



# Properties of the closed-system equilibration model for dissolved noble gases in groundwater

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## ARTICLE INFO

### Article history:

Accepted 9 August 2012

Available online 18 August 2012

### Keywords:

Noble gas temperature

Excess air models

Monte Carlo

Parameter estimation

## ABSTRACT

Among a variety of models to describe dissolved noble gas concentrations in groundwater in dependence of recharge temperature ( $T$ ), excess or entrapped air ( $A$ ), and other parameters, the closed-system equilibration (CE) model proved to be able to provide good fits to measured concentrations and physically reasonable parameter estimates in a variety of studies. Sometimes, however, it yields unrealistically high values for the parameters  $A$  and  $T$  in combination with large parameter error estimates. We analyze the origin of this behavior and investigate ways to evaluate samples affected by it. Analyses of the structure of the  $\chi^2$  space led to the insight that the  $\chi^2$  surface of well-behaved samples shows two local minima, one at realistic parameter values and another one at unphysical values. Problematic samples, however, show only a single minimum at unrealistic values, where large correlations between the CE model parameters occur, leading to large uncertainties of the parameter estimates. Monte Carlo simulations of problematic samples showed a split-up of the estimated parameters  $A$  and  $T$  in two clusters, one with realistic, one with unrealistic parameter values. This split-up also occurs to a lesser extent for normal samples as well as synthetic samples with relatively large parameter values. This behavior was found to be the cause for a bias of the CE model as recharge temperature estimator, if the mean  $T$  of the entire Monte Carlo ensembles is used as best estimate. We found that the unrealistic cluster corresponds to Monte Carlo realizations with increased Ar in combination with decreased Xe concentrations. By applying such concentration changes to synthetic samples, the problematic fitting behavior of some real samples could be reproduced. We propose a new method for dealing with the observed problems, which involves Monte Carlo analyses and a restriction of the statistical analysis to the cluster with physically realistic solutions. This method is able to retrieve the original parameter values from modified synthetic samples and yields realistic results for problematic physical samples.

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## 1. Introduction

The analysis of dissolved noble gases has become an established tool in groundwater hydrology. Noble gases have several useful properties that render them ideal tracers, especially their chemical inertness and well-known sources and sinks. As a result, noble gas data from groundwater can often be interpreted in clear and quantitative ways. In addition to several contributions to groundwater dating based on radiogenic and radioactive isotopes, one particularly important application of noble gases is the derivation of recharge temperatures

from the concentrations of the atmospheric noble gases Ne, Ar, Kr and Xe (e.g. Stute and Schlosser, 1993; Aeschbach-Hertig and Solomon, *in press*). Besides the noble gas temperature (NGT), the interpretation of noble gas data also provides information about the so-called “excess air” component (Heaton and Vogel, 1981), which itself may contain interesting climatic information (e.g. Aeschbach-Hertig et al., 2002b). Excess air originates from the (partial) dissolution of air bubbles that are entrapped in the groundwater during infiltration, and the size of the resulting gas excess depends on the hydrostatic pressure and thus on the amplitude of water table fluctuations (Ingram et al., 2007).

The fact that atmospheric noble gases in groundwater are usually not at solubility equilibrium with the atmosphere is a major complication for noble gas thermometry. A variety of models have been proposed to account for the typical gas excess above equilibrium, but in some cases also for gas deficits due to degassing (see Kipfer et al., 2002; Aeschbach-Hertig and Solomon, *accepted for publication*, for reviews). Furthermore, inverse techniques to estimate model parameters, including the

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equilibration temperature, have been developed (Ballentine and Hall, 1999; Aeschbach-Hertig et al., 1999). The general approach of these inversion algorithms is to vary several free model parameters in order to minimize the deviation between the modeled and the measured concentrations of the four atmospheric noble gases.

The inverse method made it possible to analyze in detail the performance of the various models in terms of their agreement with actual data as well as their numerical stability and ability to provide reliable parameter estimates. Ballentine and Hall (1999) had already noted that for a model with three parameters (the partial re-equilibration or PR model proposed by Stute et al. (1995)) the fit may become numerically unstable and reasonable initial parameter estimates were required to assure convergence at a global minimum. Aeschbach-Hertig et al. (1999) also observed problems with the precision of the parameter estimation for the PR model and other models with three free parameters due to parameter correlation. But in general both studies found that the inverse technique was well-behaved and did not suffer from local minima.

Among the models for dissolved atmospheric noble gases in groundwater, the closed-system equilibration or CE model (Aeschbach-Hertig et al., 2000) has been particularly widely applied, due to i) its flexibility, as it includes simpler models as limiting cases and can also describe degassing (Aeschbach-Hertig et al., 2008; Blaser et al., 2010), ii) its comparative success in providing good fits to measured noble gas data (e.g., Aeschbach-Hertig et al., 2002a; Kulongoski et al., 2009; Varsányi et al., 2011), and iii) its ability to provide realistic estimates of physically meaningful parameters (Aeschbach-Hertig et al., 2000; Aeschbach-Hertig et al., 2002b). In a laboratory study, Klump et al. (2008) found the CE model to provide a reasonable description of dissolved noble gas concentrations and NGTs that were a good approximation of the true equilibration temperatures. Ingram et al. (2007) concluded from a field study in a sandstone aquifer in England that NGTs and hydrostatic pressures derived from the CE model were realistic.

