Environmental Science: Atmospheres

ROYAL SOCIETY OF CHEMISTRY

CRITICAL REVIEW

View Article Online
View Journal | View Issue

Check for updates

Cite this: *Environ. Sci.: Atmos.*, 2023, **3**, 1045

Applications of the octanol–air partitioning ratio: a critical review

Sivani Baskaran † and Frank Wania *

Received 28th March 2023
Accepted 6th June 2023

DOI: 10.1039/d3ea00046j

rsc.li/esatmospheres

The octanol–air partition ratio (K_{OA}), also referred to as the octanol–air partition coefficient, has a wide range of applications in environmental chemistry. In this review, we explore the historical context of using octanol as a surrogate for various types of organic matter. We examine in detail the single-parameter linear free energy relationships (spLFERs) that rely on the K_{OA} to describe partitioning equilibria between the gas phase and vegetation, soil, particles, dust, surfaces, materials, and animal tissues. We further use poly-parameter linear free energy relationships (ppLFERs) to estimate how well octanol approximates the partitioning properties of these divergent phases. While the availability of ppLFERs for many environmentally and biologically relevant phases has rendered some of the spLFERs based on the K_{OA} largely obsolete, the K_{OA} still serves a useful purpose as a single parameter describing the tendency of a neutral organic chemical to partition from the gas phase into a wide variety of organic phases. As such, it is a well-defined, easy-to-comprehend and experimentally accessible descriptor of compound volatility from organic phases.

Environmental significance

There is a long tradition of using the solvent octan-1-ol as a surrogate for a large variety of organic matter when seeking to predict the phase distribution of organic compounds. While not as ubiquitous and common as the octanol–water partitioning ratio K_{OW}, the octanol–air partitioning ratio K_{OA} is widely used when studying the partitioning of organic compounds between organic matter and the gas phase. With the increasing availability and acceptance of methods for predicting the partitioning of organic vapours from air into soil organic matter, atmospheric particles, biological tissues, and polymers, that do not depend on a surrogate organic solvent phase, it is valid to explore whether there is still a role to play for simple linear regressions involving the logarithm of the K_{OA}. This review concludes that there is continued need for a single parameter quantifying organic compound volatility from organic phases and the K_{OA} is well suited to fulfill this role.

1 Introduction

Phase equilibrium processes involving the gas phase have been studied for over two centuries, beginning with an effort to understand gas solubilities (*e.g.*, Bunsen,[1] Henry,[2] and Ostwald[3]), improving drug and anesthetic delivery based on the permeability of these compounds into cells and lipids (*e.g.*, Meyer[4] and Overton[5]), for use in chemical separation processes and partition chromatography (*e.g.*, Pierotti *et al.*[6] and Porter *et al.*[7]) and understanding the behaviour and fate of chemicals in the environment.[8,9] The study of chemical partitioning between gaseous, aqueous, and organic phases has since become a fundamental aspect of environmental and physical chemistry, as well as medicinal and pharmaceutical sciences.

Chemical equilibrium partition ratios, K_{12}, hereafter simply referred to as partition ratios, describe the relative chemical concentrations in two adjacent phases at equilibrium and are dependent on environmental conditions such as temperature. In many instances, partition ratios are referred to as partition coefficients; however, because this property is influenced by external conditions (*i.e.*, temperature), IUPAC guidelines recommend the use of the term partition ratios.[10] Because partition ratios of chemicals can span many orders of magnitude, they are often expressed on a base 10 logarithmic scale (*i.e.*, $\log_{10} K_{12}$).

In this review we examine the role of the octanol–air partition ratio (K_{OA}) and its relevance to our understanding of environmental chemical fate processes. In previous work we explored the different methods used to measure and estimate the K_{OA} of an organic chemical.[11] Here, we summarize all of the different phase equilibria that have been described with the help of the K_{OA} including partitioning between the gas phase and vegetation, soil, particles, dust, surfaces, materials (*e.g.*, polyurethane), and animal tissue. We further evaluate how good a surrogate octan-1-ol is for these phases and highlight the

Department of Physical and Environmental Sciences, Environmental Sciences and Department of Chemistry, University of Toronto Scarborough, 1265 Military Trail, Toronto, Ontario, M1C 1A4, Canada. E-mail: frank.wania@utoronto.ca; Tel: +1-416-287-7225

† Current affiliation and address: Department of Environmental Engineering, Norwegian Geotechnical Institute, Sandakerveien 140, 0484, Oslo, Norway.

limitations of simple regressions between equilibrium partitioning ratios and the K_{OA}. We also explore the use of the K_{OA} in bioaccumulation and chemical risk assessments and as a coordinate in chemical space plots. Considering the availability of tools for estimating environmentally relevant phase equilibria involving the gas phase that do not rely on the K_{OA}, we further address the question of why the K_{OA} still serves a useful purpose.

1.1 What is the K_{OA}?

Partitioning between octanol and air has been described directly and indirectly with different physical–chemical properties. It is directly quantified using the octanol–air partition ratio (K_{OA}), Ostwald coefficient in octanol (L_{oct}; *e.g.*, Boyer and Bircher[12]), the Gibbs energy for octanol–air phase transfer (ΔG°_{OA}, kJ mol^{-1}; *e.g.*, Berti *et al.*[13]), and Henry's law constant in octanol (k_H^{oct}, Pa m^3 mol^{-1}; Roberts[14]). It has also been indirectly quantified by combining either a chemical's vapour pressure with the activity coefficients at infinite dilution in octanol (*e.g.*, Hussam and Carr[15]) or the octanol–water (K_{OW}) and the air–water partition ratios (K_{AW}; *e.g.*, Finizio *et al.*[16]).

K_{OA} is the concentration of a chemical in octanol divided by the concentration of a chemical in air at equilibrium (eqn (1)).

$$K_{OA} = \frac{C_O}{C_A} \quad (1)$$

The K_{OA} of a chemical can be derived from any one of the variables mentioned above. Details regarding these calculations are described in more detail by Baskaran *et al.*[11]

1.2 A brief history of partition ratios

Interest in partitioning properties and in particular the K_{OA} grew and waned throughout the years in various sub-disciplines including physical, analytical, medicinal, pharmaceutical, and environmental chemistry. Exploration of partition ratios began with investigations into the solubility of gases in water and later other solvents. Henry's law constant,[2] Bunsen absorption coefficient,[1] and Ostwald coefficient[3] were gas-solvent partition properties dependent on different external conditions.[17,18] Partitioning into organic phases and specifically lipids became of interest after the discovery of anesthesia in 1846.[19] At the turn of the 20th century, Meyer[4] and Overton[5] independently proposed that narcotics were being dissolved in lipids to cause narcosis rather than cholesterols and lipids dissolving into the narcotics.[5] In their experiments to identify chemicals partitioning to lipids, both Meyer and Overton found it challenging to use biological lipids because of their tendency to develop emulsions. They suggested the use of a partition ratio (P) between water and another organic phase instead. Overton initially used olive oil as the reference phase as it was cheaper and easier to obtain than long chain alcohols, which were known to have solvation properties closely related to those of biological lipids. Overton also noted that the high melting points of these alcohols implies that measurements would need to be made at physiologically unrealistic temperatures. In the following decades, there were few significant advances in the study of partition ratios; physical and biological chemists focused on the solubilities of different chemicals in various solvents[20] and developed manometric devices for measuring the solubilities of gases in blood.[21] In 1935, Meyer and Hemmi[22] returned to the idea of partition ratios and proposed the use of oleyl alcohol over olive oil, as oleyl alcohol would act as a better surrogate for body lipids when describing the partitioning of more polar compounds.

It was only in the early 1950s however that the use of solvent-water partition ratios was re-popularized by the work of Collander.[23–25] In 1947, Collandar published his work "On Lipoid Solubility" where he compared the solvent-water partition ratios for a number of different solvents including octan-1-ol, referred to as octanol henceforth, olive oil and oleic acid.[23] In particular, he noted that research has yet to identify a solvent that can dissolve a variety of solutes and represent the lipid phase well.[23] Collander found that the partition ratios in one alcohol/water system can be used to calculate the partition ratios in another alcohol/water system.[24] Octanol was favoured as it was, unlike ethyl ether, not very soluble in water and while hydrophilic substances and bases were more soluble in octanol, hydrophobic solutes were equally soluble in ethyl ether and octanol.[24] Over the next two decades, different solvents, including various alcohols, were considered for the organic reference phase.[26] In some of their earliest work, Hansch and colleagues found partition ratios had additive–constituent properties — which allows for fragment-based estimation techniques.[27–29] Hansch *et al.* commonly used octanol as the reference organic phase in these works.[27,28] Hansch later noted that multiple works showed good correlation between the octanol–water partition ratio and various organic bio-polymers.[30] They reported on these developments and the applicability of the octanol–water phase ratio in drug design in some of the very first volumes of the Annual Reports in Medicinal Chemistry.[30,31] The use of partition ratios, particularly the K_{OW}, in drug design took off after the publication of various works by Hansch and their colleagues, including one of the earliest review papers on partitioning, by Leo *et al.* in 1971.[29]

It is important to note that initial measurements for partition ratios would have been extremely challenging in the absence of modern analytical instruments; early methods included the use of manometers[12] and coulometry.[27] The development of partition chromatography, including gas chromatography in the 1940s and 1950s,[32] led to more measurements and increased interest in gas–liquid partition ratios. In 1959, in an effort to improve understanding of separation processes, Pierotti *et al.*[33,34] measured the infinite dilution activity coefficient of various solutes in multiple solvents using gas–liquid chromatography.

The first directly reported K_{OA} value, albeit referred to as an Ostwald coefficient, appears to be by Boyer and Bircher in 1960, while investigating the solubility of various gases in different alcohols using a modified Van Slyke-Neill blood gas apparatus.[12,21] Another set of K_{OA} data was published 13 years later in an effort to understand characteristics of solvents used in gas chromatography.[35] The next reported measurement of K_{OA} was published in 1978.[36] This work built on work by Battino and coworkers exploring gas–liquid partitioning of gaseous compounds, driven in part by the desire to find a solvent that could act as a model for partitioning of compounds (including anesthetics) between the gas phase and cell membranes.[37,38]

By the 1980s, environmental chemists had adopted the use of K_{OW} from the pharmaceutical industry for use in predicting the environmental fate and behaviour of chemicals (*e.g.*, Smith *et al.*[8]). Paterson *et al.*[39] were perhaps the first to identify the K_{OA} as a useful descriptor for plant–air partitioning and noted the dearth of experimental K_{OA} values. At the same time, octanol–air partitioning became increasingly of interest to the physical chemistry community in the mid 1980s as Pollack *et al.*,[40] Carr (*e.g.*, Hussam and Carr[15]), and Cabani (*e.g.*, Berti *et al.*[13]) and colleagues explored the thermodynamics of gas–liquid equilibria, reporting Gibbs energies of solutions and infinite dilution activity coefficients for solutes in octanol.

Exploration of the K_{OA} and other gas–liquid partition ratios to characterize the behaviour of inhaled anesthetics was renewed in the early 1990s (*e.g.*, Taheri *et al.*[41,42] and Liu *et al.*[43]). In the same decade, Harner and Carr began independently reporting K_{OA} values for various solutes. Harner's focus was on the use of K_{OA} to understand the environmental partitioning behaviour of chemicals between air and various types of organic matter.[44] Dallas and Carr[45] were interested in understanding the effect that the mutual solubility of octanol and water has on the K_{OW}. A head space sampling system developed by Carr and colleagues made measuring vapour–liquid equilibria easier.[15,45] In the following two decades interest in the K_{OA} has not waned and many more measurements of the K_{OA} have been reported.[11]

2 Single-parameter linear free energy relationships involving the K_{OA}

2.1 Phase concentration ratios involving air

In many investigations involving organic chemicals, concentrations in a phase in contact with air are measured, *e.g.*, concentration in phase X C_X in units of mol m^{-3}. It is then quite common to calculate ratios between those concentrations and the concentration in the air, *e.g.*, C_A in mol m^{-3}:

$$Q_{XA} = \frac{C_X}{C_A} \tag{2}$$

We use the variable Q to designate this concentration ratio, because we want to reserve K for equilibrium partition ratios and it is generally not established whether chemical equilibrium between phase X and the air exists. Whereas Q_{XA} is dimensionless (or rather has units of m^3 air m^{-3} phase X), other units for such concentration ratios are quite common because the concentration in phase X can be expressed in different units, *e.g.*, per mass of phase X rather than per volume of phase X. For example, the concentration ratio between atmospheric particles and the gas phase (Q'_{PA}) is often expressed in units of m^3 air μg^{-1} particles. The dimensionless Q_{PA} value can be obtained as:

$$Q_{PA} = Q'_{PA}\mathrm{TSP} \tag{3}$$

where TSP is the concentration of total suspended particulates in the air (μg m^{-3}; Finizio *et al.*[16]).

If phase X is a biological phase, *e.g.*, the foliage of a plant, the concentration ratio is sometimes referred to as a bioconcentration factor (BCF).

Generally, the C_A in eqn (1) refers to the concentration in the gas phase. However, in some cases, the total concentration in air C_{TA}, *i.e.*, concentration in both the gas and particle phase (C_P) has been measured and is used for the ratio calculation:

$$Q_{X/TA} = \frac{C_X}{C_{TA}} = \frac{C_X}{C_A + C_P} \tag{4}$$

2.2 The types of single parameter linear energy relationships involving K_{OA}

Many studies seek to relate the concentration ratios Q_{XA} obtained for different chemicals against the K_{OA} of those chemicals. This typically takes the form:

$$Q_{XA} = a{K_{OA}}^m \tag{5}$$

or, in logarithmic form:

$$\log_{10} Q_{XA} = m \log_{10} K_{OA} + \log_{10} a \tag{6}$$

These types of equations are called single parameter linear free energy relationships (spLFERs). The implicit assumption underlying these relationships is that phase X, or a constituent of phase X, has solvation properties that resemble those of octanol. An example, where the entirety of phase X is assumed to have octanol-resembling solvation properties, are organic surface films. More commonly, phase X has different constituents that may contribute to the uptake of chemicals. In this case, the concentration ratio may be expressed as the sum of the concentration ratios in the bulk phase constituents weighted by the constituents' abundance in the bulk phase, *e.g.*:

$$\begin{aligned} Q_{XA} = {} & f_{AX} + f_{WX}K_{WA} + af_{ORX}{K_{OA}}^m \\ & + f_{YX}K_{YA} + a_{Surface/X}K_{Surface/A} \end{aligned} \tag{7}$$

where f_{AX}, f_{WX}, f_{ORX}, and f_{YX} are the volume fraction of air, water, octanol-resembling phase and any other phase Y in bulk phase X and $a_{Surface/X}$ is the surface area to volume ratio of surface in phase X. K_{YA} is the equilibrium partition ratio between phase Y and air and $K_{Surface/A}$ is an equilibrium surface adsorption constant onto surface from air (with units of m).

In many cases, the assumption is then made, explicitly or implicitly, that the term $af_{ORX}K_{OA}^m$ is larger than all of the other terms in eqn (7), in which case we obtain:

$$Q_{XA} = af_{ORX}K_{OA}^m \tag{8}$$

or, in logarithmic form:

$$\log_{10} Q_{XA} = m \log_{10} K_{OA} + \log_{10} f_{ORX} + \log_{10} a \tag{9}$$

Examples of such composite bulk phases are soil, atmospheric particles and biological materials.

