

Geo Hydro Chemical and Isotopic Study of the Effects of Tannery Effluents on the Ground Water Quality in Kasur Area

¹MUHAMMAD NAEEM*, ¹ASRAR AHMED KAZI, ¹SALMA REHMAN AND ²JAVID IQBAL

¹Applied Chemistry Research Center, PCSIR, Labs. Complex, Lahore, Pakistan.

²Institute of Chemistry, University of The Punjab, Lahore, Pakistan.

(Received 20th May 2004, revised 31st May 2007)

Summary: Isotopic technique was employed to study ground water recharge mechanism and the effect of tannery effluents on the quality of ground water in Kasur area. Water samples collected were shallow ground water, deep ground water, canal water, rain water and pond water. The physicochemical parameters (pH, dissolved oxygen and electrical conductivity) were measured in the field while stable isotopes of ²D and ¹⁸O were analyzed by using GD-150 gas source isotope ratio mass spectrometer. Depleted isotopic contents of $\delta^{2}D$ and $\delta^{18}O$ are characterized by canal recharge; enriched isotopic values are associated with rains recharge and intermediate values show the mixing of water from different sources. The shallow ground water had depleted isotopic values and is being recharged by the canal. However, isotopic signature of shallow groundwater in the surroundings of the pond has been modified by the seepage of the pond water. The deuterium excess values show the effect of evaporated pond water and these values increase as the distance from the pond increases. Electrical conductivity values and chloride contents decreased along the depth. The deep groundwater that is termed as the native groundwater is being recharged by rains at piedmont area/ bedrock outcrops. Results indicate that the quality of shallow ground water has been deteriorated in the vicinity of stagnant pond water but quality of deep groundwater is good. Chromium is absent in deep ground water, its penetration is limited up to a maximum depth of 20 m.

Introduction

Groundwater is of major importance to civilization because it is the largest reservoir of drinkable water for human beings. Although groundwater is less contaminated than surface water, pollution of this major water supply has become an increasing concern in industrialized nations. A variety of activities such as industrial waste, septic tank overflow or leakage, agricultural inputs, pesticides and urban waste are the major sources of groundwater pollution. The tannery is one of major industrial sector in Pakistan, which generates considerable amount of polluting materials and is discharging without any treatment into ponds or stagnant pools. The water bodies, recipient of such highly polluted effluents are constantly making their water unfit for its uses in agriculture, industry and drinking. The history and pathway of water in different parts of the hydrological cycle can be followed by the abundance of the stable heavy isotopes of hydrogen called deuterium (²D), and oxygen (¹⁸O) [1]. Atoms with the same number of electrons and protons, but different numbers of neutrons, are called isotopes. It was discovered during the Second World War that isotopes of the same element could be separated by physical and chemical methods. This

discovery provided the basis for the methods of enrichment of the fissionable isotope of Uranium (²³⁵U, meaning that the sum of the number of protons and neutrons is 235) [2]. Hydrogen occurs in the form of three isotopes i.e Hydrogen (¹H), Deuterium (²D) and Tritium (³T), Tritium is unstable but radioactive [3-4]. Oxygen occurs in nature in three isotopic forms i.e which constituents ¹⁶O (99.765% of all oxygen atoms on earth), ¹⁸O (0.1995%) and the even rarer isotope ¹⁷O [5]. The most common isotopes of hydrogen and oxygen are present in molecular form of ¹H₂¹⁶O, H₂¹⁸O, and HD¹⁶O [6-7]. In this way, water in different environments develops isotopic "fingerprints" which help in its identification and tracing of its origin. Environmentally stable isotopes are commonly used in groundwater studies to identify the flow regime and source of recharge mechanism [8-9]. Generally, groundwater retains its stable isotopic composition, unless diluted or mixed with waters of a different isotopic composition or if warmed above 60 °C [10-11]. The stable isotopic composition is very powerful way to trace the history of recharge water in groundwater [12]. In the present study, an attempt has been made with the help of stable isotopic composition along with

*To whom all correspondence should be addressed.

