Detecting Forest Fire Emitted $PM_{2.5}$ Using a Novel Scanning Thermal Elemental Analysis (STEA) Technology:

A Progress Report

by

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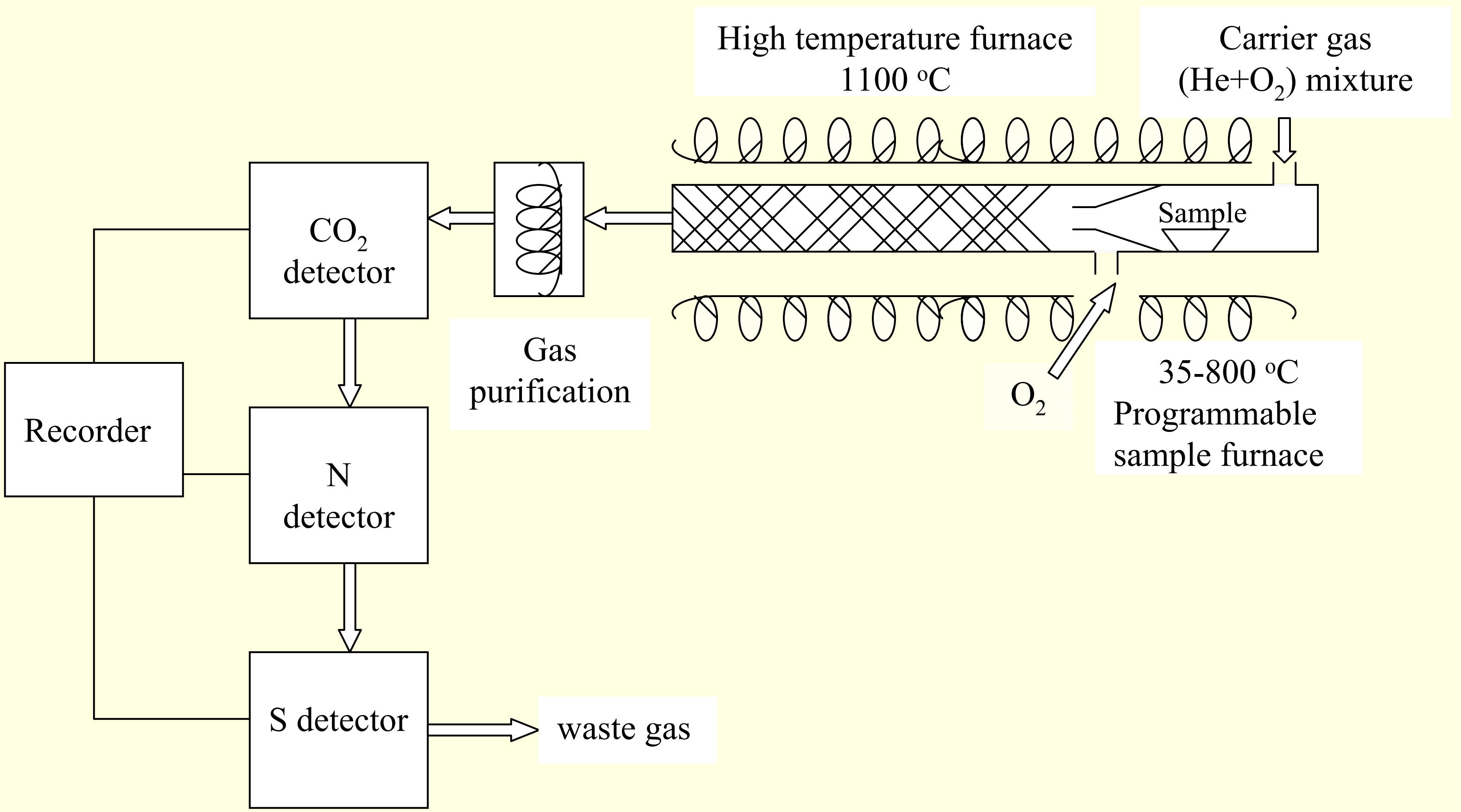
Objective

- Develop a sensitive and rapid method for the detection and chemical characterization of forest emitted $PM_{2.5}$

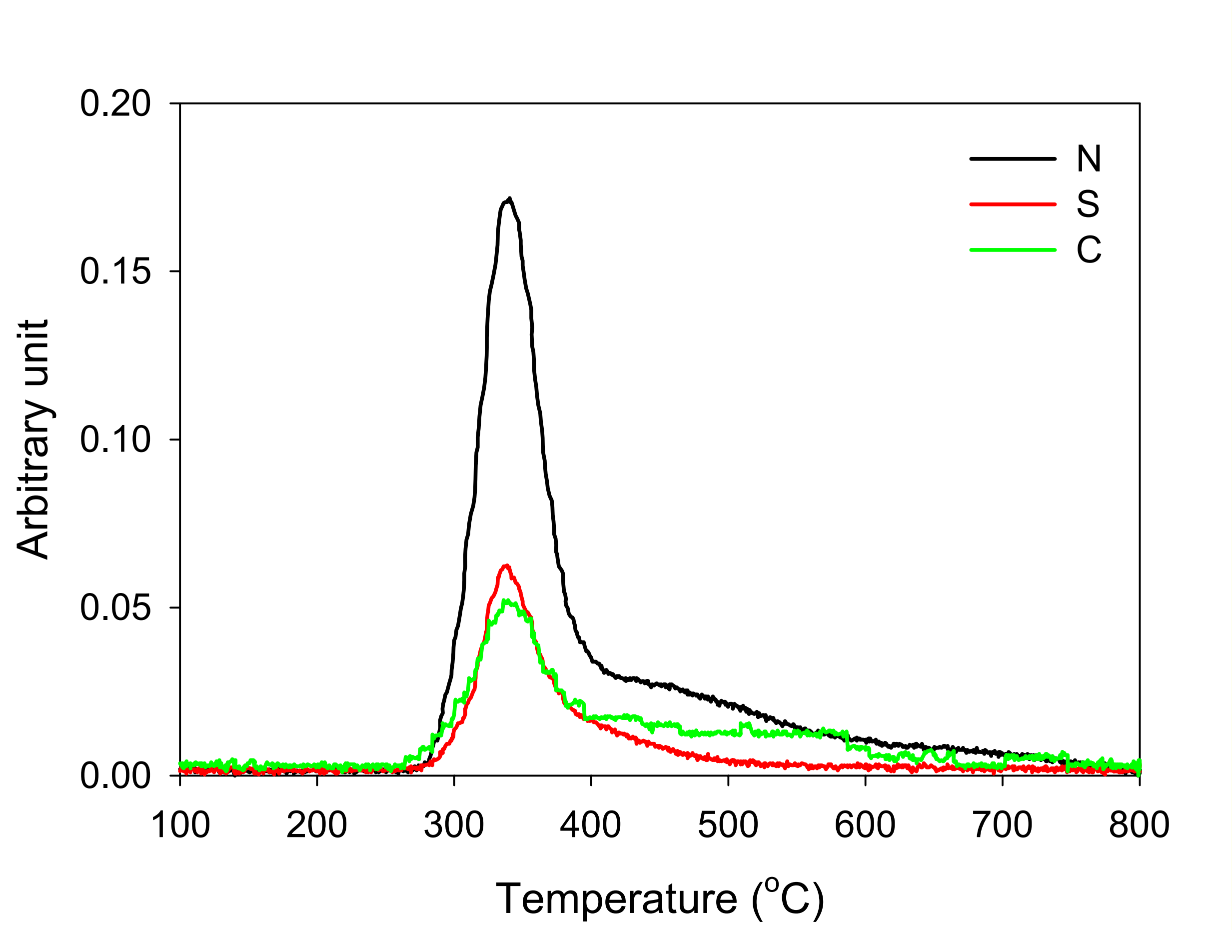
Challenges in chemical analysis of a $PM_{2.5}$ sample

- It is a solid mixture and the current analytical technology for a solid mixture is very limited.
- Very small size, not easy to handle, transfer and store, and very easily to be contaminated
- We still know very little about $PM_{2.5}$ chemically mainly due to inadequate analytical technology: e.g. the nature of black carbon (BC) and that of organic carbon (OC) in $PM_{2.5}$ are still unclear.

