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The Stability of Alkalinity, Ca, Magnesium and pH in Lake Water Samples Stored over a Period of Years

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Abstract

Lake water samples collected at various sites in the Canadian Shield were re-analysed in order to determine if loss of Ca and alkalinity had occurred. Storage periods were from 2 to $6\frac{1}{2}$ years. Magnesium and pH also were re-determined. With one possible exception there were no substantial losses of alkalinity, Ca or magnesium. As expected, however, the re-determined pH values on the whole did not agree well with the original data. On the basis of this study it is reasonable to expect meaningful data for Ca, magnesium and alkalinity based on the analysis of stored lake water samples.

Introduction

As part of the National Geochemical Reconnaissance (NGR) Surveys at the Geological Survey of Canada, sediment and water samples have been collected routinely since the mid 1970's at various sites throughout Canada. The most commonly determined constituents in the water samples were uranium, fluoride and pH. In a few areas, more complete analyses were performed (Geological Survey of Canada O.F. 899 and O.F. 900; 1984) In the mid-1980's, Ca, magnesium and alkalinity were added to the list of commonly determined constituents in lake waters collected in certain areas.

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The addition of these three parameters was in support of geochemical exploration needs as well as acid rain studies; alkalinity has a strong influence in the stability of uranium in water, (Cameron, 1980). Alkalinity also tends to promote the precipitation of hyous iron and hydrous manganese oxides which in turn co-precipitate Cu, Zn, and certain other base metals, (Cameron, 1978). Quartz-carbonate gold deposits, which are the principal mineral resource of the Canadian Shield, are enclosed by primary haloes of carbonate minerals. In favourable circumstances this may be reflected in the alkalinity of nearby lake waters. Unfortunately the presence of carbonate till around quartz-carbonate gold deposits tends to negate the usefulness of alkalinity in lake water samples as a pathfinder for these types of gold deposits.

The measurement of these three new constituents produced useful information relative to the buffering capacity of lake waters in the Canadian Shield. As a result, it was decided to extend the coverage by analysing "old" water samples which had been stored for a number of years. This would be feasible provided that there were no losses of Ca and alkalinity (bicarbonate) through the precipitation of $CaCO_3$ from lake water samples. Hence a small study was initiated to determine if there were losses of Ca, Mg or alkalinity in water samples stored for various periods of time.

Suites of lake water samples were selected where Ca, Mg and alkalinity had been measured previously. The water samples examined were collected in 1982, 1983, 1986 and 1987. In March, 1989 these

samples were re-analysed for these three parameters as well as pH. The original methods of analysis and those used in 1989 are listed below.

Constituent	Analytical Method	
	Original Analysis	1989 Analysis
Ca	AAS with buffer solutions in 1982 and 1983. ICP-ES in 1986 and 1987	ICP-ES
Magnesium	Same as Ca	ICP-ES
Alkalinity	Titration to pH 4.5 with 0.01 N H_2SO_4	Same as original analysis
pH	Combination glass-calomel electrode	Same as original analysis

AAS: Atomic Absorption Spectrometry
ICP-ES: Inductively-Coupled Plasma Emission Spectrometry

Since the main purpose of this study was to determine if there were losses of Ca and alkalinity during storage, individual samples were selected on the basis of the concentrations of these two constituents. Efforts were made to examine as broad a concentration range as possible. In a few instances there was only enough water sample stored in the bottle to determine Ca and Mg.

One of the problems encountered in this type of comparison is the fact that the differences between the original and 1989 data represent not only possible precipitation of $CaCO_3$ but also the year-to-year interlaboratory precision. For this reason samples with a broad range of concentrations of Ca and alkalinity were selected on the premise that the differences for lower

concentrations of Ca and alkalinity would not be attributable to $CaCO_3$ precipitation but would be a true measure of analytical precision. Skewing of the data for higher Ca or alkalinity values towards the x-axis (original analysis) could be indicative of the precipitation of $CaCO_3$. Sympathetic skewing of both Ca and alkalinity would reinforce the precipitation theory. As a further test, the saturation index was calculated for those samples collected in 1982 which have been analysed for all the major cations and anions.

The original data and the 1989 data for the re-analysed samples are presented in Figures 1, 2, 3 . . . 14, 15 and 16 as scatter plots along with the linear regression line. The regression coefficients, b and a (slope and y-intercept respectively) for all data sets are presented in Tables 1, 2, 3 and 4. The general equation is $y = bx + a$. The coefficient of determination, r^2, indicates the quality of fit achieved by the regression. Values of r^2 close to 1 indicate a better fit than values close to zero. The term n is the number of samples re-analysed from a particular year.

Discussion of Results

Alkalinity

Figures 1, 2, 3, and 4 are scatter diagrams of original alkalinity data vs. re-analysed alkalinity data, (Table 1); all data are expressed as ppm $CaCO_3$. With one exception (Figure 1) there are no obvious losses of alkalinity when samples are re-analysed in 1989. In Figure 1, one sample deviates substantially

from the regression line. Also because of its location, at the high concentration end of the data set, this one sample applies considerable leverage on the regression line. If this one point is deleted from the calculation there is a superior fit for the remaining data. The original linear regression equation is

$$y = 0.96 \ x + 4.93 \qquad (n = 13)$$

By removing the alkalinity data for this one sample (31D 82 1213) the equation becomes

$$y = 1.08 \ x + 0.59 \qquad (n = 12)$$

Of the thirteen 1982 samples re-analysed, twelve appear to be acceptably stable with respect to alkalinity after $6\frac{1}{2}$ years of storage. The one outlier will be examined in more detail later. The samples collected in 1983, 1986 and 1987 also appear to be acceptably stable.

Calcium

Figures 5, 6, 7 and 8 are scatter diagrams of the original Ca data plotted against the re-analysed Ca data, (Table 2). The four plots suggest that the bulk of the variance between the original data is of analytical origin since there are no substantial losses of Ca which would be indicative of precipitating $CaCO_3$. The Ca concentration for sample number 31D 82 1213 is also at the high concentration end of the regression line. Unlike the alkalinity, however the Ca value for this sample fits almost perfectly on the regression line; i.e. there is an apparent loss of alkalinity but there is no sympathetic loss of Ca.

Magnesium

The original and re-analysed data for magnesium (Table 3), are depicted in scatter plots, Figures 9 to 12. For the bulk of the data, the values cling fairly closely to the regression line. In Figure 12, two points appear to be outliers although they are on opposite sides of the regression line and tend to offset one another. For these two points there are no corresponding changes in alkalinity or Ca. Since $MgCO_3$ is almost seven times as soluble as $CaCO_3$ in water, one would not expect that conditions could favour the precipitation of $MgCO_3$ without precipitation of $CaCO_3$. Hence the deviations from the linear regression lines are most likely of analytical origin. The Mg value for sample 31D 82 1213 is quite close to the regression line.

pH

The scatter diagrams for pH (Table 4) are shown in Figures 13 to 16. In Figures 13, 14 and 15 there is considerable variance relative to the regression lines. This is especially true for original values between pH 6 and pH 8. To a certain extent this is reflected in the term r^2, the coefficient of determination for the various regression equations. The pH data for samples collected in 1983 Figure 14 give a value of 0.13 for r^2. The addition of a single synthetic point with coordinates 4.0 and 3.4 (1983 and 1989 pH data respectively) produces a value of 0.96 for r^2. Hence the mutual proximity of the six points in Figure 14 tends to produce the low value for r^2. In Figure 13, a single point A causes a

substantial shift in the regression line which is plotted in this figure both with and without point A. Although one can rationalize the lower values for r^2, overall, there is rather poor agreement between the original and the reanalysed pH values for samples collected in 1982, 1983 and 1986. The pH data for samples collected in 1987 exhibit fairly good agreement; however the data for this set have bunched above the 45° line whereas most of the data for the remaining samples have accumulated below the 45° line. The results of the pH measurements merely reinforce what has been known for many years; i.e., pH measurements on stored water samples are unreliable.

