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

Pika version 1.16

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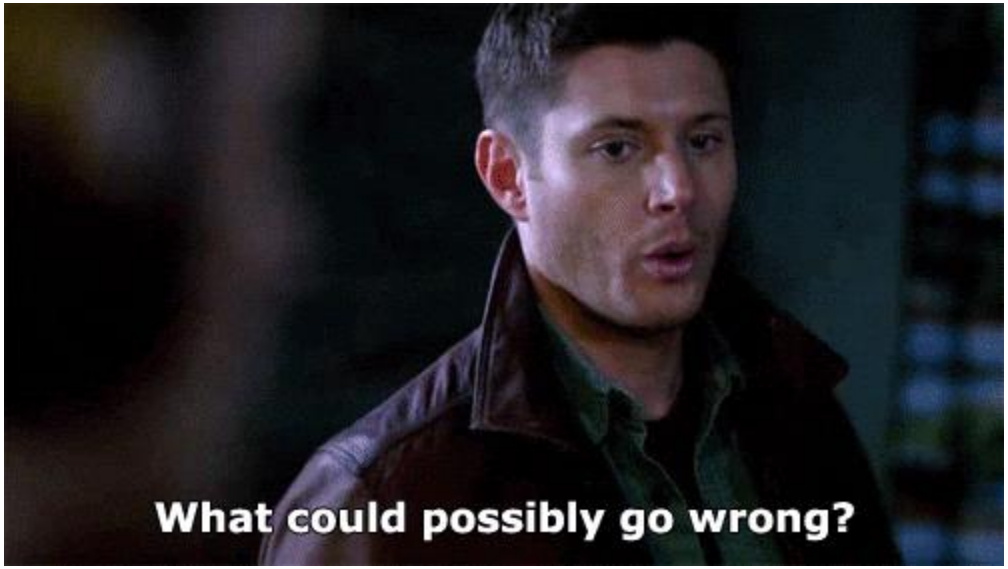
Part 1: m/z 29 HR fitting, CHO & j15NN isotope

Part 2: HROrg CO2 frag

Part 3: Elemental Analysis – Improved Ambient

Intro

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.

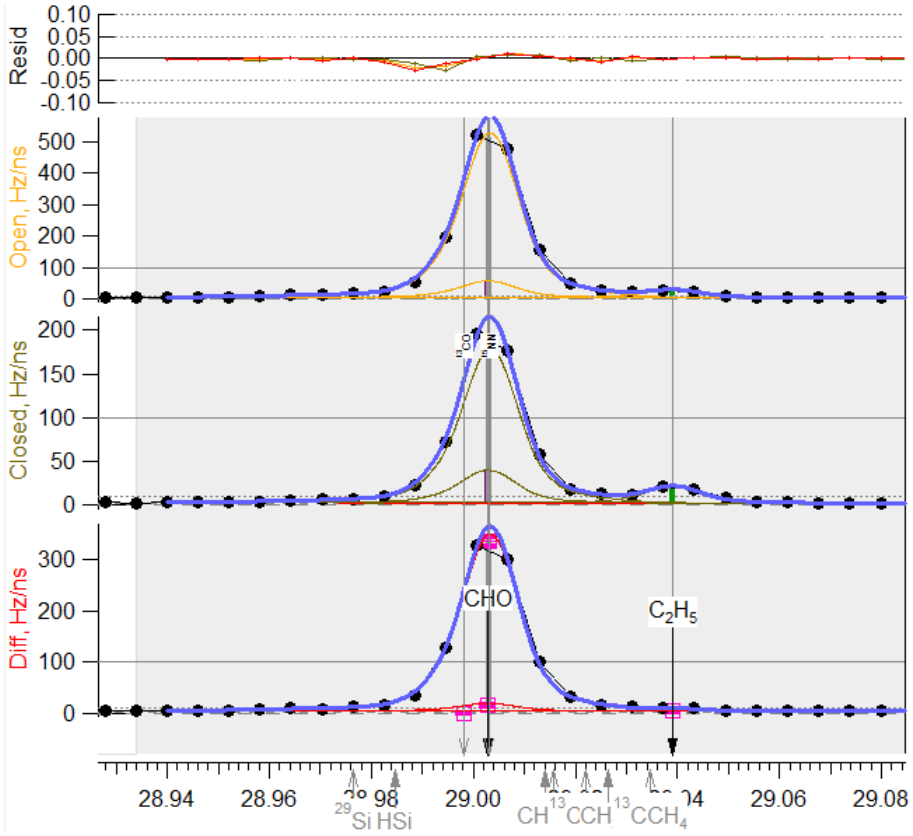
Elemental Analysis:

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.

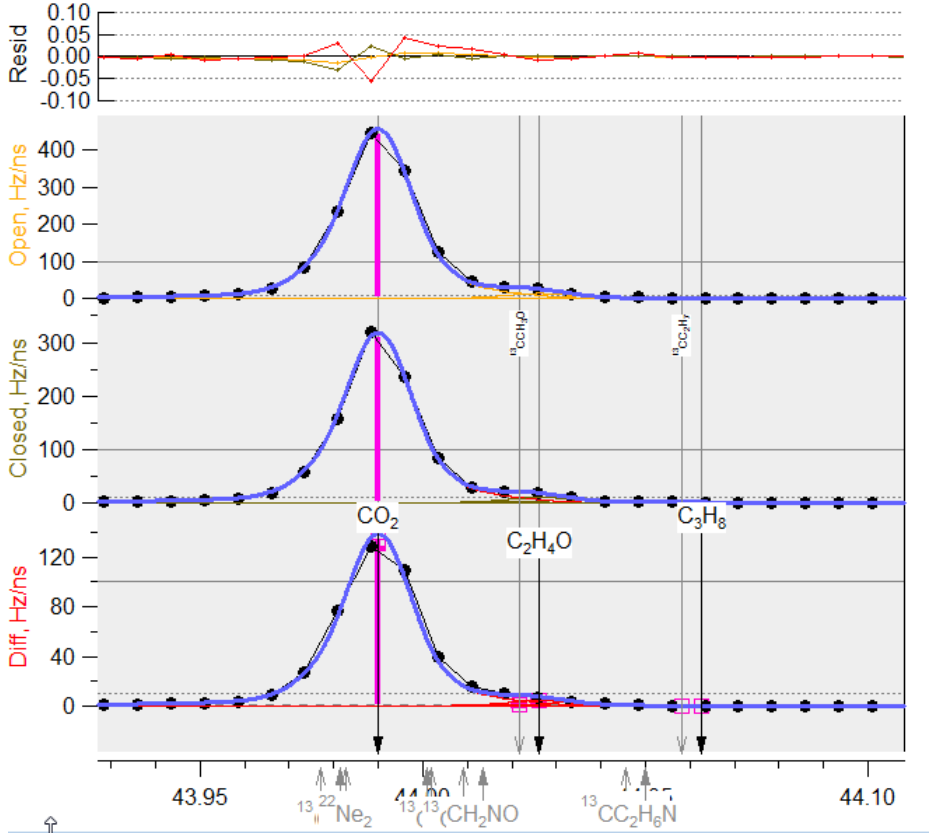
Intro

HROrg m/z29 CHO and j15NN



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.

