

## **Factors influencing biodegradation of synthetic organic chemicals in natural and engineered aquatic environments**

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**Abstract:** Synthetic organic chemicals (SOCs) are impacted by biodegradation, sorption, and volatilization in activated sludge wastewater treatment systems. However, when the bioreactor is completely mixed, the effluent concentration is determined by the kinetics of biodegradation. Volatilization and sorption affect only the capable biomass concentration, which is a fraction of the total biomass concentration. Consequently, biodegradation kinetics can be used to characterise quantitatively the biodegradability of SOC. This paper reviews the factors affecting biodegradation kinetics and methods by which they can be assessed. It also demonstrates how biodegradation kinetic parameters interact with the SOC concentration and the capable biomass concentration to determine the half-life of the SOC in aquatic environments.

### **INTRODUCTION**

There is increasing concern worldwide about the fate and effects of synthetic organic chemicals (SOCs) in the environment. This concern arises in part from the realization that some SOC are persistent and susceptible to transport over large distances, thereby subjecting organisms in diverse environments to their effects, whatever they may be. It also arises because so little is known about those potential effects, with only a small number of SOC having been subjected to toxicity testing. Since the job of testing all SOC for their effects would be enormous, a realistic approach is to focus on those SOC most likely to be persistent based on their chemical, physical, and biological properties. One part of this approach is to assess the potential environmental burden of specific SOC by examining the routes by which they may enter the environment.

One particularly important route for SOC into the environment is in effluents from wastewater treatment plants. Both industrial and municipal facilities routinely receive SOC; industrial facilities because of the manufacture and use of such chemicals in the activities of the industries they serve, and municipal facilities because of the use of SOC in the various aspects of our lives. Consequently, it is important for wastewater treatment engineers to be able to predict the fate of SOC in wastewater treatment facilities, both to properly design them and to evaluate their efficacy once they are built. The major tool used by engineers in this task is mathematical modelling, with appropriate terms for the various mechanisms acting to remove the SOC from the aqueous phase, either by destroying them or by transferring them to another phase.

The purpose of this paper is to examine the factors influencing biodegradation of SOC in activated sludge wastewater treatment systems, the most popular wastewater treatment system in use today, and in the water body receiving the effluent from the process. Although the major focus will be on biodegradation, some consideration will be given to sorption and volatilization to indicate their impacts on the assessment of biodegradation. In addition, consideration will only be given to SOC that enter the activated sludge system in the soluble state. Undissolved materials will become entrapped in the biomass, where they will undergo some degree of biodegradation, with the remainder being removed with the

waste solids. The ultimate fate of such materials will depend on the solids handling and disposal system, of which there are many variations and most of which involve ultimate disposal to the soil environment. Since biodegradation in soils is a major subject itself, no attempt will be made to cover it. Finally, to keep the topic manageable, consideration will only be given to chemicals that can serve as a carbon and energy source for microbial growth. Those interested in cometabolic biodegradation should consult the modelling work of Chang and Alvarez-Cohen (ref. 1), Criddle and co-worker (ref. 2,3), and Ely *et al.* (ref. 4).

### FATE OF SOCS IN ACTIVATED SLUDGE SYSTEMS

In its simplest form, an activated sludge system consists of a bioreactor and a final settler, with recycle of the biomass from the settler to the bioreactor. Provisions are made for oxygen transfer in the bioreactor, allowing growth of flocculent biomass through utilization of the organic compounds in the influent as their carbon and energy source, thereby mineralizing those compounds and removing them from the liquid phase. The flocculent nature of the biomass allows its removal in the final settler, providing an effluent that is low in both soluble and suspended organic matter. Because biomass is continually grown in the process, a portion of it must be wasted to maintain a steady-state concentration. This allows control of both the biomass concentration and the solids retention time (SRT), an important operational parameter (ref. 5). The bioreactor may have any of several configurations, with hydraulic characteristics anywhere between a perfect plug-flow reactor and a perfectly mixed one. Because it is simpler to analyze and model, the latter will be assumed herein. An activated sludge system employing such a bioreactor is referred to as completely mixed activated sludge (CMAS).