In earlier papers, when the K_{OA} had not been well established as a concept and when few experimental K_{OA} values were available, K_{OW}/K_{AW} instead of K_{OA} was used in relationships of type 5, 6, 8, and 9, *i.e.*, the K_{OA} was estimated as the ratio of the K_{OW} and the equilibrium air water partition ratio K_{AW}. It is believed that K_{OW}/K_{AW} in general has far higher uncertainty than K_{OA} values, especially if predicted properties are being used. This has been observed in some correlations between empirical K_{OA} and K_{OW}/K_{AW} values with Q_{XA}.[46,47]

2.3 A thermodynamic look at spLFERs involving K_{OA}

According to Goss and Schwarzenbach:[48]

$$K_{OA} = \frac{RT}{v_O \gamma_O P_L} = \frac{\rho_O RT}{M_O \gamma_O P_L} \tag{10}$$

where R, T, v_O, M_O, ρ_O, and γ_O are the ideal gas constant, absolute temperature, the molar volume, molar mass, and density of octanol at infinite dilution, and the activity coefficient of the chemical in octanol at infinite dilution, respectively. P_L is the vapour pressure of the subcooled liquid at saturation. Analogously, the equilibrium partition ratio between phase X containing the octanol-resembling constituent and air is:

$$K_{XA} = \frac{RT f_{ORX}}{v_{OR} \gamma_{OR} P_L} = \frac{\rho_{OR} RT f_{ORX}}{M_{OR} \gamma_{OR} P_L} \tag{11}$$

where v_{OR}, M_{OR}, ρ_{OR}, and γ_{OR} are the molar volume, molar mass, and density of, and the activity coefficient of the chemical in, the octanol-resembling constituent of phase X at infinite dilution. Combining eqn (10) and (11) we get:

$$K_{XA} = \frac{v_O \gamma_O}{v_{OR} \gamma_{OR}} f_{ORX} K_{OA} = \frac{M_O \gamma_O}{M_{OR} \gamma_{OR}} \frac{\rho_{OR}}{\rho_O} f_{ORX} K_{OA} \tag{12}$$

In other words, if the concentration ratio Q_{XA} reflects equilibrium partitioning, parameter a in eqn (8) is the ratio of the solubility of the solute in the octanol-resembling constituent of phase X [*i.e.*, $1/(v_{OR}\gamma_{OR})$] divided by the solubility of the solute in octanol [*i.e.*, $1/(v_O\gamma_O)$]. Also, we would expect exponent m to be 1.

Incidentally, eqn (11) corresponds to a single parameter linear free energy relationship between K_{XA} and P_L. In other words, Q_{XA} can be, and often has been, related to P_L in equations of the type:

$$Q_{XA} = a {P_L}^{-m} \tag{13}$$

or, in logarithmic form:

$$\log_{10} Q_{XA} = -m \log_{10} P_L + \log_{10} a \tag{14}$$

Equations involving K_{OA} are believed to be preferable over those involving P_L, because the ratio γ_O/γ_{OR} is less variable for different compounds than is γ_{OR}.[49] Finizio *et al.*[16] also noted that because the P_L cannot be measured directly it can incur large errors for chemicals with high melting points that are solids at environmentally relevant temperatures. However, whether spLFERs involving P_L or K_{OA} are preferable may also depend on which of these two parameters can be obtained with higher reliability.[50]

Eqn (10) and (11) also illustrate a potential issue with spLFERs involving the K_{OA} (or the P_L). Both K_{OA} and K_{XA} are inversely proportional to P_L. The P_L varies over many orders of magnitude between different chemicals, whereas γ_O and γ_{OR} vary only over a small range. K_{XA} and K_{OA} (and also K_{XA} and P_L) are therefore bound to be highly correlated if the dataset includes chemicals of divergent volatility. This auto-correlation issue has been discussed by Paterson and Mackay[51] and will be discussed further below.

2.4 Reasons why exponent/slope m in spLFERs involving K_{OA} is not 1

There are several reasons why the exponent/slope m in equations of type 5, 6, 8, and 9 can deviate from 1.

The first is that Q_{XA} does not reflect equilibrium conditions. If a chemical's K_{XA} is large, it can take a long time to reach equilibrium. If the chemical originates in the gas phase, the measured C_X is lower than it should be at equilibrium and the Q_{XA} for such high K_{XA} compounds accordingly is lower than K_{XA}. This leads to slopes m that are lower than 1. If, however, the chemical originates in phase X, non-achievement of equilibrium leads to a measured C_A that is lower than it should be at equilibrium. Q_{XA} for high K_{XA} compounds then is higher than K_{XA} and slopes m are more likely to exceed 1. An example of the latter would be a dust particle that includes polymer fragments containing the chemical of interest as an additive.

The K_{OA} threshold for non-achievement of equilibrium depends on a number of factors, such as the size, viscosity, composition and homogeneity of the octanol-resembling constituent in phase X, the mass transfer kinetics between air and that phase and the time available for equilibration. However, often several studies indicate similar threshold values. For example, vegetation is likely to reach equilibrium with gas phase chemicals with a $\log_{10} K_{OA}$ below 8.[52,53] On the other hand, compounds with a $\log_{10} K_{OA}$ in excess of 13 are unlikely to achieve equilibrium with atmospheric particles within the atmospheric lifetime of most particles.[54]

Disequilibrium may also be a result of temperature differences between air and the condensed phase X. Partitioning between gas and condensed phases are generally highly temperature dependent and the low heat capacity of air means that temperature can fluctuate far more quickly in air than in phase X. This, however, tends not to be an issue in laboratory experiments, where thermal equilibrium can typically be ensured. Some chemicals may also form non-exchangeable residues in the condensed phase, *e.g.*, in soil organic matter, and thus are not available for partitioning but can be chemically extracted during analysis.

Another reason for slopes m being lower than 1 could be the use of total air concentrations C_{TA} instead of gas phase concentrations C_A (eqn (4) *versus* eqn (2)). In that case, Q_{XA} is too small (relative to K_{XA}) for low volatility chemicals that partition to atmospheric particles.

The final reason for deviations of slopes m from 1 are differences in the solvation properties of octanol and the octanol-resembling phase. Goss and Schwarzenbach[48] show that a slope of 1 is obtained if γ_O/γ_{OR} is constant. For substances within a compound class, slopes deviating from 1 can be obtained if γ_O/γ_{OR} varies proportionally with K_{OA}.

2.5 Phase equilibria that have been described with spLFERs involving the K_{OA}

2.5.1 Vegetation–air partitioning. The uptake of many organic chemicals into plants from the air is driven largely by partitioning between air and the plant foliage. However, a mechanistic understanding of that process is often elusive due to complex composition of plant foliage and poorly defined solvation properties of the foliage constituents. For example, cellulose has a very minor capacity to sorb organic molecules and the solvation properties of cuticular waxes depend on the extent of their crystallinity. Nevertheless, repeated attempts have been made at relating empirically the measured partitioning into plants to a chemical's K_{OA}.[39] Bacci *et al.*[55] proposed a simple spLFER relating the plant bioconcentration factors (BCF), defined as the ratio of the concentration in vegetation divided by the concentration in air, to the K_{OA}, *i.e.*, eqn (8) with *a* and *m* being equal to 1. At the same time, Riederer[56] proposed to estimate BCFs in plants using an equation of type 7 based on the K_{OA} (calculated from K_{OW} and K_{AW}) and a measured cuticle–air partition ratio $K_{Cuticle/A}$, again with *a* and *m* assumed to be 1. Note that Riederer[56] considered here the plant lipids to be the octanol-resembling part of the plant, whereas the cuticle was a separate compartment. A later, simplified approach dropped the term containing $K_{Cuticle/A}$[57,58] to estimate the vegetation–air partition ratios (K_{VA}):

$$K_{VA} = f_A + f_W K_{WA} + f_L K_{OA} \tag{15}$$

which implies that the cuticle is now subsumed in the octanol-resembling phase. If the first two terms are considered negligible (Steyaert *et al.*;[58] see Section 2.2), an equation similar to that by Bacci *et al.*[55] is obtained. Muir *et al.*[59] also observed a correlation between BCFs measured in lichen and K_{OA}. Applying these concepts, a multi-compartment model for plants was developed which did not use K_{OA} directly, but used K_{OW} and K_{AW} to estimate air-leaf partitioning and bioconcentration in leaves.[60] Muller *et al.*[60] defined a different compartment for proteins, lipids, and carbohydrates, each with independent values for *a* and *m*.

Subsequently, the K_{OA} has been applied repeatedly to estimate chemical uptake in different plant species (*e.g.*, Tremolda *et al.*,[61] Dowdy and McKone,[62] Keymeulen *et al.*[63]). Tolls and McLachlan[64] reported a correlation of equation type 5 between $\log_{10} K_{VA}$ measured for welsh ray grass and $\log_{10} K_{OA}$ with R^2 values of 0.89 to 0.90. K_{OA} values that were consistently lower than the K_{VA} were attributed to differences in the temperature at which the two variables had been measured.[64] Brown *et al.*[65] also found linear correlations between the $\log_{10}$ of the whole pine needle–air partition ratio ($\log_{10} K_{Pine/A}$, $R^2 = 0.96$) and the pine needle wax–air partition ratio ($\log_{10} K_{Wax/A}$, $R^2 = 0.70$) and the $\log_{10} K_{OA}$. The regression coefficients *a* and *m* in eqn (6) are thus specific to the plant species (*e.g.*, Tolls and McLachlan,[64] Kömp and McLachlan,[66] McLachlan,[53] Nizzetto *et al.*[67]). The intercept should further be dependent on whether the concentration in vegetation is expressed on a fresh or dry weight basis. Most spLFER equations are for 25 °C but exploration of the inter-species variability of K_{VA} in relation to the K_{OA} showed that K_{VA} is more temperature dependent than the K_{OA}.[66] In a modelling effort, Taylor *et al.*[68] used eqn (6) with *m* equal to 0.7 and $\log_{10} a$ equal to 0.15 for clover–air partitioning as a general model for plant–air partitioning whenever no plant specific model is available. We stress that most of these studies were limited to non-polar organic contaminants.

The K_{OA} (or K_{OW} and K_{AW} combined) has also been related to the partitioning between specific parts of a plant and air, including leaf–air,[55,65] bark–air,[69,70] tree core–air[71] and cuticle–air.[63] The capacity to quantify these individual partition ratios in plants has advanced passive-sampling techniques in both indoor and outdoor environments for organic pollutants. For example, in indoor air, olive trees have been used to measure polycyclic aromatic hydrocarbons[72] and in outdoor environments, bark, leaf, litter, and pine needles have been used as passive samplers for PBDEs,[73] chlorobenzenes,[74] and various volatile organic compounds.[75]

In addition to partitioning between air and individual plants and plant parts, the K_{OA} can be used to describe bulk phase partitioning between the gas phase and entire forest canopies. Horstmann and McLachlan[76] measured deposition of chemicals onto deciduous and coniferous canopies in Germany and found that the distribution of chemicals with $\log_{10} K_{OA} < 10$ approached equilibrium. Accordingly, they derived equations in the form of eqn (5) to relate pseudo canopy–air partition ratios $K_{Canopy/A}$ with the K_{OA}, both for a deciduous canopy ($m = 0.76$, $\log_{10} a = 1.15$) and a coniferous canopy ($m = 0.69$, $\log_{10} a = 1.58$). Su *et al.*[77] conducted a similar study in a deciduous forest in Canada and derived a similar correlation ($m = 0.67$, $\log_{10} a = 2.04$). Many of these equations were derived from datasets comprising only a small subset of structurally related chemicals (*e.g.*, PCBs) and thus these models likely work best when applied to chemicals of similar size and structure.

The relationships above assume that chemical equilibrium is established between the vegetation and the atmospheric gas phase. However, as mentioned in Section 2.4, this is generally only a defensible assumption for relatively volatile chemicals, whereas for less volatile chemicals the kinetics of uptake and plant growth play a more important role in controlling plant bioaccumulation and bioconcentration.[78] McLachlan[53] presented a conceptual framework, which illustrates how measurements of plant uptake can be used to delineate the K_{OA} ranges within which different processes, including wet and dry deposition, are dominant. Volatile chemicals with low $\log_{10} K_{OA}$ (<8.5) reach equilibrium and the K_{VA} is directly correlated with the $\log_{10} K_{OA}$. For involatile chemicals with high $\log_{10} K_{OA}$ (>11), particle bound deposition is important which is apparent in another correlation of the $\log_{10}$ of the particle–air partition ratio $\log_{10} K_{PA}$ with $\log_{10} K_{OA}$.[53] For chemicals with intermediate $\log_{10} K_{OA}$ (8.5–11) uptake into plants from air is not a function of K_{OA}, but rather a function of the kinetics of the transport from air to the plant storage compartment and the time of exposure. Later modelling work[52] confirmed that non-volatile chemicals ($\log_{10}$

$K_{OA} > 8$) do not approach equilibrium between plants and air and so the application of the K_{OA} for estimating plant BCFs and K_{VA} is more applicable to volatile chemicals. More volatile chemicals ($\log_{10} K_{OA} < 5$) also have the potential to volatilize from a plant's stem, trunk, and leaves.[79]

2.5.2 Soil–air partitioning. The potential for the K_{OA} to describe soil–air partitioning processes was first identified by Harner and Mackay.[44] Given the lack of measured K_{OA} values, many early studies relied on the K_{OW}/K_{AW} ratio to estimate partitioning ratios between soil (organic matter) and air K_{SA} (*e.g.*, Hippelein and McLachlan[80] and Borisover and Graber[81]). Earlier, Karickhoff had shown that for a relatively small and largely non-polar group of compounds the logarithm of the organic carbon–water partition ratios ($\log_{10} K_{OC}$) is highly correlated with the $\log_{10} K_{OW}$, with a slope of ~1.[82] K_{OW}/K_{AW} and the organic carbon–air partition ratio $K_{OC/A}$ were found to be similarly related.[81] Accordingly, Hippelein and McLachlan[80] extended the Karickhoff equation to soil–air partitioning:

$$K_{SA} = 0.411 f_{OC} \rho_{OC} \frac{K_{OW}}{K_{AW}} \tag{16}$$

where f_{OC} is the fraction of organic carbon in the soil and ρ_{OC} is the density of the soil organic carbon. A regression of experimental K_{SA} values for chlorobenzenes, PAHs, and PCBs, with experimental values of both K_{OA} and K_{OW}/K_{AW} produced near identical results and the slope of these regression approached unity, suggesting that interactions between such non-polar chemicals and soil organic matter are similar to those with octanol.[80] An *m* of 1 in these relationships indicates that octanol may be a better surrogate for soil organic carbon than for plant tissues.

As more directly measured K_{OA} became available, its role in soil–air partitioning became evident and the K_{OA} was used directly to describe soil–air partitioning.[80,83] For example, volatilization fluxes of pesticides from sludge-amended soil were found to correlate with K_{OA} and the pesticide concentration in the sludge.[84,85] He *et al.*[86] found that when using directly measured K_{OA} values, the predicted K_{SA} value was ~2.7 times greater than the experimental K_{SA}, while K_{SA} values predicted using experimental K_{OW}/K_{AW} values were in better agreement with experimental K_{SA} values. This prompted He *et al.*[86] to develop a modified Karickhoff equation:

$$K_{SA} = \frac{0.411}{2.7} f_{OC} \rho_{OC} \frac{K_{OW}}{K_{AW}} \tag{17}$$

with a second correction to be applied when estimating K_{SA} below 0 °C:

$$K_{SA} = \frac{0.411}{2.7} f_{OC} \rho_{OC} \frac{K_{OW}}{K_{AW}} \times 10^{0.033(273-T)} \tag{18}$$

The use of experimental K_{OA} values in these correlation equations is preferable over using two empirical values for K_{OW} and K_{AW}.[80,86] We suspect that there are some inconsistencies in the property data used by He *et al.* to develop these correlations as some K_{OA}, K_{AW}, and K_{OW} values are from a curated review of property data for PCBs by Li *et al.*[87] which include final adjusted values. Therefore, the three partitioning values should be internally consistent and both K_{OA} and K_{OW}/K_{AW} should predict the same K_{SA} value.

