Methods of Determining Retardation Coefficients of Organic Compounds in Aquifers

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Abstract: Sorption is an important mechanism that affects the mobility of organic compounds in the subsurface environment. Sorbed compounds move slower than that of groundwater, causing retardation in their movement. Accurate determination of retardation coefficients (*R*) of organic compounds in aquifers is critical for understanding their movement, fate, and remediation. Several methods, including predictive tools, laboratory experiments, and field experiments have been utilized for determining sorption-related retardation. The objective of this paper was to review and compare between the different methods used for the determination of *R* of organic compounds, with emphasis on predictive- and laboratory-based approaches. Predictive tools are based on the use of quantitative structure-activity relationships (QSARs). Laboratory methods utilize different types of reactors including batch, stirred-flow, circulation-through-column, or miscible displacement through packed columns. In addition, data from the column method have been analyzed in various ways to determine *R*. Discrepancies between results from different methods or from different analysis approaches have been reported. This create uncertainty about the suitability of some of these methods or the used analysis approaches. This paper highlights the possible causes for the observed discrepancy and establishes the limitations and appropriateness of the used methods and analysis approaches.

Keywords: Batch method, Column method, Retardation factor, Sorption, Organic compounds, Sorption equilibrium coefficient, Groundwater contamination.

1. INTRODUCTION

Groundwater accounts for approximately 35% of all water withdrawals by humans. Thus, protecting groundwater resources from anthropogenic contamination is important especially in areas with limited surface water resources, such as arid and semi-arid countries. This has been emphasized by the World Health Organization [1] as well. However, contaminants such as synthetic organic compounds are still being released into the subsurface water. The fate of organic contaminants in the subsurface environment has received a lot of attention in the last four decades due to their impact on human health [2, 3].

Organic compounds could be ionic or nonionic, aromatic or aliphatic. Owing to the presence of these compounds in groundwater and their potential to reach underlying aquifers, several studies focused on their movement and methods of treatment. Attention was given, for example, to chlorinated organic compounds [4, 5], aromatic hydrocarbons [6, 7], polynuclear aromatic hydrocarbons [8], polychlorinated biphenyls [9], and pesticides [10]. In recent years, studies have started covering emerging compounds such as pharmaceuticals, hormones, and personal care products [11-14]. These contaminants are released in the subsurface water through different sources. The highest reported pollution source in the United States is underground storage tanks [15]. Other sources include leakage from oil pipelines [16], sewage pipelines [17], septic systems [4, 18], leaching from landfills [19, 20], irrigated lands [21], and livestock farming [22].

The mobility of dissolved organic compounds in aquifers could be influenced by several transfer and transform mechanisms. These compounds move within groundwater through advection; a process that depends on the hydraulic conductivity and the hydraulic gradient of the aquifer. These compounds also disperse during their transport due to molecular diffusion and mechanical dispersion. The sum of molecular diffusion and mechanical dispersion is termed as hydrodynamic dispersion. Advection and dispersion are transfer mechanisms that affect both conservative and nonconservative compounds. Additionally, organic compounds could be influenced by reactive transfer mechanisms or could be subject to transformation. Transform mechanisms cause degradation of the compound either through a chemical reaction (hydrolysis, oxidation-reduction, or complexation) or through biological processes. Reactive transfer mechanisms, however, do not alter the structure of the compound, but affect its mobility in the liquid phase by reducing its speed relative to that of groundwater, causing compound retardation.

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An understanding of the role of the retardation processes (as well as other transport mechanisms) of organic compounds is needed to make a proper assessment of their mobility, potential contamination of drinking-water supplies, and the effectiveness of remediation schemes. Thus, there has been an increase in studies in this field with the aim to manage, remediate, and prevent aquifer contamination. This increase in the number of research studies has also been influenced by the recent significant improvements in analytical capabilities, allowing quantification of many organic compounds at very low levels [23, 24].