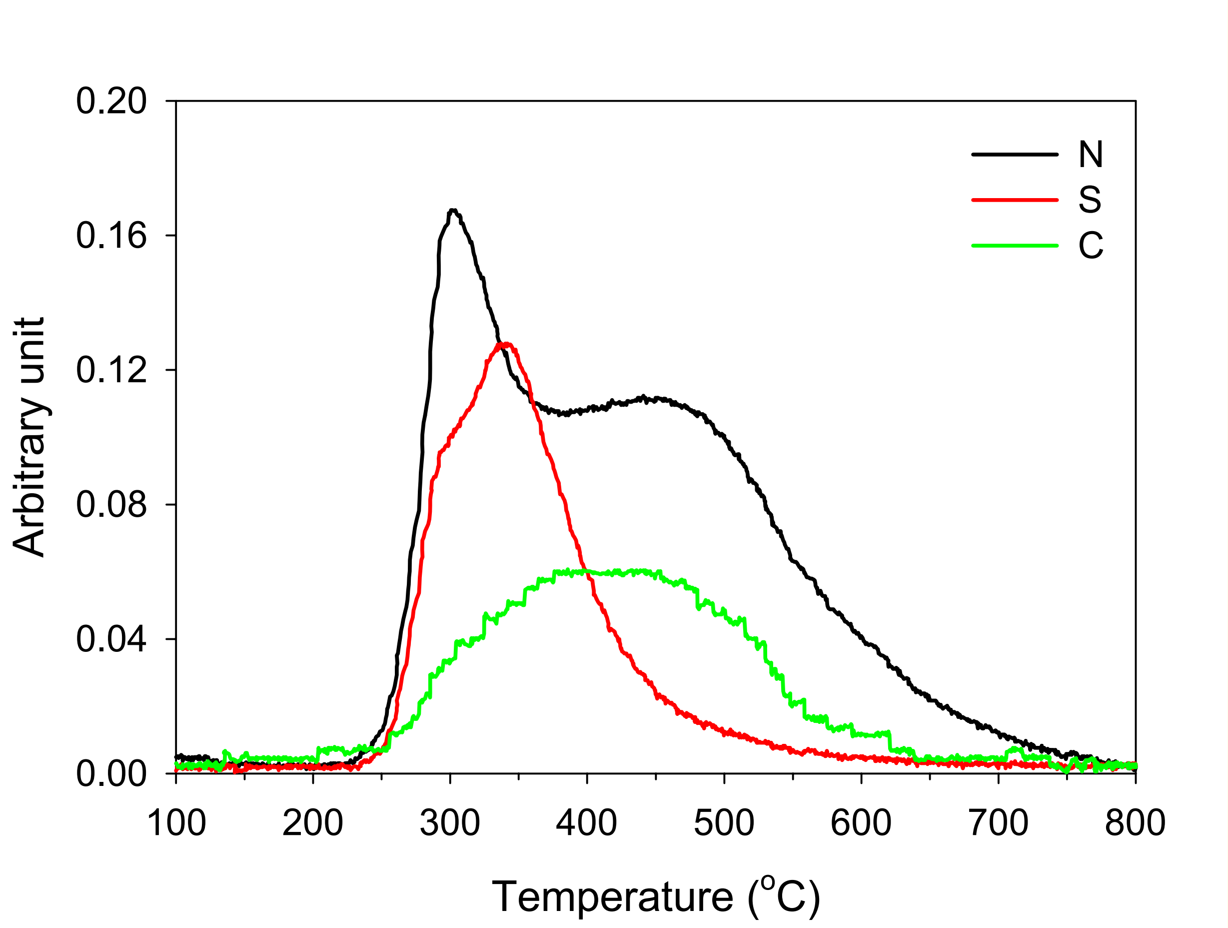
What is a STEA?



A STEA thermogram of cystine

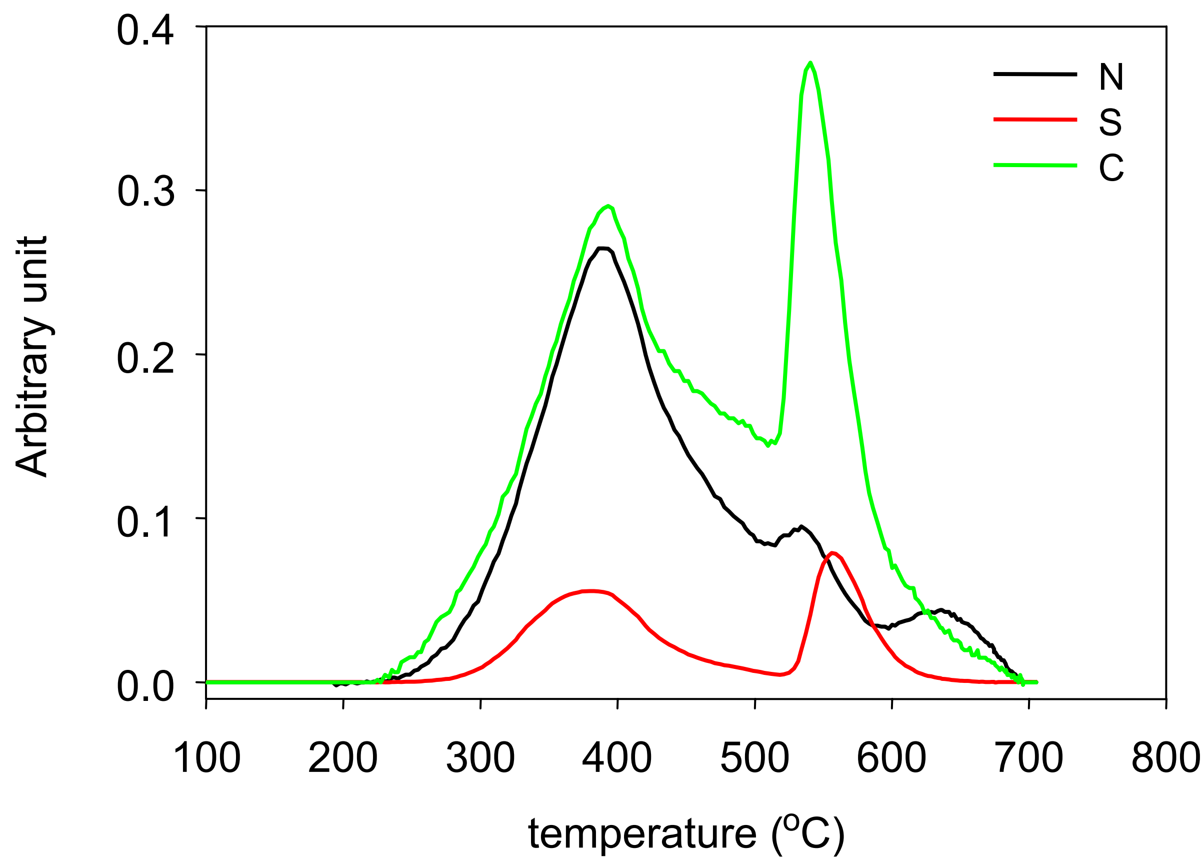


Cysteine



0.20
0.16
0.12
0.08
0.04
0.00
Arbitrary unit
100
200
300
400
500
600
700
800
Temperature (°C)
N
S
C

An air PM sample



What can STEA technology do for $PM_{2.5}$ analysis?

