CFCs and SF6 in aquifers investigations - The significance of the unsaturated zone and the origin of groundwater.

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1) Abstract

Chlorofluorocarbons (CFCs) and sulfur hexafluoride (SF_6) were used as age-dating tools and environmental tracers for groundwater flow in a field study in Central Mexico. These gaseous tracers are used because of their relatively well-known global input function. The interpretation of the CFC data led to variable residence times: in most of the investigated water the existence of young water components could be proved; whereas in only a small percentage, the CFC content is lower than the detection limit. In general, the measured contents of CFC-11 ($CFCl_3$), CFC-12 (CF_2Cl_2), and CFC-113 ($C_2Cl_3F_3$) are nearly ideally correlated and allowed unambiguous interpretations. As the unsaturated soil zone is some tens of meters thick, the significance of this part has been investigated. It could be concluded that the delay time due to transport in the unsaturated zone is relatively low, i.e. less than 20 years. A two-component-mixture-model was used. It shows that the young water component (< 50 years old) of all sample sites lies between less than 1 % and about 90 %. Assuming an exponential distribution function of the travel time between input and arrival at the well, the mean residence time in each site was calculated, based on the CFC-11 and CFC-12 concentrations. The CFC calculated ages were checked for consistency. Finally, a comparison between CFCs and SF_6 results revealed the existence of two different groundwater groups: one as a result from atmospheric input; and the second derivative from (deep) natural leaching processes of SF_6 in the aquifer.

2) Introduction

The intensive extraction of groundwater in semiarid an arid regions, can result in a water supply shortage and groundwater quality deterioration. Furthermore, information on local groundwater in such regions is often scarce, so that the water related problems become more accentuated. Because of the necessity to know the groundwater regime and to respond to these problems, hydrogeologists apply chemical and nuclear technologies on groundwater for a better understanding of these processes. One of the classical approaches is the combined use of water chemistry, stable and radioactive tracers like Cl, Br, ^{18}O, ^{2}H (deuterium), ^{3}H (tritium), and ^{14}C (radiocarbon), to meet element concentrations and parameters like groundwater origin, residence time and flow rate. In shallow groundwater, it is very common to use tritium for detection of young water components and age dating. Nowadays, the use of this isotope as age dating tool has ceased due to the low concentration in the hydrological cycle. Other tracer technologies are developed and some of them recently investigated for its applicability in hydrological studies. In this study, we investigated the relevance of the gases chlorofluorocarbons(CFCs) and sulfur hexafluoride (SF_6) as age dating tools in dry climates.

3) Theory

For the applicability of such gases, some conditions have to be met first: the most important ones are (1) the knowledge of their input function and (2) the gas-air equilibrium in the unsaturated zone. The atmospheric concentration histories of CFCs and SF6 are very well known since measurements in 1975 and can be deduced from industrial production of these gases up to the 1930s and 1950s, respectively. The enormous advantages of these gases are their globally equal distribution and their temporally increasing concentration, though in the last years the common effort of the industrialized countries to cease the CFC production - the Montreal Protocol in 1987, and the Kyoto Protocol in 1996 - has reduced their atmospheric concentration. On the other hand, the atmospheric content of SF_6 actually grows with a rate of 7% per year and is expected to increase for decades because their exists no reduction agreement although its global warming potential is considered as very high.

The second condition, the gas-air equilibrium throughout the unsaturated zone, can be guarantied only if the unsaturated zone is relatively thin (some tens of meters) or the groundwater and its characteristic gases are infiltrating fast (less than some tens of years). This is the explanation of why most of the studies with the use of CFCs or SF6 are done in shallow groundwater.

On the other hand, gaseous tracers, e.g. CFCs, ^{85}Kr and SF_6 pass the unsaturated zone by diffusive processes before they enter the groundwater at dissolved concentrations according to Henry's law. This transport is much faster than the advective transport with the seeping water and the unsaturated zone residence time can be neglected in many cases if the depth to the water table is less than 10 m (Cook and

Solomon, 1995). However, to date what happens with unsaturated layers of more than 10 m of thickness is not very well understood.

