**Drinking Water
Engineering and Science
Discussions**

# Interactive comment on "Development of a predictive model to determine micropollutant removal using granular activated carbon" by D. J. de Ridder et al.

**Anonymous Referee #2**

Received and published: 23 November 2009

The problem of predicting the adsorption behaviour of micropollutants during drinking water treatment with activated carbon is still unsolved. Therefore, the subject of this paper is of high relevance. To use QSARs as predicting tools is a new and interesting approach. Unfortunately, there are some critical points in the paper:

1. Page 192, line 22: In this sentence, cause and effect are inverted. The pKa is not a specific pH value, but the negative logarithm of the acidity constant (the equilibrium constant for the acid dissociation reaction). It follows from this definition and from the mass action law that at pH = pKa 50 % of an acid is dissociated or deprotonated and also that the degree of dissociation is 1% at pH = pKa-2 and 99% at pH = pKa+2.

2. Taking into account the definition of pKa and the relationship between pKa, pH, and degree of dissociation, it is problematic to give the solutes such absolute attributes as negatively charged, neutral, or positively charged (see table 1). Acids and bases can be neutral or charged (negatively as acid anions or positively as protonated bases) depending on pKa and pH. Within the range of pH = pKa +/- 2 both neutral and ionic forms of acids or bases are present. For instance, the authors have written that the ultrapure water has a pH of 4. If this is true (?), all of the solutes designated as positively charged are not totally positively charged, i.e., positive and neutral species coexist, because all pKa are not far from 4. In some cases (pKa >4) even the neutral species dominate. The same is true for the weak bases designated as positively charged. In the surface water (pH = 8) most of these compounds are not fully protonated, i.e., also neutral species are present, because all pKa values are lower than 10.

3. According to the definition, the pKa of neutral compounds cannot be set to 0 (see Table 1), because this would mean that these compounds are acids with an acidity constant of 1. Furthermore, it has to be distinguished between solutes which are "neutral" because they are neither acids nor bases (no pKa can be given) and solutes which are neutral only under the given pH conditions. For instance, the solute carbamazepine has a pKa of 13.9 (not 0 as written in the table 1). Therefore, it is neutral under all pH conditions in this study.

4. To characterize the charge of the species in the QSAR by a fictive parameter with the values -1, 0, +1 seems to be a strong simplification. As discussed above, a "negatively charged" solute could consist in reality e.g. of 50% neutral and 50% negatively charged species, whereas another solute at the same pH could consist of 10 % neutral and 90% negatively charged species. In the QSAR both solutes would get the same parameter value -1.

5. The pKa and therefore also the charge is considered twice in the QSAR: via charge parameter (see discussion above) and via log D definition where the dissociation/protonation leads to a reduced log KOW. Therefore, the first and the second

term of the QSAR equations are not independent.

6. The attraction/repulsion effect during adsorption onto fresh carbon depends on the charge of the solute and the charge of the adsorbent surface. An important parameter to characterize the adsorbent surface charge is the pH(pzc). If attraction/repulsion can be expected depends on the pH(pzc), the pKa, and the pH of the solution. Therefore, negative charges leads to lower adsorption (repulsion effect) only, if pH>pH(pzc) and pH > pKa-2 (negatively charged surface and negatively charged solute). The missing charge effect in case of pure water is possibly due to a positively charged adsorbent surface (the pH(pzc) of activated carbons is often in the range of 7..8). Unfortunately, the pH(pzc) is not given in table 2.

7. Page 194, line 24: The discussion on the missing MW influence is incomplete. The MW can influence the adsorption in different ways: by size exclusion (only relevant for higher MWs) and by influencing the polarizability and therefore the strengths of dispersion interactions (London forces). As long as no size exclusion occurs, the adsorption should increase with increasing MW (of course only as a trend, depending on the strength of other interactions or effects).

8. Page 195, line 5: The effect that the percentage removal is independent of the initial concentration is not a general effect. It can be observed only in trace component/NOM competitive adsorption systems and can be explained by the IAST.

9. Page 197, line 9 and the following: The deviations in Figs. 2a and b are often higher than discussed in the text. For instance, in Fig. 2a the predicted value for 30% measured removal (ultrapure water) is 60%. This is an overprediction of 100 % whereas in the text a maximum of 40% overprediction is mentioned. Possibly, the absolute deviation is discussed (in this case 60% removal-30% removal), but a percentage deviation always implies a relative value.

10. Some formal errors: Page 190, line 25 and references: The right name is Schwarzenbach, not Schwartzenbach. Page 191, line 23: replace of by or Page

191, line 23: full dissociation/protonation is not exact (exactly 99%), therefore "nearly" should be inserted. Table 2: "Activation method" is not a parameter and "steam" is not a value.

All in all, a thorough revison is recommended.