Competitive adsorption of micropollutants and NOM onto activated carbon: comparison of different model approaches

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ABSTRACT

Conventional adsorption models are not able to describe exactly the competitive adsorption of natural organic matter (NOM) and micropollutants during drinking water treatment with activated carbon. This problem is a consequence of the complex structure of natural organic matter. In the last years, two user-oriented model approaches, the tracer model (TRM) and the equivalent background compound model (EBCM), were proposed to overcome the difficulties in modelling the competitive adsorption in such multi-component systems. In this paper, these model approaches, as well as a simplified model for batch processes, are compared and opportunities and limitations are pointed out. The different aspects of model application are exemplarily discussed for the adsorption of two pesticides, atrazine and diuron, from Elbe River water onto activated carbon. As can be seen from the examples and from a series of studies, both models are suitable for modelling the micropollutant adsorption in the presence of NOM. The EBCM is somewhat easier to handle whereas the TRM allows for the consistent and parallel description of micropollutant and NOM adsorption.

Key words | activated carbon, competitive adsorption, drinking water treatment, micropollutants, NOM

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NOMENCLATURE

A parameter, defined in Equation (7)

c liquid-phase concentration, $mg\,l^{-1}$ or $mmol\,l^{-1}$

c_0 initial liquid-phase concentration, $mg\,l^{-1}$ or $mmol\,l^{-1}$

K isotherm parameter (Freundlich isotherm), $(mg\,g^{-1})/(mg\,l^{-1})^n$, or $(mmol\,g^{-1})/(mmol\,l^{-1})^n$

m_A adsorbent mass, g

N number of mixture components

n isotherm parameter (Freundlich isotherm), dimensionless

q solid-phase concentration (loading, amount adsorbed), $mg\,g^{-1}$ or $mmol\,g^{-1}$

q_T total amount adsorbed, $mg\,g^{-1}$ or $mmol\,g^{-1}$

V volume, l

z adsorbed-phase mole fraction, dimensionless

ϕ spreading pressure term in IAST, $mmol\,g^{-1}$

INTRODUCTION

Activated carbon is typically applied in drinking water treatment with the primary objective to remove organic micropollutants. During the adsorption process the micropollutants compete for the adsorption sites with natural organic matter (NOM) that occurs in all raw waters. As a consequence, the adsorption capacity for micropollutants will be reduced. Since the concentration of NOM is much higher in comparison with the micropollutants, the effect of competitive adsorption can be expected even for stronger adsorbable micropollutants. Because of the capacity reduction for the micropollutants, the NOM adsorption must be considered as a negative effect in view of micropollutant removal. On the other hand, the reduction of NOM concentration by activated carbon adsorption

reduces disinfection by-product formation during the following disinfection step with chlorine, which is a positive aspect in view of water quality. But independent of the specific assessment of the effect of NOM adsorption, there is a scientific and practical interest in modelling the competitive adsorption of micropollutants and NOM. Such competitive adsorption models are necessary to describe adsorption onto granular activated carbon (GAC) in fixed-bed adsorbers as well as adsorption onto powdered activated carbon (PAC) in batch adsorbers, in flow-through adsorbers or in ultrafiltration systems. Comparable effects can also be observed in wastewater treatment with PAC where the effluent organic matter competes with micropollutants for adsorption sites.

The mathematical description of the influence of NOM on micropollutant adsorption is complicated because NOM is not a defined substance but a multi-component mixture of unknown composition with site-specific structure and behaviour (Aiken & Cotsaris 1995). Therefore, the conventional competitive adsorption model, the ideal adsorbed solution theory (Myers & Prausnitz 1965; Radke & Prausnitz 1972), is not sufficient and has to be complemented by specific model approaches. In this paper, an overview of the actual state of modelling of competitive adsorption in the system NOM/micropollutant/activated carbon will be given. Opportunities and limitations of two model approaches, the tracer model (TRM) and the equivalent background compound model (EBCM), will be

discussed on the basis of two experimentally investigated systems: atrazine/river water and diuron/river water. An overview of other published TRM and EBCM applications can be found in Table 1.

The TRM and the EBCM are mainly intended for using in fixed-bed adsorber modelling. Their application is essential for estimating reasonable input data for subsequent breakthrough curve calculation. The TRM can be applied in combination with conventional breakthrough curve models such as the LDF model (Rabolt et al. 1998; Hartig et al. 2001). For the EBC (equivalent background compound) approach the special kinetic model COMP-SORB-GAC was developed (Schideman et al. 2006a,b). In principle, the TRM and the EBCM can also be used for batch adsorber design, but in this special case a simplified EBC approach is often sufficient. This simplified approach will also be discussed in this paper.

Since the ideal adsorbed solution theory (IAST) provides the basis of all competitive adsorption models considered in this study, a brief description of the IAST will be given in the following section.

PREDICTION OF COMPETITIVE ADSORPTION EQUILIBRIA

Currently, the ideal adsorbed solution theory (IAST) can be considered as the standard method for predicting

Table 1 | Applications of the tracer model (TRM) and the equivalent background model (EBCM)

Model	Micropollutants	Water/organic background	Reference
TRM	1,1,1-trichloroethane, trichloroethene, naphthalene-2,7-disulfonate, 4-aminonaphthalene-1-sulfonate, diuron, atrazine	River water	Rabolt (1998) and Rabolt et al. (1998)
TRM	N-n-butylbenzenesulphonamide, sulphamethoxazole	Microfiltrated tertiary effluent	Hartig et al. (2001)
TRM	Several pharmaceuticals and industrial chemicals	Biologically treated wastewater	Nowotny et al. (2007)
EBCM	2,4,6-trichlorophenol	Several natural and finished waters	Najm et al. (1991)
EBCM	2-methylisoborneol	River water, ultrafiltrate	Newcombe et al. (2002a,b)
EBCM	2-methylisoborneol	Lake water	Gillogly et al. (1998)
EBCM	2-methylisoborneol, geosmin	Lake water, river water	Graham et al. (2000)
EBCM	Simazine	River water, lake water	Matsui et al. (2001)
EBCM	Simazine, simetryn, asulam	River water, groundwater	Matsui et al. (2003)
EBCM	Atrazine	Groundwater	Schideman et al. (2006b)

competitive adsorption equilibria from single-solute isotherm parameters of the mixture constituents. The IAST was originally developed by Myers & Prausnitz (1965) for the gas-phase adsorption and was later extended to the liquid-phase adsorption by Radke & Prausnitz (1972). The IAST describes the equilibrium between the multi-component solution and a two-dimensional adsorbed phase and is based on a set of thermodynamic equations, in particular the fundamental equation for the Gibbs energy and the equations for the chemical potentials of the solutes which are partitioned between both phases. Details of this theory can be found in respective monographs (Sontheimer et al. 1988; Kümmel & Worch 1990). Therefore, only the principle and the solution equations of the IAST will be given here. Additionally, a calculation scheme is presented in Figure 1. In principle, the IAST is not restricted to a specific single-solute isotherm model (Kümmel & Worch 1990), but it is often used together with the Freundlich isotherm. For the following considerations, it will be assumed that the single-solute isotherms of the mixture components can be described by the Freundlich isotherm equation written in the following form:

