

Memorandum

To : Kean Goh  
Ag. Program Supervisor IV

Date : April 21, 1995

Place : Sacramento

Via: Don Weaver, Senior Environmental  
Research Scientist

From : Department of Pesticide Regulation - Frank Spurlock, Environmental Research  
Scientist

Subject : Determining Sources and Ages of Shallow Ground Waters, with  
Potential Application to Studies of Pesticide Transport to  
California Ground Water.

The purpose of this memo is to briefly summarize (i) methods for distinguishing different source contributions to shallow ground water using stable isotope markers, and (ii) methods for age-dating shallow ground waters using various environmental tracers.

I. INTRODUCTION

The Pesticide Contamination Prevention Act (AB2021) assumes that leaching is the mechanism responsible for non-point source pesticide pollution of ground water in California. However, studies by the Environmental Monitoring and Pest Management Branch of the California Department of Pesticide Regulation have raised important questions about the significance of other transport mechanisms. Observations of herbicides in runoff entering dry wells in Tulare County suggest that dry wells may play a significant role in transporting pesticides to ground water (Braun and Hawkins, 1991). Meanwhile in Glenn County, herbicide detections in ground water have led to the establishment of several pesticide management zones (PMZs). However, many Glenn County soils are high in swelling clay and impermeable once wetted, these being unfavorable conditions for transport by leaching. It has been suggested that preferential flow through large cracks may be a significant transport mechanism for herbicides in these soils (Graham et al., 1992). Dry wells throughout the state may provide a direct conduit to ground water for herbicide-containing runoff from highway rights-of-way (Powell et al., 1995). Age-dating of ground water parcels containing pesticides may provide valuable information for determining the relative importance of slow leaching versus other direct transport



mechanisms. In turn, more effective strategies to mitigate ground water contamination by pesticides might then be developed.

A related question concerns the lag time between changes in management practices in the field and improvement in quality of the underlying ground water. A recent PMZ well network monitoring project has been proposed for the purpose of evaluating the effectiveness of the PMZ approach in preventing further ground water contamination (Department of Pesticide Regulation, 1995a). This project proposes to monitor temporal changes in a network of contaminated wells within PMZs. However, as mentioned in the PMZ well monitoring network protocol (Department of Pesticide Regulation, 1995a), previous studies indicate that many years may be required before concentration changes in contaminated ground water can be measured. In other projects, voluntary changes in agricultural management practices (e.g., water application regimes, soil incorporation of preemergent herbicides, integrated pest management practices, etc.) by growers will be encouraged in areas sensitive to ground water contamination (Department of Pesticide Regulation, 1995b). It will be important to understand the response time between surface management activities and groundwater quality in these projects. Ground water age-dating is one tool that may give insight to this problem.

Three general categories of environmental markers are used to make inferences about the source or age of young ground waters:

- (1) stable isotope markers -  $^2\text{H}$  (Deuterium, D) and  $^{18}\text{O}$  (Oxygen-18),
- (2) radioactive isotope tracers -  $^3\text{H}$  (Tritium, T) and  $^{85}\text{Kr}$  (Krypton-85)
- (3) environmental tracers - chloroflourocarbons (CFC-11, CFC-12).

General information regarding the various environmental markers and tracers are given in Table 1.

TABLE 1. Environmental markers or tracers discussed in this report.

SOLUTE isotopes	Decay mode, half-life (yrs.)	Decay Product	Relative Abundance
<sup>1</sup> H	Stable	----	99.985
D ( <sup>2</sup> H)	Stable	----	0.015
<sup>3</sup> H	β- , 12.3	<sup>3</sup> He	-----
<sup>3</sup> He	Stable	----	0.00013
<sup>4</sup> He	Stable	----	99.99987
<sup>16</sup> O	Stable	----	99.76
<sup>18</sup> O	Stable	----	0.20
<sup>85</sup> Kr	β- , 10.7	<sup>85</sup> Rb	-----
<b>Chloro-flouorocarbons</b>	<b>Chemical Formula</b>	<b>Estimated atmospheric residence time (yrs.)</b>	
CFC-11	CCl <sub>3</sub> F	74	
CFC-12	CCl <sub>2</sub> F <sub>2</sub>	111	

## II. STABLE ISOTOPES

The stable isotopic composition of a water does not provide direct information on the age of that water. Instead, a water's stable isotopic composition provides a "fingerprint" that yields information on the source of the water. While this source information can sometimes be used to make inferences about the relative ages of two isotopically distinct waters, stable isotopes are not useful for quantitative groundwater age-dating.

Water consists of the elements hydrogen and oxygen, and these elements exist in different naturally occurring isotopic forms. The four stable isotopes of primary importance in hydrologic studies are <sup>1</sup>H, <sup>2</sup>H (i.e., D or Deuterium), <sup>16</sup>O and <sup>18</sup>O. Water molecules containing the rarer and heavier isotopes D and <sup>18</sup>O (i.e. DHO, H<sub>2</sub><sup>18</sup>O, etc.) are chemically identical to "normal" water molecules (i.e., <sup>1</sup>H<sub>2</sub><sup>16</sup>O), however, they display small but measurable differences in

physical properties such as vapor pressure and melting point (Montgomery and Perry, 1981). Consequently, all hydrologic processes that involve a phase change (e.g., evaporation, precipitation) fractionate water molecules according to isotopic composition. For instance, during evaporation, the lighter isotopes  $^1\text{H}$  and  $^{16}\text{O}$  preferentially accumulate in the vapor phase, while the heavier isotopes D and  $^{18}\text{O}$  are correspondingly enriched in the liquid water phase.

The stable isotopic composition of different waters are expressed relative to a standard known as Standard Mean Ocean Water (SMOW). For purposes here, SMOW can be considered as the isotopic composition of actual ocean water, which is essentially an isotopically homogeneous material. The isotopic composition of a given sample is then reflected by the ratio of the main isotopes of the water, i.e.,  $^{18}\text{O}/^{16}\text{O}$  and  $\text{D}/^1\text{H}$ . These ratios are given in  $\delta$  units, where  $\delta$  is defined as concentration differences in parts per thousand relative to the arbitrary standard of SMOW:

$$\delta^{18}\text{O} = \left[ \frac{(^{18}\text{O}/^{16}\text{O})_{\text{sample}}}{(^{18}\text{O}/^{16}\text{O})_{\text{SMOW}}} - 1 \right] \times 1000$$

Similarly, the hydrogen isotope compositions are also given in  $\delta$  units.

$$\delta\text{D} = \left[ \frac{(\text{D}/^1\text{H})_{\text{sample}}}{(\text{D}/^1\text{H})_{\text{SMOW}}} - 1 \right] \times 1000$$

Values of  $\delta^{18}\text{O}$  typically fall in the range of about -17 to -2 for precipitation, surface waters and shallow ground waters in California (e.g., Ingraham and Taylor, 1986, 1991), whereas  $\delta\text{D}$  typically lies between -150 to -50. The lower (more negative)  $\delta$  values are those waters that are highly depleted in the heavier isotopes, D or  $^{18}\text{O}$ . Conversely, higher (less negative) values of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  are observed for waters that are less depleted in  $^{18}\text{O}$  and D relative to SMOW.