- Very sensitive: detection limit: <0.1 µg
- Rapid and simple analytical procedure: No need for sample pretreatment
- Provide previously unavailable chemical information for testing critical hypotheses
- Provide a chemical signature for tracing sources of $PM_{2.5}$

What is BC? Why is it important?

- Black carbon (or elemental C) is a polymerized, strongly light-absorbing (dark) by-product of incomplete combustion of biomass or fossil fuel.
- BC is, supposedly, graphite-like, may be in a spectrum of polymerization and purity.
- It seems to be quite inert and thus, may be an important sink of global carbon cycle.
- It relates to forest fire and contributes to air pollution.

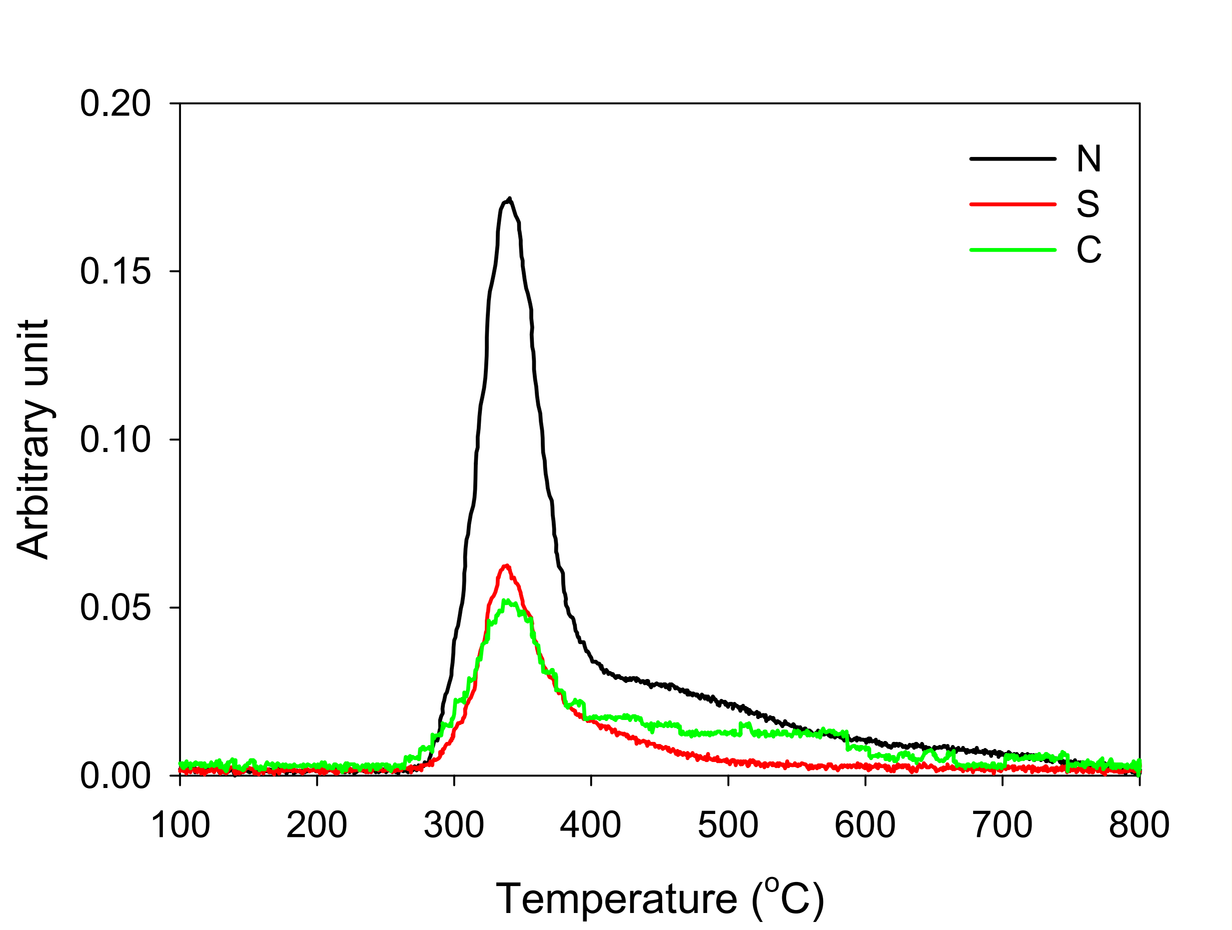
Current methods for BC determination

- Operationally defined as thermally stable at low temperature (340-370 ^{o}C) in air, highly light-absorbing fraction of the reduced (oxidizable) carbon.
- BC = total oxidizable C - OC
- BC can not have substantial N, H and O contents
- No standard method yet for separating OC and BC mainly due to a lack of methods to verify the result (a gap STEA technology can fill).

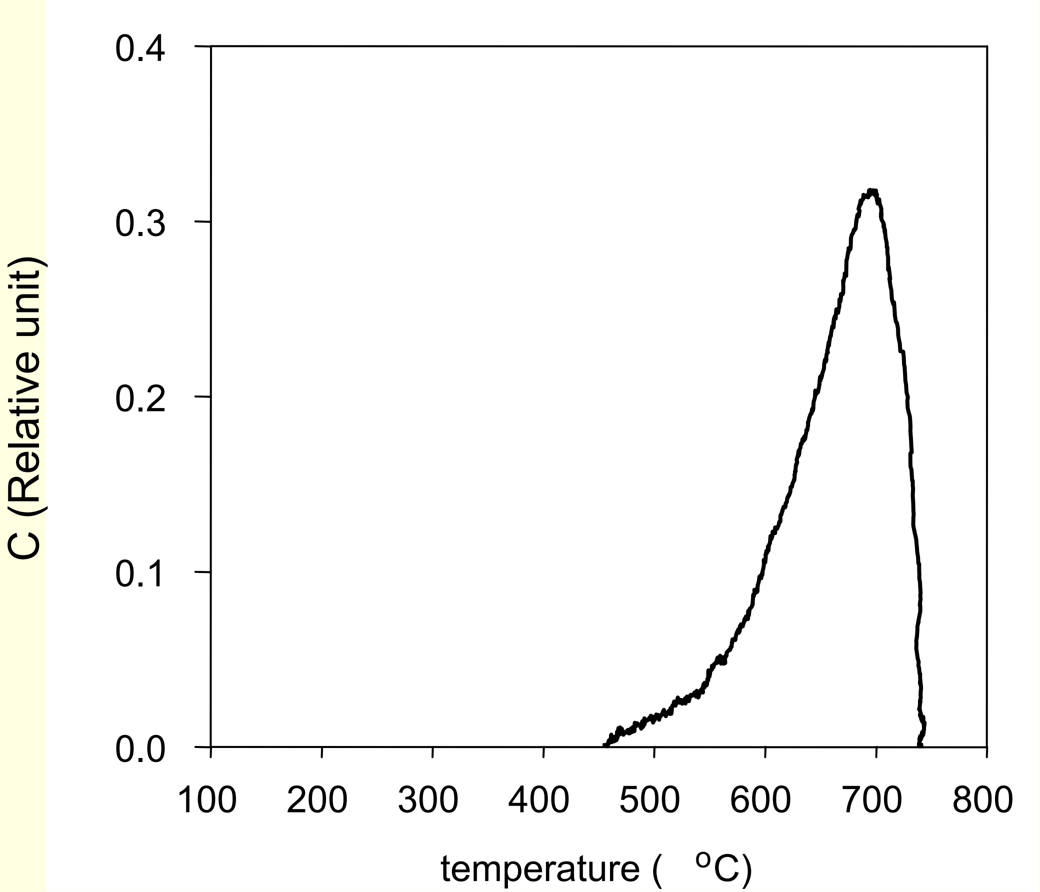
Evaluation of Current Methods for BC By the STEA technology

