

**A "TIME ZERO" PRESERVATION STUDY
OF TWENTY-EIGHT TRACE METALS,
MAJOR IONS AND NUTRIENTS**

by

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ABSTRACT

The centralization of the Water Quality Branch (WQB) laboratories has involved longer time periods between sample collection and sample analysis. If the data generated by the consolidated laboratory are to be reliable, it is essential that the sample preservation techniques currently in use be thoroughly evaluated and modified where required.

This study investigates in detail the true "time zero" preservation, where the activities were planned and coordinated to minimize the time gap between sample collection and analysis. Twenty-eight key heavy metals, major ions and nutrients were so studied. It was shown that Ag, Ba, Cd, Cr, Co, Cu, Fe, Mn, Li, Sr, Ni, Pb, Zn, Na, K, Ca, Mg, hardness, SO₄, Cl, F, alkalinity, DOC and SRP are stable up to 90 days from the actual sampling time. Ammonia, TKN and NO₃ & NO₂ are stable up to about two and a half weeks.

EXECUTIVE SUMMARY

The centralization of the Water Quality Laboratories has involved longer time between sample collection and sample analysis. If the data generated by consolidated laboratory are to be reliable, it is essential that the sample preservation techniques currently in use be thoroughly evaluated and modified where required.

The study of sample preservation techniques involved several phases. In the first three phases, 16 major ions, 11 nutrients and 19 heavy metals were studied, using natural waters collected in the regions and shipped to this laboratory for analysis. However, these waters usually arrived at different times. Thus, sample shipping and synchronizing resulted in a time gap of two-three weeks between sample collection and the first analysis and therefore it was uncertain whether some degradation occurred during this time interval. The present study addresses this issue in detail. Water samples were prepared and analyzed for key parameters immediately after sample collection. Twenty-four key parameters, namely, Ag, Ba, Cd, Cr, Co, Cu, Fe, Mn, Li, Sr, Ni, Pb, Zn, Na, K, Ca, Mg, hardness, SO₄, Cl, F, alkalinity, DOC and SRP were found to be stable up to 90 days from the actual sampling time. This finding supports the previous conclusions. Furthermore, it was found that ammonia, TKN and NO₃ & NO₂ were also stable if the samples were analyzed within two and a half weeks from sample collection.

SOMMAIRE

En raison de la centralisation des laboratoires de la Direction de la qualité des eaux, il s'écoule maintenant un délai plus long entre le prélèvement des échantillons et l'analyse. Si l'on veut pouvoir se fier aux données produites par le laboratoire unifié, il faut évaluer soigneusement et modifier au besoin les techniques employées à l'heure actuelle pour conserver les échantillons.

Dans la présente étude, les auteurs se sont efforcés de déterminer le délai réel pendant lequel les échantillons peuvent être conservés en planifiant et en coordonnant les activités de manière à réduire au minimum le temps qui s'écoule à partir du prélèvement jusqu'à l'analyse en laboratoire. L'étude a porté sur 28 oligo-éléments, ions majeurs et substances nutritives. Il s'avère que les oligo-éléments Ag, Ba, Cd, Cr, Co, Cu, Fe, Mn, Li, Sr, Ni, Pb, Zn, Na, K, Ca, Mg, la dureté de l'eau, les ions SO_4 , Cl et F, l'alcalinité, les carbone organique dissous et le phosphate réactif soluble se conservent bien jusqu'à 90 jours après la date de prélèvement de l'échantillon. L'ammoniaque, le TKN ainsi que le NO_3 et le NO_2 demeurent intacts pendant une période d'environ deux semaines et demie.

RÉSUMÉ DE L'ÉTUDE

En raison de la centralisation des laboratoires de la Direction de la qualité des eaux, il s'écoule maintenant un délai plus long entre le prélèvement des échantillons et l'analyse. Si l'on veut pouvoir se fier aux données produites par le laboratoire unifié, il faut évaluer soigneusement et modifier au besoin les techniques employées à l'heure actuelle pour conserver les échantillons.