As mentioned previously, precipitation and evaporation processes serve to isotopically fractionate water, resulting in depletion of heavier isotopes in the vapor phase. Thus, because Pacific storms travel in an easterly direction across California, precipitation becomes increasingly depleted in D and  $^{18}\text{O}$  as one traverses inland from the Pacific Ocean across the state. Furthermore, surface waters and shallow ground waters also follow the same isotopic trends to the extent that their composition is influenced by precipitation. Figures 1 and 2 illustrate the deuterium depletion trend for three West to East California sampling transects conducted by Ingraham and Taylor (1991). Different segments show different rates of isotopic depletion with distance inland due to the influences of topography and evapotranspiration. These factors influence the condensation/precipitation history of local atmospheric water vapor, hence the isotopic composition of that vapor and associated precipitation. High wintertime rainfall intensities coupled with relatively low wintertime evapotranspiration over the Western Sierra Nevada lead to increased isotopic depletion as storms traverse this reach (e.g., Fig. 2, segment c in traverses II and III). Conversely, Ingraham and Taylor explain (1991) that lower rainfall intensities and higher evapotranspiration result in lesser isotopic depletion over California's Central Valley (e.g., Fig. 2, segment b in traverse II and III).

Once water reaches the Earth's surface, evaporation from open water surfaces or the vadose zone results in isotopic enrichment, i.e., the values of  $\delta\text{D}$  and  $\delta^{18}\text{O}$  increase relative to values in the parent precipitation. Thus,  $\delta\text{D}$  and  $\delta^{18}\text{O}$  of a particular water depends on evaporative history as well as its source. Proper interpretation of the  $\delta\text{D}$  and  $\delta^{18}\text{O}$  data requires information regarding the isotopic composition of the "parent" precipitation.

In general, the isotopic composition of precipitation varies due to several factors, including topography, latitude, elevation, and climate. However,  $\delta\text{D}$  and  $\delta^{18}\text{O}$  vary systematically across virtually all precipitation. Craig (1961) evaluated isotopic composition of a large sampling of global precipitation data and found that nearly all meteoric water (e.g., rain and snow) conformed to the following relationship

$$\delta\text{D} = 8 \delta^{18}\text{O} + 10$$

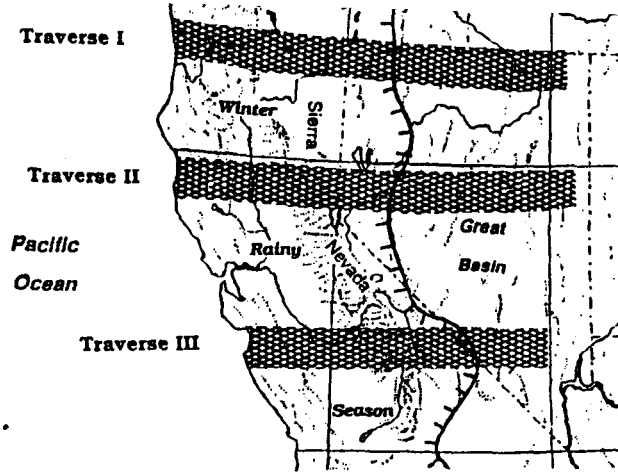


Figure 1. Ingraham and Taylor, 1991.

Location of the three east-west traverses used in this study. The traverses were positioned parallel to the atmospheric flow path and located to include most major physiographic and hydrologic provinces in California and Nevada. Also shown is the region of dominantly winter precipitation [after Markham, 1970].

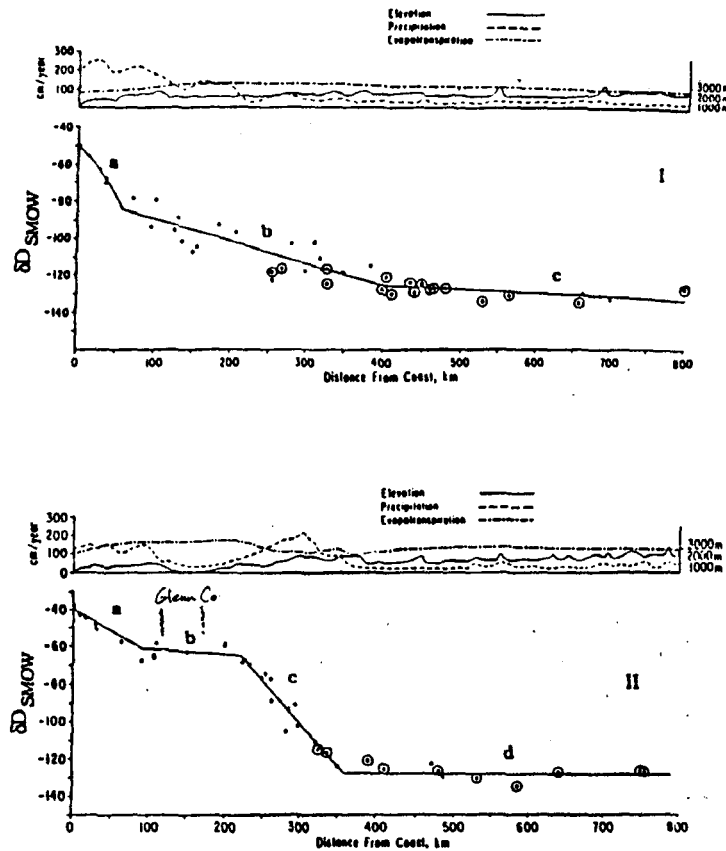
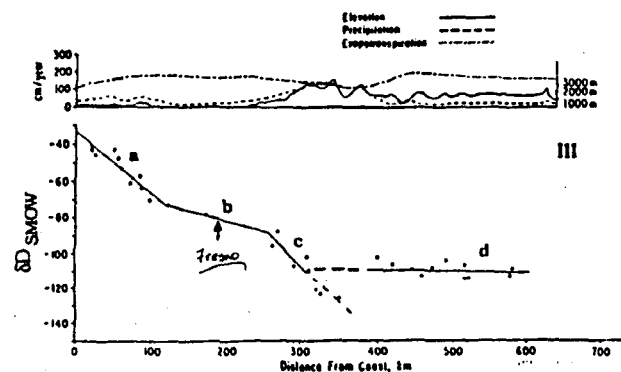


Figure 2. Ingraham and Taylor, 1991.

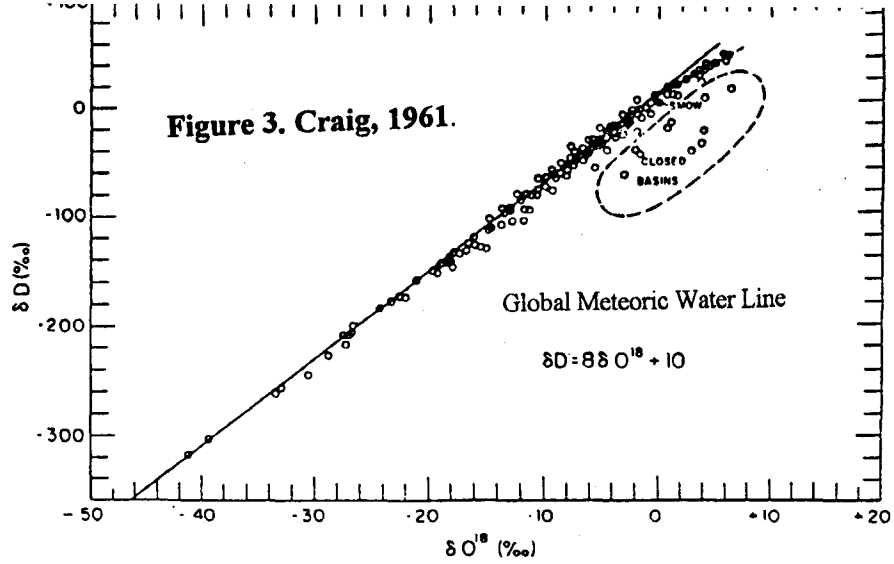


Plot of  $\delta D$  versus distance from the Pacific Ocean of traverses I-III. Precipitation data [Goodridge *et al.*, 1981], evapotranspiration data [MacGillivray *et al.*, 1975], and topography are also shown. The segments, a, b, c, and d and their regression curves (solid curves in the figures) are discussed in the text. Circled data points represent samples from thermal (temperature  $> 40^{\circ}C$ ) springs.