$$q = Kc^n \tag{1}$$

where q is the equilibrium loading (amount adsorbed), c is the equilibrium concentration, and K and n are the isotherm parameters.
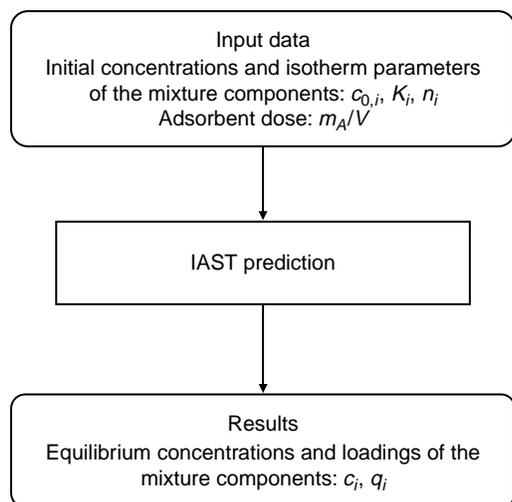

Figure 1 | Calculation scheme of the ideal adsorbed solution theory (IAST).

In the case of a batch adsorption process with given initial concentrations of the mixture constituents, $c_{0,i}$, and given adsorbent dose m_A/V (adsorbent mass per volume of solution) the equilibrium concentrations and loadings of all components can be found by solving the following set of equations:

$$\sum_{i=1}^{N} z_i = \sum_{i=1}^{N} \frac{c_{0,i}}{\frac{m_A q_T}{V} + \left(\frac{n_i \phi}{K_i}\right)^{1/n_i}} = 1 \tag{2}$$

$$\sum_{i=1}^{N} \frac{1}{n_i \phi} \cdot \frac{c_{0,i}}{\frac{m_A q_T}{V} + \left(\frac{n_i \phi}{K_i}\right)^{1/n_i}} = \frac{1}{q_T} \tag{3}$$

$$c_i = z_i \left(\frac{n_i \phi}{K_i}\right)^{1/n_i} \tag{4}$$

$$q_i = z_i q_T \tag{5}$$

The simultaneous solution of Equations (2) and (3) yields the total loading, q_T, as well as the spreading pressure term, ϕ. Furthermore, the adsorbed-phase mole fractions, z_i, are given as summands of Equation (2). Although the spreading pressure term possesses a physical meaning (for details see above-mentioned monographs), for practical use it can be considered as a simple operand. The term ϕ is only necessary for the calculation of the equilibrium concentrations of the mixture components from Equation (4). The equilibrium loadings can be found from the adsorbed-phase mole fractions and the total loading by using Equation (5).

It follows from the IAST that a prediction of mixture adsorption equilibria is only possible if the single-solute isotherm parameters, K and n, and the initial concentrations of all mixture constituents, $c_{0,i}$, are known. For NOM as a multi-component mixture of unknown composition, these data are not available. Therefore, a specific characterization of the adsorption properties of NOM is necessary prior to further mixture adsorption calculations. For this purpose, the so-called adsorption analysis can be used.

DESCRIPTION OF NOM ADSORPTION: THE ADSORPTION ANALYSIS

For NOM neither the qualitative nor the quantitative composition can be specified. In practice, the total concentration is measured as dissolved organic carbon (DOC). That means–in view of adsorption–that only total isotherms of the multi-component system (DOC loading as function of DOC concentration) can be measured experimentally. The shape of such DOC isotherms significantly differs from the shape of single-solute isotherms. In uppermost cases the DOC isotherms approach at low loadings (high adsorbent doses) a value on the concentration axis that is different from zero and corresponds to the non-adsorbable fraction of DOC. Furthermore, there is typically no uniform change in the slope of the isotherm as can be found for the single-solute Freundlich or Langmuir isotherms. This indicates that natural organic matter consists of fractions with different adsorbabilities. Consequently, DOC isotherms cannot be described by simple single-solute isotherm equations. To overcome the difficulties in the description of NOM adsorption, the method of adsorption analysis was developed. Details can be found in the monographs of Sontheimer *et al.* (1988) and Kümmel & Worch (1990). A mathematical solution was presented by Johannsen & Worch (1994).

The basic principle of the adsorption analysis consists of a formal transformation of the unknown multi-component system into a mixture of a limited number of fictive components with a defined composition. The fictive components of this mixture system stand for DOC fractions with different adsorbabilities. Within the framework of the adsorption analysis, the different adsorbabilities of the DOC fractions are defined by assigning characteristic Freundlich isotherm parameters. For simplification, the n value is normally held constant and only different K values are used to characterize the graduation of the adsorbabilities. The adsorption analysis starts with the experimental determination of the DOC isotherm for the considered NOM-containing water followed by an IAST-based search routine to find the concentration distribution of the DOC fractions. The principle of the adsorption analysis is schematically shown in Figure 2.

After running the adsorption analysis, the DOC is characterized in the same manner as a defined adsorbate
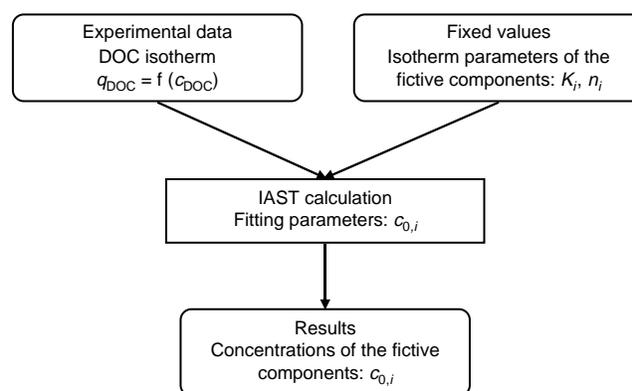

Figure 2 | Calculation scheme of the adsorption analysis.

mixture; that is, the isotherm parameters as well as the initial concentrations of the DOC fractions are now known and can be used for further process modelling purposes (e.g. for batch or fixed-bed adsorber design).

As an example, Figure 3 shows the adsorption analyses of two water samples collected from the Elbe River in Dresden, Germany, at different times. The calculation was done by using a computer program developed by the author. Table 2 shows the concentration distributions found from the adsorption analyses. As can be seen from Figure 3 and Table 2, the definition of only three components is already sufficient to describe the DOC isotherm of the Elbe River water in satisfactory quality.

