1. Introduction

Measured He, Ne, Ar, Kr and Xe concentrations in all rainwater samples from southeast Michigan are not in equilibrium with surface conditions and deviate from expected ASW values. Specifically, rainwater samples display a maximum deviation of 29%, -11%, -26%, -33% and -36% with respect to ASW for He, Ne, Ar, Kr and Xe, respectively (cf. Section 4, main text). Rainwater is typically assumed to re-equilibrate at surface conditions on the order of a few minutes [see e.g., Mazor, 1972; Klump et al., 2007]. While Mazor [1972] did not provide any calculations for this assumption, Klump et al. [2007] utilize a simple calculation based on diffusive length of noble gases to show that a water film of several millimeters in thickness would be in equilibrium with the atmosphere within 10 min. However, neither study used actual rainwater measurements to calculate the time taken by noble gases in rainwater to re-equilibrate at the surface. Below, we utilize a detailed model of diffusion in a plane sheet of water to calculate the time required for our measured maximum disequilibrium patterns in rainwater to re-equilibrate at surface conditions using realistic water depth values from precipitation data in Michigan.

2. Model Description

The total amount of noble gases diffusing into or out of a plane sheet of water is given by the infinite series solutions [Crank, 1975]:

\[
F_i = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2} \pi^2 \exp \left\{ -\left( \frac{(2n+1)^2 \pi^2 X}{4} \right) \right\} 
\]

or,

\[
F_i = 2(X)^{0.5} \left\{ \pi^{-0.5} + 2 \sum_{n=1}^{\infty} (-1)^n \text{erfc} \left( \frac{n}{\sqrt{X}} \right) \right\} \quad \text{if } X < 0.6465
\]

where, \( X = \frac{Dt}{l^2} \)

\( F_i \) is the fraction of noble gas ‘i’ (where, ‘i’=He, Ne, Ar, Kr and Xe) transferred at any given time ‘t’, ‘l’ is the depth of water (or thickness of water film), D is the diffusion coefficient of noble gases and ‘n’ is the nth term of the infinite series solution. Equations (1), (2) and (3) can be utilized to solve for parameter ‘X’ by setting \( F_i = 29\%\), -11\%, -26\%, -33\% and -36\% for He, Ne, Ar, Kr and Xe, respectively. From calculated values of ‘X’, the time ‘t’ taken to re-equilibrate can be obtained from equation (3) given the diffusion
coefficient ‘D’ of noble gases and water depth or thickness of water film ‘l’. Diffusion coefficients at a temperature of 25°C were used in our calculations because it is close to the mean measured surface air temperature at the time of collection of rainwater samples (Table S1). Values for noble gas diffusion coefficients at 25°C are given by Bourg and Sposito [2008]. In addition, water depth or thickness of water film ‘l’ was chosen based on measured hourly precipitation data from the Ann Arbor weather station during the period of sample collection (May-September, 2011). During the period of sample collection, precipitation as high as 8.2cms was recorded in one hour. While this represents an extreme value, multiple rainfall events record precipitation of 1cm or more in one hour during this time period. Consequently, we utilize a water depth of 1cm to calculate the time ‘t’ required for noble gases in rainwater to re-equilibrate using equation (3). Results of these calculations are presented below.

3. Model Results and Discussion

Considering a water depth of 1 cm, the maximum measured He excess of 29% in rainfall would take 900.5s (or ~15 minutes) at 25°C to reach equilibrium with surface conditions. Similarly, maximum deviations of -11%, -26%, -33% and -36% for Ne, Ar, Kr and Xe measured in rainfall would take ~3.3mins, ~34mins, ~72mins and ~108mins, respectively, to reach equilibrium with surface conditions for a water depth of 1 cm and 25°C. Our calculations show that re-equilibration is faster for the lighter noble gases He and Ne as compared to the heavier noble gases Ar, Kr and Xe due to both their higher diffusion coefficients and lower initial disequilibrium levels with respect to surface conditions. In addition, it should be noted that a smaller water depth ‘l’ would also lead to shorter re-equilibration times for all noble gases, in addition to processes such as turbulent mixing, if present. Nevertheless, our calculations show that the typical assumption that re-equilibration of rainwater at the surface is completed within a few minutes [see e.g., Mazor, 1972; Klump et al., 2007] is more applicable for lighter noble gases and smaller water depths (<1cms) while heavier noble gases and greater water depths require re-equilibration times on the order of hours.

Noble gas concentrations of rainfall and fog will thus be recorded in groundwater systems if the time taken to re-equilibrate with surface conditions is greater than the time taken to reach the water table. This is likely the case at high altitudes of the Galapagos Islands where rapid water infiltration due to the presence of fractures or thin soil cover [Warrier et al., 2012] allows little time for noble gas to re-equilibrate at the surface. However, sedimentary aquifer systems typically have thicker unsaturated zones and longer infiltration times allowing sufficient time for rainwater to re-equilibrate with ground air. This, in turn, allows the use of noble gases in paleoclimate reconstructions (e.g. Kipfer et al., 2002, Castro et al., 2007, 2012, Alvarado et al., 2009).
References


Bourg, I. C., and G. Sposito (2008), Isotopic fractionation of noble gases by diffusion in liquid water: Molecular dynamics simulations and hydrologic applications, Geochimica et Cosmochimica Acta, 72(9), 2237-2247.


