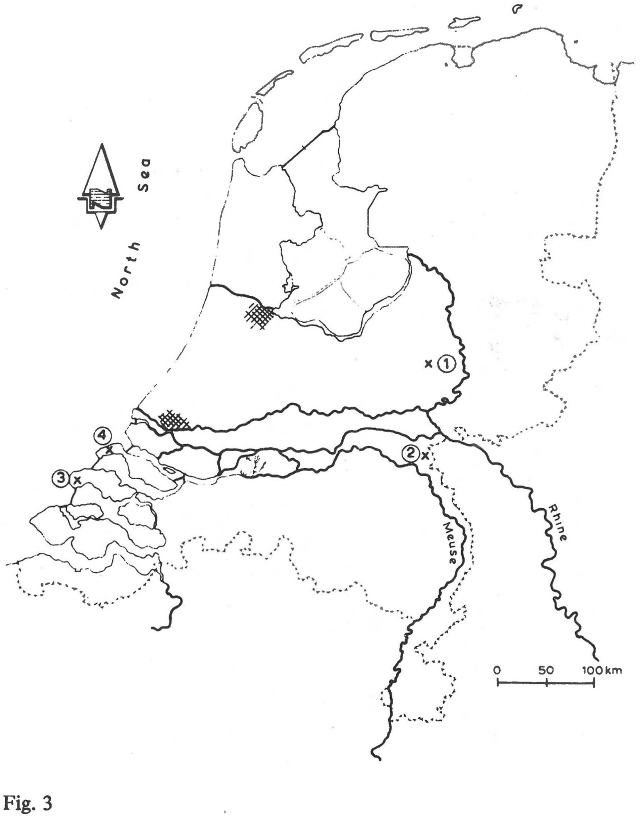

Fig. 3

The jumps are between the filters:
–142.50/–144.50 and –203.50/–205.50 for *1*
+5.40/3.40 and –11.10/–13.10 for *2* and
+10.93/8.93 and –4.07/–6.07 for *5*,
all with regard to Amsterdam water mark. The surface is at +57.5, +28.90 and +35.93 respectively with regard to Amsterdam zero at the well locations *1*, *2* and *5*. The drilling descriptions agree with the pattern of the jumps.

At well *1* the Tegelen clay is at 190-205 m below Amsterdam zero.

Well *2* shows a layer of loam at +40 Amsterdam zero; between the less deep filter and the "Uddel" lake there is no impervious layer.

Well *5* crosses clayey loam at 17-13½ and 8 m above Amsterdam water mark.

Neither well *4* (1972) nor well *3* (1970) show a jump in groundwater level. The description of *4* concerns only quartzy sand.

Well *3*, drilled from 42 m above Amsterdam zero, is described as follows: A layer of clay at 14 m below Amsterdam zero, a second layer of clay at 62 m below Amsterdam water mark, loamy layers at 81 and 120 m and clay at 131 m below Amsterdam zero. The Tegelen clay is at 155 m below Amsterdam zero.

On account of the almost certain influence of the drilling fluid, it seems less appropriate to go into the figures for Zn and Cr. Nevertheless, it might be stated that the impervious layers can be deduced from the other analysis results.

For the wells of *1*, the difference in concentrations of Cu, V, Pb, Co and Ni may be explained by assuming an impervious layer of clay.

The agreement in results for the 23.50-25.50 well of *2* and the Uddel lake on the one hand and the difference of the Cu, V and Pb percentages of both samples from the concentrations of the deep well on the other hand is in conformity with the geological situation.

The least deep filter of well *5* is between two layers of clay which explains the variations in analysis results. At well *3* the differences are particularly remarkable in the concentrations of Cu and Pb, as well as Zn and Cr to a lesser extent, in the filter at 120-123.50 m (81 m below Amsterdam zero) as compared with the concentrations in the next upper and lower filters. A pervious layer of loam (no difference in groundwater level) at this particular depth, may be the reason.

Of the measurement in the surroundings of a groundwater production well where a number of wells are sampled twice at a 2½ week interval some facts are striking.

A production well with PVC riser, situated in the neighbourhood of some observation pits where measurements are also performed, shows relatively low values for Ni, Pb, Cu and especially Zn.

Samples taken twice at a short interval from one well and without any perturbations show large differences for Cu, Pb, Zn, Co and Ni. Two weeks later, when the same well was sampled again, a peak for Cd, but reduced concentrations for Cr, Ni and Pb were found. The concentrations of Cu, Pb and Zn in a pulsed well are not very different from those in a fluid-drilled well.

The water samples of the infiltration region in which Pb, Cu, Zn and Cr are determined reveal no change between infiltration point and drainage canal. The entire trace element level of groundwater in the neighbourhood of the infiltration point is scarcely any higher than in the rest of the area, it is very low.

The samples of the real dune-water plant also have a low zinc concentration (4-72 μg/l).

CONCLUSION

Sampling was carried out in an acceptable manner. The differences between the concentrations in the Veluwe Crown estate samples and the results of the latter locations might be attributed to the fact that no production wells are present on the estate. The results obtained at the groundwater plant, however, do not completely support this explanation. Adequate information is only obtainable by sampling of observation and production wells. Especially the production wells engineered in PVC are interesting in this respect. The observation wells may be situated near sources as well as in regions without water production.

Evaluation of the obtained results will lead to a right impression of the condition of the groundwater.

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