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APPROACHES FOR GROUND-WATER DATING

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Measurements of the concentrations of atmospheric gases and isotopic substances in ground water were used to interpret the age of shallow ground water in the Chesapeake Bay Watershed. Ground-water age is defined as the time elapsed since recharge—when the water entered the ground-water system. All ages are regarded as apparent ages because they are based on an interpretation of measured concentrations of environmental tracers in ground water. Several dating techniques are used, each of which has advantages and limitations (Plummer and others, 1993; Cook and Solomon, 1997; Solomon and Cook, 1999; Plummer and Busenberg, 1999). Therefore, greater confidence in apparent age commonly is realized as multiple dating techniques are applied to the same sample. Furthermore,

by examining the relations among the various tracers, some physiochemical processes affecting the tracers become apparent. In the present study, concentrations of chlorofluorocarbons (CFCs), sulfur hexafluoride (SF_6), tritium (^3H), and tritium/helium-3 ($^3\text{H}/^3\text{He}$) ratio were used to interpret ground-water ages.

The relation between estimates of the atmospheric concentrations of CFCs and SF_6 (Plummer and Busenberg, 1999) and ^3H in precipitation at Washington, D.C., is shown in figure 7 (R.L. Michel, U.S. Geological Survey, written commun., 1999). Meteoric water recharged within the Chesapeake Bay Watershed during the past 50 years contains these tracers, and the concentrations in ground-water recharge have varied with time, making it possible to use this variation to estimate ground-water age. Dating methods that depend in part on solubilities of atmospheric gases in ground water (CFC, SF_6 , and to a lesser extent, $^3\text{H}/^3\text{He}$ dating) require evaluation of the recharge temperature.

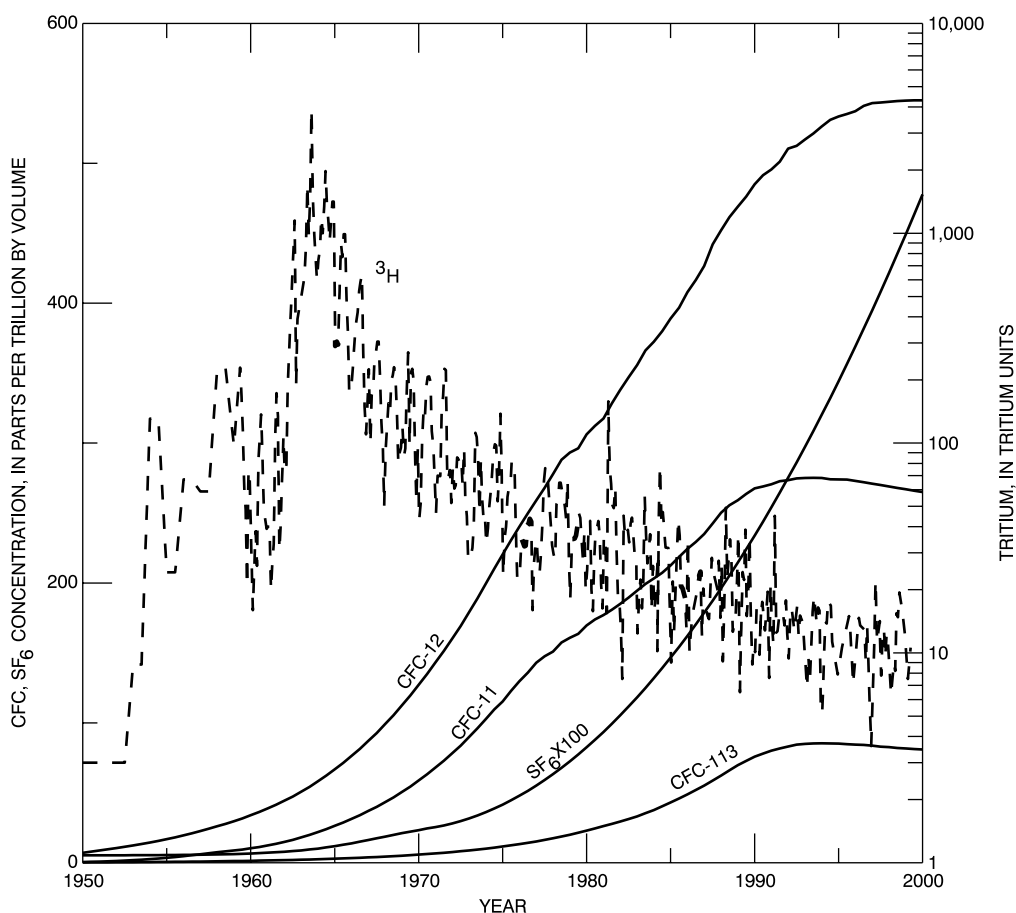


Figure 7. Chlorofluorocarbon (CFC) and sulfur hexafluoride (SF₆) air-mixing ratios for North American Air based on National Oceanic and Atmospheric Administration data from Niwot Ridge, Colo., and tritium (³H) in precipitation measured at Washington, D.C. (from R.L. Michel, U.S. Geological Survey, unpub. data, 1999).

Recharge Temperatures, Excess Air, and Quantities of Nitrogen from Denitrification

Recharge temperature is the temperature at the water table during recharge. Recharge temperatures were determined for individual samples using dissolved N₂ gas and Ar concentrations (Heaton, 1981; Heaton and Vogel, 1981; Heaton and others, 1983; Busenberg and others, 1993; Stute and Schlosser, 1999). The accuracy of this method is typically ± 0.5 °C on laboratory standards. Recharge temperatures of ground-water samples determined from concentrations of dissolved N₂ gas and Ar have larger uncertainties than those for laboratory standards because of uncertainty in recharge elevation (barometric pressure during recharge) and the

presence of excess air. Because the recharge elevation of most samples from the Chesapeake Bay Watershed probably is known to within ± 300 ft, this source of uncertainty in recharge temperatures probably is less than ± 1 °C in most cases. In reducing waters, denitrification processes can reduce dissolved NO₃⁻ to N₂ gas. If not recognized and corrected for, denitrification leads to a warm bias in the calculated recharge temperature, an overestimation of excess air in ground-water samples, and an underestimation of total NO₃⁻ initially recharged in ground water. Several procedures were utilized to refine recharge temperatures, excess air, and amounts of denitrification.