Contrary to expectations, Hippelein and McLachlan[88] observed that the absorption of organic chemicals in organic matter showed dependence on relative humidity and proposed a semi-empirical equation for predicting K_{SA}:

$$K_{SA} = A \frac{0.411}{2.7} K_{OA} e^{\frac{\Delta U_{SA}^{\circ}}{R}\left(\frac{1}{T} - \frac{1}{298}\right) - B(\mathrm{RH} - 100)} \tag{19}$$

where A is a normalization constant quantifying the similarity of octanol to organic carbon, B is the slope of the regression between K_{SA} and RH, and ΔU_{SA}° is the internal energy of soil–air phase change, which also varies with RH.[88] Hippelein and McLachlan recommend an A value of 2 and a value of 0.0437 for B as they found B to be relatively constant across penta- and hexachlorobenzene and various PCBs.[80] As both B and ΔU_{SA}° are chemical specific, or at least homologue specific, using this semi-empirical equation for predicting K_{SA} to describe general soil–air partitioning poses some challenges with data availability.[89] Instead, Davie-Martin *et al.*[89] suggest that compound group specific multiple linear regressions using K_{OA}, RH, and temperature be used for estimating K_{SA} because this approach requires fewer chemical specific properties (*i.e.*, B and ΔU_{SA}°) and performed much better than the general equation. However, there are limitations to this approach, as the f_{OC} term is not included in the regression and K_{SA} is assumed to be linearly correlated with RH.

While the relationships above all assume that partitioning of chemicals to soils from the air is solely governed by absorption on soil organic matter, this assumption is often not valid, especially in air-dry soil and soil with a low organic matter content. Under such circumstances, adsorption to mineral surfaces can become dominant.[90,91] In particular, relative humidity plays a critical role in determining the relative importance of adsorption to the mineral–air interface. If only absorption processes (*i.e.*, sorption into soil organic matter) is considered, estimates of the K_{SA} are likely to be underestimated.[91] In other words, whenever adsorption plays a role in soil–air partitioning, using octanol as a surrogate for soil will be insufficient.[91,92]

2.5.3 Particle–air partitioning in the atmosphere. Before the K_{OA} was introduced in environmental and atmospheric chemistry, the Junge–Pankow model based on the subcooled liquid vapour pressure P_L was generally used to predict the fraction of a chemical adsorbed onto particles (eqn (11); Junge[93] and Pankow[94]). This relationship would generally take the form of eqn (14), a linear regression between the $\log_{10}$ particle–air partitioning ratio (Q'_{PA}, m^3 μg^{-1}) and $\log_{10} P_L$.[95]

Whereas in its original formulation, the Junge–Pankow relationship was based on the assumption that chemicals adsorb onto the surface of the particles, Pankow[96] showed that the use of P_L is also compatible with an absorption model of particle–air partitioning, which took the form of eqn (11) and related P_L to Q'_{PA}. If chemicals are absorbed into a particle's organic matter (OM) fraction, the K_{OA} can serve as an alternative measure for estimating Q'_{PA} (see Section 2.3 and Finizio *et al.*[16]

for details). Assuming an octanol density (ρ_O) of 820 kg m^{-3},[16] a ratio $M_O\gamma_O/M_{OM}\gamma_{OM}$ equal to 1 and that all OM present in the aerosol is available for partitioning,[95] simplifies eqn (11) to an equation of type 6, where $\log_{10} a$ equals −11.91 and m is 1.

A strong relationship between Q'_{PA} and K_{OA} would suggest that interactions of neutral organic chemicals with the OM in the particles is similar to that in octanol, *i.e.*, *via* absorption, rather than surface adsorption.[16] Indeed, K_{OA} and Q'_{PA} values have been found to be correlated for a number of compound classes including PAHs, PCBs, organochlorine pesticides, and PCNs[16,95] and the K_{OA} is often considered to be a better predictor than P_L for particle–air partitioning,[95,97,98] *i.e.*, the K_{OA}-based model performs better than the Junge–Pankow model.[95,97,99] The K_{OA} based model is believed to act as a more universal model for Q'_{PA}, as structurally similar compounds tended to group together when regressing Q'_{PA} against the K_{OA}, but this did not occur when Q'_{PA} was regressed against P_L.[95,97,98]

While the regressions between K_{OA} and Q'_{PA} can be quite strong (R^2 0.60 to 0.99), slopes of the regression are often less than 1 (*e.g.*, Falconer and Harner,[97] Finizio *et al.*,[16] Harner and Bidleman,[95] Radonic *et al.*[100]). Two explanations have been proposed to explain this: octanol and OM have different solvation properties or equilibrium has not been reached (see Section 2.4). It is likely that both explanations hold true. For example, the polarity of secondary aerosol particles can differ from octanol, such that the activity ratio of a chemical in octanol and organic matter deviates from 1, thus the slope of a K_{OA} and Q'_{PA} regression will also differ from 1.[101] Yeo *et al.*[102] suggested that the activity ratio assumption of 1 held true for multi-*ortho* PCBs but not for non/mono-*ortho* PCBs based on regressions of K_{OA} and P_L from Harner and Bidleman.[95] Götz *et al.*[103] noted that the K_{OA} based model tended to overestimate the Q'_{PA} and recommended using an M_O/M_{OM} value of 0.26 in eqn (11).

The presence of soot or elemental carbon can also alter the particle–air partitioning of chemicals because then adsorption to such sorbents can occur in addition to bulk phase absorption.[104] In these instances a model based solely on K_{OA} has a tendency to underestimate the Q'_{PA},[104–106] and a second term to describe the adsorption to soot is needed:[104]

$$Q'_{PA} = \frac{M_O\gamma_O}{M_{OM}\gamma_{OM}\rho_O} f_{OM}K_{OA} + \frac{f_{EC}\alpha_{EC}}{\alpha_{AC}10^{12}}K'_{Soot/A} \quad (20)$$

where f_{EC} and α_{EC} is the fraction and specific surface area of elemental carbon in the aerosol, α_{AC} is the surface area of activated carbon, and $K'_{Soot/A}$ is the soot–air partitioning ratio in units of L kg^{-1}.[104] The 10^{12} included in the denominator is for unit conversion. However, Helm and Bidleman[107] found the opposite to be true, where the $K_{OA} - K'_{Soot/A}$ model overpredicts the Q'_{PA} whereas using K_{OA} alone better agreed with field measurements. The differing conclusions from the various studies do not reject the suitability of K_{OA} as parameter for predicting Q'_{PA}, rather suggests that better characterization of the particle phase (*e.g.*, the polarity) is needed to better understand chemical interactions between particle and gas phase.

2.5.4 Dust–air partitioning. Descriptions of indoor dust–air partitioning are largely based on particle–air partitioning systems. Weschler and Nazaroff,[108] like many others, found it more convenient to use K_{OA} instead of P_L to describe the partitioning; assuming chemicals partition into dust OM as they would in octanol, $Q_{Dust/A}$ (dimensionless) can be estimated using a form of eqn (8), where f_{ORX} is the fraction of OM in dust.[108]

Dust–air partitioning can also be defined by $Q'_{Dust/A}$ which has units of m^3 mg^{-1} and is often used in place of $Q_{Dust/A}$ (Weschler and Nazaroff;[109] see Section 2.1). Whether the equilibrium partitioning of a chemical with dust is kinetically limited depends on both the K_{OA} and size and viscosity of the particle, whereby chemicals with higher $\log_{10} K_{OA}$ values take longer to equilibrate as do larger particles.[108] Weschler and Nazaroff[109] found a correlation between measured $Q'_{Dust/A}$ and K_{OA} values—however they note that for some points in the regression the $Q'_{Dust/A}$ values are calculated using K_{OA}. For chemicals with high $\log_{10} K_{OA}$ values, the $Q'_{Dust/A}$ or $Q_{Dust/A}$ value is less than what would be expected which is attributed to non-equilibrium conditions (Weschler and Nazaroff,[109] Zhang *et al.*;[110] see Section 2.4).

Similarly, Shoeib *et al.*[111,112] found that the K_{OA} model for $Q_{Dust/A}$ tended to under-predict the concentration in the dust phase, which could be attributed to differences in how some compounds (*e.g.*, MeFOSE and EtFOSE) interact with octanol and organic matter or non-equilibrium conditions.[112] It is possible that the dust particles contain varying levels of contaminants, depending on whether they originate from the physical degradation of polymers containing the chemical as additive or whether the chemical is being taken up in the particles from the gas phase.[112] Indeed, this was observed in house dust samples, where the bromine concentration for BDE 209 contaminated samples varied highly.[113]

Using Weschler and Nazaroff's[109] equations for $Q'_{Dust/A}$ (*i.e.*, eqn (3) and (8)) and assuming values for $f_{OM,Dust}$ and ρ_{Dust}, Li *et al.*[114] present an equation for $\log_{10} Q'_{Dust/A}$ in the form of eqn (6), where m equals 1 and $\log_{10} a$ is −13.0.

Chemicals with $\log_{10} K_{OA}$ values between 8 and 11, had measured $Q'_{Dust/A}$ values similar to predicted values.[114] Chemicals with $\log_{10} K_{OA}$ values less than 8 had predicted $Q'_{Dust/A}$ values that were higher than the measured value, likely because air concentration levels were underestimated.[114] Predicted $Q'_{Dust/A}$ values lower than measured values for chemicals with $\log_{10}$ K_{OA} values greater than 11 were again attributed to disequilibrium conditions.[114]

Recently, Wei *et al.*[115] combined eqn (4) and (6) parameterized for both K_{PA} and K_{Dust} as functions of K_{OA}, to estimate a dust–total air partition ratio $K_{Dust/TA}$:

$$\log_{10} Q_{Dust/A} = (m_1 - m_2)\log_{10} K_{OA} + \log_{10} a_1 - \log_{10} a_2 - \log_{10} \text{TSP} \quad (21)$$

where m_1 and m_2 are slopes of $\log_{10} Q_{Dust/A}$ and $\log_{10} Q_{PA}$ against $\log_{10} K_{OA}$, respectively, and $\log_{10} a_1$ and $\log_{10} a_2$ are the intercepts of these regressions. If TSP × Q_{PA} is much less than 1, particle–air partitioning is negligible and the use of eqn (21) is redundant.[115] Wei *et al.*[115] observed good agreement between K_{OA} and $Q_{Dust/TA}$ for phthalates, which were estimated to have TSP × Q_{PA} values less than one. Whereas PAHs which have a wider range in TSP × Q_{PA} values, showed a poorer correlation between K_{OA} and $Q_{Dust/TA}$.[115]

2.5.5 Surface–air partitioning. Surface–air partitioning describes the process of adsorption of a gas-phase chemical onto the surface or interface of another medium.[90] Similar to soil–air partitioning, it is influenced by relative humidity; water molecules are present in higher concentrations and have the capacity to form strong hydrogen bonds, and are thus more likely to sorb onto surfaces than organic compounds.[90] Thus, any relationship between surface–air partition ratios and K_{OA} is likely to be somewhat specific to the surface, the type of compounds and relative humidity.[92]

However, the organic film present on many surfaces is often treated as a bulk-phase, and therefore an absorption model using K_{OA} has been applied to estimate film–air partition ratios $Q_{Film/A}$ (*e.g.*, Harner and Bidleman,[95] Weschler and Nazaroff[108]). Implicit in these approaches is either the assumption that surface adsorption is negligible or that adsorption to the film surface and absorption in the bulk film can be collectively described with one partitioning constant. The latter can be problematic, as the time scales for equilibration are often widely different for surface and bulk phase uptake. Also, adsorption scales with surface area and absorption with mass. In some instances, the term film–air partitioning has been used to describe partitioning between thin polymer films and air (*e.g.*, ethylene vinyl acetate[116]); these instances are described in Section 2.5.6.

$Q_{Film/A}$ values for both indoor[117,118] and outdoor[119] films were found to be correlated with, or similar to, K_{OA} values. Subsequently, studies have used organic films as passive environmental samplers relating K_{OA} and $Q_{Film/A}$ using eqn (8), where m and $\log_{10} a$ are both 1.[120,121] While the measured $Q_{Film/A}$ correlated well with K_{OA}, Wu *et al.*[122] observed very shallow regression slopes particularly for films obtained from rural environments.

Bi *et al.*[123] reported on the $Q'_{Surface/A}$ of mirrors, plates, and windows in units of m and, assuming that organic films are present on all impervious surfaces, converted these values to dimensionless $Q_{Film/A}$, by estimating a film thickness and percentage of organic material in the film. These $Q_{Film/A}$ values were in good agreement with K_{OA}.

Li *et al.*[114] presented a simplified relationship between K_{OA} and a window film–air partition ratio. As with $Q'_{Dust/A}$, estimated $Q'_{Film/A}$ values for chemicals with $\log_{10} K_{OA}$ values between 8 and 11 agreed well with experimental values, chemicals with $\log_{10} K_{OA}$ < 8 were over-predicted, and those with $\log_{10} K_{OA}$ values > 11 were under-predicted.[114]

The time needed for a chemical to reach equilibrium with a surface film is dependent on both the K_{OA}, the thickness of the film (X; m), and the mass transfer coefficient from bulk air onto the film (MTC_S in units of m h^{-1}):[108]

$$t_S = \frac{K_{OA} X}{MTC_S} \tag{22}$$

As discussed in Section 2.4, it can take several months for surface–air partitioning of chemicals with very high $\log_{10} K_{OA}$ values to reach equilibrium. For chemicals with $\log_{10} K_{OA} > 12$, this can be upwards of 1 year.[124]

While modelling film growth by SVOCs deposition, Weschler and Nazaroff[125] noted that the majority of chemicals in organic film have $\log_{10} K_{OA}$ values between 10 and 13. Because chemicals with low K_{OA} values equilibrate quickly between organic films and air, films can become enriched in chemicals with higher $\log_{10} K_{OA}$ over time.[125]

The K_{OA} has also been used to estimate a time-dependent uptake coefficient (k_a) for gaseous compounds by liquid organic films:

$$\frac{1}{k_a} = \frac{1}{\alpha} + \frac{c\sqrt{\pi t}}{4K_{OA}\sqrt{D_l}} \tag{23}$$

where α is the surface accommodation coefficient, t is the time, c is the average thermal velocity, and D_l is the liquid diffusion coefficient.[126] While predicted uptake of PAHs into organic films was underestimated, there was some correlation between the K_{OA} and k_a.[126]

2.5.6 Material–air partitioning. The partitioning of chemicals between various materials, such as polymers, physical surfaces, and clothing has often been correlated with K_{OA}. Many of these materials are used as passive-air sampling sorbents for various organic compounds. The issues associated with combining surface adsorption and bulk absorption in a single partitioning constant mentioned in the preceding section often apply also for uptake in materials.

Ockenden and colleagues[127] found that the K_{OA} was linearly correlated with the sampling rate of PCBs into triolein containing semi-permeable membrane devices (SPMD) used as passive air samplers (PASs), thus the K_{OA} could be used to estimate the amount of time required by non-polar substances to equilibrate with the PAS.

Multiple studies have shown correlations between K_{OA} and the partitioning between air and polymer material used in other PASs, including polyurethane foam,[128] low density polyethylene,[129] ethylene vinyl acetate,[130] and activated carbon and florisil.[131] De Coensel[132] noted that given the strong correlation between the K_{OA} and $K_{PDMS/A}$ (polydimethyl siloxane–air partition ratio) for *p*-dichlorobenzene and naphthalene, $K_{PDMS/A}$ could even be used to estimate K_{OA}. However such an approximation is likely to be limited to non-polar substances as the interactions of polar substances with PDMS and octanol is not the same.

The K_{OA} has also been correlated with partitioning between various textile materials such as cotton and air, generally showing fairly strong correlations.[133] Yu *et al.*[134] observed that the correlation between the cotton–air partition ratio $Q_{Cotton/A}$ and K_{OA} is specific to different homologous compound groups. However, Saini *et al.*[135] found a low correlation between K_{OA} and measured $Q_{Cotton/A}$ which was attributed to the irregularity and variance in the material itself, as polyester–air partition ratios $K_{Polyester/A}$ were more strongly correlated with K_{OA}.