The extent to which organic compounds are retarded during their movement in aquifers depends on their affinity to interact with the aquifer material. Sorption is an important mechanism that affects the mobility of these compounds in the subsurface environment. Different methods have been used for the determination of the retardation coefficients (R) of sorbed organic compounds. However, discrepancy between the results of these methods raises a question on their compatibility. The objective of this study was to review the various methods of determining sorption-related retardation of organic compounds, compare the results of these methods, and establish their suitability and limitations. Before reviewing the different methods used, a brief description of the factors that affect sorption of organic compounds is presented in Section 2 and a brief review of the conditions of nonideal sorption behavior is presented in Section 3.

2. SORPTION OF ORGANIC COMPOUNDS

Sorption involves the attachment of compounds to a solid material. When the concentration in the liquid phase is higher than the equilibrium liquid concentration, compounds move from the liquid to the solid material. When the concentration in the liquid phase is lower than that of the equilibrium liquid concentration, compounds attached to the solid material are released into the solution (a process called desorption). The attachment of the compounds could be limited to the solid surface (adsorption) or within the solid matrix as well (absorption). Sorption does not only retard the mobility of organic compounds, but also affects contaminant volatility, bioavailability, phytotoxicity, and chemical/microbial transformations [25].

The mechanisms of sorption of organic contaminants to aquifer materials are complicated. The nature of the sorption interaction could be physical, chemical, or electrostatic [26]. Physical sorption is a result of interactions between the dipole moments of the compound and the solid matrix. Chemical sorption interactions occur due to covalent and hydrogen bonding, while electrostatic sorption interactions involve ion-ion and ion-dipole forces. Several factors have been identified that affect the extent of sorption of organic compounds to aquifer materials [27]. These factors could be related to the chemical/physical properties of the compounds, the characteristics of the solution, and the properties of the aquifer material.

Soil organic matter plays a major role in the sorption of organic compounds [28-31]. The composition and structure of soil organic matter also affect the extent of sorption [32, 33]. Recently, hard-carbon components of soil organic matter, such as black carbon and kerogen, have received attention due to their high sorption capacities to organic pollutants [34,35]. The sorption equilibrium coefficient (K) of organic compounds between the solid and the liquid phase has been related to the organic carbon distribution coefficient (K_{oc}) and the fraction of soil organic carbon (f_{oc}):

$$K = K_{oc} f_{oc} \tag{1}$$

For soil material low in organic carbon (<0.1%), the contribution of minerals to sorption has been found to be significant. In reviewing sorption of organic pollutants in aquatic systems, Karickhoff [29] proposed a multiple sorptive model in which sorption onto mineral surfaces and partitioning into soil organic matter contribute to the sorption of organic compounds. Mineral contribution to sorption tends to occur with high sorbate polarity or low organic carbon content of the sorbate [29].

Clay minerals were also found to affect the sorption of organic compounds through the formation of hydrogen bonds [25]. The extent of the contribution of clay minerals to sorption depends on the ratio of clay mineral to f_{oc} as well as the nature of the organic compound [36]. Other factors that affect sorption of organic compounds are solvency [37-40] and temperature [41].

The above factors are applicable to both neutral, nonpolar organic compounds as well as ionic, polar compounds. However, sorption of polar, ionizable compounds is further influenced by pH, ionic strength, exchangeable cations, and the physicochemical nature of the compound [25]. While soil organic matter remains an important factor affecting sorption of these compounds, their K_{oc} values also depend on the solution pH and their dissociation constants (pK_a) [42-44]. Thus, the ionic and neutral forms of these compounds could have different values of K_{oc}.

3. NONIDEAL SORPTION BEHAVIOR

Ideal sorption behavior requires that sorption be linear, singular, and the sorption reactions be fast. Deviation from ideality could occur due to sorption nonlinearity, nonequilibrium interaction, sorption hysteresis, or combinations of these effects. Nonideal sorption behavior during transport of solutes in porous media has been reviewed by several researchers [26, 45-47]. Inability to accurately consider sorption nonideality could cause an improper description of transport behavior and errors in the estimation of R. The various causes of nonideal sorption behavior are described below.