- (1) In aerobic samples, with concentrations of dissolved oxygen greater than approximately 1-2 mg/L, it generally was assumed denitrification had not occurred, and in most cases, the samples were not mixtures of anaerobic and aerobic waters. The recharge temperature and excess air were calculated directly from the dissolved N₂ gas and Ar data, using the sample elevation as an estimate of the recharge elevation. The quantity of N₂ gas derived from denitrification was assumed to be zero.
- (2) In waters with concentrations of dissolved oxygen less than approximately 1-2 mg/L, there is potential for denitrification. For samples of these waters, several additional procedures were used to estimate recharge temperature, excess air, and amounts of N₂ derived from denitrification. The quantity of excess air could be calculated within $\pm 0.1 \text{ cm}^3 \text{ kg}^{-1}$ water from dissolved Ne data, because the solubility of Ne in water is relatively insensitive to temperature variations in shallow ground water (Stute and Schlosser, 1999). Having defined the excess air quantity from the Ne data, the Ar and N₂ gas data were then used to determine the recharge temperature and amount of denitrification. If no Ne data were available, average quantities of excess air or average recharge temperatures were assumed, on the basis of results from aerobic samples in the watershed or results from local samples that had Ne analyses, and then used with the dissolved N₂ gas and Ar data to estimate quantities of denitrification. The procedure usually led to consistent results for a given watershed.

Dating with Chlorofluorocarbons

Ground-water dating with chlorofluorocarbons (CFCs) is based on historical data for the atmospheric mixing ratios of these compounds over the past 50 years (fig. 7), the Henry's Law solubilities of CFCs in water, and measurements of CFC concentrations in water samples (Busenberg and Plummer, 1992; Plummer and Busenberg, 1999). Anthropogenic sources of CFCs (in addition to that of the atmosphere) cause a young bias in apparent age or result in samples with CFC concentrations that are larger than those possible for equilibrium of water with modern air (termed "contaminated"). Samples with low concentrations of dissolved oxygen may have lost CFCs because of microbial degradation, particularly CFC-11, leading to an old bias in age. The

turnover in air-mixing ratios for CFC-11 and CFC-113 in the 1990s (fig. 7) also leads to ambiguity in age, with apparently modern ages that span the 1990s. The slow rise in CFC-12 air-mixing ratios during this study permitted age interpretation of modern waters but required measurement of recharge temperature for individual samples. The CFC-12 ages of waters recharged in the 1990s thus had uncertainties larger than those associated with SF₆ or ³H/³He.

Dating with Sulfur Hexafluoride

Sulfur hexafluoride (SF₆) is accumulating rapidly in the atmosphere; the current growth rate is about 6 percent per year (Busenberg and Plummer, 2000). SF₆ can be analyzed to a precision of 1-3 percent, and, even though atmospheric mixing ratios are small (currently about 5 pptv), dating with SF₆ is possible for waters recharged from about 1970 to the present (Busenberg and Plummer, 2000). SF₆ provides a useful alternative to CFC dating in the late 1990s because CFC air-mixing ratios leveled off or declined. The historical air-mixing ratio of SF₆ (fig. 7) has been reconstructed from production records and atmospheric measurements (Maiss and others, 1996, Geller and others, 1997; Maiss and Breninkmeijer, 1998).

Apparent ground-water ages based on SF₆ concentrations can be fairly sensitive to quantities of excess air trapped and dissolved during recharge. An iterative procedure (Busenberg and Plummer, 2000) was used to resolve ages on the basis of SF₆ utilizing the measured amount of excess air and subtraction of the excess air from the sample with gas composition corresponding to the age of the sample. Natural, low-level, terrigenous sources of SF₆ also are present in some crystalline rocks (Busenberg and Plummer, 2000). Water samples containing excess SF₆ from rocks have apparent ages that are too young. This process may have affected waters from some wells sampled in the Chesapeake Bay Watershed. SF₆ apparently is not affected by microbial degradation in ground water (Busenberg and Plummer, 2000).

Tritium Dating

Large amounts of tritium (³H) were injected into the stratosphere from atmospheric testing of nuclear weapons, primarily in the mid-1960s (Rozanski and others, 1991). This bomb-related ³H continues to rain out worldwide but at much lower concentrations than during the mid-1960s. Following recharge, ³H decays in ground water with a half-life of 12.4 years. Reconstruction of local ³H records for precipitation can be used, to a first approximation, to infer some aspects of ground-

water age. For example, a smoothed record of ^3H in precipitation at Washington, D.C. is shown in figure 8. A series of parallel lines define the decay paths of points along the precipitation input function over time. For example, water recharged prior to the 1950s should contain, in the year 2000, less than 0.1 TU. Water recharged in the year 1965 would now contain approximately 70 TU. The ^3H input function of figure 8 is greatly smoothed at half-year intervals. In actuality, ^3H in precipitation is quite variable between seasons and between individual precipitation events (fig. 7). It also is apparent that, because of the multiple peaks in ^3H content of precipitation, decay lines (fig. 8) can intercept multiple possible years of recharge. During the past 25 years, the ^3H content of precipitation decreased at approximately the same rate as ^3H decay and, consequently, meteoric water recharged since about 1975 and sampled in the late 1990s to 2000 contains about 10 TU in the Washington, D.C., area (fig. 8); thus, dating with ^3H alone is qualitative at best. Still, the ^3H data can be quite useful in recognizing post-bomb waters, and together with

other atmospheric tracers, the ^3H concentration can be very useful in recognizing ground-water mixtures. Furthermore, terrigenous sources of ^3H are negligible, and ^3H is not affected by microbial degradation processes.

