

Modelling antibiotics in the aquatic environment using fugacity concepts

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Antibiotics are a major concern due to the emergence of antimicrobial resistance (AMR). In the absence of intervention to prevent the environmental spread of AMR, this could contribute to 10 million deaths per year, making it more deadly than cancer (1). Understanding how antibiotics behave in the environment is important to predict their chemical fate once discharged into surface waters. When modelling compounds such as antibiotics in the environment, fugacity describes their ability to move between two environmental compartments, such as air and surface water (2).

In modelling, equal fugacity (escaping tendency) is expected in both phases as is the vapour pressure of the compound. The relationship between fugacity (f), Concentration (C , mol m⁻³) and fugacity capacity (Z , mol m⁻³ Pa⁻¹) is shown below (Eq 1). The Z value is specific to a chemical, which is also dependent on the phase in which it is present. A compartment with a higher fugacity capacity can accept a higher concentration of a given micropollutant.

$$C = Z \times f \quad (\text{Eq 1})$$

Partition Coefficient

The partition coefficient is an extremely important parameter in fugacity calculations. There are several important partition coefficients, besides the fundamental properties of vapour pressure and aqueous solubility, which are essential for understanding chemical transfer (3) (Figure 1).

Fugacity modelling is defined by levels (1, 2, and 3), which increase with complexity. Calculations can either use fugacity principles, or specific partition coefficients, as demonstrated in Figure 1.

In this article, calculations will use fugacity principles demonstrating level 1 and 2 models.

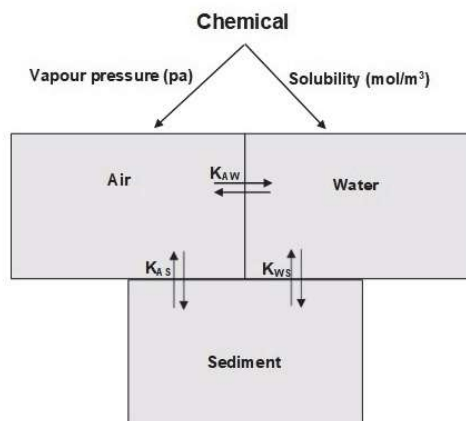


Figure 1. Illustration of the important partition coefficients that should be considered when modelling organic contaminants.

Level 1 Modelling Concepts

Level 1 assumes that the volumes of the compartments being studied are held constant, and the system is closed and in a steady state equilibrium. This means that the concentration of a contaminant in the compartment is uniform. With these assumptions, level 1 calculations can determine the partitioning behaviour of contaminants like antibiotics in the aquatic environment.

In order to accurately evaluate the concentrations of a contaminant such as an antibiotic using the fugacity method, Z values for each

phase must be defined (air, water, and sediment for three compartments). From this, equilibrium concentrations can then be deduced using fugacity as a common criterion for equilibrium. Definitions of relevant Z values are presented in Figure 2, where, H = Henry's Constant, $K_{OC} = 0.35 K_{OW}$ (organic carbon partition coefficient), y_{OC} = mass fraction of organic carbon, R = molar gas constant (8.314 Pa m³ mol⁻¹ K⁻¹).

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Using these Z values for individual antibiotics, we can define concentrations in each phase, if the volume (V) of each phase is estimated (m^3). The amount of chemical (M) in moles in a three-compartment system can be measured using the following relationships to calculate fugacity.

$$M = fZ_A V_A + fZ_W V_W + fZ_S V_S \quad (\text{Eq 2})$$

$$f = M / (Z_A V_A + Z_W V_W + Z_S V_S) \quad (\text{Eq 3})$$

Once the common fugacity has been calculated within the system, concentrations within each phase can be calculated using the specific Z -value, and f , using **Eq 1**. From

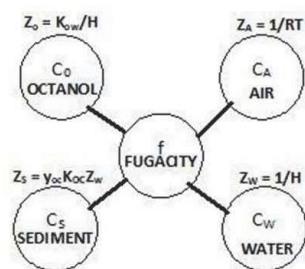


Figure 2. Relationships between fugacity, Z values and partition coefficient, where C represents concentration in a specific phase organic contaminants.

this, the moles, and percentage of the compound in each compartment can also be deduced.

It is important to consider that ionisation may occur in antibiotic chemical structures at environmental pH values. This is because of the various acid dissociation constants (pK_a values) within an antibiotic. In order to compensate for this, the Henderson-Hasselbalch equation is used to evaluate the degree of ionisation at specific pH values (**Eq 4**, where A^- is the anion and HA is the neutral compound). When considering ionisation, it is the Z_w (water phase) value, which will be affected, since ionisation will occur in the water. Therefore, the new Z_w value will be $Z_w(I + 1)$, where I is the degree of ionisation. This is important, as most antibiotics will have some degree of ionisation within the aquatic environment. Certain antibiotics may even have two dissociation constants and form Zwitterions (4).

$$pH = pK_a + \log [A^-] / [HA] \quad (\text{Eq 4})$$

Level 2 Modelling Concepts

A Level 2 fugacity model describes dynamic environ-

ments, where there are presumed inflows and outflows of chemicals within the compartment. The assumption is made that at any given instant, the different phases are in equilibrium with one another, unlike level 3 calculations, which are more complex, such that equilibrium is not assumed (5).

In level 2 modelling, the process of advection is considered. Advection can be thought of as transporting a chemical (such as an antibiotic) into or out of the region of interest by the flow of a supporting medium. The rate of advection ($N \text{ mol h}^{-1}$) (**Eq 5**), is simply the product of the flowrate of the advecting medium ($G \text{ m}^3 \text{ h}^{-1}$) and the concentration of the chemical in that medium ($C \text{ mol m}^{-3}$) (Z).

$$N = G \times C \quad (\text{Eq 5})$$

The following equations (**Eq 6, 7**) show how advection can be incorporated into fugacity calculations to define concentrations in each phase, where, I = total influx of contaminant. The important point here is that the inflow and outflow concentrations are assumed to be equal. Using a common fugacity, and applying **Eq 1**, the concentrations in each phase can be defined.

$$I = fG_A Z_A + fG_W Z_W + fG_S Z_S \quad (\text{Eq 6})$$

$$f = I / (G_A Z_A + G_W Z_W + G_S Z_S) \quad (\text{Eq 7})$$

Many contaminants degrade in the environment, and therefore this must also be considered in level 2 simulations. When applying the concept of degradation, it is convenient to use a simple first order kinetic expression to define degradation (**Eq 8**).

$$dC/dT = -ck \quad (\text{Eq 8})$$

References

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