Chapter 2

Fundamentals of SPMDs

2.1. SPMD DESCRIPTION AND RATIONALE

From the discussions thus far, the reader can infer that SPMDs are designed to mimic the passive diffusional and partitioning steps of bioconcentration while providing semi-quantitative to quantitative estimates of hydrophobic organic chemicals (HOC) concentrations in the ambient exposure medium. SPMDs (see Figure 1.1) generally consist of a thin film of the neutral triglyceride triolein (1,2,3-tri-[*cis*-9-octadecenoyl] glycerol) sealed in a layflat, thin-walled tube of low-density polyethylene (LDPE). Although fish lipid (Huckins et al., 1990a) and silicone fluids (Petty and Orazio, 1996) have been successfully used as SPMD liquid phases, triolein was chosen as the standard for use in SPMDs for the following reasons: 1) it is a major storage lipid found in most organisms; 2) its high-molecular weight (885.5 Daltons) results in extremely low LDPE membrane permeability, even during dialytic recovery of analytes; 3) triolein is commercially available in synthetic, high purity forms; 4) triolein-water partition coefficients and octanol-water partition coefficients (K_{ow}s) are similar in magnitude and are well correlated (Chiou, 1985); 5) it is a liquid down to about -4 °C; and 6) it provides a convenient reservoir for performance reference compounds (PRCs; for information on PRCs see Section 3.3.). Nonpolar liquid phases such as triolein have very low interfacial tension with LDPE, which enables the formation of a thin film with intimate membrane contact. Because solute diffusivity is 10^2 to 10^3 greater in liquids than in solids, the use of a liquid phase ensures rapid mixing of accumulated residues. In contrast, solid phase sorbents in LDPE and other nonporous hydrophobic polymer bags or enclosures are difficult to configure with

relatively high surface-area-to-sorbent-volume (AV^{-1}) ratios, and solutes in the membrane generally must vaporize to make contact with the sorbent. This step adds another potential barrier to the mass transfer or uptake of analytes.

As indicated earlier, the selection of nonporous LDPE layflat tubing for SPMDs was based on it's stability in organic solvents (required for dialysis and membrane cleaning), the low diffusion rates of triolein relative to HOCs in LDPE (both uptake and dialytic recovery processes), and it's resistance to abrasion and puncturing. The results of this research also enabled the development of polymeric film (LDPE) dialysis in organic solvent, which has been shown to be a highly effective method for separating organic contaminants from lipids (Huckins et al., 1990b; Meadows et al., 1993; Bergqvist et al., 1998). Thin-walled layflat LDPE is widely available and, because it is a thermoplastic, the lipid phase can be sealed inside the membrane tube using molecular welding (heat seals).

Although SPMDs are simple in design, the mechanisms governing their performance as passive samplers of HOCs can be quite complex (see Chapter 3). The underlying principle of molecular-size discrimination in the uptake and loss of chemicals by SPMDs is shown in Figure 2.1. The sizes of the molecules shown in the illustration are scaled to the postulated ≈10 Å diameter of the transient pores in the membrane. Temperature and the presence of plasticizers/solvent will affect the effective pore sizes.

In nonporous polymers such as LDPE, free volume is formed by random thermal motion of polymer chains in rubbery regions of the matrix (LDPE is about 50% crystalline and 50% rubbery). The volume associated with "fixed pores," which exist only in the crystalline regions of the polymer, is largely insignificant (Rogers, 1985) relative to the volume associated with the rubbery regions of the polymer. Thus, the passive sampling of dissolved and vapor phase analytes involves the dissolution of individual molecules into the rubbery regions of the polymer. The diameters of the transient polymeric cavities range up to ≈10 Å (Comyn, 1985), which precludes sampling of the waterborne residues associated with particulate organic carbon or dissolved organic carbon such as humic acids. The frequency of cavity formation is largely controlled by temperature-dependent chain segmental motility. Also, it is noteworthy that the postulated size of transient cavities in biomembranes is 9.8 Å (Opperhuizen et al., 1985). The molecular size limitation of nonporous polymers suggests that only readily bioavailable or dissolved chemicals (molecular weights <600 Daltons) will be sampled by SPMDs, which has been corroborated by the work of Ellis et al. (1995). This size exclusion characteristic of nonporous polymers is the reason for extremely low diffusion rates of triolein in LDPE (i.e., losses from SPMDs).

