Direct evaluation of organic components in soil and lake sediments using a multi-shot pyrolyzer and thermal desorption GCMS

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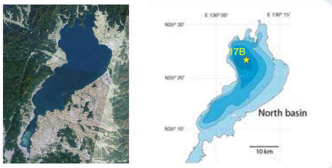
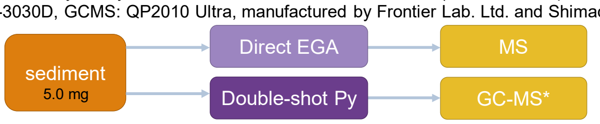
Introduction

Lake Biwa is the largest lake in Japan, with an area and water storage of approximately 670 km^2, providing water for more than 10 million people. It is essential to understand the variation of organic chemical composition in its sediments for the study of organic matter in the lake. Sediment samples are generally analyzed using a solvent extraction-GCMS method. However, information of some compounds may be damaged or lost when pretreatment is performed. Double-shot Py-GCMS method solves the above problems with fewer procedures and detailed and extensive compound information can be obtained. However, it is not easy to perform simple and macroscopic analysis of the seasonal changes of sediment layers because the excess data. The evolved gas analysis (EGA)-MS method is simpler and can analyze not only the changes of each single component, but also the changes of organic components macroscopically by profiling the thermogram. In this study, it was demonstrated that the EGA-MS method is effective in analyzing the composition of compounds in sediment layers, and that it is a simple and macroscopic method to analyze the layer and seasonal variation of sediments.



Method

Sediment layer samples collected at site 17B near the center of Lake Biwa were cut into five layers (Layer 1: 0-1 cm, Layer 2: 1-2 cm, Layer 3: 2-4 cm, Layer 4: 4-10 cm, Layer 5: 10-20 cm), freeze-dried, and analyzed by the doble-shot PY-GCMS and EGA-MS (auto-shot sampler: AS-1020E, multishot pyrolyzer: PY-3030D, GCMS: QP2010 Ultra, manufactured by Frontier Lab. Ltd. and Shimadzu corp.).



*Column : Ultra ALLOY-DTM (2.5 mm, 0.15 mm, 0.47 mm)

Direct EGA
150 ℃→15 ℃/min→600 ℃

Double shot
Part 1(TD): 150 ℃→15 ℃/min→390 ℃
Part 2(PY): 390 ℃→15 ℃/min→600 ℃

The double-shot-py GCMS method used a microjet cryotrap to trap the gas sample.

Result

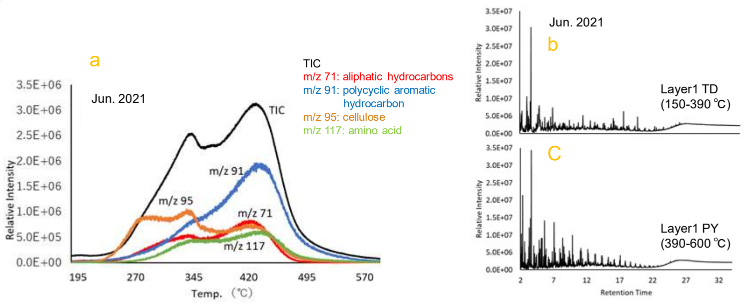


Fig.1 EGA thermograms (a) and total ion chromatogram (double-shot Py-GCMS, b:TD, c:PY) of sediment surface sample collected at site 17B in June 2021

Table1 List of compounds at m/z 95 detected by double-shot Py-GCMS (June 2021, 17B, Layer 1)

TD	PY
2,5-Dimethylfuran	**2,5-Dimethyl-furan**
Acetic acid	2-Heptene
Cycloheptane	**2-Methylfuran**
2-Ethyl-5-methyl-furan	1-Methylcyclohexene
Furfural	(E)-4-Octene
3-Methylcyclobutane-1,1-dicarboxylic acid	**2-Ethyl-5-methyl-furan**
o-Xylene	**Furfural**
1-(2-Furanyl)-ethenone	3,5-Dimethyl-cyclohexene
1,3-Dimethyl-1-cyclohexene	3,4-dimethyl-2-cyclopenten-1-one
Butyl propyl sulfone	**1-(2-Furanyl)-ethanoane**
2,4-Dimethylfuran	Phenol
Phenol	Mesitylene
N-methyl-2-(1-methylpyrrol-2-yl)ethanamine	4-Aminopyridine
1H-pyrrole-2-carboxaldehyde	N-3-pyridinylacetamide
3-Methyl-phenol	3-Methylphenol
4,8-Dimethyl-1-nonanol	2,4-Dimethylphenol
Phytol	1,8-Dimehylnapthalene
2-Decylfuran	1-Nonadecene
Squalene	

Bold: cellulose-derived components

- Fig.1
m/z 95 showed a peak at 150-390°C (TD region). m/z 91 showed a peak at 390-600°C (PY region).
- Table1 , Fig.2
The main components of m/z 95 are cellulose-derived components.
- Fig.2
The main components of m/z 71, 91, 117 are aliphatic hydrocarbon, aromatic hydrocarbons, and amino acid-derived components, respectively.
- Fig.3
The EGA-MS method is useful for the evaluation of these components because it showed a good correlation between the intensity of EGA-MS thermograms at m/z 71, 91, 95, and 117 and the intensity of aliphatic hydrocarbons, aromatic hydrocarbons, cellulose derived components, and amino acid derived components measured by double shot Py-GCMS.