At this point it has to be noted that there is a problem concerning the units in the adsorption analysis that will play a role in the further considerations. As discussed before, the IAST is based on fundamental thermodynamic equations and therefore requires the use of molar concentrations, but the DOC can only be given as mass concentration. In the IAST, mass concentrations can be used only under the unrealistic condition that all components have the same molecular weight. Therefore, an error resulting from the unavoidable use of the wrong unit $mg\,l^{-1}$ DOC has to be accepted. It follows from the theory, that the use of the wrong unit leads to wrong adsorbed-phase mole fractions (see Equation (2)) and consequently to the wrong concentration distribution. However, such a shift in the concentration distribution will be compensated in subsequent IAST applications (e.g. in process modelling) owing to the reverse direction of the calculation (adsorption analysis is

(a)

(b)
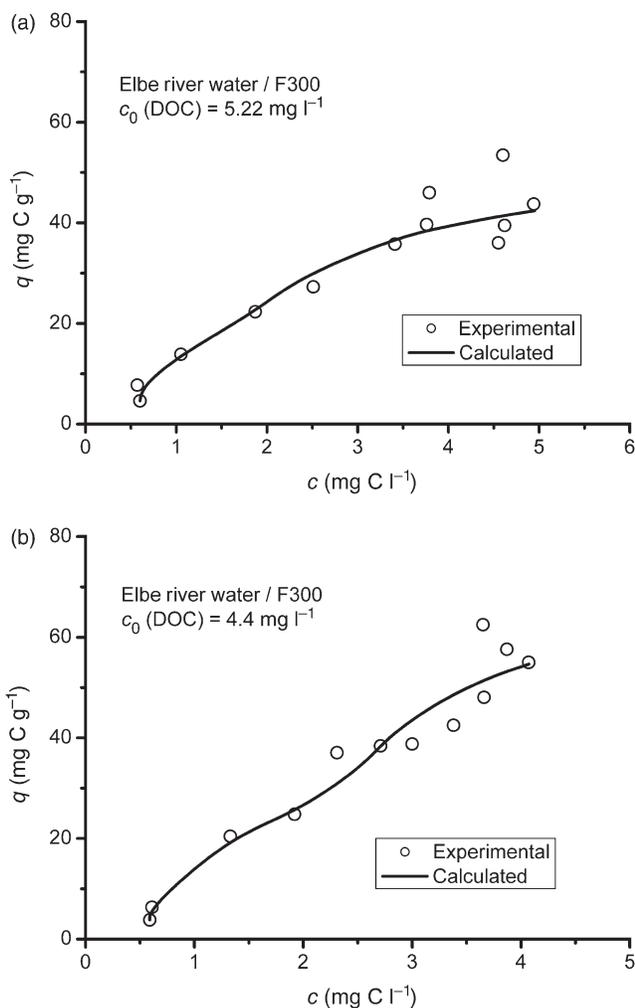
Figure 3 | Adsorption analysis of two Elbe River water samples (for concentration distribution of the fictive components see Table 2); (a) c_0 (DOC) = 5.22 mg l^{-1}; (b) c_0 (DOC) = 4.4 mg l^{-1}.

the reversal of the IAST prediction). As long as only fictive components are considered, no negative consequences will result in practical application. By contrast, difficulties in process modelling can be expected for mixture adsorbate

Table 2 | Adsorption analyses of Elbe River water ($n = 0.2$)

Sample 1, c_0(DOC) = 5.22 mg l^{-1}		Sample 2, c_0 (DOC) = 4.4 mg l^{-1}	
K (mg g^{-1})/(mg l^{-1})^n	c_0 (mg l^{-1})	K (mg g^{-1})/(mg l^{-1})^n	c_0 (mg l^{-1})
0	0.60	0	0.59
12	1.34	18	1.94
34	3.29	50	1.88

Mean percentage errors: 4.38% (sample1), 4.23% (sample 2).

systems consisting not only of fictive NOM fractions. In the following, this and other problems connected with micropollutant/NOM systems will be discussed.

PROBLEMS CONNECTED WITH THE APPLICATION OF THE IAST TO COMPETITIVE ADSORPTION OF MICROPOLLUTANTS AND NOM

It would seem at first consideration a simple matter to add the trace pollutant to the fictive-component mixture as a further component and to apply the IAST to this extended system in order to characterize the micropollutant adsorption in the presence of NOM. In principle, if the concentration and the single-solute isotherm parameters of the micropollutant are known and also the results of an adsorption analysis of the NOM-containing water are given, all required data for an IAST calculation are available. However, this kind of prediction fails in many cases. There are manifold reasons for this failure, for example:

i. The equations of the IAST are only valid for ideal conditions. All possible interactions between the adsorbates in the liquid phase as well as in the adsorbed phase are neglected. Experiences from studies with defined model mixtures show that, in most cases, the differences between experiment and prediction are relatively small, indicating no strong deviation from the ideal behaviour. On the other hand, stronger interactions and therefore larger deviations from the ideal behaviour can be expected for mixtures of NOM and micropollutants due to complex formation. Such complex formation processes with NOM are reported by several authors (Carter & Suffet 1982; Poerschmann et al. 1999; Amiri et al. 2005).

ii. As discussed in the section above, an unavoidable error results from the need to use the unit mg l^{-1} for DOC whereas the exact IAST requires molar concentrations. There are only two ways to deal with NOM/micropollutant mixtures. Either the micropollutant concentration must be transformed to DOC to get at least the same unit for all components or different units for NOM and micropollutant have to be applied in the calculation. In both cases the requirement to use molar concentrations for all components

is not fulfilled and erroneous results will be the consequence, especially obvious for the predicted micropollutant adsorption.

iii. For NOM and tracer compounds different accessibility to the micropores has to be considered as a further error source. Within the IAST it is assumed that in the case of competitive adsorption all adsorption sites are similarly accessible to all adsorbates. But it cannot be excluded that, in the case of microporous adsorbents such as activated carbons, the larger NOM molecules cannot enter the fine micropores (Pelekani & Snoeyink 1999). In this case only a fraction of the natural organic matter would be able to compete with the micropollutant in the sense of IAST.

iv. As a further effect, a possible blockage of the micropore entries by larger NOM molecules has to be considered (Carter et al. 1992; Weber 2004). In this case the micropollutant adsorption is expected to be reduced independently of the competitive adsorption. On the other hand, an uptake of micropollutants by NOM due to partitioning is also possible (Weber 2004).

To overcome the problems resulting from the application of the IAST to systems consisting of NOM and trace organic compounds, two different approaches were developed in recent years, the tracer model (TRM) and the equivalent background compound model (EBCM). Both models are based on the IAST but modify the original theory in order to make it applicable to NOM/micropollutant systems. In contrast to the original IAST, these models require the measurement of a mixture isotherm; that is, a micropollutant isotherm in the presence of NOM. This micropollutant isotherm is then used to find parameters which are able to compensate for the errors resulting from the unfulfilled preconditions of the IAST. The principal difference between the approaches consists in the fact that in the first case the isotherm parameters of the micropollutant are corrected for further application in the IAST whereas in the second case the mathematical description of the NOM adsorption is modified. These models–together with a simplified approach for the special case of batch adsorption–will be discussed in the following sections.