Ions of organic and inorganic chemicals are not sampled by SPMDs because charged species are hydrophilic and are essentially insoluble in nonpolar LDPE. Water quality variables, such as pH and salinity (Huckins et al., 1999), may affect the dissolved concentrations of some compounds in environmental waters (e.g., the residue concentrations of organic compounds with pK_as > 4 and < 9).

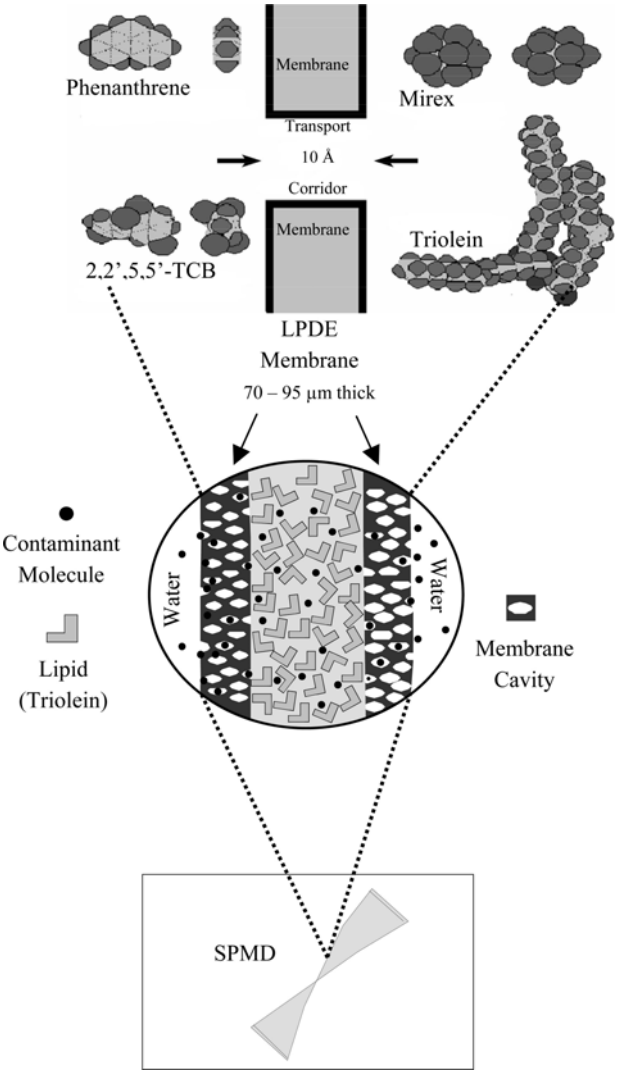

FIGURE 2.1 Exploded views showing the nonporous membrane size-exclusion phenomenon in the uptake and loss of organic compounds. Middle illustration shows the movement of contaminant molecules through transient pores in the membrane and retention (membrane exclusion) of much larger lipid molecules. Upper illustration shows similarly scaled space-filled molecular models of some organic contaminants and triolein, along with the hypothetical polymer pore (transient) size. Reprinted with permission from the American Petroleum Institute (Huckins et al., 2002).

Conceptually, SPMD data fills a gap between exposure assessments based on direct analytical measurement of total residues in water and air, and the analysis of residues present in biomonitoring organisms. SPMDs provide a biomimetic approach (i.e., processes in simple media that mimic more complex biological processes) for determining ambient HOC concentrations, sources, and gradients. Residues accumulated in SPMDs are representative of their environmental bioavailability (see Section 1.1.) in water and air and the encounter-volume rate as defined by Landrum et al. (1994) is expected to be proportional to the uptake rate. SPMD-based estimates of water concentrations can be readily compared to aquatic toxicity data (generally based on dissolved phase concentrations) and SPMD extracts can be used to screen for toxic concentrations of HOCs using bioassays or biomarker tests.

2.2. APPLICABILITY OF SPMDs

Although SPMDs concentrate a very wide range of hydrophobic organic compounds, they are not suitable for all environmental contaminants. Table 2.1 lists chemicals classes or selected compounds shown to concentrate in SPMDs, but is not all inclusive.