Because of various meteorological processes and atmospheric moisture sources (Rozanski and others, 1991), it generally is necessary to construct a local record of “ ^3H -in-precipitation” for a particular region being studied. Several scaling procedures exist for reconstruction of local ^3H records on the basis of records from parts of the United States (Michel, 1989) and reports from the International Atomic Energy Agency (IAEA). In this study, the ^3H record at Washington, D.C., was multiplied by a scaling factor determined from local measurements of ^3H in recent recharge. For example, the Washington, D.C., record was multiplied by a scaling factor of 0.73 to estimate a long-term ^3H record in the Blue Ridge in Shenandoah National Park (Plummer and others, 2001).

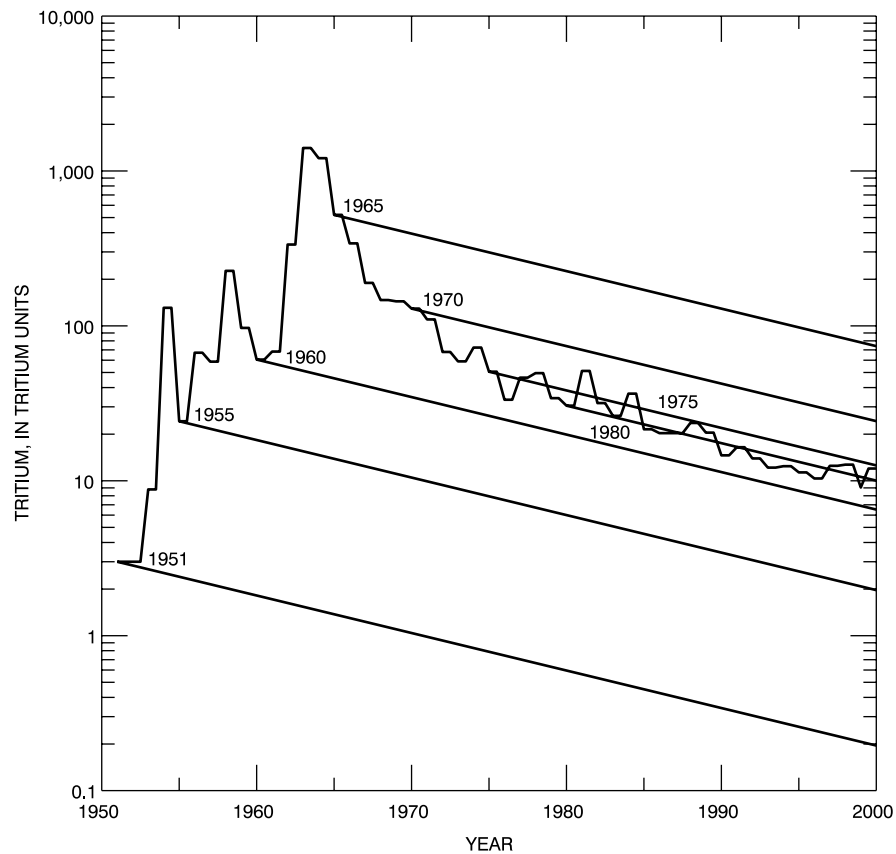


Figure 8. A smoothed record of tritium in precipitation at Washington, D.C. Parallel lines show the path of decay of tritium in ground water if recharged from precipitation in the years 1951, 1955, 1960, 1965, 1970, 1975, and 1980.

Tritium/Helium-3 Dating

Tritium/helium-3 ($^3\text{H}/^3\text{He}$) dating is based on the radioactive decay of ^3H (half-life 12.4 years). In closed systems, determination of both ^3H and tritiogenic ^3He (the daughter product of ^3H decay) in ground water can define the initial ^3H content and allow calculation of the $^3\text{H}/^3\text{He}$ age. Details of $^3\text{H}/^3\text{He}$ dating procedure are given in Schlosser and others (1988, 1989), Poreda and others (1988), Solomon and Sudicky (1991), Solomon and others (1993), Ekwurzel and others (1994), and Solomon and Cook (1999).

$^3\text{H}/^3\text{He}$ dating has two advantages over dating with atmospheric gases. First, the age is based on an isotope ratio, so mixing of young and old, ^3H -free (pre-bomb), water does not, in principle, affect the apparent age of the young fraction. Secondly, by measuring ^3H and tritiogenic ^3He , the initial ^3H content is determined analytically. The most serious limitations specific to $^3\text{H}/^3\text{He}$ dating of ground water in the Chesapeake Bay Watershed are addition of terrigenic helium from crystalline rock sources and loss of ^3He by degassing during sampling.

Mixing Models

Water pumped from a well or discharging from a spring is a mixture of the waters from all the flow lines reaching the discharge point. The age frequency distribution and mean age of the mixture affect the interpretation of the ground-water dating methods as well as the interpretation of other ground-water contaminant fluxes (Böhlke, 2002; this section). Three hypothetical mixing models that can be used to describe some of the variation normally seen in ground-water mixtures are piston flow, exponential mixing, and binary mixing (Cook and Böhlke, 1999). In some cases, the water reaching the open interval of a well or discharging at a shallow water-table spring is nearly uniform in age and can be approximated with a piston-flow model, as if the water flowed through a pipe from the point of recharge to the point of discharge without mixing during transit. Exponential mixing can describe discharge of water from well-mixed reservoirs, such as some lakes, or discharge from an unconfined aquifer receiving uniform areal recharge (Eriksson, 1958; Vogel, 1967; Maloszewski and Zuber, 1982; Maloszewski and others, 1983). One of the simplest mixing models to consider, and perhaps the most important in many fractured-rock environments, is binary mixing of young water with old (pre-tracer) water. In this case, a simple dilution occurs because the

old fraction is assumed to be free of the tracer and, consequently, the age of the young fraction can be calculated from the ratio of two tracers.

