



Letter to the Editor

Bias by the inappropriate use of the pseudo-first order approach to estimate second-order reaction rate constants: Reply to the commentary by Tratnyek (this issue)



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We thank Dr. Tratnyek (2015—in this issue) for taking an interest in our recent research on the determination of kinetic rate constants for the oxidation of several volatile organic compounds (Mahmoodlu et al., 2014). His comments provide a valuable perspective on the relevance of our results and we appreciate the opportunity to elaborate on the key aspects raised and to emphasize their importance, particularly so for the bias in second-order rate constants estimated with inappropriate use of the pseudo-first order approach.

To determine second-order rate constants experimentally, a pseudo first-order approach is routinely used experimentally and described in many chemistry textbooks (e.g. Atkins and de Paula, 2006). In this approach, one of two reactants is supplied in excess to support the assumption that its concentration change during the experiment is negligible. In the commentary, it is rightfully stressed that our study clarifies how the error in the estimated second-order rate constant decreases with increasing amounts of the actual stoichiometric excess used. Although theoretically this error never actually reaches zero, we did not mean to question the general applicability of the pseudo-first order approach. A negative bias of less than 5% in the estimate for a stoichiometric excess ratio (P/N) of over 40 (Fig. 4 in Mahmoodlu et al. (2014)) might indeed be considered acceptable by some practitioners. However, as shown, previously published pseudo-first order based estimates of the second-order rate constant for the oxidation of TCE by permanganate appear to be negatively biased by up to 20% with respect to our recalculated estimates. This bias is unnecessary, and does no service to the concept of a rate “constant”.

Many other studies have presented pseudo-first order based estimates, but did not present the raw experimental data to allow the recalculation of the second-order rate constants. Fig. 1 in the commentary presents a renewed summary of published estimates for second-order rate constants for the oxidation of TCE by permanganate as if these were all equally valid, regardless of whether the “sufficient excess” assumption was appropriate for all included pseudo-first order estimates. This goes against the key point in Mahmoodlu et al. (2014) which stresses that bias in the estimates of second-order rate constants is introduced by the inappropriate use of the pseudo-first order approach. Perhaps we should have further emphasized that studies that summarize second-order rate constants without considering these biased estimates (Waldemer and Tratnyek, (2006)) unnecessarily exaggerate the

overall range within which the rate constant appears to vary beyond analytical and experimental uncertainties.

Although the recalculation of the second-order rate constant with a second-order model would be favorable, the stoichiometric excess used in the experiments allows estimating the amount of bias in these estimates. It is important to re-emphasize here that the stoichiometric excess (P/N) is defined as the initial molar ratio between the reactants, divided by the molar ratio in the stoichiometric reaction between them, with for both ratios the reactant in excess in the numerator. As an illustration, the detailed TCE oxidation experiments by Waldemer and Tratnyek (2006, Supporting Information) were performed with stoichiometric excess (P/N) of 20 to 80. As can be derived from Fig. 4 in Mahmoodlu et al. (2014), this suggests that the lower end of these P/N values likely yielded underestimations by 5 to 10% with respect to an unbiased second-order model estimate. Since the reaction rate constant for TCE is insensitive to pH in the range of 4–8 and the temperature range (20–25° C) was limited for the included studies (Waldemer and Tratnyek, 2006), it is likely that the use of insufficient excess in the pseudo-first order approach is a major contributor to the standard deviation of 20% in reported literature estimates reported by Tratnyek (2015—in this issue).

To support the use of permanganate for particular contaminants of concern, a detailed understanding of the reaction kinetics is desirable (Waldemer and Tratnyek, 2006). Nevertheless, we agree with the commentary that there are many uncertainties in the overall field performance of a remediation effort, such as site heterogeneity and lack of characterization that limit the efficient delivery of oxidant to contaminants. Still, we see no point in adding further uncertainty by using inappropriate assumptions in the data processing from elaborate lab experiments. Moreover, in the actual removal of contaminants through oxidation, reaction rate constants are key in describing the rate with which this is expected to occur and to what extent the removal of contaminants is e.g. impacted by kinetic competition for oxidants by non-target species in a particular groundwater system.

Particularly for contaminants that are more slowly oxidized by permanganate, such as toluene and ethanol, bias in the reaction rate constant may significantly affect the rate with which they are expected to be removed in the field. In contrast with TCE, the oxidation rate of ethanol and aromatic compounds such as toluene is known to strongly depend on pH (e.g. Sen Gupta et al., 1989; Lobachev et al., 1997). Rather than presenting pH-affected estimates of reaction rate constants as a “range” (as in Fig. 1 in the commentary), it is our opinion that considering the known pH dependencies for the oxidation of such compounds is essential in the establishment of appropriate values for their rate constants. However, thus far there have been insufficient kinetic studies in the oxidation of toluene and ethanol within the full pH range that may be encountered during field application. Therefore, we agree with Dr. Tratnyek that the kinetics of permanganate oxidation of ethanol, toluene and other fuel related contaminants should be a priority area for future research.

For future kinetic research, we do consider the use of the second-order kinetic model preferable over the use of the pseudo-order rate

model for deriving second-order rate constants, because the validity of the estimate is insensitive to the degree of stoichiometric excess used in the experiment. That is not to say that reliable estimates cannot be derived from a pseudo-first order approach, just as long as the stoichiometric excesses used are sufficiently high to result in negligible bias. With our caution for the bias introduced by inappropriate use of the pseudo-first order approach (Mahmoodlu et al., 2014) we hope that the derived reaction rate constants in future studies will yield values that, for particular environmental conditions, will indeed resemble constants.

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