

## FREQUENT VARIATIONS IN THE CHEMICAL QUALITY OF GROUNDWATER - A MONITORING PROBLEM

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### ABSTRACT

Frequent variations in the concentration of 14 chemical components were observed during monthly sampling of 43 wells of the coastal and mountain aquifers of Israel. The difficulty of establishing a sampling frequency complicates the monitoring and management of groundwater quality. Relationships were found between the  $\text{NO}_3^-$  variation and technical and chemical parameters in the coastal aquifer.

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### INTRODUCTION

A groundwater quality monitoring system is being developed in Israel. An important question is the frequency of sampling in order to obtain reliable data. Owing to technical and budget constraints monitoring of groundwater quality is usually based on annual or less frequent surveys. By sampling a well once per year, a basic assumption is made; groundwater is relatively homogeneous and, therefore, the yearly changes in quality are small and continuous. The very frequent variations in the concentration of  $\text{NO}_3^-$  and  $\text{Cl}^-$  reported by others (refs. 1-6), and the observed fluctuations of pH, Eh,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , Fe and  $\text{HCO}_3^-$  (ref. 7), seem to contradict this assumption.

This paper reports on frequent variations of chemical components in wells and the bearing of this phenomenon on groundwater quality monitoring.

### METHODOLOGY

Two hydrogeologically different aquifers with groundwater of different chemical quality were tested during one year. 23 wells were sampled monthly in the sandy, phreatic, shallow (up to 180 m thick) and nitrate-polluted coastal aquifer and 20 wells were sampled in the deep (up to 900m thick), karstic and relative clean limestone aquifer of the mountain region. Wells differing in hydrogeological and environmental parameters were selected in both aquifers. All wells were being operated continuously for municipal water supply. Scattered historical data of groundwater quality, taken between 1968 and 1974, were available.

In this study 14 chemical components were tested monthly. Samples were analyzed according to standard procedures described elsewhere (ref. 8). The precision of the

analytical methods as expressed by the coefficient of variability was less than 2% for  $K^+$ ,  $HCO_3^-$ ,  $Cl^-$ ,  $NO_3^-$  and  $NH_4^+$ ; less than 3% for  $Ca^{2+}$ ,  $Na^+$  and T.D.S.; less than 10% for  $F^-$  and  $SO_4^{2-}$  and less than 5% and 28% for  $PO_4^{3-}$  and B, respectively. The coefficient of variability for  $Mg^{2+}$  ranged from 20% to 43%.

Linear correlation analysis was conducted between the variation of the chemical parameters as expressed by their range, standard deviation and coefficient of variability, measured in each well, and the following technical, hydrogeological and environmental parameters: well, filter and pumping depth; perforation depth and diameter; thickness and geological composition of unsaturated zone; transmissivity; porosity; monthly and yearly volume of water pumped; fluctuations of groundwater level; type of pollution sources and their distance from the wells. The variation of each chemical parameter was also correlated with the variation of the others and with the historical-chemical data available for each well.

## RESULTS

Variations in the concentration of all chemical components tested were detected in wells of both aquifers. Monthly concentrations of  $Cl^-$  and  $NO_3^-$  are presented in Fig. 1 exemplifying the observed fluctuations.

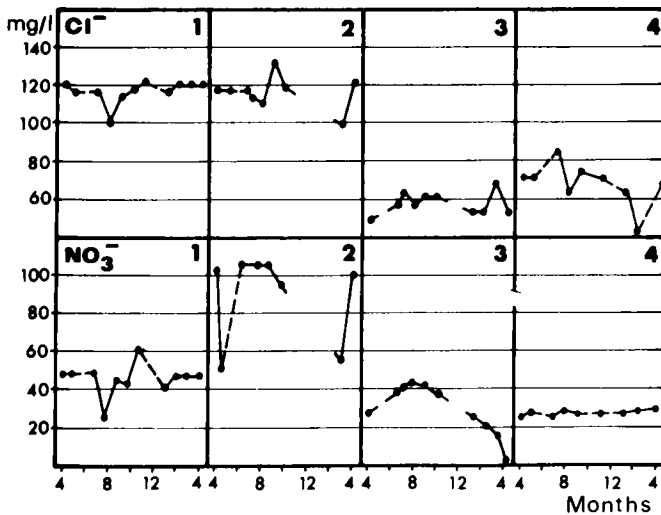


Fig. 1. Monthly variation of  $Cl^-$  and  $NO_3^-$  concentration in four wells of the coastal aquifer.