This equation is termed the global meteoric water line (MWL), and is shown in Fig. 3. Figure 4 illustrates recent data reported by Davisson et al. (1993) for rain samples in the Sacramento Valley. Globally, nearly all meteoric water data fall on or very near to the MWL, as do the resultant surface waters and ground waters that are derived from precipitation --- *provided they have not been subjected to subsequent evaporation*. Meteoric waters that evaporate from surface reservoirs have higher  $\delta D$  and  $\delta^{18}O$  values, and plot on lines that diverge from the MWL (Fig. 5). The characteristic slope of surface evaporation waters is about 5 on a  $\delta D$  vs.  $\delta^{18}O$  plot, whereas several studies (Barnes and Allison, 1983, Allison et al., 1983) have shown that waters evaporated within the vadose zone plot with a slope of about 2.5 - 3, e.g., Fig. 5.

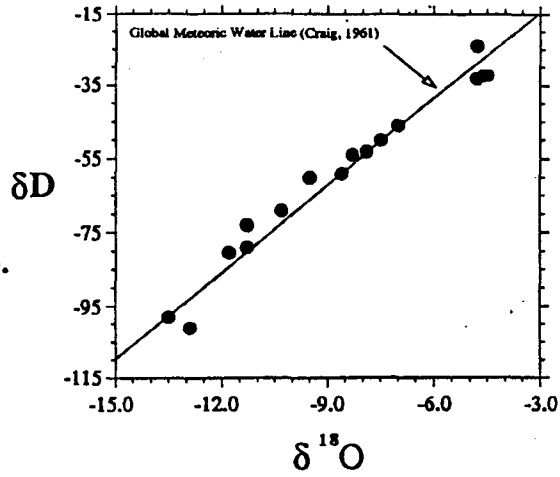
Stable Isotope Studies in California. Several recent studies have examined stable isotope methods in California ground water. Davisson and Criss (1993), Davisson et al. (1993) and Criss et al. (1994) used stable isotopic, chemical, and hydrologic data to investigate ground water sources and ground water quality in a 25 km<sup>2</sup> area around Davis, California. They reported (i) high nitrate and total dissolved salt concentrations in the shallower ground water that correlated with the  $^{18}O$  concentrations (Figs. 6a and b), (ii) higher (less negative)  $\delta^{18}O$  in the lower quality shallow ground water relative to deeper ground waters as expected for highly evaporated agricultural recharge waters, (iii) a slope of - 3 for the shallower waters on a plot of  $\delta D$  vs.  $\delta^{18}O$ , suggesting that most of the evaporation took place in the vadose zone, (iv) a modern  $^{14}C$  apparent age of the shallower low quality water (< 500 years) in contrast to  $^{14}C$  ages of 9,000 - 16,000 years for the deeper "pristine" ground water (Davisson et al., 1993), and (v) a positive relationship between  $\delta^{18}O$  and depth (Fig. 7), indicating that the shallower ground waters consisted of either local meteoric waters that had undergone vadose zone evaporation, or waters originating from another geographical area. The modern  $^{14}C$  apparent age in the shallow ground water was attributed to exchange with atmospheric carbon having modern  $^{14}C$  contents. These researchers concluded that ancient pristine ground water supplies around Davis within the 45-160m depth are being steadily mined and replaced with lower quality recharge water from agricultural irrigation.

In another study, Mohr et al. (1992) applied stable isotopic methods to investigate contaminant sources and water flow characteristics



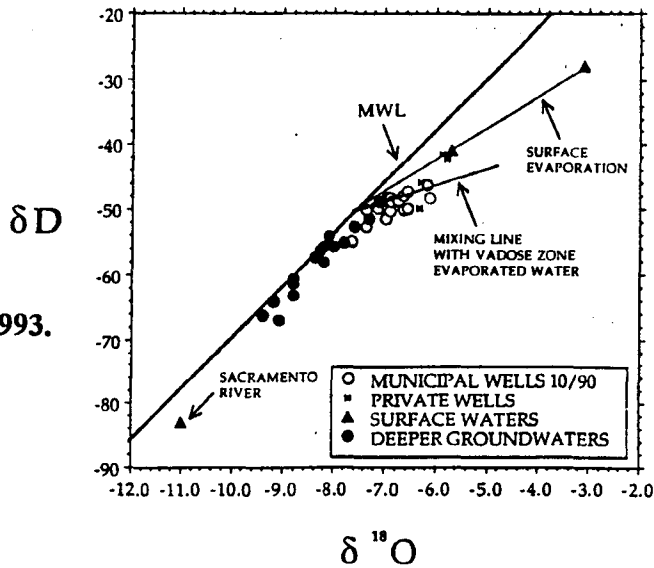
Deuterium and oxygen-18 variations in rivers, lakes, rain, and snow, expressed as per millage enrichments relative to "standard mean ocean water" (SMOW). Points that fit the dashed line at upper end of the curve are for rivers and lakes from East Africa. (Craig [77].)

Figure 4. Davisson et al. 1993.



Stable isotope distribution of rain water collected in the southwestern Sacramento Valley, 1989-1991.

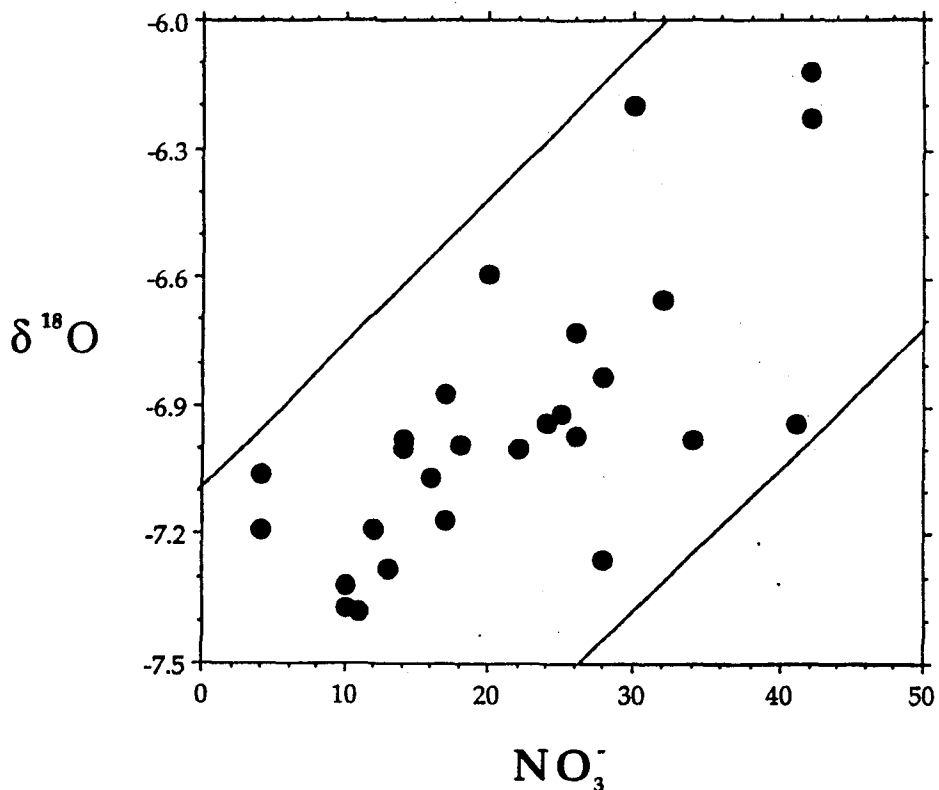
Figure 5. Davisson and Criss, 1993.



