Plynlimon 7-hourly intensive hydrochemistry data set
Metadata: Quality control and data editing

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The Plynlimon 7-hourly intensive hydrochemistry data set contains a broad suite of chemical analyses conducted on rainfall and streamflow samples that were collected every 7 hours for nearly two years. This data set is being made public in two different versions.

The Raw Data Archive (denoted by "RDA" at the end of each variable name) is an archive of the raw measurements as reported by the analytical laboratories. These data have not been altered in any way, except to correct glitches that can be traced back to the original laboratory files and analytical sheets and corrected on that basis. We are providing this raw data archive for completeness of documentation, and also in the interests of full transparency concerning data editing that has been subsequently applied. The raw data archive also provides the opportunity to go back to the original data in case new information emerges suggesting that interesting real-world phenomena may have been inadvertently edited out. However, <u>we do not recommend that the raw data archive be used for routine analyses,</u> because the raw data a number of values that are believed to be substantially in error. Instead, <u>we recommend that routine analyses use the edited version of the data</u>, where to the greatest extent possible, problematic data values have been corrected or excluded.

The edited data include only those measurements in which we have a high degree of confidence. As the name implies, they have been edited to remove unexplained flyers that defy the usual correlations among analytes and/or correlations with flow. In very few exceptional cases we have deleted flyers that are correlated among analytes, but occur as single many-sigma outliers that are not correlated in time and unrelated to flow variations. Examples include near-zero values ("drop-outs") that arise simultaneously in many elements. We suspect that these arise because of a sample labeling issue (or substitution of a blank) which unfortunately cannot be traced. Other examples include extreme flyers that are correlated among several elements, but are plausibly attributable to sample contamination.

Where we can make consistency checks (for example, SO4 and S, Alk and pH, charge balance, Gran Alkalinity and calculated ANC, N species and TDN, calculated ionic strength and conductivity), we have done so. Where clear discrepancies have been found, we have dropped the analyte that is clearly inconsistent with nearby values in its time series.

Rainfall was sampled at Carreg Wen (denoted CR in the 7-hourly data set), and streamflow was sampled at the Lower Hafren and Upper Hafren sampling sites (denoted LHF and UHF in the 7-hourly data set). These sampling locations are close to the sampling sites used in the long-term Plynlimon hydrochemistry database, but the 7-hourly sampling was done with different protocols, including autosamplers instead of manual sampling, and for rainfall, using a much larger precipitation funnel located closer to ground level. For this reason different sample location codes are used.

The long-term weekly sampling at Carreg Wen, Upper Hafren, and Lower Hafren provides an important comparison data set for the 7-hourly samples. One 7-hourly stream sample each week was collected within 3.5 hours or less of the manual sampling time at Upper Hafren and Lower Hafren. At Carreg Wen (denoted "rainfall" in the weekly sampling), the 7-hourly samples for each week can be averaged together on a volume-weighted basis for comparison with the weekly bulk sample collected during the same time interval. In some cases where weekly and 7hourly data are systematically different for the same analyte, we have exercised expert judgment concerning which one is more plausible, and omitted the other from the edited data. Where the discrepancy is not judged to be large, we have kept both in the edited data, even in cases where simultaneous measurements are not well correlated between the two data sets.

Where there are large and abrupt shifts in the pattern of variability observed for a single analyte between different blocks of the time series, we have exercised expert judgment in omitting the blocks showing implausible patterns of variability, and retaining the blocks showing more plausible patterns of variability. Examples include sudden explosions in sample-to-sample variability or sudden shifts in the upper and lower bounds of variation (indicating calibration problems). These issues are most commonly observed in trace metals and other low-level analytes, where blank levels and sample contamination are more problematic.

Another issue that arises with low-level analytes is sample carryover from a check standard that was introduced every 10 samples. The trace element concentration in this check standard was 5 ug/l, many times greater than the ambient concentrations of many trace metals. Where this sample carryover effect was visually obvious, giving rise to a "picket fence" appearance in the time series, we have culled the values that we believe to be contaminated by carryover of the check standard.

Users should be aware that conductivity, pH, Gran alkalinity, and Gran acidity were measured on samples that were settled but not filtered, whereas solute concentrations were measured on filtered samples (0.45 um membranes for cations and metals, and GF/C glass fiber for other analytes). Tests in the 1980's concluded that there was no significant difference between filtered and unfiltered samples for these analytes.

Individual samples at these sites are denoted by a unique code, consisting of the site designation (CR, UHF, or LHF) followed by a sequential integer. These unique codes will be used to refer to individual samples in the presentation below. We will first document several editing changes that affected a broad range of analytes, then review the editing changes made for each analyte in sequence.

For several samples that had flyers/zeroes in many analytes (evident sample switching or substitution of a blank), we deleted all affected values from the edited data, e.g.: LHF695, LHF883, LHF1125, UHF130, UHF753, UHF1420, UHF1496. Some examples:

- UHF1420 is an interesting example: conductivity, alkalinity, pH, and anions are similar to the points before and after, but the acidified sample (ICP-OES and ICP-MS) has very odd values for almost everything (leading to a very large discrepancy between calculated and measured alkalinity, for example).

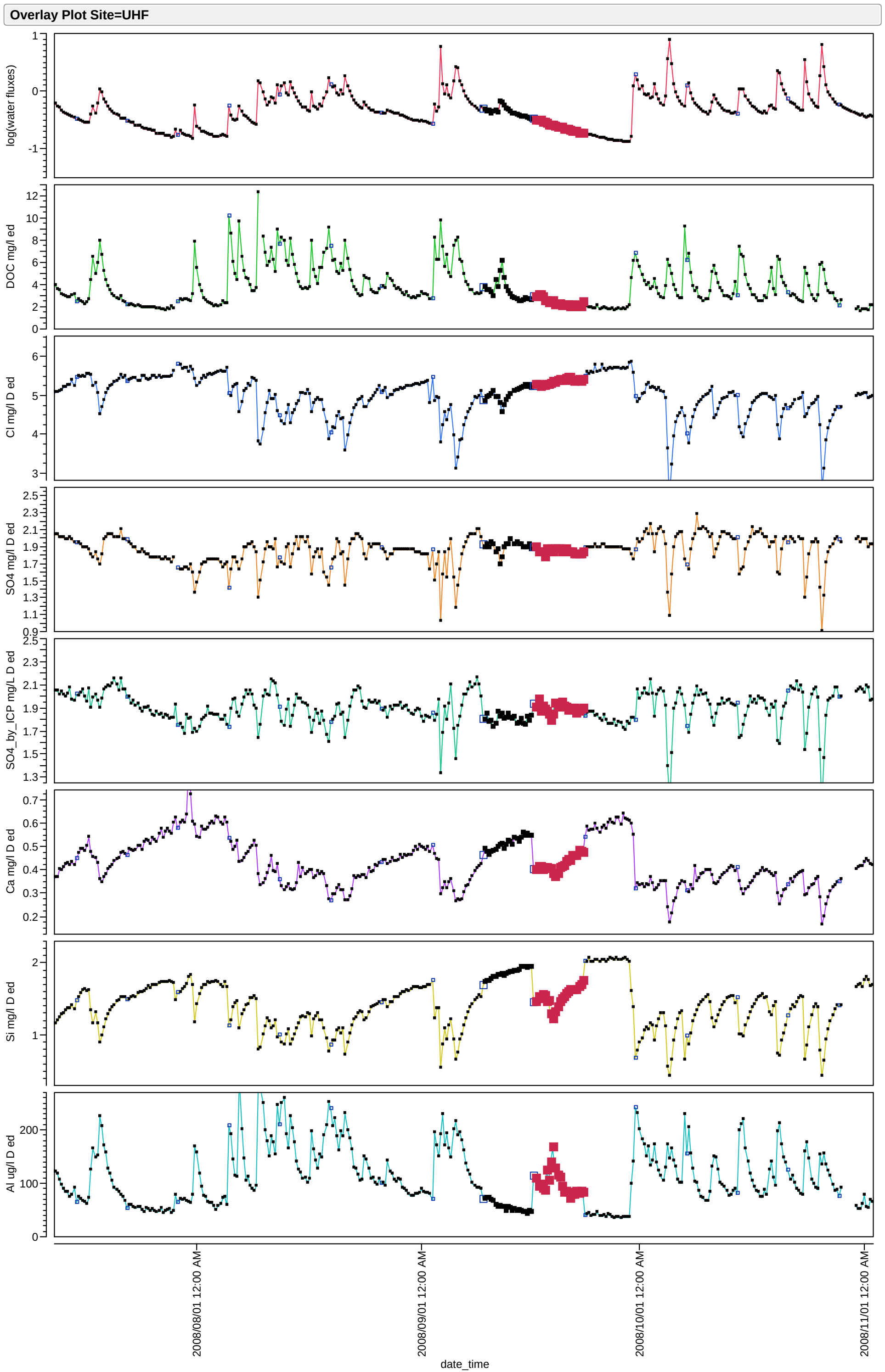
- UHF 130 has extremely high K, Cs, Rb, Fe, Al, La, Ce, and Pr, among other analytes. These are unlikely to arise from analytical issues, but rather sample contamination.

- LHF133 and LHF137 have many anomalously low values in ICPOES and ICPMS.

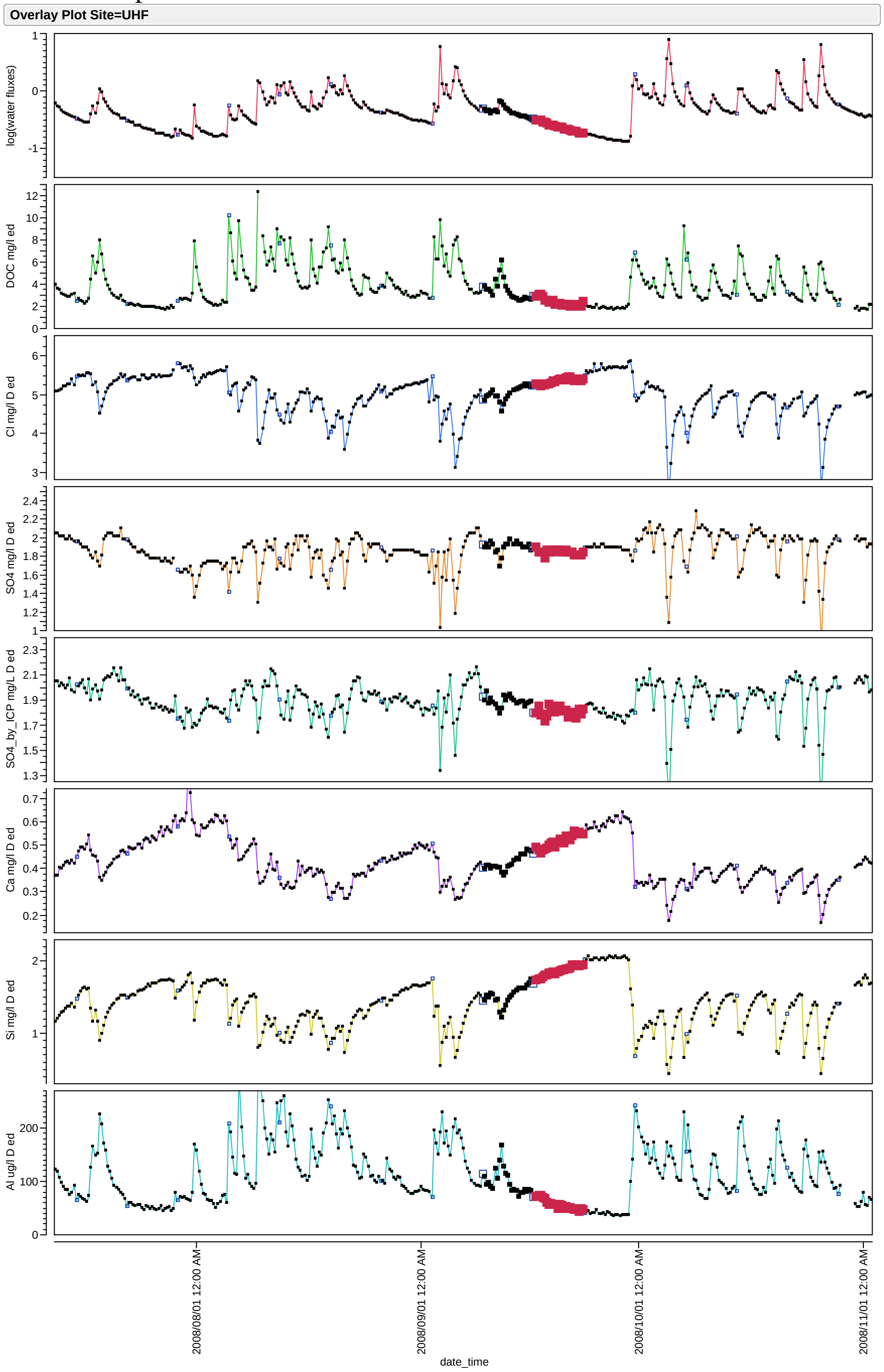
Many of these samples are flagged in the plots that follow with their sequential row numbers in the data set (3158, 3346, 5154, and so forth; note that these are not the same as the unique codes).