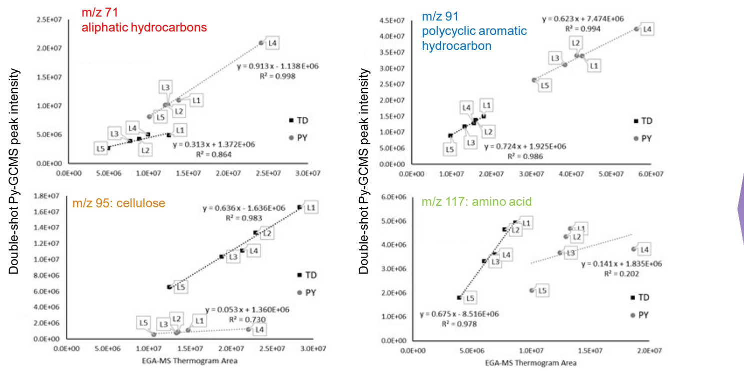


Fig.3 Intensity of EGA-MS thermograms at m/z 71, 91, 95, 117 vs. intensity of aliphatic hydrocarbons, aromatic hydrocarbons, cellulose-derived components, and amino acid-derived components in double-shot Py-GCMS

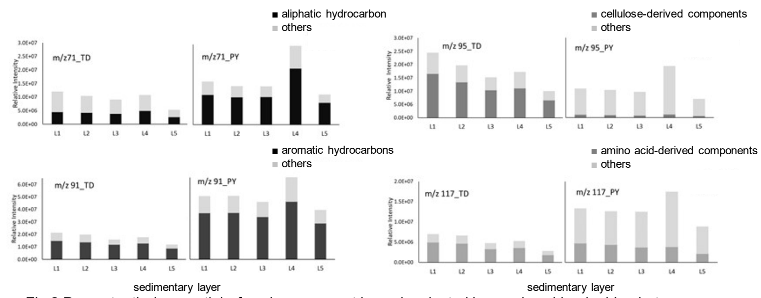
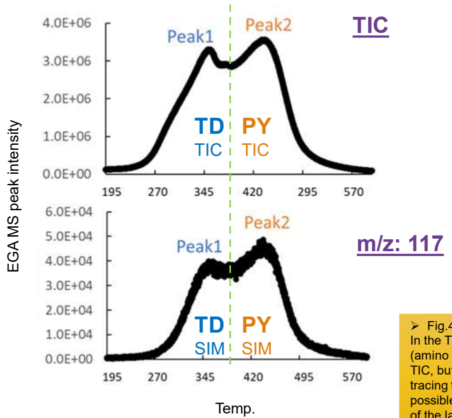


Fig.2 Present ratio (area ratio) of each component in each selected ion analyzed by double-shot Py-GCMS.



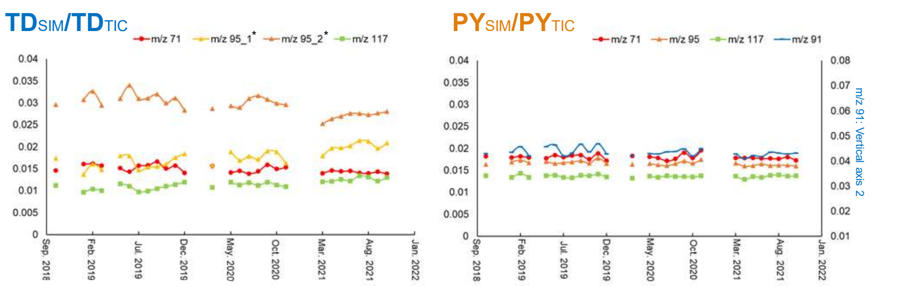


Fig.4 Annual change in the ratio of the peak of each m/z in EGA-MS to the peak of the thermogram in that temperature range (TD, PY)
*m/z 95 detected 2 peaks in the TD part

- Fig.4
In the TD region, m/z 95 (cellulose derived components), 117 (amino acid derived components) tended to change its share in the TIC, but in the PY region, no m/z changed its share in the TIC. By tracing the changes of various compounds of different origins it is possible to infer what phenomena are occurring in the environment of the lake. Compared with the results of TD, all the substances in the PY part remained almost unchanged, indicating that the highly humic substances in the PY part are more chemically stable.

Conclusion

EGA-MS method is effective in analyzing the composition of compounds in sediment layers, and that it is a simple and macroscopic method to analyze the layer and seasonal variation of sediments.