Use of Chlorofluorocarbons, Dissolved Gases and Water Isotopes to Characterize Ground-Water Recharge in an Aquifer Contaminated by Acidic, Metal-Laden Wastewater

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ABSTRACT

Chemical and isotopic analyses of ground waters sampled from the Pinal Creek Basin, near Globe, Arizona, between 1991 and 1998 provide valuable information on this highly transient ground-water flow system. Improved knowledge of the flow system and of the recharge processes affecting it is essential in predicting the chemical evolution and migration of the extensively contaminated waters in the basin. Data for dissolved nitrogen and argon indicate that most of the ground-water recharge occurs very rapidly during floods in the winter and early spring. Ground-water samples collected in 1991 have chlorofluorocarbon ages that generally increase with depth and distance downgradient in the metal- and acid-contaminated ground waters. The ground-water ages calculated from chlorofluorocarbon-11 concentra tions are reasonable—3 to 15 years for acidic ground waters and 20 to 30 years for neutralized, contaminated ground waters. Ground waters sampled in 1993 have chlorofluorocarbon ages as much as 8 years younger than the waters sampled in 1991. Ground waters sampled in 1996 and in 1998 show that the age of waters in the acidic zone of the system increased by as much as 7 years. Deuterium and oxygen-18 isotope contents measured in the ground waters and their correlation with the specific conductance of the sampled ground waters support the hypothesis that Webster Lake was a major source of metal and acid contamination of ground water in the Pinal Creek Basin. The ground-water ages presented here, however, cannot be used to determine the age of the ground-water solutes introduced by the copper mining and refining operations because the introduced solutes are affected by water-rock reactions and because of remaining uncertainties concerning the application of the chlorofluorocarbon dating technique in this extensively contaminated and highly transient ground-water system.

INTRODUCTION

Acidic, metal-laden water has contaminated shallow ground waters in the Pinal Creek Basin near Globe, Arizona (figs. 1 and 2). Chemical and isotopic ground-water data have been collected in an effort to describe and understand the movement and origin of ground waters in the unconsolidated alluvium and in the underlying consolidated basin fill, which together form the regional aquifer in the basin. The objectives of the project are (1) to determine the ages of the ground waters in the basin, (2) to determine the provenance of these ground waters, (3) to understand the recharge processes affecting ground-water flow in the basin, and (4) to understand how reactions have affected the chemical and isotopic evolution of the contaminated waters. Although the technique of using chlofluorocarbon concentrations to date young ground waters is well established, the application of the technique to such an extensively contaminated ground-water system is novel. This paper presents chemical and isotopic data for ground water sampled between 1991 and 1998 in Pinal Creek Basin, and some preliminary conclusions that may be drawn from those data.