Saturation Index

The saturation index of a water sample is the difference between the measured pH and pHs. The pHs is a calculated pH at which, without change in total alkalinity and Ca content, a water would be in equilibrium with solid Ca carbonate. By convention

$$\text{Saturation Index} = pH - pHs$$

The measurement of pHs requires analytical data for the total dissolved solids, Ca, alkalinity and the temperature of the sample. There are a number of methods available for calculating pHs: Langelier (1936), Hoover (1938), Hirsch (1942). A method described by Thomas (1953) was used in this study.

Since the samples collected in 1982 had data (Ca, Mg, Na, K, SO_4, Cl, NO_3, alkalinity) from which the total dissolved solids could be estimated, it was felt that a reasonable estimate of the

saturation index could be obtained by assuming that the temperature at which the pH was measured was 23°C (74.4°F) since this parameter was not measured when the pH was recorded in the laboratory.

The saturation indices for all of the water samples collected in 1982 are listed in Table 5. If the pH is greater than the pHs (pH - pHs > 0.00) the water will have a tendency to deposit $CaCO_3$. If the converse occurs (pH - pHs < 0.00), the water will have the potential to dissolve $CaCO_3$. An examination of Table 5 reveals that in all instances except one (sample 12D 82 1213) the saturation indices are negative which implies that all these samples except the one in question will not have a tendency to precipitate $CaCO_3$. Sample 13D 82 1213 however does have a positive saturation index for the original data which indicates that it had the potential to precipitate $CaCO_3$ (see Figure 1). On the basis of the re-analysed data, this tendency has disappeared.

Purists could argue with some veracity that the use of the saturation index under these conditions is not valid for the following reasons:

1. The pH and temperature should be measured in situ, not in the laboratory.

2. The magnitude of the saturation index is very dependent on temperature. The assumption of a specific temperature (23°C) at which the measurements were made can produce an error which would invalidate the measurement.

The rebuttal to these two arguments would be as follows:

1. The saturation index is used to determine if a particular source of water has the potential to precipitate $CaCO_3$ at any time. In this particular study, we are interested in the potential of a water to precipitate $CaCO_3$ after the original measurement, not after the time of collection. Hence the use of sample site temperature and pH would not be relevant in this particular study.

2. The samples were stored and measured at room temperature and 23°C (73.4°F) would seem to be a reasonable estimate. In the case of sample number 31D 82 1213, the temperature would have to drop to less than 40°F (4.5°C) before a negative saturation index could be achieved. Hence the positive saturation index is valid in this one instance.

In order that the reader may have an appreciation of the repeatability of the analyses done in 1989, precision data for alkalinity, Ca, magnesium and pH in three control samples are presented in Table 6.

Conclusions

With the exception of one questionable sample, the stability of alkalinity, Ca and magnesium in lake waters appears to be quite acceptable even over a period of several years. The storage of water samples however has a considerable impact on the pH measurement. The greatest variation seems to be around pH 7 ± 1.

In the case of sample 31D 82 1213, two parameters (alkalinity and saturation index) suggest that $CaCO_3$ has precipitated and one parameter (Ca) suggests that the precipitation did not occur.

On the basis of this study, it is feasible to determine Ca, magnesium and alkalinity in lake water samples after several years of storage.

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NOTE: In Tables 1, 2, 3 and 4 and in all Figures, the 1989 re-analysed data are always on the y-axis.

The general equation for the regression lines is y = bx + a.

Table 1

Regression Lines for Alkalinity: original data
vs. 1989 re-analysis data

	b	a	r^2	n
Alkalinity '82	0.96	4.93	0.98	13
Alkalinity '83	0.95	7.69	0.99	6
Alkalinity '86	1.08	-1.66	1.00	15
Alkalinity '87	1.09	1.33	1.00	17

Table 2

Regression Lines for Ca: original data
vs. 1989 re-analysis data

	b	a	r^2	n
Ca '82	0.86	0.29	0.99	13
Ca '83	0.92	0.89	1.00	10
Ca '86	0.91	0.41	1.00	16
Ca '87	1.07	-1.62	0.99	17

Table 3

Regression Lines for Magnesium: original data
vs. 1989 re-analysis data

	b	a	r^2	n
Mg '82	0.91	-0.12	0.97	13
Mg '83	0.92	0.10	0.99	10
Mg '86	1.12	-0.11	1.00	16
Mg '87	1.01	0.06	0.99	17

Table 4

Regression Lines for pH: original data
vs. 1989 re-analysis data

	b	a	r^2	n
pH '82	0.77	1.17	0.75	13
pH '83	0.98	-0.54	0.13	6
pH '86	0.81	0.78	0.90	16
pH '87	1.05	-.24	0.97	17

Table 5

Saturation Indices of Water Samples Analysed in 1982 and 1989

Sample Number	Saturation Index 1982	Saturation Index 1989
31D 82 1201	-5.84	-5.67
31D 82 1207	-2.32	-3.36
31D 82 1210	-4.05	-4.55
31D 82 1212	-3.18	-3.99
31D 82 1213	+0.40	-0.20
31D 82 1220	-1.62	-2.46
31D 82 1226	-0.23	-0.77
31D 82 1227	-0.37	-0.90
31D 82 1228	-0.35	-0.27
31D 82 1230	-1.42	-2.04
31D 82 1231	-0.54	-1.16
31D 82 1240	-1.23	-1.59
31D 82 1242	-1.28	-1.74

Table 6

Control Sample Precision

Sample Number	Alkalinity (as ppm $CaCO_3$)		Ca (ppm)		Mg (ppm)		pH	
	$\overline{X}$	σ	$\overline{X}$	σ	$\overline{X}$	σ	$\overline{X}$	σ
CR-M n=10	38.0	0.0	14.5	0.7	2.3	0.2	6.2	0.1
CR-P n=10	123.	1.	49.0	1.1	3.6	0.3	7.4	0.1
CR-R n=12	36.8	0.7	17.8	0.6	2.2	0.3	6.1	0.1