3.1. SORPTION NONLINEARITY

Nonlinear sorption of organic compounds could play an important role in their transport [48-53]. Nonlinear sorption occurs due to the presence of various sorption energies associated with the sorbent material [54]. Evidence of nonlinear sorption of organic compounds to soil and aquifer material has been documented [54-64]. Generally, nonlinear sorption occurs at high concentration [65,66] and with soils low in organic carbon (f_{oc} < 0.1%) [67].

Some researchers tend to assume a linear sorption behavior based on a good fit of a linear model to the batch sorption isotherm data. In other cases, linear sorption is assumed when the use of a nonlinear model is not statistically justified [68]. Linear sorption is also assumed when a previously developed correlation is utilized to determine a sorption equilibrium coefficient (see Section 4.1). In certain cases, nonlinear sorption isotherms have been linearized to allow the use of a transport model that employs a linear sorption behavior [68,69]. The linear sorption equilibrium model takes the form:

$$S = KC \tag{2}$$

where C and S are the equilibrium liquid- and solid-phase concentration, respectively. If sorption equilibrium is described by a linear model, then R is estimated based on the K value along with the bulk density (ρ) and moisture content (θ) of the aquifer:

$$R = 1 + \frac{\rho K}{\theta} \tag{3}$$

Nonlinear sorption of organic compounds is commonly described using the Freundlich model [26,58,60–62]. Other models that have been used to describe nonlinear sorption include the Langmuir model, the Brunauer-Emmett-Teller (BET) model, and the Polanyi-Dubinin-Manes (PDM) model [70]. The Freundlich model takes the form:

$$S = K_f C^n \tag{4}$$

where K_f is the Freundlich coefficient and n is the Freundlich exponent. R is then expressed as:

$$R = 1 + \frac{\rho K_f n C^{n-1}}{\theta} \tag{5}$$

A comparison of the movement of contaminants under linear and nonlinear sorption behavior indicates that nonlinear sorption may have a significant effect on the shape and spatial distribution of a contaminant and may explain the occurrence of scaled, retarded, and non-symmetric plumes as well as the presence of back tails and sharp front ends [52, 71]. Maraqa [53] studied the impact of the assumption of linear sorption on R under different simulated experimental conditions. The author found that R of a nonlinearly sorbed solute is a function of the input concentration, the injection period and the pore-water velocity but is independent of the length-scale.

3.2. Sorption Hysteresis

Sorption hysteresis occurs when the equilibrium distribution coefficient on the sorption path is different than the value obtained from the desorption path. Sorption hysteresis has been reported in numerous studies [72-80].

One of the suggested explanations for sorption hysteresis is the possible existence of two types of sorption sites: resistant and reversible [81]. Compounds attached to the resistant fraction during the sorption process do not easily desorb at the early stages of desorption. Another offered explanation is the possibility that the soil undergoes a physical change during the sorption/desorption process that results in variations of the number of sites available for sorption. For example, the release of lipids from soil organic matter increases the soil sorption capacity [82], while the release of humins reduces the sorption capacity

[83]. Sander and Pignatello [80] suggested that the irreversible deformation of the soil organic matter by the sorbed compounds causes an irreversible sorption.

While some researchers argue that sorption hysteresis is a true process resulting from a nonsingular value of K [80], others argue that the process could be artificially caused by experimental artifacts or by inadequate description of other transfer or transform processes [45, 84-87].

3.3. Sorption Nonequilibrium

Nonequilibrium during transport of organic compounds in aquifers could be either physical- or sorption-related. Physical nonequilibrium is caused by slow diffusion between mobile and immobile water regions [88]. Physical nonequilibrium affects both conservative and non-conservative chemicals. On the other hand, sorption nonequilibrium is due to either slow chemical interaction or slow accessibility to sorption sites. True sorption equilibrium could take months to be achieved [46]. Nonequilibrium causes higher spreading (dispersion) of the contaminant plume and may result in an apparent reduced retardation.