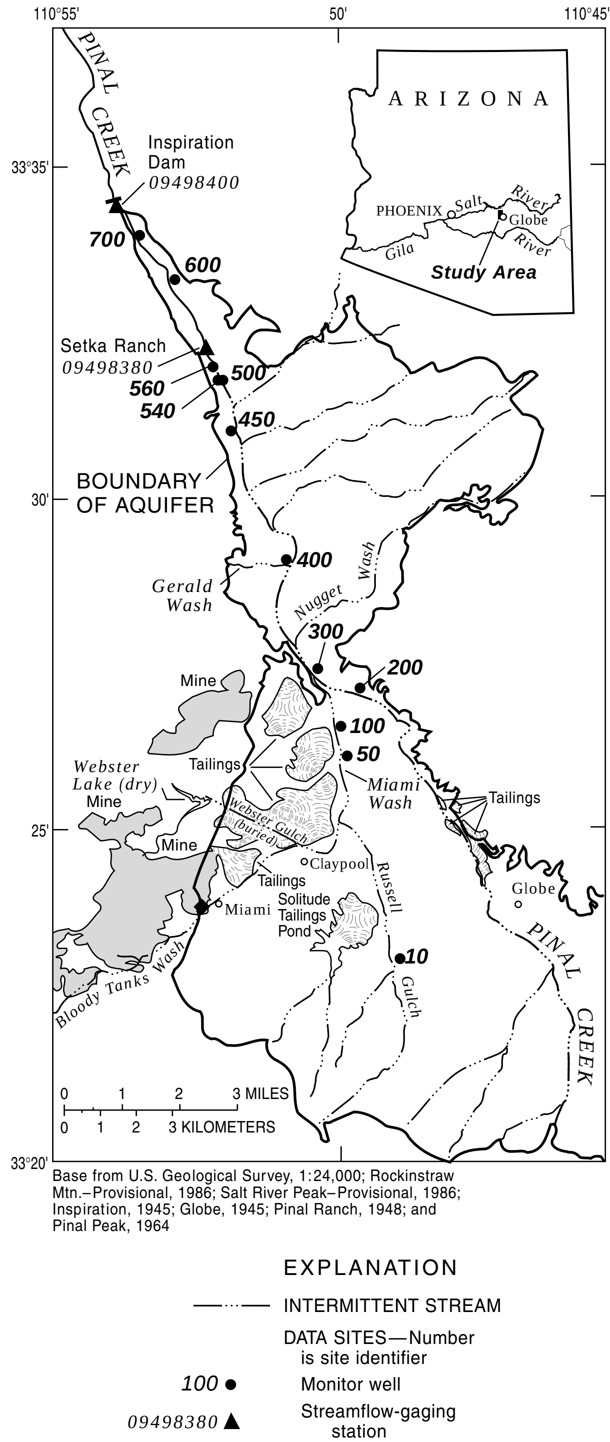

Figure 1. Pinal Creek Basin, Arizona

SUMMARY DISCUSSION

To augment routine sampling for major ions and dissolved metals, project monitoring wells were analyzed for concentrations of chlorofluorocarbon-12 (CFC-12) and chlorofluorocarbon-11 (CFC-11), dissolved gases, and stable isotopes of water in 1991, 1993, 1996, and 1998. Concentrations of dissolved nitrogen and dissolved argon in the ground waters are used to estimate recharge temperatures and the amounts of excess air trapped during recharge. The average recharge temperature calculated from the 1991 data was about 12°C±2°C—6 to 7°C colder than the average ground-water temperatures. Excess-air concentrations in 1993 were as high as 18 ml/L, indicating very rapid recharge during floods in the winter and early spring. Local precipitation records, air-temperature records and a 10°C temperature recorded in Pinal Creek during a large recharge event in February 1993 support the recharge-temperature estimates and the hypothesis of fast recharge provided by measurements of dissolved gas. Nitrogen production by denitrification is not considered a significant source of dissolved nitrogen. Indeed, concentrations of dissolved oxygen are high in all uncontaminated ground waters because of low organic-carbon contents in the water and in the aquifer materials. High partial pressures of carbon dioxide (pCO_2) were measured in the acidic ground waters and in the neutralized, contaminated ground waters. The high pCO_2 values are caused by the dissolution of carbonate minerals by the acidic ground waters.

Concentrations of CFC-11 and CFC-12 are used to calculate the dates when the sampled ground waters last equilibrated with atmospheric CFC concentrations, that is, at the time of ground-water recharge. The ground-water ages calculated from CFC-11 and CFC-12 concentrations depend on the estimated recharge temperature, recharge elevation, and excess-air concentration (Busenberg and Plummer, 1992). Concentrations of CFC-12 in ground water of Pinal Creek are abnormally high in many instances and are thought to be a consequence of a local atmospheric anomaly and of the high concentrations of excess air trapped during recharge rather than the result of point-source contamination. Ground-water ages calculated from concentrations of CFC-11 are insensitive (relative to CFC-12 ages) to excess air, and differed by no more than 1 year from age estimates that did not account for excess air.

Ground waters in the Pinal Creek Basin were first sampled for CFC analysis in 1991, following a