$\overline{X}$: mean
σ : standard deviation

List of Figures
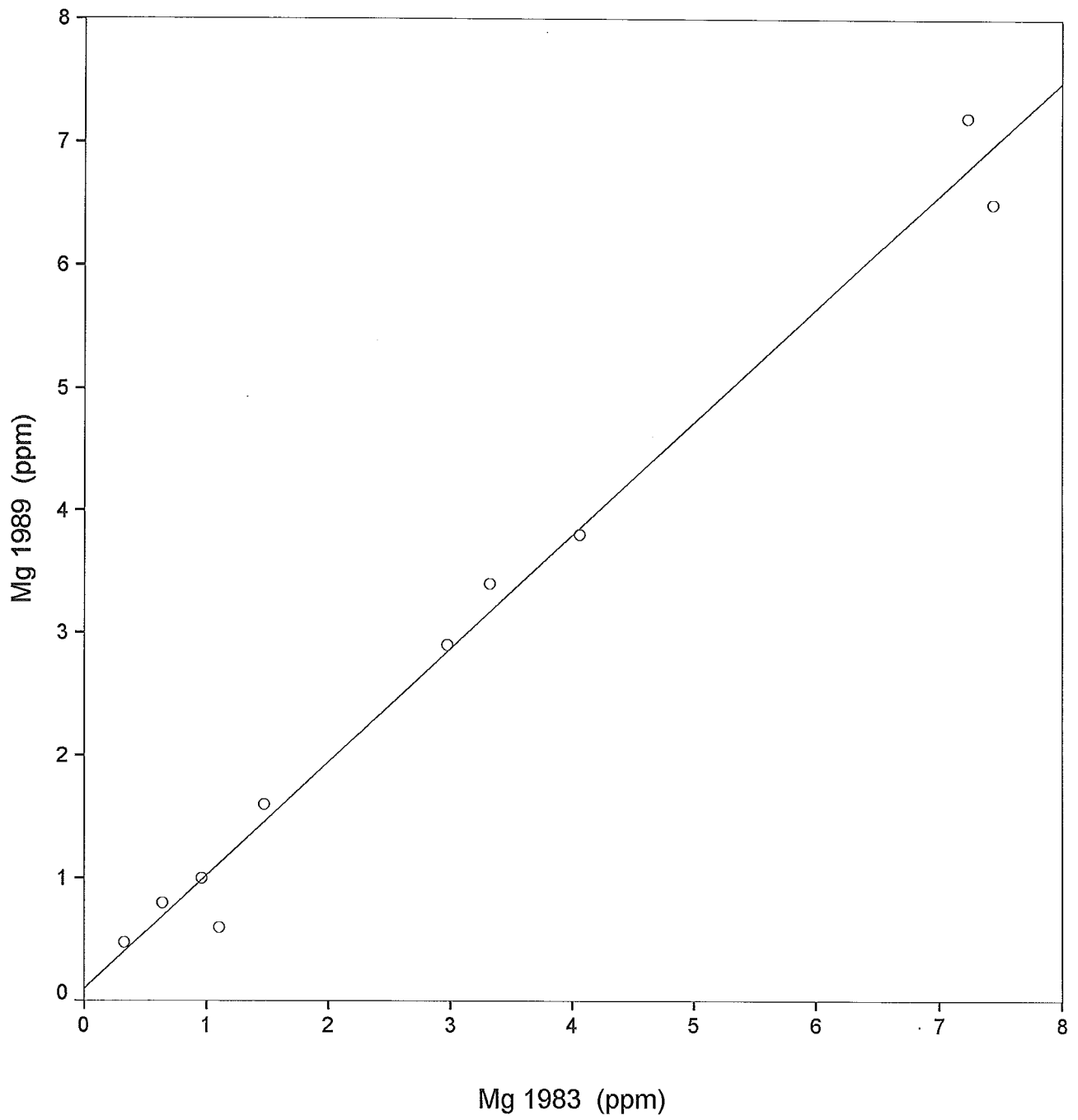
Figure 1

Figure 2

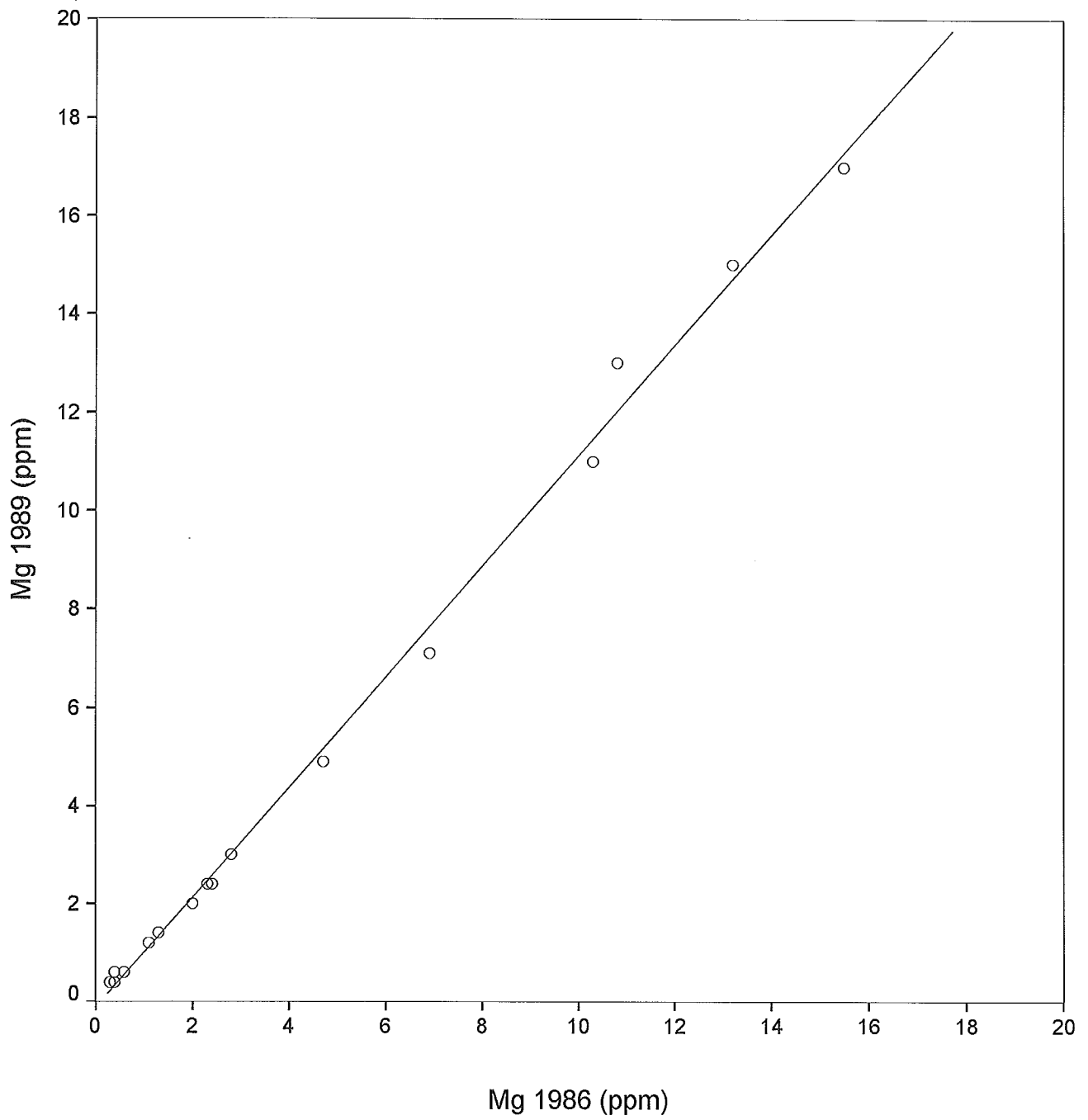