Wastewaters always contain a mixture of organic compounds; *i.e.*, they contain multicomponent feeds. Furthermore, activated sludge systems are open systems, receiving inocula from many sources. As a consequence, the biomass in activated sludge systems comprises a complex microbial community. Bacteria serve as the primary degraders in the ecosystem and are the focus of most biodegradation studies. Furthermore, the bacterial community contains many species, although the exact number is system specific and not well defined. Consequently, for engineering purposes, biomass is expressed on a mass concentration basis, rather than as numbers.

Because any specific SOC constitutes only a small fraction of the biodegradable organic matter entering an activated sludge system, a question arises concerning the amount of biomass capable of carrying out its biodegradation. While it is likely that a large percentage of the biomass is involved in the biodegradation of the biogenic organic compounds in the influent, this is not likely to be the case for a given SOC because the genetic capability to synthesize the enzymes required for its biodegradation is not likely to be widespread. Rather, it is more likely that the SOC will be degraded by specialists. If that is the case, then the concentration of this "capable" biomass can be considered to arise only from the SOC (ref. 6), allowing its concentration to be calculated as a separate entity. Such an approach is equivalent to assuming that the fraction of capable biomass in an activated sludge system is equivalent to the fraction of the biodegradable COD supplied by the SOC of interest. COD is chemical oxygen demand, a measure of the available electrons in a wastewater, and thus it is a measure of the energy available to the biomass.

We recently conducted experiments using lab-scale activated sludge systems to evaluate whether the fraction of the feed COD provided by an SOC was a reasonable approximation of the fraction of biomass capable of degrading that SOC (ref. 7). Using substrate specific most probable number analyses for the biomass capable of degrading each of six organic compounds, we found that the fraction of the COD attributable to the compound ranged from a 17 percent overestimation to a 66 percent underestimation of the capable biomass fraction. Thus, while it would be preferable to actually measure the capable biomass concentration when evaluating biodegradation kinetics, in the absence of data, use of the COD fraction provided by the SOC is a reasonable surrogate. This means that for

modelling purposes, the bacteria capable of degrading a given SOC can be calculated as a separate entity.

Because the biomass in a CMAS system is homogeneously distributed and no differential settling occurs in the final settler, the SRT is the same for all biomass. Consequently, a mass balance on either capable biomass or total biomass leads to the important relationship between the specific growth rate of biomass,  $\mu$ , and the SRT,  $\Theta_c$ :

$$\mu = \frac{1}{\Theta_c} + b \quad (1)$$

where  $b$  is the decay coefficient, which will be assumed to be the same for all biomass. The unit of SRT is time, so the units of  $\mu$  and  $b$  are reciprocal time. Equation 1 states that the engineer can exert control over the specific growth rate of the biomass in a CMAS system by controlling the SRT. This has important implications because the specific growth rate is related to the concentration of the substrate undergoing biodegradation. If the substrate is noninhibitory to its own biodegradation, the Monod (ref. 8) equation represents that relationship adequately:

$$\mu = \frac{\mu_{\max} S_s}{K_s + S_s} \quad (2)$$

where  $S_s$  is the SOC concentration and  $\mu_{\max}$  and  $K_s$  are the kinetic parameters describing its biodegradation. The units of  $K_s$  and  $S_s$  are the same, both mass per volume; the units for  $\mu_{\max}$  are reciprocal time. Substitution of Eq. 1 into Eq. 2 and rearranging gives the equation for the substrate concentration in a CMAS bioreactor (ref. 5):

$$S_s = \frac{K_s(1/\Theta_c + b)}{\mu_{\max} - (1/\Theta_c + b)} \quad (3)$$

The important point to note in Eq. 3 is that the effluent concentration of an SOC is determined solely by its biodegradation kinetics (*i.e.*,  $\mu_{\max}$  and  $K_s$ ) and the SRT of the CMAS system, which is under engineering control. It is not influenced by the influent SOC concentration. This has important implications that will be discussed later. Furthermore, the SOC concentration is not influenced by abiotic removal mechanisms, such as sorption and volatilization, as can be seen from the fact that no abiotic loss terms appear in Eq. 3. In other words, abiotic removal mechanisms have no impact on the effluent SOC concentration from a CMAS bioreactor. This is not true, however, for activated sludge systems with other configurations, particularly those that approach plug flow. Consequently, such systems are more difficult to study, which is one reason most studies for determining biodegradation kinetics for SOCs are conducted with CMAS systems.