4) Tracer techniques

CFCs

Chlorofluorocarbons (CFCs) are stable, artificially-created chemical compounds containing carbon, chlorine, fluorine, and sometimes hydrogen. They were first manufactured in the 1930s. At the present, they are used primarily to facilitate cooling in refrigerators and air conditioners, as well as cleaning agents, solvents and blowing agents in the production of foam rubber and plastics. CCl_2F_2 (F-12), CCl_3 (F-11) and $C_2Cl_3F_3$ (F-113) are the most common representatives on the CFC market. Due to there rapid accumulation in the atmosphere and catalytic chain reactions by the sun's radiation, they are contributing to the stratospheric ozone depletion and global warming effect. Additionally, these gases are long living in the stratosphere; current estimates of atmospheric lifetimes of CFC-11, CFC-12, and CFC-113 are about 45, 87, and 100 years, respectively. This all makes it that the CFCs are being phased out under the Montreal Protocol, signed by 37 nations in September 1987 as an international agreement. Later on, this agreement was strengthened ceasing the CFC production in industrialized countries in 1996 (Fabian and Singh, 1999).

The potential of chlorofluorocarbons (CFCs or Freons) as age-dating tools and transport tracers of natural waters was detected already in the 1970s in hydrological (Thompson and Hayes, 1979) and oceanographic studies (Lovelock et al, 1973). The measurement of CFCs has become routine in the 1980s (Bullister and Weiss, 1983). Extensive reports about modern CFC laboratory analyses can be appreciated in Busenberg and Plummer (1992), Oster et al. (1996b), and Hofer and Imboden (1998).

In groundwater, CFCs were used successfully in (i) contaminant hydrogeology (Böhlke and Denver, 1995; Oster et al., 1996c), (ii) in age-dating of shallow groundwater (Busenberg and Plummer, 1992; Dunkle et al., 1993, Reilly et al., 1994), and (iii) in quantification of the groundwater flow and transport system (Reilly et al., 1994, Brennwald et al., 2001).

SF_6

SF_6 is mostly man-made but also occurs naturally. Like CFCs, Sulfur hexafluoride (SF6) has increased during the past 40 years. Significant production began in the 1953 for use in high voltage electrical switches. Today, the predominant use of SF_6 is in gas-insulated switchgear and in blanketing or degassing molten aluminum and magnesium. SF_6 is extremely stable with an estimated lifetime of 3200 years (Morris et al., 1995). This feature has brought into discussion the environmental impact of SF_6 aimed at the reduction of the emission.

In groundwater, the SF$_6$ method was used successfully in (i) contaminant hydrogeology (Clark et al., 1995; Zoellmann et al., 2001), as (ii) artificial tracer (Wilson and Mackay, 1996; Schlatter et al, 1997), (iii) in age-dating of shallow groundwater (Busenberg and Plummer, 1997; Beyerle et al., 1999), and flow transport (Zoellmann et al., 2001). The analysis method has been described by Busenberg and Plummer (2000).

Groundwater can be dated with SF$_6$ for the last 30 years. As the atmospheric concentration of SF6 is expected to continue increasing, it is believed to be an excellent age-dating tool of post-1990s groundwater (Maiss and Brenninkmeijer, 1998). However, the dating method does not work when the natural background concentration of SF6 is high, i.e. volcanic rocks such as in rift zones, faults, igneous intrusions, geothermic areas, and diagenetic fluids (Busenberg and Plummer, 2000). On the other hand, this makes it to a preferable tracer for detection of leaching processes in the underground.

5) Field Site

The Alto Rio Laja study area covers approximately 6400 km^2 of predominantly agricultural land in the north of the Guanajuato State, Mexico (Figure 1).

