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Emissions of organic compounds from produced water ponds III: Mass-transfer coefficients, composition-emission correlations, and contributions to regional emissions

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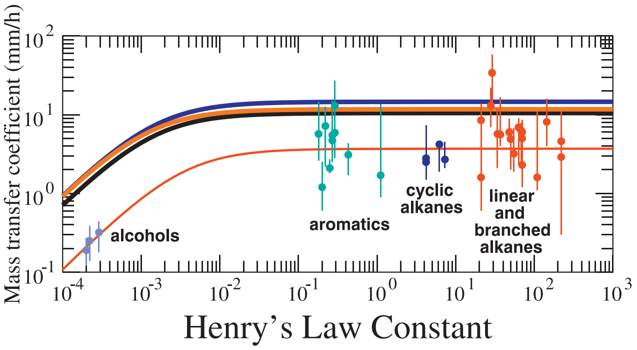
HIGHLIGHTS

- Prediction of produced water pond emissions from concentration data.
- Semi-empirical WATER9 algorithm valid to within about one order of magnitude.
- Ponds contribute significantly to total regional VOC and methanol emissions.

GRAPHICAL ABSTRACT



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ABSTRACT

A common method for treating the aqueous phase (produced water) brought to the surface along with oil and natural gas is to discharge it into surface impoundments, also known as produced water ponds. Here we analyze data on the concentration of organic compounds in the water and on the flux of the same compounds into the atmosphere. Flux data extending from about 5×10^{-2} to 10^{+3} mg m^{-2} h^{-1} are consistent with mass-transfer laws given by the WATER9 semi-empirical algorithm, although empirical data display a noise level of about one order of magnitude and predictions by WATER9 are biased high. The data suggest partitioning between hydrocarbons in aqueous solution and in suspension, especially at higher overall concentrations. Salinity of the produced water does not have a detectable effect on hydrocarbon fluxes. Recently impounded waters are stronger emitters of hydrocarbons, while emissions of older waters are dominated by CO_2. This aging effect can be explained by assuming, first, poor vertical mixing in the ponds, and second, gradual oxidation of hydrocarbons to CO_2. Our measurements account for about 25% of the produced water ponds in the Uinta Basin, Eastern Utah, and when extrapolated to all ponds in the basin, account for about 4% to 14% of all organic compound emissions by the oil and natural gas sector of the basin, depending on the emissions inventory, and about 13% and 58%, respectively, of emissions of aromatics and alcohols.

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1. Introduction

Hydrocarbon reservoirs contain a water phase that comes to the surface along with the hydrocarbons. This so-called produced water is often briny and is contaminated with organics, so that disposal into the hydrosphere is unacceptable. One common treatment is re-injection into spent oil and gas wells. Another treatment, employed frequently in arid regions of the Western USA, is to discharge it into surface impoundments, or "produced water ponds," either for the purpose of evaporation or of storage prior to re-injection. Because of the entrained organics, these ponds emit methane and non-methane volatile organic compounds. However, very little is known about the magnitude or the composition of emissions from these ponds. In two companion papers, we report extensive measurements of emissions from ponds in Eastern Utah and Western Wyoming, including a description of composition, properties, and seasonal trends, measured both by flux chamber and by inverse modeling (Lyman et al., 2018; Tran et al., 2018). This paper gives an analysis of the data reported there. We examine correlations between concentration in the water phase and emission flux into the atmosphere for a suite of organic compounds found in the water. The correlations are strong enough that an order-of-magnitude estimate of flux can be obtained by measuring the water concentration. We also extrapolate from the ponds studied to obtain a regional estimate of flux from all ponds in the Uinta Basin of Eastern Utah, and compare this estimate against total emissions as reported by several inventories. There is significant uncertainty both in our measurements and in the inventories, but we find, depending on the inventory used, that produced water ponds constitute about 4% to 14% of the total organic compound emission in the basin, and 1%, 13%, and 58%, respectively, of the total emission of methane, aromatics, and alcohols.

The data analyzed in this paper were obtained from (Lyman et al., 2018) flux chamber measurements (Eklund, 1992; Leduc et al., 2009; Hafner et al., 2010; Wang et al., 2011) of emissions of methane, non-methane hydrocarbons, light alcohols (methanol, ethanol, and isopropanol), and some carbonyls (formaldehyde and acetaldehyde) from produced water ponds in Eastern Utah and Western Wyoming; and (Tran et al., 2018) measurements of the concentrations of these same compounds in the water phase, determined by GC headspace analysis subsequent to salting, agitation, and heating of samples. These measurements were conducted from 2013 to 2016, covering all four seasons of the year. 82% of the flux chamber measurements occurred in Utah, 18% in Wyoming. For a description of the pond facilities studied and for a complete report of the measurement and analysis methods used, see the first paper in this series (Lyman et al., 2018).