Results and Discussion

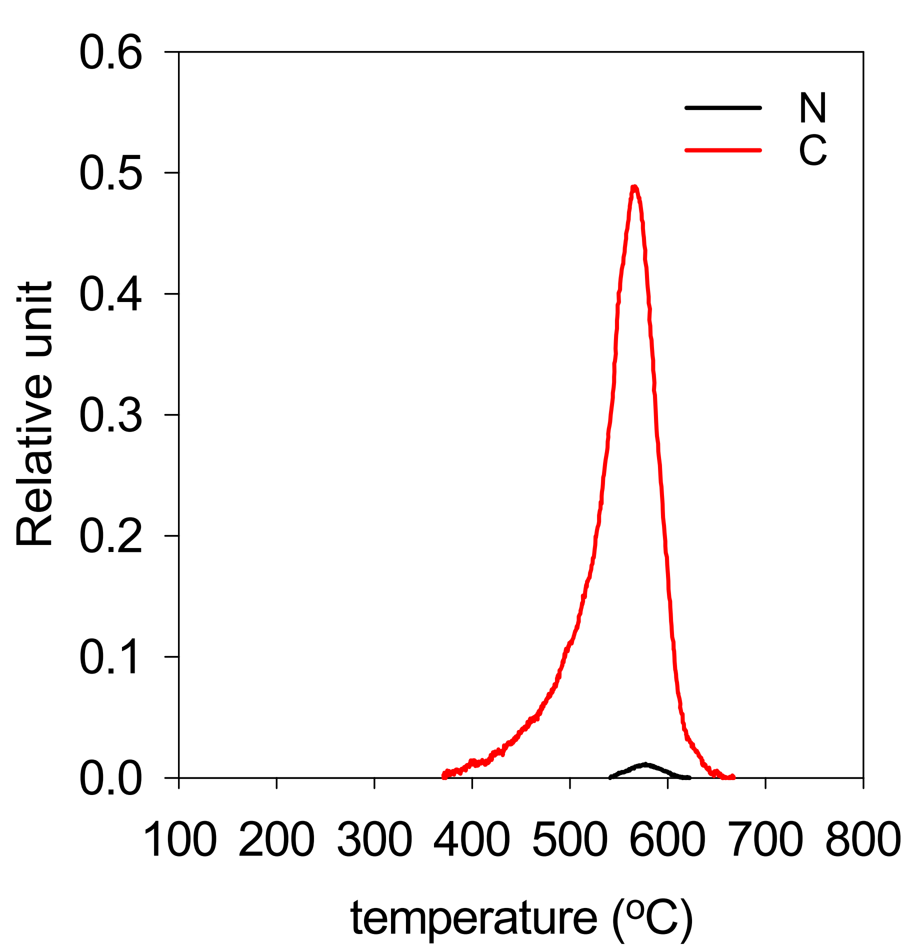
Thermogram of a cystine sample



Thermogram of a hexane soot (a BC)