Examination of Table 2.1 shows that SPMDs are not suitable for sampling very large organic molecules, ionized organic compounds, and metals. For compounds such as chlorinated phenols with different pK_as, the environmental pH determines the ratio of ionized to neutral species, which directly impacts the capacity of an SPMD to concentrate the chemical. Thus, the selectivity of SPMD sampling is limited to size exclusion properties of the low density polyethylene membrane (see Figure 2.1) and the polarity/ionization potential of the analyte. Hydrophobic or nonpolar compounds are characterized by a lack of polar functional groups and a very low potential for ionization at environmental pHs (i.e., a range of about 4.5 to 9). SPMDs will significantly concentrate ambient levels of nearly all

Table 2.1 Classes or Specific Chemicals Known to Concentrate in SPMDs

priority pollutant PAHs and alkylated PAHs	chlorinated dibenzodioxins, including 2,3,7,8-TCDD
many heterocyclic aromatics, cyclic hydrocarbons (e.g., decalin and alkylated decalins) and aliphatics	polybrominated diphenyl ethers
organochlorine pesticides	chlorinated benzenes
other pesticides: includes diazinon, endosulfans, pyrethroids, toxaphene, and trifluralin	chlorinated anisoles and veratroles
PCB congeners	alkyl phenols (nonyl phenol)
chlorinated naphthalenes	triclosan
chlorinated dibenzofurans, including 2,3,7,8-TCDF	tributyl tin
	sulfur
	essentially, any compound with log $K_{ow} \geq 3.0$[a]

[a] See Table 8.1 for additions to this list.

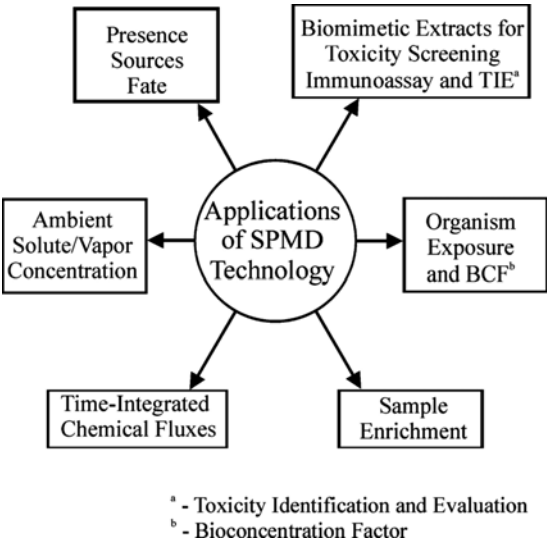

FIGURE 2.2 Various applications of SPMDs reported in the literature.

hydrophobic compounds with log K_{ow}s ≥ 3 and the sampling rates (R_ss) of most HOCs are controlled by the "encounter volume", as defined for aquatic organisms in Chapter 1. Water quality variables, such as salinity (Brown, 1978), can affect the dissolved concentrations of hydrophobic compounds in environmental waters, and thus the amounts of residues accumulated by an SPMD. However, water quality should have no effect on sampling rate constants (see Section 2.3.).

For compounds with log K_{ow}s < 3, SPMDs may not perform as well as other sampling procedures such as purge and trap methods for volatile organic compounds and the polar organic chemical integrative sampler (POCIS) for hydrophilic organic compounds (Alvarez et al., 2004). Also, for compounds with log K_{ow}s and octanol-air partition coefficients (K_{oa}s) larger than about 7.5 and 10.5, respectively, only vanishingly small amounts will be available for uptake, because of sorption to particulates and dissolved organic carbon. However, SPMDs have been successfully used for determining chemicals with very high K_{ow}s and K_{oa}s in environmental systems (McCarthy and Gale, 2001; Booij et al., 2002; Bartkow et al., 2004) but may require the use of composite SPMD samples (e.g., three to nine 1-mL triolein SPMDs).

Figure 2.2 illustrates a number of potential SPMD applications. More specifically, SPMD technology has been used for the following: 1) determination of the presence, sources, and the transport/fate of hydrophobic semi-volatile organic pollutants; 2) estimation of ambient time-weighted average (TWA) dissolved or vapor phase chemical concentrations; 3) determination of time-integrated fluxes of dissolved and vapor phase chemicals in environmental media; 4) *in situ* biomimetic sample extracts of readily available chemicals for toxicity screening (bioassays or

biomarkers), immunoassay, and toxicity identification evaluation; 5) estimation of organism exposure and bioconcentration factors (*BCF*s) for dissolved and vapor phase compounds; and 6) polymeric membrane organic solvent dialysis for enriching a wide variety of hydrophobic analytes in environmental sample extracts. Some of these applications and example studies are covered in subsequent Chapters. Herein, we briefly discuss some general considerations associated with SPMD applications.