The processes causing nonequilibrium sorption at a particle scale are complex [89]. A variety of processes may interact to give rise to the observed sorption rates [47]. Several models have been formulated to better understand sorption kinetics of organic compounds. Some models assume a single-rate mass transfer coefficient to describe sorption kinetics [26, 45, 46]. Among these models are the commonly used two-site equilibrium/kinetic models, in which the rate of sorption is modeled either as first-order or radial diffusion [77-79, 90-93]. Other recently developed and used models incorporate multiple kinetic compartments with different mass-transfer rates [89, 94-100]. Multirate models were developed based on the evidence that sorption rates decrease with the increase in the exposure time [85, 87, 95, 101-103]. Additional approaches that have been utilized to characterize solute transport with mass transfer limitations include the use of temporal moments [104-107], the use of continuous time random walk [108-111], and the use of fractional derivative [112-114].

4. DETERMINATION OF *R*

Methods for the determination of R of organic compounds are either based on the use of quantitative structure-activity relationships (QSARs) or on laboratory/field experiments. Laboratory experiments differ in the type of reactor used (*i.e.*, batch, continuous stirred flow, or packed column). For packed columns and field tests, miscible displacement experiments are conducted to obtain breakthrough data, which are then analyzed to find R. This section gives a brief description of the most commonly used methods for determination of R. These methods include the use of QSARs, the batch method, the circulation-through column method, and the column method. Other less commonly used methods have been presented elsewhere [25].

4.1. Use of QSARs

The extent of sorption of organic compounds to soil material is typically related to the organic carbon content of the soil and the compound hydrophobicity [66, 115]. As such, an organic carbon distribution coefficient (K_{oc}) has emerged as a universal parameter that represents the distribution of an organic compound between soil organic matter and aqueous solution. K_{oc} is related to K as per Eq. (1). Consequently, QSARs were developed to predict K_{oc} values. With this approach, K_{oc} can be correlated to compound properties such as the octanol-water partition coefficient (K_{ow}), aqueous solubility, molecular weight, molecular surface area, and the molecular connectivity index. Among these, the most generally appropriate relationship for estimating K_{oc} are based on K_{ow} or solubility and molecular connectivity indices [36]. A comprehensive review of the use of QSARs for predicting K_{oc} for organic chemicals has been provided by Doucette [36].

4.2. Batch Method

The batch method usually involves rate, isotherm, and control studies. One of the objectives of the rate study is to determine the equilibrium time. The rate study is typically conducted using a set of identical bottles that contain the same mass of soil material and the same volume of solution that contains the target compound. Bottles are shaken and then sampled to determine the aqueous phase concentration over time. The batch isotherm experiment is usually conducted over a range of initial concentrations of the target compound while keeping the soil-to-water ratio constant. The bottles are shaken for a period of time that is sufficient to reach equilibrium. Phase separation is usually done by centrifugation. Aqueous samples are then analyzed for the organic compound. The amount sorbed by the soil is usually determined by difference. Values of *S* and *C* at equilibrium are then plotted to determine the sorption behavior and sorption equilibrium parameters. The value of *R* is then determined using Eq. (3) or (5).

4.3. Circulation-through-Column Method

Circulation-through-column method is a closed system where a solution containing the target compound is allowed to circulate through a packed soil column until equilibrium is reached (Figure **1**). The system is thus similar to the column method in terms of soil-to-water ratio, particle spacing, and mixing level, but yet it is operated in a batch mode. As in the batch experiments, circulation-through-column experiments should include rate, isotherm, and control studies [116]. In the rate experiment, aqueous samples, with known volumes, are withdrawn from the attached bottle over the course of the experiment and analyzed for the target compound. In the isotherm experiment, a sample is withdrawn from the attached bottle after the equilibration time. A control experiment should also be conducted to assure that there is no sorption to the reactor material. In such an experiment, the solution containing the target compound is circulated through an originally empty column.