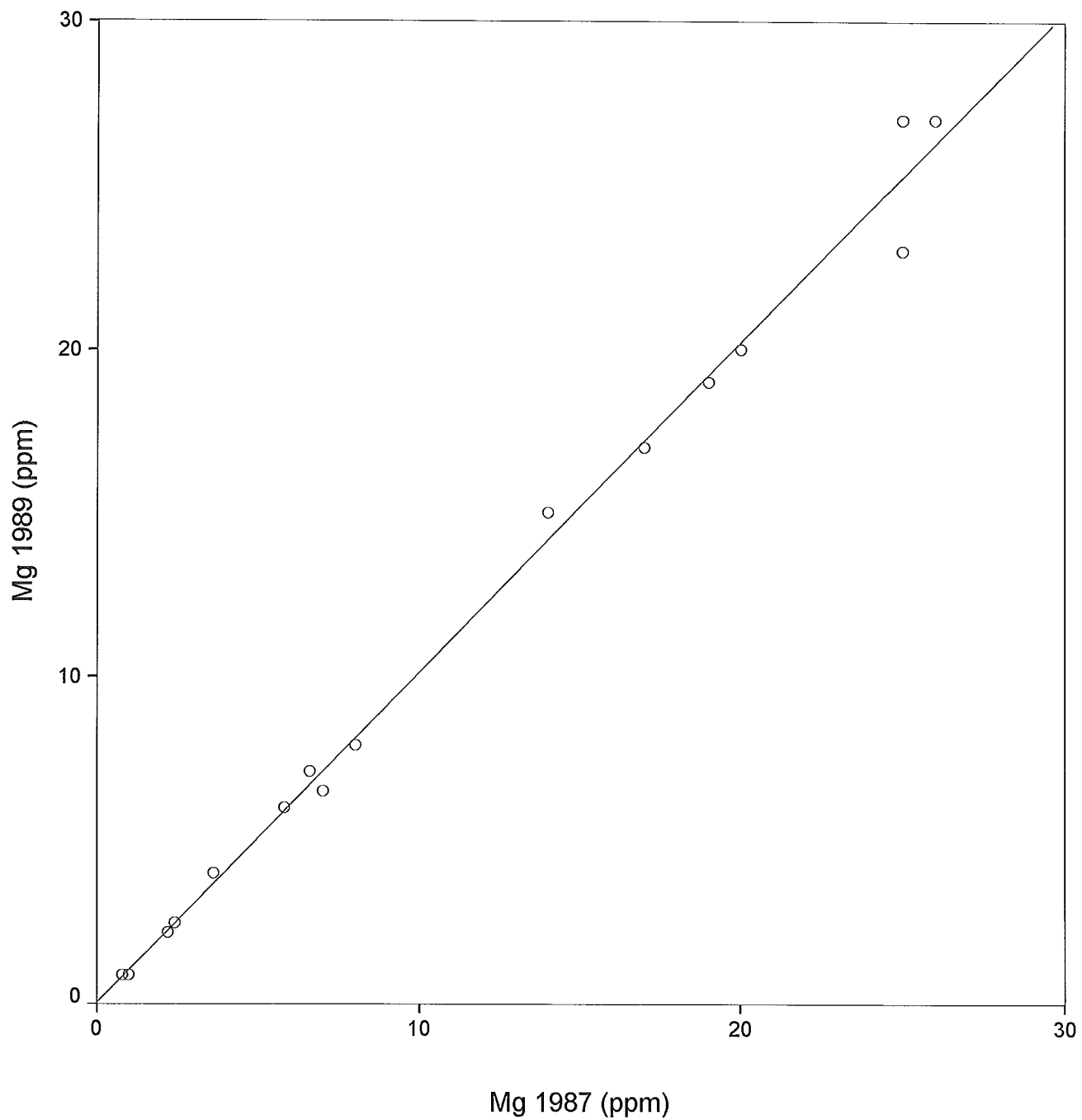Figure 3
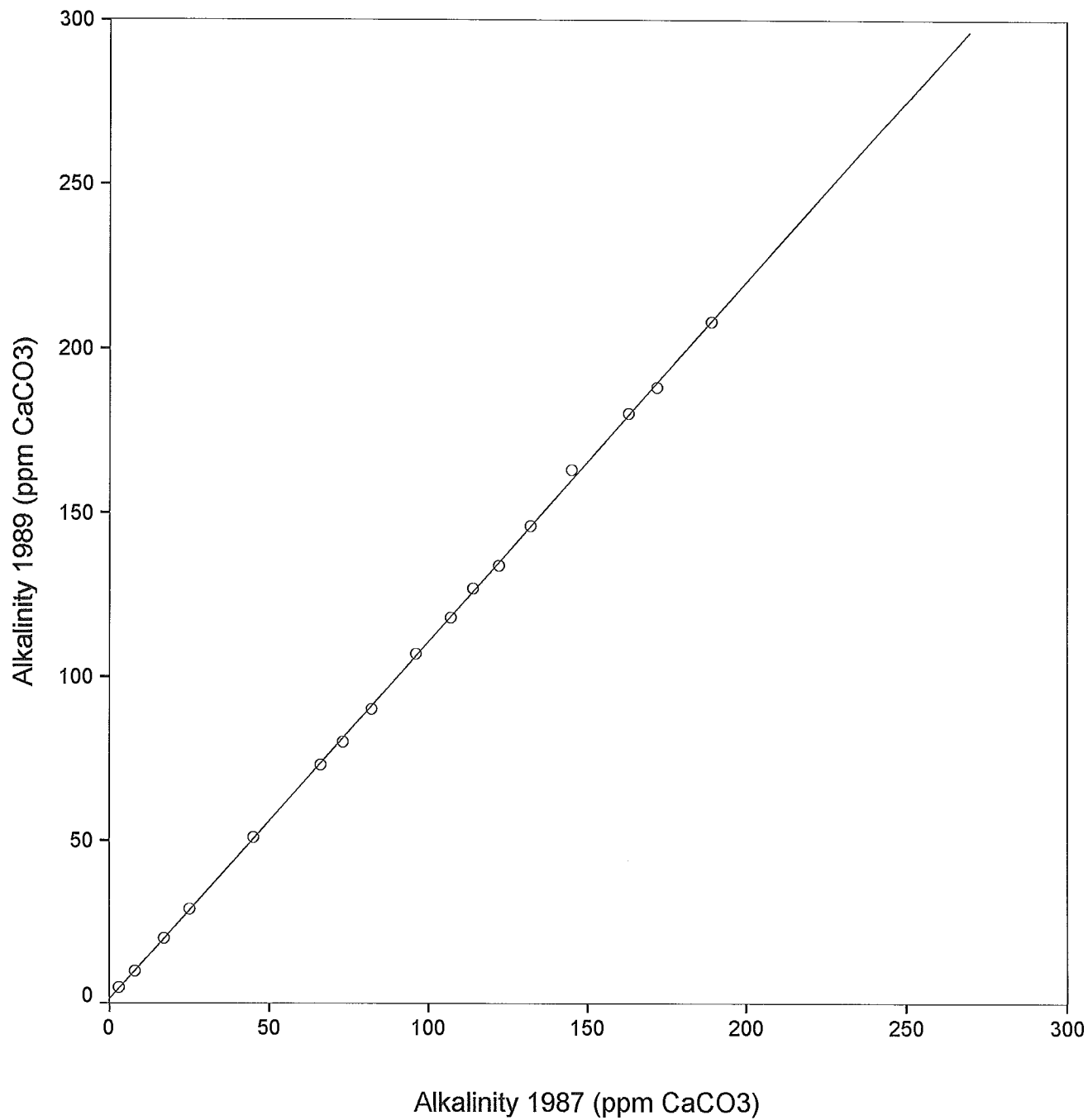
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