Similar variation patterns were detected for most components. Fig. 2 shows the variation of all components in one well (no  $\text{NH}_4^+$  or  $\text{PO}_4^{3-}$  fluctuation was detected in this well).

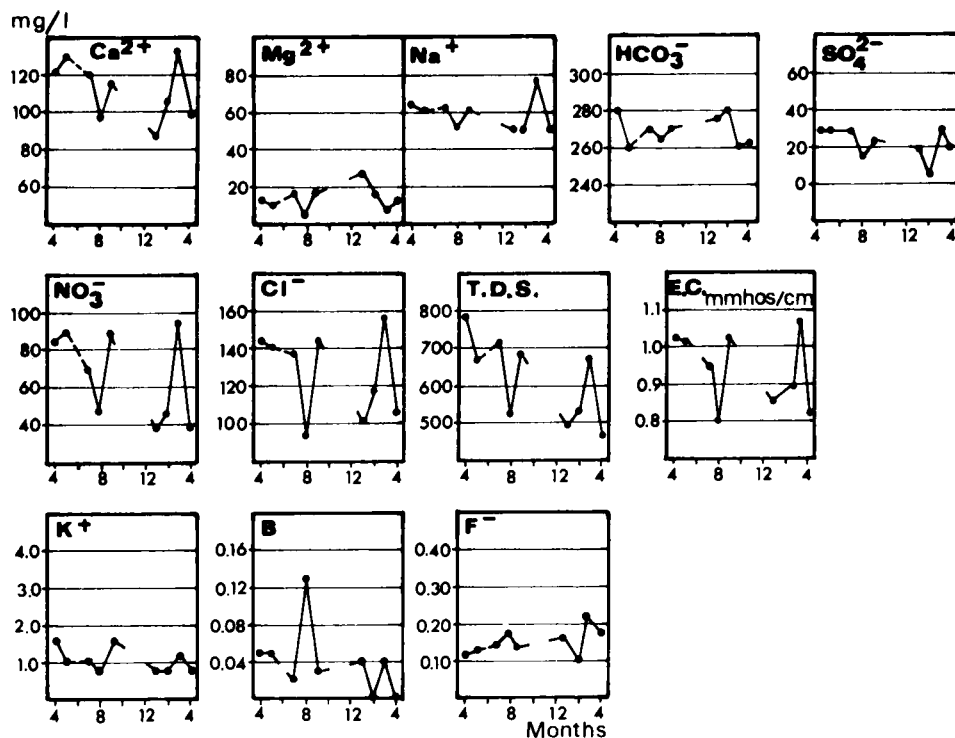


Fig. 2. Monthly variation of chemical components in well No. 9 of the coastal aquifer.

The extent of the fluctuations in all wells of the coastal aquifer is presented in Table 1. The range of maximum differences obtained for each component in each well ( $\Delta C_i$  max, range), as well as the ranges of the standard deviations (SD, range), coefficients of variability (CV, range) and average concentrations ( $\bar{C}_i$ , range) are given in columns 3, 5, 7 and 2. The same parameters averaged for all wells (Av.) are given in columns 4, 6, 8 and 1. All average values are weighted according to the number of observations in each well (65% of the wells were sampled at least nine times).

The average coefficients of variability of all components are higher than the analytical error, except for  $\text{Mg}^{2+}$ . Similar results were obtained for data from the wells of the mountain aquifer.

TABLE 1

Monthly variation of chemical components in 23 wells of the coastal aquifer in the course of one year.