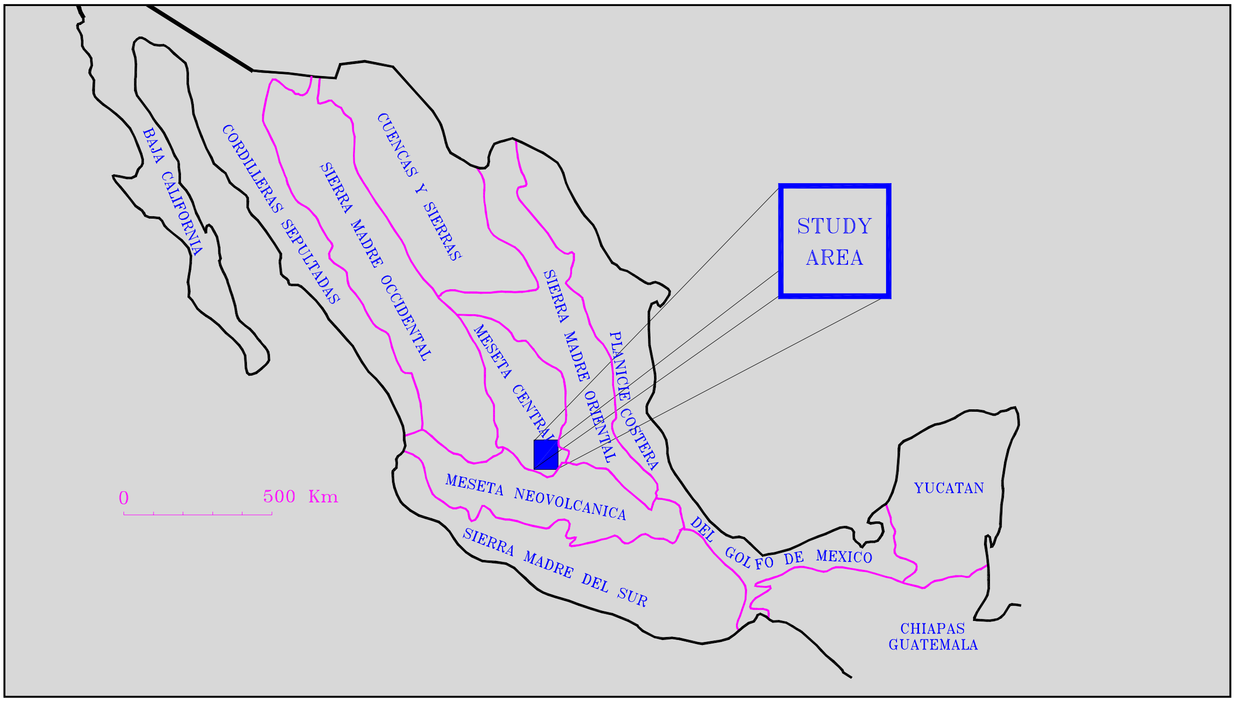

Figure 1: Physiographic location of the study area (after Raisz, 1964)

The land surface of the study area is characterized by a gently rolling plain with some topographic elevations (*mesetas*) and many intersections (*arroyos* or *canyons*), surrounded by various sierras and volcanoes. The highest elevation amounts about 2700 m above sea level (m asl), whereas the plain is about 2000 m asl. From the physiographic point of view, the study unit is situated in the Meseta Central, and in the SE part it embraces the northern portion of the Transmexican Volcano Belt (TMVB), which represents a tectonic arc crossing the central Mexican territory in W-E direction.

The lithological units that outcrop in the study area can be divided into two large packages: (i) the basal complex of the Early Cretaceous Period, and the (ii) cover complex of the Cenozoic Era. From the hydrogeological point of view, the aquifer consists in the upper part of unconsolidated sandy to silty sediments, interstratified with volcanic conglomerates and tuffs, and in the lower unit of fractured ignimbrites of mainly rhyolitic origin (Figures 2 and 3).

The rainfall season is from May to October. The mean annual and summer temperature are 17.1 and 21.0°C, respectively. The average of the annual precipitation is 556 mm/a (INEGI, 1998). The major stream in the study area, the Río Laja, carries water only during the rain season. After the nomenclature of the UNESCO, this sedimentary basin can be considered as semi-arid ($0.2 < P/PET < 0.5$, where P is the precipitation and PET the evapotranspiration).

