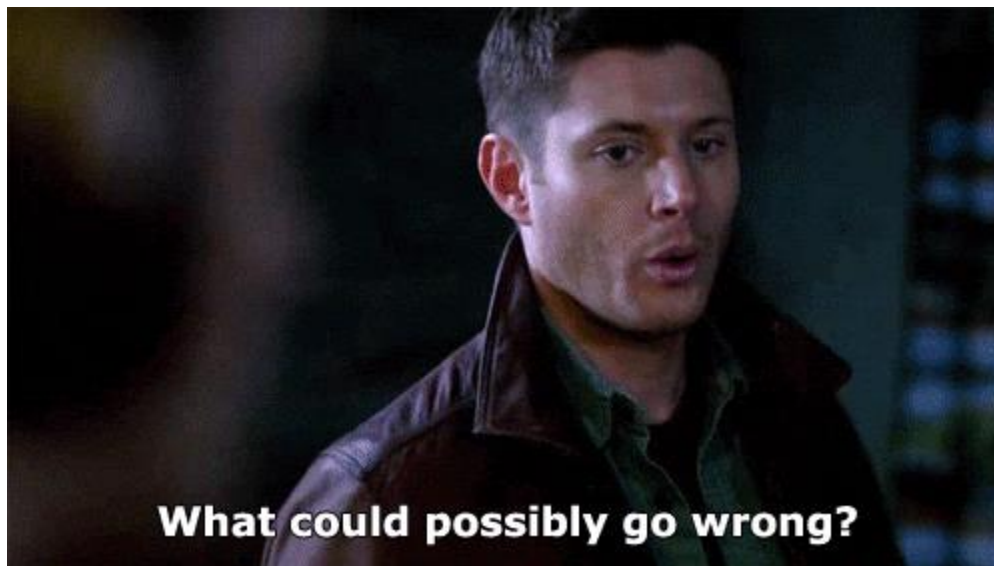


HROrg Check
&
Canagaratna et al. ACP 2015
Improved-Ambient Elemental Analysis

Pika version 1.16
Donna Sueper 6/15/2015

- Part 1: m/z 29 HR fitting, CHO & $j^{15}\text{NN}$ isotope
- Part 2: HROrg CO₂ frag
- Part 3: Elemental Analysis – Improved Ambient

HROrg (high resolution organic) Elemental Analysis (H/C, O/C OM/OC) are useful, common metrics describing aerosol composition



HROrg:

Incorrect apportionment of some HR ions

CHO (sits on top of $N^{15}N$)

CO₂ (some signal is gas phase)

To a lesser extent others:

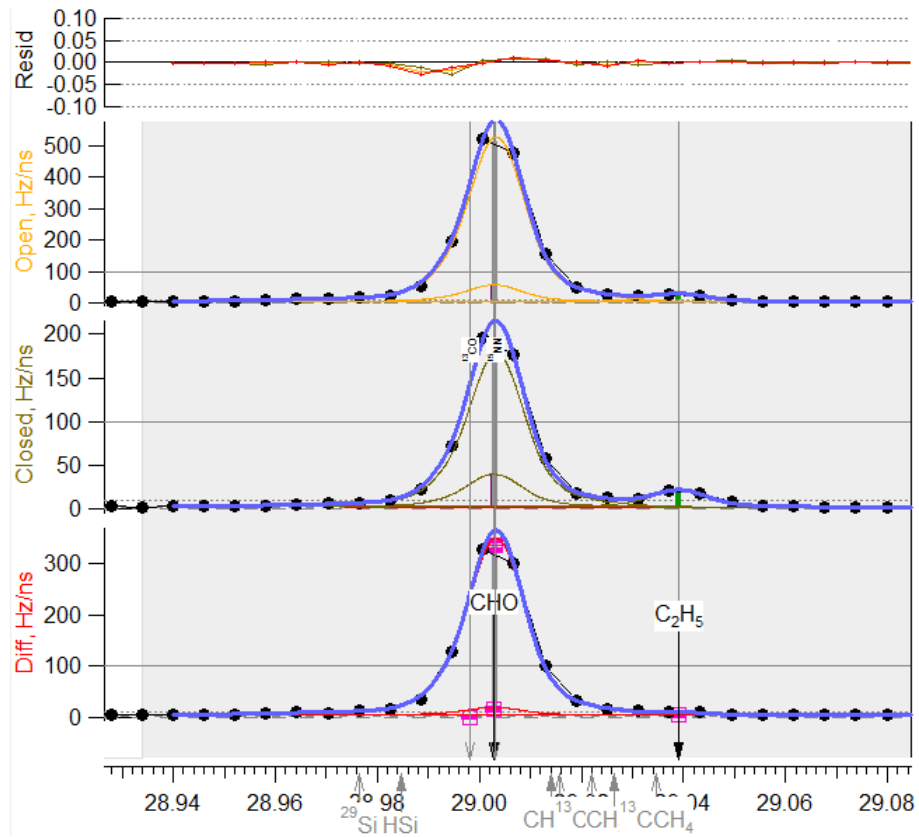
H₂O, OH, C₂H₄, etc.

Elemental Analysis:

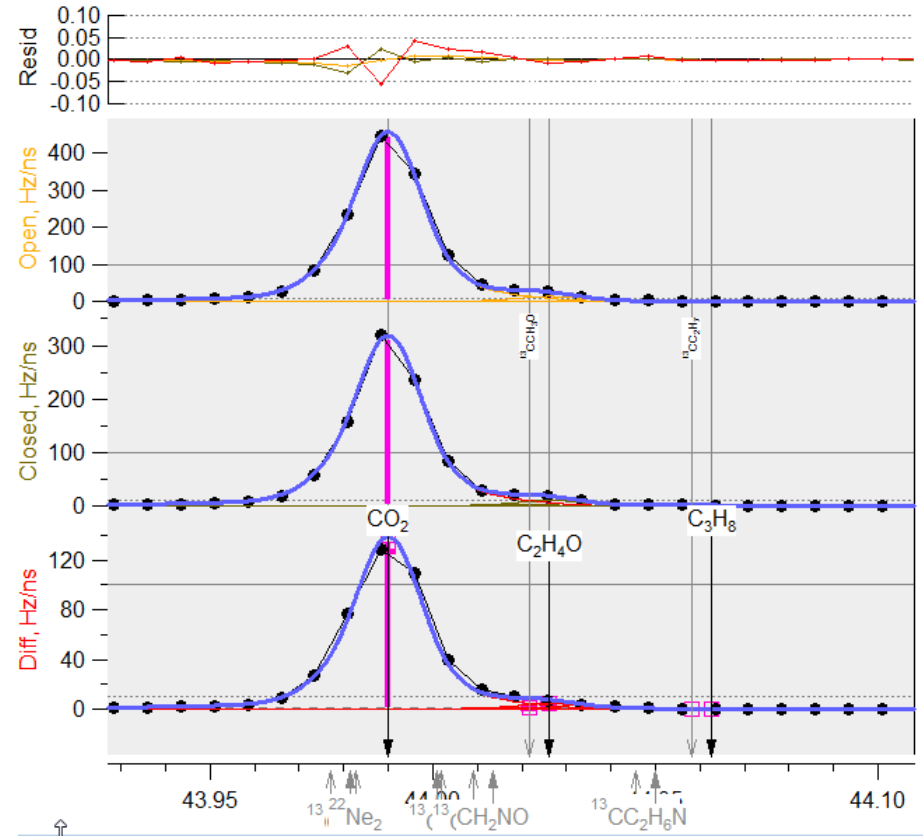
Individual HR ion signals within HROrg or HROrg can be negative when using the OMinusC data set.