SOLUTION APPROACHES FOR MODELLING THE MICROPOLLUTANT/NOM ADSORPTION

The tracer model (TRM)

The tracer model (Burwig et al. 1995; Rabolt et al. 1998) is based on the assumption that the results of the adsorption analysis can be used as input data for calculating the NOM/micropollutant competitive adsorption. The correction necessary for the correct description of the competitive adsorption by IAST is done by modifying the micropollutant single-solute isotherm parameters. The corrected isotherm parameters have to be determined from experimental mixture adsorption data (micropollutant isotherm in presence of NOM) by using a fitting procedure based on the IAST (Figure 4).

Through the correction of the isotherm parameters, all possible errors discussed in the section before will be compensated. The corrected parameters are fictive (empirical) single-solute isotherm parameters which improve the IAST calculations in comparison with the original single-solute parameters. Often, the corrected isotherm parameters differ considerably from the original single-solute isotherm parameters. They are only valid for the respective NOM-containing water and allow for IAST calculations in the system under consideration: for example, for adsorber design purposes. The benefit of this model approach is that it is based on the results of the adsorption analysis and therefore the NOM adsorption behaviour can be described in parallel to the micropollutant adsorption.
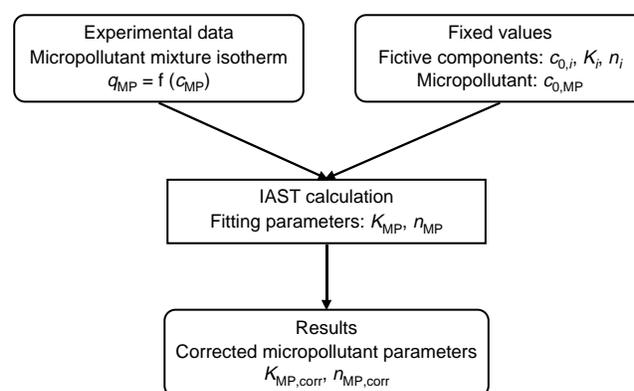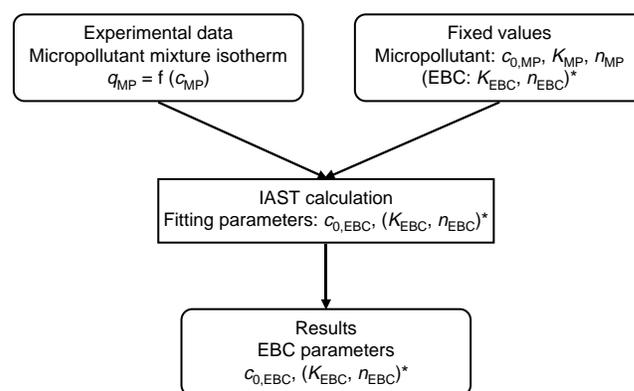

Figure 4 | Calculation scheme of the tracer model. The data for the fictive components have to be determined by adsorption analysis prior to the application of the tracer model. The subscript MP indicates the micropollutant.

The equivalent background compound model (EBCM)

The EBC model (Najm *et al.* 1991) retains all micropollutant data (concentration, single-solute isotherm parameters) and makes the corrections needed for the IAST application with the help of a simplified description of the NOM. A single NOM background component (EBC = equivalent background compound) is defined which represents that NOM fraction which is able to compete with the micropollutant within the interior of the adsorbent particle. In principle, all parameters of the EBC (isotherm parameters, concentration) are unknown and have to be determined from the mixture isotherm of the micropollutant by a fitting procedure based on IAST. But it was often found that fitting of all three parameters (c_0, n and K for EBC) does not lead to unique results. That means that different sets of parameters result in comparable fitting quality (Najm *et al.* 1991; Graham *et al.* 2000). For this reason, the EBC approach was further simplified. It was proposed to use the same Freundlich exponent, n, for the EBC as for the micropollutant and to determine only K and the concentration, c_0, by fitting (Newcombe *et al.* 2002a). It was also suggested to use both micropollutant isotherm parameters for the EBC and to fit only the EBC concentration (Schideman *et al.* 2006a,b). The latter approach is based on the assumption that a NOM component which is able to compete with the micropollutant should have more or less the same adsorption properties as the micropollutant. Of course, this is a strong simplification because competition can also be found for components with different adsorption behaviour. Figure 5 shows the calculation scheme of the EBCM.

If mmol l^{-1} is used as the unit for the initial micropollutant concentration and K is expressed in a consistent unit, the molar EBC concentration will be obtained as the fitting result. Therefore, a direct comparison of the calculated EBC concentration (in mmol l^{-1}) with the measurable DOC concentration (in mg l^{-1}) is not possible, unless a fictive molecular weight is assumed for the NOM. Furthermore, the carbon content of the NOM must be known or assumed for such a transformation. Moreover, the EBC that represents only the competing low-molecular NOM fraction is not related to the total NOM adsorption and cannot be used to describe the total DOC isotherm.

Figure 5 | Calculation scheme of the EBC model. *Optionally, K and n of the EBC can be set to the values of the micropollutant.

Within the framework of the model approach, EBC is a single solute whereas typical DOC isotherms show a multicomponent behaviour. This problem must be considered as the main drawback of the EBC model, in particular in view of the theoretical interpretation.

A comparable approach, but on the basis of multiple natural background components, was proposed by Hobby (1995). Starting with the adsorption analysis, the parameters of all fictive components were fitted to get a better description of the micropollutant adsorption in the presence of NOM. The main problem connected with this approach is the high number of fitting parameters. Because of the resulting uncertainties this approach will not be considered here.

Special case: competitive adsorption in batch adsorbers

TRM and EBCM are general model approaches which can be used to find the characteristic input data needed for subsequent batch or fixed-bed adsorber modelling. For the special case of batch reactors a simplified model approach can also be applied.

In the case of batch adsorbers, the adsorbate concentration decreases from an initial value c_0 to the residual concentration given by the adsorption equilibrium. The residual concentration decreases with increasing adsorbent dose. Under certain conditions, in particular at low concentrations of the micropollutant in comparison to NOM, the relative removal c/c_0 for the micropollutant at given adsorbent dose becomes independent of the initial

micropollutant concentration. This can be shown exemplarily by IAST model calculations. As an example, Figure 6 shows the relative concentration of diuron adsorbed from Elbe River water as a function of the adsorbent dose for different initial concentrations. For this calculation, the input data found from the TRM (see next section) were used. It can be seen that with the exception of the curve for the highest initial concentration all other curves have nearly the same shape. The differences between the curves vanish with decreasing initial concentration. From this finding it can be concluded that for a micropollutant that occurs in raw water in very low concentrations, only one curve $c/c_0 = f(m_A/V)$ has to be determined experimentally. This characteristic curve can then be used to estimate the relative removal for any adsorbent dose. Knappe et al. (1998) have demonstrated the applicability of this simple approach for a number of micropollutant/NOM systems.