Table-1: The isotopic (^{18}O and ^2D) composition in the ground water of Kasur area.

| S. No. | Sampling Site | $\delta^{18}\text{O}$ (‰) | $\delta^2\text{D}$ (‰) | S. No. | Sampling Site | $\delta^{18}\text{O}$ (‰) | $\delta^2\text{D}$ (‰) |
|--------|-------------------|------------------------------|---------------------------|--------|-------------------------|------------------------------|---------------------------|
| 1 | Canal Water | -9.63 | -45.02 | 14 | Pond Water | -2.13 | -11.03 |
| 2 | Canal Water | -8.64 | -36.04 | 15 | Shallow Ground Water | -8.98 | -39.65 |
| 3 | Canal Water | -7.86 | -43.44 | 16 | Shallow Ground Water | -9.38 | -43.36 |
| 4 | Canal Water | -9.63 | -36.05 | 17 | Shallow Ground Water | -7.92 | -39.36 |
| 5 | Canal Water | -9.02 | -25.8 | 18 | Shallow Ground Water | -9.63 | -46.32 |
| 6 | Canal Water | -8.76 | -36.56 | 19 | Shallow Ground Water | -8.35 | -41.4 |
| 7 | Canal Water | -7.78 | -38.56 | 20 | Shallow Ground Water | -5.64 | -22.29 |
| 8 | Pond Water | 3.45 | -10.56 | 21 | Shallow Ground Water | -4.63 | -25.9 |
| 9 | Pond Water | -1.05 | -10.25 | 22 | Rain Water | -10.45 | -54.36 |
| 10 | Pond Water | 1.9 | -12.3 | 23 | Rain Water | -10.15 | -52.12 |
| 11 | Pond Water | 2.01 | -10.03 | 24 | Rain Water | -9.75 | -60.26 |
| 12 | Pond Water | 3.45 | -9.05 | 25 | Rain Water | -10.27 | -55.36 |
| 13 | Pond Water | -1.02 | -10.5 | 26 | Rain Water | -10.96 | -62.36 |
| 14 | Rain Water | -11.36 | -60.25 | 31 | Deep Ground Water | -11.06 | -54.56 |
| 15 | Rain Water | -10.35 | -58.56 | 32 | Deep Ground Water | -10.96 | -55.96 |
| 16 | Deep Ground Water | -10.56 | -56.02 | 34 | Deep Ground Water | -11.20 | -53.63 |
| 17 | Deep Ground Water | -10.66 | -55.45 | 35 | Deep Ground Water | -9.87 | -61.23 |

physiochemical parameters to investigate the recharge mechanism and source of groundwater pollution in the environment of Kasur areas.

Kasur is situated 60 Km East of Lahore city. A big cluster of 237 tanneries is located at Kasur. The city has a population of approximately 250,000 inhabitants. It is spread over 2335 acres and accommodates tanning operations taking place over a wide area. Tannery units located here process at an average of 8000 hides (cattle, buffaloes) and between 12,000 and 15,000 skins (sheep and goats) each day. Municipal sewage flow is 15-20 cusecs. About 375 Kg toxic chromium is discharged every day in tannery effluents [13]. The unprocessed waste from tanneries is disposed into an open land for the last four to five decades, which has become a big pond. The sewage from the Kasur also joins the tannery effluents. Total discharge of tannery effluents is about 4.25 to 6.1 m³/min [14]. Recently the pond is being gradually diminished.

Results and Discussion

The present study covers only eighteen months period from December, 2001 to May, 2003.

All waters on the earth which have participated in evaporation and condensation have different isotopic ratios of H to ^2D and of ^{16}O to ^{18}O . The isotopic composition of ^{18}O and ^2D changes due to evaporation and condensation. The isotopic composition of all natural waters falls on a straight line, called the meteoric water line [15-16].

The pond water had $\delta^{18}\text{O}$ values in the range of -2.13 to 3.45 % and $\delta^2\text{D}$ values in the range of -9.05 to -12.13 %. The sample Nos. 8 to 14 (Table-1) which were on the periphery of the pond, had heavier isotopes of deuterium than MOSW standard. Deuterium excess values increased as the distance from the pond water decreased. The water entering pond comes from tannery effluent and sewage of Kasur town. Some people have water connections from city water supply tapping deeper zone while the others have installed their own small pumps in shallow ground water. The pond water encounters strong evaporation. This evaporated water penetrates into the shallow ground water because sample Nos. 20 and 21 (Table-1) were taken near the pond and found that heavier isotopes as in pond water.