We allow; if we forced ≥ 0 we would be biasing our results high.

HROrg m/z29 CHO and j15NN



HROrg m/z44 CO2



j15NN and CHO cannot be resolved. j15NN amount may follow exact isotopic amount if N₂ peak is saturated, bad tuning, etc. This is less of an issue for those with an ADQ card.

CO₂ signal comes from both gas and aerosol phase. We estimate CO₂ gas abundance as a multiple of N₂.

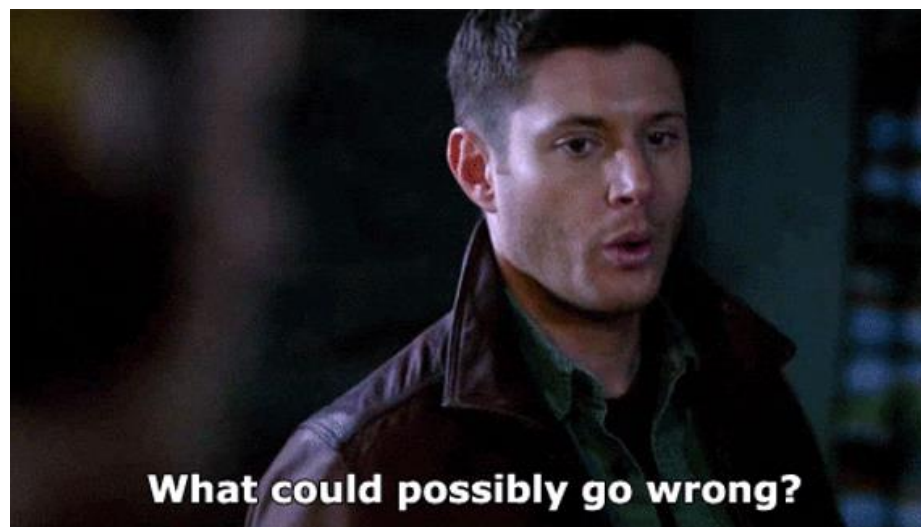
Improved – Ambient Elemental Analysis (H/C, O/C OM/OC)

$$H/C = (H/C\#) * (1.07 + 1.07 * f_{CHO})$$

$$O/C = (O/C\#) * (1.26 - 0.63 * f_{CO2} + 2.28 * f_{CHO})$$

Where f_{CHO} and f_{CO2} are surrogates for alcohols, acids

$H/C\#$ and $O/C\#$ use default Org frag, calibration factors from Aiken et al



f_{CHO} and f_{CO2} could be poor surrogates:

when **CHO is wrong** (has not been accounted for properly, i.e. HROrg is wrong)

when **CO2 is wrong** (has not been accounted for properly, i.e. HROrg is wrong)

when they are **noisy surrogates** and thus add noise to EA calculations

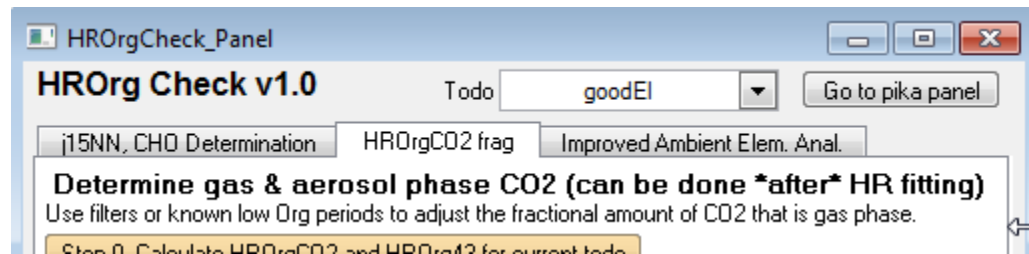
Needed: A method for systematically performing checks for
HROrg CHO HROrg CO2 (... perhaps other ions in the future)
fCHO, fCO2 for Improved Ambient Elemental Analysis

Solution: HROrgCheck panel with 3 sections

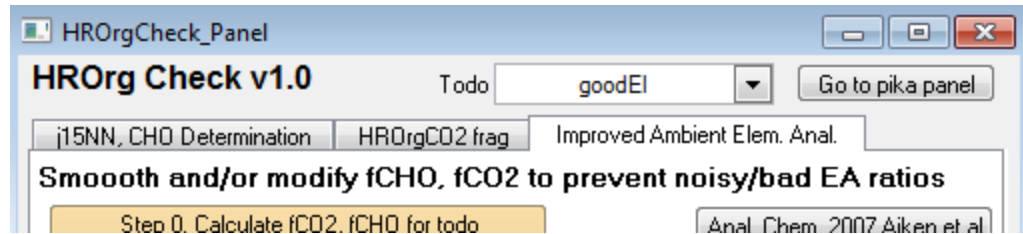
Tab 1:
m/z 29 CHO and j15NN



Tab 2:
HROrgCO2



Tab 3:
f_{CHO}, f_{CO2}



Part 1 m/z 29 HR fitting & j15NN isotope

HR_Analysis_Panel

ToF-AMS HR Analysis 1.15P

PIKA module for SQUIRREL 1.56 or higher

Todo waves: goodEI

Version Website
FAQs, Website
Upgrade Pika
Credits

Set Up HR Fits | HR Ion Groups | HR Fits One Spectra | **HR Fits for Many Runs** | HR Results

Step 5: Calculate HR sticks for each run in current todo wave.

This step is time consuming. All HR fit options in Step 4 will be used.
It is recommended that users first perform this step on a todo wave with a small number of runs (<50) and then examine step 5 diagnostics before performing HR fits on a todo wave with a large number of runs.