Before choosing SPMDs for a project, data quality requirements must be considered. Two extreme levels are litigation quality data (i.e., legally admissible) and screening data (note that rigorous quality control can be applied to screening tests). The SPMD approach can be readily used in screening projects, such as the presence/absence, sources, and relative amounts of chemicals (ranking) measured in SPMDs at different sites, to more in-depth studies designed to estimate the ambient concentrations of chemicals. For projects in the USA requiring litigation quality data, study results are typically generated by the US EPA or industry standard methods in conjunction with a formal set of quality assurance (QA) and quality control (QC) guidelines/parameters. Particular attention must be made to security issues (QA) such as sample chain of custody. Because US EPA and industry standard methods are often more than a decade behind the best available technology, there has been increased use of more current, but well-established, nonstandard methods (so-called "performance based methods") in litigation.

The SPMD approach is widely used by environmental investigators and is beginning to gain acceptance from regulatory and resource management agencies (e.g., certain EPA regions and states, the United Kingdom, and the Czech Republic). However, the authors are not aware of any studies conducted with protocols adequate for litigation. The SPMD studies presented herein may meet the criteria based on QC parameters but typically fail to meet the QA requirements for litigation, such as chain of custody documentation. However, as *a priori* acceptance of SPMD technology becomes more widespread, and studies are conducted with more stringent QA standards, the likelihood of the successful incorporation of SPMD data in litigation will increase.

Other issues of SPMD applicability relate to the type of matrix sampled. In particular, the ability to extrapolate ambient concentrations from analyte concentrations in SPMDs differs significantly depending on the matrix sampled and the variables affecting analyte concentrations in the matrix. An assumption, fundamental to the use of mathematical models for concentration extrapolations, is that the sampling process does not significantly alter ambient solute or vapor concentrations of analytes. Theory and studies to date show that this assumption is not violated when sampling surface waters and the atmosphere. However, some exceptions may occur when sampling sediments, groundwater and small, enclosed indoor spaces. To maintain pore water concentration during sampling, solute resupply via desorption from particulate and dissolved organic carbon phases of sediment must be faster than the sampler uptake rates. In the only test of this assumption in the literature, Booij et al. (2003) used LDPE strip samplers in sediments (collected

from two marine harbors) and found that pore water concentration estimates, based on linear uptake rates and PRC loss rates, corresponded well to those based on sediment-pore water equilibrium partition coefficients. These data suggest that chemical resupply of the pore water was rapid enough to offset sampler uptake or clearance rates. Because SPMDs and LDPE strips with similar surface areas sample at essentially the same rate during linear uptake, this finding likely applies to SPMDs as well (see Chapter 3 for more details).

Monitoring wells in fine grained strata often have low coefficients of permeability or recharge rates or hydraulic conductivities (see Chapter 3 for more details). In this case, SPMD sampling may significantly reduce well water concentrations of the chemicals of concern. However, knowledge of SPMD uptake rates for target compounds (see Appendix A), the groundwater hydraulic conductivity at the well site, the cross-sectional surface area of the well and the approximate volume of water in the well, should enable investigators to determine if water concentration will be significantly reduced during sampling. If so, the size (i.e., surface area) or numbers of SPMDs used in a well can be reduced as long as acceptable detection and quantitation limits can be achieved. When very low quantitation limits are required and the well's hydraulic conductivity is low, it may be possible to increase the numbers or the surface area of the SPMDs used to ensure that the extraction efficiency of target compounds from well water (dissolved phase) is $>90\%$ during an exposure period. Thus, depending on the nature of the well, SPMD sampling may deplete, moderately affect or have little effect on groundwater concentrations of target solutes.