Won *et al.*[136] also observed linear relationships between K_{OA} and partition ratios between carpet, vinyl, and drywall material and air under different conditions. Partitioning between latex paint and air was also found to be correlated with K_{OA}.[137]

Reppas-Chrysovitsinos *et al.*[138] compiled published material–air partition ratios (K_{MA}) and presented a general single parameter equation based on eqn (6), where m is equal to 1 and $\log_{10} a$ equal to −1.22. They also present K_{OA}-based equations to estimate specific material–air partitioning ratios for polyethylene, polyurethane, PDMS, carbohydrates, polyoxymethylene (POM), and nylons.[138]

Arguably, adsorption is the most relevant sorption process to describe partitioning to non-porous and non-organic material and octanol is unlikely to be a relevant surrogate for surfaces and materials whenever adsorption is the dominant uptake process.

2.5.7 Animal tissue–air partitioning. Poulin and Krishnan initially recommended against using octanol to describe tissue–air and blood–air partitioning because the solubility of hydrophobic organics is greater in octanol than in actual lipids[139] and instead used solubility in vegetable oil.[139,140] In 1996, they later presented equations for estimating $K_{Tissue/A}$ and $K_{Blood/A}$ using K_{OA} as it is easily predicted from the K_{OW} and K_{AW}.[141] Their equations were similar to what Steyaert *et al.*[58] used for plant–air partitioning and eqn (7):

$$K_{XA} = K_{OA}(f_{neutral\ lipids} + 0.3f_{phosolipids}) + K_{AW}(f_{water} + 0.7f_{phospholipids}) \quad (24)$$

where K_{XA} describes the partitioning between either blood or tissue and air and f_i is the fraction of neutral lipids, phospholipids, and water in either blood or tissue. This equation is different from the general equation presented in Section 2.2 because it assumes that chemical interactions between air and phospholipids more closely resemble those between air and water. Current approaches in bioaccumulation modelling group lipids into a single phase and add a non-lipid organic matter phase to describe proteins (*e.g.*, Li *et al.*[142]) or individually consider partitioning into each biological phase (*e.g.*, Endo *et al.*[143]).

Hau and Connell correlated odour thresholds[144] and nasal pungency thresholds[145] of chemicals with K_{OW} and K_{AW} but not with K_{OA}. This is likely because methods for measuring and estimating K_{OW} and K_{AW} were well-established and there were few measurements of K_{OA} at the time. Later, Hau *et al.*[146] showed biophase–air partitioning ratios to be related to K_{OA} and as a result the minimum alveolar concentration (MAC), which describes the potency of anaesthetics, is also related to K_{OA}. Slightly different correlations between K_{OA} and MAC were observed for alkanes and alcohols, however if the MAC of chemicals with very high K_{OW} values is corrected with the blood/brain partition ratio, then the regressions converge, and a single equation can describe the relationship between MAC and K_{OA}:[146]

$$\log_{10} MAC_{corr} = -1.10 \log_{10} K_{OA} + 2.41 \quad (25)$$

Nielsen *et al.*[147] found the K_{OA} to be a good proxy for sensory irritant receptor–air partitioning such that it can be used to estimate RD_{50}, the concentration at which a chemical causes a 50% decrease in respiratory frequency in an air-breathing organism:

$$\log_{10} RD_{50} = 0.8361 \log_{10} K_{OA} - 6.0879 \quad (26)$$

Raines *et al.*[148] similarly found a correlation between K_{OA} and the concentration of aromatic inhaled drugs needed to inhibit the *N*-methyl-D-aspartate receptor by 50%.

More recently, the K_{OA} has also been utilized in food science to estimate release behaviour of flavour compounds from an octanol–water emulsion.[149,150] Measured blood–air and milk–air partition ratios[151] and feces–air partition ratios[152] were also shown to correlate with the K_{OA}. K_{OA} has also been used as a surrogate for lipid–air partitioning to predict respiratory elimination rates[153] and human skin uptake[108] in environmental chemical fate models. Kelly and Gobas[154] noted that the estimated biomagnification factor of persistent neutral organic chemicals for wolves was correlated with K_{OA}.

Bioaccumulation assessments based solely on octanol–water partition ratios (K_{OW}) fail to take into account the role of respiratory elimination in air-breathing organisms.[153] In fact, chemicals with $\log_{10} K_{OW}$ values less than 5, and thus not considered bioaccumulative by various regulatory agencies (*e.g.*, the Government of Canada[155]), can have the potential to biomagnify in air-breathing organisms. Modelling results from Gobas *et al.*[153] indicate that persistent chemicals with $\log_{10} K_{OA}$ greater than 5 and $\log_{10} K_{OW}$ greater than 2 have the potential to bioaccumulate in terrestrial food chains. This was further supported by modelling work by Czub and McLachlan[52] who found that in humans chemicals with $\log_{10} K_{OA}$ between 6 and 10 and $\log_{10} K_{OW}$ value between 2 and 9 had high environmental bioaccumulation potentials and Kelly *et al.*[156] who noted that chemicals with $\log_{10} K_{OA}$ values greater than 6 and $\log_{10} K_{OW}$ values greater than 2 can biomagnify in air-breathing organisms. Of the chemicals listed on Canada's 2003 Domestic Substances List, 57% have an estimated $\log_{10} K_{OW}$ value between 2 and 5 and an estimated K_{OA}, value greater 5—and thus are potentially bioaccumulative.[153] Providing evidence beyond modelling studies, Moses *et al.*[157] found lipid-normalized concentrations of dieldrin, heptachlor epoxide and β-hexachlorocyclohexane to be 5–14 times higher in seals than in fish. These chemicals have $\log_{10} K_{OW}$ values around 5 or lower and $\log_{10} K_{OA}$ values greater than 8.

More recent modelling studies on compounds released indoors have also shown that inhalation exposure is the primary exposure route of persistent volatile organic compounds with $\log_{10} K_{OA}$ values less than 6,[158] while for chemicals with $\log_{10} K_{OA}$ greater than 6, non-dietary ingestion (*i.e.*, hand-to-mouth) is the primary exposure pathway, particularly in children.[158,159]

3 How good a surrogate is *n*-octanol for various types of phases?

While many studies reviewed in Section 2 reported strong linear relationships between $\log_{10} Q_{XA}$ (where X is an organic phase) and $\log_{10} K_{OA}$, it is not really possible to compare these relationships with each other, for example to assess whether the solvation properties of a particular phase more closely resemble those of octanol than those of another. This is because of divergent datasets used in those studies that include different types and numbers of chemicals and because of the unknown and variable uncertainty of the K_{OA} and Q_{XA} values used in these

Table 1 List of ppLFERs and K_{OA}-based predictions compared in Fig. 1. The K_{OA} and K_{AW} are always predicted with ppLFERs by Baskaran *et al.*[160] and Abraham *et al.*[166] NOM: natural organic matter; OC: organic carbon; POM: polyoxymethylene; PDMS: polydimethyl siloxane; PUF: polyurethane foam

Phase X	ppLFER predicted K_{XA}	$\log_{10} K_{OA}$ spLFER based prediction
NOM	Average $\log_{10} K_{NOM/A}$ for 10 different organic matter systems including humic acids, fulvic acids, and natural organic matter, predicted with ppLFER by Niederer *et al.*[167]	$\log_{10} K_{OC/A}$ predicted with spLFER by Borisover and Graber[81] using K_{OA} at 15 °C
OC	$\log_{10} K_{OC/A}$ calculated as $\log_{10} K_{WA} + \log_{10} K_{OC}$, where K_{OC} is predicted with ppLFER by Nguyen *et al.*[168]	$\log_{10} K_{OC/A}$ predicted with spLFER by Borisover and Graber[81] using K_{OA} at 25 °C
Plant cuticles	$\log_{10} K_{Plant/A}$ predicted with ppLFER by Platts and Abraham[163]	$\log_{10} K_{OA}$ at 25 °C
Storage lipid	$\log_{10} K_{Storage\text{-}lipid/A}$ calculated as $\log_{10} K_{WA}$ + $\log_{10} K_{Storage\text{-}lipid/W}$ where $K_{Storage\text{-}lipid/W}$ is predicted with ppLFER by Geisler *et al.*[164]	$\log_{10} K_{OA}$ at 37 °C
Membrane lipid	$\log_{10} K_{Membrane\text{-}lipid/A}$ calculated as $\log_{10} K_{WA}$ + $\log_{10} K_{Membrane\text{-}lipid/W}$ where $K_{Membrane\text{-}lipid/W}$ is predicted with ppLFER by Endo *et al.*[165]	$\log_{10}$ K$_{OA}$ at 37 °C
Tissue	$\log_{10} K_{Tissue/A}$ calculated as $\log_{10} K_{Tissue/W} + \log_{10} K_{WA}$ where $K_{Tissue/W}$ is predicted with a composition model by Endo *et al.*[143] using ppLFERs for $K_{Storage\text{-}lipid/W}$ by Geisler *et al.*,[164] $K_{Membrane\text{-}lipid/W}$ by Endo *et al.*,[165] $K_{Albumin/W}$ by Endo and Goss,[169] $K_{Protein/W}$ by Endo *et al.*[170]	$\log_{10} K_{Tissue/A}$ predicted using a fractional composition model with K_{OA} to 37 °C; $K_{Tissue/A} = (f_{Storage\text{-}lipid} + f_{Membrane\text{-}lipid})K_{OA} + f_W K_{WA}$
Aerosols	Average of $\log_{10} K_{PA}$ for aerosol sampled in Dübendorf fall & winter, Aspvretn, and Roost, predicted using ppLFERs by Arp *et al.*[171]	$\log_{10} K_{PA}$ predicted with spLFER by Harner and Bidleman[95] using K_{OA} at 15 °C
POM	$\log_{10} K_{POM/A}$ calculated as $\log_{10} K_{POM/W} + \log_{10} K_{WA}$ where $K_{POM/W}$ is predicted with ppLFER by Endo *et al.*[172]	$\log_{10} K_{POM/A}$ predicted with spLFER by Reppas-Chrysovitsinos *et al.*[138] using K_{OA} at 25 °C
PDMS	$\log_{10} K_{PDMS/A}$ predicted with ppLFER by Sprunger *et al.*[173]	$\log_{10} K_{PDMS/A}$ predicted with spLFER by Reppas-Chrysovitsinos *et al.*[138] using K_{OA} at 25 °C

relationships. Also, as mentioned before, it is not always assured that the Q_{XA} data refer to equilibrium conditions.

However, we can test how good a surrogate K_{OA} is for other partitioning equilibria between an organic phase X and air by comparing K_{XA} values that have either been obtained with a K_{OA}-based spLFER prediction or by a poly-parameter linear free energy relationship (ppLFER) that has been calibrated directly for phase X. In some cases (*i.e.*, plant cuticles, storage lipid, membrane lipid), we can directly compare the K_{OA} with a ppLFER-predicted K_{XA}. Furthermore, we sometimes have to rely on thermodynamic triangles to estimate a K_{XA} from ppLFER-predicted K_{XW} and K_{AW} values (natural organic matter NOM, storage lipids, membrane lipids, tissue, POM). To avoid the uncertainty in K_{OA} influencing the comparison, we can also predict the K_{OA} at the appropriate temperature with ppLFERs.[160,161] This approach is thus similar to the one used by Endo *et al.*,[143] when probing the extent to which *n*-octanol is a good surrogate for various biomaterials. Table 1 details the partition ratios that are being compared. We used 1316 organic chemicals with complete sets of experimental solute descriptors, as supplied by the UFZ-LSER database.[162] We note that this set of chemicals is limited to generally small and primarily non-polar substances. More complex multifunctional chemicals or chemicals with unusual substitutions, such as the polyflourinated alkyl substances, are not well-represented.

In general, there are very strong correlations ($R^2 > 0.89$) between the K_{OA} based spLFER and ppLFER estimated values of $\log_{10} K_{XA}$ (Fig. 1). Such good correlations can at least in part be attributed to a statistical issue discussed by Paterson and Mackay,[51] who assert that apparently significant correlations can be obtained by inadvertently correlating a quantity with itself. In the current case, $\log_{10} K_{XA}$ and $\log_{10} K_{OA}$ are almost inevitably correlated, because of the presence of the "solubility in air" in their denominator (eqn (10) and (11)). The vapour pressure, or "solubility in air", of substances ranges over many orders of magnitude, whereas the solubilities of substances in organic phases vary little and thus contribute little to the variation in partition ratios between chemicals. For similar reasons the K_{OA} is very highly correlated with the liquid saturation vapour pressure.[50] In order to eliminate this auto-correlation, we also plot the difference between ppLFER and spLFER estimates of K_{XA} against the $\log_{10} K_{OA}$ used to generate the spLFER estimate (Fig. 2).

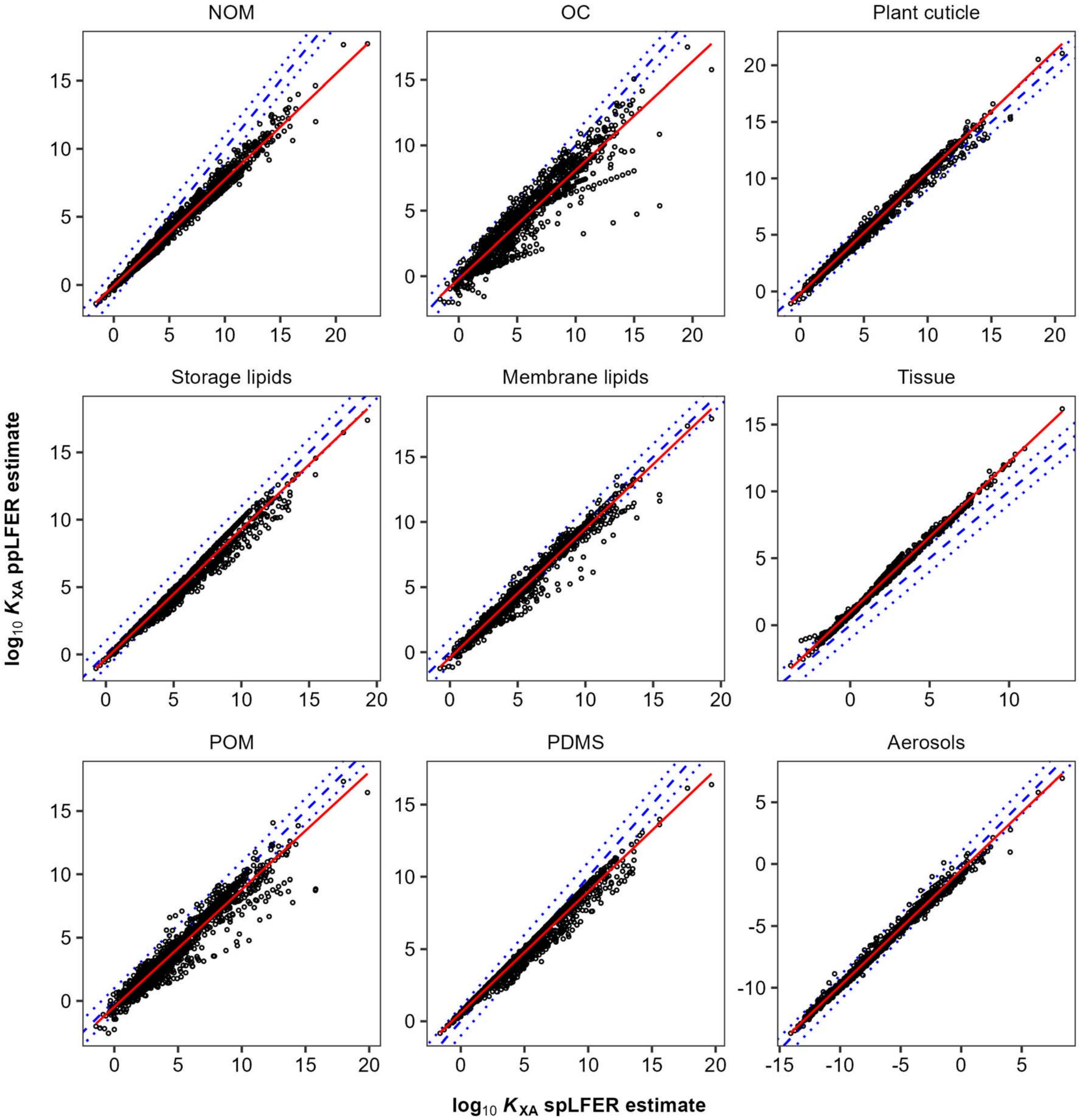

Fig. 1 Correlation between $\log_{10} K_{XA}$ predicted using system specific ppLFERs plotted against $\log_{10} K_{XA}$ predicted using spLFERs using $\log_{10} K_{OA}$. The red solid lines show the line of best fit, blue dashed lines indicate a 1 : 1 relationship, and blue dotted lines have slopes of 1 and intercepts of ±1 $\log_{10}$ unit. NOM: natural organic matter; OC: organic carbon; POM: polyoxymethylene; PDMS: polydimethyl siloxane; PUF: polyurethane foam.