L'étude de la conservation des échantillons s'est déroulée en plusieurs étapes. Au cours des trois premières étapes, les chercheurs ont analysé des échantillons d'eau naturelle recueillis en région et envoyés au laboratoire pour dépister seize ions majeurs, onze substances nutritives et dix-neuf oligo-éléments. Les échantillons ne sont pas tous parvenus au laboratoire en même temps de sorte qu'il s'est écoulé de deux à trois semaines entre le moment où les échantillons ont été prélevés et l'analyse en laboratoire. Par conséquent, on était en droit de se demander si les échantillons s'étaient dégradés au cours de cette période. La présente étude permet de répondre à cette question. Des échantillons ont été préparés et analysés immédiatement après avoir été prélevés. On a pu ainsi déterminer que 24 paramètres clés dont les oligo-éléments Ag, Ba, Cd, Cr, Co, Cu, Fe, Mn, Li, Sr, Ni, Pb, Zn, Na, K, Ca, Mg, la dureté de l'eau, les ions SO_4 , Cl et F, l'alcalinité, le carbone organique dissous et le phosphate réactif soluble se conservent bien jusqu'à 90 jours après la date de prélèvement de l'échantillon. L'étude a en outre révélé que l'ammoniaque, le TKN ainsi que le NO_3 et le NO_2 ne se dégradent pas si les échantillons sont analysés dans un délai de deux semaines et demie après le prélèvement.

INTRODUCTION

Due to laboratory centralization, test samples have to be sent from the various regions across Canada to the Water Quality National Laboratory (WQNL) Burlington, for analysis. In order for the analyses to be meaningful, the sample integrity must be demonstrated. For this, Water Quality Branch/Headquarters requested NWRI to carry out a thorough evaluation of preservation procedures to ensure stability of all parameters.

The objective of the task was to evaluate and improve, where necessary, the existing preservation practices for all parameters that the National Laboratory analyzes. These parameters include trace metals, major ions, nutrients, physical parameters and the whole spectrum of organic constituents.

Three phases of preservation studies have been carried out to date: major ions and physical parameters¹, nutrients and residue² and heavy metals³. In these studies, several regional waters were collected and shipped to this laboratory. The various waters usually arrived at different times. Thus, before the analysis could begin, some time had already elapsed because of the time taken for sample shipping and for synchronizing the week "0" analyses. This time gap, which was about 2-3 weeks, could be critical as far as the degradation of samples is concerned. Therefore, the purpose of this study was to investigate this time gap in detail in order to supplement the previous findings¹⁻³. Thus, in this study, the analyses began

immediately after sample collection and continued for two and a half weeks. As a final step to tie this study to the first three studies, the analyses were also made three months after sample collection. Twenty-eight key parameters of metals, major ions and nutrients were investigated: Ag, Al, Ba, Cd, Cr, Co, Cu, Fe, Mn, Li, Sr, Ni, Pb, Zn, Na, K, Ca, Mg, hardness, SO₄, Cl, F, alkalinity, DOC, SRP, NH₃, TKN, and NO₃ and NO₂.

EXPERIMENTAL

Study Design

The design called for planning and coordinating activities so that the analyses could begin immediately after each of several sample collections. The working definition for each parameter was that the first analyses represented the "true" initial values, whose average was taken as the day "0" value. After the day "0" analyses, the investigation continued daily for one week, then every other day for a week and a half. To harmonize with the previous studies¹⁻³, the final analyses were carried out at day 90.

Sample Preparation and Analytical Schedule

Hamilton Harbour water was chosen to be the model water. Several water collections were made for different groups of parameters by the

Field Operations Unit of the Technical Operations Division using a Van Dorn bottle. Each water sample was poured into a large container with or without an appropriate amount of preservative (see below). Immediately after homogenization, subsampling was made into test bottles and analysis made (about 15 minutes from sampling time).

Test bottles were prearranged into groups of storage time, which corresponded to analysis time as follows: day "0", day 1, 2, 3, 6, 8, 10, 13, 15 and day 90. Each group contained three to six replicate test samples, thus 3 to 6 replicate analyses, depending on the parameters studied.

Preservatives and Chemicals

For major ions and nutrients, the samples were stored without preservative at 4°C until analysis. For all metals except Ag, 0.2% HNO₃ preservative was used. Silver samples were preserved with 0.4 g Na₂ EDTA per 100 mL of water. All chemicals were of reagent grade or atomic absorption standards.

