Comparative Assessment of GC and GC×GC Characterization Techniques for Estimating Aquatic Toxicity of Complex Petroleum Mixtures

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INTRODUCTION

Evaluation of aqueous toxicity of complex mixtures of petroleum hydrocarbons using chemical characterization is challenging given analytical limitations associated with chemical identification. Traditionally, chemical analysis has been conducted using gas chromatography-mass spectrometry (GC-MS) and GC-flame ionization detection (GC-FID), both of which are capable of quantifying a few hundred individual compounds in a complex petroleum mixture, a small fraction of the compounds typically present. Recently, comprehensive two dimensional GC, combined with either FID (GC×GC-FID) or time-of-flight MS (GC×GC-ToF-MS), has been used to identify thousands of individual compounds in complex petroleum mixtures. The increased resolution of the GC×GC approaches may be valuable for assessing potential aquatic toxicity. This study evaluates the relative performance of three approaches (GC-FID and GC-MS, GC×GC-FID, and GC×GC-ToF-MS) by comparing the predicted aquatic toxicity estimates derived using the Petrotox model across a range of crude and refined petroleum mixtures.

METHODOLOGY

- Two crude oils (North Slope Crude and Louisiana Light Sweet Crude) and two distillates (gasoline and diesel fuel) were extracted and analyzed by three approaches:
  1. Single-dimensional GC (GC-MS and GC-FID)
  2. GC×GC-ToF-MS
  3. GC×GC-FID
- Each of the resultant datasets was "binned" and modeled using the Petrotox model
  - Petrotox calculates the petroleum product solubility and uses the Target Lipid Model (TLM) (Di Toro et al. 2000) and toxic unit theory of additivity

Table 1: Example of Petrotox model input. Note that each of the values represents the mass fraction.

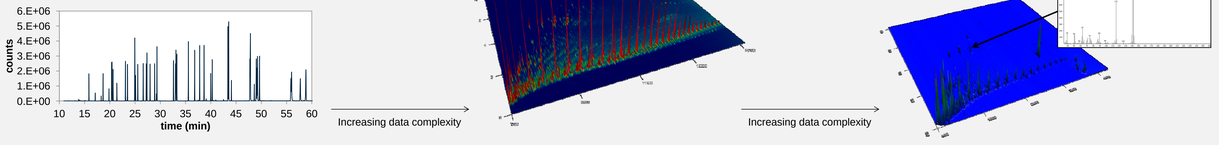
Carbon Number	Aliphatic Sulfur-Bearing Struct.	Aromatic Sulfur-Bearing Struct.	Di-Aromatics	Di-Naphthenics	Other Naphthenics	i-Olefins	i-Paraffins	Mono-Aromatics	Naphthenic Di-Aromatics	Naphthenic Mono-Aromatics	Substituted Cyclopentanes	Substituted Cyclohexanes	n-Olefins	n-Paraffin	Poly-Aromatics	Poly-Naphthenics
6	0.000	0.000	0.000	0.000	0.000	0.000	0.014	0.017	0.000	0.000	0.016	0.037	0.000	0.000	0.000	0.000
7	0.000	0.000	0.000	0.000	0.017	0.000	0.049	0.110	0.000	0.000	0.078	0.016	0.083	0.000	0.000	0.000
8	0.000	0.033	0.000	0.003	0.051	0.019	0.048	0.411	0.000	0.000	0.144	0.119	0.000	0.014	0.000	0.000
9	0.000	0.234	0.000	0.115	0.053	0.051	0.175	0.675	0.000	0.003	0.019	0.209	0.031	0.023	0.000	0.000
10	0.000	0.482	0.254	0.022	0.107	0.094	0.178	0.774	0.000	0.465	0.040	0.176	0.075	0.034	0.000	0.000
11	0.000	0.415	1.196	0.015	0.061	0.157	0.303	0.997	0.000	0.778	0.013	0.033	0.141	0.050	0.000	0.000
12	0.000	0.193	2.321	0.037	0.283	0.127	0.394	0.595	0.053	1.244	0.000	0.022	0.050	0.097	0.000	0.000
13	0.000	0.150	2.344	0.017	0.156	0.173	0.398	0.722	0.056	0.758	0.046	0.054	0.285	0.159	0.000	0.000
14	0.000	0.115	1.937	0.003	0.118	0.078	1.074	0.558	0.233	0.337	0.000	0.034	0.416	0.225	0.125	0.000
15	0.000	0.000	0.968	0.021	0.107	0.192	1.342	0.480	0.121	0.243	0.000	0.037	0.310	0.260	0.273	0.000
16	0.000	0.002	0.360	0.003	0.062	0.220	0.701	0.167	0.007	0.000	0.000	0.039	0.080	0.279	0.180	0.000
17	0.000	0.002	0.000	0.006	0.038	0.250	0.519	0.258	0.000	0.000	0.000	0.016	0.080	0.287	0.131	0.000
18	0.000	0.000	0.000	0.009	0.058	0.193	0.526	0.131	0.000	0.000	0.000	0.000	0.026	0.290	0.050	0.000
19	0.000	0.000	0.000	0.002	0.037	0.048	0.395	0.056	0.000	0.000	0.000	0.011	0.029	0.269	0.000	0.000
20	0.000	0.000	0.000	0.000	0.029	0.157	0.444	0.023	0.000	0.000	0.000	0.000	0.000	0.269	0.000	0.000
21	0.000	0.000	0.000	0.000	0.006	0.112	0.325	0.018	0.000	0.000	0.000	0.000	0.000	0.223	0.000	0.000
22	0.000	0.000	0.000	0.000	0.008	0.048	0.057	0.003	0.000	0.000	0.000	0.000	0.058	0.183	0.000	0.000
23	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.141	0.000	0.000
24	0.000	0.000	0.000	0.000	0.042	0.014	0.074	0.000	0.000	0.000	0.000	0.000	0.000	0.162	0.000	0.000
25	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.137	0.000	0.000
...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
34	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