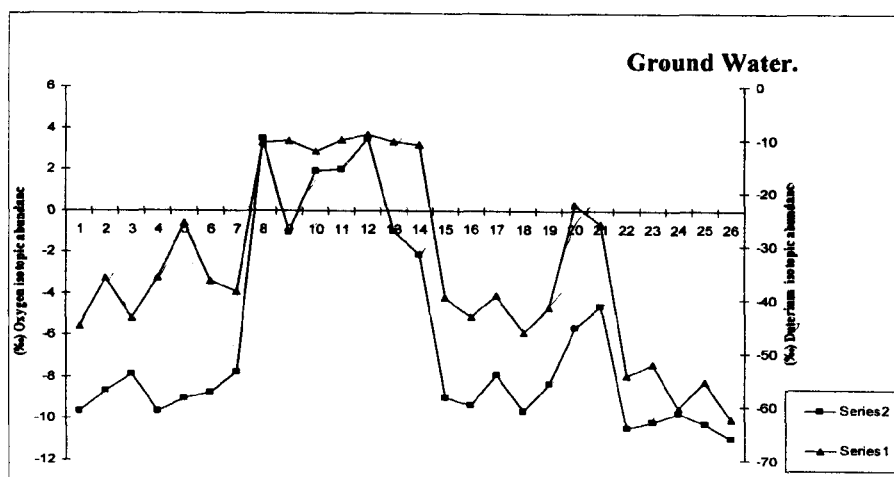


Fig.1. Isotopic abundance in pond canal and shallow ground water

Series-1 Deuterium isotopic abundance
Series-2 Oxygen isotopic abundance

The isotopic index of the canal in the study area was estimated in the range of -7.78 to -9.63 % for $\delta^{18}\text{O}$ and -25.80 to -45.02 % for $\delta^2\text{D}$ and the same range of isotopes of $\delta^{18}\text{O}$ and $\delta^2\text{D}$ was found in shallow ground water have been plotted in Fig. 1. The long term isotopic data of precipitation is not available for the project area. The deep groundwater that can be termed as the native ground water is being recharged by the rains at the piedmont area/ bedrock outcrops. The deep ground water samples were collected from tube wells of water supply schemes of public health engineering department, penetrating up to a depth of 180m, has mean $\delta^{18}\text{O}$ value of -57.61 % and $\delta^2\text{D}$ value of 10.47 %. The isotopic index of rains at the piedmont area was estimated in the range of -9.75 to -11.36 % for $\delta^{18}\text{O}$ and -52.12 to 60.26 % for $\delta^2\text{D}$. The isotopic results of rain water and deep ground water sample Nos. 22 to 35 (Table-1) were collected from project area and plotted in Fig. 2. The $\delta^{18}\text{O}$ values range from -9.87 to -11.25 % and $\delta^2\text{D}$ values range from -54.56 to -61.23 % in the deep groundwater.

The data showing spread of isotopic water suggests that the ground water is being recharged by different sources. Depleted isotopic values correspond to canal recharge, lighter than MOSW standard isotopic values represent rains recharge, highly enriched isotopic values with low deuterium

excess values, show contribution of the pond water and the intermediate isotopic values show the mixing of above mentioned sources in varying proportions. It is evident from the isotopic data that the canal passing through the project area is mainly recharging the shallow groundwater.

Electrical conductivity of groundwater varied from 578 $\mu\text{S}/\text{cm}$ to 10778 $\mu\text{S}/\text{cm}$. Deep ground water had low EC value than the canal water. The EC of pond water varied from 6690 $\mu\text{S}/\text{cm}$ to 20400 $\mu\text{S}/\text{cm}$. Low value of EC of pond water was recorded in August. It may be due to mixing of water from monsoon rains and that is supported by the relatively depleted isotopic values of pond water during same period. The contours of electrical conductivity of ground water have been plotted in Fig. 3. This indicates that contaminants from pond water migrated up to certain depths. Similarly, the data regarding concentration chloride ions shows identical behavior as electrical conductivity. As far the downward penetration of the pollution is concerned, it is limited to a shallow depth. The EC of deep ground water at 180m depth is about 650 $\mu\text{S}/\text{cm}$. Wells penetrating up to a depth of about 40 m (Table-2) had EC values up to a maximum of 2120 $\mu\text{S}/\text{cm}$. It shows that EC decreases rapidly with depth. It is clear that EC of groundwater decreases exponentially with depth. At this location, penetration is restricted up to 40m