Major surgery: We deleted the first analytical block in precip samples (EE215), because it has many extreme flyers, and as the first block it is the most vulnerable to instrument glitches and contamination effects.

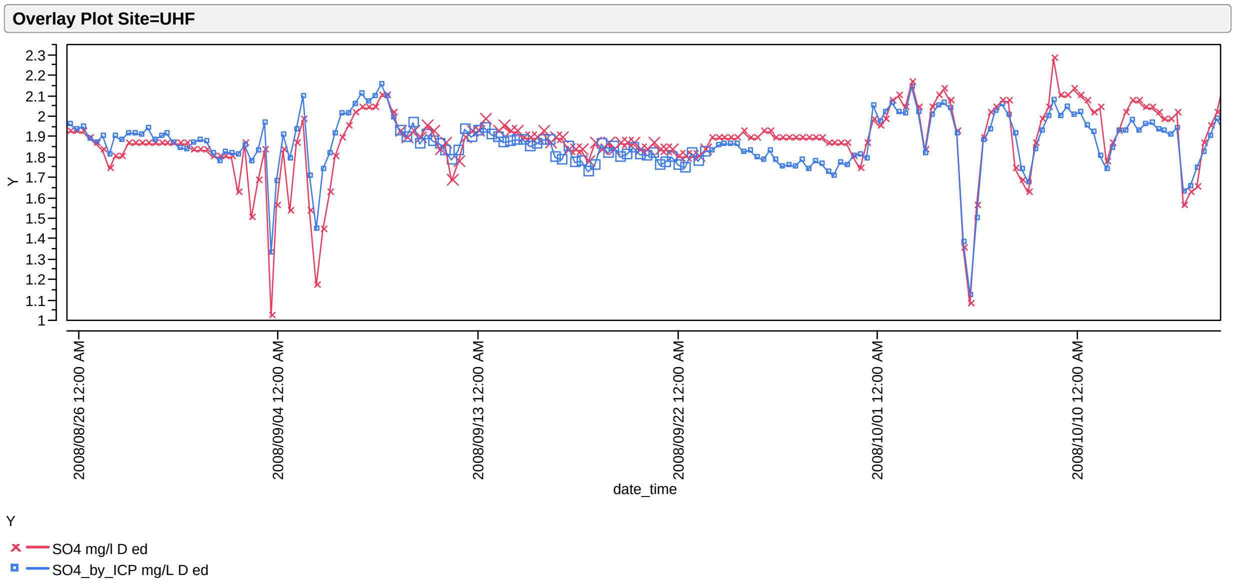
Major surgery: Samples were analyzed in batches corresponding to each field trip that was made to download the autosamplers (indicated in the "Trip" column of the data set). There has evidently been an inadvertent swap in analysis (or mislabeling) of the acidified samples (ICP-OES and ICP-MS) between Trip 81 (UHF1920-1943) and Trip 80 (UHF1896-1919). The problem is illustrated by the figure on the next page, where the two trips are shown in heavy black and red symbols.



The small flow peak in Trip 80 produces a corresponding spike in DOC, Cl, and SO4 (by IC), which all come from the un-acidified sample splits, but this peak is missing in SO4_by_ICP, Ca, Si, and Al, which all come from the acidified sample splits; instead the peak comes a week later. The apparent swapping of samples also results in a bizarre "top hat" in many of the time series from the ICP-OES and ICP-MS. We cannot trace this error without the original bottles, which we no longer have. However if the apparent swap is reversed, the correspondence among the different samples becomes almost exact. Therefore we have swapped the acidified analyses for these two trips at UHF. The results are shown below.



An important check is that the wiggles in SO4 (by IC) and SO4_by_ICP are now synchronized. This is significant because these are almost identical analytes, determined in both the acidified and un-acidified bottles. Below is a zoom-in on the highlighted region above, with SO4 and SO4_by_ICP overlain with each other. The enlarged symbols are the two trips in question.



Correlations among analytes:

We used scatterplot matrices of correlated analytes to distinguish flyers that are correlated with other co-varying analytes (and thus could be real), and those that are inconsistent with normal patterns of correlation with other analytes (and thus are probably anomalies). The following table enumerates the co-varying analytes that were used for each "target" analyte:

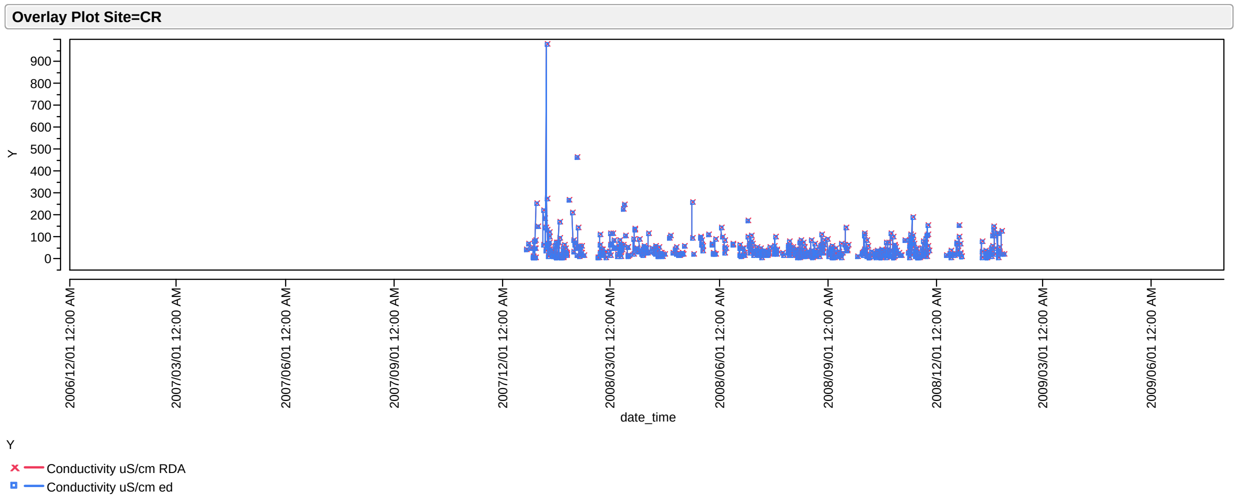
F: NH4 (in rain), log(Q), alkalinity
NO2: (nothing correlates!)
Br: Si
DOC: DON, Fe, Ce, La, Pr
Cl: Mg, Na, conductivity, Sr
NO3: SO4, TDN, Mg
NH4: TDN
SO4: SO4_by_ICP
SO4_by_ICP: SO4
TDN: NO3, NH4, DOC
DON: (calculated quantity, not edited)
K: Rb
Mg: Sr, Na, Ca, Cl
Na: Cl, Mg, conductivity, Sr
Ca: Mg, Si, alkalinity, pH, Sr
B: DOC, U
S: SO4
Si: log(Q), Ca, pH, Al
pH: Alk, Ca, Si, Al
cond: Cl, Na, Mg, ionic strength

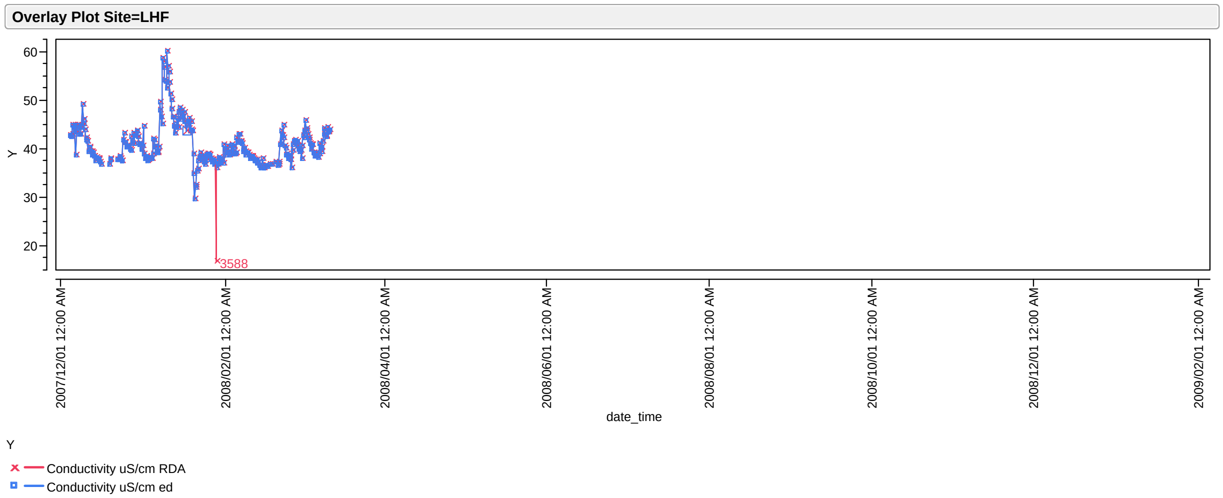
Li: log(Q), Ca, Si, Sr
Be: Si, pH, Ni, Al, Ce, Pr
Al: Si, log(Q), Fe, La, Ce, Pr, DOC, Be
Sc: Mo, alkalinity
Ti: As, DOC, U
V: Al, Fe, La, Ce, Pr, U
Cr: V, Fe
Mn: Co, DOC
Fe: DOC, As, La, Ce, Pr
Co: Mn
Ni: Mn, Be, Zn, Ba
Cu: Ca, Pb, alkalinity, pH
Zn: Alk, pH, Mn
As: Fe, V, Sr, U
Se: As, U
Rb: K
Sr: Ca, Cs, Mg, Na, Cl
Mo: log(Q), Ca, Mg, Na
Cd: Ba, Zn, Ni, Be, Al, Co
Sn: Cd, Cl, Zn
Sb: U, Fe, DOC
Cs: Sr, Ca, Si, pH, alkalinity
Ba: Cd, Cl, Ni, Co, Mn
W: (nothing correlates)
La: Ce, Pr, Al, DOC, Si
Ce: La, Pr, Al, DOC, Si
Pr: La, Ce, Al, DOC, Si
Pb: Si, Cu, Cd, Al
U: La, Ce, Pr, As, DOC, V