The ratios of CFCs and SF_6 over time are shown in figure 9. If the old fraction is CFC-free, and no other processes affect CFC concentrations other than air-water equilibrium, then the CFC-11/CFC-12 ratio will define the age of the young fraction if the ground water recharged between the late 1940s and about 1977 (fig. 9). Similarly, the CFC-113/CFC-12 ratio will define the age of the young fraction if the ground water recharged in the 1980s to the early 1990s (fig. 9). The ratio $\text{SF}_6/\text{CFC-12}$ also may prove useful in dating mixtures of young and old water. Once the age of the young fraction is determined (using tracer ratios), the fraction of young water in the mixture is determined from the ratio of the tracer concentration in the sample to the concentration expected for an un-mixed sample of age corresponding to the young-fraction age.

Because the various environmental tracers considered here have differing temporal patterns to their input functions, plots of one tracer against another can be useful in distinguishing hypothetical mixing processes that may affect the samples, in addition to recognizing samples affected by microbial degradation and (or) anthropogenic contamination. In the plots used in this report, the CFC and SF_6 concentrations were expressed as the atmospheric gas-mixing ratios (in parts per trillion by volume) that would be in equilibrium with the measured concentrations in the water at the N_2 -Ar-based recharge temperature, adjusted for the effect of recharge elevation. The normalized gas-mixing ratios are preferred to the measured concentrations because the normalization removes effects of local variations in recharge temperature and elevation and permits direct comparison of the data to regional records of atmospheric-mixing ratios.

Theoretical variations in the concentrations of CFCs, SF_6 , and ^3H in response to piston flow, exponential mixing, and binary mixing are shown in figure 10. Measured values for water samples will plot within the areas in the diagrams bounded by the curves representing the different concentrations of the modeled tracer, if no other processes have affected them. Samples with tracer concentrations that plot far outside the bounded areas may be contaminated or degraded. For example, it is relatively common for anaerobic ground waters to plot below the curves in figure 10; relatively low CFC-11/CFC-12 ratios indicating degradation of CFC-11. Water from many springs in the Chesapeake

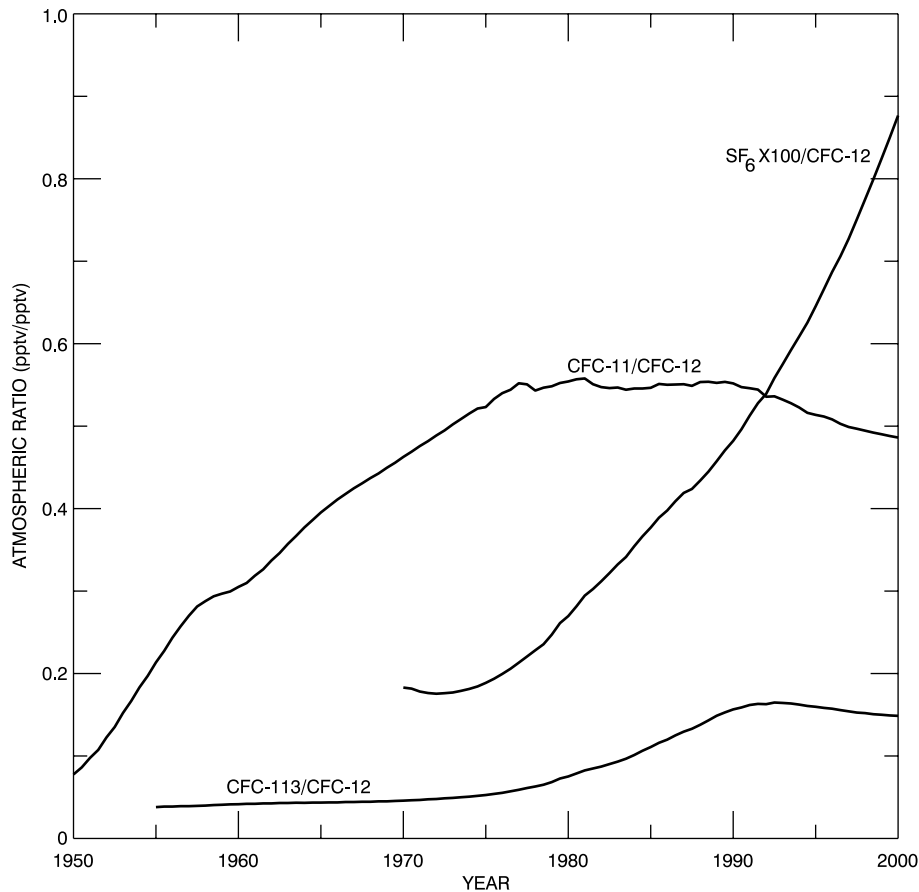


Figure 9. Atmospheric ratios of chlorofluorocarbon (CFC) and sulfur hexafluoride (SF_6) used in dating water or in dating the young fraction in mixtures of young water and old (tracer-free) water.

Bay Watershed plot outside the curves because of local CFC or SF_6 contamination. The model calculations for CFCs are nearly insensitive to expected variations in the amount of excess air, but similar calculations involving SF_6 are sensitive to variations in excess air because of the low Henry's law solubility of SF_6 relative to solubilities of CFCs.

If all tracers were reliable (no contamination, no degradation), it should be possible to derive information about the age frequency distribution and the magnitude of the mean age in a sample. A water sample that is not a mixture should plot somewhere along the solid piston-flow curves for all the tracers at points corresponding to the single age of the water. For example, point A would represent the composition of water recharged in 1984, with an age of 15 years when collected in 1999 (fig. 10). Samples that do not plot on the piston-flow curves are more likely to represent mixtures. An exponential mixture should plot somewhere along the exponential-mix-

ing curves at points corresponding to a single mean age. For example, point B would represent the composition of water with an exponential model mean age of 25 years when collected in 1999 (fig. 10). Binary mixtures could plot almost anywhere within the bounded area depending on the ages of the end members. The simplest case (represented by the heavy dashed line in figure 10) would be a binary mixture of modern (1999) water and old (pre-tracer) water. For a sample plotting on this limiting mixing line, the fractions of the two end members could be determined by the lever rule. For example, point C would represent the composition of a binary mixture consisting of 50 percent 1999 water and 50 percent pre-tracer water). Mean ages for binary mixtures of this type are not known because the age of the old fraction is not known. However, minimum mean ages for binary mixtures can be derived from the mixing fractions and the minimum age of the appropriate tracer-free water (for example, a sample plotting at point C,