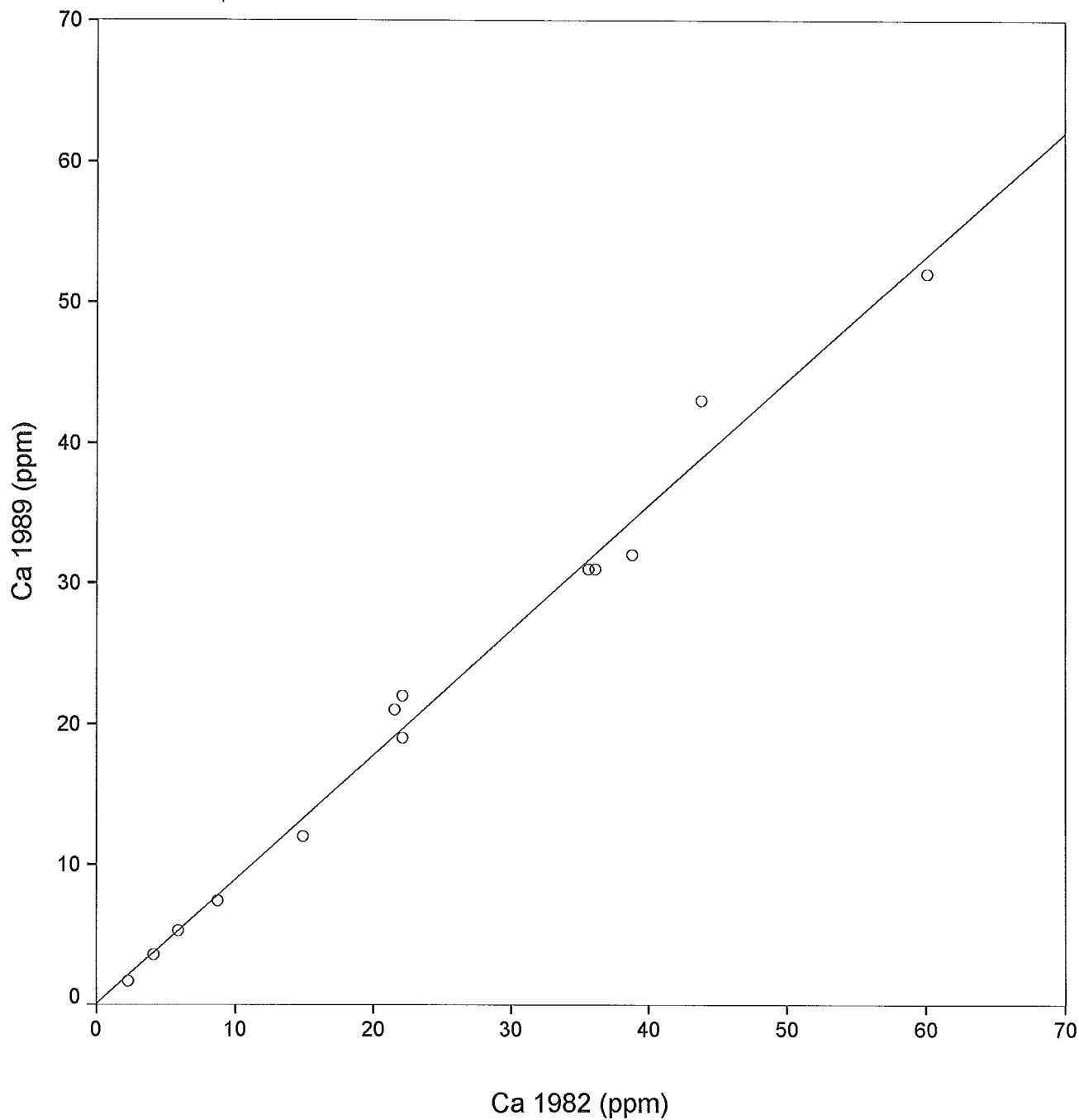
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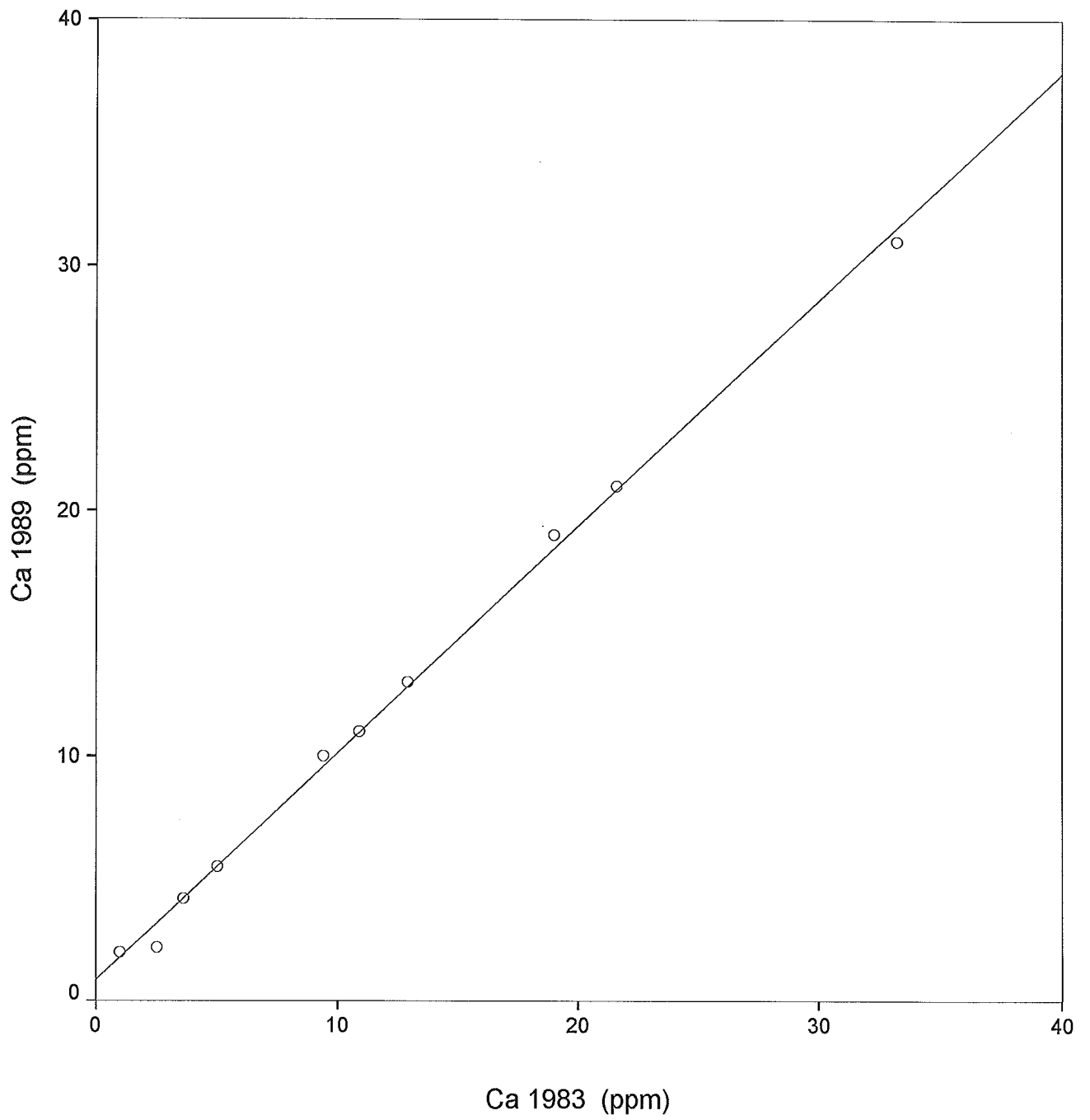
