Supplement of Hydrol. Earth Syst. Sci. Discuss., 12, 1397–1436, 2015
http://www.hydrol-earth-syst-sci-discuss.net/12/1397/2015/
doi:10.5194/hessd-12-1397-2015-supplement

Hydrology and
Earth System
Sciences
Discussions
Open Access

Supplement of

Assessment of Halon-1301 as a groundwater age tracer

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Supplementary information

This supplementary material consists of 3 parts. In the first part the mathematical background on the determination of equivalent atmospheric concentrations is described including solubility determination, correction for access air and headspace. The second part gives a comprehensive assessment of inferred Halon-1301 ages. The third part contains detailed assessment of elevated Halon-1301 ages/reduced Halon-1301 concentrations compared to tritium and SF_6.

List of Supplementary Material

S1- Mathematical background

S2 - Detailed assessment of elevated Halon-1301 ages

References of Supplementary Material

S1- Mathematical background

Solubility determination

For most calculations the Henry coefficient (K_H) is used. It defines the ratio of compound in water and gas: $K_H = \frac{c_{aqu}}{p_g}$ (S1)

Where c_{aqu} is the aqueous concentration of Halon-1301 (and SF_6) in mol/L; p_g is the partial pressure of Halon-1301 (and SF_6) in the gas phase (often atmosphere), which can be determined from the known atmospheric ratio (pptv) and pure air pressure (difference between total pressure and vapor pressure of water): $p_g = x_m \, x \, (p_T - p_{H_2O})$ (S2)

Where the p_T is the total air pressure and p_{H2O} is the vapor pressure of water. The total air pressure (p_T) is a function of elevation (H) using an approximation for elevations less than 3000m (Eqn. S 3 A). And the vapour pressure of water (p_{H2O}) is a function of temperature at equilibrium, in groundwater application at recharge (Eqn. S3 B):

A: $\ln p_T = -\frac{H}{8300}$; B: $\ln p_{H_2O} = 24.4543 - 67.4506 \times \left(\frac{100}{T}\right) - 4.8489 \times \ln\left(\frac{T}{100}\right) - 0.000544$ (S3)

The Henry coefficient (K_H) and other commonly used solubility coefficients, such as the Ostwald or Bunsen coefficient, can be determined from measurable solubility parameters by using the Clarke-Glew-Weiss fit [Warner and Weiss, 1985]:

$$\ln K_x = A + B\frac{100}{T} + C\ln\frac{T}{100} \qquad \text{(S4)}$$

where K_x is the solubility estimated as Henry's (K_H), Bunsen (K_B) or Ostwald (K_O) coefficient, A, B, C are the solubility fit parameters, given in Table 2, and T is the equilibrium/recharge temperature (in K), determined using Ar and N_2 concentrations. A salinity term can be added to Eqn. A4, but this is negligible for most groundwater applications so ignored here.

Corrections for excess air and headspace

Due to degassing of the water sample after sampling, a gas bubble/headspace can be formed in the sample bottle. The gas bubble will contain a certain amount of Halon-1301 (and SF_6), depending on its size. This leads to an underestimation of total amount of Halon-1301 (and SF_6) in the water sample during analysis. The amount of Halon-1301 (and SF_6) 'lost' into the bubble (headspace) can be determined using the solubility relationships as described earlier [see also Pankow, 1986]. The total amount of Halon-1301 (and SF_6) contained in the sample can then be determined as sum of amount determined via analysis in the water sample (dissolved) and the amount contained in the bubble/ headspace.

Additionally the total amount of Halon-1301 (and SF_6) in the sample has to be corrected by any present excess air trapped in the sample during recharge. Trapped excess air introduces additional amounts of Halon-1301 (and SF_6) into the sample. This leads to an overestimation of the total amount of Halon-1301 (and SF_6) in the water sample when the sample is analysed. The amount of excess air is determined by dissolved Ar and N_2 determination [Heaton and Vogel, 1981].

S2 - Detailed assessment of elevated Halon-1301 ages

Analytical issues

We linearly up-scaled the calibration curve for data where the calibration curves did not cover the entire concentration range due to the use of calibrated air. This might introduce some additional uncertainty, but we consider this to be fairly minor. The slight non-linearity of the 'true' calibration curve relationship would mostly affect the modern water samples, which is 1 of the 5 affected groundwater wells with reduced concentration of Halon-1301 (Johnston and with 3 years tritium MRT). Uncertainties related to calibration cannot have caused the significant differences in concentrations/ inferred ages observed for the older groundwater age sites (e.g. Seaview Wools with ca. 16 years MRT obtained with tritium and SF_6), hence cannot explain the found reduced concentrations (higher inferred ages) of Halon-1301 in in George, Buick, CDC south, IBM 2 and Seaview Wools.