4.4. Column Method

Column experiments, commonly referred to as miscible displacement, are conducted on disturbed or undisturbed packed soil/aquifer material. Glass or stainless-steel are the most commonly used column materials. Details of the column experiment setup including column material, fittings, tubes, pumps, and column size have been presented by Banzhaf and Hebig [27]. The boundary conditions applied to the column setting may vary and include continuous injection of a solution that contains the target compound (step increase), injection of a solution for a limited duration (Dirac or square-wave pulse), or injection of a compound-free solution to an already contaminated column (step decrease or leaching experiment). Effluent samples are collected and analyzed for the target compound to generate a normalized breakthrough curve (BTC). Figure **2** shows a schematic diagram of normalized BTCs for the three types of column experiments. Generated BTCs are then utilized to determine *R*.

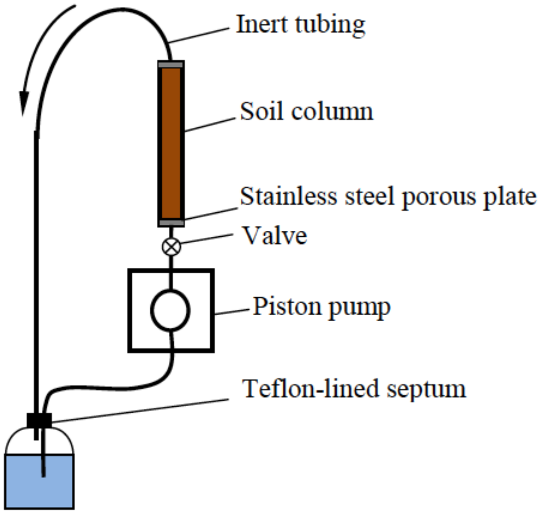

Figure 1: Schematic of a circulation-through-column experiment [116].

Though different estimation methods have been used to determine *R* from a column study, moment analysis and curve fitting have been the most widely used methods. In the moment analysis method, *R* is determined from breakthrough data using the normalized first temporal moment [107, 117]. Several researchers have used moment analysis for the determination of *R* [41, 68, 116, 118-123]. As for the curve fitting method, different models have been used to predict *R* by optimization including equilibrium models [124, 125], single-rate models [68, 77-79, 91, 126-131], and multirate models [90].

Other column methods that have been used to determine *R* include the area above the front limb of a normalized BTC [116, 132, 133], the area under the elution part of a step decrease experiment [134], the half-mass method [135], and the number of pore volumes at C/C_o=0.5 [132, 136, 137]. It should be noted that *R* determined by the area above the front limb of a normalized BTC is identical to that determined by moment analysis of a step increase [117]. Similarly, *R* determined by the area under the elution part is identical to that determined by moment analysis of a step decrease experiment.

5. DISCREPANCY AMONG DIFFERENT METHODS

Several studies have shown that experimentally-determined *R* values deviate from those predicted based on QSARs [120, 138-141]. Some researchers have attributed this deviation to the presence of mechanisms other than hydrophobic interactions that have not been accounted for in the QSARs [139-141].

The use of QSARs to estimate *R* has some limitations [36, 142]. Generally, the approach is acceptable for sorption of neutral hydrophobic compounds on soil with $f_{oc} > 0.1\%$. However, for soils with $f_{oc} < 0.1\%$ and high clay contents, or for highly polar, ionizable organic compounds, the contribution of soil minerals to the sorption process may dominate.