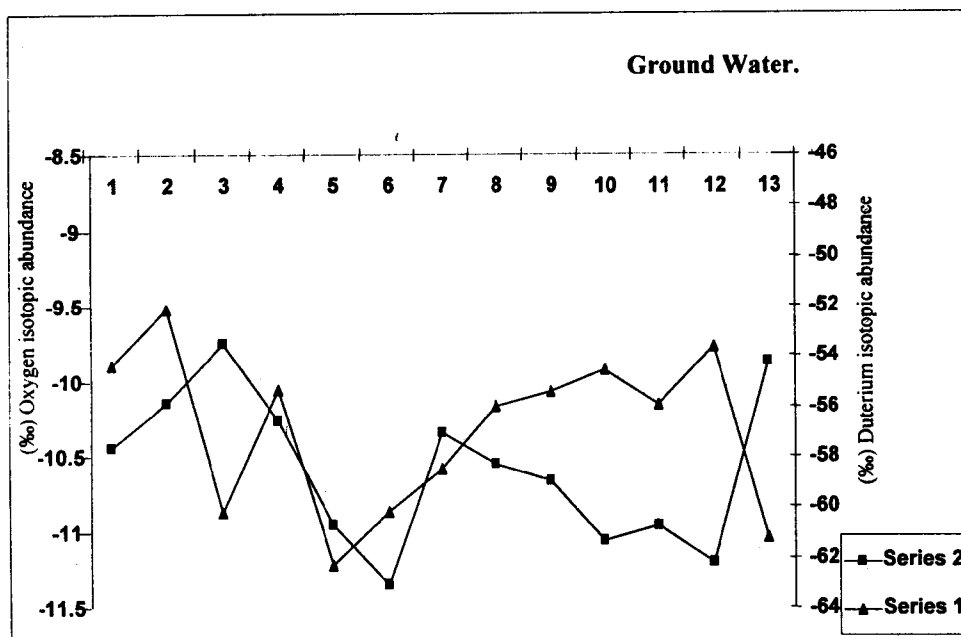


Fig. 2. Isotopic in rains and deep ground water

Series-1 Deuterium isotopic abundance
 Series-2 Oxygen isotopic abundance

But on the other side of the pond, along the plume flow direction, depth of penetration is about 45m. In this area upper soil layer is sandy and extends up to water table.

The pH of ground water samples varies from 6.53 to 8.64. The dissolved oxygen (DO) concentrations for ground water ranged from 1.7mg/ l to 6.7mg/ l, whereas DO of pond water varied from 3.1mg/ l to 5.5mg/l. The temperature of groundwater had minimum value of 20.8°C and maximum 28.9°C. The EC values support the isotopic data. The ground water having contribution

from pond water had low deuterium excess and high EC values. As distance from the pond increased, the EC decreased and deuterium excess values increased. The EC values at sample Nos.1, 2, 3, 4, and 5 (Table-2) were highest and had a decreasing trend away from the pond. This indicates that the maximum contribution of the pond is near its vicinity and it decreases with an increase in the distance from the pond. One of the tube wells was situated just at the boundary of the pond, but isotopic data show no effect of evaporated pond water. This indicates that penetration of pond water is limited to shallow

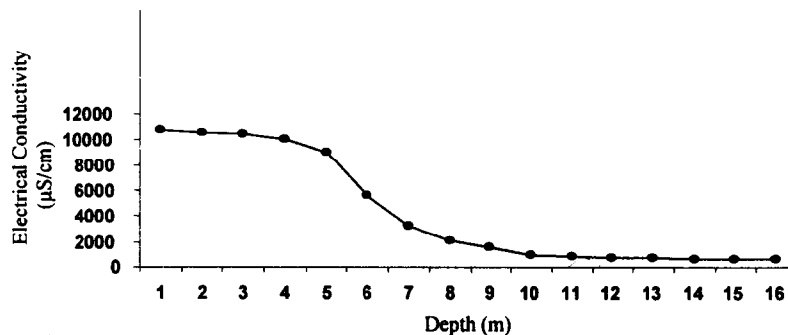


Fig. 3: Electrical Conductivity with respect to depth in all type of water.

