Global Inventory of Natural Gas Molecular & Isotopic Compositions

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Introduction
Top-down models of the global atmospheric methane budget use isotopic and/or molecular data to constrain source-specific emissions. These models are sensitive to end-member signatures ($\delta^{13}$C(CH4), $\delta^{13}$C(C2H6), ethane-methane ratios) for the three main source categories, microbial methanogenesis, biomass burning, and fossil fuels. However, the end-member values are poorly constrained and based on data of unknown or limited sample count, regional extent and global representation. For fossil fuels in particular, few modeling studies reference primary data, despite a vast literature in petroleum geology reporting on the isotopic and molecular composition of natural gas.

Table 1: Natural gas and coal $\delta^{13}$C(CH4) source signatures used in some top-down models of the global methane budget. Citation pathways indicated by arrows. Only one study (Whiticar 1989) is based on a large empirical dataset; however, the data were proprietary and therefore of unknown global or regional representation.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Natural Gas $\delta^{13}$C(CH4) (%)</th>
<th>Coal $\delta^{13}$C(CH4) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Whiticar 1989</td>
<td>-44 (-37)</td>
<td>-39 (-37)</td>
</tr>
<tr>
<td>Gupta 1996</td>
<td>-38 (-37)</td>
<td>-37 (-37)</td>
</tr>
<tr>
<td>Quay 1999</td>
<td>-43 (-36)</td>
<td>-7 (-36)</td>
</tr>
<tr>
<td>Milkov 2004</td>
<td>-46 (-37)</td>
<td>-14 (-37)</td>
</tr>
<tr>
<td>Lissi 2007</td>
<td>52 (-35)</td>
<td>-36 (-35)</td>
</tr>
<tr>
<td>Naed 2010</td>
<td>60 (-35)</td>
<td>-35 (-35)</td>
</tr>
<tr>
<td>Monnai 2011</td>
<td>-65 to -25</td>
<td>N/A</td>
</tr>
<tr>
<td>Kirschka 2013</td>
<td>-61.3 ± 2.7</td>
<td>-36.2 ± 0.1</td>
</tr>
</tbody>
</table>

Global Representation
The inventory contains data from 45 countries, 179 basins, >597 geological formations, and 8734 unique samples. On a country-level basis, the data represent 82.5% of world natural gas production and 80.2% of world coal production over the period 2000-2014 (BP 2014). Note over-representation of some countries (e.g. USA, China, Australia) and under-representation of others (e.g. Norway, Qatar, Algeria, Saudi Arabia, Turkmenistan).

Caveats
- Focus was on publications having isotope data; much more gas concentration data exist in the literature/reports.
- No way to verify isotopic calibration/standardization (esp. Soviet era papers).

Database
We compiled a global inventory of natural gas molecular and isotopic measurements from the peer-reviewed literature and government reports (Fig. 1). Samples were categorized into conventional oil/gas, coal and shale gas. Recorded parameters include concentrations of C2-C6 alkanes and permanent gases and $\delta^{13}$C and $\delta^{18}$O of C2-C6 alkanes.

Fig. 2: Comparison of country-specific production (as percent of global production) vs. sample count for conventional gas (left) and coal (right).

Implications for Top-Down Models
Data distributions are shown in Fig. 3. Note significantly lower mean and median $\delta^{13}$C(CH4) values for conventional gas and especially coal, than typically used in top-down models (Table 1). This is due to the importance of 1) primary and secondary microbial methanogenesis in approximately 20% of global oil and gas reservoirs (Rice & Claupey 1981; Milkov 2011) and in coal (Rice 1993 and 2) isotopically light signatures in low-maturity, oil-association gas (Fig. 4). For example, giant Cenomanian gas pools of western Siberia, which account for 17% of global gas production, have mean $\delta^{13}$C(CH4) ≈ -51 ‰. Revision of $\delta^{13}$C(CH4) end-member signatures has a significant effect on modeled fossil fuel contributions to the global methane budget (Schwietzke et al. submitted).

Fig. 4: Plot of $\delta^{13}$C(CH4) vs. $\Delta$D(CH4) for conventional gas, coal, and shale gas, with density distributions and genetic domains. Microbial methanogenesis (via fermentation and microbial CO2 pathways) in conventional gas reservoirs and coal accounts for negatively-skewed $\delta^{13}$C(CH4) distributions.

Conclusions
- Most complete database of natural gas compositions ever compiled.
- Includes isotopic ($\delta^{13}$C & $\delta^{18}$O) and molecular compositions.
- Data represent ~80% of global natural gas and coal production.
- At global level, $\delta^{13}$C and $\delta^{18}$O values are skewed to lower values because of microbial methanogenesis and low thermal maturity oil-associated gases.
- Previous inversion studies may have underestimated the fossil fuel flux due to use of end-member values that were too high.
- Database will be published as a stand-alone manuscript and is available by download through:

References