GC AND GC×GC APPROACHES

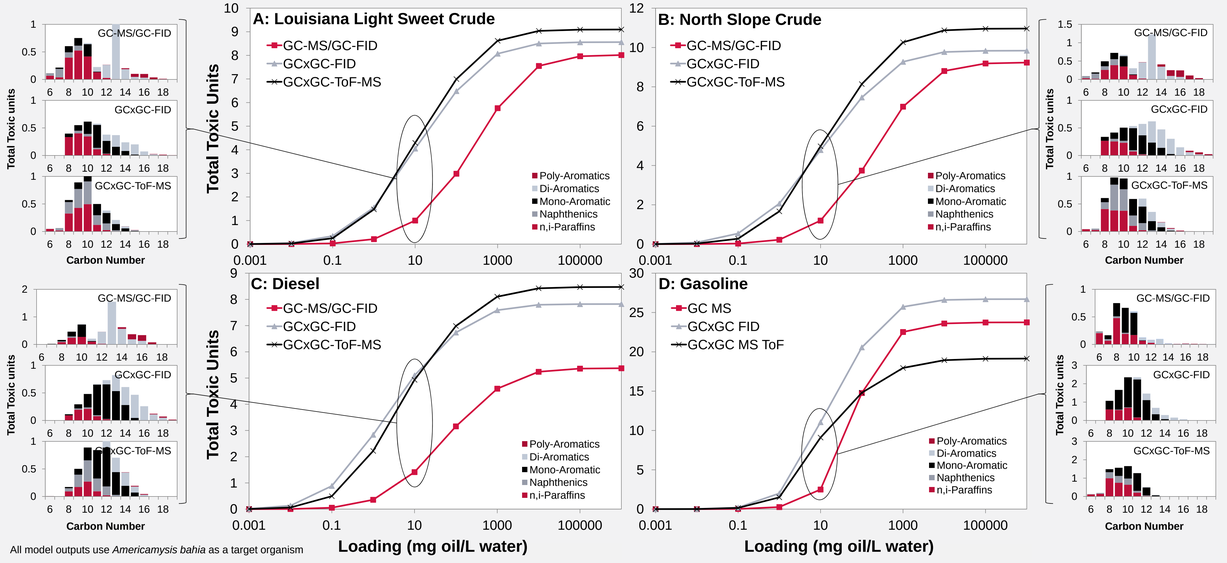
GC-MS and GC-FID
- Separates compounds in one dimension (volatility)
- Robust and sensitive analysis of hundreds of individual compounds
- GC methods are the standard tool for most petroleum hydrocarbon analyses
- Usually requires multiple injection methods for measuring all GC-amenable compounds

GC×GC-FID
- Separates compounds in two dimensions (volatility and polarity)
- FID detector responds to carbon only
- Can sensitively detect thousands of individual compounds in crude oil

GC×GC-ToF-MS
- Separates compounds in two dimensions (volatility and polarity)
- ToF mass analyzer generates mass spectra
- Can detect thousands of individual compounds in crude oil with the ability to search mass spectra against MS libraries



MODEL OUTPUTS



All model outputs use *Americamysis bahia* as a target organism

RESULTS

- *For both crude oils and the diesel fuel…*
  - At all loadings, the model outputs using both GC×GC datasets predicted greater toxicity than that of GC-MS/GC-FID
  - The model outputs using the GC×GC-FID and GC×GC-ToF-MS datasets predicted nearly identical toxicity across the entire range of loadings
- *For the gasoline…*
  - At low loadings (10 mg/L or less), the model output using the GC×GC-FID and GC×GC-ToF-MS datasets predicted greater toxicity than that of GC-MS/GC-FID
  - At high loadings, the model output using the GC×GC-FID dataset predicted the greatest toxicity, and the GC-MS and GC-FID data predicted whereas that of the GC×GC-ToF-MS data predicted the least amount of toxicity
- *Relative contribution of compounds based on carbon number and compound class…*
  - The modeled toxicity of all three GC approaches is attributable to C_{20} and smaller components
  - The model output using the three different approaches attributed different distributions of toxicity across all five compound classes (poly-aromatics, di-aromatics, mono-aromatics, naphthenics, and n-/i-paraffins)

CONCLUSIONS/FUTURE WORK

- Variability between the GC approaches and the GC×GC approaches is attributed to the fact that the latter detects many more compounds in complex petroleum mixtures
- The difference in attribution of toxic units to different compound classes may be attributable to the response factors across the GC×GC-ToF-MS and GC×GC-FID planes *or* the relative selectivities of GC×GC-ToF-MS and GC×GC-FID
  - *It is important to note that the overall dose responses for both GC×GC approaches were often similar*
- Model outputs need to be validated against laboratory toxicity tests

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