A  $\delta D$  vs.  $\delta^{18}O$  plot of groundwaters and surface waters in the southwestern Sacramento Valley. Note the distinctive evaporation trends that intersect the meteoric water line (MWL) at approximately  $-7.5\%$  for  $\delta^{18}O$  and  $-50\%$  for  $\delta D$ , values representing average meteoric precipitation. The trend for surface evaporation has a slope of 5.0, and that for vadose zone evaporation has a slope of 2.5. Enrichment along the slope 2.5 mixing line corresponds to increased nitrate levels (Fig. 11(a)) and higher  $^{18}O$  plumes (Figs. 12(a)-(d)). Deeper groundwaters (300-650 mbs) have lower  $\delta^{18}O$  values (to  $-9.4$ ) and lie close to the MWL. Sacramento River water ( $-11.0$ ) represents combined meteoric waters from the mountains east and north of the Sacramento Valley, moderately modified by surface evaporation.



Figure 6. (a) Criss et al., 1993.



The  $\delta^{18}\text{O}$  values plotted against nitrate for individual wells sampled between November 1990 and July 1991. The dilute end of this trend approximates values for average meteoric precipitation.

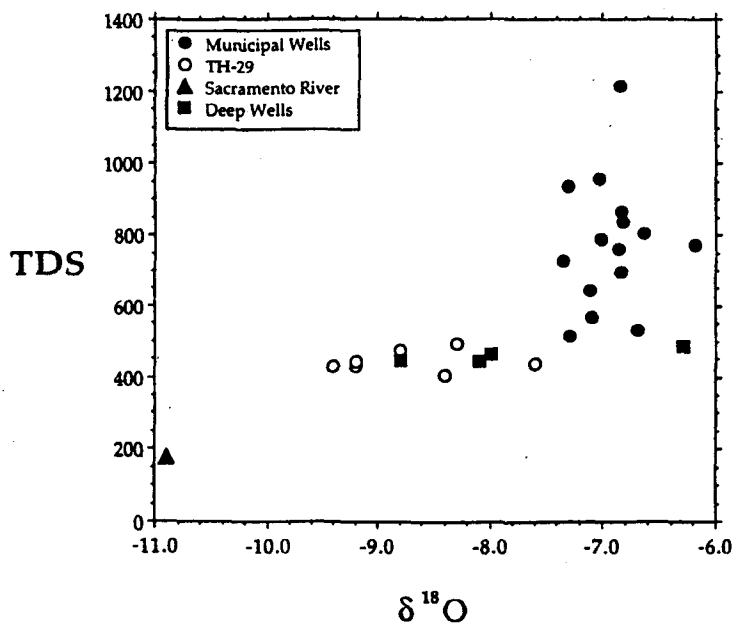
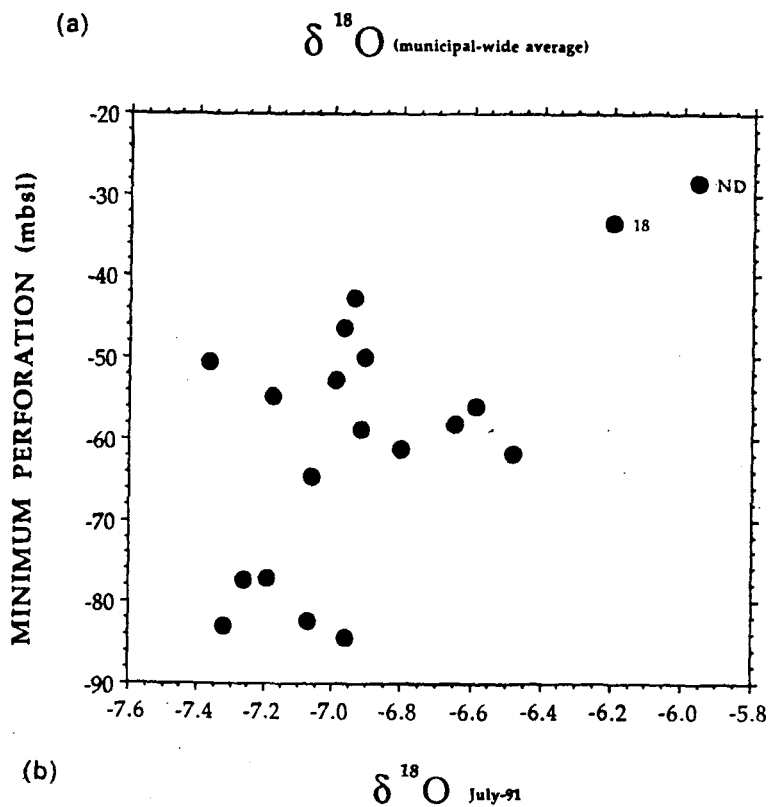


Figure 6 (b) Davisson and Criss, 1993.

Graph of TDS vs.  $\delta^{18}\text{O}$  values for the Sacramento River water, deep groundwaters from TH-29, other deep groundwaters, and the average values for the municipal wells. The plot suggests that groundwater modification by long-standing irrigation practices has significantly altered the groundwater, and that recycling of groundwater is common in the municipal system.

Figure 7. Davisson and Criss, 1993.



(b) The July 1991 (low water table)  $\delta^{18}\text{O}$  values plotted as a function of minimum perforation depth measured as meters below sea-level (mbs) in each municipal well. The plot demonstrates that higher  $^{18}\text{O}$  groundwater (irrigation water) resides in the upper part of the aquifer. Note that wells ND and 18 have the highest  $\delta^{18}\text{O}$  values and the shallowest minimum perforation depths. These two wells furthermore show negligible temporal isotopic variation.

below the Yolo County landfill. They were able to distinguish three different source waters at the landfill site: a local shallow ground water upgradient of the landfill, cannery effluent from a local tomato cannery that disposes of effluent in the area, and municipal wastewater that is disposed of nearby in treatment fields.

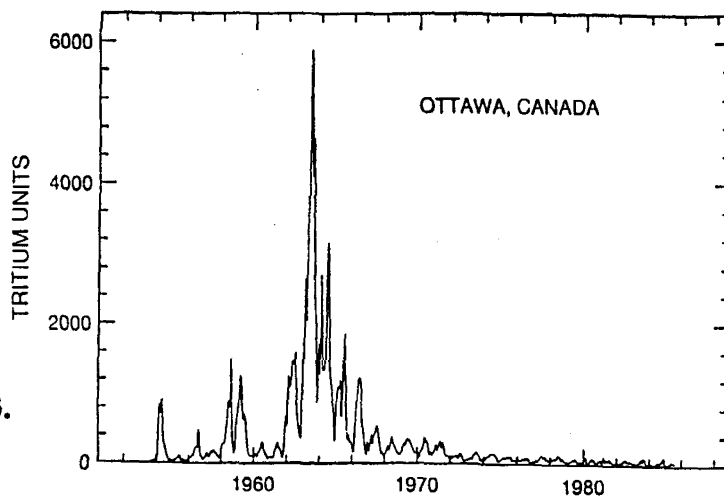
In summary, the stable isotopic composition of a water provides a "fingerprint" that is characteristic of that water's source and/or evaporative history. In ground water studies, the stable isotopes are most useful for differentiating between two or more waters of different origin or evaporative history, and isotopic composition data are most effective when interpreted in conjunction with regional hydrologic and/or chemical data.