SPMDs are biomimetic only when partitioning-diffusion processes mediate bioconcentration. The appropriateness of using SPMD data to predict equilibrium concentrations of bioconcentratable contaminants in aquatic organisms is dependent on a number of factors, as discussed in Chapter 7 and by Huckins et al. (2004). Briefly, SPMDs and other passive samplers cannot account for physiological and behavioral differences among species such as residue metabolism, dietary uptake and trophic transfer, which can cause residue concentrations in tissues to vary considerably from equilibrium partition levels (Connell, 1990; Huckins et al., 2004). Also, unlike many aquatic invertebrates, shellfish and finfish, SPMDs generally do not reach equilibrium with hydrophobic chemicals (i.e., for compounds with log K_{ow}s >5) during exposures of 42 d or less. Thus, direct comparisons of SPMD-water partition coefficients (K_{sw}s) and *BCF*s often are not feasible. However, SPMDs provide reasonably accurate estimates of *in situ* TWA concentrations of dissolved-phase chemical concentration. Use of SPMD-derived water concentrations and biomonitoring organism (BMO) tissue concentrations may enable the development of improved regression models for estimating HOC *BCF*s. This statement is based on the assumption that some of the scatter in *BCF*s derived from existing regression models relates to the inability of previous investigators to determine TWA concentrations of bioavailable residues in exposure waters. Regardless of the difficulties in directly relating SPMD concentrations to *BCF*s, SPMDs provide reasonable estimates of aquatic organism exposure to

persistent HOCs (e.g., Meadows et al., 1998; Huckins et al., 2004), via the dissolved phase.

The case for using SPMDs as a biomimetic device for estimating TWA atmospheric exposure of HOCs to terrestrial organisms is less well developed. The possible exception to this statement is the exposure of humans to semi-volatile organic compounds (SVOCs) in indoor air. Determination of TWA values for volatile organic compounds using passive samplers is widely accepted as the method of choice for assessing occupational exposure. Because K_{oa}s are very large for hydrophobic SVOCs, sampling is generally integrative for months. Note that TWAs can only be determined by integrative passive samplers. Furthermore, the sampling rates and capacities of SPMDs for vapors of SVOCs are much higher than traditional passive samplers. This permits the isolation of sufficient target compound mass for bioassay and lower quantitation limits.

2.3. ACCUMULATION OF CHEMICALS BY SPMDs

Although "Theory and Modeling" is more extensively discussed in Chapter 3, it is helpful to briefly discuss some basic concepts related to the accumulation of chemicals by SPMDs. Huckins et al. (1993) have shown that the uptake process obeys first-order kinetics (Figure 2.3). This type of exchange kinetics is characterized by "half-lives" ($t_{1/2}$), which are constant for a particular set of conditions and

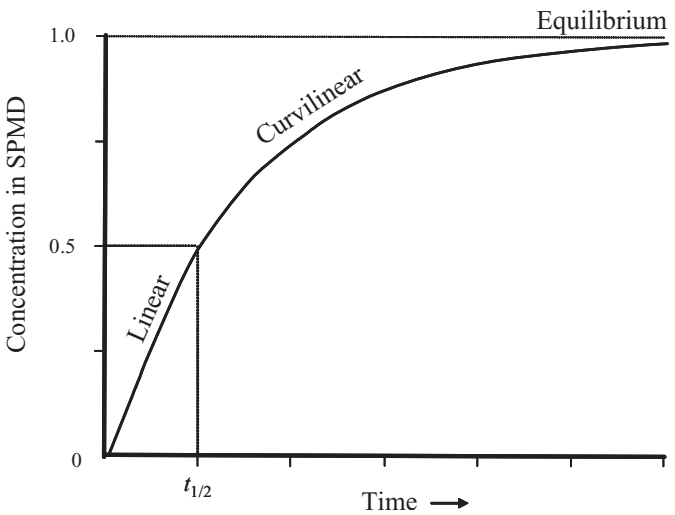

FIGURE 2.3 Plot of the three phases of SPMD uptake, illustrating first-order exchange kinetics. Time is given in halflives or $t_{1/2}$, which in this case is the time required to reach half of the equilibrium concentration of a chemical. This figure is reproduced courtesy of the American Petroleum Institute (Huckins et al., 2002).

