SUPPLEMENTARY MATERIAL

A new processing routine for ultra-high resolution direct infusion mass spectrometry data

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Adjusting isotope abundance

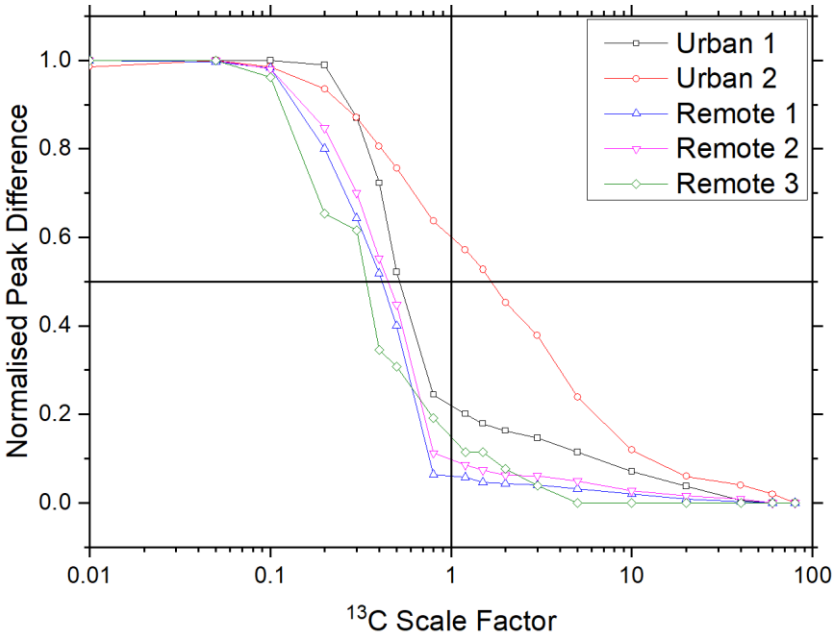
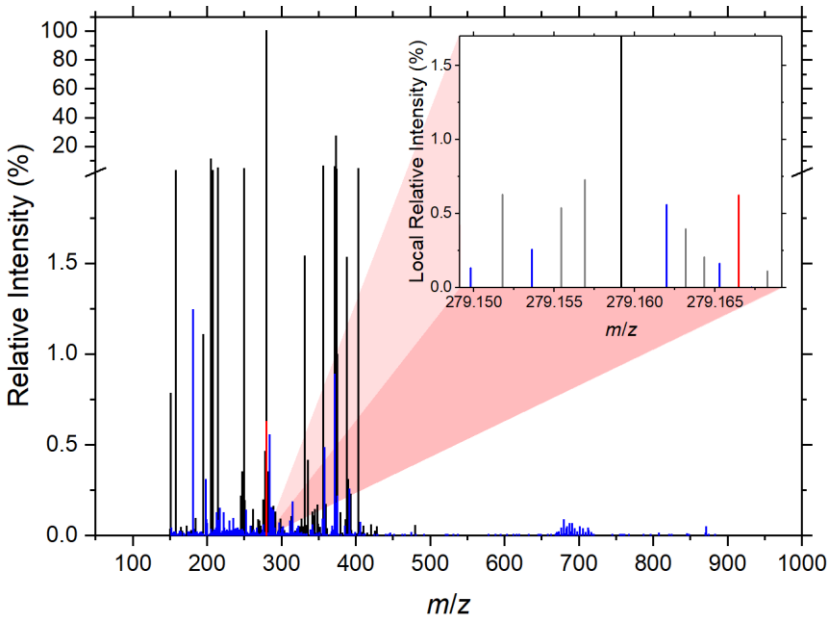


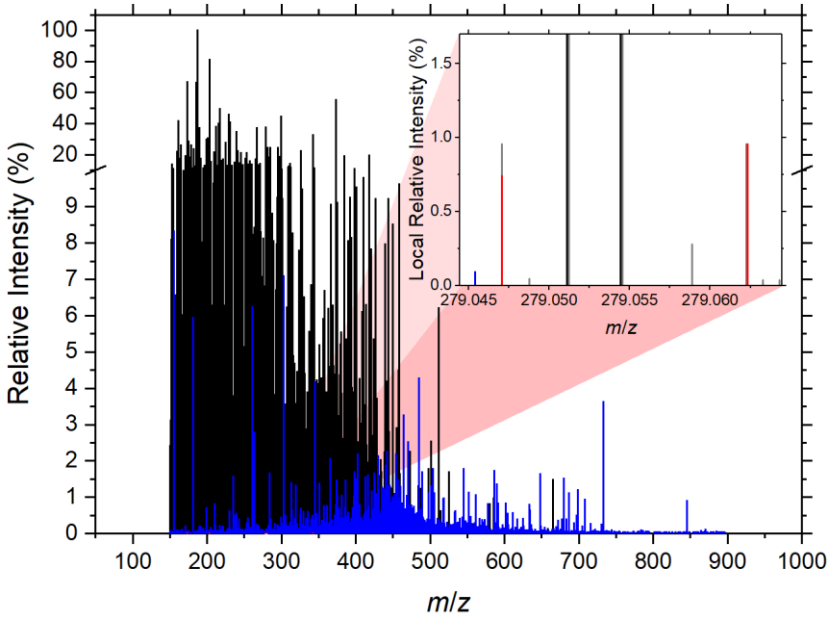
Figure S1 Influence on final peak count of varying the isotopic ratio cut-off for $^{13}C/^{12}C$ based on scaling (*x*-axis) the natural abundance (1.1%). The change in peak number is normalised from the maximum (*i.e.* 1.0) to minimum (*i.e.* 0.0) number of peaks for each different environmental sample (two urban, three remote). Significant changes in peak count typically only occurred when lowering the cut-off below the natural abundance in agreeance with the likelihood of underestimation by Orbitrap analysers. All samples were processed using negative ESI.

Detailed post-processing spectra for sample application

Figure S2 summarises the common ion and shoulder ion processing stages for both APPI positive and ESI negative modes. The black peaks show the final spectra after all processing (including post-processing). Blue peaks are peaks removed as uncommon ions and the red peaks were removed as shoulder ions. The insets, similar to Figure 6 in the main text, show a sample of shouldering with respect to a localised, centred peak (note the change in *y*-axis). The insets feature additional grey peaks which are from one of the four replicates to highlight that shoulder peaks were also removed during the main processing stage. The overlapping of initial sample (grey) peaks with others, for example the red shoulder peaks, highlights minor changes produced by the common ion code. Firstly, the output intensity is the average of the four samples which, in the case of the *m*/*z* 279.047 ESI negative peak was lower than the initial peak from the selected replicate. Secondly, the common ions are filtered based on the chemical formulae which may be assigned to slightly different *m*/*z* values. The output of the common ion code arbitrarily selects one of the replicate *m*/*z* values which explains the minor *m*/*z* shifts in the grey peaks relative to the red and blue peaks.



(a)



(b)

Figure S2 Mass spectra of the final post-processing steps for (a) APPI+ and (b) ESI−. The black lines denote the final spectra with the blue and red lines denoting peaks that were removed during the common ion and shoulder ion stages, respectively. Inset highlights shoulder ion removal with the *y*-axis being relative to the dominant local peak (centred within inset). The grey lines are from the initial spectrum of one of the sample replicates to highlight that many of the shoulder peaks were removed prior to the shoulder peak processing stage.