Step 5 preliminary. j15NN isotope analysis using UMR data (HROrg Check Panel)

Fit PTof groups selected

Save experiment after completion

Step 5. Calc HR sticks for all runs in todo wave

Info for last instance of Step 5
Todo wave: goodEI Num. of HR ions: 567
Time Completed: Tue, Jun 02, 2015 4:01:56 PM
Num. of failed fits: 0
Use Peak Shape: 1
Constrain Isotopes: 1 Let Peak Width Vary: 0
Use separate O,C m/z params: 0
MS

Step 5a (Optional) PTof data set subtraction

PTof HR data set 'Open' Get List

PTof HR data set 'Closed' Get List

Name of the new HR PTof data set
PTof_

Calculate PTof 'Open' - PTof 'Closed'

Step 5i: (For HR sticks found previous to 1.09H) Calculate total ion count error in todo wave.
Find HRTtotalIDMinusClonCountErr

Step 5ii: (For HR sticks found previous to 1.12N) Calculate total signal error in todo wave.
Find HRTtotalIDMinusCSigErr

Step 5A. View diagnostics for HR fits of todo wave

Diagnostic 5a:
Ten UMR parameters time series panel

Diagnostic 5b:
Graph, table of runs, amus where HR fit failed

There is now a gold button, 'Pika Step 5 preliminary'

It is necessary to apportion the peak of CHO and j15NN correctly before HR fits so that CHO isotopes at ^{13}CHO etc can be propagated correctly.

This is the only HR ion for which it is not possible to fix within the HR frag table.

The purpose of this tab is to aid the user in determining the j15NN contribution (air at m/z 29)

A graph shows UMR (or HR)
- Org29 vs Org43 (HROrg29 vs HROrg43)

Optimally, the user would chose a todo wave with filters and nonfilter data.

The goal is to adjust the variable such that data clusters near origin (for filter data) and/or fit line has an intercept of 0 (for non-filter data).

When the user updates the scalar (above the Step 2 gold button) the data, plot, and fit line updates.

HROrgCheck v1.1 Todo: all Go to pika panel

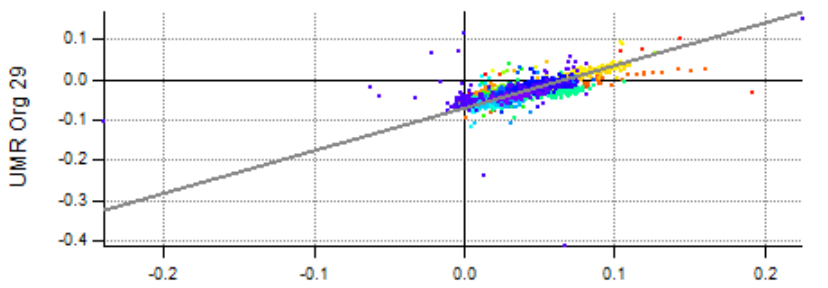
j15NN, CHO Determination HROrgCO2 frag Improved Ambient Elem. Anal.

Determine CHO abundance by by modifying j15NN abundance
 CHO and j15NN are <0.001 m/z apart. These ions are resolved by constraining j15NN by N2; remaining signal at this peak is fit to CHO. Use filters or known low Org periods to adjust the isotopic scalar to get Org29 = 0 at these periods. Use the UMR option if HR data has not been fit; else use the HR option.

UMR HR Step 0. Calculate Org29 and Org43 for current todo Go to pika fitting gr

Step 1. Adjust the j15NN scalar to get data clustering the origin (filters) or fit intercept near the origin.
 frag_air[29] = 1 * 0.0073066 * frag_air[28] Revert to previous value

Step 2. Declare isotope value for j15NN in HR and frag_air[29] in UMR Pop Graph



Details

Step 3. Perform HR fits using this j15NN isotopic abundance (Pika step 5)

HR Org Check v1.0

Todo: all

Go to pika panel

j15NN Estimation | HROrgCO2 frag | Improved Ambient Elem. Anal.

Estimate j15NN as a scalar multiple of m/z 28 (UMR) or N2 (HR)

CHO and j15NN are <0.001 m/z apart. These ions are resolved by constraining j15NN; remaining signal at this peak is fit to CHO in HR. Use filters or known low Org periods to adjust the scalar to get Org = 0 at these periods. Use the UMR option if HR data has not yet been fit; else use the HR option.

UMR HR

Step 0. Calculate HROrg29 and HROrg43 for current todo

Go to pika fitting.gr

Step 1. Adjust the j15NN scalar below so that intercept lies near or clusters on the origin.
(Decreasing the scalar increases Org)

j15NN = 0.825 * 0.0073066 * {N2}

Revert to previous value

Step 2. Declare scalar value for j15NN in HR and frag_air29 in UMR

Pop Graph

UMR Org 29

UMR Org 43

Details

Step 3. Perform HR fits using this isotopic abundance for j15NN.

Optionally, if the 'Details' checkbox is checked two tables will appear:

- HR ion table at j15NN row
- UMR frag table at mz29 row

The goal is to obtain good a good setting for j15NN for HR fitting.

For simplicity, users may want to maintain identical settings for UMR, frag_air[29], as for the HR setting.

However, as the UMR case cannot apportion C2H5 exactly the UMR correction will be slightly different than HR.

Tab 1 j15NN, CHO Determination at m/z29

HROrg Check v1.1

Todo: all [Go to pika panel]

j15NN, CHO Determination | HROrgCO2 frag | Improved Ambient Elem. Anal.

Determine CHO abundance by by modifying j15NN abundance

CHO and j15NN are <0.001 m/z apart. These ions are resolved by constraining j15NN by N2; remaining signal at this peak is fit to CHO. Use filters or known low Org periods to adjust the isotopic scalar to get Org29 = 0 at these periods. Use the UMR option if HR data has not been fit; else use the HR option.

UMR HR [Step 0. Calculate Org29 and Org43 for current todo] [Go to pika fitting gr]

Step 1. Adjust the j15NN scalar to get data clustering the origin (filters) or fit intercept near the origin.

frag_air[29] = 0.83 * 0.0073066*frag_air[28] [Revert to previous value]

Step 2. Declare isotope value for j15NN in HR and frag_air[29] in UMR [Pop Graph]

UMR Org 29 vs UMR Org 43 scatter plot

Details [Declare value for j15NN in HR table (Step 2 only for HR)] [Pop HR Table]

Point	HR ion	Mass	Fit Mask	Comments	Fit Mask Default	Isotope Abund.
79	j15NN	29.00318	1	0.83*0.0073066	1	0.00806448

[Declare value for frag_air29 in UMR table (Step 2 only for UMR)] [Pop UMR Table]

m/z	frag_air	frag_organic
29	0.83*0.00730666*frag_air[28]	29,-frag_air[29]

Step 3. Perform HR peak fitting with this j15NN isotopic abundance

When optimal settings have been found, the user presses the Step 2 gold button. Three things happen:

- (1) Entries identified in the tables are overwritten.
- (2) In the history window this statement is added:
"// The user declared the j15NN isotope scalar to be 0.83 at time x, day y."
- (3) The text "Step 3.." which indicates that the user should now perform HR fits is enlarged & red.