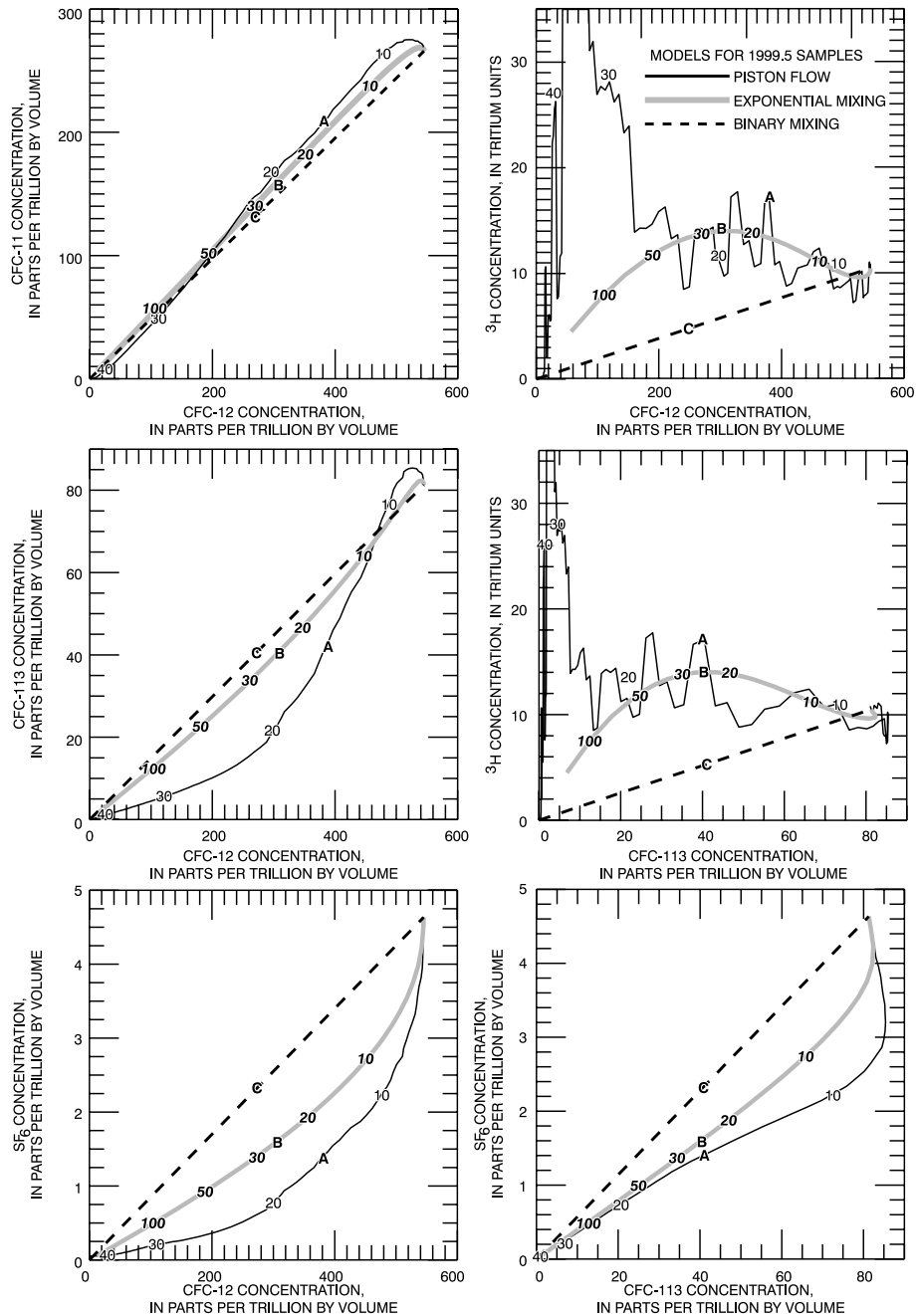


Figure 10. Environmental tracers in ground waters sampled in 1999. Abundance of tracer pairs are shown as continuous curves corresponding to different ground-water mixing models: (1) Thin solid lines (including points “A”) indicate compositions of discrete water parcels with single ages (corresponds to the “piston-flow” model); numbers in normal type indicate compositions corresponding to apparent ages ranging from 0 to 40 years. (2) Heavy curves (including points “B”) indicate compositions of mixtures with exponential age distributions (“exponential model”); numbers in bold italics indicate compositions corresponding to mean ages ranging from 0 to 100 years. (3) Dashed lines (including points “C”) indicate compositions of binary mixtures with varying fractions of “young” water with age of 0 years and “old” water that has no detectable tracer (for example, age > 47 years for ³H, > 60 years for CFC-12, etc.).

halfway between the limiting end members for CFC-12 and ^3H , would have a minimum mean age corresponding to $[0.5 \times 0] + [0.5 \times 60] = 30$ years).

The most common assumption made about binary mixtures in the Chesapeake Bay samples is that they contain a fraction of old (pre-tracer) water and a fraction of younger water with a piston-flow age somewhere between the pre-tracer age and the date of collection (Plummer and Busenberg, 1999). A sample of this type would plot on a mixing line from the origin to a point on the piston-flow curve corresponding to the age of the young fraction. The slope of a mixing line emanating from the origin would be equal to the tracer ratio shown in figure 9 for the young fraction. For example, ages of young fractions in many of the waters from fractured-rock environments in the Chesapeake Bay Watersheds (such as at the Mahantango Creek Watershed and the Muddy Creek Watershed) were calculated using the CFC-113/CFC-12 ratio, and the fraction of the young water in the mixture was calculated from the ratio of the measured parts per trillion by volume to that corresponding to the recharge year. It is evident from figure 10 that the uncertainties in calculated ages of mixing fractions will depend on the tracer used and on the value of the age of the young fraction. For example, it would not be possible to distinguish from the CFC-113/CFC-12 ratio of a binary mixture whether the young fraction had an age of 0 or 10 years (fig. 10). Also, because of the way the different tracer concentrations in the atmosphere have changed over time, it may not be possible to distinguish between mixing models for some combinations. For example, because CFC-11 and CFC-12 have similar historical records, the piston-flow, exponential-mixing, and binary-mixing models all yield similar curves (fig. 10) despite the fact they could represent very different age distributions and magnitudes.