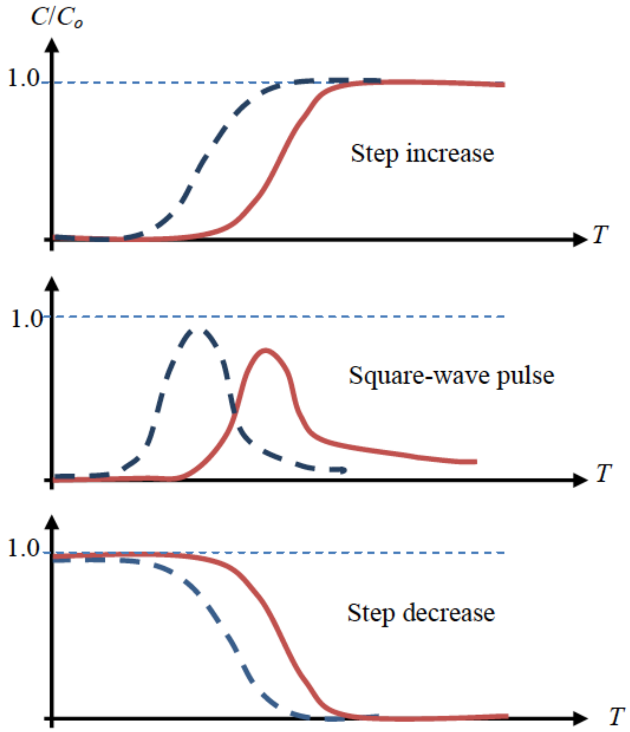

Figure 2: Schematic diagram of normalized BTCs (solid line) for step increase, pulse input, and step decrease experiments. The dotted line is for a conservative chemical. The y-axis represents normalized concentration (C/C_o) and the x-axis represents normalized time or the number of pore volumes (*T*).

While the QSAR approach is useful for obtaining approximate values for *R*, considerable variations in K_{oc} values have been observed for single compounds. Meanwhile, larger variations have been observed for polar, ionizable compounds as compared to those for nonpolar compounds [25]. These variations were attributed to differences in the sorption characteristics of soil organic matter, variations in the methods used to determine K_{oc}, the impact of other soil properties, and the properties of chemicals being sorbed [36]. Because of the possibility of high variations in the estimated K_{oc} value, some researchers suggested that QSARs should be used with extreme caution [143].

A majority of the experimentally-determined *R* values are based on the batch and one or more of the column methods. Results determined by both methods have been reported in several studies with few studies reporting similar results [44, 102, 123, 133, 144-146]. Other studies reported a discrepancy between the results of the two methods. In most cases, the batch-determined values were found to be higher than those determined by any of the column methods [41, 68, 91, 116, 118-121, 124, 125, 127-129, 132, 136, 137, 140, 145, 147-152]. The extent of deviation between the results of the two methods varies from slight/intermediate differences [68, 116, 128, 132, 147, 153] to very high differences that reached several orders of magnitude [41, 122]. In a few studies, *R* values based on the batch method were lower than those based on the column method [130, 154, 155].

In many of the studies that reported a discrepancy between the batch and column methods, the cause could not be clearly identified. However, several reasons have been suggested. Some of these reasons are related to fundamental differences between the batch and column methods including the level of mixing [156], particle spacing [147], and soil-to-water ratio [115, 122, 157, 158]. Other reasons that have been suggested are related to improper interpretation of transport behavior, including failure to account for sorption nonlinearity [159, 160], hysteresis [68, 72], nonequilibrium [68, 128, 137, 149, 161-163], and not accounting for some of the transfer or transform mechanisms [120]. Another set of causes that have been suggested are related to the possible existence of experimental artifacts including loss of sorbent from the column [164], analytical difficulties [117, 163], and unaccounted for immobile water regions in the column [165, 166].

Maraqa [167] fitted single-rate models to simulated breakthrough data using a transport model with multirate sorption kinetics. It was shown that *R* of a system with a multirate sorption behavior is under-predicted if the parameter value is determined by curve fitting a single-rate model. The author suggested that a major potential cause of the previously reported discrepancy between batch- and column-determined *R* could be due to the use of single-rate models for parameter prediction.