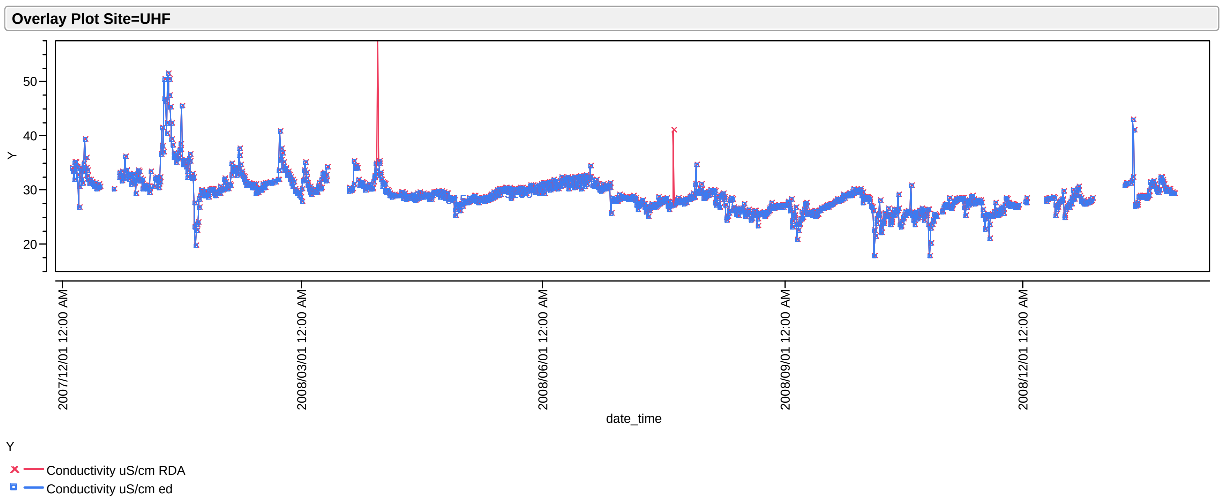
Notes on individual analytes:

The following pages present notes and sample time-series plots for each analyte, to illustrate the editing that has been applied. Raw data values that have been culled or changed are shown in red; those that have been kept (or changed) in the edited data are shown in blue.

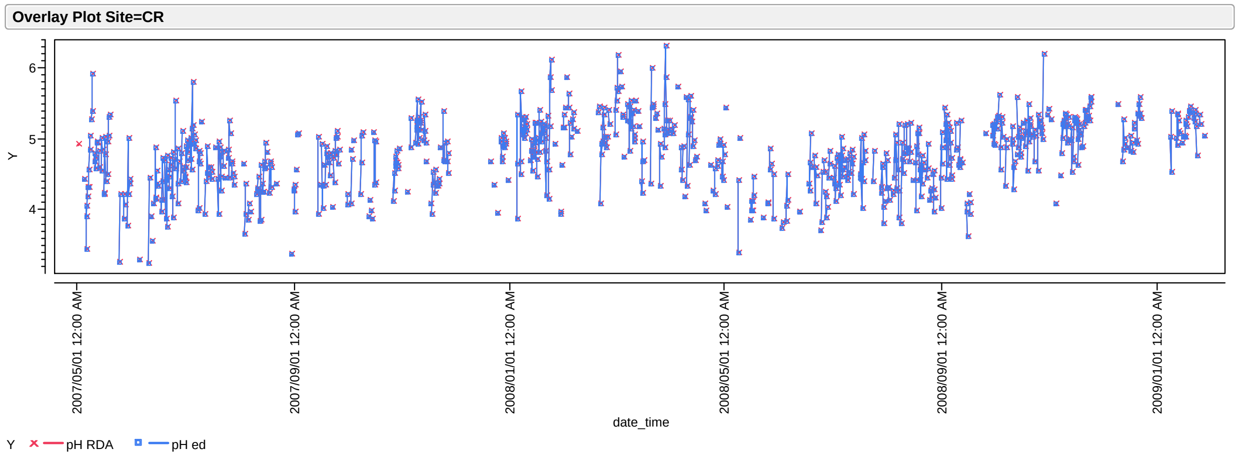
The analytes are arranged in two groups in the data set (and also in the presentation below). First, we present those analytes that are determined by ion chromatography, electrochemical methods, autoanalysis, and so forth, in order of increasing atomic number. Thus, for example, Gran alkalinity and DOC, representing atomic number 6 (carbon), come before the nitrogen species representing atomic number 7. Next we present the cations and metals, analyzed by ICP-OES and ICP-MS, again in order of increasing atomic number.

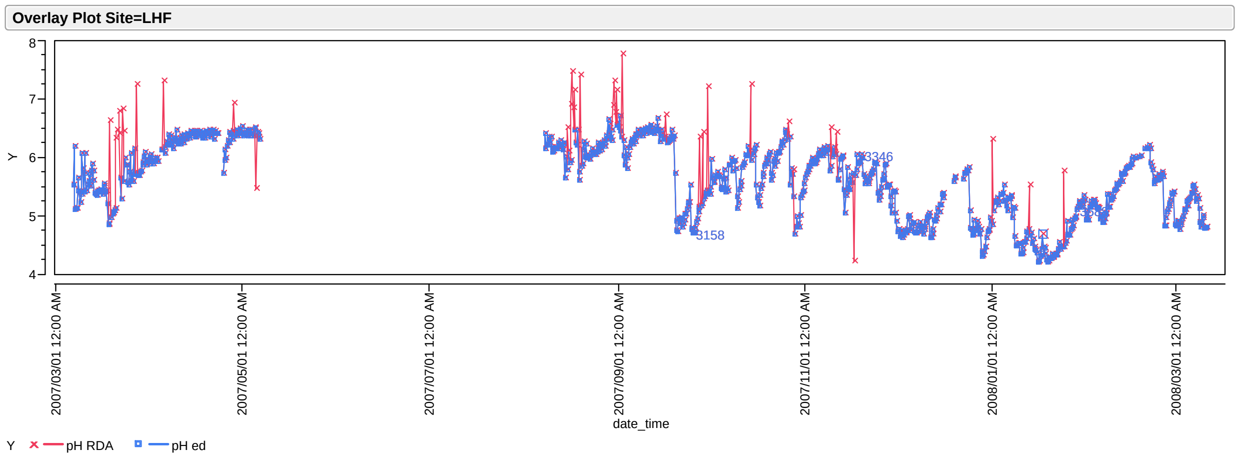


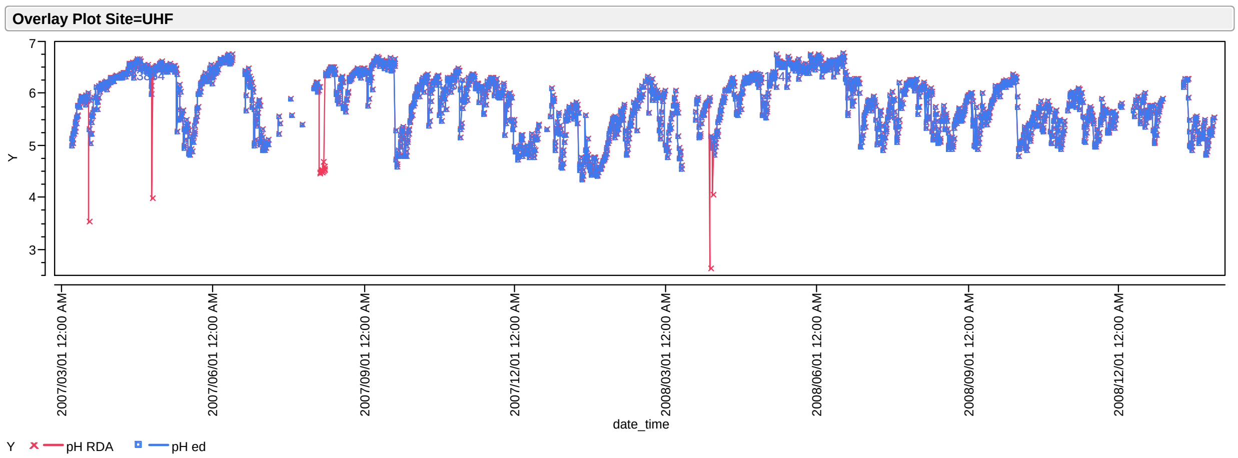




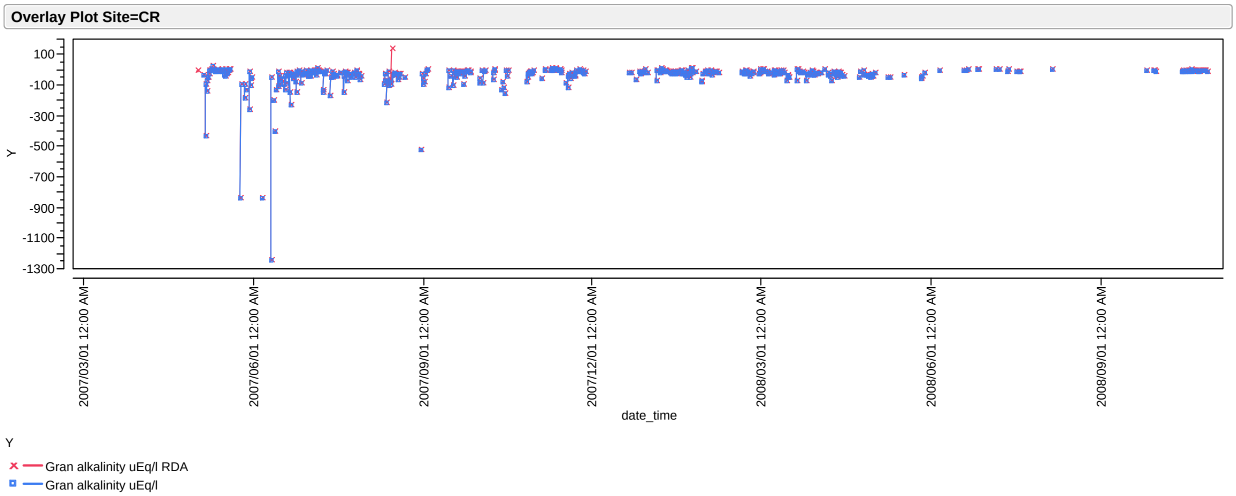
Conductivity: Conductivity flyers were culled where they were inconsistent with calculated ionic strength.