Analysis

"Total" Cd, Cu, Co, Cr, Ni, Zn, Pb, Al, Fe, Mn, Li and Sr were analysed by atomic absorption following a concentration procedure, where 200 mL of each sample was acidified with 4 mL of concentrated HNO₃ and boiled to dryness in a volumetric flask. Two millilitres of

of concentrated HCl was then added to the flask, which was again brought to dryness. Fifteen millilitres of deionized distilled water was then added to dissolve the residue, and this 15 mL concentrate was used for analysis. For each storage time, five test samples and five standards were so digested and analysed.

Fluoride, chloride and sulfate were analysed by automated ion chromatography. Other constituents were determined using the methods described in the Analytical Methods Manual for unfiltered samples⁴; sodium and potassium by automated flame photometry; Ca and Mg by atomic absorption; total alkalinity by the 2-end point titration; dissolved organic carbon (DOC) by infrared carbon analyser; soluble reactive phosphate (SRP) by colorimetry with stannous chloride reduction; ammonia by colorimetry (automated colorimetric phenate); TKN by colorimetry (Berthelot reaction); NO₃ & NO₂ by colorimetry with Cd reduction; "extractable" Ag and "total" Ba by atomic absorption direct aspiration technique.

RESULTS AND DISCUSSION

Criteria for Stability

The working criteria was that for a particular parameter in all the waters studied, if 95% of the data are randomly within 10% of the day "0" mean values, the parameter is considered stable.

Metals

The data for the 14 metals studied are summarized in Table 1 and plotted in Figure 1. All metals except Al show good stability as the results are within $\pm 10\%$ of day "0" values. Aluminum results are erratic, probably because of the Al originally present in the Pyrex flasks used for sample digestion. It is recommended that "extractable" Al rather than "total" Al be measured under these conditions.

Major Ions and Nutrients

Table 2 and Figure 2 summarize the data of the 14 major ions and nutrients studied. Calculations on these data indicate that all the constituents (except NH_3 , TKN, and NO_3 & NO_2) satisfy the stability criteria and thus are stable up to day 90. The NH_3 , TKN, and NO_3 & NO_2 , as Figure 2 clearly indicates, remain stable up to day 15 but drastically change at day 90: ammonia and TKN decrease whereas NO_3 & NO_2 increases. This observation supports a previous conclusion² that, for these parameters, the samples should be analyzed as soon as possible. The increase behaviour was also observed for nitrate species in two other repeat studies at two different times of the year, using ion chromatography. Some analyses were also made between day 15 and day 90, and the data indicated that the nitrate

concentration started to increase after about 2-1/2 weeks of storage. All this suggests that the three constituents should be analysed within two-three weeks of sample collection.

CONCLUSIONS

This study complements the previous investigations¹⁻³ and shows that 24 key parameters (namely, Ag, Ba, Cd, Cr, Co, Cu, Fe, Mn, Li, Sr, Ni, Pb, Zn, Na, K, Ca, Mg, hardness, SO₄, Cl, F, alkalinity, DOC and SRP) are stable up to 90 days from the actual sampling time (time "0"). Ammonia, TKN, and NO₃ & NO₂ are stable up to about two and a half weeks of storage at 4°C. For these parameters it would be best to analyse the samples within two weeks from sample collection. For Al, it is advisable to analyse for "extractable" metal only.

ACKNOWLEDGEMENTS

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2. V. Cheam, A.S.Y. Chau, J. Sherry and K.K. Kwan. Preservation of nutrients and residue in water samples. Being approved.
3. V. Cheam and A.S.Y. Chau. 1985. Preservation of 19 heavy metals in ten regional waters. NWRI Contribution No. 86-82.
4. Analytical Methods Manual. 1981. Inland Waters Directorate, Water Quality Branch, Ottawa.

TABLE 1 "Total" heavy metals data (mean \pm standard deviation of five replicates in ppb).

