Obtaining accurate data for the contents of biogenic and fossil carbon in thermally-treated waste is essential for determination of the environmental profile of waste technologies. Relations between the variability of waste chemistry and the biogenic and fossil carbon emissions are not well described in the literature. This study addressed the variability of biogenic and fossil carbon in combustible waste received at a municipal solid waste incinerator. Two approaches were compared: (1) radiocarbon dating (14C analysis) of carbon dioxide sampled from the flue gas, and (2) mass and energy balance calculations using the balance method. The ability of the two approaches to accurately describe short-term day-to-day variations in carbon emissions, and to which extent these short-term variations could be explained by controlled changes in waste input composition, was evaluated. Finally, the measurement uncertainties related to the two approaches were determined. Two flue gas sampling campaigns at a full-scale waste incinerator were included: one during normal operation and one with controlled waste input. Estimation of carbon contents in the main waste types received was included. Both the 14C method and the balance method represented promising methods able to provide good quality data for the ratio between biogenic and fossil carbon in waste. The relative uncertainty in the individual experiments was 7–10% (95% confidence interval) for the 14C method and slightly lower for the balance method.