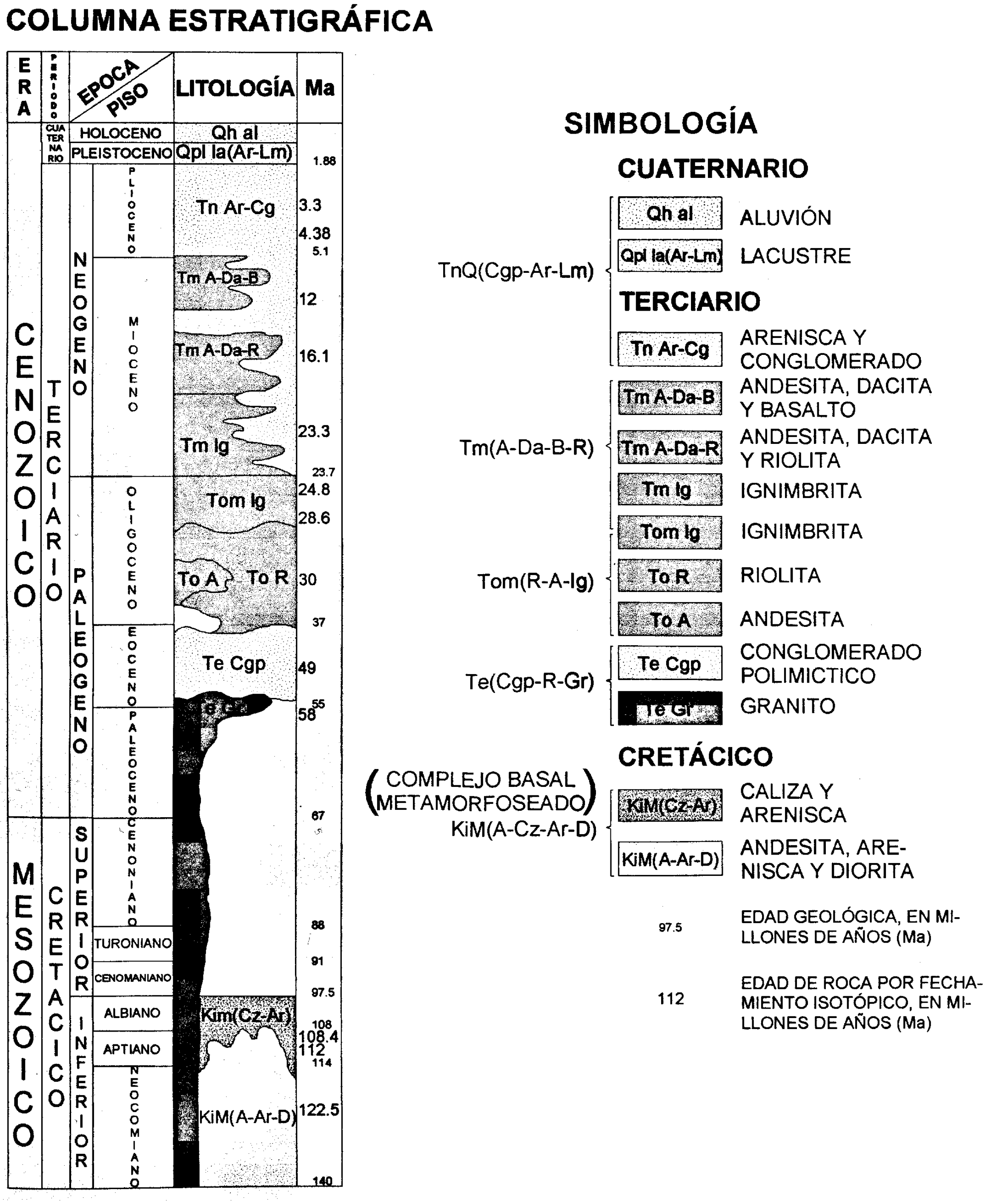

Figure 2: Stratigraphy of the study unit, after CODEREG (2000).