2. Correlations between water-phase concentrations and emissions to the atmosphere

We examine the correlations between the concentration of a volatile compound in a produced water pond and its flux into the atmosphere. If correlations can be found, then it will be possible to quantify emissions by taking water samples. Compounds such as formaldehyde and acetaldehyde that react in the water phase require special treatment, see below. Emissions generally satisfy a mass-transfer law of the form

$$f = Sc \tag{1}$$

where c is the concentration of a volatile compound in the water phase and f is its flux into the atmosphere (Schwarzenbach et al., 2003). The proportionality constant, S, is the "mass-transfer coefficient" or the "transfer velocity." We expect S to be a function of wind speed, of the water and air temperature, and of the partition coefficient between air and water phases, or Henry's Law constant.

Mass-transfer theory holds that thin stagnant films on both the water and air sides of the boundary are the bottlenecks to transport of solutes across the boundary. Turbulent mixing cannot persist across the boundary and is therefore damped out in these films. Solutes must cross them by the relatively slow process of molecular diffusion. Inverse mass-transfer coefficients ("resistivities") for adjacent boundary films are additive (Lyman et al., 2018.; Schwarzenbach et al., 2003; *Air Emissions Models for Waste and Wastewater*, 1994):

$$\frac{1}{S} = \frac{1}{S_w} + \frac{1}{HS_a} \tag{2}$$

where S_w and S_a are respectively transfer coefficients for the water and the air film. H is Henry's Law constant for the compound in water, and here, we use its air-over-water dimensionless form:

$$H = \frac{c_a}{c_w} \tag{3}$$

where c_a and c_w are equilibrium mass or molar concentrations in the air and liquid phases, respectively. Presumably because the measurements are difficult, literature values of H are often not well constrained: Different independent measurements can vary by as much as an order of magnitude (Sander, 1999). Fortunately, most of our compounds are in a regime for which S is insensitive to H, see below. The values we employed are shown in Table 1 and were mainly extracted as means or as consensus values from Sander (1999). Because Henry's constants vary among compounds by many orders of magnitude, one term or the other in Eq. (2) usually dominates, and we have

$$S = S_w \tag{4}$$

and

$$S = HS_a \tag{5}$$

respectively for large and small H.

Fig. 1 displays box-and-whisker plots of the ratio f/c for 36 compounds. There is usually a difference of many orders of magnitude between each maximum and minimum, but the central half of each dataset usually spans about an order of magnitude or less. Effects such as uneven mixing in the ponds; the possibility that organics in the water phase might actually be in suspension rather than solution (below we examine this possibility further); or differences in temperature, wind speed, and salinity probably contribute to the data spread. Table 1 gives empirical S values as the medians of f/C, and the error bars are the 25-th and 75-th percentiles.

Fig. 2 examines the ability of the data to agree with Eq. (1) for methane, benzene, cyclohexane, and the three alcohols. Similar plots, not shown, were developed for all of the compounds studied. On a log-log plot, a proportionality appears as a straight line of slope 1. The solid red line is the best-fit unit-slope line. The pink band is drawn to have a total width of one order of magnitude centered on the red line. It indicates the approximate noise level for these measurements. The blue line is the prediction based on the WATER9 model explained below. Although noisy, many proportionalities hold over 3 or 4 orders of magnitude.

Fig. 3 displays the empirical values of S from Table 1 as functions of H. Our empirical data, although noisy, are consistent with these values of S_a and S_w, obtained by least-squares fitting:

$$S_a = 1110\ \frac{\text{mm}}{\text{h}}, \qquad S_w = 3.7\ \frac{\text{mm}}{\text{h}} \tag{6}$$

Eq. (6) represents S_a and S_w as constants, whereas they are expected to vary with solute, temperature, and salinity. Because our data are noisy, we are able to obtain reasonable fits using just these constants. Fig. 3 indicates that aromatic and alkane compounds obey Eq. (4), i.e., their behavior is independent of H, while the alcohols obey Eq. (5).

We next compare our results with a standard model for S_A and S_W, the so-called WATER9 software package (*Air Emissions Models for*