chemicals, and "rate constants" that are independent of chemical concentration. In this case, the rate of change of the concentration in an SPMD (C_s) is given by

$$dC_s/dt = k_u C_w - k_e C_s \tag{2.1}$$

where k_u is the uptake rate constant, k_e is the elimination rate constant, C_w is the concentration in the water phase, and t is time. In the case of SPMD-air exchange, it is only necessary to replace the subscript "w" by "a". In the initial stages of the uptake, the term $k_e C_s$ is much smaller than $k_u C_w$ and Eq. 2.1 reduces to

$$dC_s/dt \approx k_u C_w \tag{2.2}$$

Equation 2.2 shows that C_s increases linearly with time when the aqueous concentration is constant. This is why the initial stage of the uptake process is called the "linear uptake phase" (Figure 2.3). Integrating Eq. 2.2 over time shows that sampling is "integrative", and that C_s is linearly proportional to the TWA concentration in the water phase ($C_{w,TWA}$)

$$C_s(t) = \int dC_s = k_u \int C_w \, dt \equiv k_u C_{w,TWA} t \tag{2.3}$$

When equilibrium is attained, the rate of uptake balances the rate of loss, and Eq. 2.1 reduces to

$$C_s = C_w k_u / k_e \tag{2.4}$$

This stage of the uptake process is therefore called the "equilibrium sampling phase".

The time it takes to reach 50% of the equilibrium concentration ($t_{1/2}$) is related to the elimination rate constant (k_e) by

$$t_{1/2} = \ln 2 / k_e \tag{2.5}$$

where ln 2 is the natural logarithm of 2. Figure 2.3 shows that analytes accumulated by an SPMD may be in the linear (integrative), curvilinear, or equilibrium partitioning phases of uptake, depending on the chemical sampled, environmental conditions, and the duration of the exposure. Also, Figure 2.3 shows that sampling is essentially integrative up to $t < t_{1/2}$. For $t > 4t_{1/2}$, equilibrium is essentially complete (>94%). Although the limits between the linear uptake phase, the curvilinear phase, and the equilibrium phase are somewhat arbitrary, these times can be used to get a feeling for the extent to which sampling is integrative.

Modeling SPMD residue exchange as two compartments (membrane and lipid) adds complexity (Huckins et al., 1993, 1999). A single compartment model can be applied to SPMD residue exchange when using K_{sw}, resistance is controlled by the boundary layer, and equilibrium exists between the membrane and lipid phases. The K_{sw} is the volume-averaged partition coefficient of the membrane and lipid phases and is given by Eq. 3.11. In simple one-compartment models (Figure 2.4), the concentration at any moment in time is determined by competing

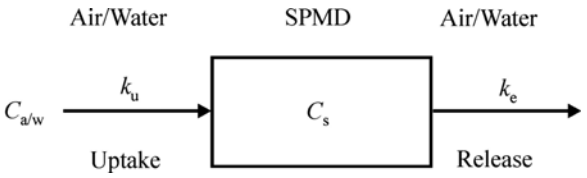

FIGURE 2.4 Single compartment model for the uptake and release of hydrophobic organic compounds. The a/w subscript refers to air or water.

rates of chemical uptake and release, as given in Eq. 2.1. This common modeling approach is widely used for estimates of the concentration of hydrophobic chemicals in the lipids of aquatic organisms.

2.4. PASSIVE SAMPLER FUNDAMENTALS AND TERMINOLOGY

Until the advent of SPMDs and solid phase microextraction (SPME) fibers, passive sampling devices were generally limited to integrative "diffusion" or "permeation" samplers (Fowler, 1982), with engineered barriers that control uptake rates. The engineered rate-limiting barriers of these classical samplers consist of a structural feature with stagnant air or water (diffusional samplers) or a nonporous polymeric membrane (permeation samplers). In both cases, these barriers are designed to account for >90% of the total resistance to solute or vapor uptake by the sampler. The advantage of using the engineered barrier approach is that changes in facial velocity and turbulence have little effect on sampling rates and thus can be neglected. Also, the diffusion samplers are relatively simple to calibrate because equations for calculating diffusion coefficients in air and water are well developed and the relevant diffusional pathway or length is fixed by design. The disadvantage of both of these engineered diffusion and permeation samplers is that their uptake fluxes (e.g., ng cm^{-2} d^{-1}) are generally more than an order of magnitude lower than the uptake rates of samplers under external boundary layer control such as SPMEs and SPMDs.

