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The isotopic composition of formaldehyde in urban air

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The isotopic composition of atmospheric formaldehyde was measured in air samples collected in urban Seattle, Washington. A recently developed gas chromatography-isotope ratio mass spectrometry analytical technique was used to extract formaldehyde directly from whole air, separate it from other volatile organic compounds, and measure its $^{13}C/^{12}C$ and D/H ratio. Measurements of formaldehyde concentration were also made concomitant with isotope ratio. Results of the analysis of nine discrete air samples for $\delta^{13}C$–HCHO have a relatively small range in isotopic composition (–31 to –25‰ versus VPDB) over a considerable range of concentrations (0.8–4.4 ppb). In contrast, analyses of 17 air samples for δD–HCHO show a large range (–296 to +210‰ versus VSMOW) over the concentrations measured (0.5–2.9 ppb). Observations of δD are weakly anti-correlated with concentration. Isotopic data are interpreted using both source and sink-based approaches. Results of $\delta^{13}C$–HCHO are similar to those observed previously for a number of non-methane hydrocarbons in urban environments and variability can be reconciled with a simple sink-based model. The large variability observed in δD–HCHO favors a source-based interpretation with values depleted in deuterium from primary sources of HCHO (i.e., combustion) and values enriched in deuterium from secondary photochemical sources (i.e., hydrocarbon oxidation).