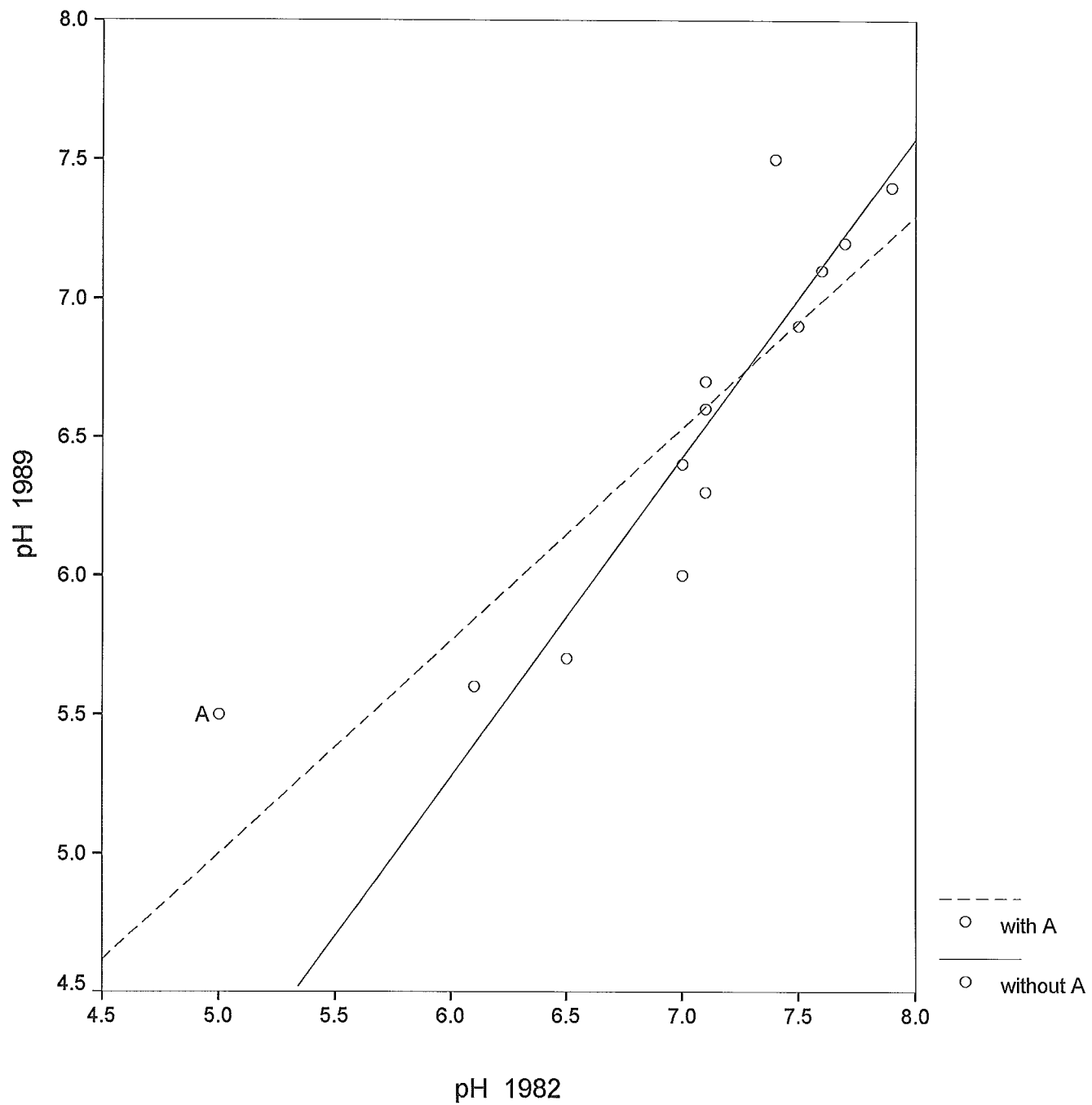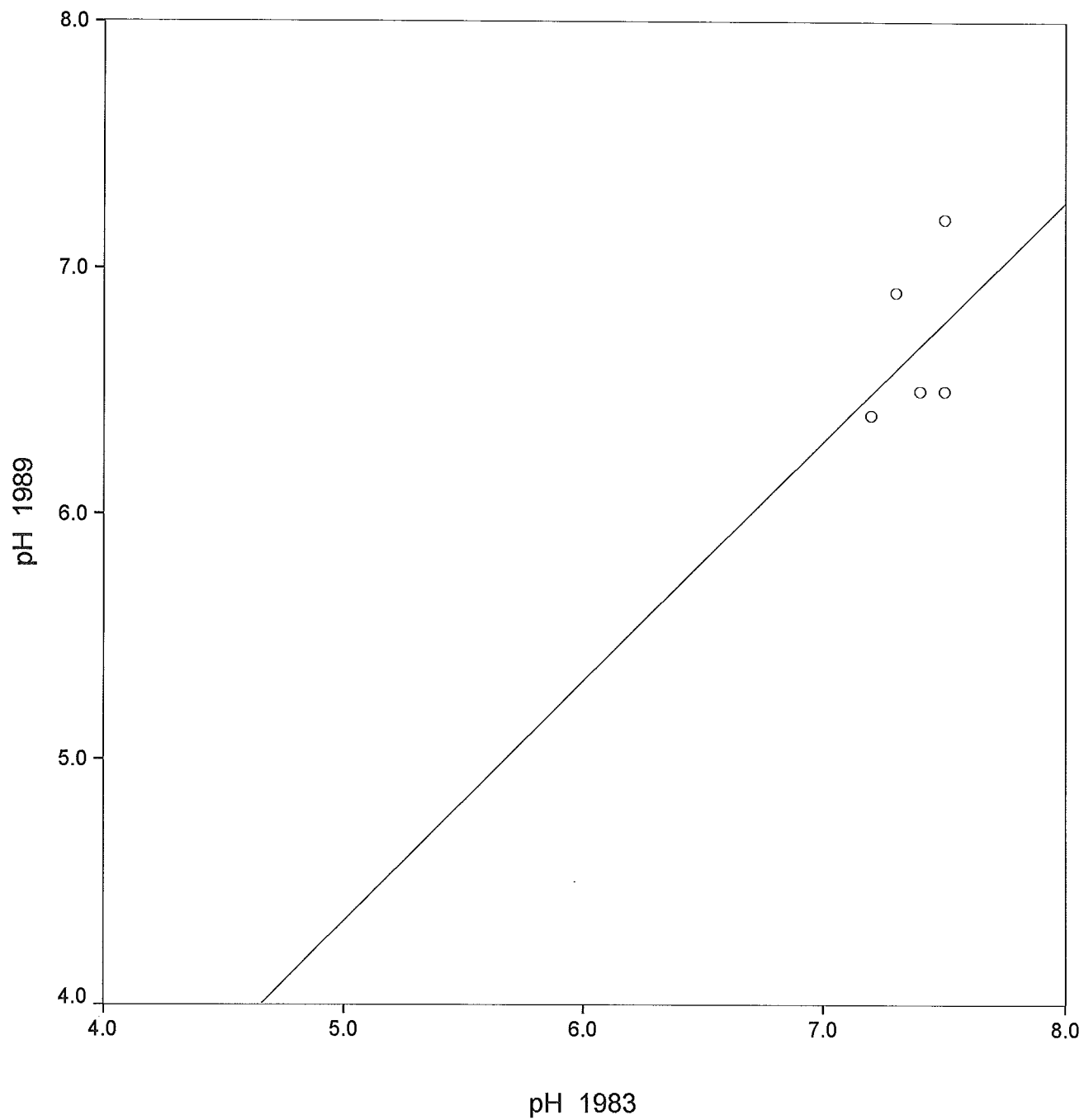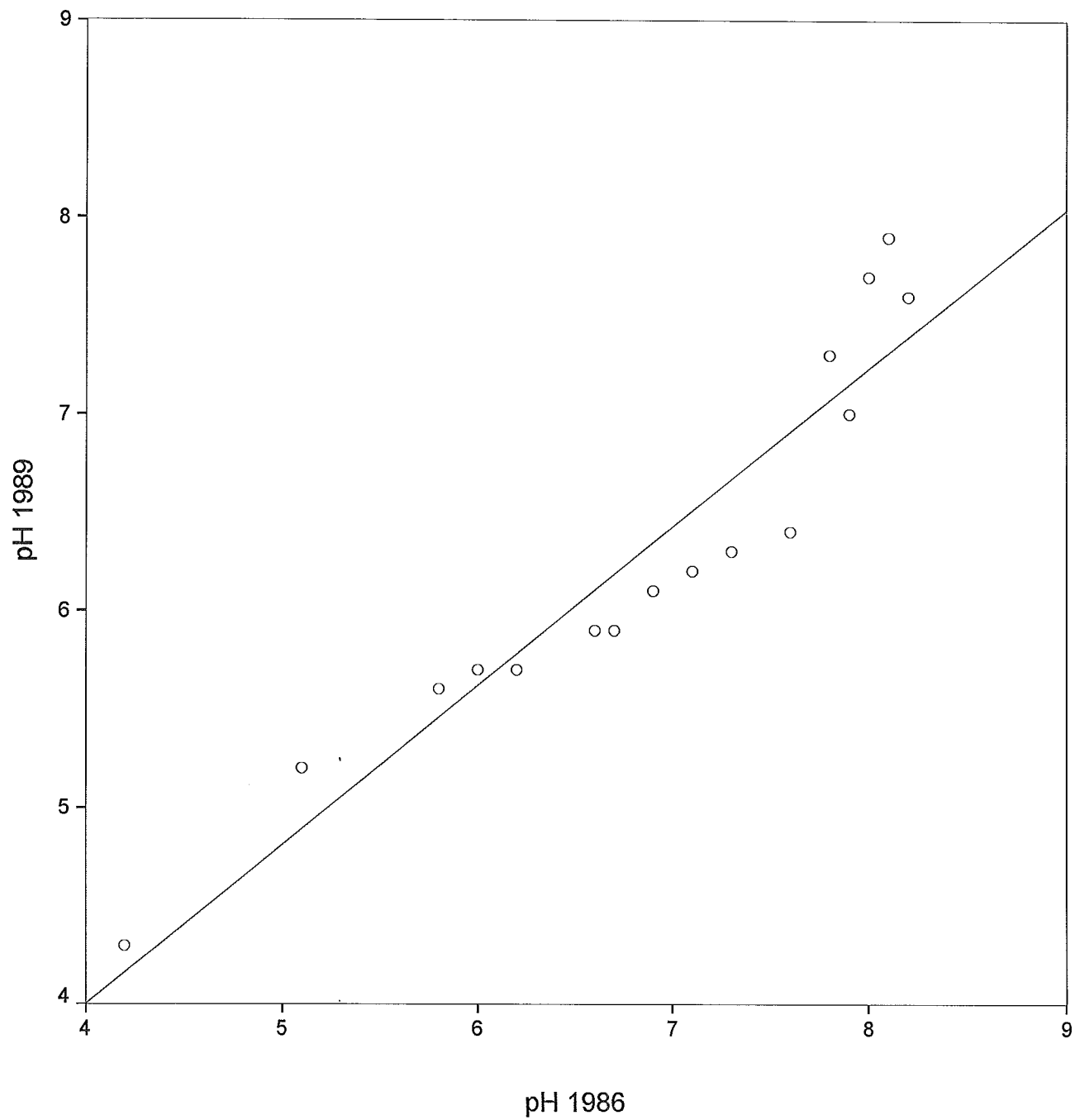Figure 6