High uncertainty in inferred age for water recharged before 1975 and after 2000

Results of uncertainty calculations showed an overall average relative uncertainty of 4.6 % for Halon-1301 determination. Due to its characteristic S-shaped input function (less difference in concentration from year to year before 1975 and after about 2000), a larger uncertainty in inferred piston flow age is faced for waters recharged before 1975 and after about 2000. In Johnston and potentially CDC south higher uncertainties due to a reduced growth rate might explain reduced Halon-1301 concentrations (compared to other gaseous tracers). However, significantly reduced Halon-1301 concentrations in the remaining affected groundwater of higher MRT, are not likely to have been caused by a reduced growth rate and/or seasonal fluctuations, because they were recharged before 2000 and after 1975.

Interference of the Halon-1301 signal with co-eluting compounds

We previously showed that interference of the Halon-1301 signal with co-eluting compounds, such as CFC-13, does not appear to be a major problem when (calibrated) air is analysed, due to the lower sensitivity of the ECD towards CFC-13 and potential co-eluting compounds at concentrations present in air. The same applies for water samples. However we could not exclude interference of the Halon-1301 signal in groundwater, because we cannot exclude contamination of the water with potentially co-eluting compounds.

Since we can exclude the interference in (calibrated) air, reduced concentrations of Halon-1301 (compared to other gaseous tracers) are unlikely to have been caused by an erroneous calibration curve caused by interference of co-eluting compounds. Similarly reduced concentrations of Halon-1301 are unlikely to have been caused by signal interference of co-eluting compounds in groundwater, because this would lead to increased concentrations.

Halon-1301 property related issues

Degradation

Similarly to CFCs, degradation of Halon-1301 only seems possible in anoxic/anaerobic conditions. The groundwater wells where reduced concentrations of Halon-1301 occur are Buick, George, Seaview Wools, IBM 2and Duffy deep with 0.26, 0.02, 0.2, 0.3, and 2.3 mg/L DO, respectively (Table 1). Duffy deep is methanogenic. For all sites anoxic conditions could allow degradation of Halon-1301 which would lead to reduced Halon-1301 concentrations (in line with reduced CFC concentrations). However this cannot be verified in this study.

Lag time in unsaturated zone

Differences in gas ages and tritium age can also occur, due to diffusive travelling of tracer gases through the unsaturated zone and associated lag time [Cook and Solomon, 1995]. The time lag is a function of the tracer's diffusion coefficient, tracer solubility in water, and soil water content [Weeks et al., 1982; Cook and Solomon, 1995]. Gooddy et al. (2006) simulated lag times for SF_6, CFC-11 and CFC-12 and showed lag times in order SF_6<CFC-12<CFC-11 in the given environment, which only resulted in a significant age difference with unsaturated zone depth of more than 10 m. An existing lag time would affect all gas tracers (including SF_6), which we do not observe for any of the sites.

Degassing

Degassing of gas tracers into gas bubbles/headspace created due to de-nitrification, production of methane or when groundwater is brought to the ground surface might occur [Blicher-Mathiesen et al., 1998; Visser et al., 2007; Fortuin and Willemsen, 2005]. However this should also affect SF_6 concentrations, actually to a higher extend than Halon-1301, due to its lower solubility in water compared to Halon-1301. Reduced Halon-1301 concentrations are not observed along with even further reduced SF_6 concentrations any affected site. Hence degassing cannot explain reduced Halon-1301 concentrations in our study.

Adsorption in aquifer or material used

Another reason for the offset in determined Halon-1301 ages in regards to SF_6 and tritium ages is potential absorption to organic material and therefore retardation in the aquifer (as reported for CFCs in e.g. Cook et al. (1995) and Brown, (1980)). We cannot exclude this for any site, because little is known regarding the sorption behaviour of Halon-1301. Reported estimated K_{oc} values for Halon-1301 vary highly ranging from moderately mobile to very mobile (organic carbon coefficient (K_{oc}) of 244.8 [e.g. Ansul Incorporated, 2009 and other safety data sheets] or 49 (estimated, using a log K_{ow} of 1.86 [Hansch et al, 1995] and a regression-derived equation [Lyman et al., 1990]) or 102 (estimated using method by Chiou et al. (1979) [Montgomery, 2007]).

Sorption to well casing or sampling equipment may also lead to reduced gas tracer concentrations of certain (halo-)carbons [Glenn et al, 1990]. This could potently occur at well casings and sampling equipment of certain plastic material other than the recommended

Nylon and glass ware. However, we presume the effect of sorption to sampling equipment or well material in our study to be of minor importance, since the time the water is in contact with the well or sampling material is very short in the order of seconds to minutes.

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