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Reply to the Comment on "Structural characterization of dissolved organic matter: a review of current techniques for isolation and analysis" by E. C. Minor, M. M. Swenson, B. M. Mattson, and A. R. Oyler, Environ. Sci.: Processes Impacts, 2014, 16, 2064

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Davies et al.[1] have provided a well-written and well-referenced letter that points out the missing CRAM (carboxyl-rich alicyclic molecules) label in Figure 5 of our review paper[2] and the importance of CRAM and MDLT (material derived from linear terpenoids) as DOM components in aquatic samples. Minor et al. 2012[3], which applies a different extraction approach but the same mass spectrometry techniques to Lake Superior DOM, discusses that CRAM fits within the van Krevelen space labeled "lignin-like" but this discussion was not included in our review[2]. Davies et al. [1] make the point much more thoroughly than Minor et al. 2012[3]and add the MDLT idea as well. As was briefly discussed in our review[2], van Krevelen compositional-space identifications from FT-ICR-MS data are tentative as they are based solely on elemental ratios within the identified molecular—not structural—formulas, and their relationships to the elemental ratios in likely model compounds. Thus for more definitive information on the molecular structures in inshore Tasmanian marine surface water[1], additional mass spectrometric or NMR analyses would be appropriate to tease apart whether lignin, CRAM, and MDLT co-occur in this sample. Such coastal marine samples are likely to have multiple autochthonous and allochthonous organic matter sources.

Davies et al.[1] also suggest adding color-coding to increase the information content in van Krevelen visualizations. We employ color-coding in our current work (as shown in Fig. 1) and agree that such an approach should become common practice. When this color-coding is done, CHON and CHONP compounds overlap considerably with the area labeled lignin and/or CRAM based upon O:C and H:C ratios, thus highlighting that such compositional-space determinations are an oversimplification. Screening the compounds to plot only specific formula types (such as the CHO formulas in Davies et al.'s[1] Figure 1a) is one approach to clarify data visualization. However, perhaps the mass spectrometry community needs to investigate additional visualization approaches to improve our ability to investigate the rich data sets delivered by FT-ICR-MS.

References cited:

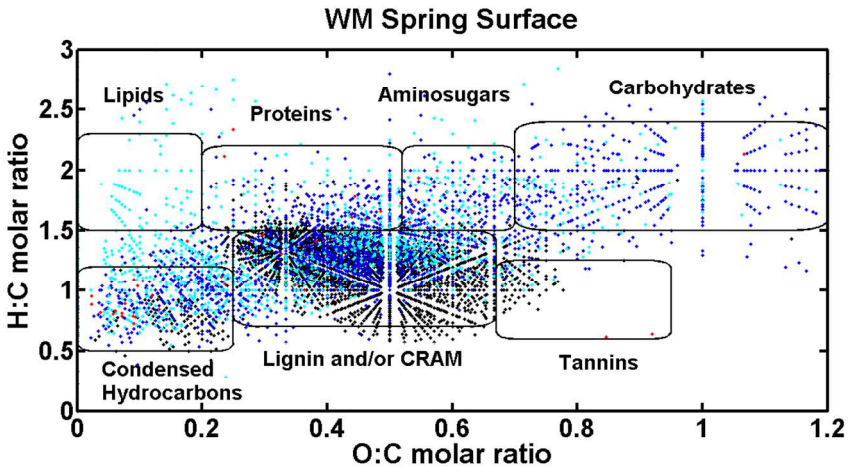
[1.] N. W. Davies, S. Sandron, P. N. Nesterenko, B. Paull, R. Wilson, P. Haddad, R. Shellie, A. Rojas, Environ. Sci.: Processes Impacts, 2015, DOI:C4EM00631C

[2.] E. C. Minor, M. M. Swenson, B. M. Mattson, and A. R. Oyler, Environ. Sci.: Processes Impacts, 2014, 16, 2064-2079.

[3.] E. C. Minor, C. J. Steinbring, K. Longnecker and E. B. Kujawinski, Org. Geochem., 2012, 43, 1–11.

Figure Caption:

Fig. 1. Van Krevelen diagram of formulae (m/z) in solid-phase (SDB-XC) extracted DOM from Lake Superior surface water sampled during spring mixing at 47°19’N, 89°51’W. CHO and CH compounds (black) are overlaid with CHON (blue) compounds which are overlaid with CHONP compounds (cyan). Any CHOP compounds (red) are placed in the top layer. The van Krevelen spaces are divided into seven discrete regions, modified from the diagrams proposed by Hockaday et al. 2009, Kim 2003; Sleighter and Hatcher 2007.



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