HROrg m/z44 CO2



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

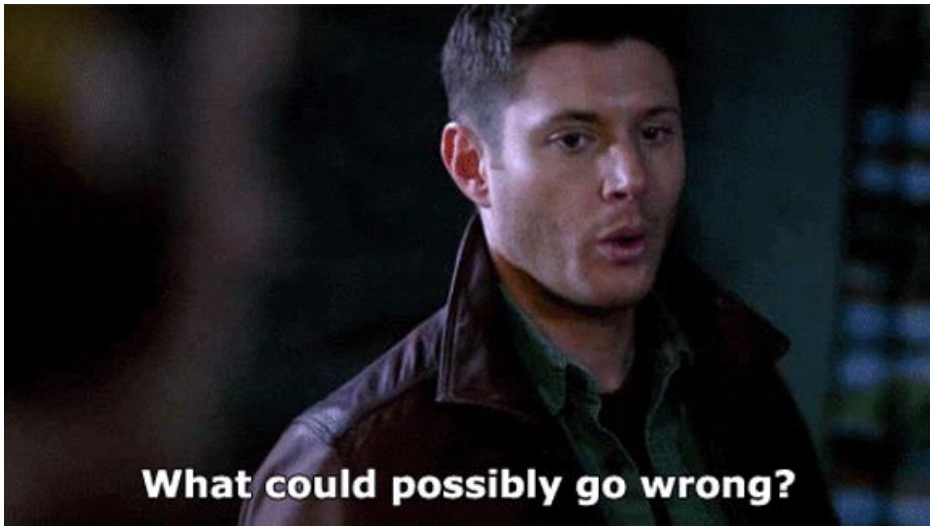
Improved – Ambient Elemental Analysis (H/C, O/C OM/OC)

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

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

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 <u>wrong</u>** (has not been accounted for properly, i.e. HROrg is wrong)

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

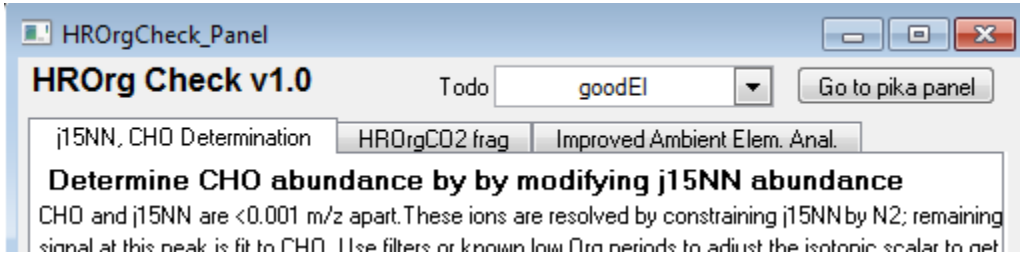
when they are **<u>noisy surrogates</u>** and thus add noise to EA calculations

Intro

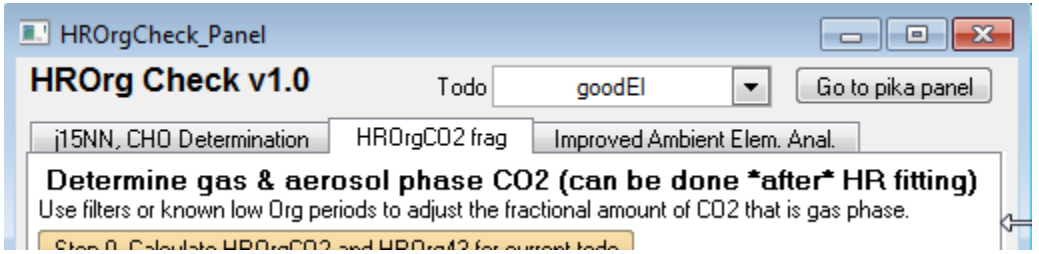
Needed: A method for systematically performing checks for
HROrg CHO HROrg CO2 (… perhaps other ions in the future)
fCHO, fCO2 for Improved Ambient Elemental Analysis

