

***Interactive comment on* “Substrate effects in the photoenhanced ozonation of pyrene” by S. A. Styler et al.**

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We thank the reviewer for the careful reading of the MS. Below, we respond to each point in turn.

Comment: On page 27828, the authors state that oxidation of PAH in films may have implications for human health. I do not think it is likely as in most cases the oxidation products remain in the film and therefore cannot easily come in direct contact with humans. Is there evidence of significant health effects through skin contact with urban surfaces?

Response: We have modified this section to more clearly reflect the current state of knowledge regarding urban film-related health concerns. In the revised manuscript,

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this portion now reads:

“Given that the products of PAH ozonation are themselves photoactive (Mmereki et al., 2004), these results imply that oxidative processes occurring within urban films not only may significantly influence the lifetime and relative abundance of PAH species but also may promote other heterogeneous photoprocesses. The products of PAH ozonation, which typically display enhanced toxicity (Luster-Teasley et al., 2005; Luster-Teasley et al., 2002), would not be expected to partition into the gas phase. Rather, their residence time in the film would be expected to be limited by rain-induced washoff, which has been shown to transfer the vast majority of PAH species to urban surface waters regardless of polarity (Labencki et al., unpublished manuscript). This phenomenon has the potential to act as a pathway for contamination of urban soils and vegetation.”

Comment: On page 27830, I would replace “5X” by “5 times”. Same comment applies to Fig. 3 caption.

Response: The revised manuscript incorporates this suggestion.

Comment: On page 27834, the authors state that “At the surface of a more dilute pyrene solution, the same dependence upon ozone concentration was observed.” There is no evidence to support this statement in Figure 3. There is just one point measured at a lower concentration - not enough to infer the dependence.

Response: Although we performed a set of experiments in which the heterogeneous loss rate of dilute solutions of pyrene was explored as a function of gas-phase ozone concentration, the data obtained in these experiments were omitted from Figure 3 for purposes of clarity. We have revised the manuscript to more clearly reflect this omission: “At the surface of a substantially more dilute pyrene solution, we again observed a linear dependence of pyrene loss rate on ozone concentration (not shown in Figure 3).”

Comment: I found the discussion of the mechanism R1–R6 on page 27840 and the

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statement “We attribute this change in mechanism to an increased favourability of A-type pathways at the highly polar air–aqueous interface” too qualitative. I would prefer to see this mechanism contrasted with the Langmuir–Hinshelwood for the illuminated as well as dark oxidation so that the differences these mechanisms can be better emphasized.

Response: We have included the following discussion after the mechanism R1–R6 in order to address these comments:

“If the electron-transfer/hydrolysis steps (R3 and R4) are sufficiently fast, the concentration of adsorbed ozone at the illuminated aqueous surface will be small. Under these conditions, loss of pyrene at the interface may be dominated by reaction with hydroxyl radical (R5) rather than with adsorbed ozone (R2). In this manner, the Langmuir–Hinshelwood mechanism observed in the dark, which would involve reaction between co-adsorbed pyrene and ozone, would evolve into one in which the ozone dependence reflects the delivery of gas-phase ozone to the surface, where its reduction is very rapid.”

Comment: Finally, can the authors rule out the possibility that Langmuir–Hinshelwood still applies at the aqueous illuminated surface but the parameter B is increased significantly?

Response: On the basis of our data alone, we cannot explicitly rule out this possibility. Nonetheless, we see no plausible mechanism by which the propensity of ozone to adsorb to the aqueous surface would be changed by illumination, especially given that our previous results have shown that the B parameter for ozonation is identical for illuminated and dark pyrene solid films (Styler et al., 2009). While our results suggest that illumination of pyrene at the aqueous surface leads to the formation of polar charge-transfer intermediates, the surface density of these polar intermediates is likely too small to significantly influence macroscale partitioning processes. Work by Kwamena et al. (Kwamena et al., 2007), which found that the B parameter for ozonation

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of a variety of PAHs varies primarily as a function of substrate identity rather than as a function of the organic species sorbed to it, provides support for this assertion.

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