Based on the IAST and the EBC (two-component) approach, Qi et al. (2007) have derived a simplified equation that describes the micropollutant (component 1) removal in presence of EBC (component 2) as a function of the adsorbent dose. Inspecting their simplified model, the same effect as discussed above (independence of percentage removal on the initial concentration) can be seen. Furthermore, this approach provides the opportunity to describe mathematically the characteristic micropollutant removal
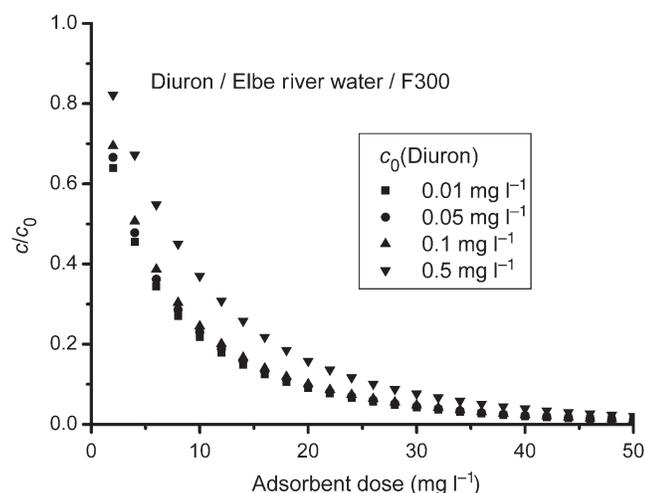
curve. In the following this approach will be referred to as simplified EBCM (SEBCM).

Under the assumption that the EBC is much better adsorbed than the micropollutant ($q_2 > > q_1$) and the values of the Freundlich exponents are comparable ($n_1 \approx n_2$) the following equation can be found from the IAST

$$\frac{c_{0,1}}{c_1} = \frac{1}{A}\left(\frac{m_A}{V}\right)^{1/n_1} + 1 \qquad (6)$$

with

$$A = c_{0,2}^{1/n_1 - 1}\left(\frac{n_1}{n_2 K_1}\right)^{1/n_1} \qquad (7)$$

where $c_{0,1}$ is the initial concentration of the micropollutant, c_1 is the residual concentration of the micropollutant, $c_{0,2}$ is the initial concentration of the EBC, n_1 and n_2 are the Freundlich exponents of the respective components, and K_1 is the Freundlich coefficient of the micropollutant.

As can be seen from the right-hand sides of the Equations (6) and (7), there is no influence of the initial concentration $c_{0,1}$ on the relative removal $c_1/c_{0,1}$. The logarithmic form of Equation (6) can be used to find the parameters A and n_1 from an experimentally determined curve $c_1/c_{0,1} = f(m_A/V)$ by linear regression

$$\ln\left(\frac{c_{0,1}}{c_1} - 1\right) = \frac{1}{n_1}\ln\left(\frac{m_A}{V}\right) - \ln A \qquad (8)$$

Once the two parameters A and n_1 are known, Equation (6) can be used to calculate the relative removal of the micropollutant from NOM-containing water at any adsorbent dose. For this type of calculation it is not necessary to know the exact values of the parameters included in A.

In contrast to the other models discussed above, only one experimental curve has to be determined as a precondition for subsequent prediction of the micropollutant batch adsorption behaviour in the presence of NOM. The adsorbent dose needed for a given treatment objective can be read directly from the curve or can be calculated after estimating n_1 and A. Therefore, this simplified model is very easy to use. But there are also some limitations:

i. The simplified approach is restricted to batch adsorption processes whereas the results of TRM and EBCM

Figure 6 | Diuron adsorption in a batch reactor in the presence of NOM: influence of the micropollutant initial concentration (model calculation based on IAST).

can be used not only for batch processes but also as input data for calculating fixed-bed adsorber break-through curves.

ii. It is not easy to verify the fulfilment of the precondi-tions for the simplified approach. The simplified IAST presented by Qi *et al.* (2007) is based on the assumption that $q_2 >> q_1$ and $n_1 \approx n_2$. In their paper the authors have shown that the deviation of the simplified IAST from the original IAST is less than 10% in the full range of expected n_1 and n_2 values if the EBC dominates over the trace compound by a factor of 130 or more on the adsorbent surface. It can be assumed that this condition is fulfilled in the uppermost practical cases, but it cannot be proved exactly because typically only the concentrations of micropollutant and NOM (DOC) are available but the EBC parameters are unknown.

iii. Since the simplified approach is a special case of EBCM it underlies the same restrictions. In particular, it is not possible to describe the NOM adsorption behaviour in parallel to the micropollutant adsorption.

EXAMPLE: ATRAZINE AND DIURON ADSORPTION IN THE PRESENCE OF NOM

The application of the models discussed above will be demonstrated by taking the adsorption of two pesticides, atrazine and diuron, onto activated carbon F 300 as an example. The single-solute and multi-component isotherms were measured by Rabolt (1998) at room temperature. River water from the Elbe River was used as NOM-containing water after biological stabilization (removal of the biode-gradable NOM fraction). The DOC concentration of the stabilized water was different in both experiments ($5.22\ \text{mg}\,l^{-1}$ and $4.4\ \text{mg}\,l^{-1}$, respectively). The results of the adsorption analyses are given in Table 2. The single-solute isotherms were measured with solutions of the adsorbates in pure water (Milli-Q). The Freundlich iso-therm parameters found by nonlinear regression are $K = 92.4\ (\text{mg}\,\text{g}^{-1})/(\text{mg}\,l^{-1})^n$ and $n = 0.48$ for atrazine and $K = 125\ (\text{mg}\,\text{g}^{-1})/(\text{mg}\,l^{-1})^n$ and $n = 0.44$ for diuron, respectively. All competitive adsorption calculations were done with software developed by the author.