Table- 2: Important Hydro geophysical parameters of ground water of Kasur area

| Sr. No. | Depth (m) | EC ($\mu\text{S}/\text{cm}$) | pH | DO (ppm) | Chloride (ppm) |
|---------|-----------|--------------------------------|------|----------|----------------|
| 1 | 00 | 10778 | 8.51 | 6.7 | 3000 |
| 2 | 05 | 10580 | 8.05 | 6.2 | 2503 |
| 3 | 10 | 10500 | 7.92 | 5.8 | 2015 |
| 4 | 15 | 10025 | 8.15 | 5.7 | 2013 |
| 5 | 20 | 9005 | 8.13 | 5.4 | 1800 |
| 6 | 25 | 5600 | 7.56 | 5.4 | 1500 |
| 7 | 30 | 3200 | 7.85 | 5.1 | 1102 |
| 8 | 40 | 2120 | 7.23 | 4.2 | 1012 |
| 9 | 60 | 1550 | 7.45 | 4.1 | 692 |
| 10 | 80 | 900 | 7.55 | 3.7 | 605 |
| 11 | 100 | 850 | 7.86 | 3.0 | 556 |
| 12 | 120 | 775 | 7.05 | 2.6 | 523 |
| 13 | 140 | 698 | 6.82 | 2.1 | 521 |
| 14 | 160 | 665 | 6.53 | 1.9 | 512 |
| 15 | 180 | 650 | 7.31 | 1.7 | 502 |
| 16 | 200 | 578 | 6.25 | 1.8 | 452 |

depths and the deep groundwater is still safe from contamination that is also supported by the low EC values. The groundwater samples and soil samples from project area were also analyzed for the determination of chromium concentration.

All the deep ground water samples for chromium were below the detection limit. The concentration of chromium in soil along depth is plotted in Fig. 4. It is clear from result that shows that concentration of chromium in soil decreases with depth and is not detectable beyond 20m of depth. The water table in the area is below 20m from the surface.

Experimental

Water and Soil Sampling

Water samples were collected for the analysis from existing tube-wells, hand pumps, canal, and the pond receiving the tannery effluents

and the sewage of the city. For isotope analysis, water samples were collected in pre-cleaned, leak proof double-stoppard glass bottles. The soil samples were collected from three different sites around the effluent disposal pond for the determination of chromium.

Analytical Method

Physiochemical parameters such as pH (Hydac), dissolved oxygen (DO meter Hanna) and electrical conductivity (Hydac) were measured in the field. Oxygen and hydrogen isotopes are reported in the standard delta (δ) notation (\square for difference in measurement between standard and sample) and delta values for the isotopic composition are expressed in parts per thousands (‰) relative to Vienna Standard Mean Ocean Water (VSMOW) an average value for the isotopic composition of ocean water.

Table- 3: Chromium in soil

| Sr. No. | Depth (m) | Chromium (ppm) |
|---------|-----------|----------------|
| 1 | 0 | 98 |
| 2 | 1 | 87 |
| 3 | 2 | 79 |
| 4 | 3 | 77 |
| 5 | 4 | 68 |
| 6 | 5 | 68 |
| 7 | 6 | 62 |
| 8 | 7 | 58 |
| 9 | 8 | 56 |
| 10 | 9 | 47 |
| 11 | 10 | 41 |
| 12 | 11 | 35 |
| 13 | 12 | 29 |
| 14 | 13 | 24 |
| 15 | 14 | 19 |
| 16 | 15 | 15 |
| 17 | 16 | 08 |
| 18 | 17 | 07 |
| 19 | 18 | >5 |

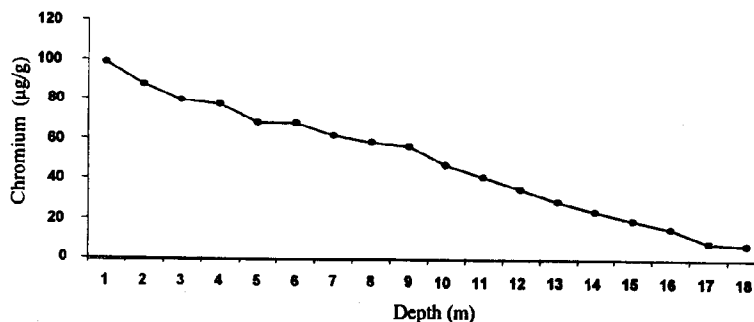


Fig. 4: Chromium profile in soil along the depth.

