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Carbon Isotope Anomaly in the major Plant C_1 Pool and its biogeochemical Implications

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Stable isotope analysis has become a powerful tool for environmental scientists, plant biologists, ecologists and geochemists studying global elemental cycles or past climatic conditions. Thus most plant species have been photosynthetically characterised as Calvin cycle (C_3), Slack-Hatch cycle (C_4) and Crassulacean acid metabolism (CAM) categories using carbon isotope signatures. Moreover variations in the carbon isotope composition ($\delta^{13}C$) of compounds, produced and destroyed in the global carbon cycle, are often used to investigate biogeochemical cycles and global source-sink relationships, as well as the underlying mechanisms. Stable isotope techniques are increasingly applied to the study of atmospheric budgets of volatile organic compounds (VOCs).

We report evidence that methoxyl groups in terrestrial plants (in esters and aromatic ethers) have a unique carbon isotope signature exceptionally depleted in ^{13}C. Plant-derived C_1 volatile organic compounds (VOCs) are also highly depleted in ^{13}C compared with C_{n+1} VOCs. Our observations suggest that the plant methoxyl pool is the predominant source of C_1 compounds of plant origin in the biosphere such as

methanol, chloromethane, bromomethane, iodomethane, and cyanomethane. Moreover this pool, which comprises *ca* 2.5% of carbon in plant biomass and represents an important substrate for methanogenesis, is likely to be a significant source of highly depleted methane entering the atmosphere.

The distinct ^{13}C depletion of methoxyl groups in plants which is reflected in isotope signatures of C_1 VOCs may provide a helpful tool in constraining complex environmental processes. These isotope anomalies have a tremendous potential to improve our understanding of the global cycles of atmospheric trace gases and the biochemical pathways involved. Furthermore methoxyl groups could act as markers for biological activity in organic matter of terrestrial and extraterrestrial origin.