Metals	Day "0"	Day 1	Day 2	Day 3	Day 6	Day 8	Day 10	Day 13	Day 15	Day 90
Cd	3.3 \pm 0.0	3.3 \pm 0.0	3.24 \pm 0.05	3.28 \pm 0.04	3.34 \pm 0.05	3.26 \pm 0.05	3.28 \pm 0.05	3.26 \pm 0.05	3.18 \pm 0.11	3.05 \pm 0.10
Cu	3.72 \pm 0.04	3.58 \pm 0.16	3.65 \pm 0.06	3.66 \pm 0.09	3.68 \pm 0.08	3.68 \pm 0.04	3.63 \pm 0.15	3.66 \pm 0.05	3.60 \pm 0.14	3.65 \pm 0.17
Co	4.0 \pm 0.0	4.0 \pm 0.0	4.0 \pm 0.0	4.0 \pm 0.0	4.0 \pm 0.0	4.0 \pm 0.0	4.0 \pm 0.0	4.0 \pm 0.0	3.8 \pm 0.3	4.0 \pm 0.0
Cr	9.2 \pm 0.3	9.5 \pm 0.4	9.4 \pm 0.2	9.2 \pm 0.3	9.2 \pm 0.3	9.1 \pm 0.3	9.4 \pm 0.4	9.1 \pm 0.2	9.2 \pm 0.3	10.0 \pm 0.0
Ni	9.4 \pm 0.2	9.3 \pm 0.3	9.4 \pm 0.2	9.5 \pm 0.0	9.0 \pm 0.0	9.3 \pm 0.3	9.4 \pm 0.4	9.1 \pm 0.2	9.0 \pm 0.0	9.9 \pm 0.3
Zn	18.4 \pm 0.2	18.5 \pm 0.0	18.8 \pm 0.3	18.6 \pm 0.4	18.4 \pm 0.5	19.0 \pm 0.0	18.5 \pm 0.4	18.3 \pm 0.4	18.8 \pm 0.3	18.5 \pm 1.0
Pb	13.0 \pm 0.0	13.0 \pm 0.0	13.0 \pm 0.0	13.0 \pm 0.0	12.4 \pm 0.6	12.8 \pm 0.5	12.8 \pm 0.4	12.4 \pm 0.6	12.6 \pm 0.5	13.0 \pm 0.0
Al	63.8 \pm 9.0	53.6 \pm 4.0	56.4 \pm 3.5	54.8 \pm 5.5	64.6 \pm 6.8	56.8 \pm 1.8	59.8 \pm 8.5	63.0 \pm 4.0	60.0 \pm 4.6	57.0 \pm 2.7
Fe	165.0 \pm 0.0	162.2 \pm 3.8	163.3 \pm 3.5	162.7 \pm 4.0	161.5 \pm 4.0	154.3 \pm 7.5	155.8 \pm 11.1	150.3 \pm 6.1	159.5 \pm 11.0	160.0 \pm 0.0
Mn	46.0 \pm 1.0	45.6 \pm 1.3	46.6 \pm 0.9	45.8 \pm 1.5	44.8 \pm 0.4	44.8 \pm 0.5	44.8 \pm 0.5	44.3 \pm 0.5	45.8 \pm 2.0	51.0 \pm 2.2
Li	37.2 \pm 1.8	37.0 \pm 3.0	38.4 \pm 2.9	38.0 \pm 0.0	35.6 \pm 2.2	36.4 \pm 2.2	37.8 \pm 2.5	37.8 \pm 2.5	36.4 \pm 2.2	39.0 \pm 1.2
Sr	128.0 \pm 0.0	121.6 \pm 3.6	129.4 \pm 3.1	128.0 \pm 0.0	127.8 \pm 10.8	126.0 \pm 4.0	126.0 \pm 4.0	123.2 \pm 4.4	126.0 \pm 4.0	125.4 \pm 3.2
Ba, ppm	0.5 \pm 0.0	0.5 \pm 0.0	0.5 \pm 0.0	0.5 \pm 0.0	0.5 \pm 0.0	0.5 \pm 0.0	0.5 \pm 0.0	0.5 \pm 0.0	0.5 \pm 0.0	0.5 \pm 0.0
Ag	34.9 \pm 0.7	36.0 \pm 0.7	34.5 \pm 1.1	34.1 \pm 0.4	34.0 \pm 0.8	32.9 \pm 0.3	32.3 \pm 0.6	32.3 \pm 0.6	32.3 \pm 0.4	32.8 \pm 1.0

(extractable)

TABLE 2 Major ions and nutrients data (mean \pm standard deviation of three to six replicates in ppm).