Component	C <sub>i</sub>		ΔC <sub>i</sub> max		SD		CV	
	Range	Av.	Range	Av.	Range	Av.	Range	Av.
	mg/l						%	
Ca <sup>2+</sup>	42 - 133	91	10 - 44	21	3 - 15	7	3 - 27	7
Mg <sup>2+</sup>	3 - 36	13	5 - 23	14	2 - 8	5	16 - 99	42
Na <sup>+</sup>	25 - 102	52	5 - 39	18	2 - 13	6	4 - 18	12
HCO <sub>3</sub> <sup>-</sup>	124 - 343	224	12 - 134	38	4 - 41	12	2 - 33	5
SO <sub>4</sub> <sup>2-</sup>	6 - 52	23	5 - 38	20	3 - 12	7	12 - 140	37
Cl <sup>-</sup>	35 - 260	104	7 - 60	21	2 - 23	7	2 - 27	6
NO <sub>3</sub> <sup>-</sup>	16 - 90	54	3 - 57	22	1 - 24	8	3 - 47	14
T.D.S.	262 - 928	512	51 - 417	156	14 - 113	49	5 - 20	9
F.C. mmhos/cm	0.41 - 1.40	0.78	0.04 - 0.27	0.10	0.01 - 0.10	0.03	1 - 13	4
K <sup>+</sup>	0.7 - 8.1	1.5	0.0 - 4.7	0.9	0.0 - 1.5	0.3	0 - 33	22
NH <sub>4</sub> <sup>+</sup>	0.00 - 0.03	0.00	0.00 - 0.30	0.04	0.00 - 0.10	0.01	0 - 333	55
B	0.01 - 0.10	0.03	0.05 - 0.16	0.09	0.02 - 0.05	0.03	34 - 173	93
PO <sub>4</sub> <sup>3-</sup>	0.00 - 0.02	0.00	0.01 - 0.09	0.02	0.00 - 0.02	0.00	34 - 223	109
F <sup>-</sup>	0.07 - 0.27	0.14	0.08 - 0.34	0.20	0.03 - 0.10	0.06	24 - 84	54

This study also revealed, as reported before (ref. 2), that the range of maximum differences obtained by monthly sampling may be similar or higher than the long term changes measured by yearly sampling. In the coastal aquifer this phenomenon was observed for Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> in 50% and 30% respectively, of the wells sampled. This observation is exemplified in Fig. 3.

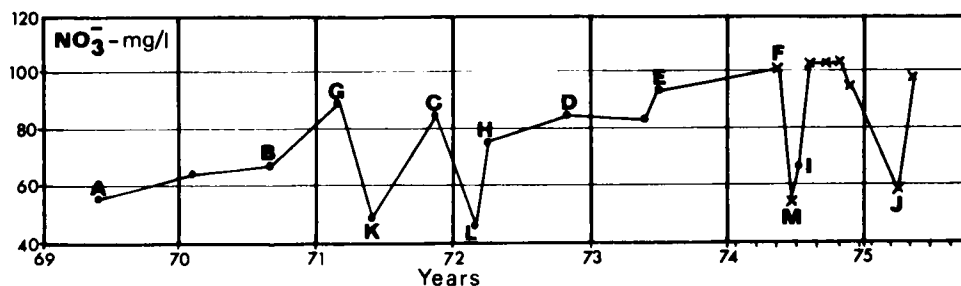


Fig. 3. Long-term and monthly changes of NO<sub>3</sub><sup>-</sup> in well No. 2 of the coastal aquifer, (•) historical data, (x) data obtained in the course of this study.

From results reported in previous studies (refs. 2 and 3), it was observed that in some wells the patterns of variation of a chemical component change from year to year and are not long term characteristics of the well. Similar observations are reported by others (ref. 9).

Different patterns were also detected for different components in the same well (Figs. 1 and 2).

Few significant relationships were evident as a result of the correlation analysis and most of them related to the  $\text{NO}_3^-$  variation in the coastal aquifer. Nitrate relationships are summarized in Table 2.

TABLE 2

Linear relationships between  $\text{NO}_3^-$  variation and chemical/technical parameters ( $Y = a + b X_i$ )

Y	$X_i$	a	b	Correlation factor	Significance level
	Pumping depth (m)	13.4	-0.17	-0.43	5
	Av. $\text{NO}_3^-$ in 1974 (mg/l)	-1.43	0.18	0.62	1
SD of $\text{NO}_3^-$ 1974	SD of E.C., 1974 (mmhos/cm)	0.57	202.65	0.73	0.1
	SD of T.D.S, 1974 (mg/l)	-2.31	0.23	0.78	0.1
	SD of $\text{NO}_3^-$ , 1968-1974 (mg/l)	-0.54	0.91	0.84	0.1
	Av. $\text{NO}_3^-$ , 1968-1974 (mg/l)	-1.40	0.21	0.56	1

## DISCUSSION

The bearing of this phenomenon on groundwater quality management and monitoring can not be disregarded. The problem faced becomes more critical when comparing concentrations with permissible standards (e.g.  $\text{NO}_3^-$  drinking standard of 90 mg/l). According to this standard, for example, drinking water should not have been supplied from wells No. 2 and 9 for three and four months of the year, respectively (Figs. 1 and 2).