Despite its relative success, the CE model also has its drawbacks. Aeschbach-Hertig et al. (2002a) already noted that fitting the CE model to one specific sample (MD6.2) out of a data set of 23 wells from the Aquia Aquifer in Maryland yielded an unrealistically large and highly uncertain result for the parameter  $A$ , describing the concentration of entrapped air. This sample also stood out with a rather high estimate of the temperature parameter (the equilibration or noble gas temperature, denoted simply by  $T$  in the following) and in particular a very high error of  $T$ . Some samples with extraordinarily high  $T$  uncertainties also occurred in other noble gas studies (e.g. Weyhenmeyer et al., 2000; Hall et al., 2005; Blaser et al., 2010), without a further explanation or discussion of this phenomenon. Castro et al. (2007) noted that the CE model exhibited severe non-uniqueness issues leading to systematic large parameter uncertainties and occasionally even a complete inability to estimate certain parameters.

While the problems of parameter identification with the CE model have not been sufficiently discussed so far, it is known that parameter correlation in general can lead to a poor identifiability of the affected parameter combinations. This effect has particularly been observed and described for the case of the pressure and temperature parameters, which simultaneously cannot be well determined in the presence of excess air (Aeschbach-Hertig et al., 1999; Ballentine and Hall, 1999; Manning and Solomon, 2003). Hall et al. (2005) also showed examples of parameter combinations for several models that seem to exhibit strong correlation. This well-known problem underlies the fact that the so-called oxygen depletion (OD) model (Hall et al., 2005; Castro et al., 2007) shows numerical instabilities and large temperature errors if its pressure parameter is allowed to vary freely, i.e. when all three parameters ( $T$ ,  $A$  and  $P_{OD}$ ) are fitted to a single sample. A possible way to deal with such situations is to assume that one parameter is constant for a set of samples and estimate its value from the complete data set (Ballentine and Hall, 1999; Hall et al., 2005). Sun et al. (2010) noted this fact and its similarity to problems with fits of the CE model. The

question thus arises, whether similar reasons of parameter correlation underlie the problems that are observed when fitting the CE model to some samples.

Sun et al. (2010) compared the statistical properties of various groundwater noble gas models and found that the CE model, in contrast to other models, exhibited a bias in estimating the equilibration temperature. This bias manifests itself by slightly too high mean  $T$  estimates in Monte Carlo analyses of synthetic samples. We suspect that the bias is related to the occasional occurrence of solutions with unphysically high values of the entrapped air parameter, which furthermore can be identified by high temperatures with large uncertainties.

The aim of this study is to better characterize and understand the behavior of the CE model in fitting real and synthetic noble gas data sets. We investigate under which conditions the observed effects such as non-uniqueness, high estimates of  $A$  and  $T$ , and high parameter uncertainties occur. We study the relationship of these issues with the bias of the CE model in estimating the equilibration temperature, and furthermore search for methods to improve the parameter estimation with the CE model and to eliminate its bias as a paleotemperature estimator.

## 2. Methods

In the following analyses the noble gas concentrations in groundwater were assumed to consist of two components: dissolved air at solubility equilibrium and excess air. The other component – radiogenic isotopes – is important primarily for He where it plays an important role. Therefore, this study, like most studies about noble gas temperatures from groundwater, concentrates on Ne, Ar, Kr and Xe. Moreover, we focus exclusively on the CE model for the concentrations of these atmospheric gases in groundwater. The model equations are (Aeschbach-Hertig et al., 2000):

$$C_i^{\text{mod}}(T, S, P, A, F) = C_i^*(T, S, P) + \frac{(1-F)Az_i}{1 + FAz_i/C_i^*} \quad (i = \text{Ne, Ar, Kr, Xe}) \quad (1)$$

where  $C_i^*(T, S, P)$  are the moist-air solubility equilibrium concentrations as functions of temperature  $T$ , salinity  $S$ , and pressure  $P$ . Ne, Ar, and Kr equilibrium concentrations were calculated using the empirical equations determined by Weiss (1970, 1971) and Weiss and Kyser (1978). The solubilities reported by Clever (1979) were used for Xe.  $z_i$  are the volume fractions of the noble gases in dry air.

The model parameters  $A$  and  $F$  describe the size and composition of the excess air component. They have a physical interpretation that enables a check of the plausibility of the fit results (Aeschbach-Hertig et al., 2000, 2002b).  $A$  describes the initial volume of entrapped air per unit mass (or volume) of water.  $F$  describes the reduction of the trapped air volume  $A$  by partial dissolution and compression. Values of  $F > 1$  describe degassing (Aeschbach-Hertig et al., 2008), but here we restrict the discussion to the case of excess air, when  $F$  ranges between 0 and 1. In the limiting case of  $F = 0$ , the CE model reduces to the simplest excess air model, which describes the complete dissolution of unfractionated atmospheric air (UA model).

For the sample evaluation with the CE model,  $S$  was assumed to be 0 and  $P$  was set to a fixed value estimated from the altitude of the infiltration area. The remaining model parameters  $A$ ,  $F$  and  $T$  were determined using inverse modeling as described by Aeschbach-Hertig et al. (1999). In this approach the error-weighted square sum of the deviations between measured and modeled concentrations, denoted by  $\chi^2$ , is minimized.

$$\chi^2 = \sum_i \frac{(C_i - C_i^{\text{mod}})^2}{\sigma_i^2} \quad (i = \text{Ne, Ar, Kr, Xe}). \quad (2)$$

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