Figure 7 shows the pesticide adsorption isotherms for the adsorption from pure water and from Elbe River water as well as the results of model calculations based on the conventional IAS theory without any data correction. As can be seen from the isotherms, the adsorption of atrazine and diuron is strongly reduced in the presence of NOM. However, the conventional IAST based on the micropollu-tant single-solute adsorption data and the adsorption analysis overestimates the NOM influence. Both micro-pollutants were better adsorbed than predicted by the IAST. Similar results were also found for other micropollutants (Rabolt 1998) adsorbed from the same river water. It seems that the weaker competition effects in real water in comparison to the IAST prediction supports the assumption
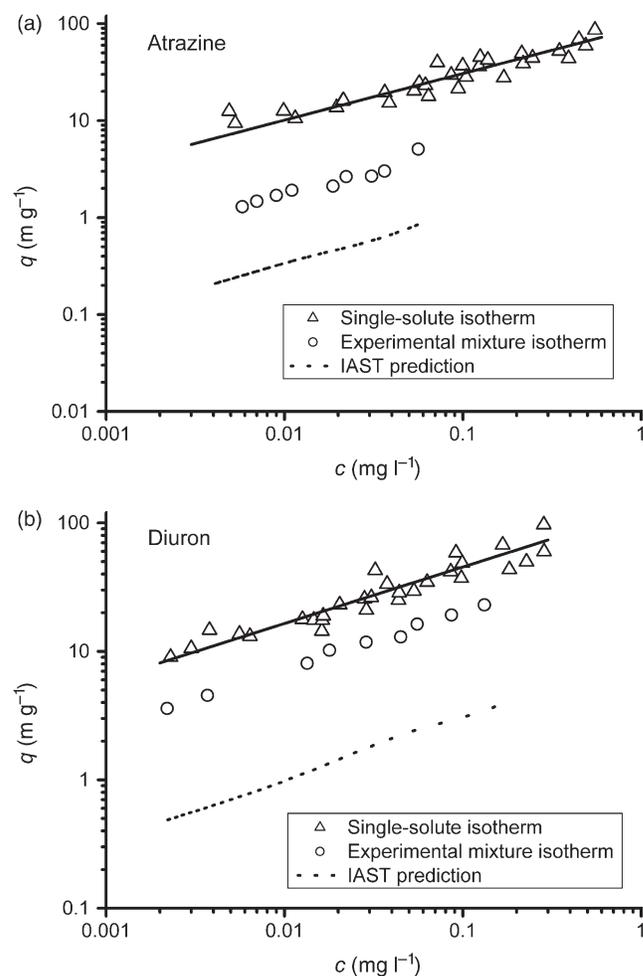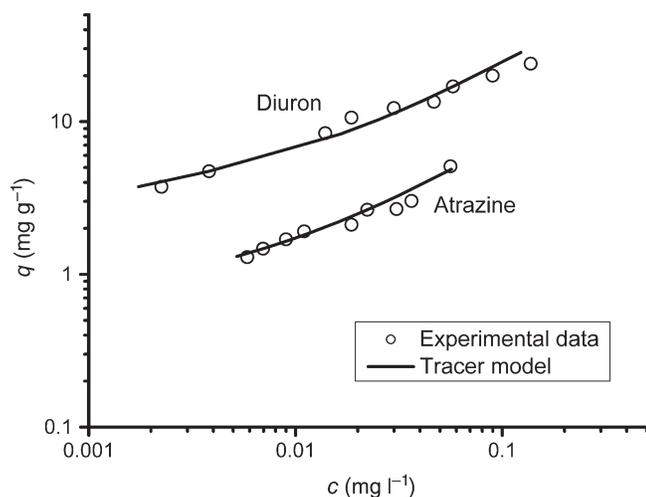

Figure 7 | Adsorption isotherms of atrazine (a) and diuron (b) on activated carbon F 300 from pure water and from Elbe River water. DOC concentrations of the river water: $5.22\ \text{mg}\,l^{-1}$ (a), $4.4\ \text{mg}\,l^{-1}$ (b).

of the EBC model that only a fraction of NOM is able to compete with the micropollutant. However, as shown in the discussion above, other reasons for the differences between experiment and prediction have to be taken into account.

In Figure 8 the results of the application of the tracer model are shown. In TRM calculations the same concentration units (related to C) for the micropollutant and the fictive components were used. Therefore, also the Freundlich K values of the micropollutant given here are related to the C content. From the fitting procedure based on the TRM the corrected single-solute isotherm parameters $K = 31.2$ (mg C g^{-1})/(mg C l^{-1})^n and $n = 0.13$ were found for atrazine. For comparison, the original isotherm parameters found from the single-solute isotherm are $K = 60.6$ (mg C g^{-1})/(mg C l^{-1})^n and $n = 0.48$. The corrected parameters found for diuron were $K = 72.8$ (mg C g^{-1})/(mg C l^{-1})^n and $n = 0.19$ (original: $K = 81.2$ (mg C g^{-1})/(mg C l^{-1})^n and $n = 0.44$).

By using these corrected parameters together with the results of the adsorption analyses, a good description of the experimental data can be achieved. The mean percentage error of the equilibrium concentrations and loadings is 5.3% for atrazine and 8.3% for diuron, respectively.

When using the EBC model the number of fitting parameters can vary between one and three. One-parameter fitting means that n and K of the EBC is set to the values of the respective micropollutant and the EBC concentration is the only fitting parameter, whereas in two-parameter fitting only n is set to the micropollutant value and K is fitted together with the EBC concentration. In the case of three-parameter fitting, the concentration and both isotherm parameters of the EBC are determined by curve fitting. If both isotherm parameters as well as the initial concentration of the equivalent background component are used as fitting parameters, problems may arise in view of the uniqueness of the results. Reducing the number of fitting parameters leads to unique results, but the fitting quality slightly decreases (Table 3). But in the examples discussed here, the assumption of an EBC that has the same isotherm parameters as the micropollutant (atrazine: $K = 5.6$ (mmol g^{-1})/(mmol l^{-1})^n, $n = 0.48$; diuron: $K = 5.9$ (mmol g^{-1})/(mmol l^{-1})^n, $n = 0.44$) would be absolutely sufficient to describe the competitive adsorption of NOM and micropollutant (Figure 9). In this case the only fitting parameter, the EBC concentration, was found to be 0.009 mmol l^{-1} for the system NOM/atrazine and 0.003 mmol l^{-1} for the system NOM/diuron.

As already discussed, a direct comparison of the EBC and the measured DOC concentration is not possible because the molecular weight and the carbon content of the EBC are unknown. However, to get an impression of the order of magnitude of the EBC concentration in terms of DOC, the DOC concentrations were calculated for an assumed NOM molecular weight of 500 g mol^{-1} and an assumed carbon content of 50%. Under these conditions the

Figure 8 | Mixture isotherms of atrazine and diuron: experimental data in comparison with results of the tracer model. Activated carbon: F 300, NOM background: Elbe River water (for fictive components see Table 2).

**Table 3** | EBC parameters found from the pesticide mixture isotherms by one-, two-, and three-parameter fitting

Fitted EBC parameter	c_0 mmol l^{-1}	K (mmol g^{-1})/ (mmol l^{-1})^n	n	Mean percentage error %
NOM/atrazine				
1 (c_0)	0.009	5.60 (A)	0.48 (A)	5.13
2 (c_0, K)	0.009	4.97	0.48 (A)	5.04
3 (c_0, K, n)	0.003	0.67	0.26	4.08
NOM/diuron				
1 (c_0)	0.003	5.9 (D)	0.44 (D)	3.70
2 (c_0, K)	0.003	5.22	0.44 (D)	2.98
3 (c_0, K, n)	0.008	34.62	0.71	2.49

(A) Set to the value of atrazine (fixed value), (D) set to the value of diuron (fixed value).
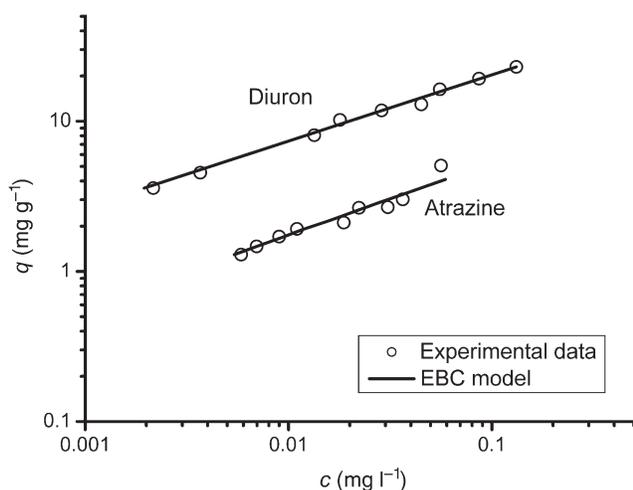
Figure 9 | Mixture isotherms of atrazine and diuron: experimental data in comparison with results of the EBC model. Activated carbon: F 300, NOM background: Elbe River water (for EBC characteristics see Table 3).