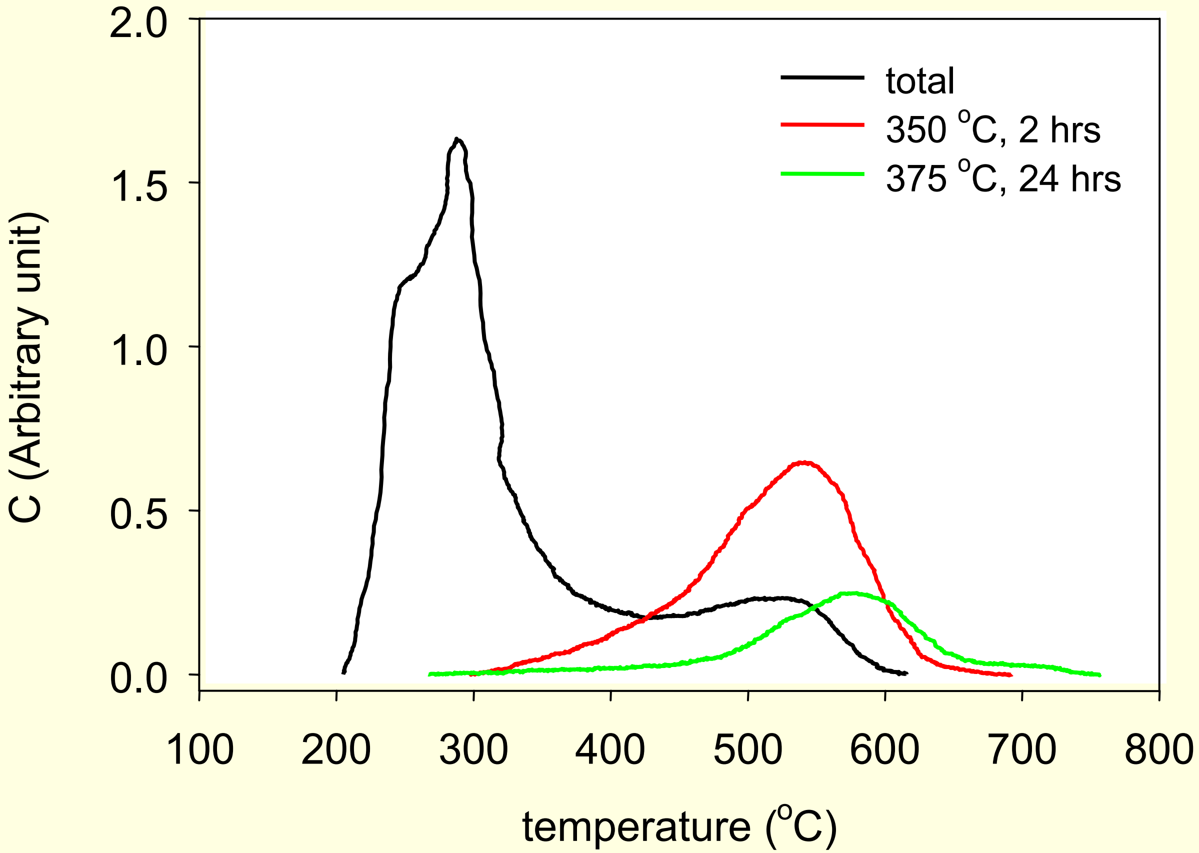
Thermogram of an activated charcoal



1. The step-heating method for BC

- OC: Oxidizable in air at 340-375 ^{o}C.
- BC = total oxidizable C - OC

Glucose



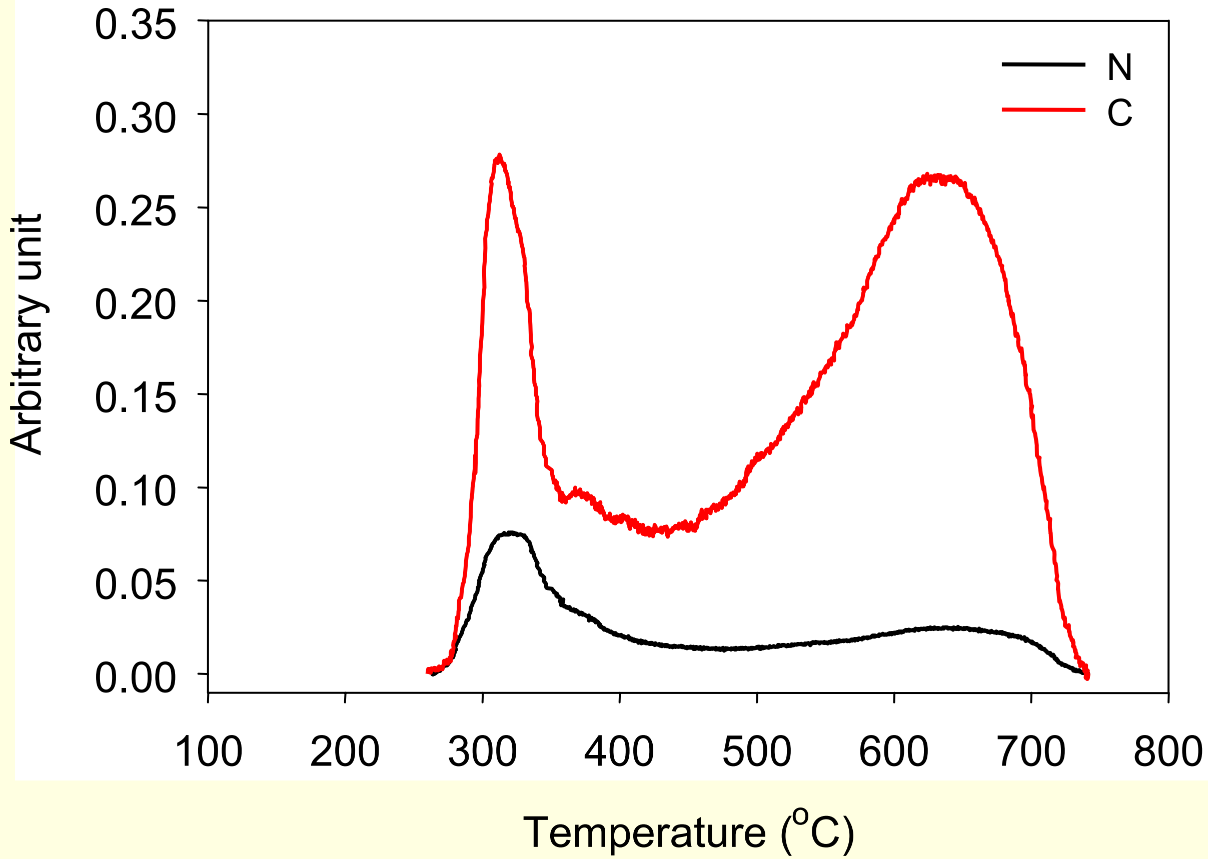
total
350 °C, 2 hrs
375 °C, 24 hrs
C (Arbitrary unit)
2.0
1.5
1.0
0.5
0.0
100
200
300
400
500
600
700
800
temperature (°C)

- The step-heating method could over estimated BC, because 1) OC may not be completely burned at low temperature, and 2) 2nd BC may form from OC during heating, 3) BC may be partially oxidized under prolonged low temperature heating.

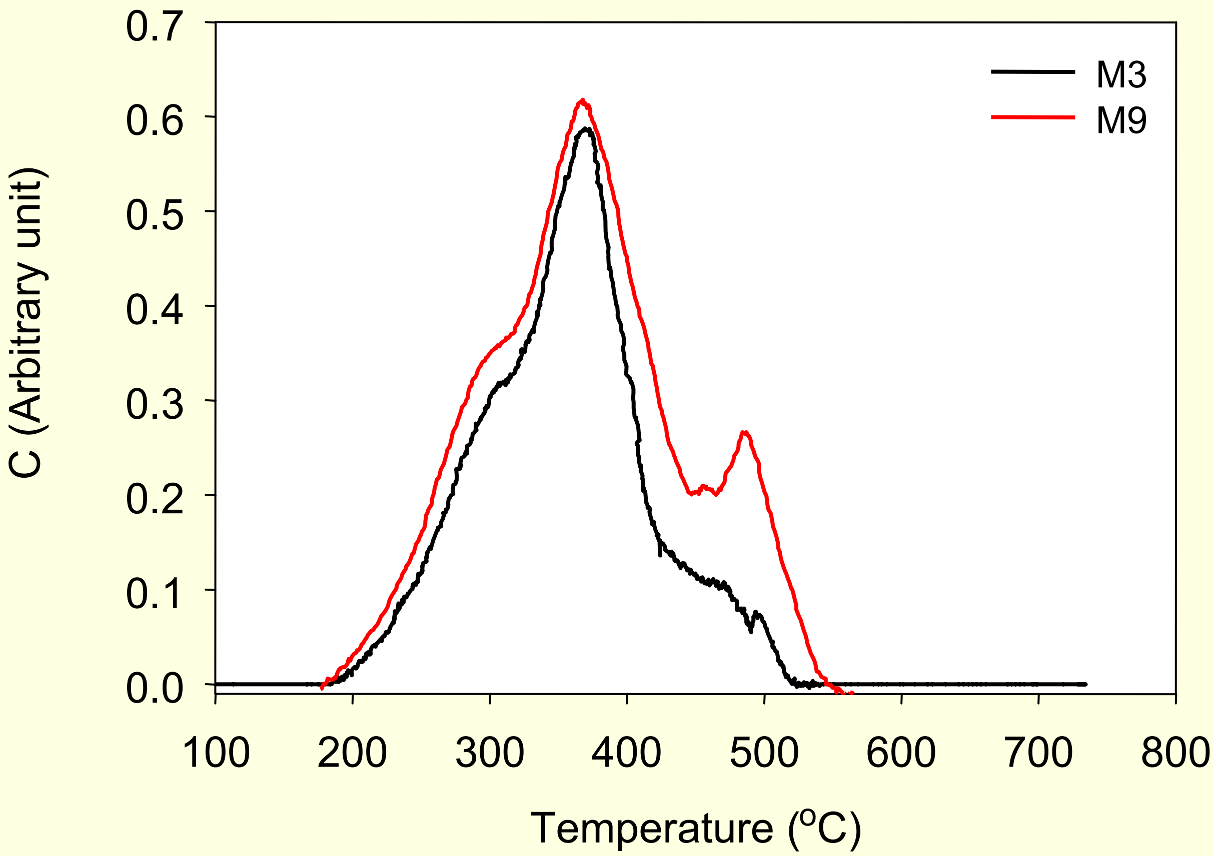
The 2nd formed BC

- Formed from OC during heating.
- The degree of 2nd BC formation depends on the nature of a compound, the oxygen content of the atmosphere and the rate of heating
- OC may be occluded in a shell of 2nd BC