Consti- tuents	Day "0"	Day 1	Day 2	Day 3	Day 6	Day 8	Day 10	Day 13	Day 15	Day 90
Na	27.7 \pm 0.2	27.9 \pm 0.4	27.9 \pm 0.2	27.5 \pm 0.1	27.8 \pm 0.0	28.9 \pm 0.1	28.5 \pm 0.3	28.5 \pm 0.2	28.3 \pm 0.1	28.5 \pm 0.8
K	4.00 \pm 0.06	4.08 \pm 0.07	4.03 \pm 0.05	4.01 \pm 0.04	4.04 \pm 0.01	3.93 \pm 0.01	3.87 \pm 0.04	4.02 \pm 0.02	4.05 \pm 0.05	3.87 \pm 0.03
Ca	50.0 \pm 0.0	50.0 \pm 0.0	50.0 \pm 0.0	50.0 \pm 0.0	50.0 \pm 0.0	50.0 \pm 0.0	50.0 \pm 0.0	50.0 \pm 0.0	50.0 \pm 0.0	51.2 \pm 0.8
Mg	10.8 \pm 0.0	10.8 \pm 0.0	10.8 \pm 0.0	10.8 \pm 0.0	10.8 \pm 0.0	10.8 \pm 0.0	10.8 \pm 0.0	10.8 \pm 0.0	10.8 \pm 0.0	11.0 \pm 0.0
Hardness,										
CaCO ₃	169.3 \pm 0.0	169.3 \pm 0.0	169.3 \pm 0.0	169.3 \pm 0.0	169.3 \pm 0.0	169.3 \pm 0.0	169.3 \pm 0.0	169.3 \pm 0.0	169.3 \pm 0.0	173.1 \pm 2.1
SO ₄	54.9 \pm 0.9	55.9 \pm 0.5	55.2 \pm 0.6	56.1 \pm 0.3	54.5 \pm 0.2	55.9 \pm 0.5	55.8 \pm 0.3	55.8 \pm 0.2	55.2 \pm 0.8	55.1 \pm 0.5
Cl	55.2 \pm 0.5	54.9 \pm 0.2	56.1 \pm 0.4	54.8 \pm 0.2	55.1 \pm 0.2	55.2 \pm 0.6	54.7 \pm 0.1	54.7 \pm 0.2	55.0 \pm 0.2	55.1 \pm 0.2
F	0.449 \pm	0.455 \pm	0.459 \pm	0.451 \pm	0.448 \pm	0.447 \pm	0.466 \pm	0.467 \pm	0.457 \pm	0.483 \pm
	0.019	0.017	0.007	0.007	0.006	0.014	0.010	0.013	0.018	0.006
Alkalinity,										
CaCO ₃	103.3 \pm 2.2	104.0 \pm 0.0	103.6 \pm 0.9	104.8 \pm 0.5	104.3 \pm 0.5	104.8 \pm 0.5	104.8 \pm 0.5	103.8 \pm 0.5	104.6 \pm 0.9	100.1 \pm 0.5
DOC	3.0 \pm 0.0	3.1 \pm 0.1	2.9 \pm 0.1	2.8 \pm 0.1	2.9 \pm 0.1	3.0 \pm 0.1	3.0 \pm 0.0	3.1 \pm 0.1	2.8 \pm 0.2	3.1 \pm 0.1
SRP (ppb)	44.7 \pm 1.1	45.5 \pm 1.9	43.4 \pm 1.2	43.2 \pm 0.9	43.5 \pm 0.4	46.9 \pm 3.5	49.2 \pm 3.2	48.9 \pm 0.4	45.3 \pm 2.5	43.8 \pm 0.5
NH ₃	0.64 \pm 0.01	0.65 \pm 0.01	0.66 \pm 0.01	0.65 \pm 0.01	0.64 \pm 0.02	0.67 \pm 0.01	0.65 \pm 0.01	0.63 \pm 0.02	0.57 \pm 0.03	0.06 \pm 0.01
TKN	0.94 \pm 0.06	1.00 \pm 0.07	0.95 \pm 0.04	1.00 \pm 0.05	0.87 \pm 0.03	0.96 \pm 0.05	0.93 \pm 0.02	0.95 \pm 0.04	1.01 \pm 0.03	0.47 \pm 0.07
NO ₃ &NO ₂	2.03 \pm 0.08	1.96 \pm 0.04	1.91 \pm 0.00	1.90 \pm 0.00	1.90 \pm 0.00	1.93 \pm 0.02	1.93 \pm 0.01	1.98 \pm 0.01	1.92 \pm 0.02	2.68 \pm 0.02