Thus, if the K_{OA} is a good surrogate for a partitioning equilibrium, we expect to see a regression with a slope m of near unity in Fig. 1 (ref. 47) and a horizontal regression line in Fig. 2. By normalizing ppLFER estimated values of K_{XA} by spLFER estimates of K_{XA} we can better visualize the variation in K_{XA} with K_{OA} that is not easily observed in Fig. 1. For example, a negative slope in Fig. 2 indicates that as the K_{OA} of a chemical increases, the K_{OA} based estimate (*i.e.*, the spLFER estimate) is greater than the ppLFER estimate. This suggests that when the slope is negative (<0), the activity ratio (γ_O/γ_X) is greater than 1 whereas a positive slope suggests that the activity ratio is less than 1. In Table 2 we present the slopes and intercepts of the regressions and coefficients of determination (R^2) of both plots and the root mean squared error (RMSE) between the spLFER and ppLFER-based estimates.

Slopes near 1 in Fig. 1 and near 0 in Fig. 2 and RMSE values of 0.50 and 0.53 respectively, indicate that the K_{OA} value is a good surrogate for the partitioning between storage and membrane lipids and the gas phase and a very good predictor for partitioning into tissue. The results for PDMS are similar to those of storage and membrane lipids. The K_{OA} also appears to be a reasonable surrogate for the partitioning between aerosols[95] and plant cuticles[163] and the gas phase, with RMSE values of 0.33 and 0.39 respectively. In the case of partitioning to soil organic matter from the gas phase, the spLFERs based on the K_{OA} have the highest RMSE and tend to give predictions that are

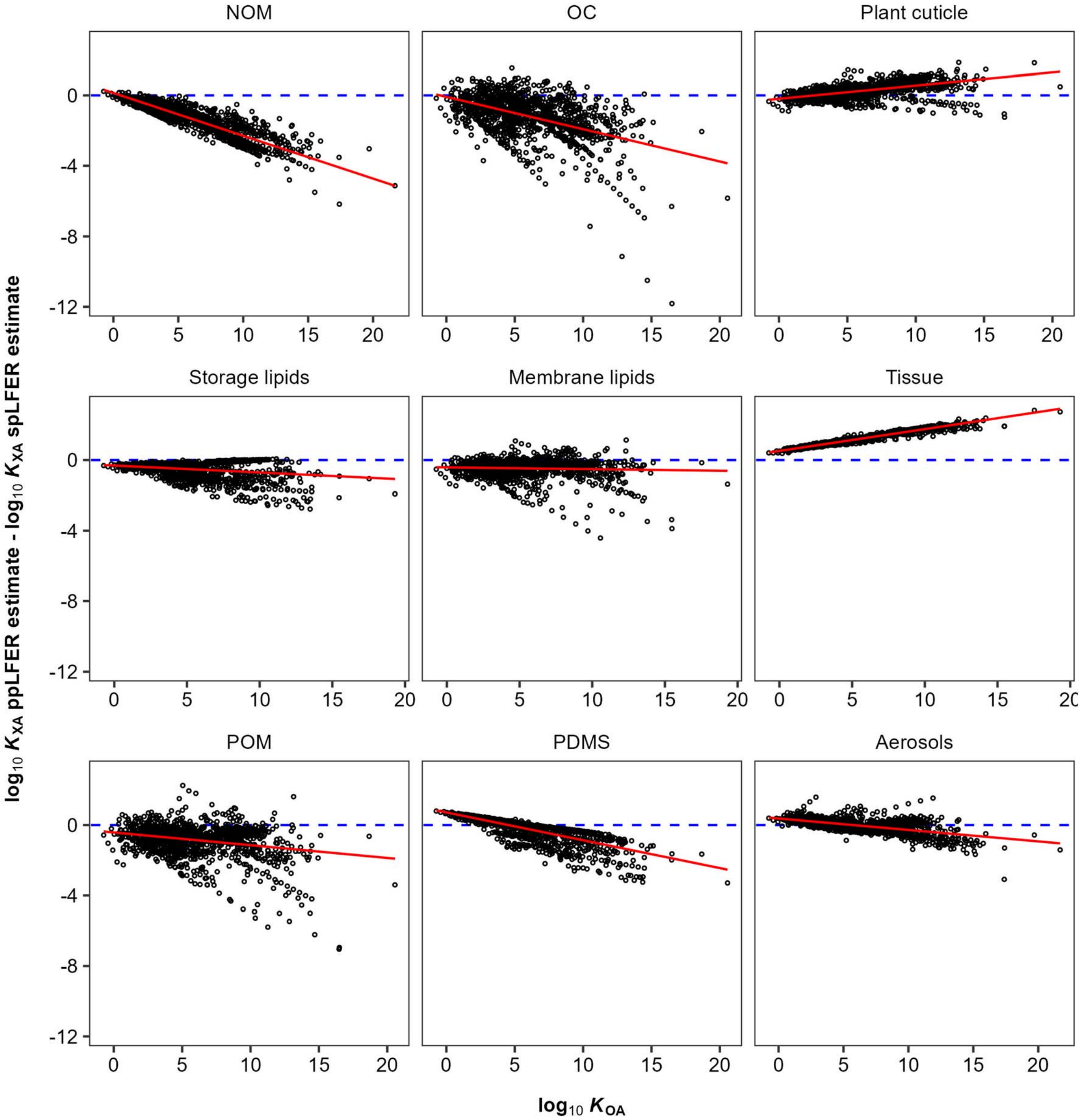

Fig. 2 The difference between ppLFER and spLFER estimates for $\log_{10} K_{XA}$ plotted against the $\log_{10} K_{OA}$ used to derive the spLFER estimate.

Table 2 Statistics on the regressions presented in Fig. 1 and 2. The slopes and intercepts reported here are not the same as the spLFERs used to calculate the respective K_{XA} values

	Fig. 1			Fig. 2			
Phase X	Slope	Intercept	R^2	Slope	Intercept	R^2	RMSE
NOM	0.78	−0.04	0.98	−0.24	0.14	0.79	0.42
OC	0.83	−0.22	0.89	−0.18	−0.08	0.25	1.02
Plant cuticle	1.07	−0.19	0.99	0.07	−0.19	0.28	0.39
Storage lipids	0.96	−0.31	0.97	−0.04	−0.31	0.06	0.50
Membrane lipids	0.99	−0.41	0.97	−0.01	−0.41	0.00	0.53
Tissue	1.12	0.97	0.99	0.12	0.52	0.95	0.26
POM	0.93	−0.47	0.92	−0.07	−0.42	0.07	0.87
PDMS	0.84	0.58	0.97	−0.16	0.72	0.57	0.45
Aerosols	0.93	−0.50	0.99	−0.07	0.37	0.31	0.33

biased low for compounds with high K_{OA} values, indicated by the slopes in the plots in Fig. 2 being negative and the large scatter below the regression line. To a smaller extent that is also the case for the K_{OA}-based spLFERs for POM and PDMS[138] and the storage[164] and membrane lipids.[165] The opposite is the case for the K_{OA} and K_{AW}-based fractional composition model for $K_{Tissue/A}$ where a positive slope in Fig. 2 suggest that relying on K_{OA} to estimate partitioning into tissues leads to an overestimation for low volatility compounds.

4 Is the K_{OA} obsolete?

4.1 Alternative means for predicting environmental phase equilibria involving the gas phase

A major motivation for introducing the K_{OA} as an equilibrium partitioning property was to use it in the prediction of other equilibria between environmental phases and the gas phase. Accordingly, the literature is replete with linear free energy relationships that regress an environmentally relevant partitioning ratio involving the gas phase against K_{OA} (see also Section 2). Those predictive equations suffer from the same shortcomings as other single-parameter linear free energy relationships, namely they have no universal applicability, but require different regression coefficients for different compound groups capable of undergoing a variety of intermolecular interactions.[92] The longevity and popularity of those equations can be explained in part by their robustness for largely non-polar substances and the prevalence of such substances among the contaminants of historical concern.

Major progress in predicting environmental phase equilibria has been made in the decades since the K_{OA} has first been introduced. In particular, poly-parameter linear free energy relationships (ppLFERs) have become a viable method for predicting partition ratios involving environmental phases, mostly, because (i) calibrations have been performed to determine system constants (the regression constants of the ppLFER equations) for most environmentally relevant phase equilibria or can be estimated,[162,174] (ii) solute descriptors for numerous contaminants have been experimentally determined.[175] When carefully calibrated system constants and experimental solute descriptors are combined, ppLFERs can achieve prediction accuracy on the order of 0.3 $\log_{10}$ units.[176] Even for substances, for which no experimental solute descriptors exist, those descriptors can now be predicted with the help of QSPRs[162,177] and still result in a prediction accuracy for environmental phase equilibria better than one order of magnitude.[176] K_{OA}-based spLFERs would be hard pressed to match such accuracy, even if they were only applied to substances appropriate for a particular regression, *i.e.*, similar to the substances used in the calibration of that spLFER. In other words, there is no longer the need for a parameter such as K_{OA} to predict contaminant partitioning from the gas phase into organism lipids,[164] soil organic matter,[167] atmospheric particles,[171] or sampling sorbents.[178]

The merit of ppLFER extends beyond the provision of estimates that tend to be more precise than estimates from K_{OA}-based spLFERs. By describing the different intermolecular interactions involved in partitioning, ppLFERs also provide a mechanistic understanding of organic chemical solvation in various phases.[179]

The question therefore arises whether there is still a need for the K_{OA}. The answer is two-fold. First there are still some partitioning equilibria between air and organic phases, which need to be predicted with the help of K_{OA}-based spLFERs. Second, the utility of the K_{OA} is not limited to the prediction of specific environmentally relevant phase equilibria.

4.2 Continued need for K_{OA}-based predictions of environmental phase equilibria

Currently, there are no robust ppLFERs that would be able to predict partitioning into plants. The ppLFER for plant cuticles by Platts and Abraham[163] suffers from (i) a limited suitability of isolated tomato cuticles to represent plant foliage more generally and (ii) a calibration that had not a sufficiently diverse set of substances to be widely applicable with confidence. Therefore, K_{OA}-based prediction methods are still required for the very plant–air phase equilibria, for which the K_{OA} was first introduced.[39] Important examples include the empirical K_{OA}-based equations for predicting partitioning in forest canopies (eqn (9) and (10) in Horstmann and McLachlan,[76] eqn (11) in Su *et al.*[77]).

While many environmentally relevant phase equilibria can now be predicted directly, the availability of tools to predict partition ratios at a variety of temperatures is much more limited. For example, while ppLFERs for predicting gas particle partitioning at 15 °C exist,[171] atmospheric temperatures range over more than 60 K. The K_{OA} for many contaminants has been determined as a function of temperature or can be predicted using a ppLFER for the internal energy of phase transfer from octanol to gas phase ΔU°_{OA}.[161,180] It is thus possible to estimate an environmentally relevant equilibrium partition ratio at any temperature by either (i) applying K_{OA}-based spLFERs by inserting (empirical or predicted) K_{OA} values at the relevant temperatures or by (ii) adjusting the environmentally relevant partition ratio to the desired temperature using van't Hoff's equation and the (empirical or predicted) ΔU°_{OA}. Implicit in either approach is that the temperature dependence of the partitioning between the environmentally relevant phase and the gas phase is well described by the temperature dependence of octanol–air partitioning. Admittedly, one can obviously also adjust an equilibrium partitioning ratio derived from a ppLFER using such a ΔU°_{OA}. Note, since the K_{OA} and many other environmentally relevant phase equilibrium ratios are commonly defined using molar volumetric concentration in the gas phase (rather than a partial pressure), the ΔU°_{OA} needs to be used in the van't Hoff equation. ΔU°_{OA} can be obtained from the enthalpy of phase transfer ΔH°_{OA} by deducting the product of the ideal gas constant and absolute temperature.

There is need to further explore the extent of agreement between the internal energy of phase transfer between various environmentally relevant phases X and the gas phase ΔU°_{XA} and ΔU°_{OA}. This is currently limited by the availability of measurements for K_{XA} at different temperatures, but there are indications that ΔU°_{XA} can deviate from ΔU°_{OA}.[66]

4.3 The need for a single parameter describing partitioning from the gas phase into a wide variety of environmentally relevant organic phases

However, even if well-calibrated ppLFER equations existed for all relevant partitioning equilibria between air and organic phases at all desired temperatures, it would still be useful to have a single parameter that can serve to describe the tendency of a neutral organic chemical to partition from the gas phase into a wide variety of organic phases of environmental relevance. For such a parameter to be most useful, it needs to be (i) well-defined, (ii) directly accessible to measurement, and (iii) a reasonable surrogate for a wide

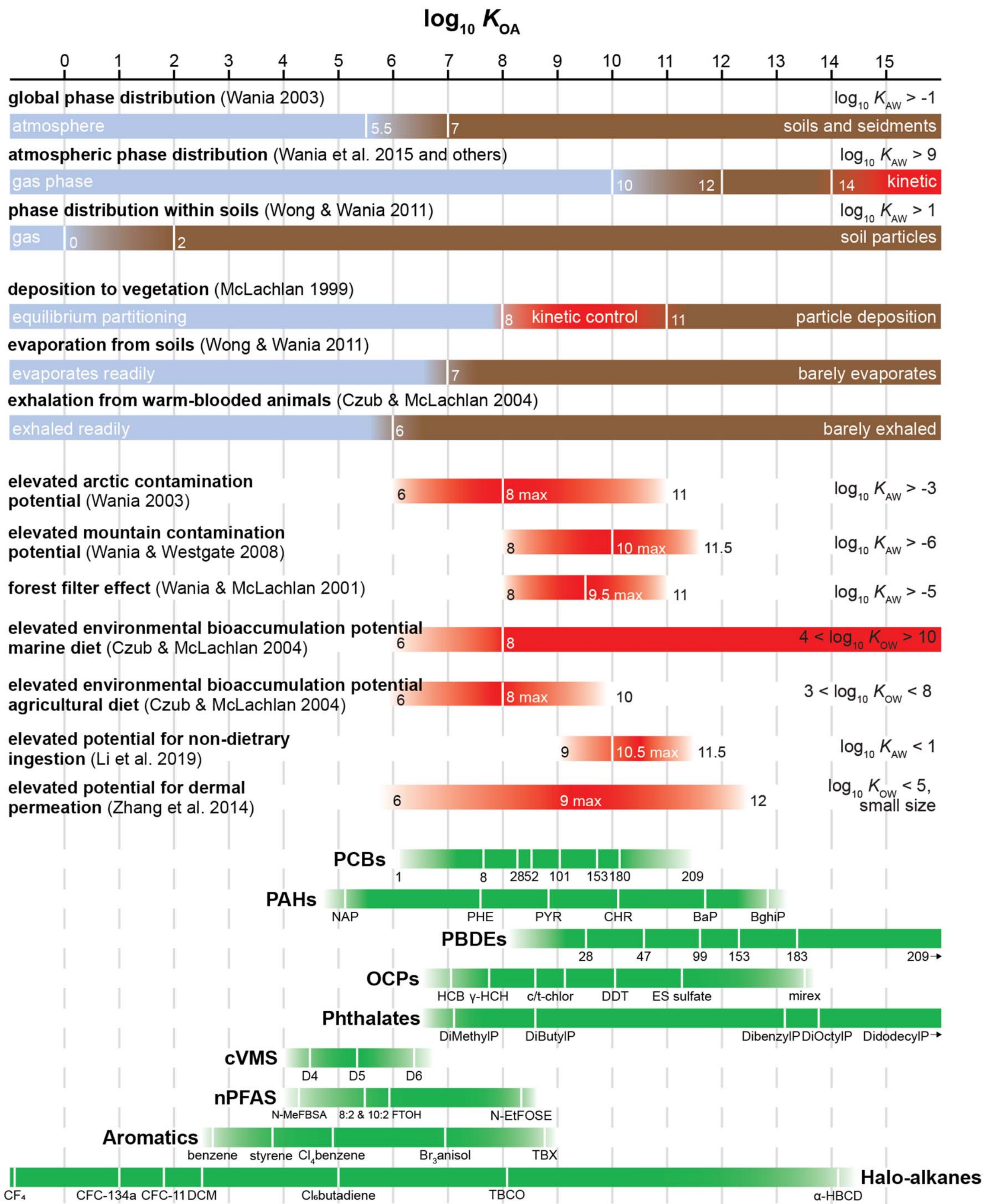

Fig. 3 Relationship between K_{OA} range and the environmental fate of common contaminants. Vertical lines are indicative of the $\log_{10} K_{OA}$, blue and brown bars indicate the relative dominant phase a chemical will be present in,[52,53,181–183] red bars indicate the bioaccumulation potential of chemicals within a K_{OA} range,[52,158,181,184–186] and green bars indicate the K_{OA} range of various compound groups. PCBs: polychorinated biphenyls; PAHs: polycyclic aromatic hydrocarbons; PBDEs: polybrominated diphenyl ethers; OCPs: organochlorine pesticides; cVMS: cyclic volatile methylsiloxanes; nPFAS: per- and poly-fluoroalkyl substances.

variety of organic phases. The K_{OA} is better suited to this role than other parameters:

• An equilibrium partition ratio involving a real environmental organic phase is not a good choice because environmental phases are of variable composition and therefore not sufficiently well-defined.