Solution: HROrgCheck panel with 3 sections

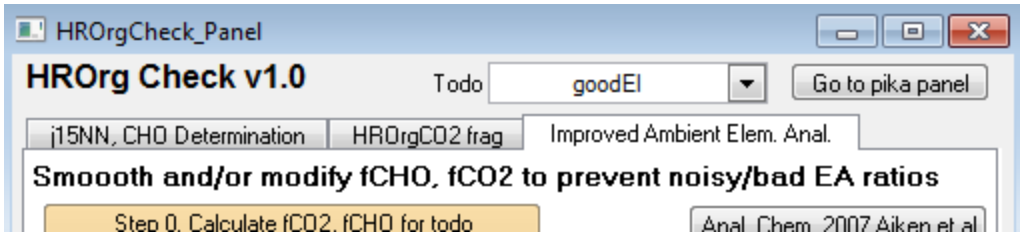
Tab 1:
m/z 29 CHO and j15NN



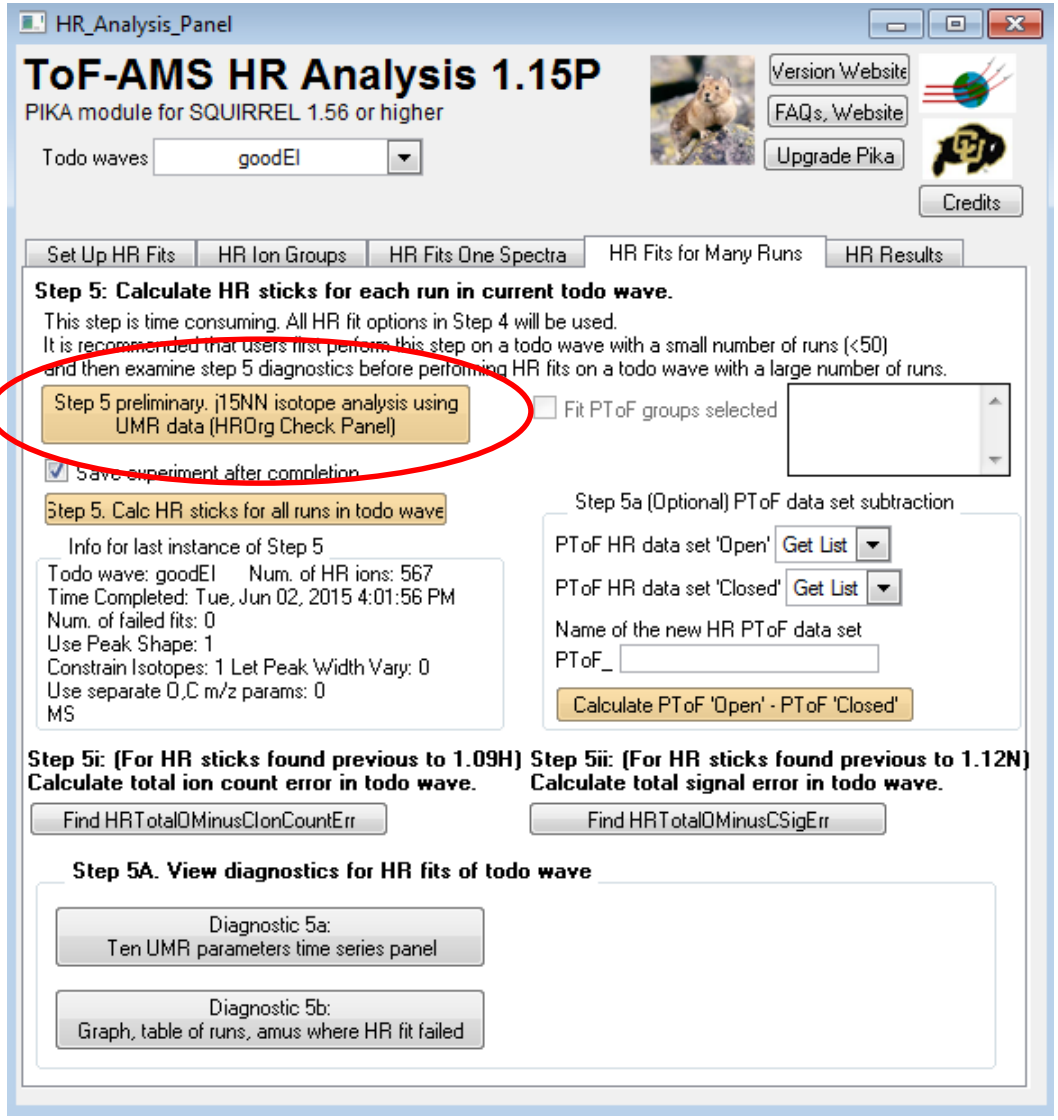
Tab 2:
HROrgCO2



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



Part 1 m/z 29 HR fitting & j15NN isotope

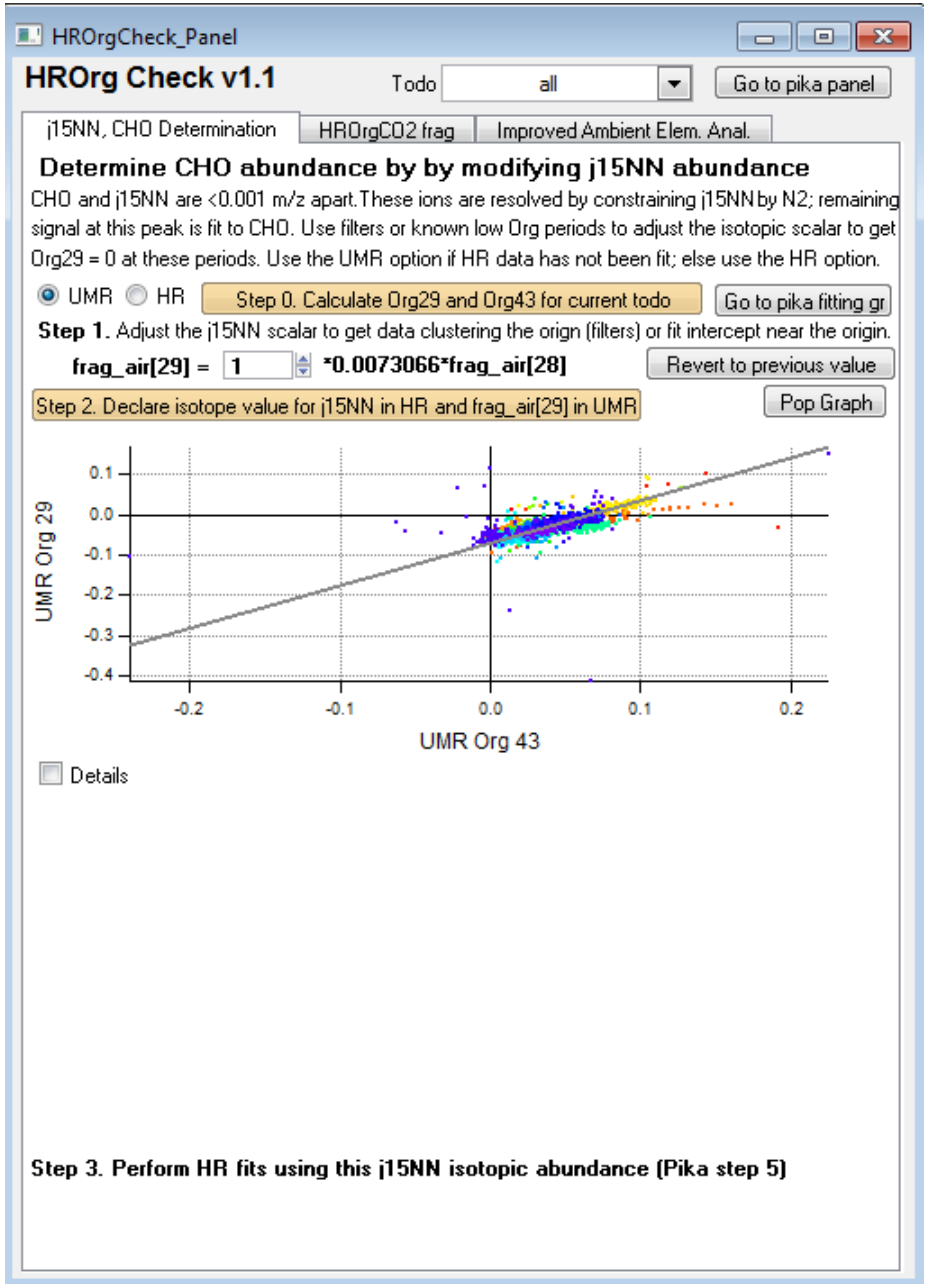


There is now a gold button, 'Pika Step 5 preliminary'

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.

Tab 1 j15NN, CHO Determination at m/z29



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

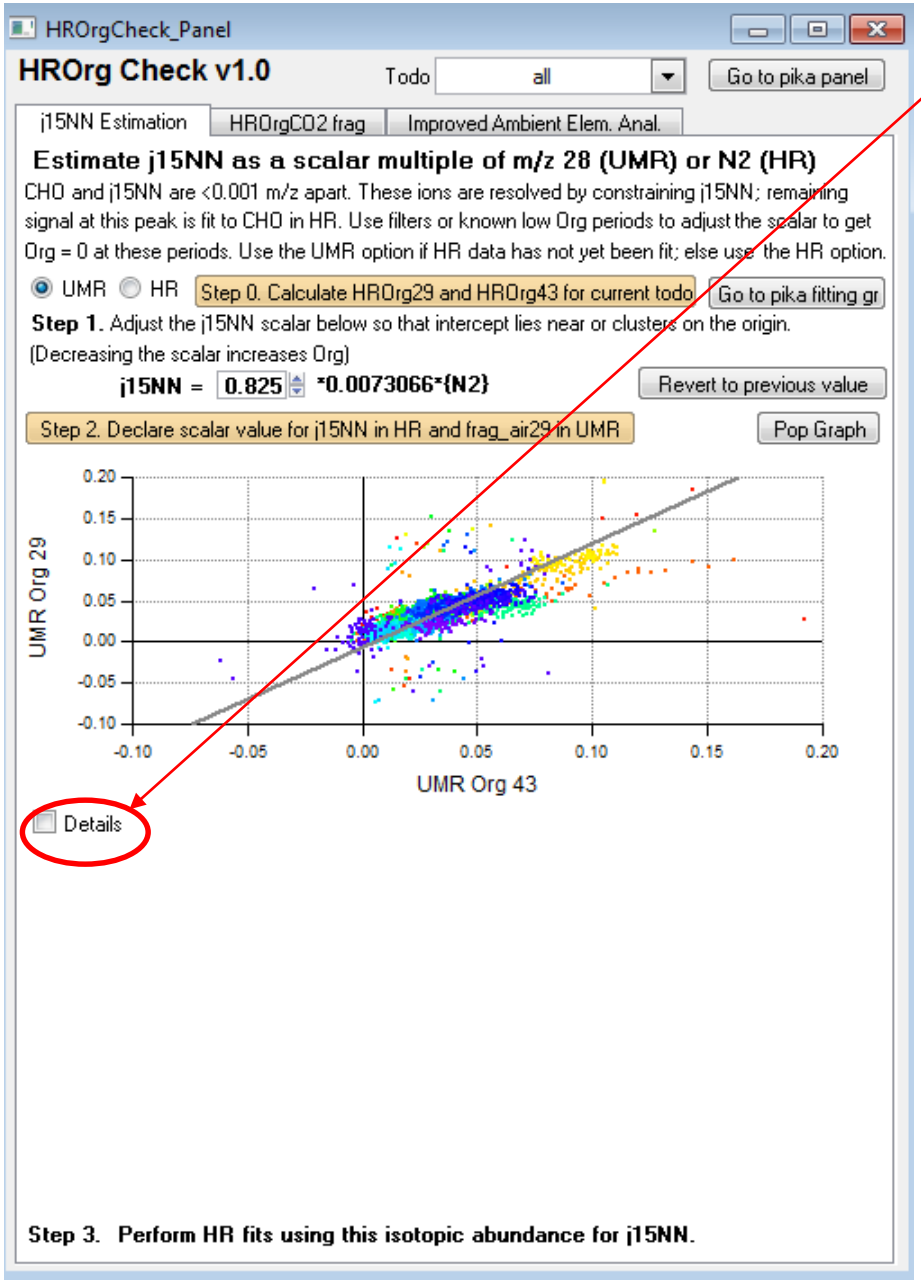
A graph shows UMR (or HR)
- Org29 vs Org43 (HROrg29 vs HROrg43)

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.