A STEA thermogram of arginine



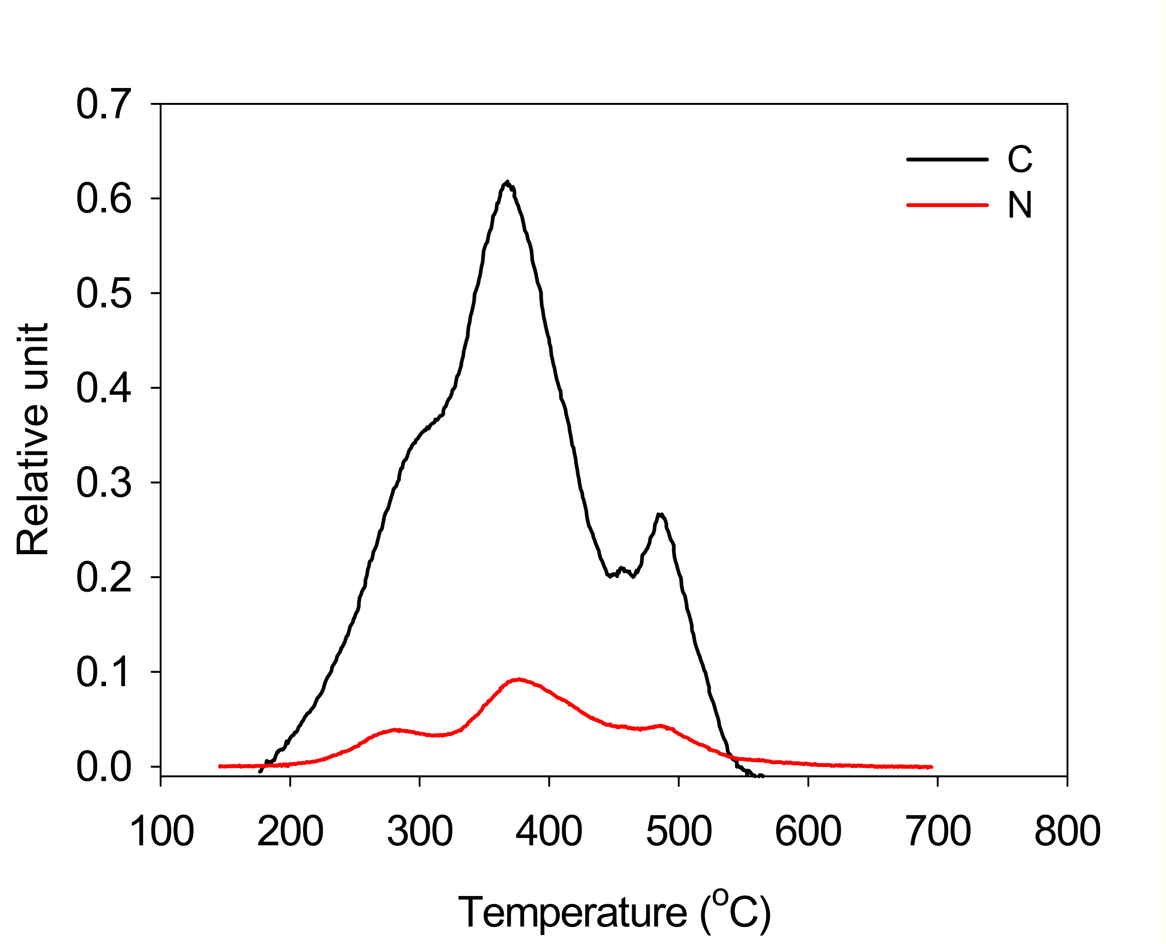
A STEA thermogram of humic acid at 50 ^{o}C/min (M3) and 110 ^{o}C/min (M9) heating rate



2. Thermal-optical method for BC

- Heating at 340-370 ^{o}C in air and monitoring optical absorption changes to estimate 2nd formed BC
- BC = total oxidizable C – low temp. oxidizable C + 2nd BC (estimated from light absorption)
- Problem: 1) May over estimate BC because OC may be occluded in a shell of 2nd BC.

Occluded OC in 2nd BC of a humic acid sample

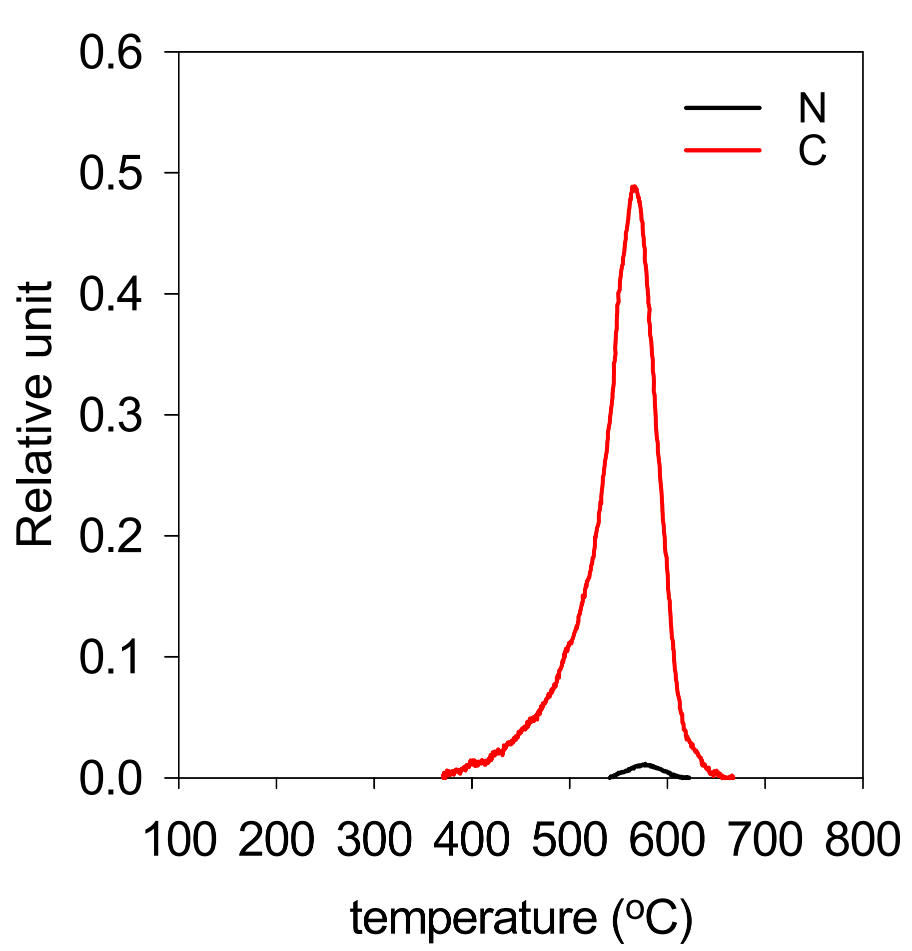


- The current methods may all over estimated BC to some extent due to incomplete separation of 2nd BC from OC and 2nd BC formation during heating analysis.

How does STEA determine BC?