Some of the most useful indicators of binary mixtures of old and young waters are combinations of ^3H and gas-tracer data. Because atmospheric ^3H concentrations have been elevated for a long time, old-water components can be identified by anomalously low ^3H concentrations in comparison with CFCs or SF_6 (for example, point C). Similarly, apparent piston-flow ages based on CFCs and SF_6 , if not corrected for mixing with old water in fractured-rock systems, can be biased old relative to $^3\text{H}/^3\text{He}$ ages. Because of ambiguities in distinguishing age-distribution models, and the possibility of degradation or contamination of various constituents,

it is important to consider simultaneously as many different tracer measurements as possible in a single sample to determine its history and age.

Environmental Tracer Data from the Chesapeake Bay Watersheds

Age information obtained as a part of this study was based on CFCs, SF_6 , ^3H , and $^3\text{H}/^3\text{He}$. Most tracer measurements are compared in figures 11 and 12. Samples with elevated concentrations of CFCs (CFC-11 > 300 pptv, CFC-12 > 600 pptv, and CFC-113 > 100 pptv) and SF_6 (> 5 pptv) were considered “contaminated,” could not be used for dating purposes, and are not shown on figures 11 and 12. Sources of CFC contamination usually are anthropogenic in nature (Plummer and Busenberg, 1999), and SF_6 concentrations in excess of air-water equilibrium and excess air values are usually from terrigenous sources.

Concentrations of CFCs and SF_6 in figures 11 and 12 are expressed in parts per trillion by volume, which was calculated from the measured concentration in water at the N_2 -Ar-based recharge temperature and estimated recharge elevation. Concentrations of SF_6 were corrected for the presence of excess air, assuming a piston-flow model (Busenberg and Plummer, 2000). ^3H concentrations are in tritium units and are compared to the record of ^3H in precipitation at Washington, D.C., decayed to the year 1999. Each plot compares one tracer to another. Model lines are included for piston flow, exponential mixing, and binary mixing of modern (1999) and old (pre-tracer) water. The “+” signs on the piston-flow line indicate specific recharge dates and the dots along the exponential-mixing lines correspond to mean residence times. Similar plots are presented in later sections of this report showing data specific to each watershed.

Examination of all samples from the Chesapeake Bay Watershed suggests some general features regarding applicability of particular tracers for dating. Overall, CFC-11 tends to be depleted relative to CFC-12 (fig. 11A) and may be degraded microbially relative to CFC-12 (Plummer and Busenberg, 1999) in soils or in ground-water environments with low concentrations of dissolved oxygen. Except in a few specific cases, CFC-11 data generally were not used for dating the samples from the Chesapeake Bay Watershed. Many water samples have CFC-12 and CFC-113 concentrations that plot within regions bounded by piston flow and binary mixing of young and old water (fig. 11B) and may be useful for dating. Many samples plot parallel to