• While the saturation vapour pressure is the traditional parameter for expressing compound volatility, the solid state vapour pressure is not an appropriate parameter to describe the volatility of a substance from any organic phase other than its own pure solid phase, because of the strong influence of the lattice energy.

• Although this can be in principle corrected by using the saturation vapour pressure of the sub-cooled liquid, it has the drawback that this parameter cannot be determined directly by experiment. It also implies that the organic reference phase is a different one for every substance.

• While other organic solvents or polymers may be equally good (and possibly even better) surrogates of environmental organic phases relative to octanol, the knowledge of how good a surrogate octanol is, is much better than for any other organic solvent (see Section 3).

As such, the K_{OA} can still play an important role as a measure of volatility from organic phases. It is an easy to comprehend, single chemical characteristic that can be used to judge a chemical's propensity to undergo a very wide range of environmental processes. Just by knowing a compound's K_{OA}, it is possible to infer a tremendous amount of information on its environmental behaviour. This is illustrated in Fig. 3. For example, instead of requiring separate parameters to assess a chemical's equilibrium phase distribution in atmosphere and soils, its susceptibility to evaporate or be exhaled, and the importance of processes controlling its deposition to plants, this can all be deduced from the compound's K_{OA}. At the same time, it can inform you about the suitability of a sampling sorbent for the compound and which human exposure pathways are likely to be relevant.

Another example for the utility of such a parameter is that it can serve as a volatility threshold for classification, prioritization and possibly even regulation of chemicals (Section 2.5.7). For example, K_{OA} is being used as a threshold for the potential to bioaccumulate in air-breathing species.[187]

Another advantage of K_{OA} is the possibility to use it in analyses that require the display of model results as a function of the chemical partitioning space. By taking advantage of octan-1-ol being able to represent a wide variety of organic phases reasonably well, the K_{OA} facilitates the display of model-derived contaminant behaviour in a chemical partitioning space defined by coordinates of hydrophobicity and volatility. For example, when Czub *et al.*[188] plotted the model calculated combined Arctic Contamination and BioAccumulation Potential (AC-BAP) of organic chemicals as a function of K_{OA} and K_{AW}, octan-1-ol simultaneously serves to approximate the solvation properties of soil and sedimentary organic matter, forest canopies, organic aerosol particles and lipids in a variety of organisms (plants, food animals, humans). Similarly, in Li *et al.*'s[158] analysis of human exposure pathway, the K_{OA} is used simultaneously to estimate partition equilibria between a very large variety of phases and the gas phase. This includes soil and sediment organic matter, atmospheric particles, house dust, various indoor surfaces, plant and animal lipids and human skin. While it would be possible to perform the type of model calculations performed by Czub *et al.*[188] and Li *et al.*[158] using partitioning ratios that are not estimated from K_{OA}, it would be much more difficult to perform the systematic investigation of how the model results depend on the partitioning characteristics of an organic chemical without relying on partitioning ratios involving octan-1-ol. It would clearly be impossible to display them in a two-dimensional partitioning space.

5 Conclusion

This review examines the role of the K_{OA} in environmental chemistry. We examined the historical context of partition ratios and the various ways the K_{OA} is used to predict and describe gas partitioning properties in the real environment. The K_{OA} is shown to be a reasonable surrogate for multiple environmental phases and has applications in environmental, atmospheric, physical chemical, medical, and food sciences. It is more advantageous to use the K_{OA} to describe these partitioning processes instead of vapour pressure, because it is well defined, has broader applicability, and can be reliably estimated and measured.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was funded by the European Chemical Industry Council (CEFIC) through project ECO 41 of the Long-range Research Initiative (LRI).

References

1 R. Bunsen, XV. On the law of absorption of gases, *London, Edinburgh Dublin Philos. Mag. J. Sci.*, 1855, **9**, 116–130.
2 W. Henry III., Experiments on the quantity of gases absorbed by water, at different temperatures, and under different pressures, *Philos. Trans. R. Soc. London*, 1803, **93**, 29–42.
3 W. Ostwald, *Solutions*, Longmans, Green, and Co., London, New York, 1891.
4 H. Meyer, Zur theorie der alkoholnarkose, *Arch. Exp. Pathol. Pharmakol.*, 1899, **42**, 109–118.
5 C. E. Overton, *Studien über die Narkose: Zugleich ein Beitrag zur allgemeinen Pharmakologie*, Fischer, Jena, 1901.
6 G. J. Pierotti, C. H. Deal, E. L. Derr and P. E. Porter, Solvent effects in gas–liquid partition chromatography, *J. Am. Chem. Soc.*, 1956, **78**, 2989–2998.
7 P. E. Porter, C. H. Deal and F. H. Stross, The determination of partition coefficients from gas–liquid partition chromatography, *J. Am. Chem. Soc.*, 1956, **78**, 2999–3006.

8 J. H. Smith, W. R. Mabey, N. Bohonos, B. R. Holt, S. S. Lee, T. W. Chou, D. C. Bomberger and T. Mill, *Environmental Pathways of Selected Chemicals in Freshwater Systems Part 1: Background and Experimental Procedures*, Environmental Protection Agency, 1977, Technical Report 600778074.
9 D. R. Branson, *Estimating the Hazard of Chemical Substances to Aquatic Life*, American Society for Testing and Materials, 1978, pp. 55–70.
10 The IUPAC, *Compendium of Chemical Terminology: the Gold Book*, IUPAC, International Union of Pure and Applied Chemistry (IUPAC), Research Triangle Park, NC, 4th edn, 2019.
11 S. Baskaran, Y. D. Lei and F. Wania, A database of experimentally derived and estimated octanol–air partition ratios (K_{OA}), *J. Phys. Chem. Ref. Data*, 2021, **50**, 043101.
12 F. L. Boyer and L. J. Bircher, The solubility of nitrogen, argon, methane, ethylene and ethane in normal primary alcohols, *J. Phys. Chem.*, 1960, **64**, 1330–1331.
13 P. Berti, S. Cabani, G. Conti and V. Mollica, Thermodynamic study of organic compounds in octan-1-ol. Processes of transfer from gas and from dilute aqueous solution, *J. Chem. Soc., Faraday Trans. 1*, 1986, **82**, 2547–2556.
14 J. M. Roberts, Measurement of the Henry's law coefficient and first order loss rate of PAN in n-octanol, *Geophys. Res. Lett.*, 2005, **32**, L08803.
15 A. Hussam and P. W. Carr, Rapid and precise method for the measurement of vapor/liquid equilibria by headspace gas chromatography, *Anal. Chem.*, 1985, **57**, 793–801.
16 A. Finizio, D. Mackay, T. Bidleman and T. Harner, Octanol–air partition coefficient as a predictor of partitioning of semi-volatile organic chemicals to aerosols, *Atmos. Environ.*, 1997, **31**, 2289–2296.
17 R. Battino and H. L. Clever, The solubility of gases in liquids, *Chem. Rev.*, 1966, **66**, 395–463.
18 A. E. Markham and K. A. Kobe, The solubility of gases in liquids, *Chem. Rev.*, 1941, **28**, 519–588.
19 D. H. Robinson and A. H. Toledo, Historical Development of Modern Anesthesia, *J. Investig. Surg.*, 2012, **25**, 141–149.
20 A. Seidell, *Solubilities of Inorganic and Organic Compounds, a Compilation of Quantitative Solubility Data from the Periodical Literature*, New York, Van Nostrand, 1919.
21 D. D. Van Slyke and J. M. Neill, The determination of gases in blood and other solutions by vacuum extraction and manometric measurement. i, *J. Biol. Chem.*, 1924, **61**, 523–573.
22 K. Meyer and H. Hemmi, Beitrage zur theorie der narkose. III, *Biochem. Z.*, 1935, 39–71.
23 R. Collander, On lipoid solubility, *Acta Physiol. Scand.*, 1947, **13**, 363–381.
24 R. Collander, The partition of organic compounds between higher alcohols and water, *Acta Chem. Scand.*, 1951, 774–780.
25 R. Collander, The permeability of nitella cells to non-electrolytes, *Physiol. Plant.*, 1954, **7**, 420–445.
26 C. Hansch, *Drug Design*, Academic Press, New York, 1971, vol. 1, pp. 271–342.
27 C. Hansch, P. P. Maloney, T. Fujita and R. M. Muir, Correlation of biological activity of phenoxyacetic acids with Hammett substituent constants and partition coefficients, *Nature*, 1962, **194**, 178–180.
28 T. Fujita, J. Iwasa and C. Hansch, A new substituent constant, π, derived from partition coefficients, *J. Am. Chem. Soc.*, 1964, **86**, 5175–5180.
29 A. Leo, C. Hansch and D. Elkins, Partition coefficients and their uses, *Chem. Rev.*, 1971, **71**, 525–616.
30 C. Hansch, *Annual Reports in Medicinal Chemistry*, Academic Press, 1968, vol. 3, pp. 348–357.
31 C. Hansch, *Annual Reports in Medicinal Chemistry*, Academic Press, 1967, vol. 2, pp. 347–359.
32 R. Wixon, *Chromatography: a Century of Discovery 1900–2000: the Bridge to the Sciences/Technology*, Elsevier Science, Ltd, Amsterdam; New York, 1st edn, 2001, pp. 1–38.
33 G. J. Pierotti, C. H. Deal and E. L. Derr, Activity coefficients and molecular structure, *Ind. Eng. Chem.*, 1959, **51**, 95–102.
34 J. Gmehling and J. Menke, *Activity Coefficients at Infinite Dilution. Pt. 5: C1–C16*, DECHEMA, Frankfurt/Main, 2007, vol. 9.
35 L. Rohrschneider, Solvent characterization by gas–liquid partition coefficients of selected solutes, *Anal. Chem.*, 1973, **45**, 1241–1247.
36 R. J. Wilcock, R. Battino, W. F. Danforth and E. Wilhelm, Solubilities of gases in liquids II. The solubilities of He, Ne, Ar, Kr, O_2, N_2, CO, CO_2, CH_4, CF_4, and SF_6 in n-octane 1-octanol, n-decane, and 1-decanol, *J. Chem. Thermodyn.*, 1978, **10**, 817–822.
37 R. Battino, F. D. Evans and W. F. Danforth, The solubilities of seven gases in olive oil with references to theories of transport through the cell membrane, *J. Am. Oil Chem. Soc.*, 1968, **45**, 830–833.
38 J. E. Byrne, R. Battino and W. F. Danforth, The solubility of gases in liquids 7. The solubilities of N_2, O_2, Ar, CO, CO_2, and c-C_3H_6 in benzene and isobutanol solutions of cholesterol, lecithin, and cephalin at 310.65 K, *J. Chem. Thermodyn.*, 1974, **6**, 245–250.
39 S. Paterson, D. Mackay, D. Tam and W. Shiu, Uptake of organic chemicals by plants: a review of processes, correlations and models, *Chemosphere*, 1990, **21**, 297–331.
40 G. L. Pollack, J. F. Himm and J. J. Enyeart, Solubility of xenon in liquid n-alkanols: Thermodynamic functions in simple polar liquids, *J. Chem. Phys.*, 1984, **81**, 3239–3246.
41 S. Taheri, M. J. Halsey, J. Liu, E. I. I. Eger, D. D. Koblin and M. J. Laster, What solvent best represents the site of action of inhaled anesthetics in humans, rats, and dogs?, *Anesth. Analg.*, 1991, **72**, 627–634.
42 S. Taheri, M. J. Laster, J. Liu, E. I. I. Eger, M. J. Halsey and D. D. Koblin, Anesthesia by n-alkanes not consistent with the Meyer-Overton hypothesis: Determinations of the solubilities of alkanes in saline and various lipids, *Anesth. Analg.*, 1993, **77**, 7–11.