## II. RADIOACTIVE ISOTOPES.

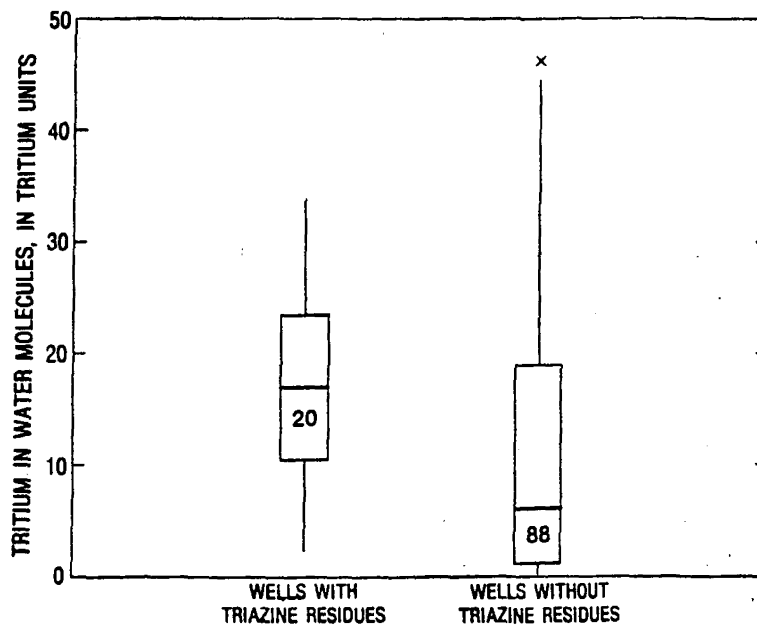
In contrast to the stable isotopes D and  $^{18}\text{O}$  that provide information about a water's source or history, radioactive isotopes can be used to provide information about the "age" of a ground water. For the purpose of this report, *ground water age refers to the period of time since the water has moved deep enough into the subsurface to be considered isolated from the earth's atmosphere.*

Tritium. The most commonly used radioactive isotope for age-dating young ground waters is tritium,  $^3\text{H}$ . Tritium is a short-lived isotope of hydrogen with a half-life of 12.3 years, decaying by  $\beta$  emission to stable and inert  $^3\text{He}$ . The sole natural source of tritium is from the interaction of cosmic rays with stratospheric constituents. This source provided a relatively constant global inventory of tritium until 1953. Prior to 1953,  $^3\text{H}$  concentrations in precipitation were about 2-8 tritium units (TU, where 1 TU is equal to 3.24 picoCuries/L). After the beginning of atmospheric fusion bomb testing in 1953,  $^3\text{H}$  levels in precipitation began to increase, and further large-scale bomb tests in 1962-1963 led to  $^3\text{H}$  increases in precipitation of as much as three orders of magnitude (Fig. 8). Therefore, by accounting for radioactive decay, ground waters consisting solely of pre-1953 recharge water are expected to display  $^3\text{H}$  concentrations no higher than about 0.5 TU. Significantly higher  $^3\text{H}$  ground water concentrations indicate at least some contribution from post-1953 "modern" or "bomb" water. Theoretically, ground water  $^3\text{H}$  concentrations can be used to estimate the age of post-1953 ground waters providing the  $^3\text{H}$

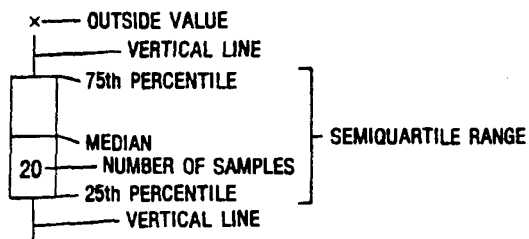
Figure 8. Plummer et al., 1993.



Monthly tritium concentration in precipitation at Ottawa, Canada, 1953 through 1985. (Data from IAEA 1969, 1970, 1971, 1973, 1975, 1979, 1983, 1986, 1990.)



EXPLANATION



Outside values are between 1.5 and 3.0 times the semiquartile range from the top or bottom of the rectangle

Vertical lines extend a distance equal to 1.5 times the semiquartile range away from the top or bottom of the rectangle or to the limit of the data, whichever is least

Tritium in water samples from wells with and without detections of triazine herbicide residues; regional aquifer study, 1985-87.

concentration at the time of infiltration is known. In practice,  $^3\text{H}$  concentrations in precipitation are subject to the same seasonal and geographic variations as the stable isotopes discussed previously, as well as further local variability due to the seasonal nature of tritium exchange rates between the stratosphere (the source of naturally produced "cosmic-ray" tritium) and the lower troposphere. Moreover, the enhanced  $^3\text{H}$  levels in precipitation due to atmospheric testing in the early 1960s have now declined, increasing the uncertainty of ground water age estimates based on  $^3\text{H}$  alone.

Tritium/Helium-3. Because of the foregoing difficulties in accurately defining the local  $^3\text{H}$  input to infiltration waters, recent studies have attempted to determine  $^3\text{H}$  concentrations at the time of infiltration (i.e., time of a water's isolation from the atmosphere) by measuring both  $^3\text{H}$  and the tritium decay product  $^3\text{He}$  (Schlosser et al., 1988, 1989; Solomon and Sudicky, 1991; Solomon et al., 1992, 1993). Thus, the sum of  $^3\text{H}$  and tritiogenic  $^3\text{He}$  is equal to the original  $^3\text{H}$  input concentration. Two issues that must be considered in the  $^3\text{H}/^3\text{He}$  dating method are determination of tritiogenic  $^3\text{He}$  from total  $^3\text{He}$ , and potential exchange losses of  $^3\text{He}$  with the vadose zone atmosphere. Schlosser et al. (1988, 1989) have discussed a mass balance method for evaluating tritiogenic  $^3\text{He}$  and vadose losses from total  $^3\text{He}$  and dissolved neon concentrations. They concluded that their method is accurate for shallow ground waters providing extreme flow velocities and/or high dispersion are not present, however, further studies are necessary to validate their method.

Applications of  $^3\text{H}$  and  $^3\text{H}/^3\text{He}$  dating. Domagalski and Dubrovsky (1991) conducted a regional study of pesticide residues in the San Joaquin Valley, California. Well monitoring data from the CDFA data base (1975-1988) were supplemented with results from 183 additional wells sampled by the U.S. Geological Survey. In the wells sampled by U.S.G.S., they found that nitrate concentrations were not significantly related to the presence of triazine herbicides in ground water. In contrast, wells containing triazine residues were significantly higher in  $^3\text{H}$  concentrations (Fig. 9,  $\alpha = 0.05$ , Mann-Whitney nonparametric rank test). Although not all wells containing triazines displayed high  $^3\text{H}$  concentrations, no triazine residues were found in samples with no detectable tritium. This result is expected because higher  $^3\text{H}$  concentrations reflect recent waters

quantitative dating of the sampled ground waters was not attempted due to the previously mentioned inherent inaccuracies associated with dating on the basis of  $^3\text{H}$  alone (N. Dubrovsky, personal communication).