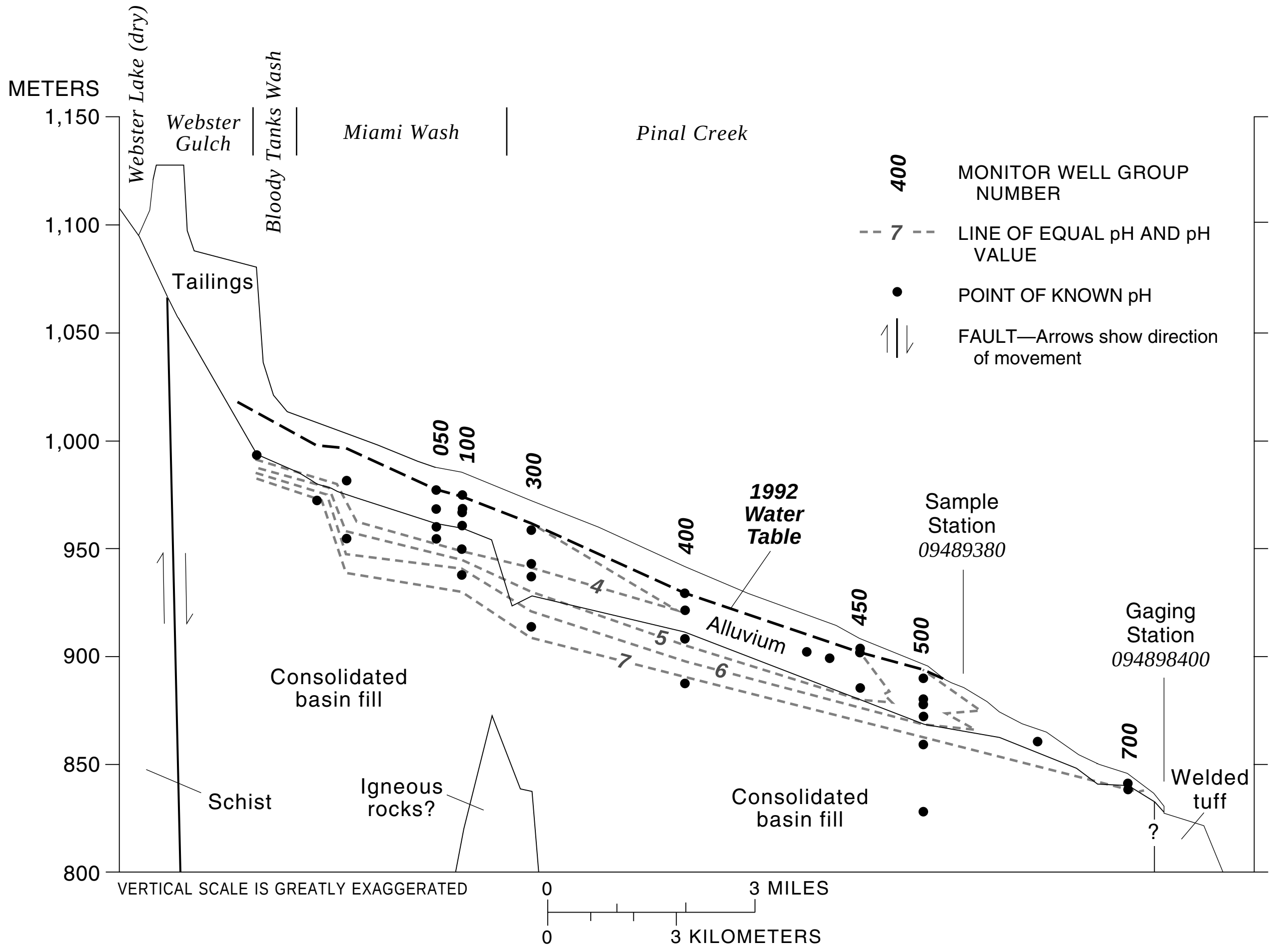

Figure 2. Distribution of pH in the aquifer in 1992. Line of section approximates the principal ground-water-flow line from Webster Lake to Inspiration Dam along the channels of Webster Gulch, Bloody Tanks Wash, Miami Wash, and Pinal Creek (Brown and Harvey, 1996).

period of steadily declining ground-water levels that began in about 1987. The ground waters were resampled in 1993, several months after a large winter flood recharged large amounts of water to the aquifer and caused the water table to rise by as much as 15 m in the southern part of the basin. Ground-water levels have again steadily declined since late 1993. In anticipation of increased remedial pumping and of the installation of a subsurface, impermeable barrier in the alluvium about 6 km upstream from Inspiration Dam, ground-water samples were collected and analyzed for CFC concentrations in 1998.