43 J. Liu, J. Laster, S. Taheri, E. I. Eger, D. D. Koblin and M. J. Halsey, Is there a cutoff in anesthetic potency for the normal alkanes?, *Anesth. Analg.*, 1993, **77**, 12–18.
44 T. Harner and D. Mackay, Measurement of octanol–air partition coefficients for chlorobenzenes, PCBs, and DDT, *Environ. Sci. Technol.*, 1995, **29**, 1599–1606.
45 A. J. Dallas, PhD thesis, University of Minnesota, United States – Minnesota, 1995.
46 H. V. Andersen and M. Frederiksen, Sorption of PCB from air to settled house dust in a contaminated indoor environment, *Chemosphere*, 2021, **266**, 129139.
47 T. Salthammer and T. Schripp, Application of the Junge- and Pankow-equation for estimating indoor gas/particle distribution and exposure to SVOCs, *Atmos. Environ.*, 2015, **106**, 467–476.
48 K.-U. Goss and R. P. Schwarzenbach, Gas/solid and gas/liquid partitioning of organic compounds: critical evaluation of the interpretation of equilibrium constants, *Environ. Sci. Technol.*, 1998, **32**, 2025–2032.
49 J. F. Pankow, Further discussion of the octanol/air partition coefficient K_{OA} as a correlating parameter for gas/particle partitioning coefficients, *Atmos. Environ.*, 1998, **32**, 1493–1497.
50 H. Xiao and F. Wania, Is vapor pressure or the octanol–air partition coefficient a better descriptor of the partitioning between gas phase and organic matter?, *Atmos. Environ.*, 2003, **37**, 2867–2878.
51 S. Paterson and D. Mackay, Correlation of tissue, blood, and air partition coefficients of volatile organic chemicals, *Br. J. Ind. Med.*, 1989, **46**, 321–328.
52 G. Czub and M. S. McLachlan, Bioaccumulation potential of persistent organic chemicals in humans, *Environ. Sci. Technol.*, 2004, **38**, 2406–2412.
53 M. S. McLachlan, Framework for the interpretation of measurements of SOCs in plants, *Environ. Sci. Technol.*, 1999, **33**, 1799–1804.
54 F. Zhao, I. Riipinen and M. MacLeod, Steady-state mass balance model for predicting particle–gas concentration ratios of PBDEs, *Environ. Sci. Technol.*, 2021, **55**, 9425–9433.
55 E. Bacci, M. J. Cerejeira, C. Gaggi, G. Chemello, D. Calamari and M. Vighi, Bioconcentration of organic chemical vapours in plant leaves: the azalea model, *Chemosphere*, 1990, **21**, 525–535.
56 M. Riederer, Estimating partitioning and transport of organic chemicals in the foliage/atmosphere system: discussion of a fugacity-based model, *Environ. Sci. Technol.*, 1990, **24**, 829–837.
57 M. Riederer, *Plant Contamination: Modeling and Simulation of Organic Chemical Processes*, 1995.
58 N. L. L. Steyaert, M. Hauck, S. W. H. Van Hulle and A. Jan Hendriks, Modelling bioaccumulation of semi-volatile organic compounds (SOCs) from air in plants based on allometric principles, *Chemosphere*, 2009, **77**, 727–732.
59 D. C. G. Muir, M. D. Segstro, P. M. Welbourn, D. Toom, S. J. Eisenreich, C. R. Macdonald and D. M. Whelpdale, Patterns of accumulation of airborne organochlorine contaminants in lichens from the Upper Great Lakes Region of Ontario, *Environ. Sci. Technol.*, 1993, **27**, 1201–1210.
60 J. F. Müller, D. W. Hawker and D. W. Connell, Calculation of bioconcentration factors of persistent hydrophobic compounds in the air/vegetation system, *Chemosphere*, 1994, **29**, 623–640.
61 P. Tremolada, V. Burnett, D. Calamari and K. C. Jones, Spatial distribution of PAHs in the U.K. atmosphere using pine needles, *Environ. Sci. Technol.*, 1996, **30**, 3570–3577.
62 D. L. Dowdy and T. E. McKone, Predicting plant uptake of organic chemicals from soil or air using octanol/water and octanol/air partition ratios and a molecular connectivity index, *Environ. Toxicol. Chem.*, 1997, **16**, 2448–2456.
63 R. Keymeulen, G. De Bruyn and H. Van Langenhove, Headspace gas chromatographic determination of the plant cuticle–air partition coefficients for monocyclic aromatic hydrocarbons as environmental compartment, *J. Chromatogr. A*, 1997, **774**, 213–221.
64 J. Tolls and M. S. McLachlan, Partitioning of semivolatile organic compounds between air and Lolium multiflorum (Welsh ray grass), *Environ. Sci. Technol.*, 1994, **28**, 159–166.
65 R. H. A. Brown, J. N. Cape and J. G. Farmer, Partitioning of chlorinated solvents between pine needles and air, *Chemosphere*, 1998, **36**, 1799–1810.
66 P. Kömp and M. S. McLachlan, Interspecies variability of the plant/air partitioning of polychlorinated biphenyls, *Environ. Sci. Technol.*, 1997, **31**, 2944–2948.
67 L. Nizzetto, C. Pastore, X. Liu, P. Camporini, D. Stroppiana, B. Herbert, M. Boschetti, G. Zhang, P. A. Brivio, K. C. Jones and A. Di Guardo, Accumulation Parameters and Seasonal Trends for PCBs in Temperate and Boreal Forest Plant Species, *Environ. Sci. Technol.*, 2008, **42**, 5911–5916.
68 M. Taylor, S. M. Lyons, C. L. Davie-Martin, T. S. Geoghegan and K. J. Hageman, Understanding trends in pesticide volatilization from agricultural fields using the pesticide loss via volatilization model, *Environ. Sci. Technol.*, 2020, **54**, 2202–2209.
69 Y. Zhao, L. Yang and Q. Wang, Modeling persistent organic pollutant (POP) partitioning between tree bark and air and its application to spatial monitoring of atmospheric POPs in mainland china, *Environ. Sci. Technol.*, 2009, **43**, 8469–8470.
70 Y. Zhao, L. Yang and Q. Wang, Modeling persistent organic pollutant (POP) partitioning between tree bark and air and its application to spatial monitoring of atmospheric POPs in mainland China, *Environ. Sci. Technol.*, 2008, **42**, 6046–6051.
71 C. Rauert, A. Kananathalingam and T. Harner, Characterization and Modeling of Polycyclic Aromatic Compound Uptake into Spruce Tree Wood, *Environ. Sci. Technol.*, 2017, **51**, 5287–5295.
72 M. F. Sari, F. Esen and Y. Tasdemir, Characterization, source apportionment, air/plant partitioning and cancer risk assessment of atmospheric PAHs measured with tree components and passive air sampler, *Environ. Res.*, 2021, **194**, 110508.
73 X. Fu, J. Wang, X. Zhou, J. Deng, Y. Liu, W. Zhang, L. Liu, L. Dong and K. Lin, Tree bark as a passive air sampler to

indicate atmospheric polybrominated diphenyl ethers (PBDEs) in southeastern China, *Environ. Sci. Pollut. Res.*, 2014, **21**, 7668–7677.

74 J. Leppich, J. H. Pardue and W. A. Jackson, *Wetlands & Remediation: an International Conference*, Columbus, 2000, pp. 17–24.

75 T. A. Wetzel and W. J. Doucette, Plant leaves as indoor air passive samplers for volatile organic compounds (VOCs), *Chemosphere*, 2015, **122**, 32–37.

76 M. Horstmann and M. S. McLachlan, Atmospheric deposition of semivolatile organic compounds to two forest canopies, *Atmos. Environ.*, 1998, **32**, 1799–1809.

77 Y. Su, F. Wania, T. Harner and Y. D. Lei, Deposition of polybrominated diphenyl ethers, polychlorinated biphenyls, and polycyclic aromatic hydrocarbons to a boreal deciduous forest, *Environ. Sci. Technol.*, 2007, **41**, 534–540.

78 W. J. Doucette, C. Shunthirasingham, E. M. Dettenmaier, R. T. Zaleski, P. Fantke and J. A. Arnot, A review of measured bioaccumulation data on terrestrial plants for organic chemicals: Metrics, variability, and the need for standardized measurement protocols, *Environ. Toxicol. Chem.*, 2018, **37**, 21–33.

79 M. Limmer and J. Burken, Phytovolatilization of organic contaminants, *Environ. Sci. Technol.*, 2016, **50**, 6632–6643.

80 M. Hippelein and M. S. McLachlan, Soil/air partitioning of semivolatile organic compounds. 1. Method development and influence of physical-chemical properties, *Environ. Sci. Technol.*, 1998, **32**, 310–316.

81 M. D. Borisover and E. R. Graber, Specific interactions of organic compounds with soil organic carbon, *Chemosphere*, 1997, **34**, 1761–1776.

82 S. W. Karickhoff, Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils, *Chemosphere*, 1981, **10**, 833–846.

83 A. Finizio, T. Bidleman and S. Szeto, Emission of chiral pesticides from an agricultural soil in the Fraser Valley, British Columbia, *Chemosphere*, 1998, **36**, 345–355.

84 T. F. Bidleman, Atmospheric transport and air-surface exchange of pesticides, *Water, Air, Soil Pollut.*, 1999, **115**, 115–166.

85 I. T. Cousins, N. Hartlieb, C. Teichmann and K. C. Jones, Measured and predicted volatilisation fluxes of PCBs from contaminated sludge-amended soils, *Environ. Pollut.*, 1997, **97**, 229–238.

86 X. He, S. Chen, X. Quan, Z. Liu and Y. Zhao, Temperature-dependence of soil/air partition coefficient for polychlorinated biphenyls at subzero temperatures, *Chemosphere*, 2009, **77**, 1427–1433.

87 N. Li, F. Wania, Y. D. Lei and G. L. Daly, A comprehensive and critical compilation, evaluation, and selection of physical–chemical property data for selected polychlorinated biphenyls, *J. Phys. Chem. Ref. Data*, 2003, **32**, 1545–1590.

88 M. Hippelein and M. S. McLachlan, Soil/air partitioning of semivolatile organic compounds. 2. Influence of temperature and relative humidity, *Environ. Sci. Technol.*, 2000, **34**, 3521–3526.

89 C. L. Davie-Martin, K. J. Hageman, Y.-P. Chin, V. Rougé and Y. Fujita, Influence of temperature, relative humidity, and soil properties on the soil–air partitioning of semivolatile pesticides: Laboratory measurements and predictive models, *Environ. Sci. Technol.*, 2015, **49**, 10431–10439.

90 K.-U. Goss, The air/surface adsorption equilibrium of organic compounds under ambient conditions, *Crit. Rev. Environ. Sci. Technol.*, 2004, **34**, 339–389.

91 K.-U. Goss, J. Buschmann and R. P. Schwarzenbach, Adsorption of Organic Vapors to Air-Dry Soils: Model Predictions and Experimental Validation, *Environ. Sci. Technol.*, 2004, **38**, 3667–3673.

92 K.-U. Goss and R. P. Schwarzenbach, Linear free energy relationships used to evaluate equilibrium partitioning of organic compounds, *Environ. Sci. Technol.*, 2001, **35**, 1–9.

93 C. Junge, *Fate of Pollutants in the Air and Water Environments*, Wiley, New York, 1977, vol. 1, pp. 7–26.

94 J. F. Pankow, Review and comparative analysis of the theories on partitioning between the gas and aerosol particulate phases in the atmosphere, *Atmos. Environ.*, 1987, **21**, 2275–2283.

95 T. Harner and T. F. Bidleman, Octanol–air partition coefficient for describing particle/gas partitioning of aromatic compounds in urban air, *Environ. Sci. Technol.*, 1998, **32**, 1494–1502.

96 J. F. Pankow, An absorption model of the gas/aerosol partitioning involved in the formation of secondary organic aerosol, *Atmos. Environ.*, 1994, **28**, 189–193.

97 R. L. Falconer and T. Harner, Comparison of the octanol–air partition coefficient and liquid-phase vapor pressure as descriptors for particle/gas partitioning using laboratory and field data for PCBs and PCNs, *Atmos. Environ.*, 2000, **34**, 4043–4046.

98 H. Kaupp and M. S. McLachlan, Gas/particle partitioning of PCDD/Fs, PCBs, PCNs and PAHs, *Chemosphere*, 1999, **38**, 3411–3421.

99 J.-E. Oh, J.-S. Choi and Y.-S. Chang, Gas/particle partitioning of polychlorinated dibenzo-p-dioxins and dibenzofurans in atmosphere; evaluation of predicting models, *Atmos. Environ.*, 2001, **35**, 4125–4134.

100 J. Radonic, M. Vojinovic-Miloradov, M. Turk-Sekulic, J. Kiurski, M. Djogo and D. Milovanovic, The octanol–air partition coefficient K_{OA} as a predictor of gas-particle partitioning of polycyclic aromatic hydrocarbons and polychlorinated biphenyls at industrial and urban sites, *J. Serb. Chem. Soc.*, 2011, **76**, 447–458.

101 B. Chandramouli, M. Jang and R. M. Kamens, Gas–particle partitioning of semi-volatile organics on organic aerosols using a predictive activity coefficient model: analysis of the effects of parameter choices on model performance, *Atmos. Environ.*, 2003, **37**, 853–864.

102 H.-G. Yeo, M. Choi, M.-Y. Chun and Y. Sunwoo, Gas/particle concentrations and partitioning of PCBs in the atmosphere of Korea, *Atmos. Environ.*, 2003, **37**, 3561–3570.

103 C. W. Götz, M. Scheringer, M. MacLeod, C. M. Roth and K. Hungerbühler, Alternative approaches for modeling gas–particle partitioning of semivolatile organic

chemicals: Model development and comparison, *Environ. Sci. Technol.*, 2007, **41**, 1272–1278.

104 J. Dachs and S. J. Eisenreich, Adsorption onto aerosol soot carbon dominates gas-particle partitioning of polycyclic aromatic hydrocarbons, *Environ. Sci. Technol.*, 2000, **34**, 3690–3697.

105 P. Fernández, J. O. Grimalt and R. M. Vilanova, Atmospheric gas-particle partitioning of polycyclic aromatic hydrocarbons in high mountain regions of Europe, *Environ. Sci. Technol.*, 2002, **36**, 1162–1168.

106 N. Vardar, Y. Tasdemir, M. Odabasi and K. E. Noll, Characterization of atmospheric concentrations and partitioning of PAHs in the Chicago atmosphere, *Sci. Total Environ.*, 2004, **327**, 163–174.

107 P. Helm and T. Bidleman, Gas–particle partitioning of polychlorinated naphthalenes and non- and mono–ortho-substituted polychlorinated biphenyls in arctic air, *Sci. Total Environ.*, 2005, **342**, 161–173.

108 C. J. Weschler and W. W. Nazaroff, Semivolatile organic compounds in indoor environments, *Atmos. Environ.*, 2008, **42**, 9018–9040.

109 C. J. Weschler and W. W. Nazaroff, SVOC partitioning between the gas phase and settled dust indoors, *Atmos. Environ.*, 2010, **44**, 3609–3620.

110 X. Zhang, M. L. Diamond, M. Robson and S. Harrad, Sources, emissions, and fate of polybrominated diphenyl ethers and polychlorinated biphenyls indoors in Toronto, Canada, *Environ. Sci. Technol.*, 2011, **45**, 3268–3274.

111 M. Shoeib, T. Harner, M. Ikonomou and K. Kannan, Indoor and outdoor air concentrations and phase partitioning of perfluoroalkyl sulfonamides and polybrominated diphenyl ethers, *Environ. Sci. Technol.*, 2004, **38**, 1313–1320.

112 M. Shoeib, T. Harner, B. H. Wilford, K. C. Jones and J. Zhu, Perfluorinated sulfonamides in indoor and outdoor air and indoor dust: Occurrence, partitioning, and human exposure, *Environ. Sci. Technol.*, 2005, **39**, 6599–6606.

113 T. F. Webster, S. Harrad, J. R. Millette, R. D. Holbrook, J. M. Davis, H. M. Stapleton, J. G. Allen, M. D. McClean, C. Ibarra, M. A.-E. Abdallah and A. Covaci, Identifying transfer mechanisms and sources of decabromodiphenyl ether (BDE 209) in indoor environments using environmental forensic microscopy, *Environ. Sci. Technol.*, 2009, **43**, 3067–3072.

114 H.-L. Li, L.-Y. Liu, Z.-F. Zhang, W.-L. Ma, E. Sverko, Z. Zhang, W.-W. Song, Y. Sun and Y.-F. Li, Semi-volatile organic compounds in infant homes: levels, influence factors, partitioning, and implications for human exposure, *Environ. Pollut.*, 2019, **251**, 609–618.

115 W. Wei, C. Dassonville, S. Sivanantham, A. Gregoire, F. Mercier, B. L. Bot, L. Malingre, O. Ramalho, M. Derbez and C. Mandin, Semivolatile organic compounds in French schools: Partitioning between the gas phase, airborne particles and settled dust, *Indoor Air*, 2021, **31**, 156–169.

116 J. B. Wilcockson and F. A. P. C. Gobas, Thin-film solid-phase extraction to measure fugacities of organic chemicals with low volatility in biological samples, *Environ. Sci. Technol.*, 2001, **35**, 1425–1431.

117 U. M. Shahin, Y.-H. Li and T. M. Holsen, Dry deposition of gas-phase polycyclic aromatic hydrocarbons to greased surrogate surfaces, *Aerosol Sci. Technol.*, 1999, **31**, 446–455.

118 Y. Wu, C. M. A. Eichler, W. Leng, S. S. Cox, L. C. Marr and J. C. Little, Adsorption of phthalates on impervious indoor surfaces, *Environ. Sci. Technol.*, 2017, **51**, 2907–2913.

119 M. L. Diamond, S. E. Gingrich, K. Fertuck, B. E. McCarry, G. A. Stern, B. Billeck, B. Grift, D. Brooker and T. D. Yager, Evidence for organic film on an impervious urban surface: characterization and potential teratogenic effects, *Environ. Sci. Technol.*, 2000, **34**, 2900–2908.

120 C. M. Butt, M. L. Diamond, J. Truong, M. G. Ikonomou, P. A. Helm and G. A. Stern, Semivolatile organic compounds in window films from lower manhattan after the september 11th World Trade Center attacks, *Environ. Sci. Technol.*, 2004, **38**, 3514–3524.