Tab 1 j15NN, CHO Determination at m/z29



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

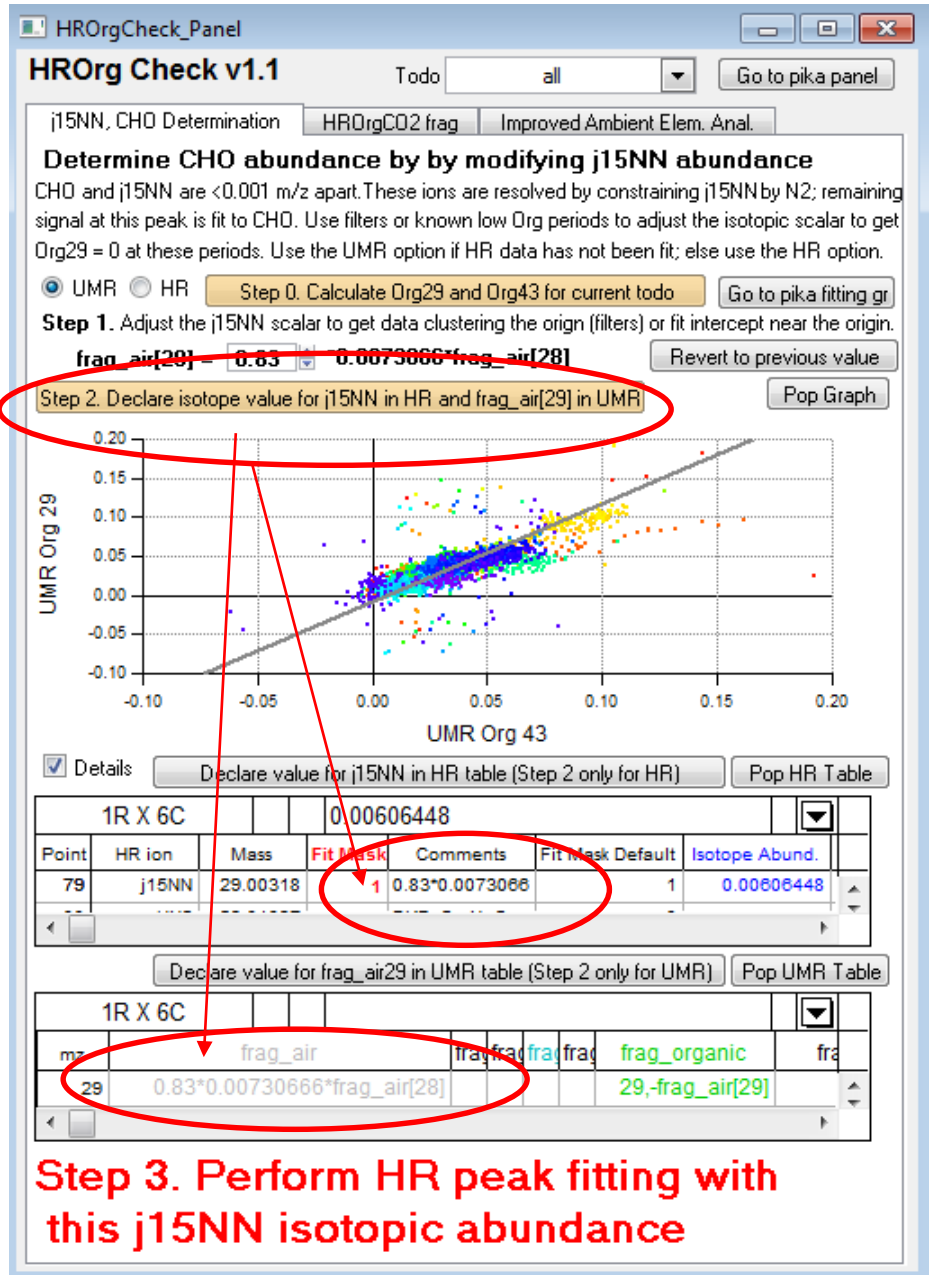
- HR ion table at j15NN row
- UMR frag table at mz29 row

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



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

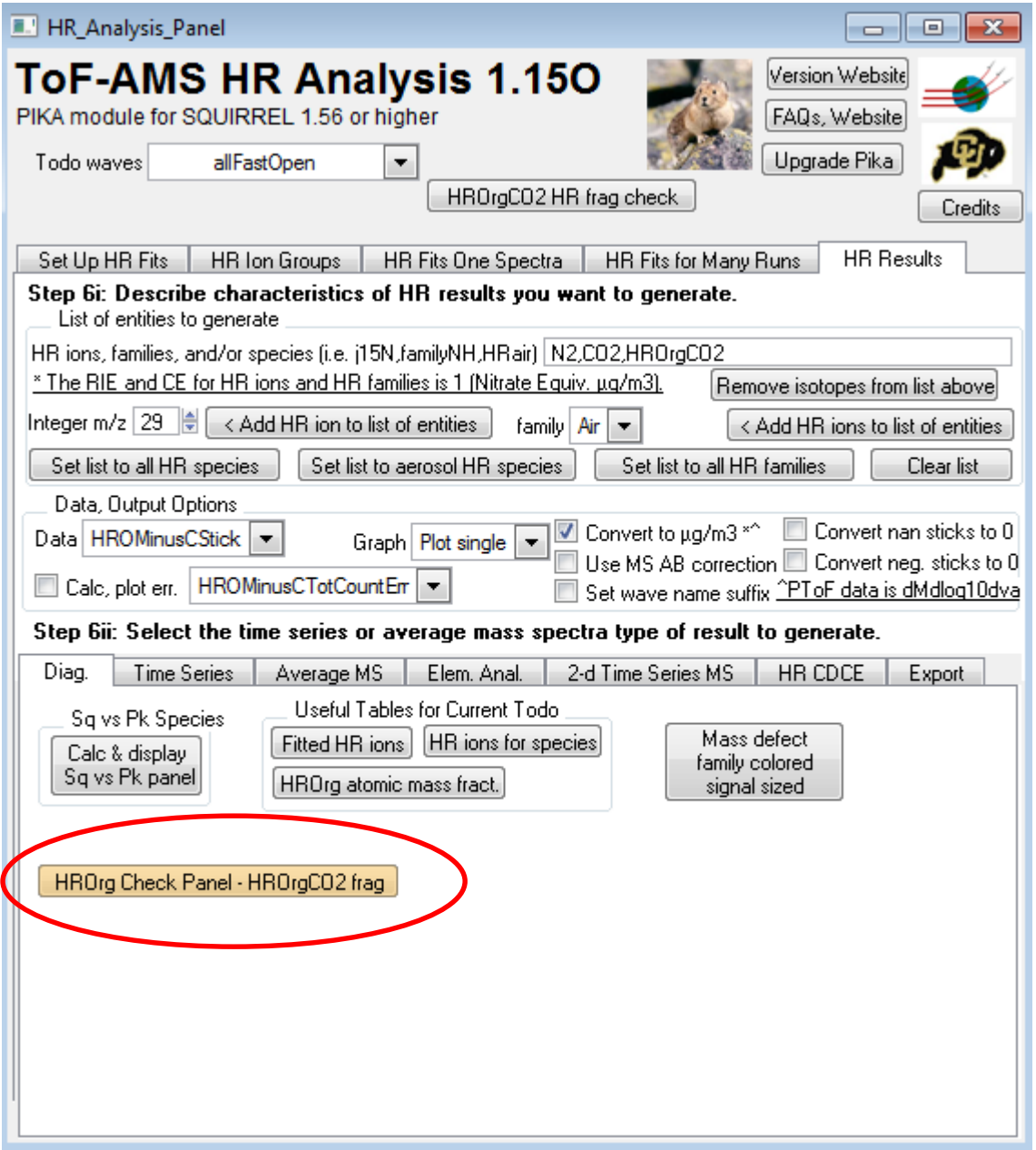
(1) Entries identified in the tables are overwritten.

(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.