Samples collected in 1991 generally increase in age with depth and distance downgradient in the metal- and acid-contaminated ground waters (fig. 3). Ground-water ages calculated from CFC-11 concentrations are reasonable—3 to 15 years for acidic ground waters and 20 to 30 years for neutralized, contaminated ground waters. Deep uncontaminated ground waters have little or no measurable CFC-11 or CFC-12, which indicates that they are more than 50 years old. This observation also is supported by the low tritium contents (<0.1 TU) measured in those waters, which indicates that the deep waters were recharged before atmospheric nuclear testing started in the 1950's.

Ground-water recharge in winter and spring of 1993 significantly altered the ages calculated on the basis of CFC-11 and CFC-12 concentrations. Ground-water ages were as much as 8 years younger in samples collected in 1993 than in those collected in 1991, probably because recharge in the late winter and early spring of 1993 resulted in the mixing of ground water of different ages (fig. 4). Ground-water ages in water from the deepest wells at well group 400 and well group 500 were not affected by the recharge event; the ages of waters

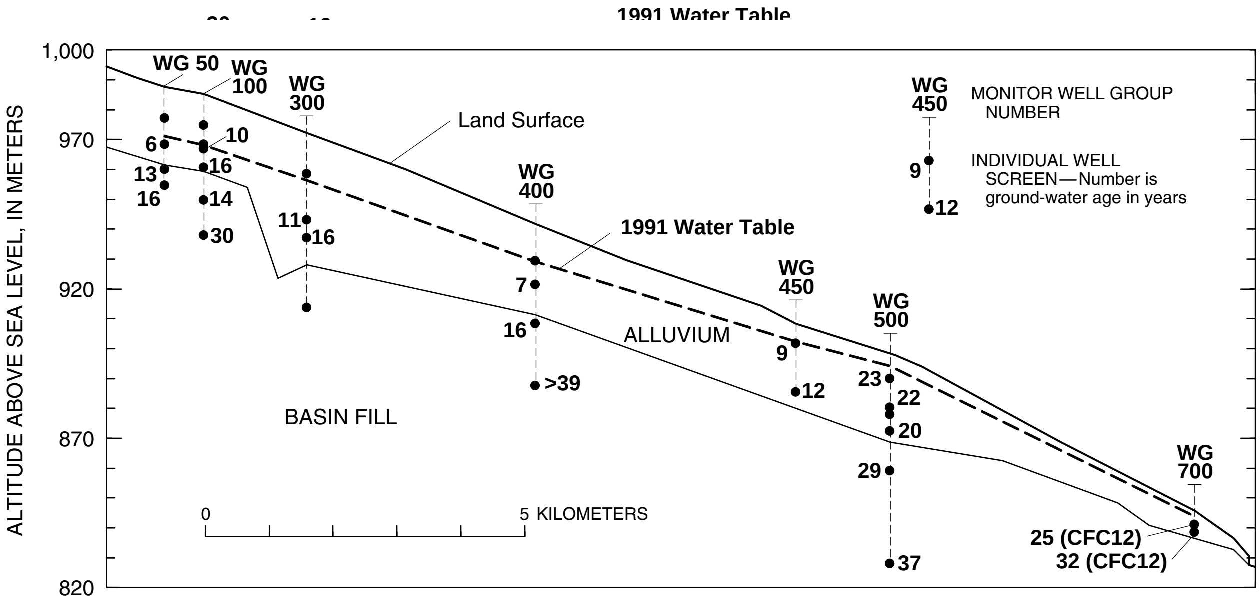

Figure 3. Hydrogeologic section showing ground-water ages based on chlorofluorocarbon 11 [and some chlorofluorocarbon 12(CFC12)] concentrations in Pinal Creek Basin, 1991.