6. DISCUSSION

The different methods for determining *R* of organic compounds have their own advantages and limitations as summarized in Table **1**. However, discrepancies in the results obtained by these methods have caused uncertainties regarding the appropriate method to use.

Given the uncertainty associated with the use of the developed QSARs, their use should probably be limited to obtaining approximate values of *R*. In other words, conducting laboratory or field experiments becomes necessary for an accurate determination of *R*. It should be emphasized that experimental methods for the determination of *R* should produce the same estimate value if the value represents sorption equilibria. Otherwise, the value of *R* will be in error [168].

Processes, such as sorption nonlinearity or nonequilibrium, which result in asymmetrical BTCs render several methods unsuitable for determining *R* by the column method. These include the half-mass method, the number of pore volumes at C/C_o=0.5, and curve fitting a transport model that assumes equilibrium, linear sorption behavior.

An easy and simple way to obtain *R* is to conduct a batch isotherm study. Some researchers, however, questioned the ability to utilize results obtained from the batch method to describe transport in dynamic systems [169]. These doubts have mainly originated as a result of the previously reported discrepancy between the batch and column methods. However, such discrepancy could be due to an improper determination of *R* by the column method [167]. Thus, batch isotherm studies would still be useful for obtaining information about the sorption equilibrium behavior as long as they are conducted for a duration sufficient to reach equilibrium. Otherwise, batch-determined *R* would be underestimated.

A limitation of the batch method is that it could entail high uncertainty in the value of *R* of weakly sorbing compounds. For these compounds, the extent of sorption, with the practical limits of soil-to-water ratio employed in batch systems, could be lower than the desirable range needed to have an appreciable drop (20 to 50%) in the initial liquid concentration [170]. The problem will be further amplified if the compounds are subjected to mechanisms other than sorption to soil material [171]. In any case, other mechanisms should be eliminated or at least accounted for. Otherwise, sorption equilibrium parameters will be over-estimated if the parameter estimation is based on the difference in the initial and equilibrium liquid concentrations. Attention, therefore, should be given to possible volatilization, degradation, or sorption of the chemical to the bottle material. Control bottles should be employed to test sorption to bottle material, volatilization should be eliminated by avoiding headspace in the bottles, and biodegradation should be eliminated by using an appropriate and effective biocide.

Table 1: Advantages and Limitations of the Methods used for the Determination of *R* [1].

Method	Analysis approach	Advantages	Limitations
QSARs		• Does not require experimental work	• Provides approximate values for *R*, but deviations from the actual values could be high especially for ionic organic compounds
Batch		• Easy, simple, and relatively cheap	• Equilibrium must be achieved • High uncertainty for low sorbing compounds • Employs S/W ratio different than reality
CTC		• Suitable for low sorbing compounds • Employs S/W ratio similar to reality	• Harder and more expensive than the batch method • Requires multiple column runs at different initial input concentration to construct a sorption isotherm curve
Column	Moment	• Employs S/W ratio similar to reality • Not affected by sorption nonequilibrium	• Harder and more expensive than the batch method • Requires breakthrough data with no truncation • Requires multiple column runs at different initial input concentration to assess sorption behavior (linear versus nonlinear)
	Curve fitting	• Employs S/W ratio similar to reality	• Harder and more expensive than the batch method • Not suitable if the used model does not accurately describe the sorption behavior
	Others [2]	• Employs S/W ratio similar to reality	• Harder and more expensive than the batch method • Not suitable if nonlinear or nonequilibrium sorption exist

[1] S/W ratio means soli-to-water ratio. CTC means circulation-through-column.
[2] Other approaches include half mass and pore volume at C/C_o=0.5.