The effect of abiotic removal mechanisms in a CMAS system is to reduce the concentration of capable biomass, and this must be considered when such systems are used for biodegradation studies. The fractional reduction in capable biomass concentration by abiotic mechanisms is equal to the fraction of the SOC removal that can be attributed to those mechanisms (ref. 9). Recognizing this, it is possible to derive an expression for the fractional reduction that can be used to estimate either the capable biomass concentration or the fraction of SOC removal due to abiotic mechanisms. The derivation is available elsewhere (ref. 9), so only a few important points will be made here. First, the only abiotic mechanisms of importance in activated sludge systems are volatilization and sorption. Photolysis is not important because of shading by the biomass. Volatilization losses from a CMAS system can be quantified using a first-order volatilization rate coefficient,  $k_v$ , provided the gas-phase concentration of the SOC remains essentially negligible. This condition is generally met during surface aeration (ref. 10,11), and during diffused aeration when the air flow rate is high, the Henry's Law coefficient of the SOC is high, and the exit air is less than 10% saturated in the SOC (ref. 12). Similarly, in a CMAS bioreactor where everything is homogeneous and the hydraulic retention time (HRT),  $\tau$ , and SRT are typical, sorption occurs rapidly (ref. 13) and the concentration of the SOC sorbed on the biomass can be considered to be at equilibrium (ref. 14,15,16). Any individual SOC generally represents only a small part of the influent biodegradable COD, in which case the concentration of capable

biomass,  $X_B$ , will be a small fraction of the mixed liquor suspended solids (MLSS) concentration,  $X_M$ , and the MLSS will dominate the sorption effect. As a consequence, the loss of the SOC by sorption will be due to the wastage of mixed liquor from the bioreactor. At low SOC concentrations, the solid phase SOC concentration can be related to the liquid phase SOC concentration by a linear sorption isotherm with sorption coefficient  $k_s$ . Using these simplifications the fraction of the SOC removal that can be attributed to abiotic mechanisms,  $\gamma$ , which is equal to the fractional reduction in capable biomass concentration by abiotic mechanisms, can be calculated as:

$$\gamma = \frac{\alpha_a \left( \frac{S_s}{S_{so}} \right)}{\left( 1 - \frac{S_s}{S_{so}} \right)} \quad (4)$$

where  $\alpha_a$  is a dimensionless abiotic loss coefficient. It is made up of the dimensionless volatilization loss coefficient,  $\alpha_v$ , and the dimensionless sorption loss coefficient,  $\alpha_s$ :

$$\alpha_a = \alpha_v + \alpha_s \quad (5)$$

where:

$$\alpha_v = \tau \cdot k_v \quad (6)$$

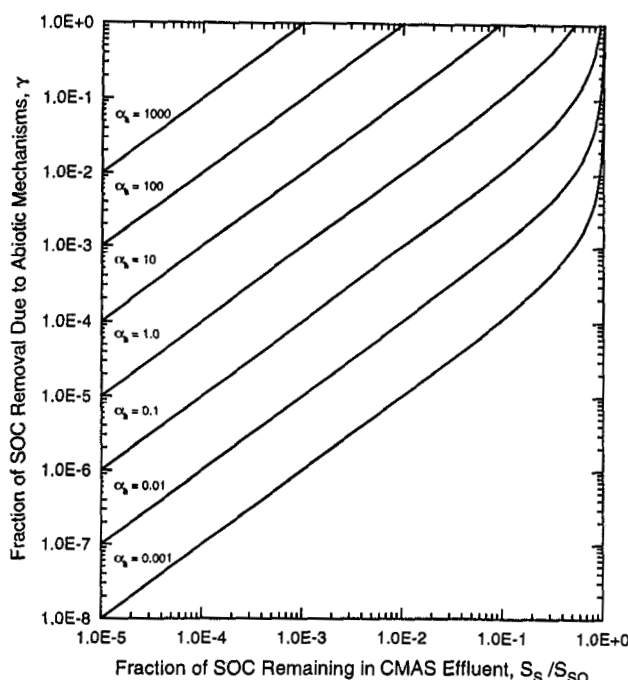
and

$$\alpha_s = \frac{\tau \cdot k_s \cdot X_M}{\Theta_c} \quad (7)$$

Equation 4 is plotted in Fig. 1 to allow visualization of its implications. The main point to draw from it is that abiotic removal mechanisms play a more important role as the fractional removal of the SOC by the activated sludge system declines. Three things can contribute to small fractional removals. First, the kinetics of biodegradation can be slow so that the effluent soluble SOC concentration as given by Eq. 3 is high. Obviously, under that circumstance biodegradation would be slow compared to other removal mechanisms, leading to a large contribution by abiotic mechanisms and a loss of capable biomass relative to the amount that would be present in the absence of the abiotic removal. Second, the SRT could be too short to give good biological removal. Increasing the SRT will decrease  $S_s$ , which decreases the fraction of SOC remaining in the effluent. However, for a fixed MLSS concentration, increasing the SRT will increase the system HRT almost proportionally, which increases the volatilization loss coefficient relative to the sorption loss coefficient, causing the total abiotic loss coefficient to increase. Consequently, the overall effect of an increase in SRT on the importance of abiotic losses will depend on the characteristics of the particular system. The third thing that can cause a low fractional removal of an SOC is a low influent concentration. Recall that the effluent SOC concentration from a CMAS system is independent of the influent SOC concentration (Eq. 3). Consequently, for a fixed SRT the fraction of the SOC remaining in the effluent will increase as its influent concentration is decreased, thereby increasing the importance of abiotic mechanisms in its removal and reducing the amount of capable biomass relative to the amount that would be formed in the absence of the abiotic removal. This suggests that careful consideration must be given to the importance of abiotic removal mechanisms when the influent concentrations of SOC's used in biodegradation studies are low. Methods for evaluating the abiotic loss coefficients from the chemical/physical characteristics of an SOC are discussed elsewhere (ref. 9).

## PREDICTING EFFLUENT SOC CONCENTRATIONS

Predicting the concentration of an SOC leaving a CMAS system is "simply" a matter of applying Eq. 3. However, this activity assumes that the kinetic parameters describing biodegradation are known, and obtaining representative values for them is not a "simple" matter. Even a cursory examination of the literature reveals that when multiple data sets can



**Fig. 1:** Graphical presentation of Eq. 4, showing the fraction of SOC removal from a CMAS system resulting from abiotic mechanisms. From ref. 9; copyright © Water Environment Federation; reprinted with permission.

be found describing biodegradation of a particular SOC, a large degree of variation exists among them. One reason for this is a failure to recognize the importance of physiological state in determining the outcome from biodegradation testing (ref. 17). The history of a microbial culture determines the levels of enzymes and RNA within the cells, and they in turn, determine how rapidly the cells respond during kinetic testing. Because testing conditions have not been standardized, different labs often utilize cultures in different physiological states, leading to some of the variability observed. To help increase the awareness of this effect, a nomenclature system has been proposed in which kinetic parameters are divided into two categories based upon the physiological conditions of the biomass during a kinetic test (ref. 17). At one extreme are intrinsic parameter sets. These are reflective of biomass that have a fully developed biodegradative system capable of using a test compound at the highest rate possible. They are obtained in tests requiring extensive cell division. As a consequence, all biomass used in intrinsic tests have a similar physiological state, making intrinsic parameters independent of the history of the culture and reflective of only the nature of the test compound and the organisms employed. At the other extreme are extant parameter sets. These are reflective of biomass with a physiological state unchanged from the environment from which they came, and indeed, the name implies parameters that are "currently existing" in the original environment. They are obtained in tests that minimize cell division and enzyme synthesis and are reflective of the compound, the culture, and its history. In between these two extremes lies a range of conditions that may be either defined or undefined, depending upon the care of the investigator.

The question therefore arises as to the best type of kinetic parameters to use to predict the effluent SOC concentrations from CMAS systems. To answer this question, we measured both intrinsic and extant biodegradation kinetic parameters for six SOC's fed to lab-scale CMAS systems as part of a multicomponent feed and evaluated their ability to predict effluent SOC concentrations (ref. 18). Twenty-nine data sets were obtained for which predictions could be made from both intrinsic and extant parameter sets and compared to measured effluent concentrations. In 27 of those sets, extant parameter values provided the better estimate of effluent SOC concentration and in two, there was no statistically significant

difference between the two types of estimates. However, in the majority of cases, both types of parameters overestimated effluent SOC concentrations, with extant predictions being higher than measured values by a factor of five or less and intrinsic predictions by one to two orders of magnitude. This suggests that extant kinetic parameters are better for predicting SOC biodegradation in CMAS systems but that the effluent concentrations predicted from application of Eq. 3 will be conservative. Intrinsic parameter sets appear to be more useful for comparing the relative biodegradabilities of organic compounds under a standard condition.