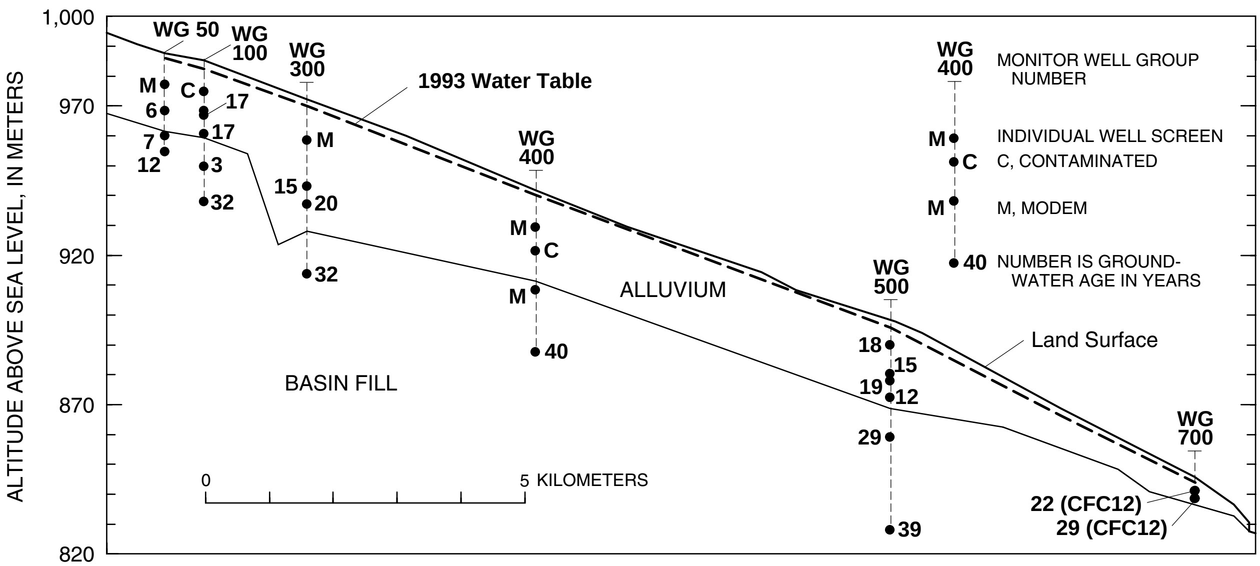

Figure 4. Hydrogeologic section showing ground-water ages based on chlorofluorocarbon 11 [and some chlorofluorocarbon 12(CFC12)] concentrations in Pinal Creek Basin, 1993.

sampled from those wells were the oldest of all the samples collected from the Pinal Creek Basin in 1993. Ground waters sampled in 1993 from wells that were dry in 1991 gave CFC ages that were either "modern" or "contaminated." Waters with "modern" CFC ages are defined here as those in which CFC concentrations were near equilibrium with the standard atmospheric concentrations at the time of sampling (after correction for excess air). Waters with "contaminated" CFC ages had CFC concentrations that were above equilibrium with the standard atmospheric concentrations at the time of sampling (after correction for excess air). By 1996, CFC concentrations in these same wells produced ages that ranged from 9 to 33 years as a result of the continued mixing of ground water of different ages (fig. 5). By 1998, ground-water