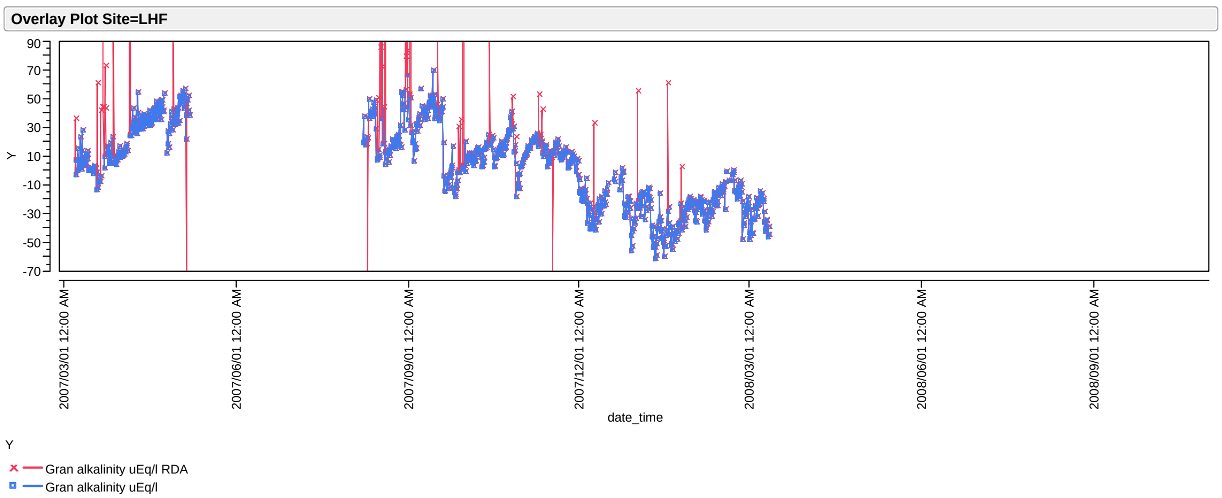


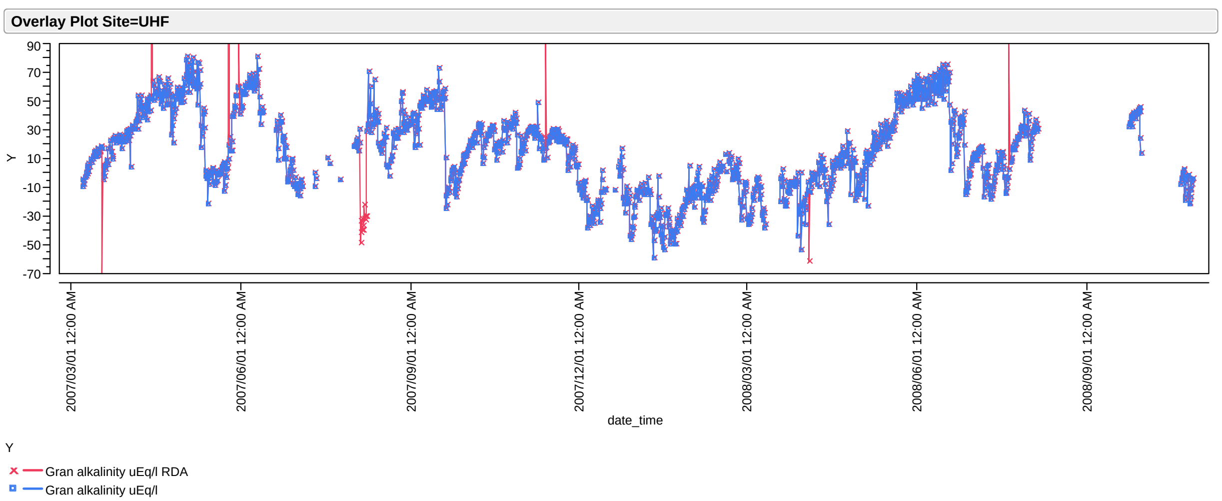




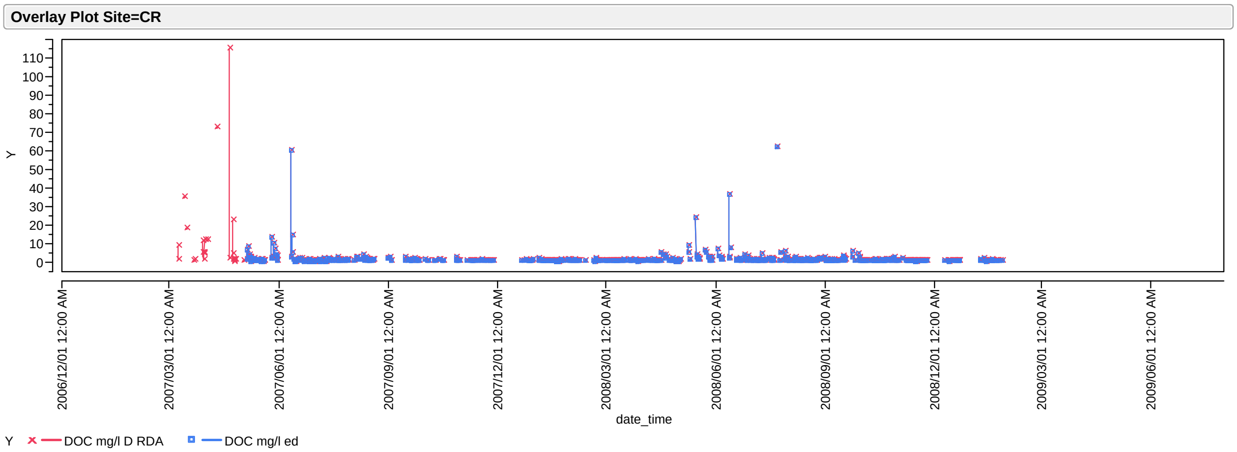
pH: pH flyers were deleted where they were inconsistent with Gran alkalinity, or where they were associated with the forest of Ca spikes at LHF (see the discussion of Ca, below, for more on this issue).

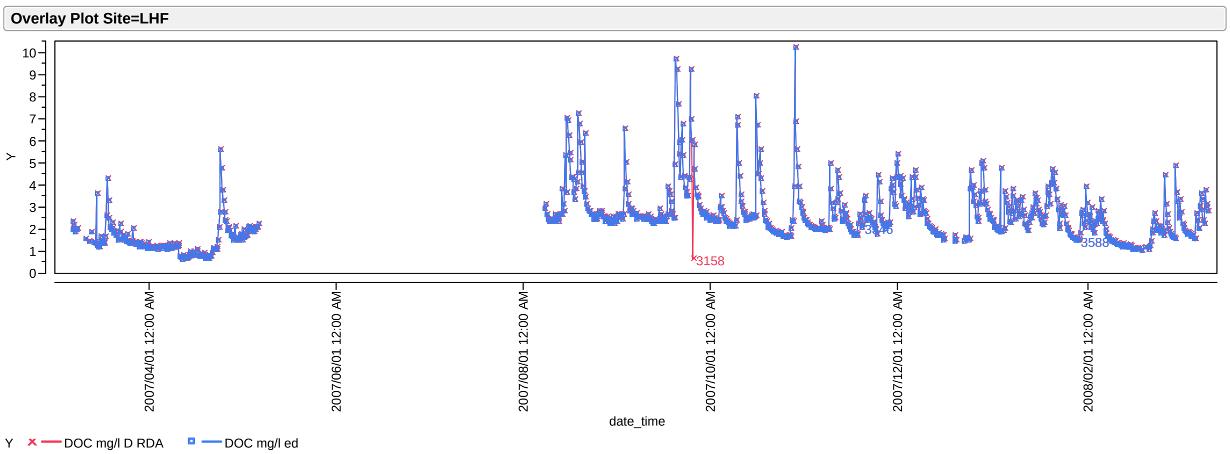


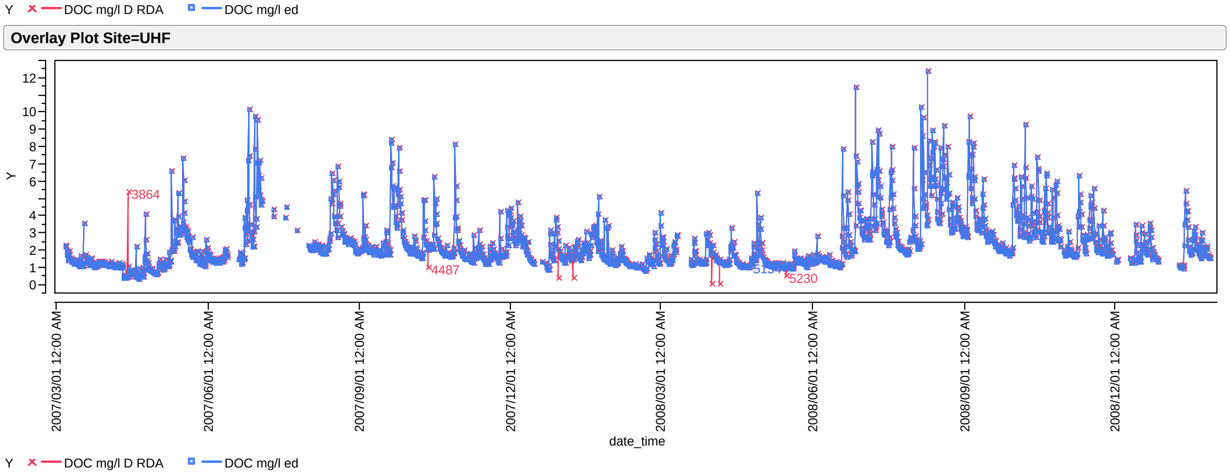




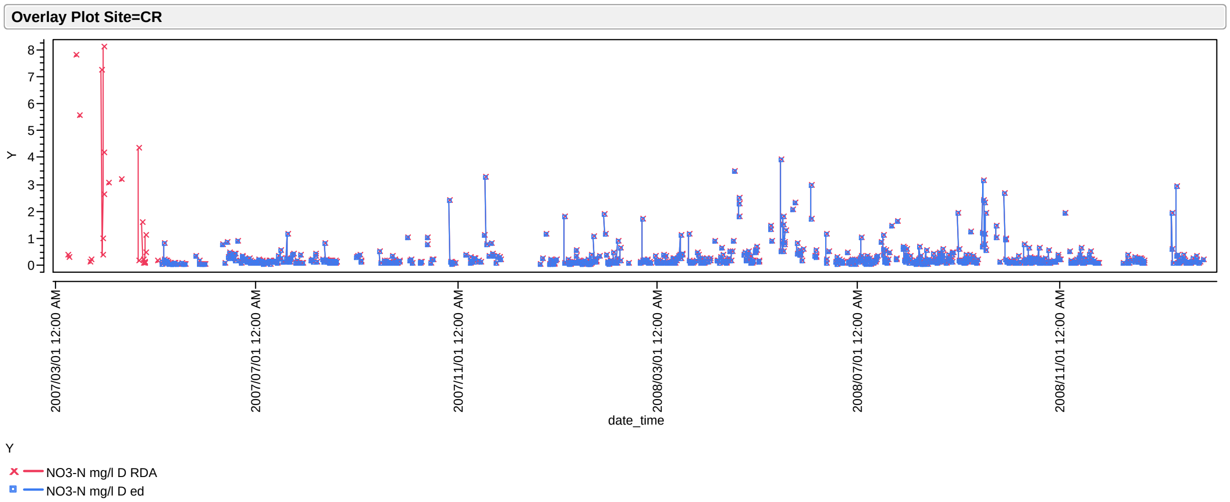
Gran alkalinity: Gran alkalinity flyers were culled where they were inconsistent with pH, or where they were associated with the forest of Ca spikes at LHF (see the discussion of Ca, below, for more on this issue).