Advanced users & high loading data sets may opt to have different settings for HR and UMR data. This can be achieved through buttons above each table.

Tab 2 HROrg CO2 frag

HR_Analysis_Panel

ToF-AMS HR Analysis 1.150

PIKA module for SQUIRREL 1.56 or higher

Version Website
FAQs, Website
Upgrade Pika
Credits

Todo waves: allFastOpen

HROrgCO2 HR frag check

Set Up HR Fits | HR Ion Groups | HR Fits One Spectra | HR Fits for Many Runs | **HR Results**

Step 6i: Describe characteristics of HR results you want to generate.

List of entities to generate

HR ions, families, and/or species (i.e. j15N,familyNH,HRair) N2,CO2,HROrgCO2

* The RIE and CE for HR ions and HR families is 1 (Nitrate Equiv. $\mu\text{g}/\text{m}^3$). Remove isotopes from list above

Integer m/z 29 < Add HR ion to list of entities family Air < Add HR ions to list of entities

Set list to all HR species | Set list to aerosol HR species | Set list to all HR families | Clear list

Data, Output Options

Data HROrgMinusCStick Graph Plot single Convert to $\mu\text{g}/\text{m}^3$ Convert nan sticks to 0

Calc, plot err. HROrgMinusCTotCountErr Use MS AB correction Convert neg. sticks to 0

Set wave name suffix ^PTof data is dMdlq10dva

Step 6ii: Select the time series or average mass spectra type of result to generate.

Diag. | Time Series | Average MS | Elem. Anal. | 2-d Time Series MS | HR CDCE | Export

Sq vs Pk Species

Calc & display Sq vs Pk panel

Useful Tables for Current Todo

Fitted HR ions | HR ions for species

HROrg atomic mass fract.

Mass defect family colored signal sized

HROrg Check Panel - HROrgCO2 frag

A new button has been entered in the HR Results – Diagnostics tab.

When this gold button is pressed, the code automatically goes to the 2nd tab of the previous panel.

The purpose of this tab is to aid the user in determining the CO2 gas phase and CO2 aerosol phase components.

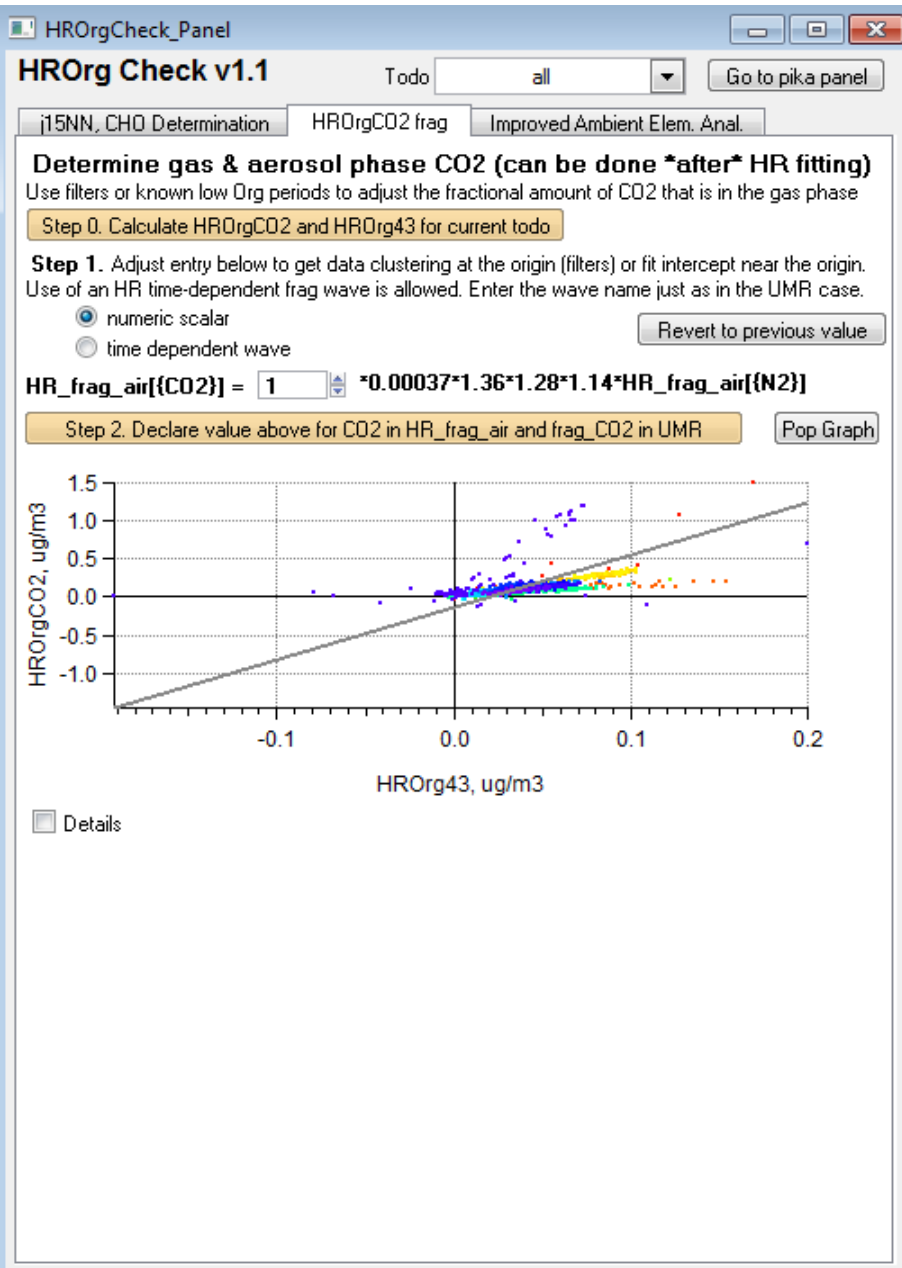
A graph shows
- HROrg44 vs HROrg43

Optimally, the user would chose a todo wave with filters and nonfilter data.

The goal is to adjust the variable such that data clusters near origin (for filter data) and/or fit line has an intercept of 0 (for non-filter data).