- 1) Direct estimation from a STEA thermogram
- 2) The nitrate oxidation method

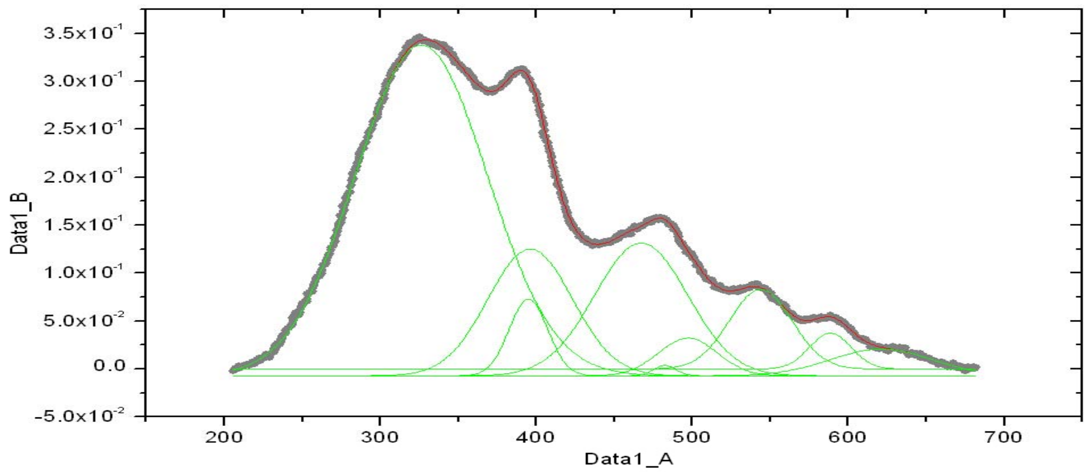
A thermogram of activated charcoal



Direct estimation from STEA thermogram

Peak Analysis Title

Source File: Data1	Data Set: Data1_B	Date:4/18/2005
Chi^2=5.079482637E-6	COD=0.9996	# of Data Points=1174
SS=0.005821087102	Corr Coef=0.9998	Degree of Freedom=1146