Other recent studies have evaluated the  $^3\text{H}/^3\text{He}$  dating method. Poreda et al. (1988) estimated hydraulic conductivities within a shallow Tennessee aquifer, finding agreement between conductivities obtained by estimating ground water flow rates using  $^3\text{H}/^3\text{He}$  and conductivities measured using conventional aquifer tests. Solomon et al. (1992) found recharge rates determined from  $^3\text{H}/^3\text{He}$  data in good agreement with estimates obtained from different methods in the well characterized Borden aquifer. While the method appears to give reasonable estimates of shallow ground water age within an accuracy of about 1-4 years in these studies, the accuracy of the method in general has yet to be established. Site-specific application requires careful evaluation of the surrounding aquifer and multi-level well sampling to characterize flow velocities and dispersion.

Krypton-85. As  $^3\text{H}$  concentrations decrease with increasing time since the large-scale atmospheric testing of the 1960s, Krypton-85 has generated interest as an age dating tracer for young ground waters. Krypton-85 is a radioactive inert gas that decays by  $\beta$  emission to Rubidium-85 with a half-life of 10.8 years, and has several advantages as a ground water dating tool. Natural sources of  $^{85}\text{Kr}$  are insignificant compared with the principal anthropogenic source: the fission reactions of uranium and plutonium in bomb testing and especially in nuclear reactors. The main releases of  $^{85}\text{Kr}$  occur during fuel rod reprocessing (Smethie et al., 1992; Ekwurzel et al., 1994). As a result, tropospheric  $^{85}\text{Kr}$  concentrations are relatively homogeneous and, in contrast to tritium, have increased smoothly over the last forty years (Fig. 10). Perhaps the greatest advantage of  $^{85}\text{Kr}$  in ground water dating is that the age of a water parcel can be determined from the specific activity of  $^{85}\text{Kr}$ , i.e., the ratio of  $^{85}\text{Kr}$  to total dissolved Kr (Smethie et al., 1992). Thus, loss to the vadose zone atmosphere is relatively unimportant because such losses would affect all dissolved Kr similarly. The half-life of 10.7 years is similar to that of  $^3\text{H}$ , and should allow dating over the range of about 2-50 years. Finally, Krypton is an inert gas, hence unaffected by chemical or biological processes. The primary disadvantage of

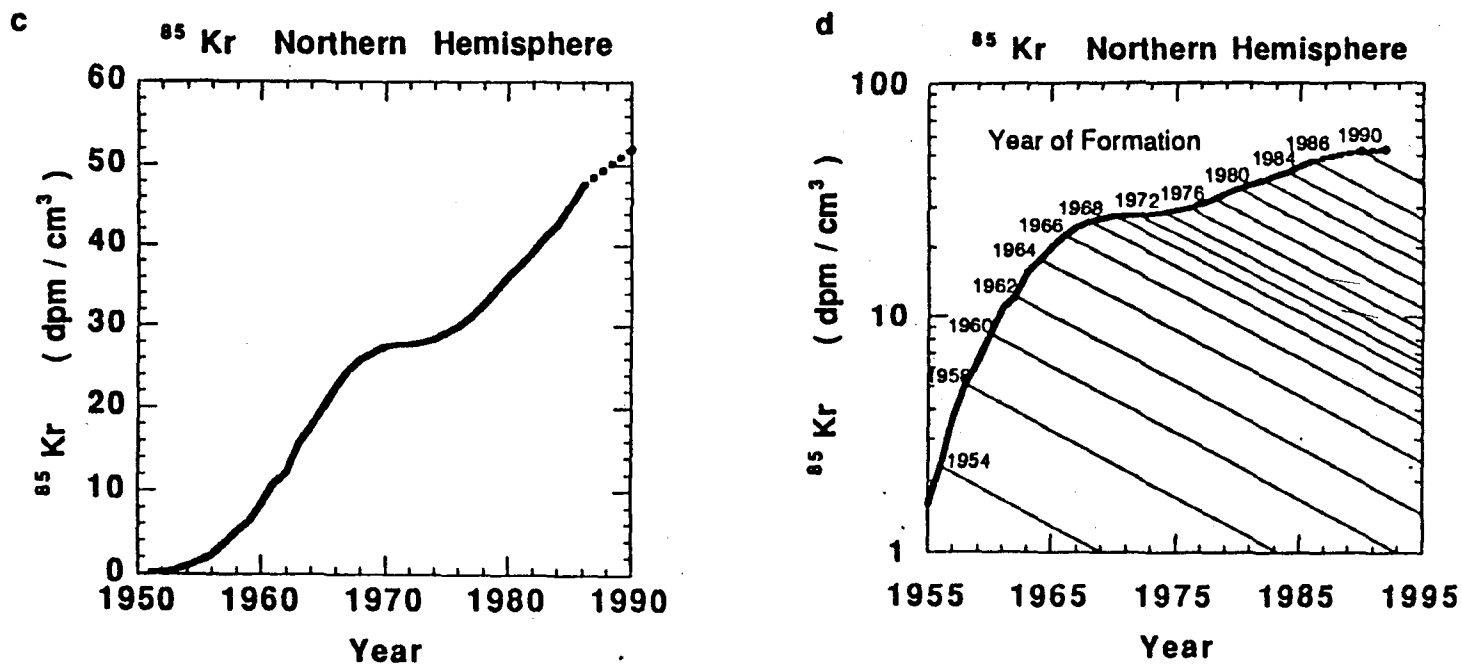


Figure 10. Ekwurzel et al., 1994.

(c) Krypton 8

specific activity (i.e., the ratio of <sup>85</sup>Kr to stable krypton in disintegrations per minute per cubic centimeter krypton) in the troposphere of the northern hemisphere between 40° and 55°N as a function of time [Sittku and Stockburger, 1976; Rozanski, 1979; Weiss et al., 1983]. The <sup>85</sup>Kr specific activity is extended to pass through the atmospheric specific activity measured at Locust Grove in November 1991. (d) Same curve as in Figure 2c, but plotted on a logarithmic scale. Diagonal lines represent radioactive decay after groundwater is isolated from the atmosphere [Smethie et al., 1992].

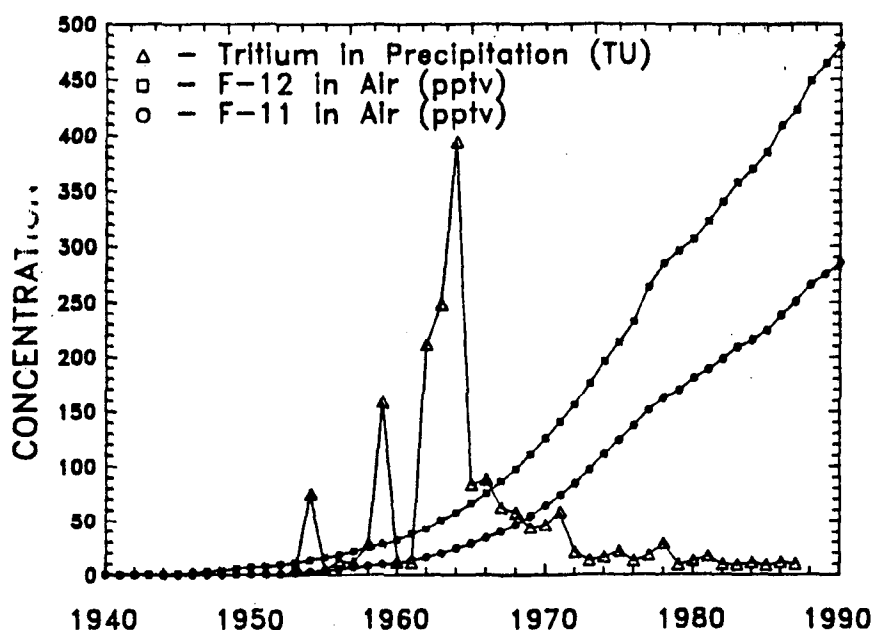


Figure 11. Busenberg and Plummer, 1992.