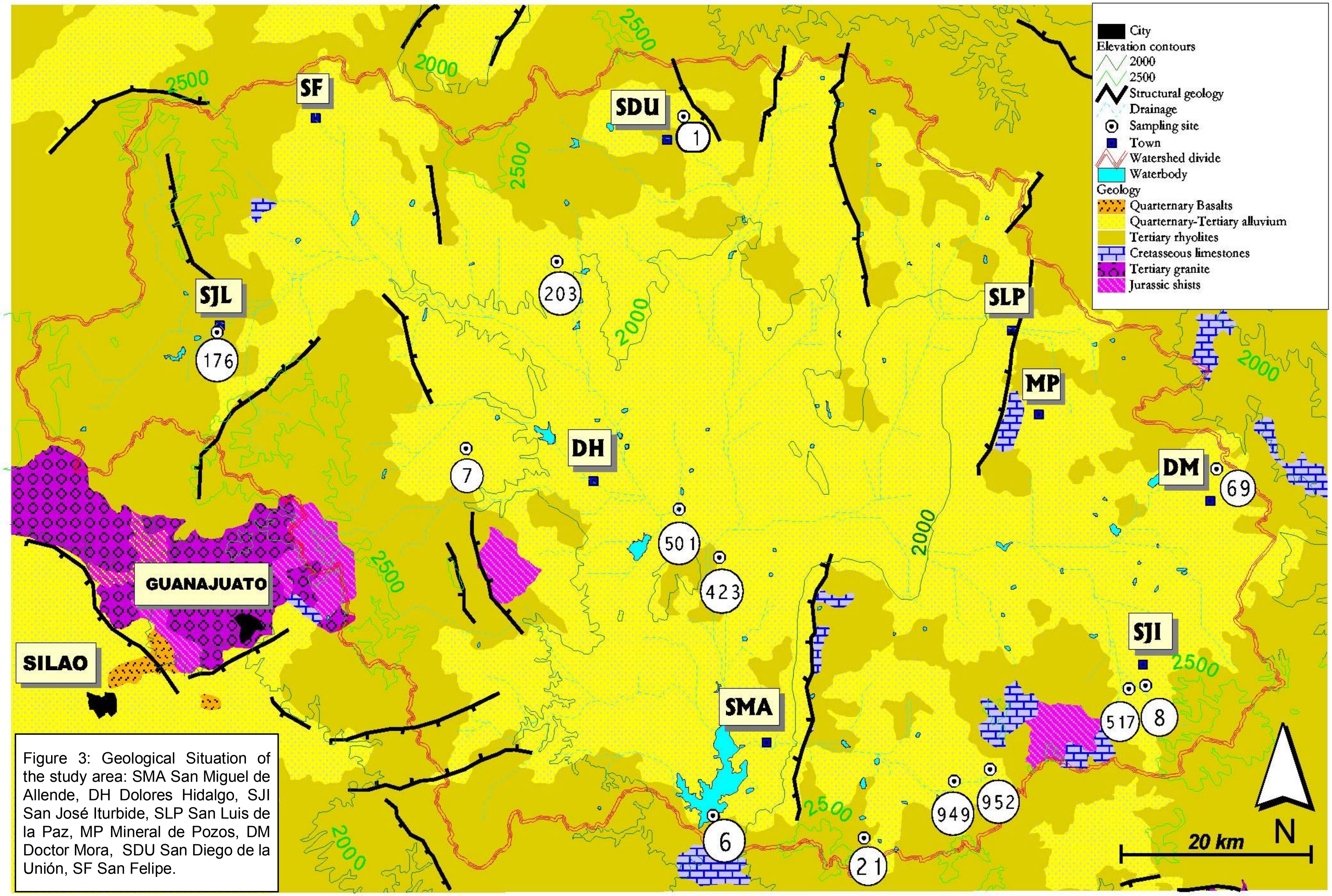

Figure 3: Geological Situation of the study area: SMA San Miguel de Allende, DH Dolores Hidalgo, SJI San José Iturbide, SLP San Luis de la Paz, MP Mineral de Pozos, DM Doctor Mora, SDU San Diego de la Unión, SF San Felipe.

6) *Sampling and measurements*

Thirteen sampling sites were used for measurements of piezometric heads, well completion depth and groundwater sampling. Prior to sampling, the borehole and all fittings were flushed with groundwater of at least three times the borehole volume. Then oxygen concentration, water temperature, electrical conductivity, alkalinity and pH were measured. For sampling of CFCs and SF_6, a special 1000-ml glass bottle with glass fittings was used. To restrict air contamination and to remove all gas bubbles, the glass bottle was filled directly using a copper tube, and flushed about ten times of its volume (10 L). For transport, the tightly tapped bottle was placed in a lamina box which itself was filled with water and sealed. Analyses were done in less than 15 days after sample collection at the Spurenstofflabor Dr. Oster in Wachenheim, Germany, using a gas chromatograph with an electron capture detector as described by Oster et al. (1996a).