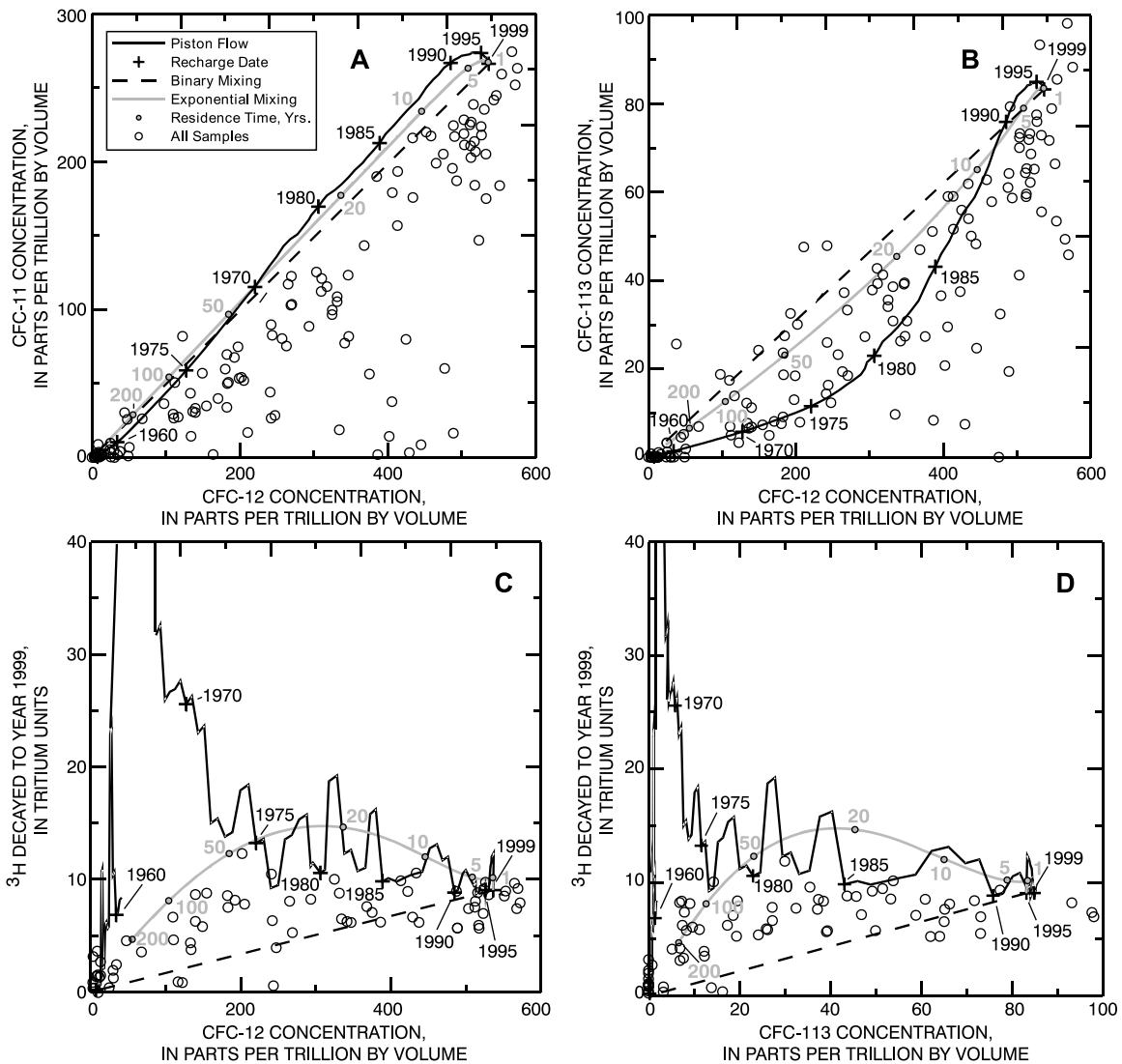


Figure 11. Relation between concentrations of environmental tracers in waters from the Chesapeake Bay Watersheds. A. CFC-11 and CFC-12; B. CFC-113 and CFC-12; C. ^3H and CFC-12; and D. ^3H and CFC-113. Model lines are included for piston flow, exponential mixing and binary mixing of modern (1999) and old (pre-tracer) water. The “+” signs on the piston-flow line indicate specific recharge dates and the dots along the exponential-mixing lines correspond to mean residence times.

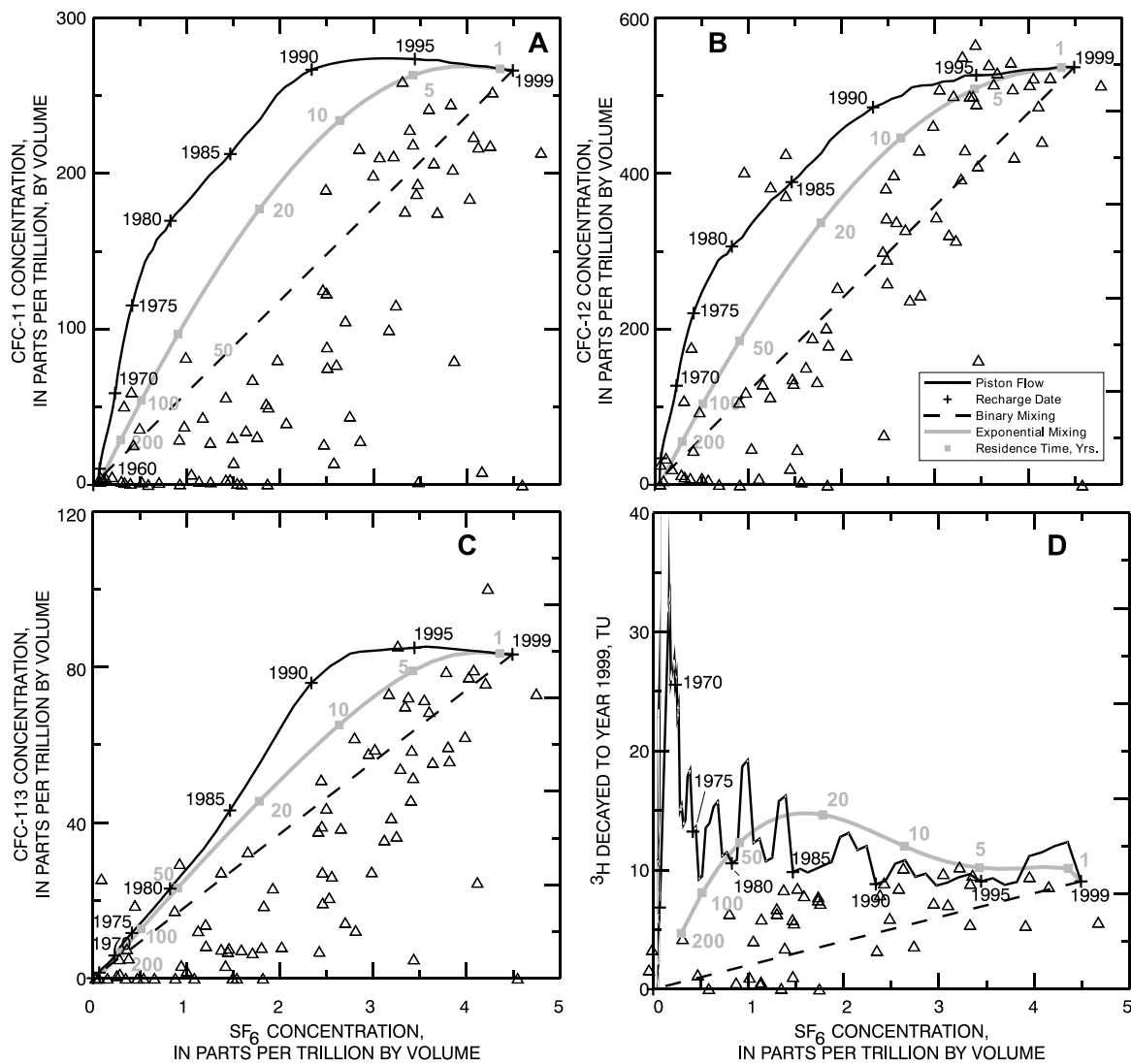


Figure 12. Relation between concentrations of environmental tracers in waters from the Chesapeake Bay Watersheds. A. CFC-11 and SF₆; B. CFC-12 and SF₆; C. CFC-113 and SF₆; and D. ³H and SF₆. Model lines are included for piston flow, exponential mixing and binary mixing of modern (1999) and old (pre-tracer) water. The "+" signs on the piston-flow line indicate specific recharge dates and the dots along the exponential-mixing lines correspond to mean residence times.