Use of an optional time dependent CO2 wave is allowed & syntax, use is the same.

When the user updates the scalar (above the Step 2 gold button) the data, plot, and fit line updates.



Tab 2 HROrg CO2 frag

HROrgCheck_Panel

HROrg Check v1.0 Todo: goodEl Go to pika panel

[15NN, CHO Determination] HROrgCO2 frag Improved Ambient Elem. Anal.

Determine gas & aerosol phase CO2 (can be done *after* HR fitting)
 Use filters or known low Org periods to adjust the fractional amount of CO2 that is gas phase.

Step 0. Calculate HROrgCO2 and HROrg43 for current todo

Step 1. Adjust the entry to get data clustering the origin (filters) or fit intercept near the origin.
 Use of an HR time-dependent frag wave is allowed. Enter the wave name just as in the UMR case.

numeric scalar Revert to previous value
 time dependent wave

HR_frag_air[CO2] = * 0.00037 * 1.36 * 1.28 * 1.14 * HR_frag_air[N2]

Step 2. Declare value above for CO2 in HR_frag_air and frag_CO2 in UMR Pop Graph

Details Declare value for air CO2 in HR table (Step 2 only for HR) Pop HR Table

Point	HR_specMass	HR_frag_air	HR_fr
17	CO2	1.175*0.00037*1.36*1.28*1.14*HR_frag_air[N2]	

Declare value for air CO2 in UMR table (Step 2 only for UMR) Pop UMR Table

mz	frag_air	frag_CO2	frag_O
44	frag_CO2[44]	1.175*0.00037*1.36*1.28*1.14*frag_air[28]	

Optionally, if the 'Details' checkbox is checked two tables will appear:

- HR frag table at CO2 row
- UMR frag table at mz44 row

The goal is to obtain good a good setting for CO2 gas vs aerosol contribution.

For simplicity, users may want to maintain identical settings for UMR, frag_CO2[44], as for the HR setting.

However, as the UMR case does not consider contributions from C2H4O nor C3H8 the UMR correction will be slightly different than HR.

Part 2 HROrg CO2 frag

Estimate gas phase CO2 signal (can be done *AFTER* HR fitting)
 $HR_{OrgCO2} = (1/RIE * CE) * (CO2) - HR_frag_air\{CO2\}$ This is similar to the UMR case.

Step 0. Calculate HROrg29 and HROrg43 for current todo

Step 1. Modify the HR_frag_air CO2 entry below so that intercept lies near or clusters on the origin. Use of an HR time-dependent frag wave is allowed. Enter the wave name just as in the UMR case.

time dependent wave numeric scalar

HR_frag_air[CO2] = 0.9 * CO2wave*1.36*1.28*1.14*HR_frag_air[N2]

Step 2. Declare value above for CO2 in HR_frag_air and frag_CO2 in UMR

HR_frag_air[CO2] = 0.9 * CO2wave*1.36*1.28*1.14*HR_frag_air[N2]

HR_frag_air[CO2] = 0.9 * CO2wave*1.36*1.28*1.14*HR_frag_air[N2]

Point	HR_spa	HR_frag_air	HR_fra
17	CO2	0.9*CO2wave*1.36*1.28*1.14*HR_frag_air[N2]	

mz	frag_air	frag_CO2	frag_O
44	frag_CO2[44]	0.9*CO2wave*1.36*1.28*1.14*frag_air[2]	

When optimal settings have been found, the user presses the Step 2 gold button. Two things happen:

(1) Entries identified in the tables are overwritten.

(2) Additionally, in the history window this statement is added:

"// The user declared the CO2 air contribution to be *** at time x, day y."

Advanced users & high loading data sets may opt to have different settings for HR and UMR data. This can be achieved through buttons above each table.

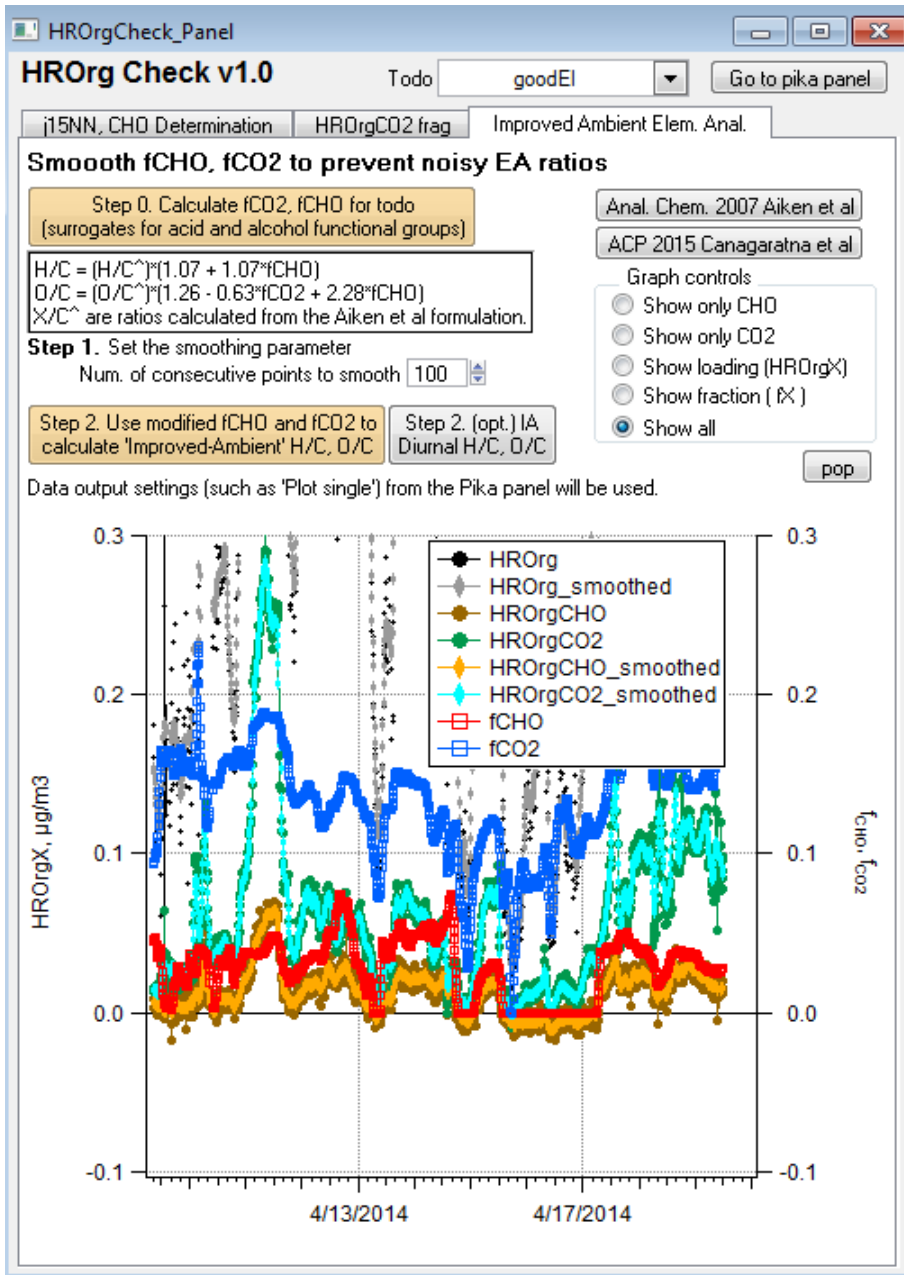
Part 3 Elemental Analysis – Improved Ambient

