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## Ten years of high precision methane isotope data for Mace Head and London: a tale of Canadian and European sources

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Greenhouse gas data records for the Mace Head background station (Irish west coast) and Egham, (western edge of London), provide complementary controls on the changing nature of sources in western Europe and beyond. During summer Egham often records near background signals under the influence of Azores high pressure systems from the SW, while at the same time the Mace Head station is receiving air masses enriched by carbon gases from wetland or forest fire sources in Canada. Mace Head is infrequently visited by air masses from continental Europe while SE England is a more frequent recipient. An example was the heat wave of summer 2003 which resulted in anomalously high carbon gases in London for the following 6 months, but had only minor influence on the growth rate at Mace Head.

Carbon isotopes are good discriminants between major sources of methane. This demands high precision. The records constrain source types responsible for excess over background. The Royal Holloway time series has long term precisions for  $\delta^{13}$ C of  $\pm 0.04$  per mil and for replicate tank sample analyses of  $\pm 0.03$  per mil or better. This is particularly important for the Mace Head record. These spot samples have isotopic shifts of < 0.15 per mil and excess mixing ratio of <20 ppb CH<sub>4</sub> for Canadian air masses compared to Atlantic background. The dominant methane summer source has  $\delta^{13}$ C averaging –63 per mil, typical of Canadian wetland emissions. A signal averaging –27 per mil was detected during the autumns of 1998 and 2002, recording anomalously large forest fire emissions in parts of Canada. Carbon monoxide records for Mace Head support these findings. Air masses from central Europe to Mace Head are infrequent, and less frequently sampled for isotopic analysis, but they do give an estimate of the changing European source mix, from -54 per mil in 1996 to -56 per mil in 2001. This is consistent with reductions in coal use, a shift from North Sea to Russian gas supply, and better landfill practice. Atlantic air masses that sample only Irish sources have a source mix averaging -65 per mil representing the ruminant and peat bog sources which make up as much as 80% of Irish emissions.

The Egham site receives near-background air from the SW, but with London to the east it cannot be used to interpret changes in continental European sources. During anticyclonic conditions, or when Arctic air masses arrive via the North Sea, it is possible to distinguish local and London sources. London itself is dominated by gas leaks and vehicle emissions, with a <sup>13</sup>C-enriched source signal. In contrast, the London fringes have important landfill emissions, with a <sup>13</sup>C-depleted source signal. We are developing continuous isotope monitoring of Egham air using automated continuous flow techniques. This will aid the understanding of diurnal and seasonal variations in source mix in an urban area, but also detect isotopic shifts related to unexpected events, such as the recent Buncefield oil terminal fire.