the piston-flow line but are somewhat elevated in CFC-12 relative to CFC-113 (fig. 11B), especially for the relatively young samples (post-1985 recharge dates). Plummer and others (2001) observed enrichment of approximately 2 percent on average in CFC-12 in air samples from Shenandoah National Park, Va., relative to that at Niwot Ridge, Colo., during the course of this study. Although local enrichment of air may account for some elevation in CFC-12, many samples are enriched by 10 percent or more in CFC-12 relative to Niwot Ridge, an enrichment greater than that measured in air samples at Shenandoah National Park. Because the piston-flow line for CFC-113 turns over in post-1995 samples, many samples that appear enriched in CFC-12 could be mixtures of recent and somewhat older water. Only a few samples appear to be elevated in CFC-113 relative to CFC-12; a greater proportion of samples are depleted in CFC-113 relative to CFC-12 (fig. 11B). There may be a removal process that preferentially lowers CFC-113 relative to CFC-12—possibly sorption onto organic matter in shallow ground water. Not all samples appear to be affected by this process.

Another group of samples from the Chesapeake Bay Watershed appears to be very old, based on the low concentrations of CFC-113 and CFC-12, though these samples also could be from methanogenic environments where all CFCs can be degraded microbially. Dissolved CH_4 was measured routinely for the Chesapeake Bay samples and is used in later sections of this report to screen those samples that could have concentrations of CFC-113 and CFC-12 lowered by microbial degradation. Further evidence for old water in samples with low CFC concentrations is low ^3H activities (figs. 11C and 11D). Other samples plot very close to the piston-flow line, particularly those with apparent recharge dates between 1970 and 1975, and may be largely unmixed. Other samples are consistent with binary mixtures of modern (1999) water and old, pre-CFC and pre- ^3H water. Most other samples appear to be mixtures, some with apparent exponential (mean residence time) ages of 10-20 years (fig. 11B).

The relations between ^3H and CFC-12 (fig. 11C) and CFC-113 (fig. 11D) show that most samples from the Chesapeake Bay Watershed can be interpreted as mixtures that lie between the lines for piston flow and binary mixing of modern and old (pre- ^3H and pre-CFC) water. Strong evidence for mixing (of any type) is indicated by the absence of any samples retaining the decayed, initial ^3H activity from the mid- and late-1960s bomb peak (figs. 11C and 11D).

Concentrations of CFC-11, CFC-12, CFC-113, and ^3H are compared to SF_6 concentrations in figures 12A-12D for all the samples from the Chesapeake Bay Watershed. Although there are specific cases where SF_6 appears to be a useful tracer, its application to dating is complicated by potential, unknown amounts of excess SF_6 . SF_6 concentrations can be elevated in samples with low concentrations of CFCs and ^3H (fig. 12A-12D). This suggests that SF_6 accumulates in water samples with increasing age, presumably from terrigenous sources. Many samples from the Chesapeake Bay Watershed probably have elevated SF_6 concentrations (fig. 12). In the comparison of SF_6 and CFC-12, which is the CFC least affected by microbial degradation, the youngest samples plot within the region bounded by the piston-flow and simple binary-mixing curves (fig. 12B), but with increasing age (lower CFC-12 concentration), many samples are shifted off the piston-flow line with elevated SF_6 concentrations that exceed that of simple binary mixing of modern and old water (fig. 12B). A few samples from the Chesapeake Bay Watershed plot along the piston-flow lines for CFC-12 relative to SF_6 and CFC-113 relative to SF_6 (figs. 12B and 12C) and may be unaffected by terrigenous SF_6 . The least useful combination of tracers is CFC-11 and SF_6 , where effects of microbial degradation on CFC-11 and contamination of SF_6 from terrigenous sources combine to shift most samples from the Chesapeake Bay Watershed outside of the regions bounded by any possible mixing models (fig. 12A).

Figure 12D compares ^3H to SF_6 and was constructed using the ^3H record for precipitation in Washington, D.C. These data are probably better suited for application to the Muddy Creek, Va., and Mahantango Creek, Pa., Watersheds, than for watersheds south and east of Washington, D.C. In moving south and east of Washington, D.C., moisture from continental air masses apparently mixes with greater proportions of Atlantic moisture, resulting in a general lowering of ^3H content of precipitation. Consequently, points south and east of Washington, D.C. (such as at the Polecat Watershed, central Virginia), and particularly on the Delmarva, Eastern shore region (areas of Green Run, Forth Fork Green Run, and Wayne Tulls Farm) probably have ^3H concentrations in precipitation that are lower than those recorded at Washington, D.C. It will be shown later that most of the relatively young points plotting below the binary-mixing line on figure 12D are from the Delmarva, Eastern shore region, and if a lowered ^3H in precipitation input function is used, these samples plot in the modern region or along the simple mixing line

between modern and old water. Along the Delmarva Eastern shore region, a ^3H function was estimated by multiplying the Washington, D.C., record by the factor 0.66. Inspection of figure 12D suggests that, in general, samples from the Chesapeake Bay Watersheds that are older than about 20 years may be more significantly affected by excess sources of SF_6 than samples younger than 20 years.

Lithology is probably an important consideration in determining regions best suited for application of SF_6 to dating. Busenberg and Plummer (2000) found excess SF_6 in ground waters from crystalline rocks and Paleozoic limestones but not in sand aquifers such as in the Delmarva, Eastern shore region. Of the four regions investigated, SF_6 appears least suited for dating in the siliciclastics of the Mahantango Creek Watershed and the Paleozoic carbonates at Muddy Creek, Va., and better suited for dating water in the Piedmont regolith of the Polecat Creek Watershed and best for dating water in the sands of the Delmarva, Eastern shore region.

Age information specific to individual watersheds is discussed separately in later sections of this report and tabulated in the appendixes.

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