An alternative to the batch method is the circulation-through-column method. This method was found to be compatible with the batch method [116], but it is more difficult to conduct since it requires a separate column run to generate each data point on the sorption isotherm curve. To reduce the cost and time to generate a sorption isotherm curve using this method, one could employ several parallel columns injected with different low initial concentrations within the range of interest. Once the experiments are completed, the concentrations in the bottle are increased to a medium level and the solution is then recirculated until a new equilibrium value is reached. The process is then repeated to cover the high level of concentrations of interest. Losses to reactor material should be assessed by running a control column either empty or filled with an inert material. Meanwhile, biodegradation should be eliminated by using an appropriate biocide.

Another method to determine *R* is by using moment analysis of column BTCs. This method is not influenced by sorption kinetics [107], but it is usually constrained by tail truncation of BTCs due to either analytical limitations or premature termination of the experiment. Tail truncation may cause underestimation of *R* by moment analysis even when a good mass recovery is achieved [117, 167, 172-174]. Young and Ball [117] simulated data truncation for a wide range of experimental and boundary conditions, assuming a single rate nonequilibrium process. The authors provided guidance toward the experimental designs that are needed to keep the estimation error of *R* within specific bounds. Maraqa [167] demonstrated that, for a system undergoing heterogeneous sorption kinetics, the value of *R* obtained by moment analysis could be under-estimated even if the recovered mass obtained from the area underneath the BTC is almost complete. The author indicated that collection of sufficient data on the tail side of the BTC could be constrained by time and analytical capabilities. Similar to the circulation-through-column experiments, losses in the column experiments should be eliminated or properly accounted for.

R could also be estimated by fitting a transport model to the generated BTCs. In this case, the model being used should closely represent the processes affecting solute mobility. Since curve fitting is based on minimizing the sum of squares residuals, the goodness of fit does not necessarily mean accurate parameter values. In other words, the goodness of fit cannot be used to confirm an assumed mechanism. Ngo *et al.* [175] noted that the optimization results of curve fitting could lead to high uncertainty in the fitted parameter values. Thus, it is advisable that the number of optimized parameters is minimized either by determining some parameters independently or by isolating mechanisms in different column settings. For example, dispersivity is typically determined using an ideal tracer concurrently injected with the organic compound. Biodegradation parameters could be isolated by using a biocide. Retardation itself could be determined by moment analysis or by independent batch or circulation-through-column methods.

In case the transport model does not closely resemble actual conditions, optimized parameters could be inaccurately determined by curve fitting. In some cases, the optimized parameters may show dependency on the applied experimental conditions. In other cases, inadequate description of a process could cause an effect on the fitted parameters of other processes. Maraqa [53], for example, cautioned that the assumption of linear sorption for nonlinearly sorbed chemicals under equilibrium conditions could in some cases erroneously be interpreted as evidence of the presence of nonequilibrium. It is, therefore, necessary that the used transport model is proven robust by testing the sensitivity of fitted parameter values to changes in system conditions [176].

7. CONCLUSION

Several methods have been used for the determination of sorption-related retardation of organic compounds. However, discrepancies between the results of these methods have caused uncertainties regarding their appropriateness. Though the cause of discrepancy in many cases remained unclear, identification of the cause is important to assure the reliability of the data obtained by these methods. The QSAR approach is useful for obtaining approximate values for *R* but should be used with caution as the true value of *R* could, in some cases, deviate significantly from the predicted ones. The batch method is an easy and simple method to obtain a true value of *R* as long as equilibrium is reached, but the method could entail high uncertainty for low sorbing compounds. The circulation-through-column method is more difficult to conduct but could be used as an alternative to the batch method. *R* could be determined by moment analysis of generated breakthrough data from laboratory columns but the method requires complete mass recovery with good analytical capabilities to detect low concertation on the tail side of the BTCs. The use of curve fitting a transport model to column BTCs is not a preferred option but could be used if the transport model is proven robust. Otherwise, inadequacy of the used model in properly accounting for the transport mechanisms may produce errors in predicted *R* and other optimized parameters to achieve a good fit.

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