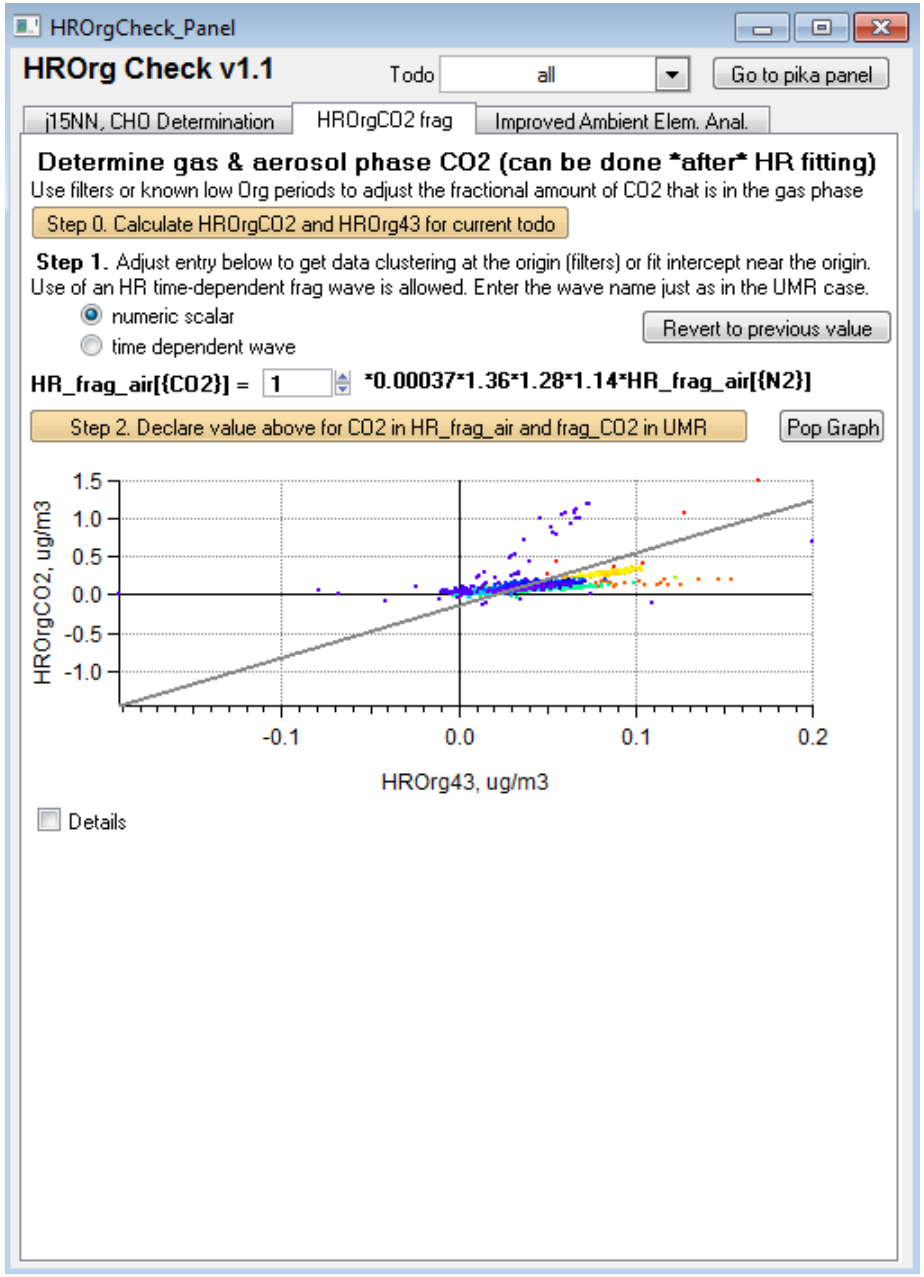
Tab 2 HROrg CO2 frag



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.

Tab 2 HROrg CO2 frag



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

A graph shows
- HROrg44 vs HROrg43

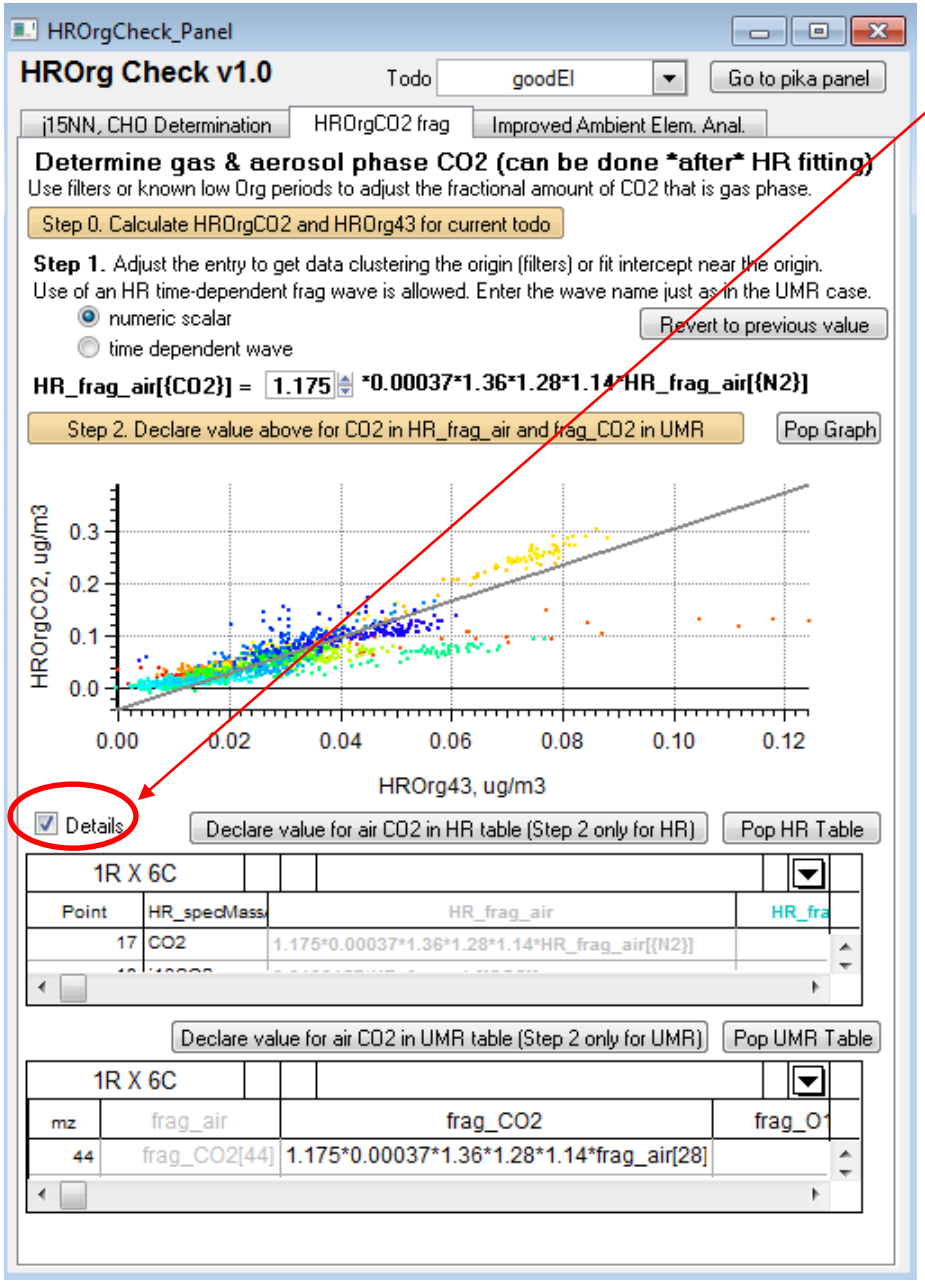
Optimally, the user would chose a todo wave with filters and nonfilter data.

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



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

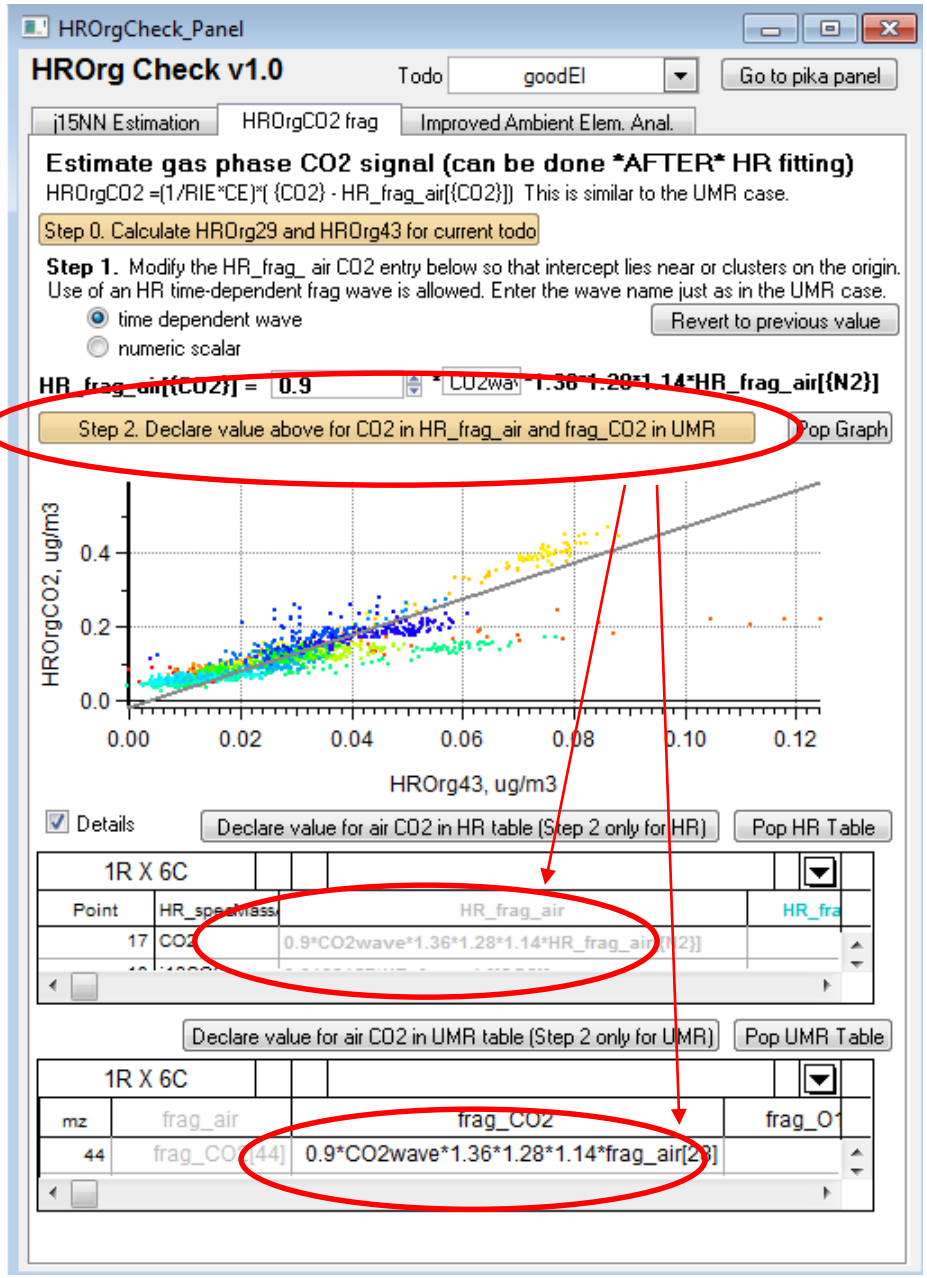
- HR frag table at CO2 row
- UMR frag table at mz44 row

