

# Influences of pH and oxidation on the leaching potential of As, Cu, Pb and Zn from sediments through a pH<sub>stat</sub>-leaching test in combination of a BCR 3-step extraction

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Since contaminated river-bed sediments in Haiphong Harbor (Vietnam) are regularly dredged and disposed on land, an understanding about the influences of key parameters such as pH and oxidation on the leachability of As, Cu, Pb and Zn is necessary for management and treatment of these dredged wastes. A 96h pH<sub>stat</sub>-leaching test examining the leaching behaviors of elements at pre-set pH values (2, 4, 6, 8 (natural), 9 and 11), is performed on a freshly-collected wet sediment and a 2 month-ripened dry sediment. Additionally, a BCR 3-step extraction is also used to clarify the differences in leachability between 2 types of sediment. The results indicate that the pH-dependent leaching behavior reflects a concave curve with the lowest value at pHs 6 or 8 and the highest value at pH 2 in case of Cu, Pb and Zn, or at pH 11 in case of As. Generally, due to oxidation, the leachability of As and Zn has decreased considerably at highly-acid and highly-alkaline pHs (2–4 and 9–11) while, for Cu and Pb, it has increased at acid pHs (2–6), but decreased at highly-alkaline pHs (9–11). As shown by results of BCR 3-step extraction, for As and Zn, there is a transfer from easily-soluble exchangeable & carbonate fraction to hardly-soluble reducible fraction through oxidation. As a consequence, the smaller exchangeable & carbonate fraction in the oxidized sediment is the cause for the lower leachability of As and Zn at almost all pH values. In contrast, for Cu and Pb, there is a transfer from the oxidizable fraction to the reducible fraction. Therefore, the more important reducible fraction in the oxidized sediment contributes to the higher leachability of Cu and Pb at acid pHs (2–4) while the smaller oxidizable fraction contributes to their lower leachability at alkaline pHs (9–11) if compared with the fresh sediment.

# Is TEX<sub>86</sub> paleothermometry applicable in the polar regions?

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TEX<sub>86</sub> paleothermometry [1] is an organic sea surface temperature (SST) proxy based on the archaeal glycerol dialkyl glycerol tetraethers (GDGT) lipids, which are ubiquitous in the global ocean. This relatively recent proxy potentially offers an advantage over its more established counterpart, i.e. the alkenone unsaturation index, that has limited success in the polar regions due to its absence or extremely low abundance in this realm. Furthermore, the polar regions, especially the Southern Ocean, are severely under-represented in the global TEX<sub>86</sub>-SST calibration data set. Therefore, this study aims to investigate the distribution pattern of GDGTs and to evaluate the applicability of TEX<sub>86</sub> paleothermometry in the polar regions. A principal component analysis (PCA) on the GDGTs data shows that the variance in the relative distribution of the GDGTs in our study region is similar to that of the global data set, suggesting that the lipids are probably contributed by a common group of source organism. However, the TEX<sub>86</sub>-SST relationship in the Arctic differs substantially from that of the Southern Ocean, resulting in poor overall correlation ( $r^2 = 0.06$ ). Meanwhile, the TEX<sup>L</sup><sub>86</sub> [2] fares much better than TEX<sub>86</sub> ( $r^2 = 0.50$ ). Seasonality does not lead to a different TEX<sub>86</sub>- and TEX<sup>L</sup><sub>86</sub>-SST relationship, relative to that of the annual mean. Interestingly, the TEX<sub>86</sub> and TEX<sup>L</sup><sub>86</sub> are found to correlate well, if not better, with the temperature at the base of thermocline and the oxygen minimum zone. At this stage, the explanation for this finding is still elusive. Nevertheless, its implication for paleo reconstruction work could be significant. Therefore, future work shall be focused on the elucidation of the relationship of TEX<sub>86</sub> with the temperature at different water depths, and the reason for the large scatter in the TEX<sub>86</sub> data in the polar regions.

[1] Schouten, Hopmans, Schefuss & Sinninghe-Damsté (2002) *Earth Planetary Science Letters* 204, 265-274. [2] Kim, van der Meer, Schouten, Helmke, Willmott, Sangiorgi, Koc, Hopmans & Sinninghe-Damsté (2010) *Geochimica et Cosmochimica Acta* 74, 4639-4654.