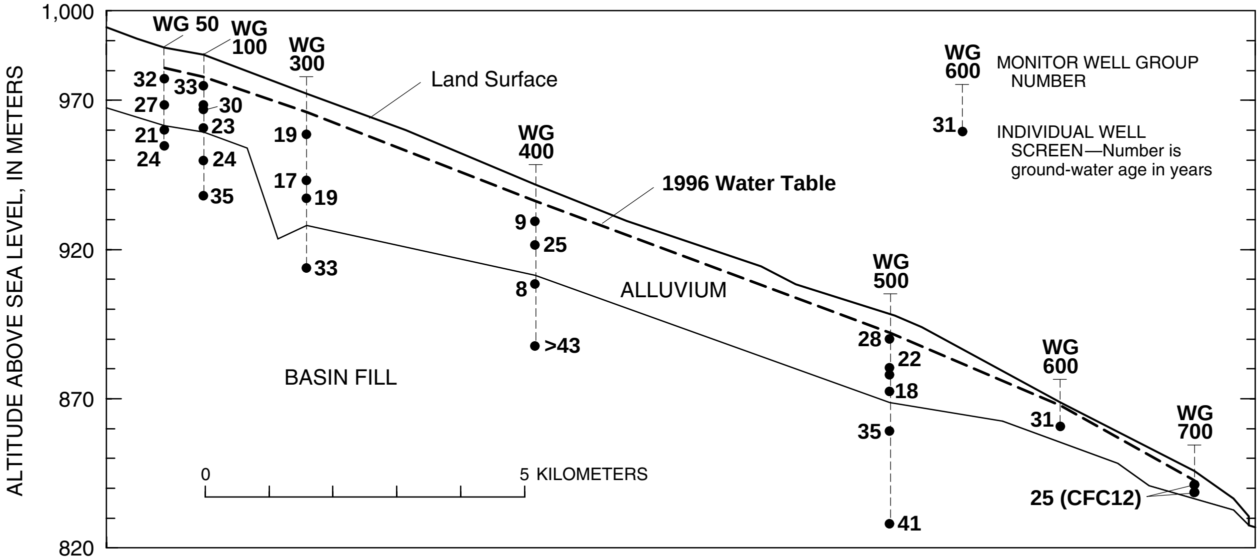

Figure 5. Hydrogeologic section showing ground-water ages based on chlorofluorocarbon 11 [and some chlorofluorocarbon 12(CFC12)] concentrations in Pinal Creek Basin, 1996.

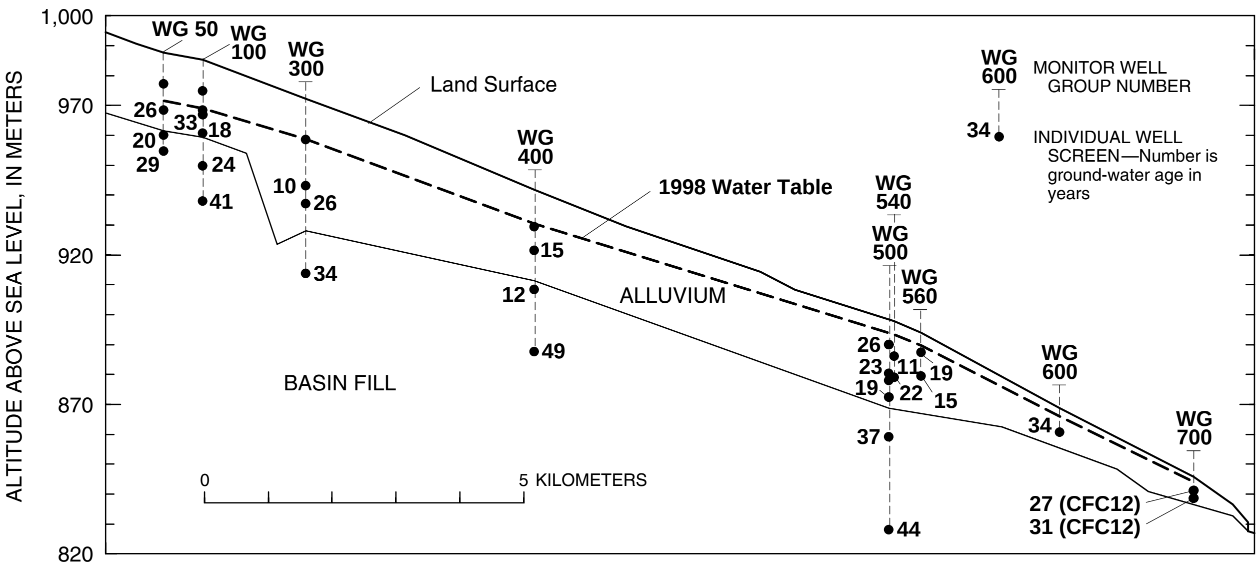

Figure 6. Hydrogeologic section showing ground-water ages based on chlorofluorocarbon 11 [and some chlorofluorocarbon 12(CFC12)] concentrations in Pinal Creek Basin, 1998.

levels had declined below the well screens of the shallowest wells in the acidic zone (fig. 6).

From 1996 to 1998, ground-water ages in the acidic ground water changed by as much as 7 years. In some wells, ground-water ages increased; in others, ground-water ages decreased. In neutralized ground waters, ages changed 3 years or less in most cases. The lack of an apparent trend is an indication of the complexity inherent in a transient-flow system that is affected by occasional large recharge events, by pumping for water supply and remediation, and by the removal of recharge sources (contaminated and uncontaminated) to the aquifer.