DOC concentrations of the EBC would be $2.25 \, mg \, l^{-1}$ in the NOM/atrazine system and 0.75 in the NOM/diuron system. Both values are lower than the total DOC concentrations of 5.22 and $4.4 \, mg \, l^{-1}$ and therefore in accordance with the assumption of the EBCM that only a fraction of the DOC can compete with the micropollutant. On the other hand, the EBC is a fictive component which cannot be characterized independently in view of molecular weight, carbon content and isotherm parameters. Consequently, despite the plausible theoretical explanation, the EBC model is only a formal correction method for IAST
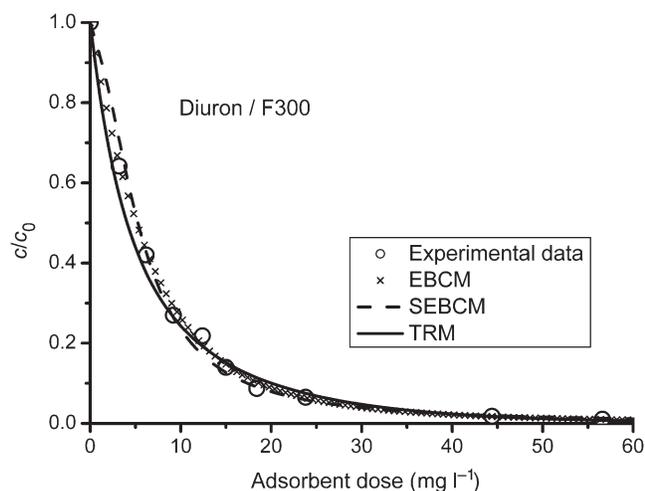
Figure 10 | Relative diuron removal as a function of adsorbent dose. Comparison of the tracer model (TRM), the equivalent background model (EBCM), and the SEBCM approach by Qi et al. (2007).

calculation in NOM/micropollutant systems. From this point of view, the EBCM provides no advantage over the TRM. Because of the uncertainties in the fitting procedure and the limited comparability of the EBC data with measured DOC concentrations, no further conclusions can be drawn in view of a closer characterization of the NOM.

In addition to the more general models, EBCM and TRM, the simplified EBC model (SEBCM) was also used to describe the competitive adsorption in the atrazine/NOM and diuron/NOM systems. Fitting the raw data (c/c_0, adsorbent dose) from the isotherm experiments by using Equation (8), the parameters $n_1 = 0.73$ and $\ln A = -6.33$ were found for atrazine and $n_1 = 0.55$ and $\ln A = -9.55$ for diuron. These parameters can be used to calculate removal curves $c/c_0 = f(m_A/V)$ for the micropollutant. As an example, Figure 10 shows a comparison of the removal curves for diuron calculated by the SEBCM and the more general models TRM and EBCM. The curves found from the different models are nearly identical and all curves reflect the experimental data well. It is obvious that, in the system diuron/NOM, Equation (6) is a good approximation for the IAST/EBCM. Comparable results were found for atrazine/NOM.

CONCLUSIONS

- The presented examples, as well as the results of several other studies, show that the conventional IAS theory is not able to predict the competitive adsorption of micropollutants and NOM exactly. The IAST overestimates the competition and predicts a weaker adsorption of the micropollutant in comparison to experimental findings.
- The tracer model as well as the EBC model can be used to overcome this problem, but this is accompanied by the loss of the opportunity to predict the equilibrium data without any mixture adsorption data. Both models require a mixture isotherm of the micropollutant measured with the NOM-containing water. The parameters found from the models can be used for any other adsorption modelling with the same micropollutant/NOM system: for example, for adsorber design. For other waters, these parameters have to be re-determined.

- In contrast to the tracer model, the EBC model was developed on the basis of the theoretical assumption that there is a limited accessibility of the NOM to the adsorbent micropores. But in the practical use, both models inhibit the character of an empirical IAST correction method. The parameters found from the models do not allow for any further interpretations.

- In view of the experimental effort there are only slight differences between the models. Both models require the determination of two experimental isotherms. In the case of the TRM, the DOC isotherm (as the basis for the adsorption analysis) and the micropollutant mixture isotherm are needed. Under favourable conditions both isotherms can be determined in parallel within a single set of experiments because the contribution of the micropollutant to the DOC is negligible and both concentrations can be independently measured from the same water sample. The knowledge of the micropollutant single-solute isotherm is not obligatory for this model. The EBC model requires the knowledge of the single-solute as well as the mixture isotherm of the micropollutant.

- The results of the adsorption analysis determined for the tracer model can also be used to calculate the adsorption behaviour of NOM. That means that the same parameter set can be used to characterize the NOM adsorption and the micropollutant adsorption under the influence of NOM. This is an advantage in comparison to the EBC model, because the EBC data are only suitable to describe the micropollutant mixture isotherm but they are not able to characterize the typical NOM adsorption in terms of DOC.

- The EBC model considers only two components and is therefore less complex than the TRM. In particular, if the same K and n values for EBC and micropollutant are used (one-parameter fitting), a further simplification of the IAST equations is possible. But because of the availability of user-friendly IAST software this simplification does not provide a notable advantage.

- At the present level of knowledge, there is no clear advantage for one of the models as long as only the micropollutant adsorption in NOM-containing water is of interest. If the NOM adsorption should be characterized in addition to the micropollutant adsorption, the application of the tracer model is to be recommended.

- For batch adsorption systems a simplified approach can be used to describe competitive adsorption. Under the condition that NOM dominates the surface loading, the relative micropollutant removal as a function of adsorbent dose becomes independent of the initial micropollutant concentration. In this case a 'characteristic' removal curve exists that can be described by a simple equation with two parameters. Therefore, only one experimental curve is necessary to determine all parameters needed for characterizing micropollutant adsorption in the presence of NOM. There are three limitations of the simplified model: i) the model is restricted to batch adsorber design; ii) the preconditions for the simplification cannot be proved independently; and iii) the NOM adsorption cannot be described.

REFERENCES

Aiken, G. & Cotsaris, E. 1995 Soil and hydrology: their effect on NOM. *J. Am. Water Works Assoc.* **87**(1), 36–45.