Atmospheric concentrations of F-12 and F-11 for central Oklahoma as a function of time (See text for details.). The tritium concentrations in March precipitation are also shown [Michel, 1989]. Tritium concentrations have been corrected for radioactive decay to the year 1988.

Krypton as an age dating tool is the difficulty in sampling and analytical determinations. Total Krypton concentrations are usually very low, typically requiring water sample volumes on the order of 100 - 300L, along with extensive vacuum degassing and trapping procedures necessary to obtain sufficient gas for analysis (Smethie et al., 1992; Plummer et al. 1993).

### III. ENVIRONMENTAL TRACERS - CHLOROFLOUROCARBONS.

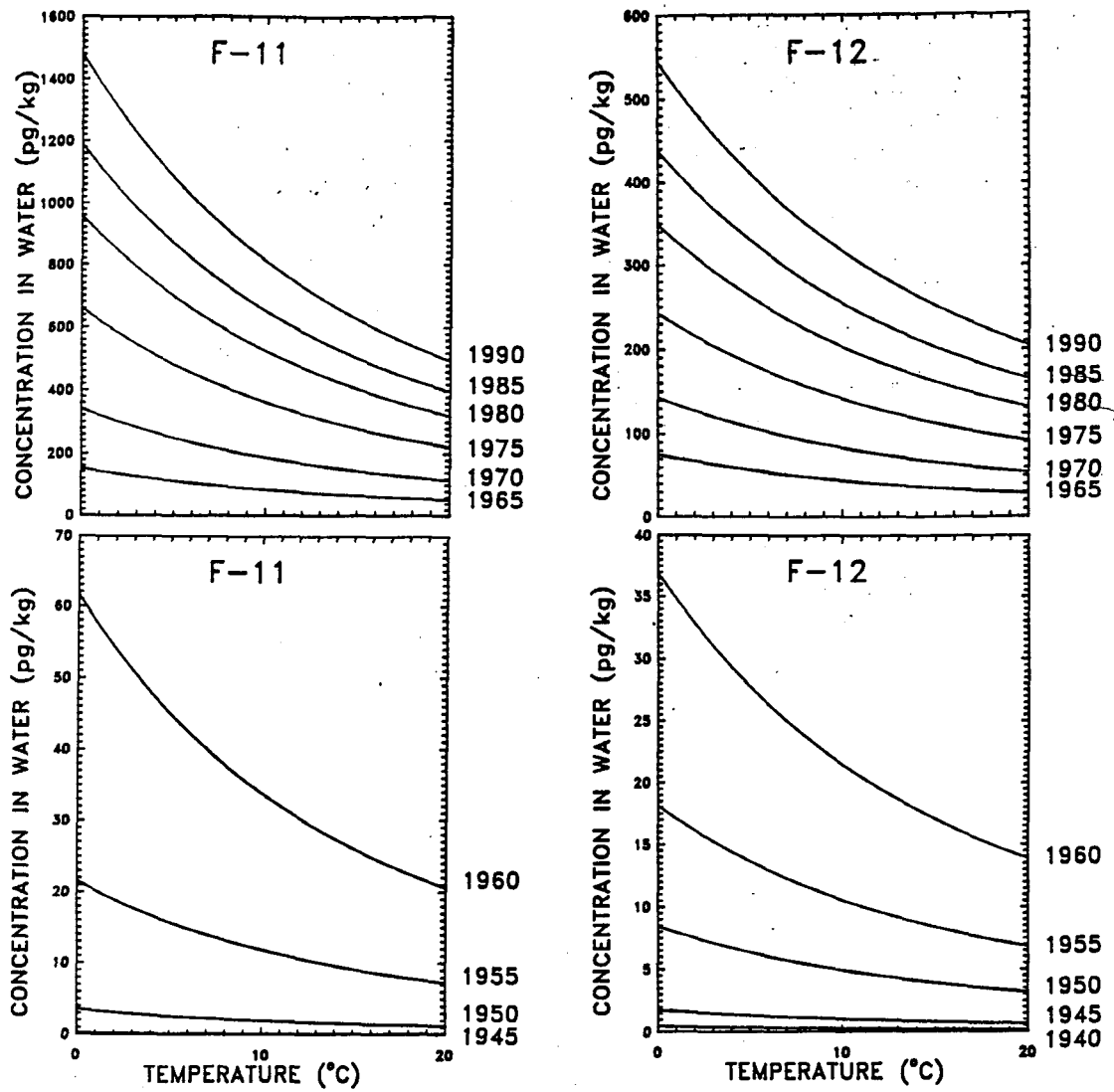
Similar to  $^{85}\text{Kr}$ , tropospheric concentrations of chloroflourocarbons (CFCs) have increased smoothly since they were first manufactured in the 1930s; no known natural CFC sources exist (Plummer et al. 1993). Two Freon compounds, CFC-11 ( $\text{CCl}_3\text{F}$ ) and CFC-12 ( $\text{CCl}_2\text{F}_2$ ) have accounted for nearly 80 percent of global CFC production. The northern hemisphere tropospheric concentrations of these compounds are relatively homogeneous (with the exception of local, near-surface concentration anomalies in or near large metropolitan areas), with average annual atmospheric concentrations of CFC-11 and CFC-12 shown in Figure 11.

Estimation of apparent ground water age using CFCs requires knowledge of CFC-11 or CFC-12 concentrations in the ground water, and knowledge of the recharge temperature. Using these data, the aqueous CFC concentration is assumed proportional to the atmospheric CFC concentration at the time of recharge. The constant of proportionality is the (known) Henry's law constant of the CFC. One implicit assumption is that the vadose zone air concentration is similar to that in the ambient atmosphere. Limited data suggests this to be case for depths below the surface of around 5-10m (Weeks et al., 1982). Because of the strong dependence of CFC solubility on temperature, recharge temperature is an important variable as shown in Fig. 12. However, methods exist for estimating recharge temperature that appear to be relatively accurate (Busenberg and Plummer, 1992).

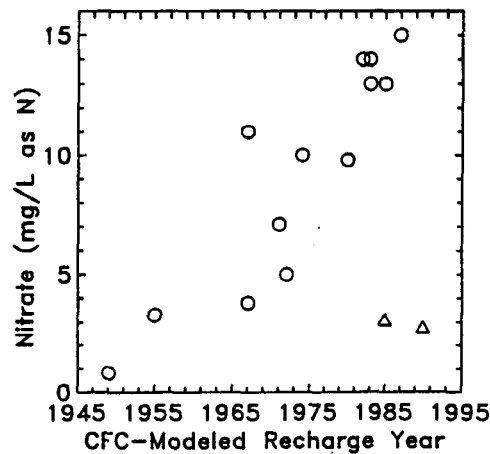
CFCs are typically analyzed by purge-and-trap gas chromatography with electron capture detection. This analytical method is relatively simple and inexpensive. Typical detection limits for CFCs are around 1 pg/L, low enough to permit ground water dating back to about 1950. The uncertainty in age dating due to the analytical determinations are about 1 year. While analytical CFC determinations are relatively straightforward, sampling is difficult. Busenberg and Plummer (1992) developed a sampling



Figure 12. Plummer et al., 1993.