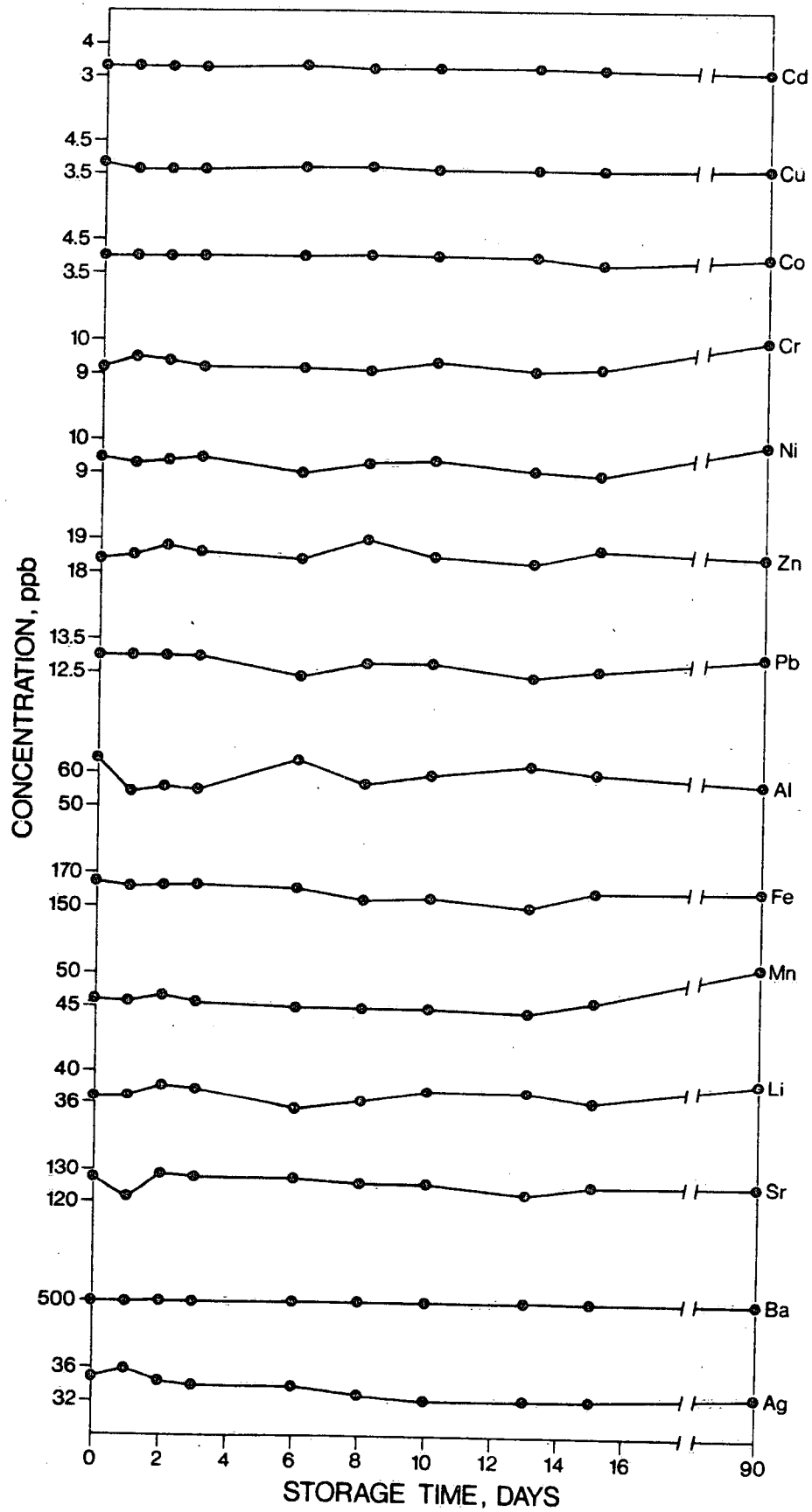


FIGURE 1. METAL STABILITY DATA