The recharge ages determined on the basis of of CFC-11 concentrations are consistent with available tritium, deuterium, oxygen-18, and dissolved-gas data, as well as with travel times calculated using observed ground- water levels and estimated aquifer characteristics. Deuterium and oxygen-18 values in water do not plot on the global meteoric water line (GMWL), but instead plot on a line with a slope of 5 (instead of 8 for the GMWL; fig. 7). These results imply that the ground waters are mixtures of deep, uncontaminated waters recharged at high elevations and cold temperatures and shallow contaminated waters that have undergone extensive evaporation. The specific conductance of the waters is highly correlated with their deuterium (or oxygen-18) content (fig. 8). This correlation is consistent with the hypothesis that Webster Lake was a major source of metal and acid contamination of ground water in the Pinal Creek Basin. Webster Lake was an artificial lake used between 1940 and 1988 for the storage of acidic, metal-laden, process water from the copper-refining industry.

The ground-water ages presented in this paper cannot be used to determine the age of the various ground-water solutes introduced by copper mining and refining operations. Indeed, many of the introduced solutes are affected by water-rock reactions (sorption, precipitation and dissolution) and generally will be retarded with respect to movement of the water and CFC molecules. Eychaner (1991), Stollenwerk (1994), Glynn and Brown (1996) and Brown and others (1998) discuss in detail the chemical and physical processes controlling the chemical evolutions of ground waters in Pinal Creek. Additionally, many

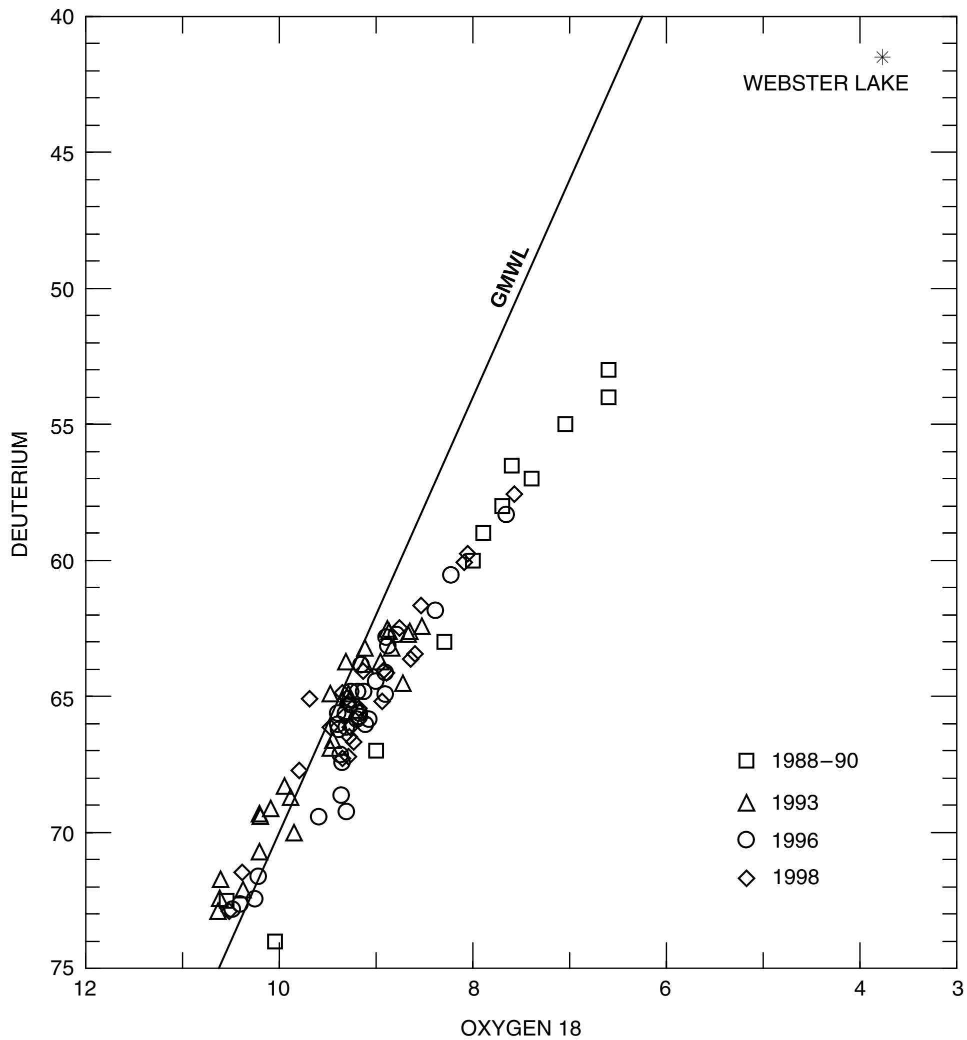

Figure 7. Oxygen 18 and deuterium concentrations in ground water and lake water, 1988–98.