7) *Results*

In general, the results for the three analyzed CFCs - CFC-11, CFC-12, and CFC-113 - show that there exists a significant analytical level of concentration. This demonstrates that the waters parcels contain young water components. There exists a good agreement between the measured values of these three gases.

Significance of the unsaturated soil zone

Due to the very effective diffusive process in the soil air, the existence of an equilibrium state between the CFC concentration in the soil zone and the infiltrating water can be assumed. Thus, it is very important to meet the dynamic interaction between the atmospheric increase of CFCs and the concentration history in the soil air. A raw estimation demonstrates that a thickness of about 50 m of unsaturated soil zone results in a lag time of the input signal of about 10 years, which is relatively low.

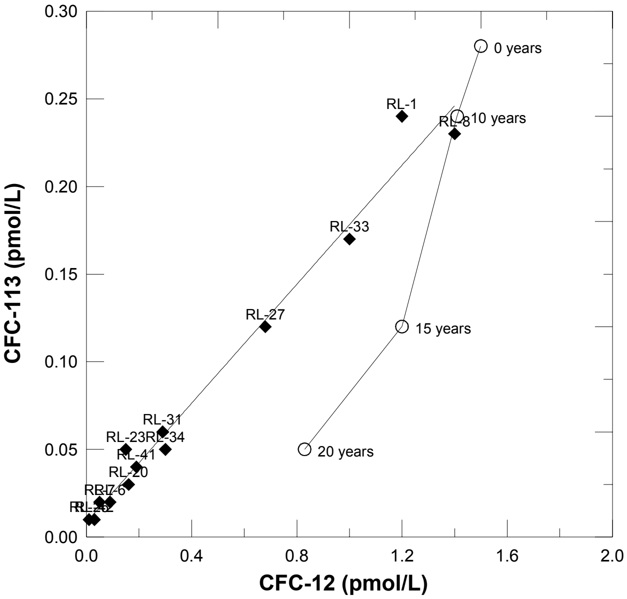

Figure 4: CFC-12 vs. CFC-113 concentration. Additionally, the expected CFC-12 and CFC-113 concentration depending on the lag time due to diffusive transport (0, 10,15, and 20 years, respectively; open circles) is matched.

The unsaturated zone depth in the study area is extremely variable with an average of about 80 m. The sampling sites present depths between 10 and 120 m to the water table. The CFC-12 vs. CFC-113 concentrations of the well samples are demonstrated in Figure 4. Additionally, the expected CFC-12 and CFC-113 concentration depending on the lag time due to transport (0, 10,15, and 20 years, respectively) is matched (open circles). As the measured sampling data coincide very well with the relatively low lag time, the system indicates a minor time lag of the input function, despite of the relatively thick unsaturated soil zone. Cook & Solomon (1995) observed similar results in the Surgeon Falls Surficial aquifer, Ontario: 6-10 years for 45 m of aeration zone.

Age dating

The tracer data can be interpreted by the box model approach. Generally, a transfer function is assumed a priori. We used a mixing model for determination of components, and an exponential model for interpretation of the average residence time.

Two-component-mixture

The assumption of this model is the existence of a mixture between an old (> 50 years and free of tritium) and a recent (0 to 10 years old) component:

$$e_{\text{young}} \cdot c_{\text{young}} + (1 - e_{\text{young}}) \cdot c_{\text{old}} = c_{\text{measured}}$$

where $e_{\text{young/old}}$ is the contribution of young/old water, and $c_{\text{young/old/measured}}$ the concentration of young/old/measured water. By using this equation, it was possible to calculate the young component contribution. Additionally, the recharge temperature was necessary. The temperature at the groundwater table was estimated to be equal to the average annual air temperature, 17° C, and the infiltration height of about 2,100 m a.s.l. The therein-resulting reference concentration for the study area is about 1.5 pmol/L, 3.2 pmol/L, and 0.28 pmol/L, for CFC-11, CFC-12, and CFC-113, respectively.