For the determination of $\delta^2\text{D}$ concentrations, water samples were totally reduced to hydrogen gas by using zinc shots [17] and for $\delta^{18}\text{O}$ values of water samples were determined by using $\text{CO}_2\text{-H}_2\text{O}$ equilibration method [18]. Analysis of $\delta^{18}\text{O}$ and $\delta^2\text{D}$ was performed on GD-150 gas source isotope ratio mass spectrometer with analytical errors of 0.15‰ and 1.0‰ respectively. Per mille units (‰) is the difference in the ratio of the heavy to light isotope relative to the ratio in the standard, times 1000, or alternatively as 10 times the percent change [15-16]:

$$\delta = \frac{R_u - R_{\text{std}}}{R_{\text{std}}} \times 1000, \text{‰}$$

where R is the ratio of the heavy to light isotope, u is the unknown or sample, and std is the international standard. The commonly used standard for ^2D and ^{18}O in water is Standard Mean Ocean Water (SMOW). A relative abundance of 0‰ is identical with SMOW, a negative relative abundance indicates less heavy isotope than SMOW, and a positive relative abundance indicates more heavy isotope than SMOW. The concentration of chromium in the soil samples was determined by using Inductive Couple Plasma-Optical Emission Spectrometer (Model ARL 3580). Chloride content was determined by ion-selective electrode using Orion Micro-Processor Ion Analyzer-901. All the instruments were calibrated with standard solutions from NIST, Myron-L, Merck, NPSL, and VSMOW for pH, electrical conductivity, chromium, chloride and isotopes respectively.

Conclusions

On the basis of present investigations, it can be concluded that the shallow groundwater is being recharged by the canal water and the contribution of pond water has charged isotopic composition of shallow ground water. The deep groundwater is being recharged by rains at piedmont area and is still safe from any kind of pollution (below 45m depth). The quality of shallow groundwater has been deteriorated in the vicinity of the pond water up to a depth of 45m and up to a distance of 7 Km along the Kasur Khudian road. The quality of deep groundwater is good. The chromium is absent in the groundwater, its penetration is limited up to a maximum depth of 20m.

References

1. Z Latif, M. Sajjad, M. A. Tasneem, I. H. Khan, M. Fazil and M. Ali, *J. Anal. & Envir. Chem.*, **4**, 21 (1999).
2. M. Bender, D. H. Boschelli, D. T. Connor and P. J. Kuipers, *J. Geophys. Res.*, **95**, 2243 (1990).
3. S. B. Yaakov, Y. Saitoh and H. Nakano, *Geo Cosmo Acta.*, **36**, 1395 (1972).
4. A. H. Gorrel, O. V. Litvinov, A. A. Saonova, S. N. Chalaya and V. G. Kharchenko, *A A P G Bulletin*, **42**, 2513 (1958).
5. A. W. Rose, H. E. Hawkes and J. S. Webb, "Geo Chemistry in Mineral Exploration" *2nd Ed.*, Academic Press, London, **23**, 657 (1979).
6. M. Dole, L. Breydo, H. Zang and K. S. Gates, *J. Am. Chem. Soc.*, **57**, 2731 (1935).
7. G. Dongmann, H. W. Nürnberg, H. Förstel and K. Wagener, *Environm. Biophys.*, **11**, 41 (1974).
8. P. Fritz, C. S. Hennings, O. Suzuki and E. Salati, *IAEA. Proceeding Series, Vienna, Austria*, **15**, 525 (1979).
9. Y. Yurtsever and B. R. Payne, *IAEA. Proceeding Series, Vienna, Austria*, **75**, 465, (1979).
10. J. C. Fontes. "Handbook of Environmental Isotopes Geochemistry" *Elsevier Scientific Publishing Company, Netherlands*, **1**, 75, (1980).
11. J. R. Gat, J. H. Gatten, and R. Gonifantini, *IAEA. Proceeding Series, Vienna, Austria*, **64**, 223 (1981a).
12. A. Khurshid, A. Aziz and M. M. Akhtar, *J. Sci. Tech. & Dev.* **14**, 27 (1995).
13. M. L. Coleman, T. J. Shepherd, J. J. Durham, J. E. Rouse and G. R. Moore, *Anal. Chem.*, **54**, 993 (1982).
14. S. Epstein and T. Mayeda, *Geo. Cosmo. Acta*, **4**, 213 (1953).
15. J. P. Severinghaus, T. Sowers, E. J. Brook, R. B. Alley, and M. L. Bender, *Nature*, **391**, 141 (1998).
16. D. D. Jensen, K. Mosegaard, N. Gundestrup, G. D. Clow, S. J. Johnson, A. W. Hansen, and N. Balling, *Science*, **282**, 268 (1998).
17. M. Bender, T. J. Sheperd and J. J. Durham, *J. Geophys. Res.*, **95**, 2268 (1990).
18. M. Dole, B. R. Payne and J. S. Webb, *J. Am. Chem. Soc.*, **57**, 2731 (1935).