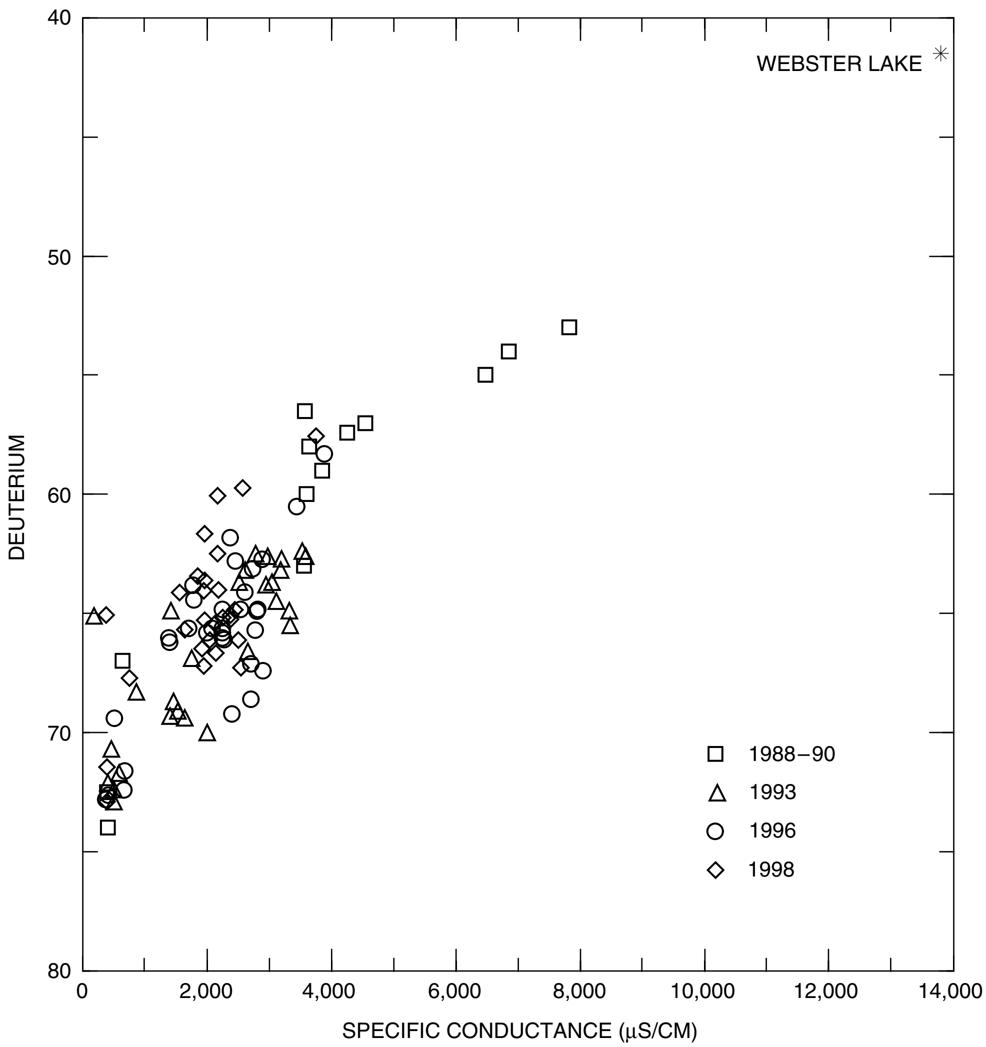

Figure 8. Specific conductance and deuterium concentrations in ground water and lake water, 1988–98.

uncertainties remain concerning the application of the CFC dating technique in this extensively contaminated and highly transient ground-water system.

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