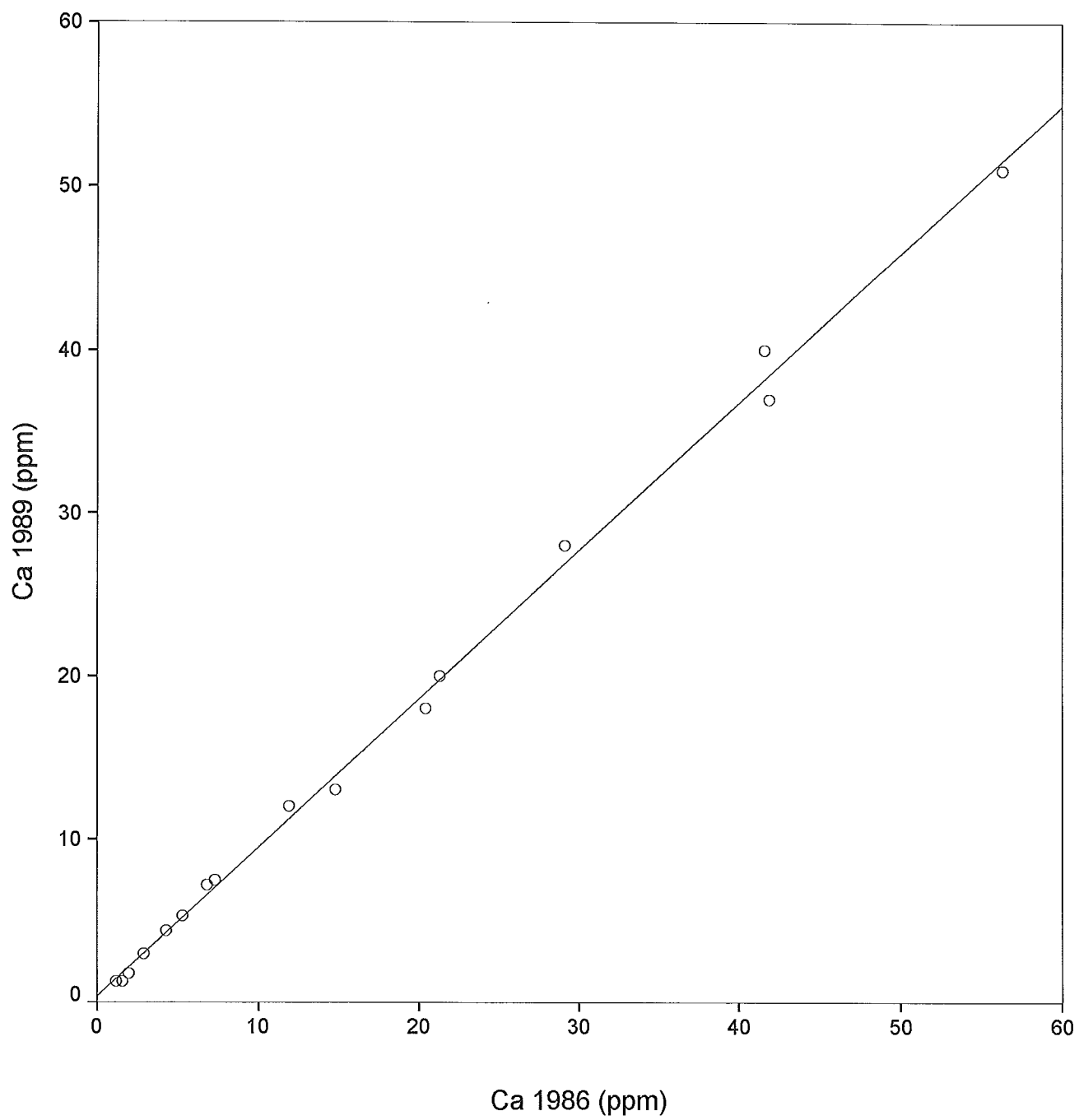
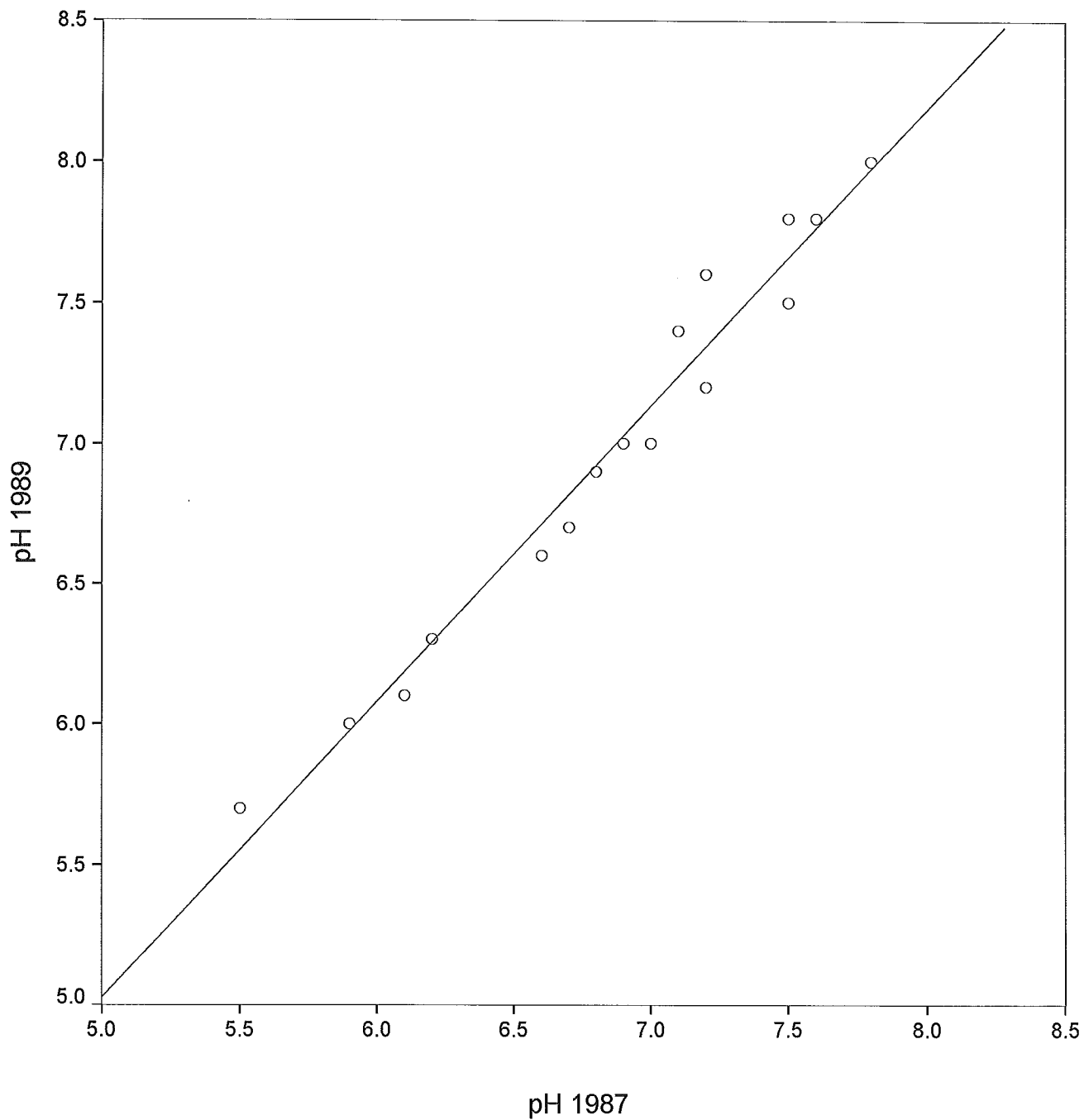Figure 7
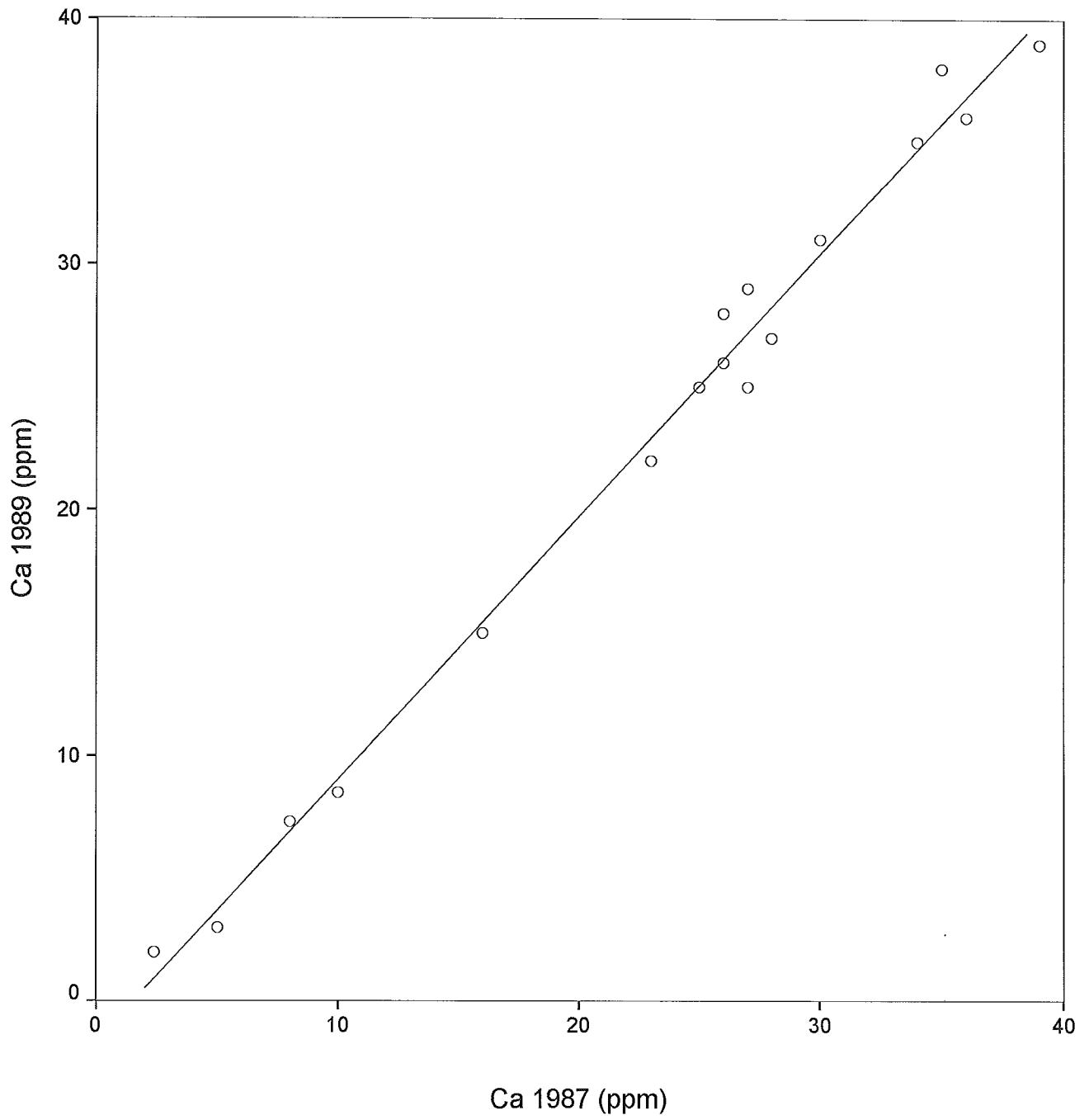
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