SHIFTS IN THE NATURAL ABUNDANCE $\delta^{13}C$ SIGNATURES OF ESTUARINE PLFAS WITH INCREASED COPPER

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INTRODUCTION

Many antifouling paints, applied to ships' hulls and other marine structures, contain copper (Cu) as an active ingredient. As a result many European waterways are becoming increasingly Cu contaminated. Implications of this on estuarine ecosystem functioning is unknown.

MATERIALS AND METHODS

Figure 1: Sediment was collected from the top ~2 cm of a mud flat on the Ythan estuary (grid ref: NK020275; 57° 20.085'5N, 02° 0.206'5W) Aberdeenshire, UK; then sieved to remove debris and macrofauna.

Figure 2: Sixty mesocosms were constructed containing sediment to a depth of 9 cm and covered in filtered sea water (Fig 2A). The experiment was a factorial design of six Cu concentrations (0 – 1000 mg Cu kg^{-1} dry sediment); in the presence and absence of the marine invertebrate *Corophium volutator* (Fig 2B) and with five replicates.

Figure 3: After 10 d sediment was freeze dried and phospholipid fatty acids extracted. Following derivitisation to their methyl esters; the concentration and $\delta^{13}C$ signatures of individual PLFAs were determined using a GC-C-IRMS (Trace GC, GC II interface and Delta V, all Thermo Scientific, Germany).

RESULTS

- Increased [Cu] caused a reduction in the concentration of many PLFAs (e.g. Fig 4).
- The extent of the reduction was PLFA dependent and resulted in a shift in the microbial community structure (Fig 5). The effect of Cu was greater in the presence of *C. voluator* (Fig 5) possibly due to this organism mixing the sediment.
- Increased [Cu] also caused shifts in the natural abundance $\delta^{13}C$ signatures of individual PLFAs (e.g. Fig 6) and also in the $\delta^{13}C$ signature of the overall PLFA population (Fig 7).

Figure 4: Typical response of an individual PLFA (20:5w3) to increased Cu concentration. Points are mean of 5 replicates ± SD.

Figure 5: Principal component analysis of the proportions of molar PLFA concentrations; points occupying different space indicate a difference in overall PLFA composition and hence a difference in microbial community structure (only two Cu concentrations are shown for clarity).

Figure 6: An illustration of the shift in $\delta^{13}C$ of an individual PLFA (C15:0) caused by increasing Cu concentration. Points are mean of 5 replicates ± SD.

Figure 7: Principal component analysis of the $\delta^{13}C$ signatures of the PLFAs (only two Cu concentrations are shown for clarity).

DISCUSSION

- Observed PLFA $\delta^{13}C$ signatures represent a mean signature from several microbial groups.
- Changes in this mean with increased [Cu] may occur due to differential sensitivity of microbial groups to Cu.
- In the presence of *C. voluator* a further mechanism is possible; greater mortality of *C. voluator* with increased [Cu] providing a new source of carbon with a distinct $\delta^{13}C$ signature.
- No change in the substrates used by the microbes with increased [Cu] is implied, though it may occur.

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