Several techniques are available for measuring both intrinsic and extant biodegradation kinetic parameters and many were discussed at a recent SETAC-Europe workshop (ref. 19). One particularly popular technique is respirometry, which can be used for both types of measurements. The main reason for the popularity of respirometry is that it allows collection of a continuous data record via microcomputer, providing a sufficiently large and robust data set to allow use of nonlinear parameter estimation (ref. 20). Consequently, we have focused on respirometry as our technique of choice in the procedures we have developed for measuring both intrinsic (ref. 21) and extant (ref. 22) parameter sets. Although different types of respirometers are used for the two techniques, the problems associated with the parameter estimation routines are similar. Care must be exercised in experimental design and execution to ensure that the resulting respirometric data sets meet the criteria for the applicability of the Monod model. Consequently, we have developed a screening protocol to assist investigators in determining whether their data sets are valid for parameter evaluation (ref. 23).

Questions arise about the nature of the chemicals that can be tested in the respirometric protocols. Current models of biodegradation assume that rates are governed by the liquid phase concentration. Consequently, the only process that the parameter estimation routines incorporate is biodegradation. If a compound is present in the test environment at a concentration above its solubility limit, the rate of dissolution may well govern the observed biodegradation rate, making it impossible to obtain an accurate assessment of the biodegradation parameters (ref. 24). A more complicated problem exists when an SOC is sorbed to a carrier, such as noncapable biomass or soil particles. In this case, the observed kinetics in the system may well reflect rates of desorption rather than just biodegradation (ref. 25). Modelling of such systems is not straightforward and many questions still remain to be answered. For example, bacteria selected by growth on sorbed substrates appear to facilitate their desorption (ref. 26), which raises questions as to how the kinetics of desorption and biodegradation can be independently estimated in such systems. Unfortunately, our current techniques are not adequate for handling such situations. Finally, if a compound is volatile, it may partition between the gas and liquid phases in the respirometer, requiring modification of the parameter estimation routine to properly evaluate the parameters (ref. 27). However, once that has been done, the effects are transparent to the analyst and the protocols may be applied in the same manner as for a nonvolatile compound.

As stated earlier, wastewaters contain many organic chemicals that can serve as growth substrates, but Eq. 3 reflects only the concentration of the SOC of interest as if the capable biomass were specialists growing only on it. However, in a multisubstrate environment will simultaneous biodegradation of other substrates influence the biodegradation kinetics of a specific SOC? In other words, should the values of  $\mu_{\max}$  and  $K_S$  in Eq. 3 reflect the multicomponent nature of the substrate or can parameter values measured in single substrate experiments be used to predict effluent quality? Two lines of evidence suggest that the latter is true; that single substrate experiments are adequate for assessing the kinetic parameters describing biodegradation in activated sludge systems. The first is from the experiments mentioned previously in which predicted concentrations were compared to measured concentrations. All of those predicted values were from single substrate kinetic experiments, yet they did an adequate job of predicting effluent concentrations from a bioreactor receiving a multicomponent feed. The fact that the differences between measured and predicted values were within a five-fold range suggests that the presence of other substrates in the CMAS feeds did not have a large impact on the biodegradation kinetics. However, because that evidence was suggestive, and not direct, experiments were conducted