The analysis of the data discloses also the possibility of drawing different isoconcentration maps and calculating different average values in each month. In the coastal aquifer the  $\text{NO}_3^-$  average varied from 53 mg/l to 59 mg/l between April to September, and the number of wells with  $\text{NO}_3^-$  content above the drinking standard increased from 4% to 20%.

The conclusions about the concentration trend of a chemical parameter in a well can depend on the sampling scheme. A concentration increase (A,B,C,D,E,F), decrease (G,C,H,I,J) or an almost non-change pattern (A,K,L,M,J) could be detected in well No. 2 (Fig. 3).

As aquifers are not isotropic and both extensive and intensive pollution sources

are not uniformly distributed it is to be expected that groundwater quality will not be uniform. Therefore, the concentration of chemical components may change in the course of a year.

In order to determine the optimal frequency of sampling for groundwater monitoring several approaches are possible. One of them is to study the relationship between fluctuations and responsible or related factors. At this stage, certain relationships were determined which can enable anticipation of  $\text{NO}_3^-$  variation in the coastal aquifer by means of assessing the pumping depth of the wells or by means of such chemical parameters as are presented in Table 2. Another approach is to develop statistical models that will enable the calculation of an optimal number of samples for a well to estimate the average concentration of any chemical component (refs. 10 and 11).

#### ACKNOWLEDGEMENT

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#### REFERENCES

- 1 K.T. Crabtree, Nitrate Variation in Groundwater, Technical Completion Report, OWRR B-004-Wis, OSW UI-00556-01, DNR 133-6451 Wis, The University of Wisconsin, 1970.
- 2 D. Ronen, Nitrate Contamination of Groundwater in the Rishon Le Zion - Rehovot District, Report No. HR/72/046, Tahal, Israel, 1972, (in Hebrew).
- 3 I. Kaanovitch and D. Blanck, Groundwater Pollution by Nitrates in Israel, Report No. 01/74/47, Tahal, Israel, 1974, (in Hebrew).
- 4 F. Schwillie, Hydrogeological Studies on the Origin of High Nitrate Content in Well Waters in the Federal Republic of Germany, Proc. Groundwater Quality Control and Management Seminar, Brussels, November 4 - 8, 1974.
- 5 Y. Bar-Yoseph, Salinity Problems in the Yarkon Tanninim Aquifer, Report No. 01/75/37 Tahal, Israel, 1975, (in Hebrew).
- 6 K.D. Schmidt, Water Quality Variations for Pumping Wells, Ground Water, 15(1977)130-137.
- 7 C.C. Davison and J.A. Vonhof, Spatial and Temporal Hydrochemical Variations in a Semiconfined Buried Channel Aquifer. Esterhazy, Saskatchewan, Canada, Ground Water 16(1978)341-351.
- 8 Y. Kanfi and D. Ronen, The Chemical Quality of Groundwater in the Coastal Plain Aquifers of Israel, Report No. 76/1, Water Commissioner's Office, Israel, 1976, (in Hebrew).
- 9 P.G. Saffigna and D.R. Keeney, Nitrate and Chloride in Groundwater Under Irrigated Agriculture in Central Wisconsin, Ground Water, 15(1977)170-177.
- 10 R.C. Ward, J.C. Loftis, K.S. Nielsen and R.D. Anderson, Statistical Evaluation of Sampling Frequencies in Monitoring Networks, Journal WPCF, 51(1979)2292-2300.
- 11 M. Ben-Tzvi, D. Blanck and S. Aberbach, Design of a Network for Groundwater Quality in "Mekorot's" Wells, Tahal, Israel, 1979, (in Hebrew).