All passive monitoring devices operate on the basis of diffusive transfer, regardless of whether they are classified as diffusion, permeation or unclassified (e.g., SPMDs), and the rate-limiting barrier is the step with the greatest resistance to mass transfer (see Figure 3.1). Fick's first law is the fundamental law of diffusion. It states that the flux of a chemical in the x-direction (j_x, e.g., ng cm^{-2} d^{-1}) is proportional to the concentration gradient ($\partial C/\partial x$)

$$j_x = -D_i(\partial C/\partial x) = -D_i \Delta C/\delta_i \tag{2.6}$$

where D_i is the diffusion coefficient in the rate limiting barrier, δ_i is the effective thickness of the rate limiting barrier, and ΔC is the concentration difference across the barrier. Fick's first law appears to apply to diffusion of trace levels of HOCs through SPMD membranes and associated boundary layers. However,

the polymer permeability literature contains many references (e.g., Comyn, 1985) where membrane-diffusion coefficients are not constant, requiring the application of Fick's second law.

Unlike the aforementioned classical samplers, the barrier limiting chemical uptake by SPMDs is dependent on physicochemical properties of the target compound and the exposure conditions. For example, under conditions of low water flows and turbulence (i.e., <1 cm s^{-1}), the water boundary layer (WBL) is relatively thick and compounds with log K_{ow}s ≥ 4.5 are generally under WBL control and δ_w represents the effective thickness of the WBL. In this case, SPMDs act as diffusion samplers (Huckins et al., 1999). However, under the same conditions, compounds with log K_{ow}s < 4.5 are under membrane control (δ_m), and SPMDs act as permeation samplers. The reason for this bimodal rate control is that the magnitude of the membrane-water or membrane-air partition coefficient affects the resistance to mass transfer across the membrane (Eqs. 3.8 and 3.9). More specifically, high membrane-water partition coefficients effectively reduce resistance to mass transfer across the membrane. The transition point between membrane and boundary layer rate control varies (see Figure 7.2) depending on flow and turbulence conditions at the external surface of the membrane (i.e., thinning of the boundary layer reduces resistance to mass transfer). Because SPMD sampling rates are affected by environmental conditions, *in situ* sampling rates may vary greatly (see Section 3.6.) across sites. As mentioned in Chapter 1 and discussed in Chapter 3, PRCs were developed to provide a means of determining the effects of environmental exposure conditions on SPMD sampling rates.

Some introductory comments on the conceptual basis of SPMD uptake (k_u) and release (k_e) rate constants and the associated sampling rates (i.e., R_s) are in order. The k_u can be conceptualized as the volume of air or water cleared of chemical per unit sampler mass or volume per unit time (e.g., mL g^{-1} d^{-1} or mL mL^{-1} d^{-1}) and R_s is the volume of air or water cleared per unit time (e.g., L d^{-1}). Thus, the only difference between k_u and R_s is that R_s is not normalized to a unit mass or unit volume of sampler. In the context of organism exposure (see Section 1.1.), the SPMD k_u is equivalent to the "encounter volume" times the fractional bioavailability of the chemical (which excludes dietary uptake). The release rate constant (d^{-1}) is equal to $k_u K_{sw}^{-1}$.

Equation 1.1 gives the "clearance or sorption capacity" (E_v) of a thin polymeric film sampler for nonpolar organic compounds, which equals $V_s K_{sw}$ in the case of water sampling by SPMDs. E_v can be visualized as the volume of water cleared of a target compound, when an SPMD has attained equilibrium with the ambient environment. For moderate to high K_{ow} compounds, the E_v of an SPMD is generally not approached in most exposures, but E_v is often attained for relatively low K_{ow} compounds, exposed under similar conditions. In these cases, an investigator can estimate E_v volumes by using measured or estimated values of $K_{sw,}$ or by assuming that $K_{ow} \approx K_{sw}$. The E_v volumes thus derived can be used to compare to the volumes of air or water extracted by other methods, to determine if

analyte mass is sufficient for analytical determination or bioassay screening, and to evaluate the need for compositing SPMDs. For the case of air sampling, Cao (1991) has proposed that sorbents capable of clearing >0.1 m^3 g^{-1} (i.e., SPMD-air partition coefficient $[K_{sa}] \approx 10^5$) are suitable for the integrative sampling of organic vapors. In aquatic environments, the minimal value is equivalent to about 0.12 L g^{-1} (i.e., $K_{sw} \approx 120$). For most passive samplers, this $K_{s(a/w)}$ value is far too low to maintain linear uptake for periods greater than one week and the corresponding E_vs would be inadequate to accumulate sufficient residues for trace to ultra-trace analyses.