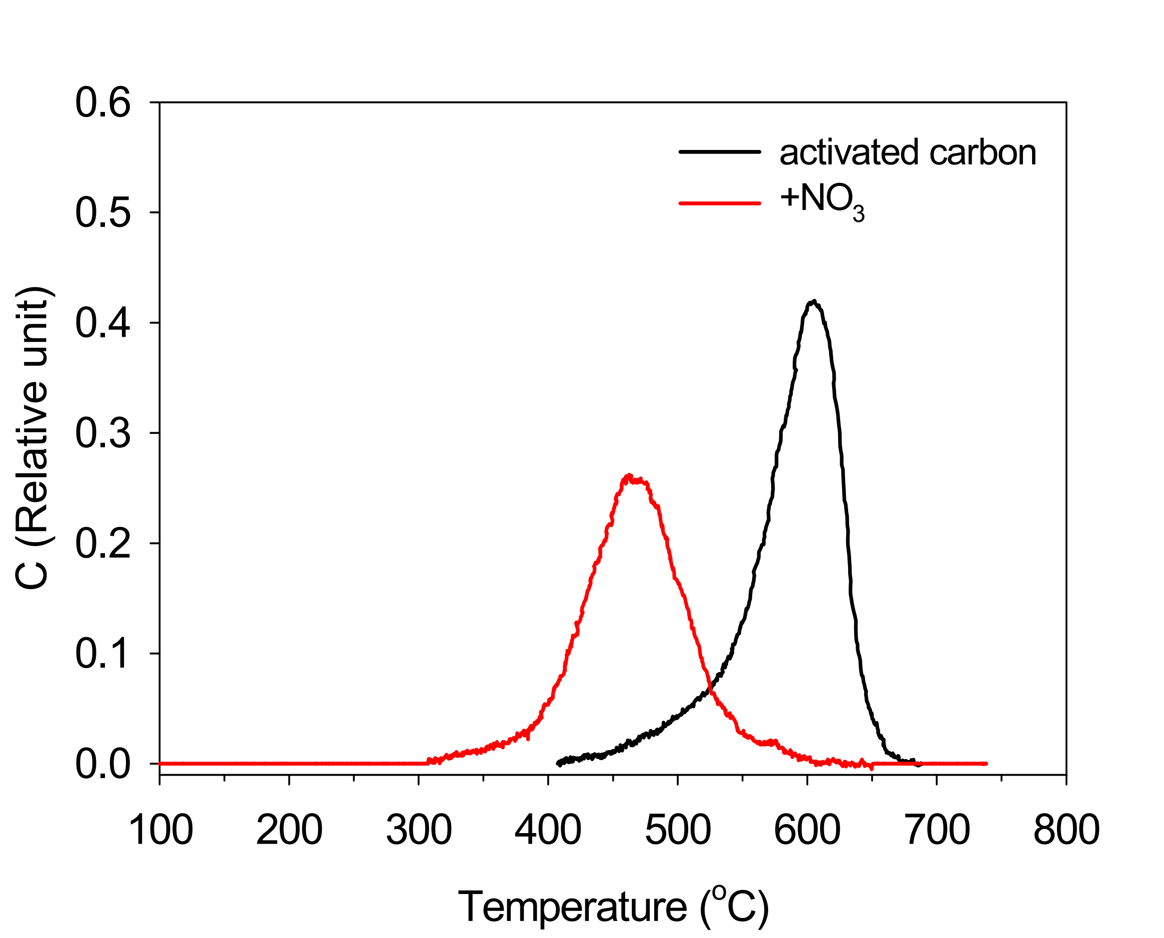


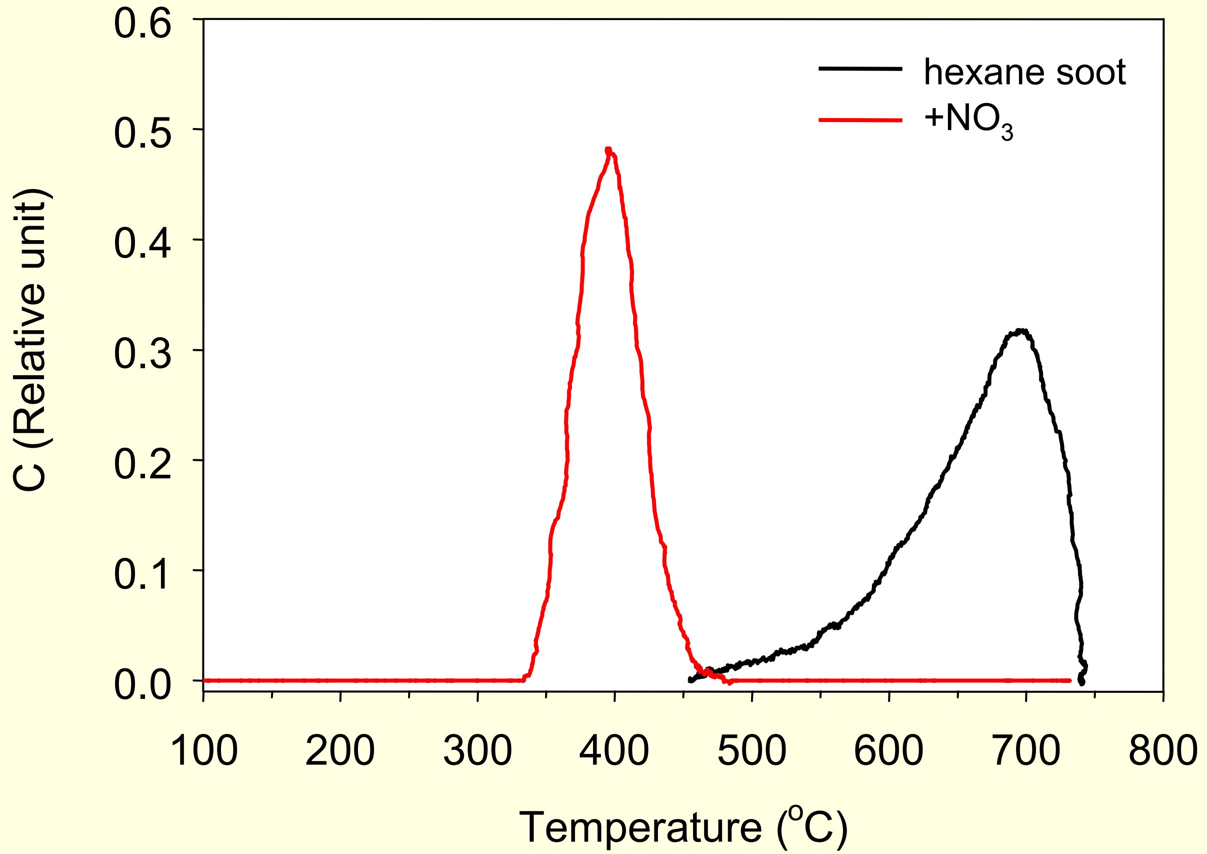
Fitting Results

Peak #	Peak Type	AreaFitT	FWHM	MaxHeight	CenterGrvty	AreaFitTP
1	Gaussian	24.42339	99.82457	0.34473	326.29841	53.69857
2	Gaussian	5.9955	63.85667	0.13196	396.12318	13.18203
3	Gaussian	1.66062	29.12648	0.07988	395.03769	3.65113
4	Gaussian	6.93326	70.54029	0.13818	467.21353	15.24384
5	Gaussian	1.23808	44.22867	0.0393	497.18517	2.72212
6	Gaussian	1.46662	76.55841	0.02775	621.00211	3.22459
7	Gaussian	0.12996	16.80789	0.01079	482.27155	0.28573
8	Gaussian	2.79682	47.36187	0.08292	543.78012	6.14925
9	Gaussian	0.83812	31.44808	0.03736	588.55227	1.84275
		45.48239				

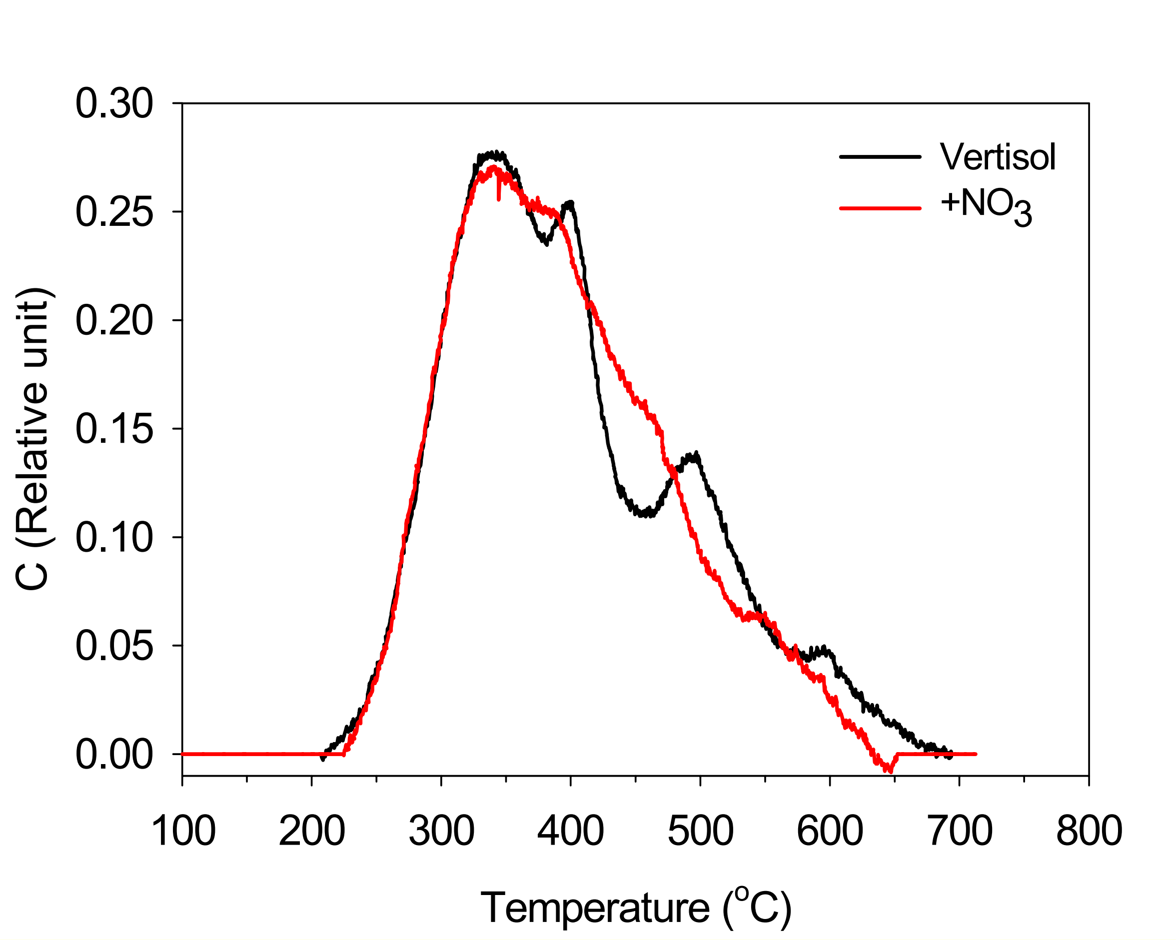
BaseLine: CONSTANT

The nitrate oxidation method




hexane soot
+NO3
C (Relative unit)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
100
200
300
400
500
600
700
800
Temperature (oC)

STEA thermogram of a vertisol



Comparison of methods of BC determination

Sample	Total C mg/g	BC 350 °C, 2 hrs mg/g	BC 375 °C, 24 hrs mg/g	BC Direct STEA mg/g	BC NO_3 method mg/g
Mollisol [1]	25.0±1.0	9.0±0.0	N.A.	2.2	0.5±0.0
Vertisol [2]	43.0±0.0	14.7±0.0	3.9	4.8	1.5±0.0
SRM1649a [3]	195.0±7.0	103.5±0.6	23.4±0.1	n.d	3.7
activated carbon	750.0±35.0	669.0	112.5	466.5	606.0
coal	981.0±2.0	611.2±0.0	0.0	723.0	582.7
hexane soot	1000.0	895.0±0.0	710.0	1000.0	995.0
marsh HA	778.3	N.A.	24.9	48.3	3.1
glucose	400.0	222.0	24.0	27.2	23.6
cystine	300.0	N.A.	11.4±0.0	0.0	N.A.

Reported BC: 1) 4.7 mg/g, 2) 10.4 mg/g, 3) 13.3-81.3 mg/g

Conclusion and Future Direction

- STEA is a sensitive and rapid method which is promising to the study of $PM_{2.5}$
- Correct measurement of BC and OC in PM samples has a critical importance to our understanding of the effects of forest fire on air quality and the global C cycle.

Conclusion and Future Direction (continued)

- We will continue to develop the STEA technology for detecting, characterizing and tracing forest fire emitted $PM_{2.5}$.
- We welcome and look forward to the opportunity of collaborating with other research teams in the application STEA technology to air quality studies.