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



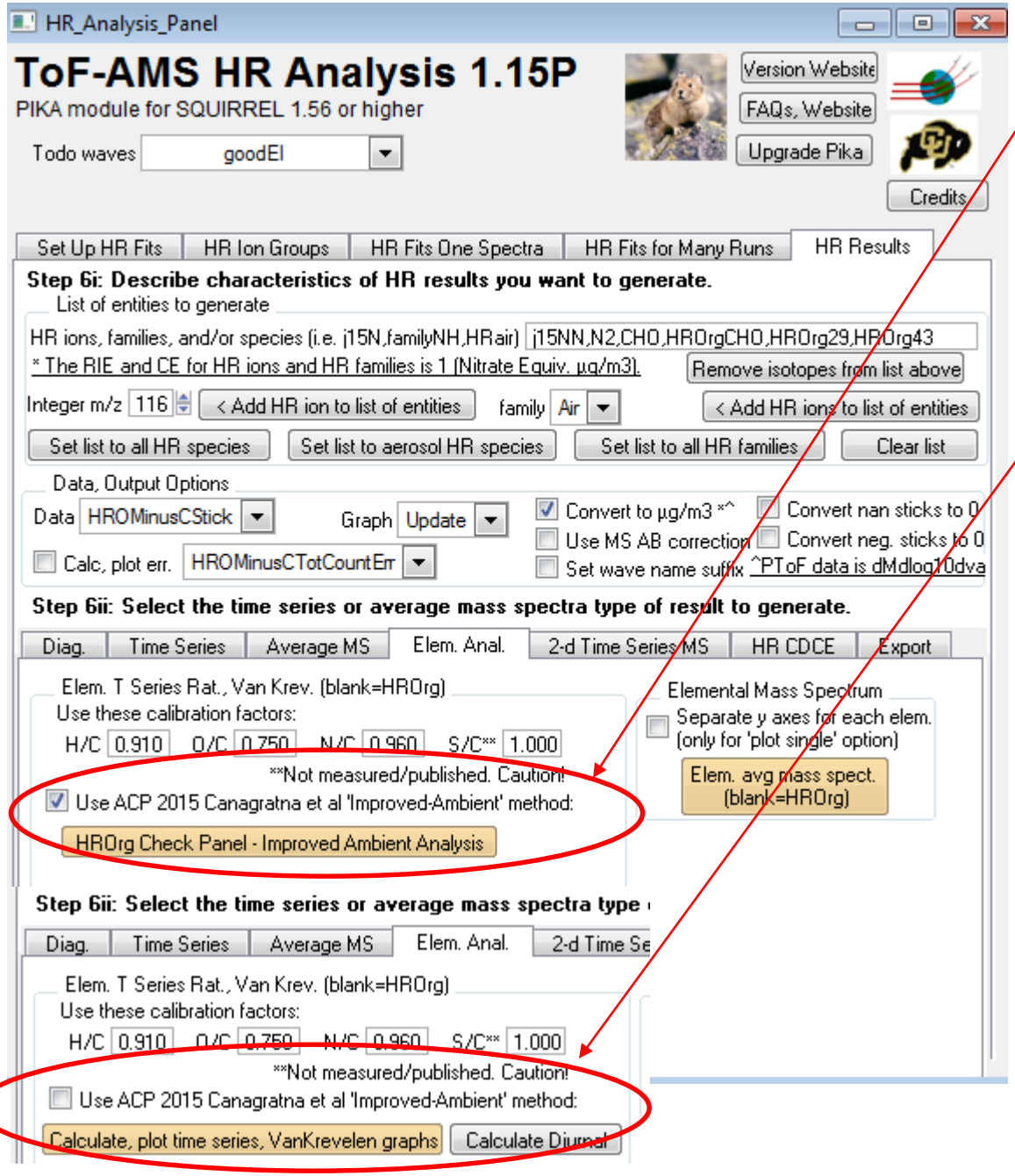
When optimal settings have been found, the user presses the Step 2 gold button. Two things happen:

(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

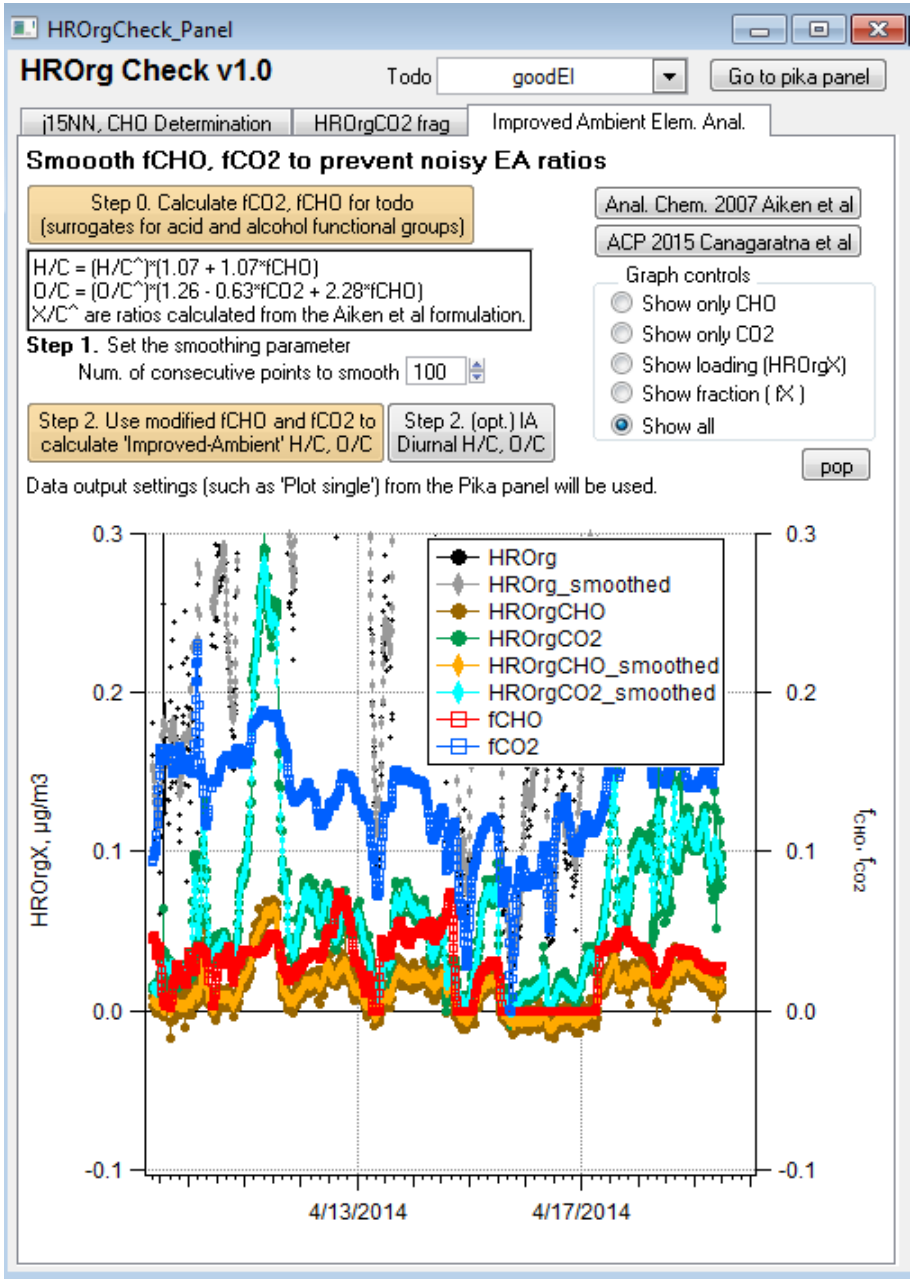


Slightly rearranged EA tab.