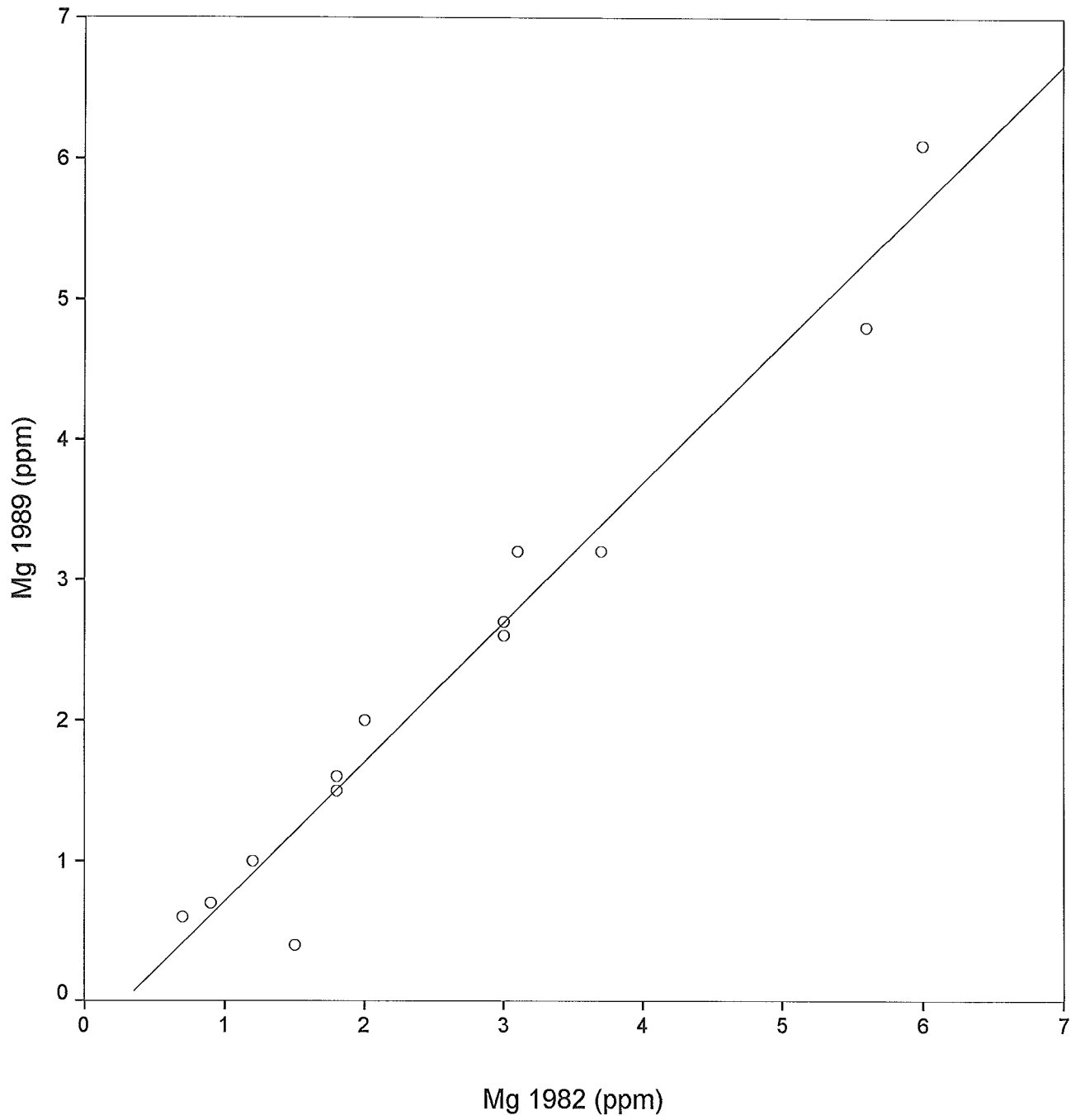
Figure 9

Figure 10

Figure 11

Figure 12

Figure 13

Figure 14

Figure 15

Figure 16