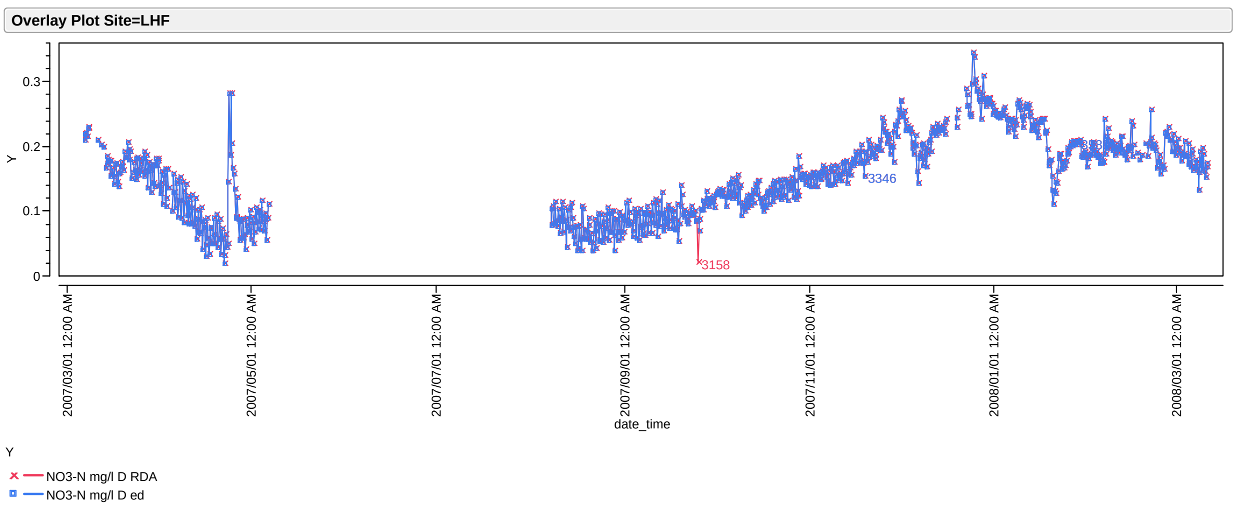


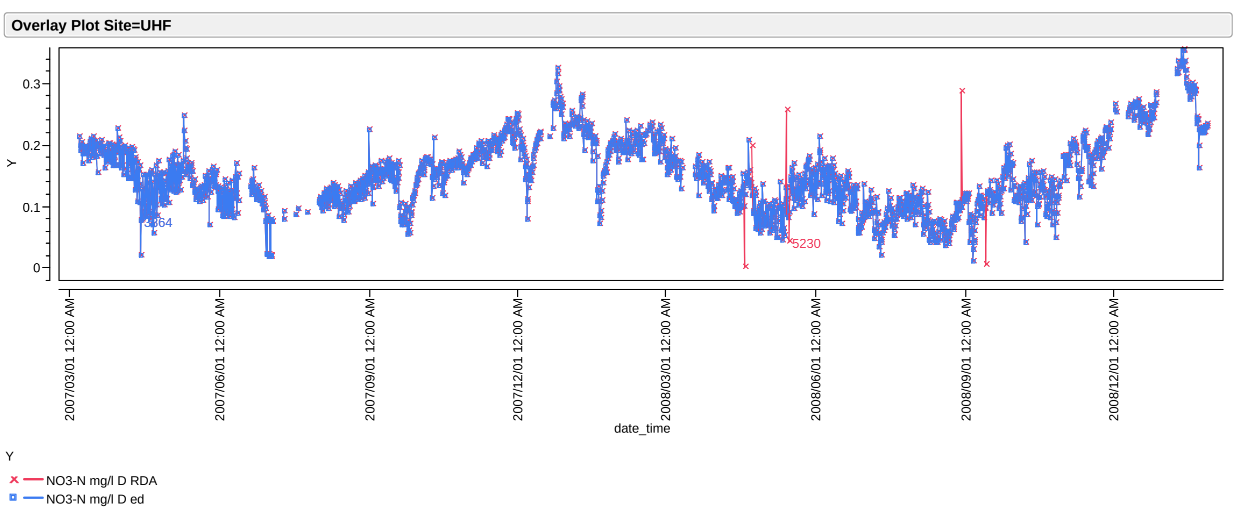




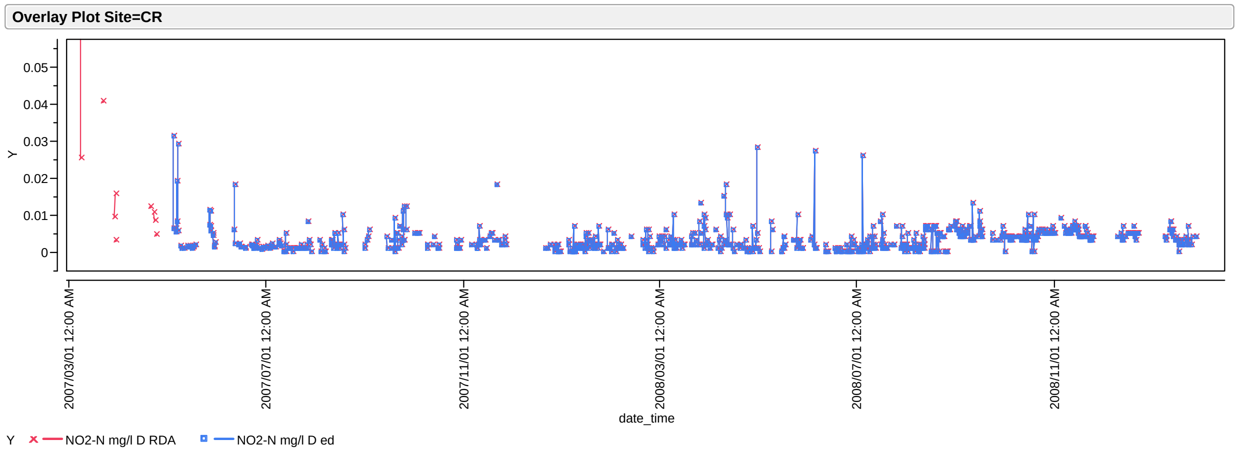
DOC: A few dissolved organic carbon spikes or drop-outs that did not correspond with flow excursions and did not correlate well with Fe etc. were deleted.

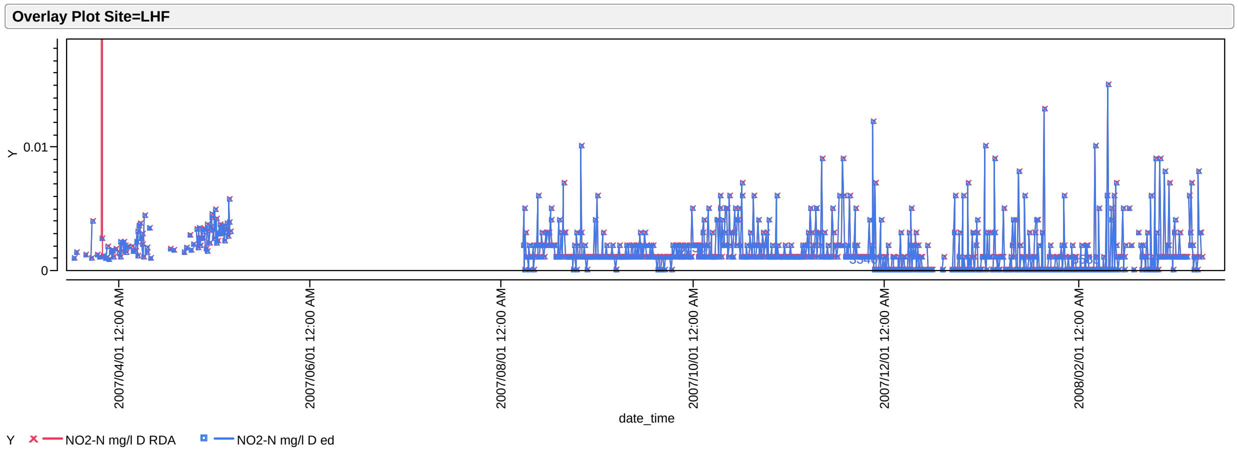


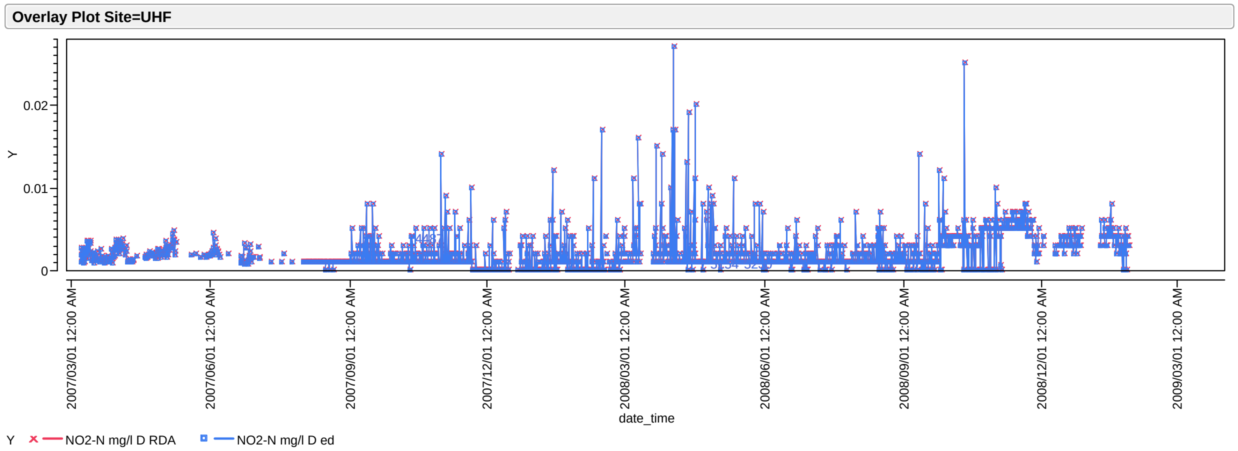




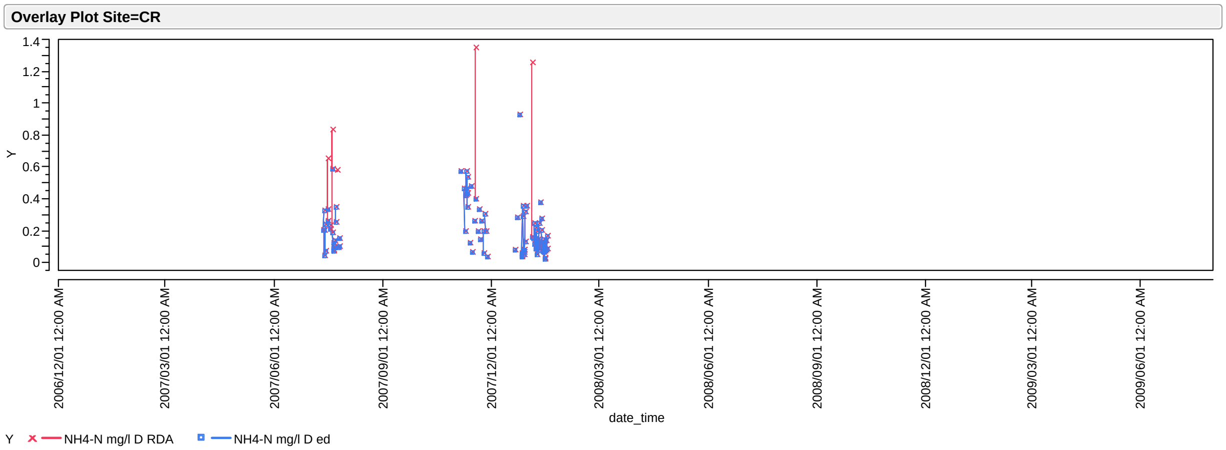
NO_3-N: Nitrate spikes were culled where NO_3+NH_4>TDN. Several NO_3 drop-outs (low values) were also deleted.