If the aim of a study is to estimate TWA concentrations, an integrative sampler must be used. In this case, the response time (t_r) provides useful information on sampler performance in environments where concentrations vary through time. Following a step change in ambient exposure concentration, t_r can be defined as the time required for the sampling flux ($R_s C_w$) of a passive monitoring device to largely adjust to the full concentration change in the ambient environment (Fowler, 1982). Values of t_r are representative of the average time an analyte spends within the rate-limiting barrier. If a linear concentration gradient is assumed across the rate-limiting barrier, then

$$t_r = \delta_i^2 / 2D_i \tag{2.7}$$

where t_r is the response time for both integrative and steady state samplers and subscripts were defined earlier. Other non-linear derivations of t_r using Fick's second law show that t_r is the time required to achieve approximately 63% increase (relative to full change induced) in the concentration of a chemical in the rate limiting zone or region due to a step change in ambient exposure concentration. Using Eq. 2.7, values of D in water for phenanthrene, benzo[*g,h,i*]perylene and decachlorobiphenyl (PCB congener 209) from Hofmans (1998), and an estimate of SPMD boundary layer thickness under low flow conditions (<1 cm s^{-1}) by Gale (1998), t_rs for these compounds were 131, 157 and 197 s, respectively. Note that the compounds used in this example are known to be under WBL control at low-flow rates. Under higher flow conditions, these response times would be expected to be reduced by at least 4-fold. Fowler (1982) has suggested that a t_r of a few minutes or less is satisfactory for most applications of passive samplers.

If the aim of an investigator is to determine equilibrium concentrations in samplers, then the "residence time" (t_m) is a logical parameter to compare among samplers. The t_m is the mean length of time that a molecule spends in a passive sampling device, where solute exchange follows first-order kinetics. Residence time is given by

$$t_m = 1/k_e \tag{2.8}$$

where t_m is about 1.5 $t_{1/2}$s. This parameter can be determined by curve fitting when analyte concentrations reach the curvilinear or equilibrium phases of exchange kinetics (Figure 2.3) or it can be calculated when the k_u and K_{sw} are known. Residence times of chemicals in an SPMD are much larger than response times.

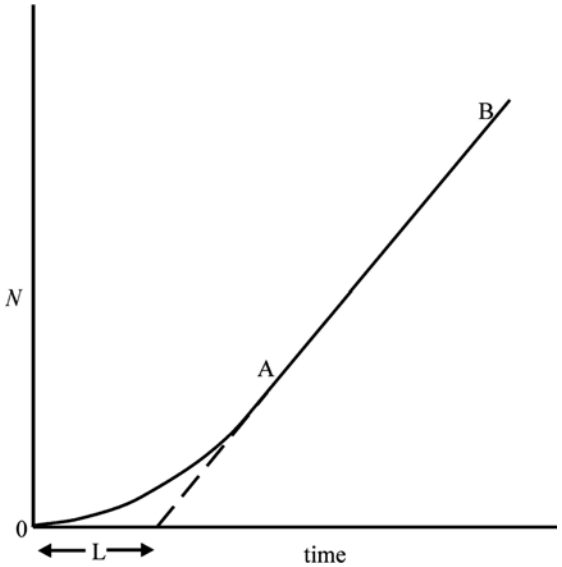

FIGURE 2.5 The amount of a chemical absorbed by a sampler through time, where the lag time (L) is the time represented by the x-intercept of the extension (dashed line) of the steady state line AB.

For example, under low flow conditions and at a temperature of 18 °C, the SPMD residence time for phenanthrene is 45.4 d and k_e values for benzo[*g,h,i*]perylene are too small to measure, which suggests a residence time of $>10^3$ d.

The lag time t_L is a closely related parameter to t_r but is generally used for diffusional processes under membrane control. This term is given by

$$t_L = \delta_i^2/6D_i \tag{2.9}$$

The meaning of this term is shown by Figure 2.5 and it is essentially the time required to attain steady state flux across a barrier. When the resistance in the boundary layer is negligible, the lag-time equation provides a convenient means of calculating membrane or polymer-diffusion coefficients.

2.5. REFERENCES

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