Slightly rearranged EA tab.
When this gold button is pressed, the code automatically goes to the 3rd tab of the previous panel. The only way a user can calculate Improved-Ambient EA ratios is via this new HROrgCheck panel

When the Use ACP... checkbox is not checked, the old buttons for time series and diurnals appear and the HROrgCheck panel button disappears.

Part 3 Elemental Analysis – Improved Ambient

The purpose of this tab is to aid the user in determining the fCHO and fCO2 values that will be used in the improved ambient (IA) O/C and H/C ratios.



- A graph of time series of
- HROrgCO2, HROrgCO2_smoothed,
 - fCO2
 - HROrgCHO, HROrgCHO_smoothed, fCHO

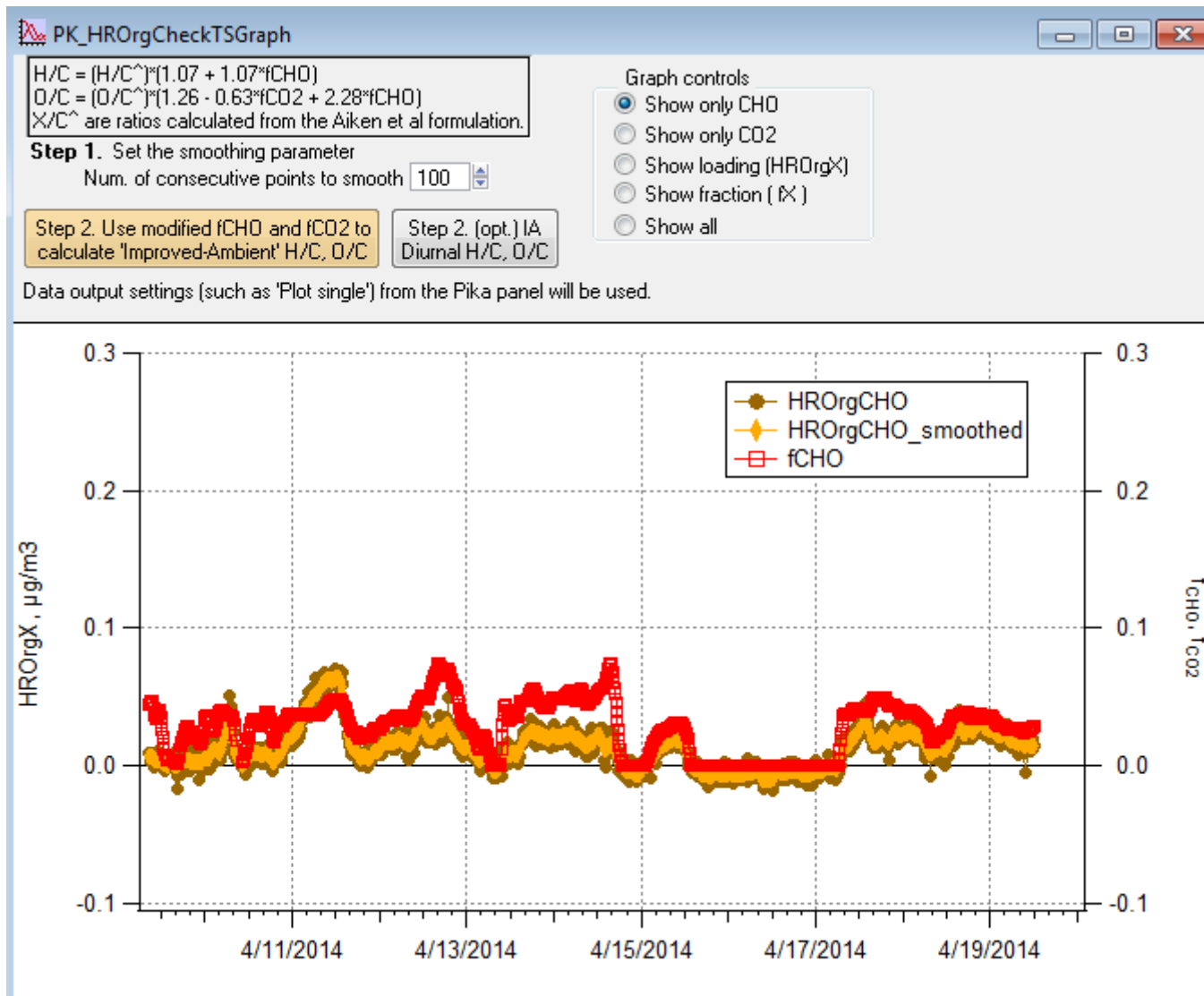
Radio buttons help users display only one set of data at a time.

- The goal is to
- (1) adjust the smoothing parameter such that fX doesn't contain noise but retains real atmospheric variability
 - (2) Review time series of HROrgCHO
 - (3) Review time series of HROrgCO2