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

When the Use ACP… checkbox is <u>not</u> 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
<u>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</u>.

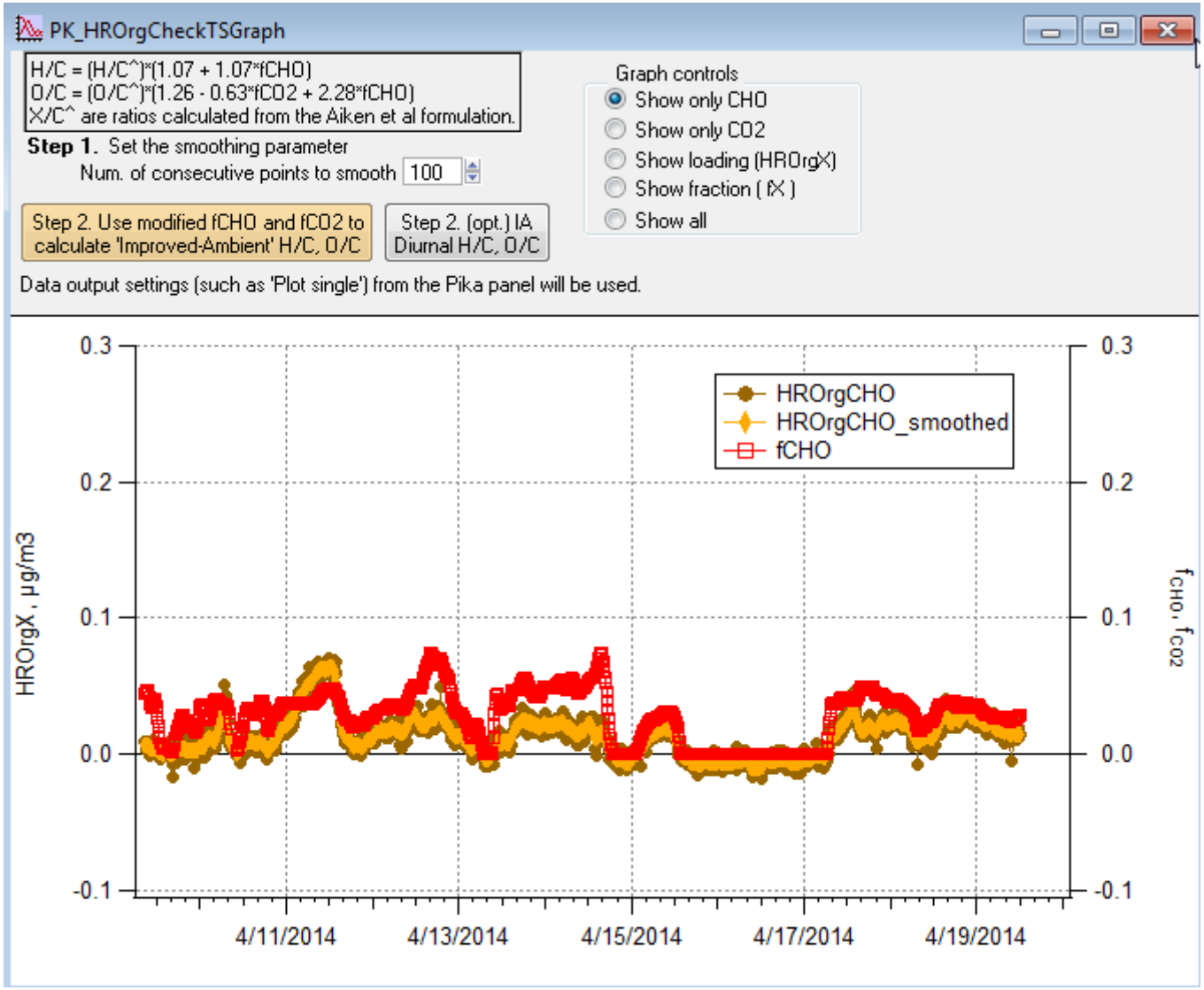
A graph of time series of
- HROrgCO2, HROrgCO2_smoothed,
- fCO2
- HROrgCHO, HROrgCHO_smoothed, fCHO

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 = smoothed(X)/smoothed(HROrg)
fX = limit(fX[p],0, 1)

Part 3 Elemental Analysis – Improved Ambient

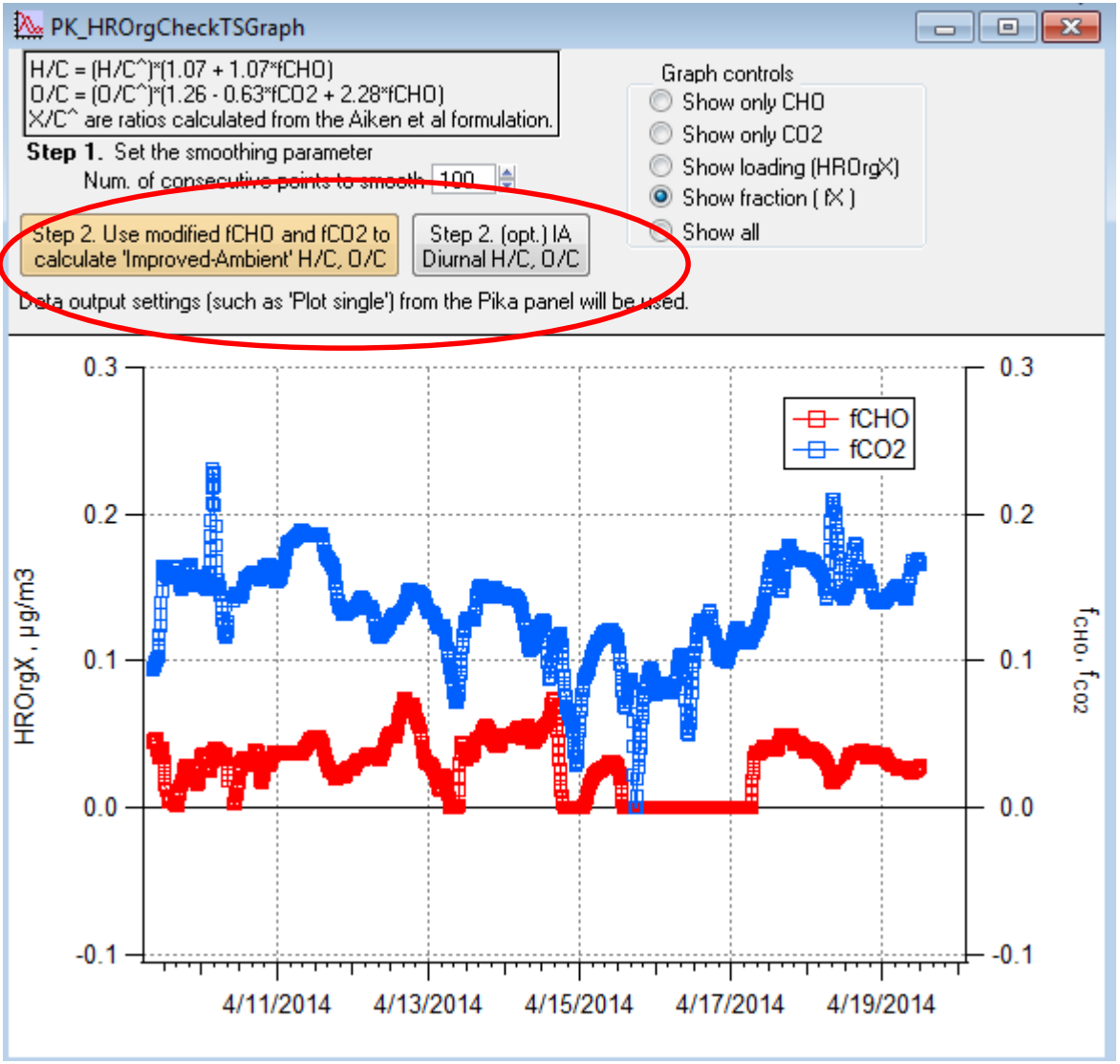


An example of the popped graph and showing only the CHO waves.