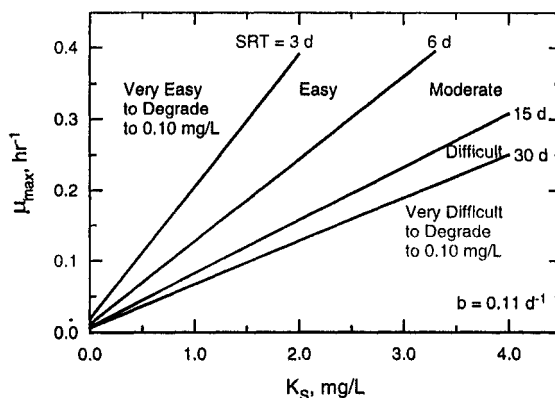
to address the question directly (ref. 28). Extant kinetic tests were run in a fed-batch respirometer to determine how simultaneous biodegradation of a multicomponent biogenic substrate influenced the measured biodegradation kinetics of several SOCs, each measured singly. In the fed-batch respirometer, the multicomponent biogenic substrate was supplied continuously to the test biomass at the same rate per unit of biomass that the substrates had been supplied in the CMAS system from which the biomass was obtained. The test SOC was then supplied as a pulse of substrate and the response of the culture was observed as a transient increase in oxygen consumption. Subtraction of the background oxygen consumption rate from the total response gave the net response to the test SOC, which could be used in a nonlinear parameter estimation routine to evaluate the kinetic parameters. Parallel experiments were run in the absence of fed-batch feed to determine the kinetic parameters when the SOCs were supplied as sole substrates. Tests were run with five test compounds (acrylamide, ethylene glycol, 4-chlorophenol, phenol, and *m*-toluate) and the only statistically significant effects seen were on  $\mu_{\max}$  for acrylamide, which was 29 percent higher (a positive effect) in the presence of the other substrates, and on  $K_S$  for *m*-toluate, which was 41 percent higher (a negative effect) in the presence of the other feeds. More extensive studies were done with phenol in which the nature of the fed-batch feed and its application rate were varied. These studies showed that the effect of the fed-batch feed depended on its application rate, with a maximum increase in  $\mu_{\max}$  being observed when it was fed at 300 percent of the rate to the CMAS system. Overall, however, the major conclusion from the study was that extant batch kinetic tests with single substrates are adequate measures of biodegradation kinetics in multisubstrate environments (ref. 28).

## ESTIMATION OF FATE IN CMAS SYSTEMS

One utility of biodegradation kinetic parameters is that they provide a framework within which rational assessments can be made of the potential problems associated with SOCs in CMAS systems. One level of that assessment could be the potential for significant interphase transfer. Equation 3 could be used to predict the effluent concentration of an SOC in a given CMAS system, allowing computation of the fraction of the SOC remaining in the effluent. That fraction could then be used in Fig. 1 to determine the fraction of the SOC removal due to abiotic mechanisms, which could be used in combination with the mass input rate of the SOC to determine the mass rate of loss to the atmosphere and to biosolids. That quantity could then be partitioned to the two phases in proportion to their abiotic loss coefficients, as given by Eqs. 6 and 7.

Another level of assessment is the degree of relative biodegradability in CMAS systems. Figure 2, adapted from McAvoy *et al.* (ref. 29), represents Eq. 3 in rearranged form and facilitates such an assessment. To use it, the point corresponding to the biodegradation kinetic parameters for an SOC is located on the chart, thereby identifying its biodegradation potential. An output SOC concentration of 0.10 mg/L was arbitrarily chosen for this chart, but any value could be used. Four CMAS SRT values were chosen to represent ease of biodegradability, based upon their use in practice. An SRT of 3 days represents a high-rate system such as might be used in a municipality and an SRT of 30 days represents a low-rate system such as might be used in an industrial wastewater treatment facility. The other two values are simply intermediate between those extremes. If the kinetic parameters for an SOC lie on or to the left of the 3 day SRT line, the compound is very easy to biodegrade because an effluent concentration of 0.1 mg/L could be achieved in a CMAS system with an SRT of 3 days or less. Conversely, if the kinetic parameters for an SOC lie on or to the right of the 30 day SRT line, the compound is very difficult to degrade because an SRT of 30 days or more would be required to degrade it to 0.1 mg/L. Intermediate levels of biodegradability are associated with the other zones. The utility of a chart like Fig. 2 lies in its ease of use and its visual presentation. Although it is simply a rearrangement of Eq. 3, it makes it immediately clear what is needed to remove the SOC, thereby giving a rational basis for assessments of

biodegradability in wastewater treatment systems. The task now is for the profession to decide on the target effluent SOC concentration to be used in such assessments.



**Fig. 2:** Diagram for determining the ease of biodegradability of SOCs in CMAS systems. Adapted from ref. 29.

### ESTIMATION OF FATE IN RECEIVING STREAMS

Environmental engineers' concern with SOCs does not stop with their fate in wastewater treatment systems. Rather, it also includes their fate in receiving streams. One measure of that concern is the possibility of the SOC being persistent; *i.e.*, resisting degradation, as measured by its half-life in the receiving medium. In water, a half-life of two months has been proposed as the threshold for classifying a chemical as persistent by the UN Economic Council for Europe (UNECE). Thus, the question arises as to whether any SOC that is able to serve as a carbon and energy source for microbial growth is likely to be persistent in a receiving stream as long as the environmental conditions (*i.e.*, temperature, pH, redox state, etc.) are favorable for microbial growth on the compound. Biodegradation kinetics can be used to address this question in part by assuming that other degradative processes are inactive and that biodegradation is the major destructive mechanism. It is uncertain whether intrinsic or extant kinetic parameter estimates should be used in such an exercise, although one might argue that extant parameters representative of the physiological state of the bacteria in the receiving stream would be most appropriate. This is a question that needs to be addressed.