$$fX = \text{smoothed}(X) / \text{smoothed}(\text{HROrg})$$

$$fX = \text{limit}(fX[p], 0, 1)$$

Part 3 Elemental Analysis – Improved Ambient

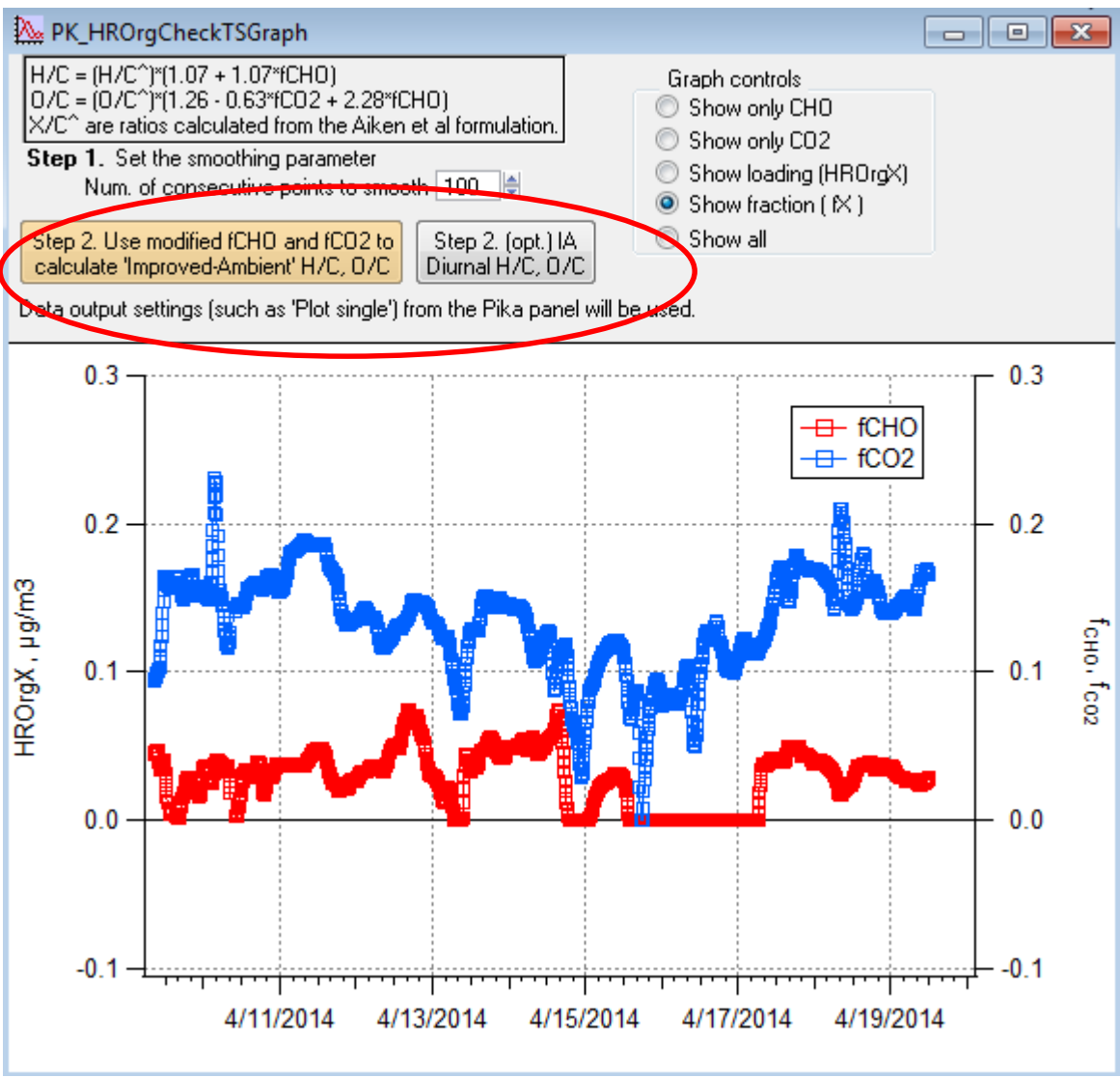


An example of the popped graph and showing only the CHO waves.

When the user updates the scalar (above the Step 2 gold button) the data, plot updates.

Unlike the previous variables users adjust, the exact value of the smoothing parameter is subjective.

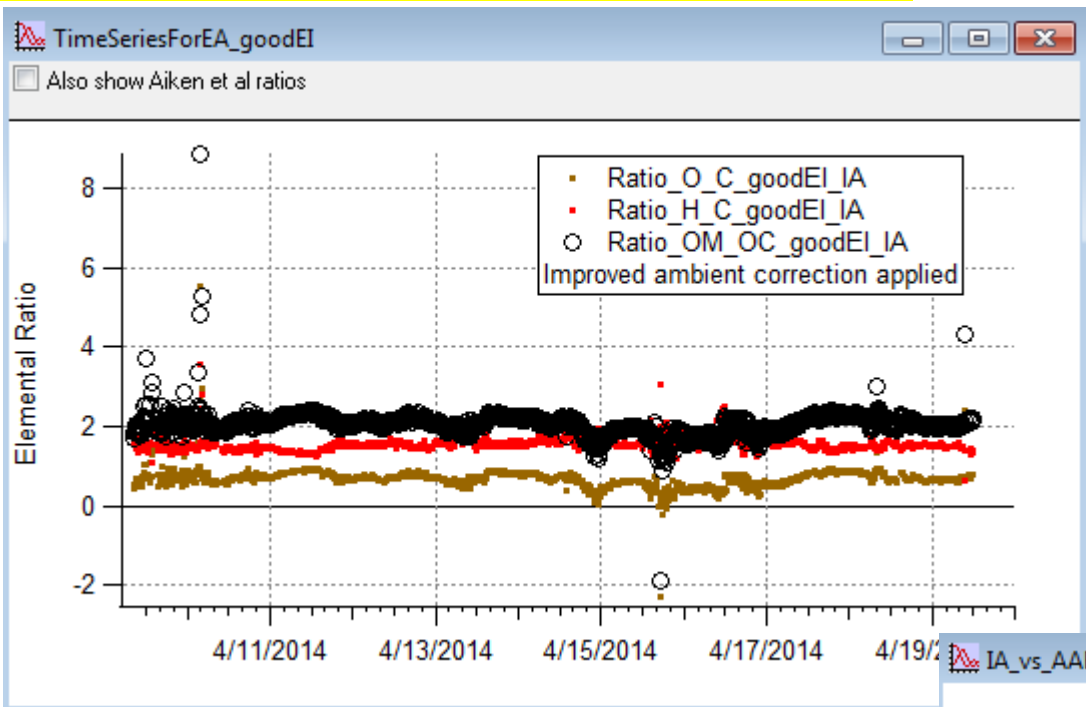
Part 3 Elemental Analysis – Improved Ambient



The actual generation of time series graphs, van Krevlin diagrams, and the Improved-Ambient vs Aiken_Ambient scatter plot, and the diurnal plot are generated from the HROrgCheck_Panel or the popped graph.