Amiri, F., Börnick, H. & Worch, E. 2005 Sorption of phenols onto sandy aquifer material: the effect of dissolved organic matter (DOM). *Water Res.* **39**(5), 933–941.

Burwig, G., Worch, E. & Sontheimer, H. 1995 A new method to calculate the adsorption behaviour of organic trace compounds in mixtures (Eine neue Methode zur Berechnung des Adsorptionsverhaltens von organischen Spurenstoffen in Gemischen). *Vom Wasser* **84**, 237–249.

Carter, C. W. & Suffet, I. H. 1982 Binding of DDT to dissolved humic materials. *Environ. Sci. Technol.* **16**(11), 735–740.

Carter, M. C., Weber, W. J., Jr & Olmstead, K. P. 1992 Effects of background dissolved organic matter on TCE adsorption by GAC. *J. Am. Water Works Assoc.* **84**(8), 81–89.

Gillogly, T. E. T., Snoeyink, V. L., Elarde, J. R., Wilson, C. M. & Royal, E. P. 1998 14C-MIB adsorption on PAC in natural water. *J. Am. Water Works Assoc.* **90**(1), 98–108.

Graham, M. R., Summers, R. S., Simpson, M. R. & MacLeod, B. W. 2000 Modelling equilibrium adsorption of 2-methylisoborneol and geosmin in natural waters. *Water Res.* **34**(8), 2291–2300.

Hartig, C., Ernst, M. & Jekel, M. 2001 Membrane filtration of two sulphonamides in tertiary effluents and subsequent adsorption on activated carbon. *Water Res.* **35**(16), 3998–4003.

Hobby, R. 1995 *Removal of Organic Pollutants by Powdered Activated Carbon (Entfernung organischer Störstoffe im Spurenbereich mit pulverförmiger Aktivkohle)*. PhD Thesis, Gerhard Mercator Universitat, Duisburg, Germany.

Johannsen, K. & Worch, E. 1994 A mathematical method for realizing adsorption analyses (Eine mathematische Methode zur Durchführung von Adsorptionsanalysen). *Acta hydrochim. hydrobiol.* **22**(5), 225–230.

Knappe, D. R. U., Matsui, Y., Snoeyink, V. L., Roche, P., Prados, M. J. & Bourbigot, M.-M. 1998 Predicting the capacity of powdered activated carbon for trace organic compounds in natural waters. *Environ. Sci. Technol.* **32**(11), 1694–1698.

Kümmel, R. & Worch, E. 1990 *Adsorption from Aqueous Solutions (Adsorption aus wässrigen Lösungen)*. Deutscher Verlag für Grundstoffindustrie, Leipzig.

Matsui, Y., Colas, F. & Yuasa, A. 2001 Removal of synthetic organic chemical by PAC-UF systems. II: Model application. *Water Res.* **35**(2), 464–470.

Matsui, Y., Fukuda, Y., Inoue, T. & Matsushita, T. 2003 Effect of natural organic matter on powdered activated carbon adsorption of trace contaminants: characteristics and mechanisms of competitive adsorption. *Water Res.* **37**(18), 4413–4424.

Myers, A. L. & Prausnitz, J. M. 1965 Thermodynamics of mixed-gas adsorption. *Am. Inst. Chem. Eng. J.* **11**(1), 121–127.

Najm, I. N., Snoeyink, V. L. & Richard, Y. 1991 Effect of initial concentration of a SOC in natural water on its adsorption by activated carbon. *J. Am. Water Works Assoc.* **83**(8), 57–63.

Newcombe, G., Morrison, J., Hepplewhite, C. & Knappe, D. R. U. 2002a In the (adsorption) competition between NOM and MIB, who is the winner, and why? *Water Sci. Technol. Water Suppl.* **2**(2), 59–67.

Newcombe, G., Morrison, J., Hepplewhite, C. & Knappe, D. R. U. 2002b Simultaneous adsorption of MIB and NOM onto activated carbon. II. Competitive effects. *Carbon* **40**(12), 2147–2156.

Nowotny, N., Epp, B., von Sonntag, C. & Fahlenkamp, H. 2007 Quantification and modeling of the elimination behavior of ecologically problematic wastewater micropollutants by adsorption on powdered and granulated activated carbon. *Environ. Sci. Technol.* **41**(6), 2050–2055.

Pelekani, C. & Snoeyink, V. L. 1999 Competitive adsorption in natural water: role of activated carbon pore size. *Water Res.* **33**(5), 1209–1219.

Poerschmann, J., Kopinke, F. D., Plugge, J. & Georgi, A. 1999 Interactions of organic chemicals (PAH, PCB, triazines, nitroaromatics and tinorganic compounds) with dissolved humic matter. In: Davies, G. & Ghabbour, E. A. (eds) *Understanding Humic Substances: Advanced Methods, Properties and Applications*. The Royal Society of Chemistry, Cambridge, pp. 223–240.

Qi, S., Schideman, L., Mariñas, B. J., Snoeyink, V. L. & Campos, C. 2007 Simplification of the IAST for activated carbon adsorption of trace organic compounds from natural water. *Water Res.* **41**(2), 440–448.

Rabolt, B. 1998 *Investigation of the Competitive Adsorption of Micropollutants and Natural Organic Water Constituents (Untersuchungen zur konkurrierenden Adsorption von Mikroverunreinigungen und natürlichen organischen Wasserinhaltsstoffen)*. PhD Thesis, Dresden University of Technology, Dresden.

Rabolt, B., Heubach, J., Schilling, H. & Worch, E. 1998 Investigations into the competitive adsorption of chlorinated hydrocarbons and organic background compounds of the Elbe River (Untersuchungen zur konkurrierenden Adsorption von chlorierten Kohlenwasserstoffen und organischen Hintergrundkomponenten der Elbe). *Vom Wasser* **90**, 135–151.

Radke, C. J. & Prausnitz, J. M. 1972 Thermodynamics of multisolute adsorption from dilute liquid solutions. *Am. Inst. Chem. Eng. J.* **18**(4), 761–768.

Schideman, L. C., Mariñas, B. J., Snoeyink, V. L. & Campos, C. 2006a Three-component competitive adsorption model for fixed-bed and moving-bed granular activated carbon adsorbers. Part I. Model development. *Environ. Sci. Technol.* **40**(21), 6805–6811.

Schideman, L. C., Mariñas, B. J., Snoeyink, V. L. & Campos, C. 2006b Three-component competitive adsorption model for fixed-bed and moving-bed granular activated carbon adsorbers. Part II. Model parameterization and verification. *Environ. Sci. Technol.* **40**(21), 6812–6817.

Sontheimer, H., Crittenden, J. C. & Summers, R. S. 1988 *Activated Carbon for Water Treatment*. DVGW-Forschungsstelle, Engler-Bunte-Institut, Universität Karlsruhe.

Weber, W. J., Jr. 2004 Preloading of GAC by natural organic matter in potable water treatment systems: Mechanisms, effects and design considerations. *J. Water Supply Res. Technol.–AQUA* **53**(7), 469–482.