Exponential Model

The exponential model assumes an ideally exponential distribution of the residence time from the site of recharge to the withdrawal at the production well. The “exponential” age corresponds to the mean residence time in the groundwater reservoir:

$$c_{out}(t) = \int_{-\infty}^{t} c_{in}(t') \cdot \frac{1}{\tau} \exp\left[-\frac{t-t'}{\tau}\right] dt'$$

where t is the time, c_{in} the input concentration, and τ the mean residence time. The mean residence time can be determinate independently for each, CFC-11 and CFC-12, respectively. The weighted average value is a good estimation for the mean residence time. In our case, CFC-113 was not considered, because its measurements were within the proximity of the accuracy limit and hence contained analytical errors.

Consistency of CFC Ages

The consistency of the CFC ages was checked in shallow water. Based on the assumption, that the vertical velocity at the water table surface is simply a function of the recharge rate r and the porosity p given by the following relation:

$$v_{vert} = \frac{r}{p}$$

the time of travel t for vertical movement from water table to a point at a given depth near the water table is then given:

$$t = \frac{d}{v_{vert}} = \frac{d \cdot p}{r}$$

Ranges of travel time can than be calculated for shallow wells for a reasonable range of recharge rates and porosities (Table 1). Of three wells examined, the recommended CFC model recharge age of the two wells no. 1 and no. 501 lie in the range of the expected travel time.

Table 1: Calculated range of travel time for three shallow wells and recommended CFC model recharge age.

Well number	Depth below water table of center of well screen (m)	Range of recharge Rate (mm/y)	Range of Porosity (unitless)	Range of Time of Travel (years)	Recommended CFC Age (years)
1	0.7	21 - 41	0.25 - 0.40	4.3 – 13.7	9.0 ± 3.0
8	1.4	25 - 49	0.25 – 0.40	7.1 – 22.8	6.0 ± 1.0
501	2.0	26 - 52	0.25 - 0.40	9.6 – 30.7	15.0 ± 3.0

Comparative results with SF6

In Figure 5, the contents of sulfur hexafluoride (SF_6) are matched versus the young water contribution obtained from CFC results. Some of the waters align very well at the correlation line (group 1). However, there can be detected an excess of concentration. The observed values for young groundwater is about 15 fmol/L; this is about 15 times more than expected from atmospheric input. The excess can be interpreted as a results from SF_6 leaching from rocks: other studies reported SF_6 concentrations greater than that possible for equilibrium with modern air in springs issuing from igneous and volcanic rocks at or near fault contacts separating crystalline and sedimentary rocks; the therein reported maximum SF_6 concentrations are 42.1 fmol/L (Busenberg & Plummer 2000). In our study, we suggest that because rhyolite and granite have higher fluoride concentrations than basalts and mafic rocks, and the silicic rocks may be the source of the natural SF_6. Additionally, there could be detected a correlation between high Cl concentration and shallow water, and low Cl concentrations corresponding to deep water (Figure 6a).

In combination with SF_6, the final interpretation led to the following statement: some of meteoric water has infiltrated and circulates as shallow water (no. 501, 1) with high Cl and "normal" air equilibrated SF_6 concentrations indicating evaporation processes. Others evolve as intermediate to deep water with both, Cl and SF_6 in low concentration (no. 952, 8, 203). Finally a group of deep water (more than 75 m depth to water table) owing low to high Cl and SF_6 in excess (no. 176, 6, 69, 423), indicating mixture with Cl diluted waters and natural enrichment with SF_6 resulting from leachates (Figure 6b).