Consider the receiving stream to behave as a plug-flow reactor, receiving both the SOC and capable bacteria from a wastewater treatment plant as a point source. The half-life of the SOC in the stream as a result of biodegradation can be estimated by using the Monod-growth model (ref. 30), which assumes that the capable bacteria grow on the SOC as sole substrate with Monod kinetics as expressed by Eq. 2. Integration of the model and substitution of the definition of the half-life,  $t_{0.5}$ , as the time required to reduce the concentration to half of the initial concentration,  $S_{SO}$ , leads to the following expression:

$$t_{0.5} = \frac{0.693YK_s + \left[ 1 + \frac{S_{so}Y}{X_{BO}} \left( 1 + \frac{K_s}{S_{so}} \right) \right] \ln \left( 1 + 0.5 \frac{S_{so}Y}{X_{BO}} \right)}{\left( 1 + \frac{S_{so}Y}{X_{BO}} \right) \mu_{max}} \quad (8)$$

where  $S_{SO}$  and  $X_{BO}$  are the concentrations of the SOC and capable biomass, respectively, in the receiving stream after mixing, and  $Y$  is the growth yield of the biomass on the SOC. Examination of Eq. 8 reveals that the half-life of an SOC due to biodegradation depends on the initial SOC and capable biomass concentrations and the biodegradation kinetic parameters. If we define three dimensionless groups, Eq. 8 can be presented in a single plot. The three groups are:



$$\text{Dimensionless Half-life} = t_{0.5} \mu_{\max} \quad (9)$$

$$\text{Dimensionless SOC Concentration} = \frac{S_{SO}}{K_S} \quad (10)$$

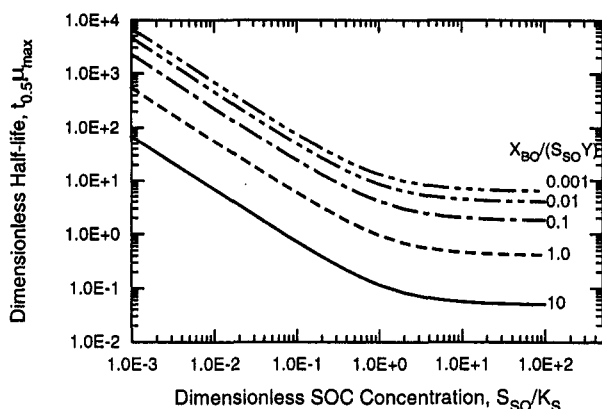
and

$$\text{Dimensionless Capable Biomass Concentration} = \frac{X_{BO}}{S_{SO} Y} \quad (11)$$

The dimensionless capable biomass concentration represents the amount initially present relative to the amount that would be grown if all of the SOC were degraded biologically.

Figure 3 shows the plot of Eq. 8 in which the dimensionless half-life is presented as a function of the initial SOC concentration with the initial biomass concentration as a parameter. Several things about the persistence of SOCs in receiving streams can be learned from this plot. First, the half-life is inversely proportional to  $\mu_{\max}$ . Consequently, if  $\mu_{\max}$  is small, the half-life will be large. Second, as long as SOCs are present at initial concentrations greater than their  $K_S$  values, the initial concentration has little effect on half-life. However, examination of Eq. 3 shows that SOCs will seldom be discharged from CMAS systems at concentrations approaching their  $K_S$  values, so we can expect the initial SOC concentration in the receiving stream to influence the half-life, with lower concentrations causing longer half-lives. Furthermore, if  $K_S$  is large, the dimensionless SOC concentration will be very small, which will extend the half-life. Third, the initial capable biomass concentration also has a strong effect on half-life, although not as strong as the initial SOC concentration, with lower biomass concentrations increasing the half-life. Thus, in the case of SOCs that are degraded by specialized bacteria present in the activated sludge system, but perhaps not naturally present in the receiving stream, efforts to reduce effluent bacterial concentrations by disinfection may greatly extend the half-lives of those SOCs in the environment.