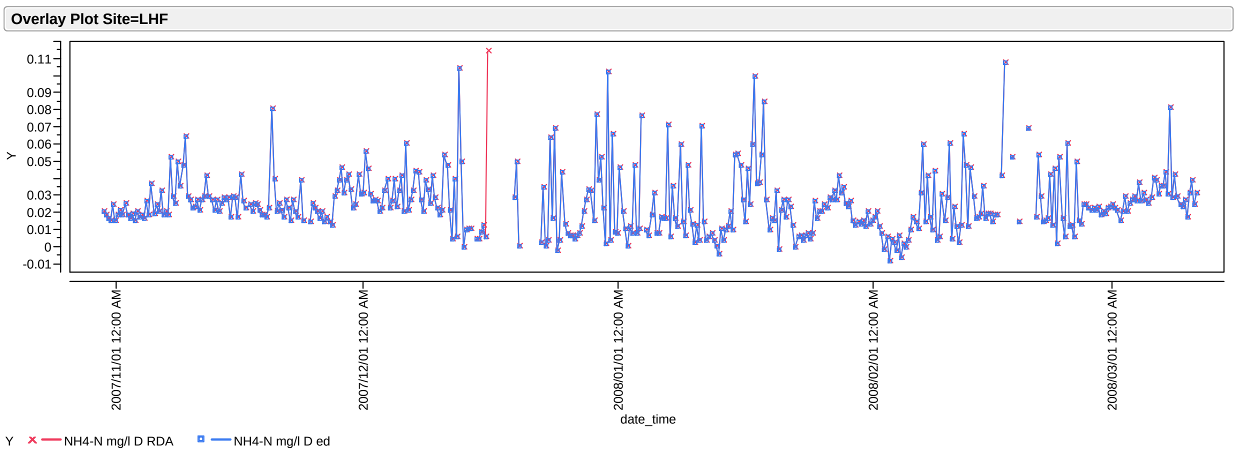


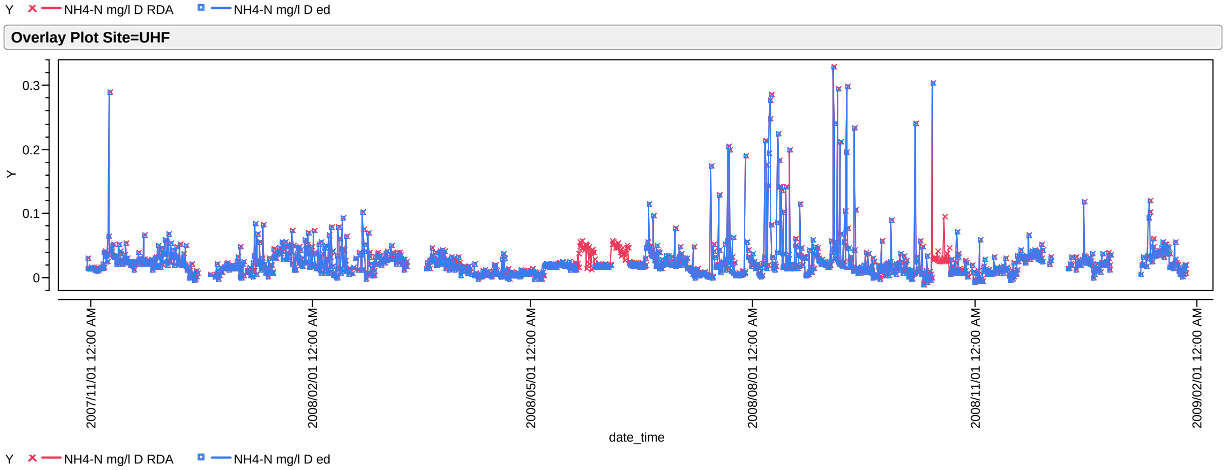




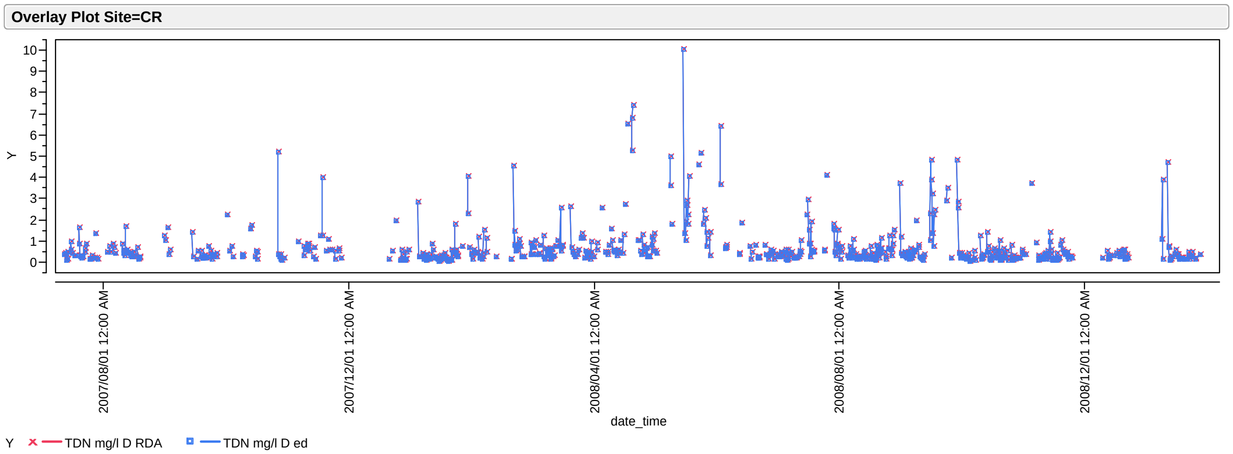
NO_2-N: Nitrite concentrations are very low, and their dynamics are noisy. We have left them in the edited data but they should be used only with caution.

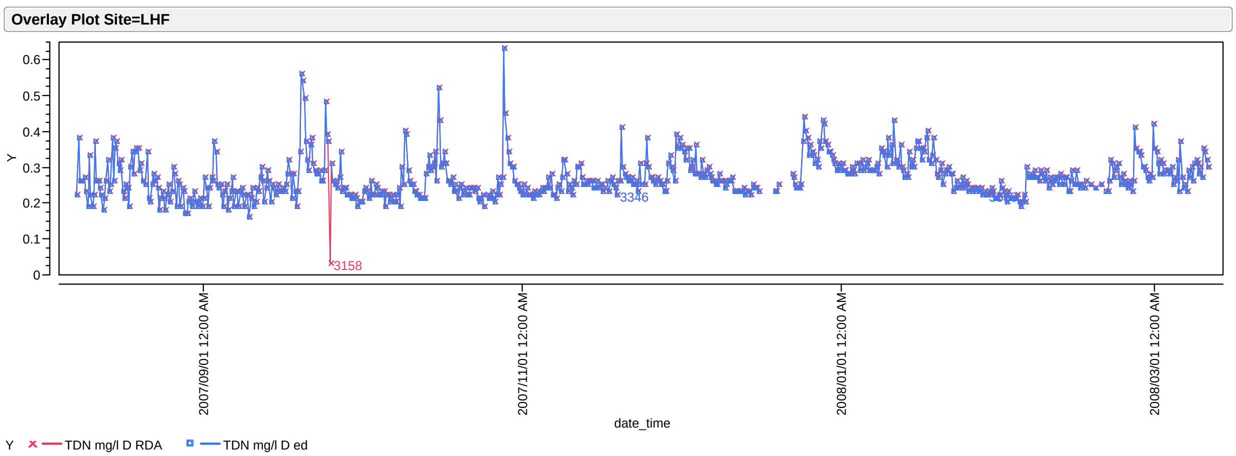


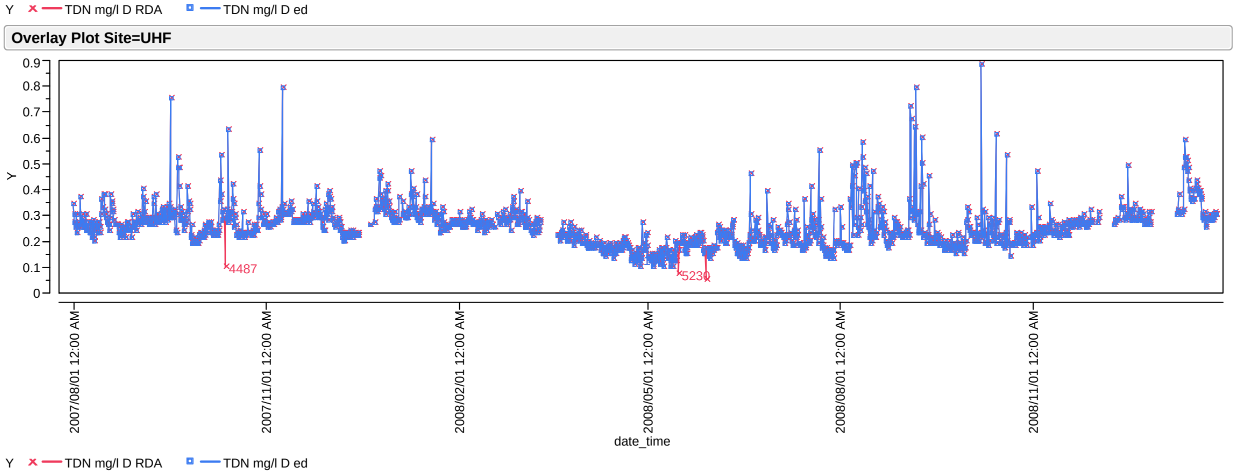




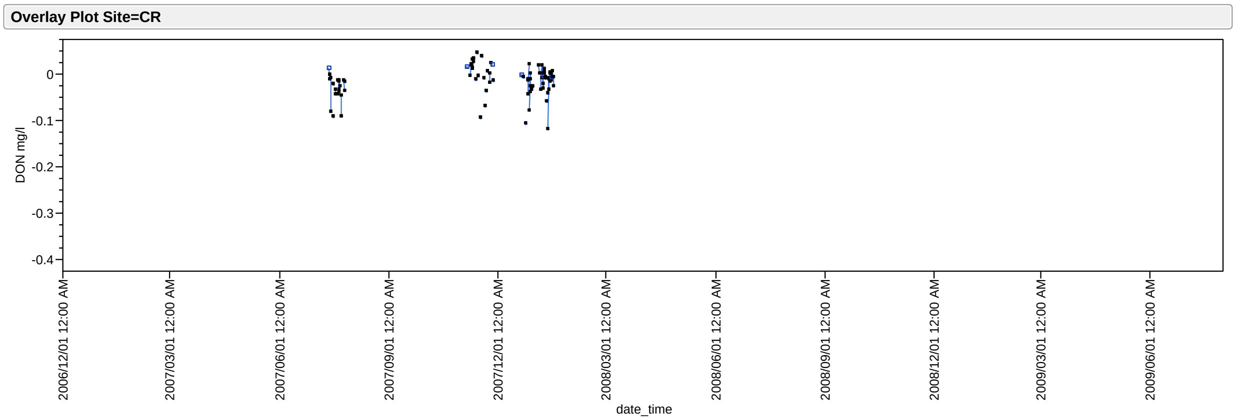
NH_4-N: We culled several ammonium flyers in precip because they led to negative calculated DON (NO_3+NH_4>TDN). We did not cull the NH_4 spikes at UHF because they also show up in TDN; users should nonetheless be aware that these could represent sample contamination. Users should also be aware that there are background correction "baseline" shifts between different analytical blocks in NH_4 at UHF (corresponding to different instrument calibrations); the most anomalous blocks have been culled but smaller shifts remain.