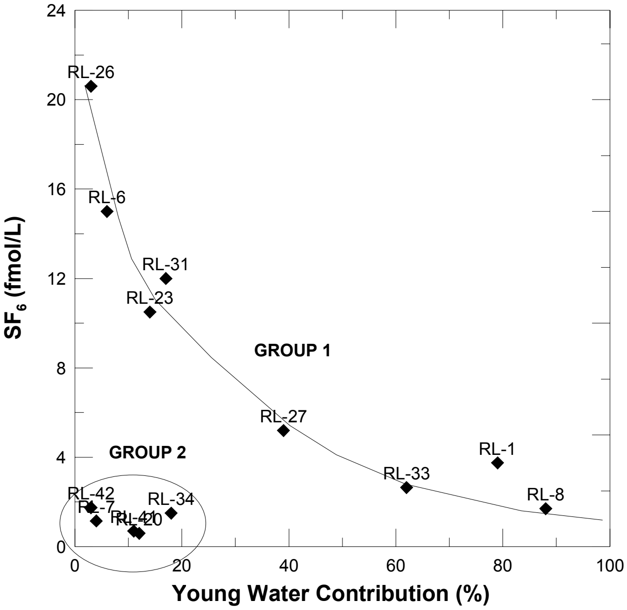

Figure 5: SF_6 concentration as function of the young water contribution obtained from CFCs.

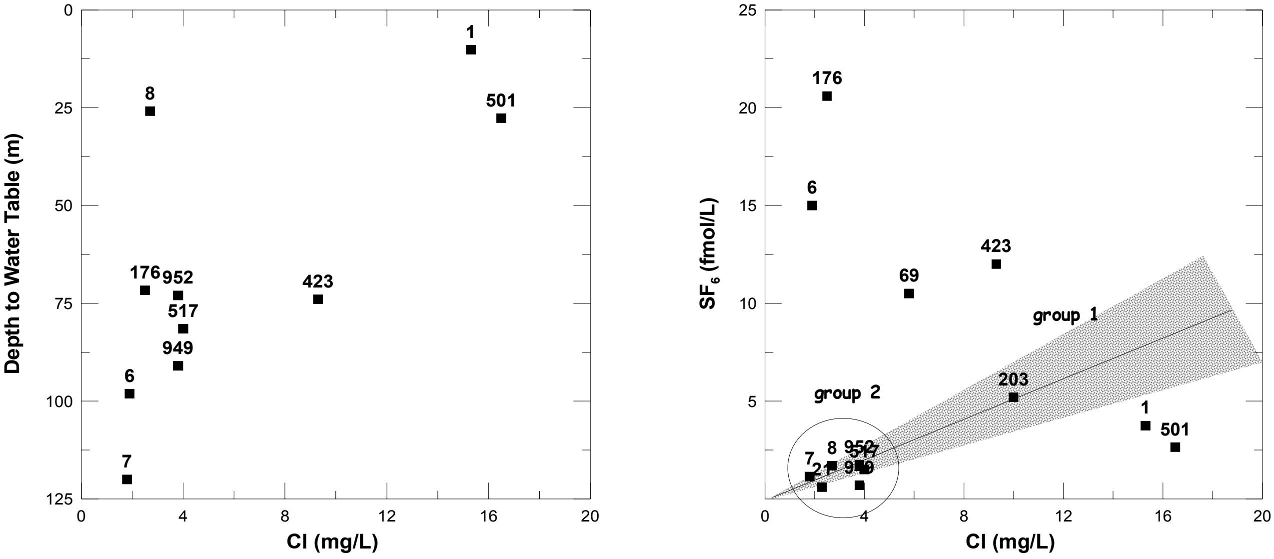

Figure 6: a) Cl as function of depth to water table. b) Comparison of SF_6 with dissolved Cl: two assemblies are differentiated: group 1 with low SF_6 and Cl concentrations owing a positive correlation, whereas group 2 is wide scattered and inhomogeneous with dilution (end member well no. 176) and evaporation tendency (end member no. 501).

8) Conclusion

The combined use of CFCs (CFC-11, CFC-12, and CFC-113) produce reliable results in age-dating of young groundwater. Additionally, it is possible to determinate the contribution of young water in mixed waters. Due to its excellent input curve, SF_6 can be used as age dating tool of young groundwater, too. However, it could be revealed that in volcanic rocks and in the nearby of tectonic faults leaching processes of SF_6 alternate the SF_6 concentration considerably. On the other hand, this makes it an excellent tracer for detection of the origin of groundwater. The results of CFCs and SF_6 must be checked for consistency and calibrated with the output of hydraulic modeling. This leads to a good knowledge of the local groundwater patterns and represents a valuable tool for responding to groundwater problems like scarcity of water and deterioration of quality in dry climate zones.

9) Acknowledgements

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