Using Fig. 3, we can now address the issue of whether an SOC that is biodegradable would be persistent in a receiving stream. Consider as a first example the detergent sodium dodecyl sulfate, which has intrinsic kinetic parameters of  $\mu_{\max} = 0.60 \text{ h}^{-1}$  and  $K_S = 0.56 \text{ mg/L}$  (ref. 31). Entering Fig. 2 with these parameters reveals that it is very easy to biodegrade in CMAS systems, and that low effluent concentrations can be obtained, as has been found in practice. Now, assume that a concentration of  $0.10 \text{ mg/L}$  is discharged to a stream in the effluent from a wastewater treatment plant and that it is diluted there to  $0.010 \text{ mg/L}$ . What type of half-life would it have? Entering Fig. 3 with a dimensionless SOC concentration of  $0.018$  (i.e.,  $0.010 \text{ mg/L} \div 0.56 \text{ mg/L}$ ) reveals that the dimensionless half-life would be  $400$  if the dimensionless initial biomass concentration was only  $0.001$ , a very low value. Since  $\mu_{\max} = 0.60 \text{ h}^{-1}$ , this suggests that the half-life would be  $677 \text{ h}$  (i.e.,  $400 \div 0.60 \text{ h}^{-1}$ ), a value



**Fig. 3:** Graphical presentation of Eq. 8 showing the effects of SOC biodegradation kinetic parameters, initial SOC concentration, and capable bacterial concentration on the SOC biodegradative half-life in an aquatic environment.

well below the persistence level proposed by the UNECE. This demonstrates that SOCs with good biodegradative characteristics are unlikely to be persistent as long as environmental conditions are suitable for growth of bacteria capable of degrading them.

Now consider an SOC that is known to be very difficult to remove biologically, 1,4-dioxane. At 25°C its intrinsic biodegradation kinetic parameters are  $\mu_{\max} = 0.010 \text{ h}^{-1}$  and  $K_S = 13.5 \text{ mg/L}$  (ref. 32). Entering Fig. 2 with these values shows clearly that it would be impossible to reach an effluent substrate concentration of 0.10 mg/L for this compound from a CMAS system, suggesting that it is an unsuitable treatment system, which is well known. However, suppose that another type of treatment reduced its discharge concentration to a level that made the in-stream concentration 0.10 mg/L below the outfall. What would its half-life be? Entering Fig. 3 with a dimensionless SOC concentration of 0.0074 (*i.e.*, 0.10 mg/L + 13.5 mg/L) and assuming a moderate dimensionless inoculum of 0.01 gives a dimensionless half-life of 700, which corresponds to a half-life of 70 000 h (*i.e.*,  $700 + 0.010 \text{ h}^{-1}$ ). Thus, according to the UNECE protocol, 1,4-dioxane would be considered to be persistent. Furthermore, the dimensionless inoculum concentration would have to approach 10, an unlikely occurrence, to prevent 1,4-dioxane from being classified as persistent. Thus, we must conclude that SOCs of known slow biodegradability can be persistent simply because of their unfavorable biodegradation kinetics. This suggests that biodegradation testing should play an important role in the characterization of SOCs.

## CLOSURE

We have seen that the use of biodegradation kinetics in mathematical models provides valuable information about the fate of SOCs in aquatic environments. Thus, much can be gained from extending our database of biodegradation kinetic parameters. However, in doing that, careful consideration must be given to the use to which the parameters will be put. If they are to be used to assess the biodegradability of the SOCs in activated sludge wastewater treatment systems, extant measurements should be made, ensuring that the parameters are reflective of the rates likely to exist in such systems. Furthermore, the available evidence suggests that extant tests may be run with single substrates, which greatly simplifies the required protocol. Those tests, however, must be run with soluble substrates for the parameters to reflect only the biodegradation rate. Parameters reflecting the contributions of volatilization and sorption can be estimated adequately from the physical/chemical properties of the SOCs. Once all parameters are known, the relative contributions of biotic and abiotic removal mechanisms can be assessed with the use of Fig. 1 whereas the ease of biodegradability can be evaluated with Fig. 2. Finally, biodegradation kinetic parameters can also be used to assess the potential of an SOC to be persistent in aquatic environments using Fig. 3. At this time, however, it is unclear whether intrinsic or extant parameter values should be used in making that assessment.

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