Equilibrium air-water concentrations of F-11 and F-12 in ground water calculated using the solubility data of Warner and Weiss (1985) and the atmospheric F-11 and F-12 data of Figure 11-6. Contours show solubilities for a particular year as a function of recharge temperature.



Correlation of dissolved nitrate concentrations and CFC-modeled recharge years for Locust Grove groundwater. Triangles indicate shallow wells located adjacent to the roadway.

difficult. Busenberg and Plummer (1992) developed a sampling apparatus that allows sample collection without allowing sample contact with air. After sampling, samples are welded shut inside borosilicate glass ampules until analysis.

While the potential of CFCs for ground water dating was recognized as early as the mid-1970s, several recent studies by personnel of the U. S. Geological Survey have detailed the method and evaluated it's application in several geographic areas of the United States (Busenberg and Plummer 1992, Ekwurzel et al. 1994, Reilly et al. 1994, Dunkle et al. 1993). Busenberg and Plummer (1992) found CFC-estimated ground water recharge dates in central Oklahoma in close agreement with both tritium-estimated dates and local precipitation records. They concluded that under "optimum conditions" (to be discussed later) that CFC recharge ages appear to be definable to within 2 years. Dunkle et al. (1993) conducted a detailed investigation of shallow ground water in the Delmarva Peninsula, concluding that their CFC estimated recharge rates were consistent with local hydrogeologic interpretations based on geologic, hydraulic, chemical, and  $^3\text{H}$  data. In addition, a high correlation between  $\text{NO}_3$  and the CFC concentrations was found in the largely agricultural Locust Grove area (Fig. 13). However, Dunkle et al. (1993) also indicate that potential effects of CFC sorption and degradation require further study; degradation of CFC-11 appears to be a greater problem than with CFC-12. In addition, potential contamination from surface waters must be carefully evaluated on a site-specific basis, particularly in or around large metropolitan areas and landfills (Plummer et al. 1993). Finally, preliminary results from a study of CFCs and pesticides in San Joaquin Valley ground waters suggest that CFCs may hold potential for estimating pesticide transport times to ground water (Dubrovsky, N., personal communication).

Plummer et al. (1993) have reviewed the CFC dating literature and summarized site conditions best suited for CFC age dating. They state that the aquifers most amenable to CFC dating have the following properties:

- ▶ Located in rural areas where aqueous concentrations are determined by air-water equilibrium only
- ▶ Relatively thin unsaturated zones (< ~ 10m) where vadose zone air is mixed rapidly and similar to local atmospheric concentrations

- ▶ Oxidic ground water so that microbial reductive breakdown of ground water is not a problem
- ▶ Low organic carbon content of the vadose zone and aquifer so that sorption is minimized.
- ▶ Temperate climates so that drying periods between successive recharge events are minimized
- ▶ Shallow waters containing measurable quantities of CFCs (i.e., post-1940 recharge).

#### IV. DISCUSSION.

Plummer et al. (1993) have presented an excellent review of ground water dating methods. They point out that while many of the aforementioned tracers have been extensively used in oceanographic studies for age-dating parcels of water, tracing water mass movement, and defining mixing proportions, applications to ground water investigations are relatively recent. Ground water tracers are impacted by additional chemical and physical processes that are unimportant in oceanographic investigations. These include:

- ▶ hydrodynamic dispersion (e.g., mixing of waters as they move through porous media),
- ▶ sorption, which may influence CFC measurements under certain conditions,
- ▶ exchange with unsaturated zone atmospheres, which may potentially effect any of the gas phase tracer compounds,
- ▶ degradation, which may potentially influence CFC measurements,
- ▶ additional source terms, e.g., the excess  $^{85}\text{Kr}$  near nuclear fuel reprocessing plants.

Quantitative age dating of ground waters is a complex problem, and there exists no "magic bullet" analyte that provides the age of a water parcel based on a single sample or analysis. Many shallow ground waters are mixtures, and the process of hydrodynamic dispersion in the aquifer (e.g., mixing) requires spatial sampling in order to characterize the tracer/marker distribution throughout the ground water system. Thus, hydrologic evaluations in conjunction with site history, and specific well information substantially increase the confidence in ground water age estimates and subsequent conclusions regarding sources of contamination, transport mechanisms, and characteristic transport time between surface and water table. Therefore, ground water age-dating techniques hold the greatest potential for regional studies, where information from several wells can be used to hydrologically

characterize a study area. However, qualitative dating information can be obtained from single samples. For instance, the presence of measurable  $^3\text{H}$  or high CFC concentrations indicates that at least some modern water is present.

## V. CONCLUSION.

Several methods for dating or sourcing ground water are available. Stable isotope composition ( $^2\text{H}$  and  $^{18}\text{O}$ ) is not a true dating method, but can provide valuable information about the source or history of a ground water parcel. Stable isotopic differentiation of a ground water is most useful when at least two isotopically distinct waters contribute to the ground water composition, but cannot yield any information concerning recharge rates, hence transport times to ground water.

The use of  $^3\text{H}$  is limited, in part due to difficulties in characterizing the highly variable atmospheric source function of  $^3\text{H}$ , and also because of the continued decay of the  $^3\text{H}$  bomb signal with time. The  $^3\text{H}/^3\text{He}$  method is attractive because measurement of both  $^3\text{H}$  and tritogenic  $^3\text{He}$  yields the original  $^3\text{H}$  input directly. Indirect methods (e.g., dissolved neon and  $^4\text{He}$  determinations) can be used to estimate possible  $^3\text{He}$  losses to the vadose zone atmosphere. These losses may be significant in arid California climates, particularly for shallow ground water parcels. The  $^3\text{He}$  mass balance model to assess these potential losses appears sound, however, the approach is analytically intensive, requiring mass spectral determinations of  $^3\text{He}$ ,  $^4\text{He}$ , and Ne, as well as low level  $^3\text{H}$  scintillation counting in every sample. The relatively new method based on  $^{85}\text{Kr}$  obviates the need to consider gas exchange between ground water and the vadose zone atmosphere because the method is based on the specific activity of  $^{85}\text{Kr}$ , i.e., the ratio of  $^{85}\text{Kr}$  to total Kr in the sample. Furthermore, the  $^{85}\text{Kr}$  atmospheric source function has increased smoothly since the early 1950s. Unfortunately, Krypton gas sampling requires very large sample volumes (ca 100 - 300 liters) and specialized gas purification and low-level scintillation counting techniques are required for analysis.

The  $^3\text{H}/^3\text{He}$ ,  $^{85}\text{Kr}$ , and CFC methods are all potentially useful for age-dating post-1950 to post-1960 ground waters, with resolutions that can approach 2-3 years under optimum conditions. A comparison of the  $^3\text{H}/^3\text{He}$ , CFC, and  $^{85}\text{Kr}$  methods was conducted in the Delmarva

peninsula, Maryland, and comparable ages were obtained using the three methods (Ekwurzel et al. 1994). Therefore, while selection of an appropriate ground water dating or sourcing method may depend to some extent on particular site conditions and study goals, costs associated with sampling and analysis are likely to be a major factor in choice of method. The relative ease of CFC analytical determinations is a strong argument in favor of this method. Although some questions remain about CFC age dating method limitations (e.g., vadose zone depths, sorption, degradation), work is currently being conducted that should provide insight into the usefulness of this method under California conditions.

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