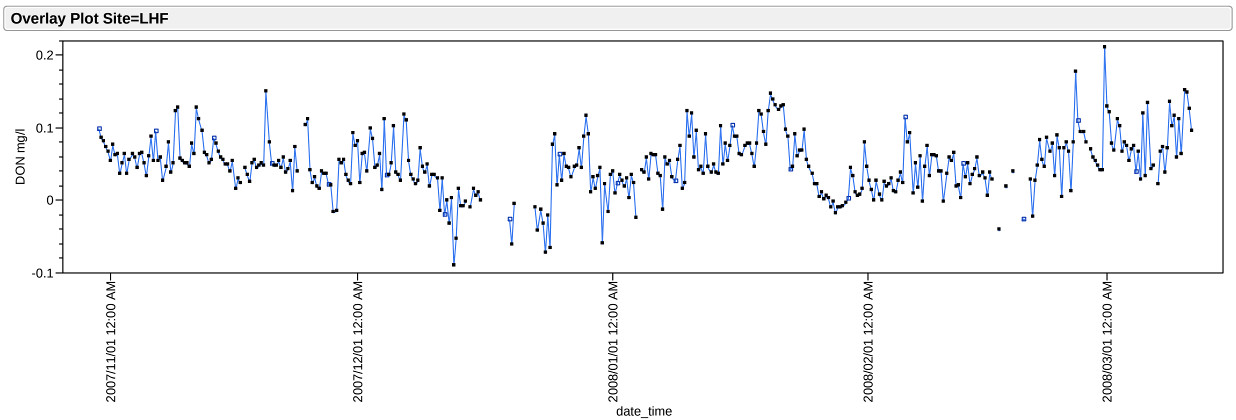


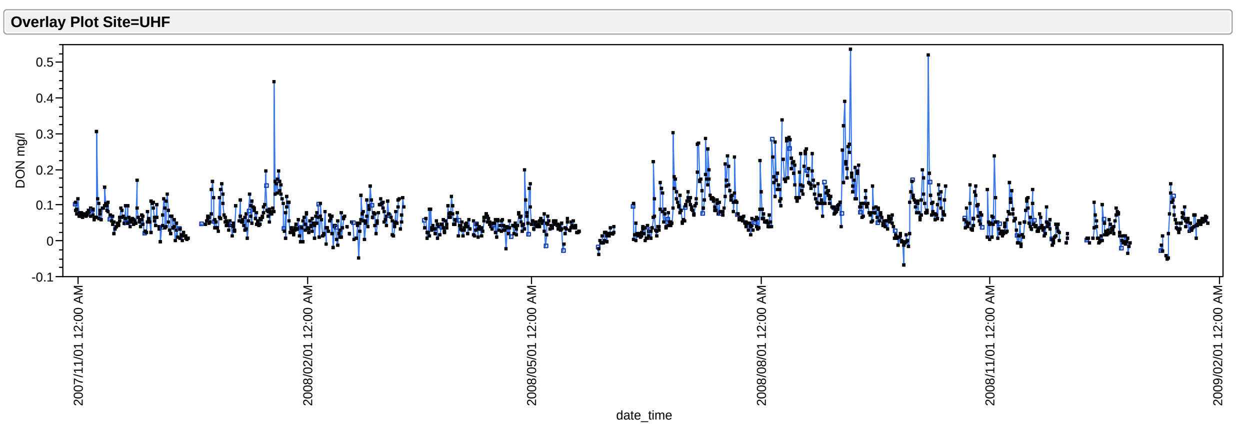




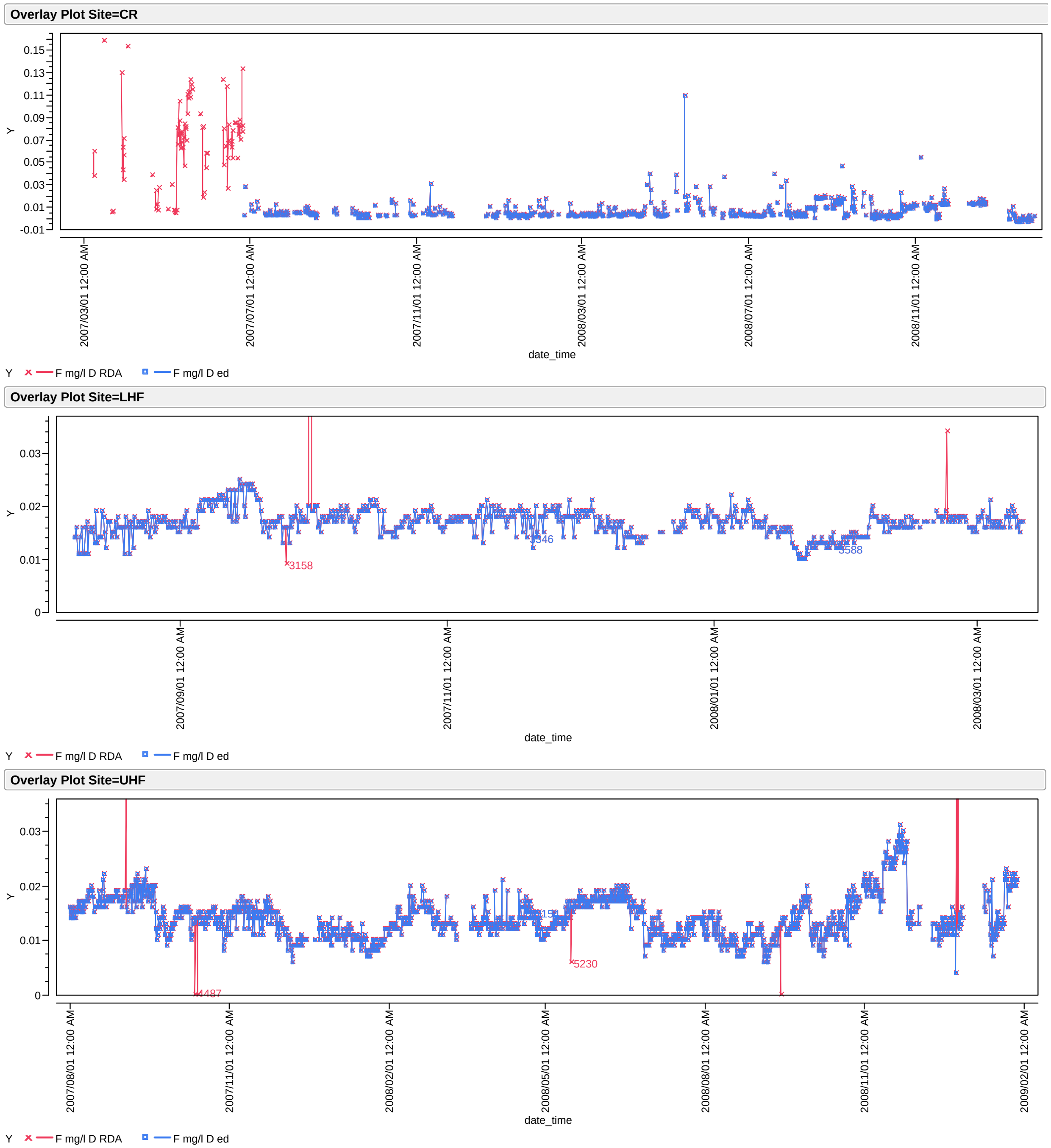
TDN: only a few TDN (total dissolved nitrogen) drop-outs were culled. Many flyers were kept because they were mirrored in NH_4 and DOC; nonetheless they could arise from sample contamination.



