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Quantification and characterization of Black Carbon using Rock-Eval analysis

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Introduction

Black Carbon (BC) has been reported to play an important role in the sorption of persistent organic pollutants. BC is a chemical continuum ranging from slightly charred biomass to highly condensed soot and graphite. A whole range of different methods are used for the quantification of BC, each method detecting a different part of the BC continuum. In the present study, we show the potential of Rock-Eval 6 analysis for BC quantification and characterization.

Objective

- Comparison of Rock-Eval analysis to traditional BC quantification methods

Method

- sediment sampled in four European catchments: Meuse, Ebro, Elbe and Danube.
- reference materials developed by the BC Steering Committee complemented with several other pure BC materials.
- BC content measured by chemo-thermal oxidation (CTO375).
- Rock-Eval 6 analysis for determination of total organic carbon (TOC), residual carbon (RC) and $T_{50\%}$. RC is thought to consist of refractory organic carbon (e.g. soot, char, coal). Consequently, we propose that RC can be used as a measure of the BC content. $T_{50\%}$ is the temperature at which 50% of the organic carbon is oxidized in a Rock-Eval oxidation only analysis. $T_{50\%}$ has been shown to correlate with BC/TOC measured by CTO375 (Oen et al., 2006).
- Data from Rock-Eval analysis for pure BC (reference) materials analysis was compared to literature data of four different BC quantification methods: CTO (chemo-thermal oxidation), acid dichromate (chemical oxidation), BPCA (molecular marker) and TOT/TOR (optical method).

Results

- Rock-Eval analysis detects RC in the whole BC continuum from slightly charred material upto highly condensed soot.
- For pure BC materials, RC correlates significantly with BC measured by CTO and TOT/TOR (Table 1).TOT/TOR also detects the whole BC continuum, but CTO detects only the most refractory BC fractions (soot). $T_{50\%}$ correlated only significantly with CTO (Table 2).
- For sediment samples RC also correlates significantly with BC measured by CTO (Fig. 1).
- Pure BC materials show distinct range in thermal stability (Fig. 2a). For sediment samples the thermogram could be used to differentiate RC in different BC types (Fig. 2b).

Table 1. Linear regression of RC (g Kg-1) and $T_{50\%}$ (℃) of pure BC (reference) materials against literature data on BC content (g Kg-1) and BC/TOC respectively.

method	R	slope	intercept	significance	N
regression against RC					
CTO	0.649	0.358	-91.1	0.016	13
Acid dichromate	0.717	0.516	-86.6	0.173	5
BPCA	0.854	0.345	-47.8	0.0656	5
TOT/TOR	0.977	1.21	-114	0.00428	5
regression against $T_{50\%}$					
CTO	0.882	0.231	-94.3	<0.0001	5
Acid dichromate	0.548	0.227	-63.7	0.081	5
BPCA	0.525	0.09	-23.5	0.097	5
TOT/TOR	0.515	0.163	-2.60	0.11	5

Table 2 Linear regression of RC (g Kg-1) and $T_{50\%}$ (℃) of sediment samples against CTO375 measured BC content (g Kg-1) and BC/TOC respectively.

independant variable	R	slope	intercept	significance	N
RC (g Kg^{-1})	0.882	0.031	1.0	0.034	33
$T_{50\%}$ (℃)	0.237	0.0002	-0.008	0.177	33

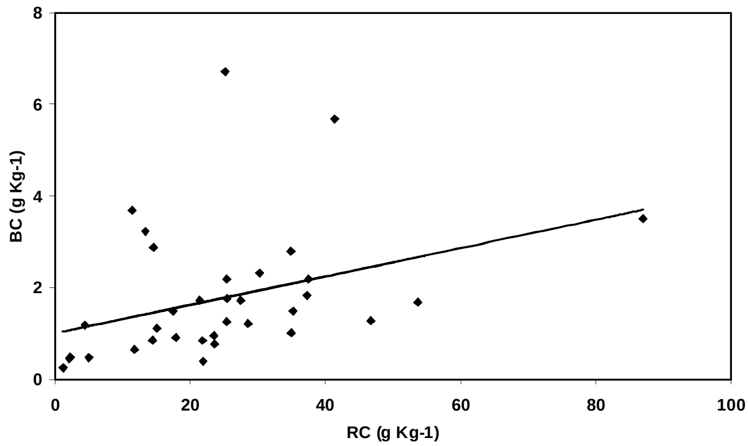

Figure 1. Correlation between BC measured by CTO375 and RC measured by Rock-Eval analysis for all sediment sample. Solid line indicates regression line (see Table 2).

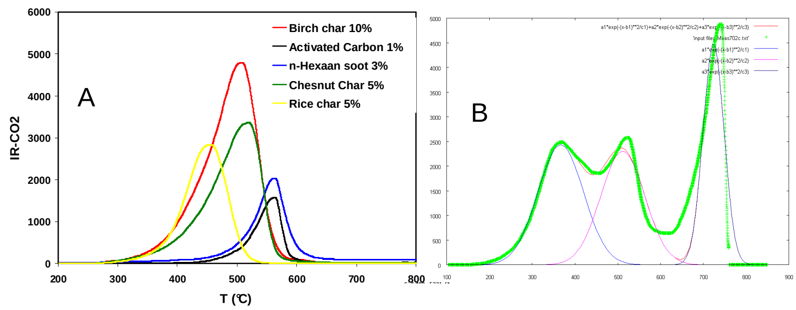

Figure 2. a) CO2 evolution (IR signal) during oxidation stage of Rock-Eval analysis for pure BC (reference) materials mixed with precombusted silica (percentage denotes % organic carbon of the mixture). b) Example of deconvolution of Rock-Eval thermogram for a sediment sample with different types of BC.

Conclusions

Rock-Eval analysis can quantify a major part of the BC continuum by making use of the RC and T50% variables. In addition, it has the potential to characterize BC through deconvolution of the dominant peaks in the thermogram, making it a powerful tool in BC analysis

References
Oen, A.M.P., Breedveld, G.D., Kalaitzidis, S. and K. Christanis (2006). Env. Tox. Chem. 25:1258-1267.

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