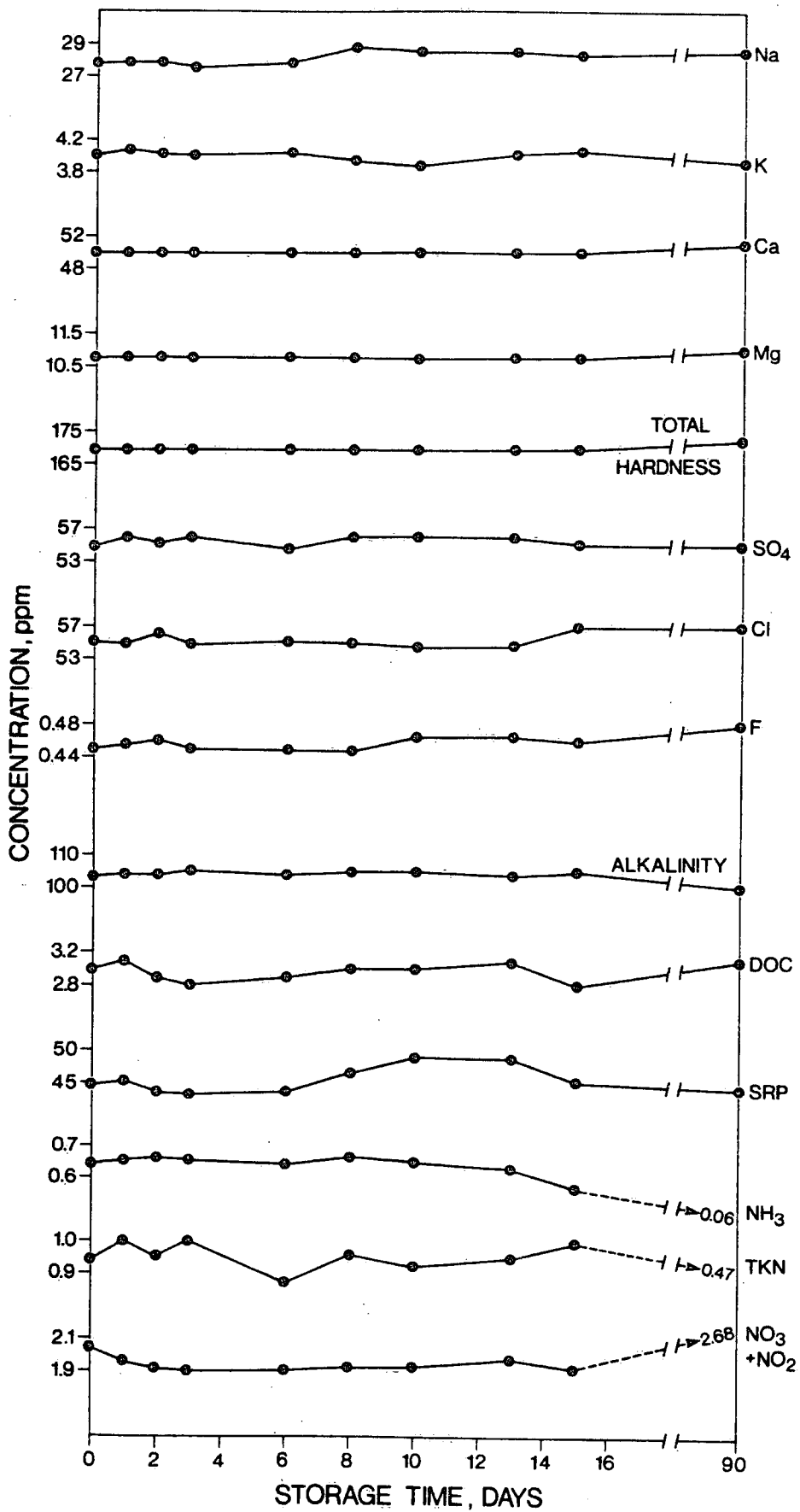


FIGURE 2. MAJOR IONS AND NUTRIENTS STABILITY DATA