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.

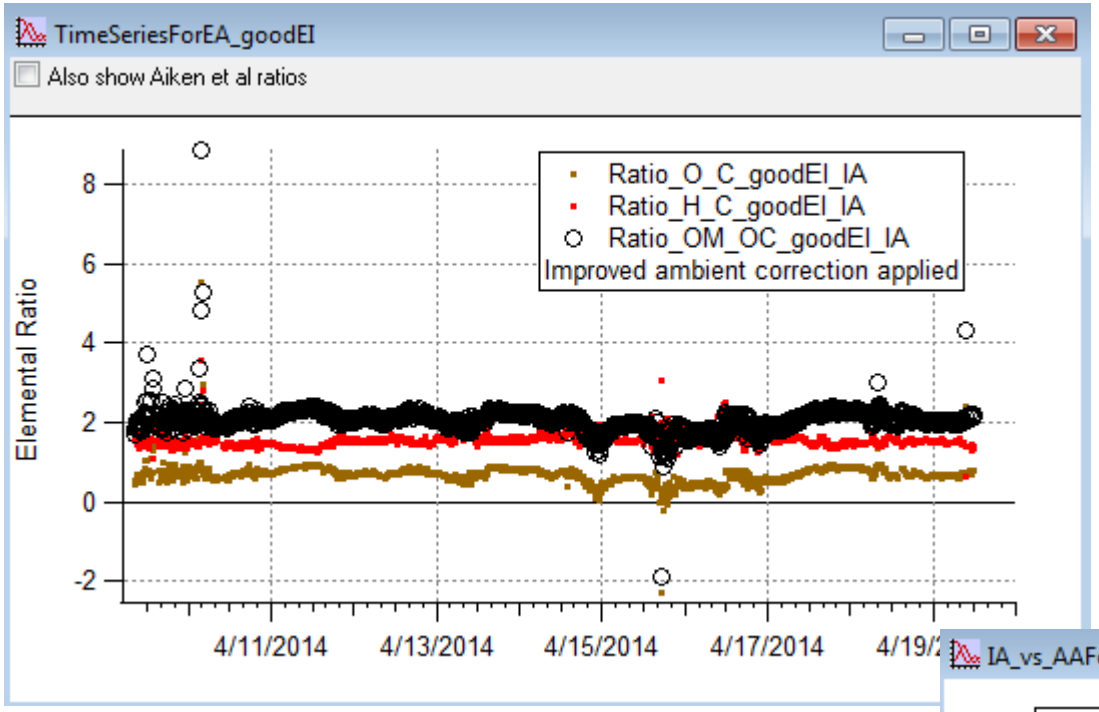
Part 3 Elemental Analysis – Improved Ambient



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.

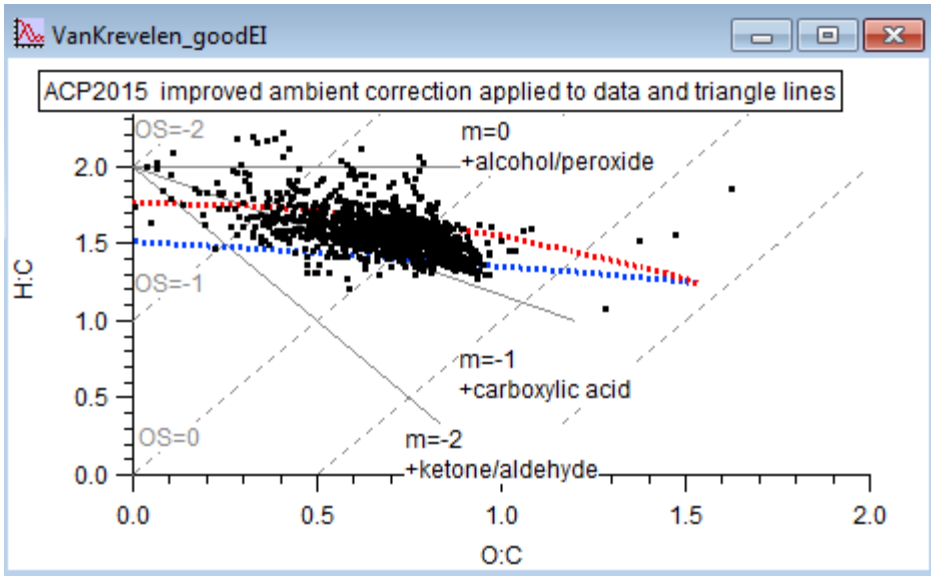
If a user wanted a new graph or appended graph, i.e. they would have to make that selection in the main Pika panel.

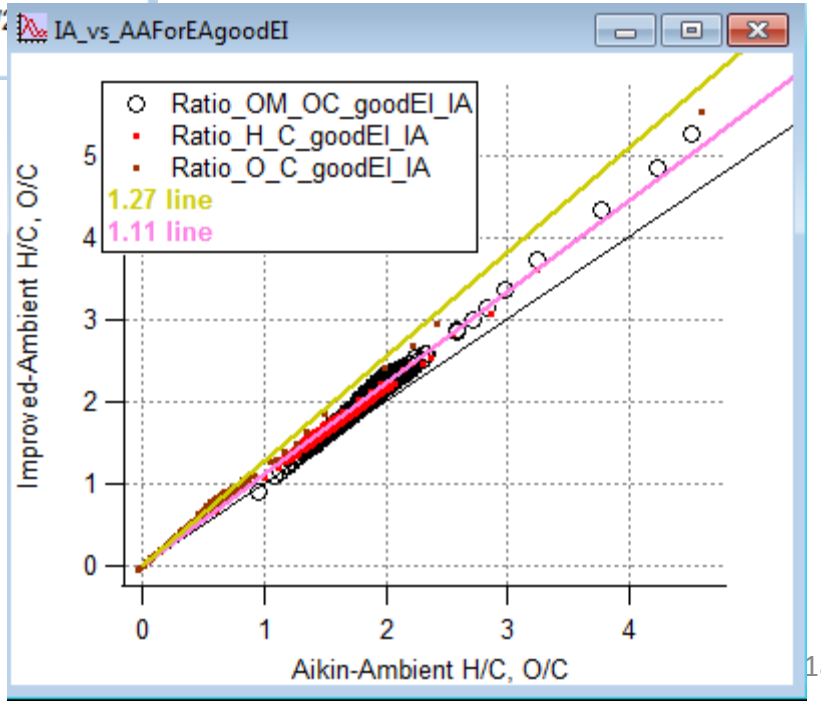
Part 3 Elemental Analysis – Improved Ambient



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.





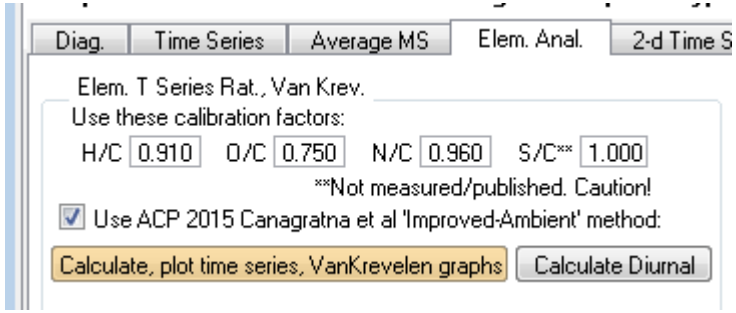
Details:

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.



HRFragTable

R14

Point	HR_specMassA	HR_f	HR_fra	HR_fra	HR_fra	HR_fra	HR_frag_organic
0	C						0.25*HR_frag_organic[{H2O}]
1	j13C						0.0108157*HR_frag_organic[{C}]
2	N	{N},-			0.04*I		0.25*HR_frag_organic[{H2O}]
3	j15N	0.00:			0.003		
4	O	0.35:	0.04*I			0.04*I	0.04*HR_frag_organic[{H2O}]
5	HO	0.00(	0.25*I			0.25*I	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*I	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*I	

Part 3 Conclusions & Recap

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_{CO2} 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