121 C. M. Butt, M. L. Diamond, J. Truong, M. G. Ikonomou and A. F. H. ter Schure, Spatial distribution of polybrominated diphenyl ethers in Southern Ontario as measured in indoor and outdoor window organic films, *Environ. Sci. Technol.*, 2004, **38**, 724–731.

122 R. Wu, T. Harner, M. Diamond and B. Wilford, Partitioning characteristics of PCBs in urban surface films, *Atmos. Environ.*, 2008, **42**, 5696–5705.

123 C. Bi, Y. Liang and Y. Xu, Fate and transport of phthalates in indoor environments and the influence of temperature: a case study in a test house, *Environ. Sci. Technol.*, 2015, **49**, 9674–9681.

124 B. Cetin and M. Odabasi, Polybrominated diphenyl ethers (PBDEs) in indoor and outdoor window organic films in Izmir, Turkey, *J. Hazard. Mater.*, 2011, **185**, 784–791.

125 C. J. Weschler and W. W. Nazaroff, Growth of organic films on indoor surfaces, *Indoor Air*, 2017, **27**, 1101–1112.

126 D. J. Donaldson, B. T. Mmereki, S. R. Chaudhuri, S. Handley and M. Oh, Uptake and reaction of atmospheric organic vapours on organic films, *Faraday Discuss.*, 2005, **130**, 227–239.

127 W. A. Ockenden, H. F. Prest, G. O. Thomas, A. Sweetman and K. C. Jones, Passive air sampling of PCBs: Field calculation of atmospheric sampling rates by triolein-containing semipermeable membrane devices, *Environ. Sci. Technol.*, 1998, **32**, 1538–1543.

128 M. Shoeib and T. Harner, Characterization and comparison of three passive air samplers for persistent organic pollutants, *Environ. Sci. Technol.*, 2002, **36**, 4142–4151.

129 M. E. Bartkow, D. W. Hawker, K. E. Kennedy and J. F. Müller, Characterizing uptake kinetics of PAHs from the air using polyethylene-based passive air samplers of multiple surface area-to-volume ratios, *Environ. Sci. Technol.*, 2004, **38**, 2701–2706.

130 K. E. Kennedy, D. W. Hawker, J. F. Müller, M. E. Bartkow and R. W. Truss, A field comparison of ethylene vinyl acetate and low-density polyethylene thin films for equilibrium phase passive air sampling of polycyclic aromatic hydrocarbons, *Atmos. Environ.*, 2007, **41**, 5778–5787.

131 S. Ly-Verdú, F. A. Esteve-Turrillas, A. Pastor and M. de la Guardia, A passive sampling-based analytical strategy for the determination of volatile organic compounds in the air of working areas, *Anal. Chim. Acta*, 2010, **677**, 131–139.
132 N. De Coensel, K. Desmet, T. Górecki and P. Sandra, Determination of polydimethylsiloxane-air partition coefficients using headspace sorptive extraction, *J. Chromatogr. A*, 2007, **1150**, 183–189.
133 J.-Y. Lao, C.-C. Wu, L.-J. Bao, L.-Y. Liu, L. Shi and E. Y. Zeng, Size distribution and clothing–air partitioning of polycyclic aromatic hydrocarbons generated by barbecue, *Sci. Total Environ.*, 2018, **639**, 1283–1289.
134 J. Yu, F. Wania and J. P. D. Abbatt, A New Approach to Characterizing the Partitioning of Volatile Organic Compounds to Cotton Fabric, *Environ. Sci. Technol.*, 2022, **56**, 3365–3374.
135 A. Saini, C. Rauert, M. J. Simpson, S. Harrad and M. L. Diamond, Characterizing the sorption of polybrominated diphenyl ethers (PBDEs) to cotton and polyester fabrics under controlled conditions, *Sci. Total Environ.*, 2016, **563–564**, 99–107.
136 D. Won, R. L. Corsi and M. Rynes, Sorptive interactions between VOCs and indoor materials: Sorptive interactions between VOCs and indoor materials, *Indoor Air*, 2001, **11**, 246–256.
137 T. Schripp, T. Salthammer, C. Fauck, G. Bekö and C. J. Weschler, Latex paint as a delivery vehicle for diethylphthalate and di-n-butylphthalate: Predictable boundary layer concentrations and emission rates, *Sci. Total Environ.*, 2014, **494–495**, 299–305.
138 E. Reppas-Chrysovitsinos, A. Sobek and M. MacLeod, Screening-level models to estimate partition ratios of organic chemicals between polymeric materials, air and water, *Environ. Sci.: Processes Impacts*, 2016, **18**, 667–676.
139 P. Poulin and K. Krishnan, A tissue composition-based algorithm for predicting tissue:air partition coefficients of organic chemicals, *Toxicol. Appl. Pharmacol.*, 1996, **136**, 126–130.
140 P. Poulin and K. Krishnan, A mechanistic algorithm for predicting blood:air partition coefficients of organic chemicals with the consideration of reversible binding in hemoglobin, *Toxicol. Appl. Pharmacol.*, 1996, **136**, 131–137.
141 P. Poulin and K. Krishnan, Molecular structure-based prediction of the partition coefficients of organic chemicals for physiological pharmacokinetic models, *Toxicol. Methods*, 1996, **6**, 117–137.
142 L. Li, J. N. Westgate, L. Hughes, X. Zhang, B. Givehchi, L. Toose, J. M. Armitage, F. Wania, P. Egeghy and J. A. Arnot, A Model for Risk-Based Screening and Prioritization of Human Exposure to Chemicals from Near-Field Sources, *Environ. Sci. Technol.*, 2018, **52**, 14235–14244.
143 S. Endo, T. N. Brown and K.-U. Goss, General model for estimating partition coefficients to organisms and their tissues using the biological compositions and polyparameter linear free energy relationships, *Environ. Sci. Technol.*, 2013, **47**, 6630–6639.
144 K. M. Hau and D. W. Connell, Quantitative structure-activity relationships (QSARs) for odor thresholds of volatile organic compounds (VOCs), *Indoor Air*, 1998, **8**, 23–33.
145 K. M. Hau, D. W. Connell and B. J. Richardson, Quantitative structure-activity relationships for nasal pungency thresholds of volatile organic compounds, *Toxicol. Sci.*, 1999, **47**, 93–98.
146 K. M. Hau, D. W. Connell and B. J. Richardson, A Study of the Biological Partitioning Behavior of n-Alkanes and n-Alkanols in Causing Anesthetic Effects, *Regul. Toxicol. Pharmacol.*, 2002, **35**, 273–279.
147 G. D. Nielsen, E. S. Thomsen and Y. Alarie, Sensory irritant receptor compartment properties. Equipotent vapour concentrations related to saturated vapour concentrations, octanol-water, and octanol-gas partition coefficients, *Acta Pharm. Nord.*, 1990, **2**, 31–44.
148 D. E. Raines, F. Gioia, R. J. Claycomb and R. J. Stevens, The N-methyl-D-aspartate receptor inhibitory potencies of aromatic inhaled drugs of abuse: evidence for modulation by cation-pi interactions, *J. Pharmacol. Exp. Ther.*, 2004, **311**, 14–21.
149 S. Tamaru, N. Igura and M. Shimoda, Effectiveness of water–air and octanol–air partition coefficients to predict lipophilic flavor release behavior from O/W emulsions, *Food Chem.*, 2018, **239**, 712–717.
150 S. Tamaru, A. Ono, N. Igura and M. Shimoda, High correlation between octanol–air partition coefficient and aroma release rate from O/W emulsions under non-equilibrium, *Food Res. Int.*, 2019, **116**, 883–887.
151 S. Batterman, L. Zhang, S. Wang and A. Franzblau, Partition coefficients for the trihalomethanes among blood, urine, water, milk and air, *Sci. Total Environ.*, 2002, **284**, 237–247.
152 G. A. Moser and M. S. McLachlan, Partitioning of polychlorinated biphenyls and hexachlorobenzene into human faeces, *Chemosphere*, 2002, **46**, 449–457.
153 F. A. P. C. Gobas, B. C. Kelly and J. Arnot, Quantitative structure activity relationships for predicting the bioaccumulation of pops in terrestrial food-webs, *QSAR Comb. Sci.*, 2003, **22**, 329–336.
154 B. C. Kelly and F. A. P. C. Gobas, Bioaccumulation of persistent organic pollutants in lichen-caribou-wolf food chains of Canada's Central and Western Arctic, *Environ. Sci. Technol.*, 2001, **35**, 325–334.
155 Government of Canada, *Persistence and Bioaccumulation Regulations*, 2022, https://laws-lois.justice.gc.ca/PDF/SOR-2000-107.pdf.
156 B. C. Kelly, M. G. Ikonomou, J. D. Blair, A. E. Morin and F. A. P. C. Gobas, Food web-specific biomagnification of persistent organic pollutants, *Science*, 2007, **317**, 236–239.
157 S. K. Moses, J. R. Harley, C. L. Lieske, D. C. Muir, A. V. Whiting and T. M. O'Hara, Variation in bioaccumulation of persistent organic pollutants based on octanol–air partitioning: influence of respiratory elimination in marine species, *Mar. Pollut. Bull.*, 2015, **100**, 122–127.

158 L. Li, J. A. Arnot and F. Wania, How are humans exposed to organic chemicals released to indoor air?, *Environ. Sci. Technol.*, 2019, **53**, 11276–11284.
159 N. Aurisano, L. Huang, L. Milà i Canals, O. Jolliet and P. Fantke, Chemicals of concern in plastic toys, *Environ. Int.*, 2021, **146**, 106194.
160 S. Baskaran, Y. D. Lei and F. Wania, Reliable prediction of the octanol–air partition ratio, *Environ. Toxicol. Chem.*, 2021, **40**, 3166–3180.
161 S. Baskaran, A. Podagatlapalli, A. Sangion and F. Wania, Predicting the Temperature Dependence of the Octanol–Air Partition Ratio: A New Model for Estimating $\Delta U_{OA}°$, *J. Solution Chem.*, 2023, **52**, 51–69.
162 N. Ulrich, S. Endo, T. Brown, G. Bronner, M. H. Abraham and K.-U. Goss, *UFZ-LSER Database V 3.2 [Internet]*, 2017.
163 J. A. Platts and M. H. Abraham, Partition of volatile organic compounds from air and from water into plant cuticular matrix: an LFER analysis, *Environ. Sci. Technol.*, 2000, **34**, 318–323.
164 A. Geisler, S. Endo and K.-U. Goss, Partitioning of organic chemicals to storage lipids: Elucidating the dependence on fatty acid composition and temperature, *Environ. Sci. Technol.*, 2012, **46**, 9519–9524.
165 S. Endo, B. I. Escher and K.-U. Goss, Capacities of membrane lipids to accumulate neutral organic chemicals, *Environ. Sci. Technol.*, 2011, **45**, 5912–5921.
166 M. H. Abraham, A. Ibrahim and W. E. Acree, Partition of compounds from gas to water and from gas to physiological saline at 310 K: Linear free energy relationships, *Fluid Phase Equilib.*, 2007, **251**, 93–109.
167 C. Niederer, R. P. Schwarzenbach and K.-U. Goss, Elucidating differences in the sorption properties of 10 humic and fulvic acids for polar and nonpolar organic chemicals, *Environ. Sci. Technol.*, 2007, **41**, 6711–6717.
168 T. H. Nguyen, K.-U. Goss and W. P. Ball, Polyparameter linear free energy relationships for estimating the equilibrium partition of organic compounds between water and the natural organic matter in soils and sediments, *Environ. Sci. Technol.*, 2005, **39**, 913–924.
169 S. Endo and K.-U. Goss, Serum albumin binding of structurally diverse neutral organic compounds: data and models, *Chem. Res. Toxicol.*, 2011, **24**, 2293–2301.
170 S. Endo, J. Bauerfeind and K.-U. Goss, Partitioning of neutral organic compounds to structural proteins, *Environ. Sci. Technol.*, 2012, **46**, 12697–12703.
171 H. P. H. Arp, R. P. Schwarzenbach and K.-U. Goss, Ambient gas/particle partitioning. 2: the influence of particle source and temperature on sorption to dry terrestrial aerosols, *Environ. Sci. Technol.*, 2008, **42**, 5951–5957.
172 S. Endo, S. E. Hale, K.-U. Goss and H. P. H. Arp, Equilibrium partition coefficients of diverse polar and nonpolar organic compounds to polyoxymethylene (POM) passive sampling devices, *Environ. Sci. Technol.*, 2011, **45**, 10124–10132.
173 L. Sprunger, A. Proctor, W. E. Acree and M. H. Abraham, Characterization of the sorption of gaseous and organic solutes onto polydimethyl siloxane solid-phase microextraction surfaces using the Abraham model, *J. Chromatogr. A*, 2007, **1175**, 162–173.
174 T. N. Brown, QSPRs for predicting equilibrium partitioning in solvent–air systems from the chemical structures of solutes and solvents, *J. Solution Chem.*, 2022, 1101–1132.
175 S. Endo and K.-U. Goss, Predicting partition coefficients of polyfluorinated and organosilicon compounds using polyparameter linear free energy relationships (PP-LFERs), *Environ. Sci. Technol.*, 2014, **48**, 2776–2784.
176 A. Stenzel, K.-U. Goss and S. Endo, Prediction of partition coefficients for complex environmental contaminants: Validation of COSMOtherm, ABSOLV, and SPARC, *Environ. Toxicol. Chem.*, 2014, **33**, 1537–1543.
177 T. N. Brown, *IFSQSAR – A Python Package for Applying QSARs*, 1.0.1, https://github.com/tnbrowncontam/ifsqsar.
178 I. Kamprad and K.-U. Goss, Systematic investigation of the sorption properties of polyurethane foams for organic vapors, *Anal. Chem.*, 2007, **79**, 4222–4227.
179 S. Endo and K.-U. Goss, Applications of polyparameter linear free energy relationships in environmental chemistry, *Environ. Sci. Technol.*, 2014, **48**, 12477–12491.
180 C. Mintz, K. Burton, T. Ladlie, M. Clark, W. E. Acree and M. H. Abraham, Enthalpy of solvation correlations for gaseous solutes dissolved in dibutyl ether and ethyl acetate, *Thermochim. Acta*, 2008, **470**, 67–76.
181 F. Wania, Assessing the Potential of Persistent Organic Chemicals for Long-Range Transport and Accumulation in Polar Regions, *Environ. Sci. Technol.*, 2003, **37**, 1344–1351.
182 F. Wania, Y. D. Lei, C. Wang, J. P. D. Abbatt and K.-U. Goss, Using the chemical equilibrium partitioning space to explore factors influencing the phase distribution of compounds involved in secondary organic aerosol formation, *Atmos. Chem. Phys.*, 2015, **15**, 3395–3412.
183 F. Wong and F. Wania, Visualising the equilibrium distribution and mobility of organic contaminants in soil using the chemical partitioning space, *J. Environ. Monit.*, 2011, **13**, 1569–1578.
184 F. Wania and J. N. Westgate, On the Mechanism of Mountain Cold-Trapping of Organic Chemicals, *Environ. Sci. Technol.*, 2008, **42**, 9092–9098.
185 F. Wania and M. S. McLachlan, Estimating the Influence of Forests on the Overall Fate of Semivolatile Organic Compounds Using a Multimedia Fate Model, *Environ. Sci. Technol.*, 2001, **35**, 582–590.
186 X. Zhang, J. A. Arnot and F. Wania, Model for Screening-Level Assessment of Near-Field Human Exposure to Neutral Organic Chemicals Released Indoors, *Environ. Sci. Technol.*, 2014, **48**, 12312–12319.
187 European Chemicals Agency, *Guidance on Information Requirements and Chemical Safety Assessment Chapter R.7c: Endpoint Specific Guidance.*, 2017.
188 G. Czub, F. Wania and M. S. McLachlan, Combining long-range transport and bioaccumulation considerations to identify potential arctic contaminants, *Environ. Sci. Technol.*, 2008, **42**, 3704–3709.