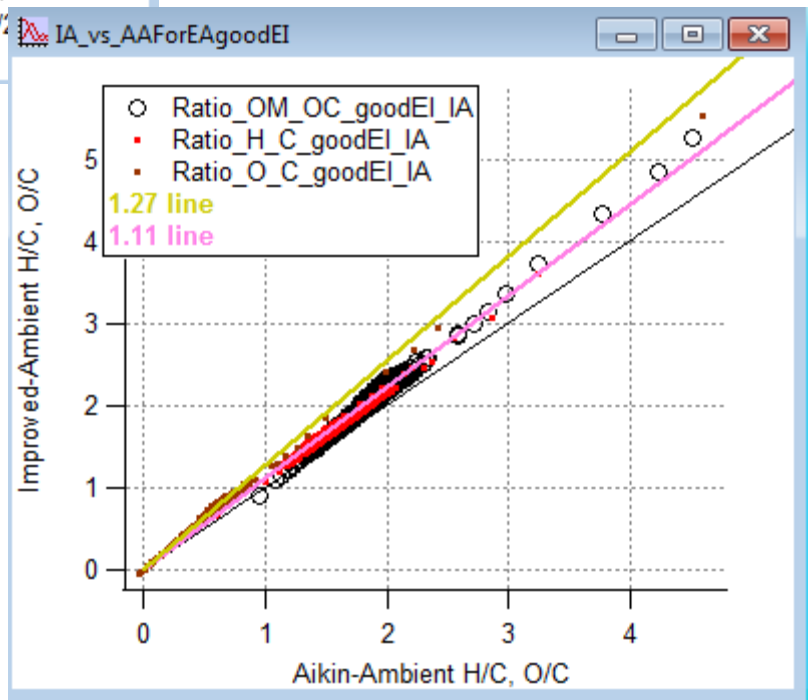
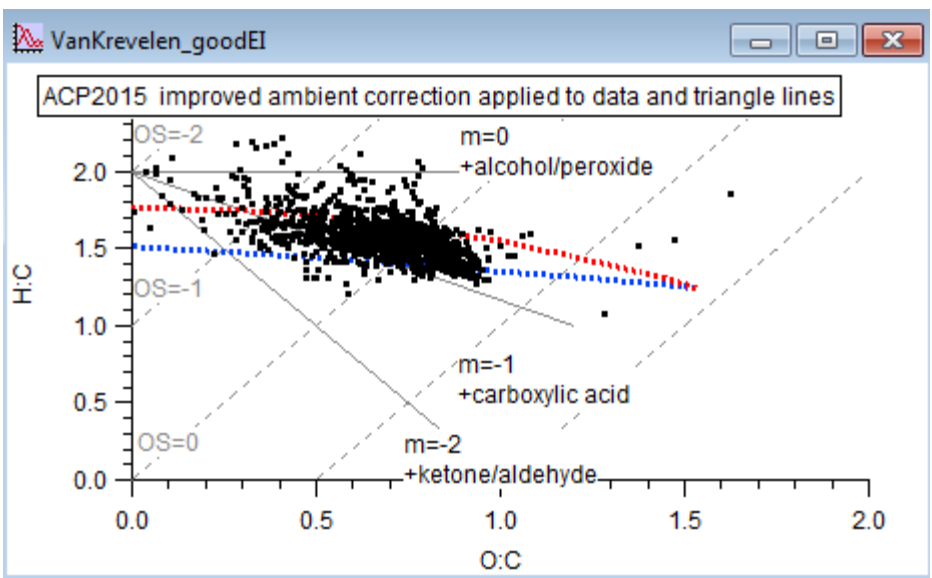
If a user wanted a new graph or appended graph, i.e. they would have to make that selection in the main Pika panel.

Part 3 Elemental Analysis – Improved Ambient



Examples of plots generated by pressing the gold button in the previous slide.

For these Improved-Ambient graphs, no N/C or S/C values were changed from Aiken et al, so no plots are generated using the old Aiken et al formulation.



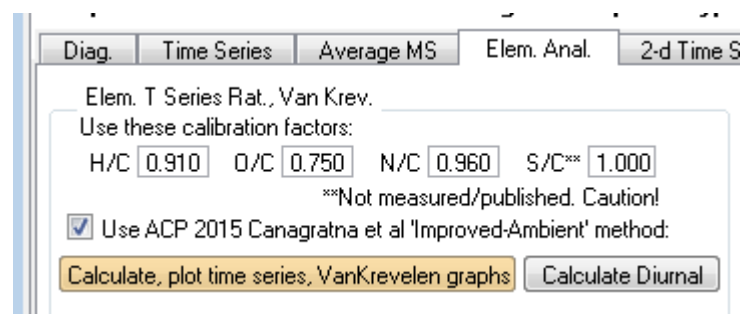
Details:

The Improved-Ambient method relies on

(A) the use of the calibration factors found in Aiken et al. The code automatically checks to see if these values have been changed from their defaults.

(B) The use of the Aiken et al Organic frag entries for CO, H₂O, HO, O. If these entries have been changed from their defaults, the code saves a copy of the changes, performs the calculations using the Aiken defaults and returns the frag values to the original values

As indicated in Canagaratna et al ACP 2015, the Aiken Explicit method (i.e. for some lab studies) is still valid.



Point	HR_specMass	HR_f	HR_fr	HR_fr	HR_fr	HR_fr	HR_frag_organic
0	C						0.25*HR_frag_organic[{H2O}]
1	j13C						0.0108157*HR_frag_organic[{C}]
2	N	{N},-			0.04*†		0.25*HR_frag_organic[{H2O}]
3	j15N	0.00;			0.003†		
4	O	0.35;	0.04*†			0.04*†	0.04*HR_frag_organic[{H2O}]
5	HO	0.00;	0.25*†			0.25*†	0.25*HR_frag_organic[{H2O}]
6	j18O	0.00;	0.002†			0.002†	0.00205499*HR_frag_organic[{O}]
7	H2O	0.01†	{H2O}			0.67*†	0.225*HR_frag_organic[{CO2}]
8	Hj18O	0.00;	0.002†			0.002†	0.00205499*HR_frag_organic[{HO}]
9	H2j18O	0.00;	0.002†			0.002†	0.00205499*HR_frag_organic[{H2O}]
10	CO2plus2						{CO2plus2}
11	CO						HR_frag_organic[{CO2}]
12	j13CO	0.01†					0.0108157*HR_frag_organic[{CO}]
13	Cj18O	0.00;					0.00205499*HR_frag_organic[{CO}]
14	S					0.21*†	

HROrg is more precise than UMR Org, however care is still needed in a few places

- m/z 29 - CHO is very close to j15NN
- m/z 44 - CO₂ still need to partition gas and aerosol phase
- Checks for Other HROrg ions may be coming but the two above are most important.

Improved Ambient Elemental analysis from Canagaratna et al ACP 2015 needs care

- f_{CHO} and f_{CO_2} should reflect accurate estimates of alcohols and acids
- Uses Aiken et al defaults for HROrg frag table and calibrations

HROrgCheck panel will help users address above issues