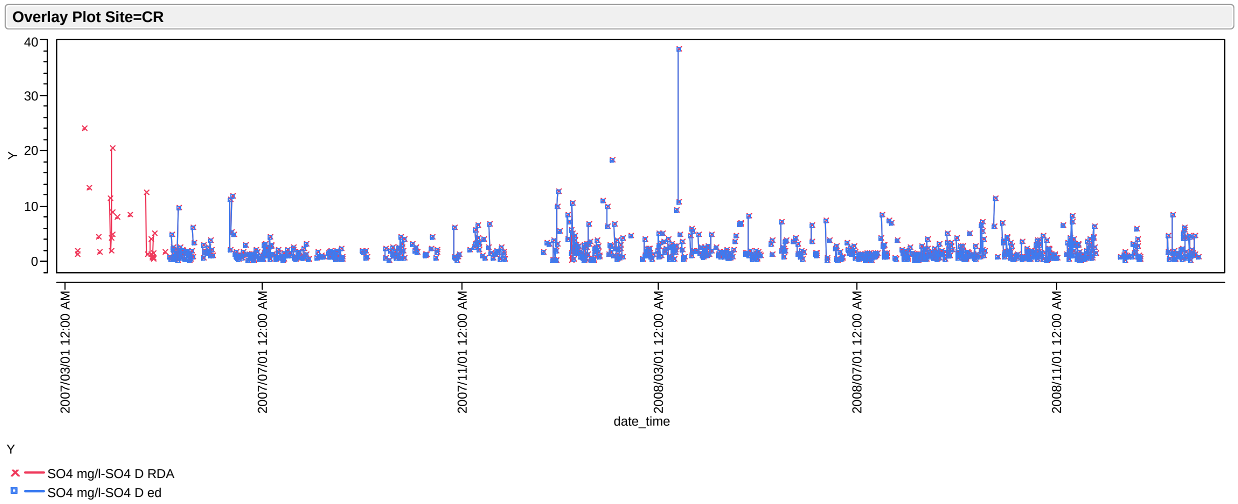


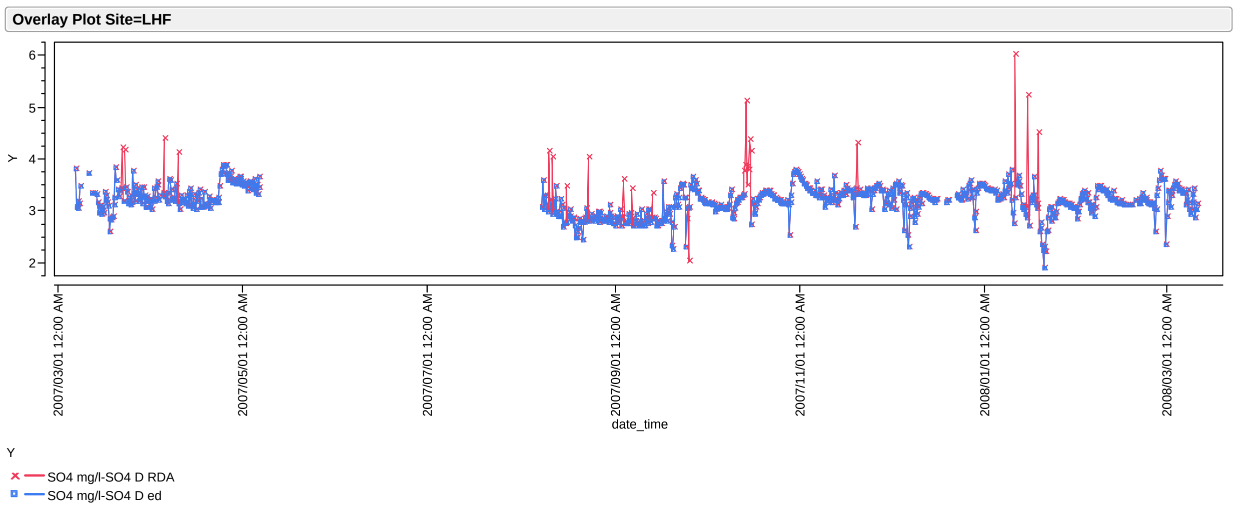


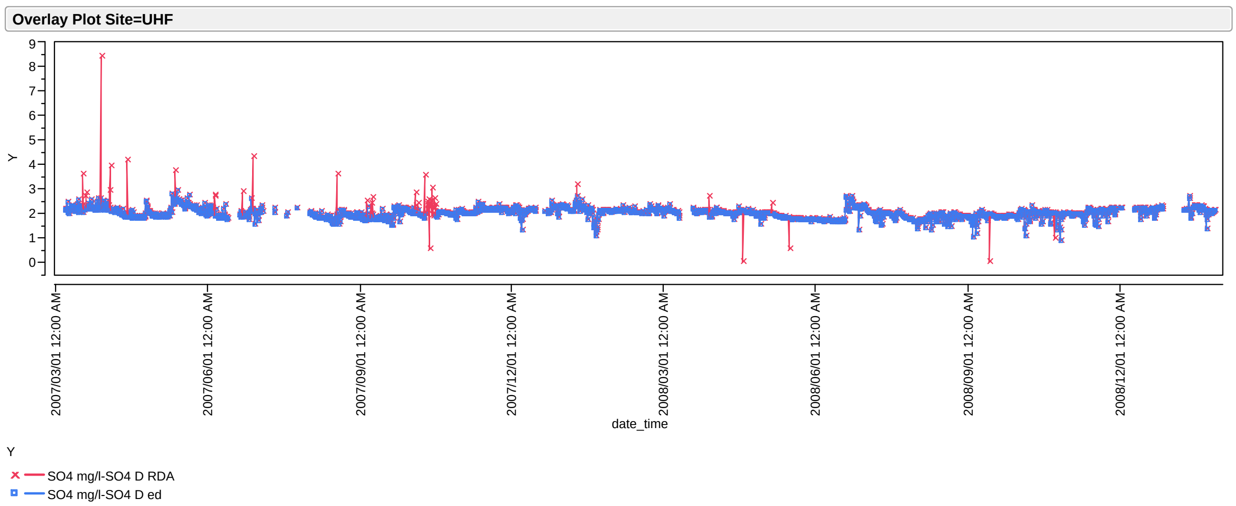
DON: Dissolved organic nitrogen is calculated as TDN – NO_3 – NO_2 – NH_4 (all in mg/l of N) using the edited values of these analytes; thus DON has no Raw Data Archive values. Where NO_2 is missing it is replaced with its average value, 0.02 mg/l, with little influence on the resulting DON values. In a few cases, DON values far below zero were used as clues to discrepancies between TDN and NO_3, leading either TDN or NO_3 to be culled. Some negative DON values remain, reflecting unavoidable uncertainties in DON estimation.



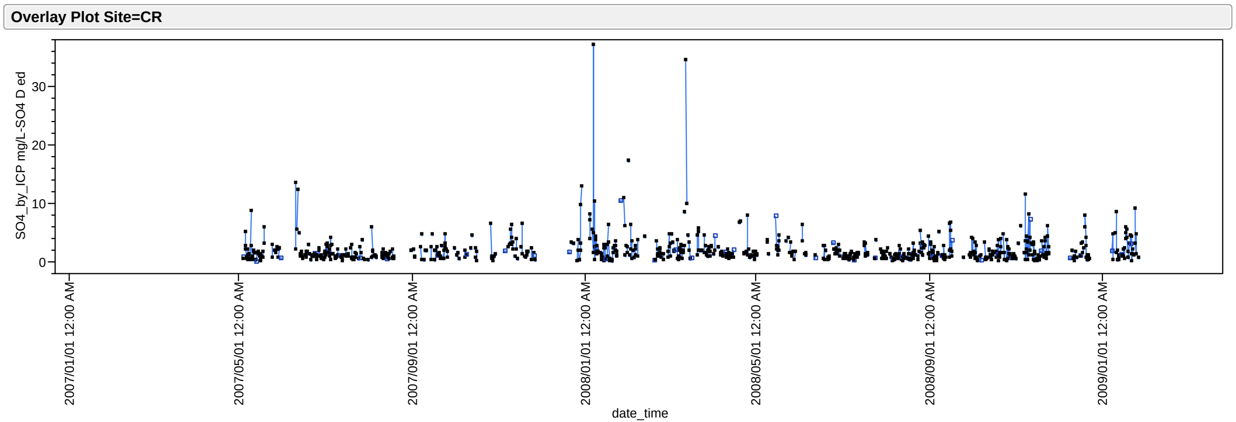
F: Only a few obvious fluoride flyers have been culled. Early F values in precipitation were culled because of evident calibration issues.

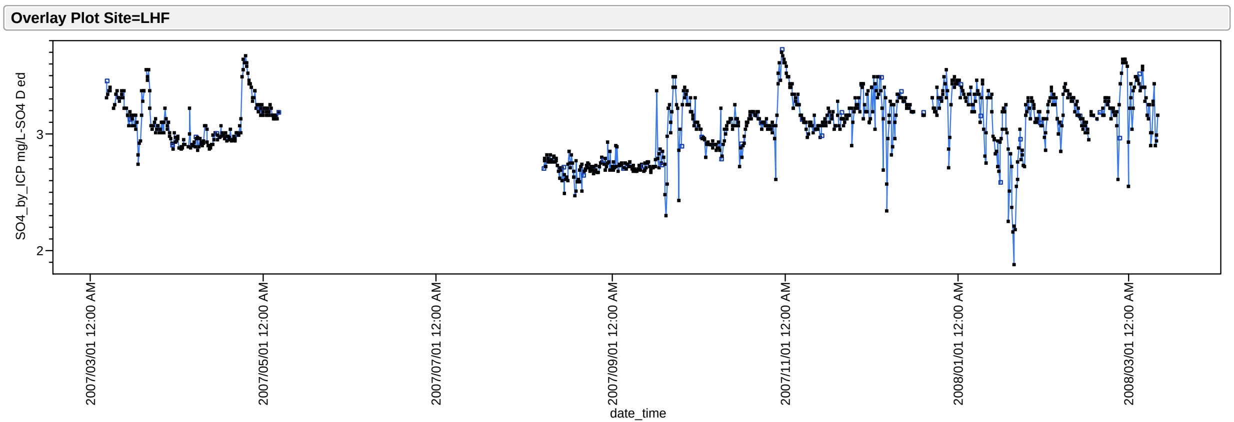


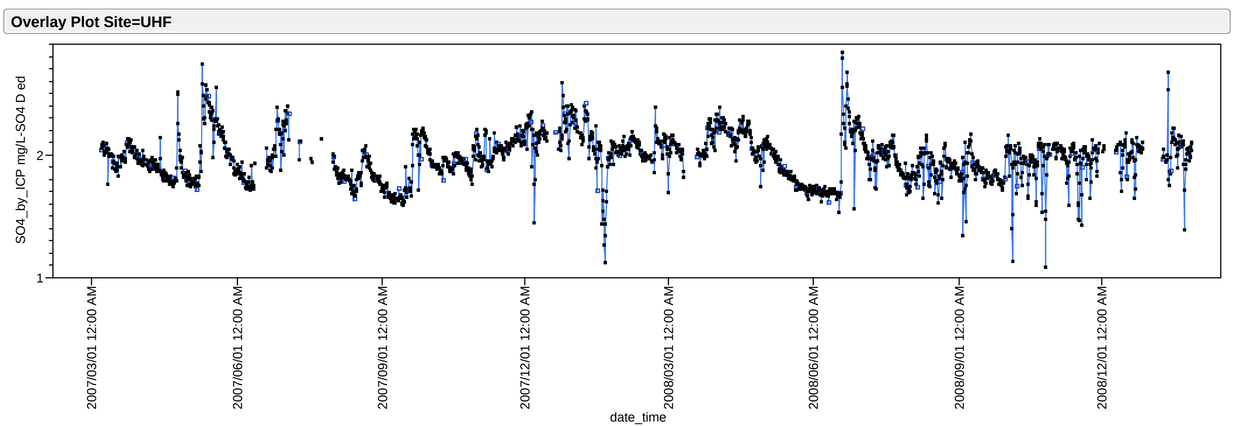




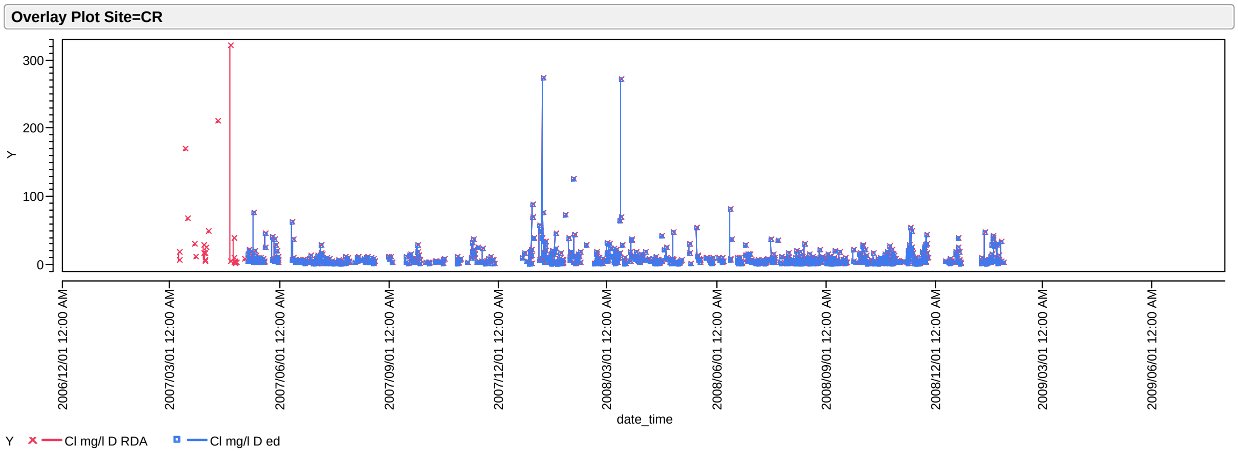
SO_4: The variable "SO_4" in the data set contains sulfate measured by ion chromatography, and expressed as mg/l of the ion. Flyers and drop-outs have been culled where they are not matched by similar extremes in total S determined by ICP-OES.

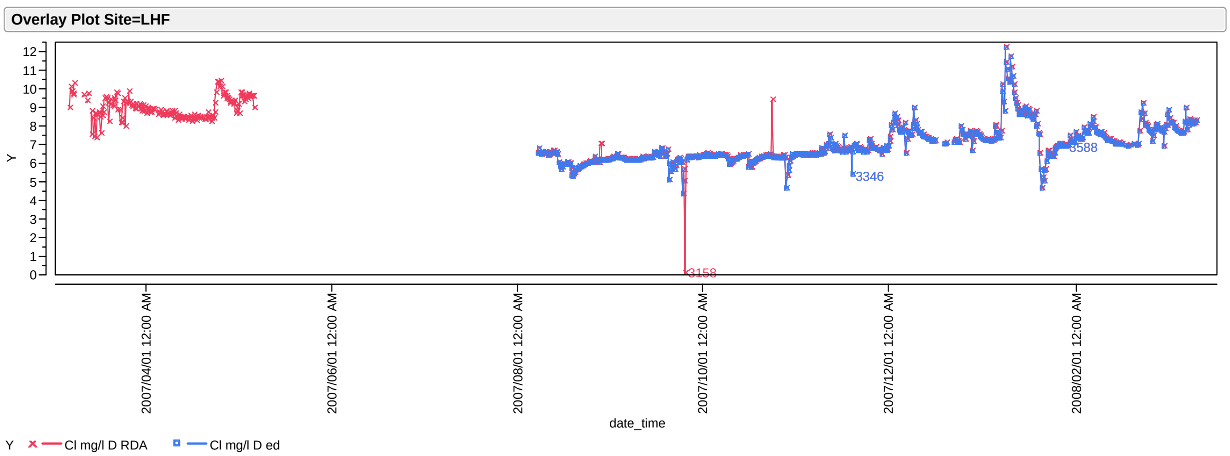


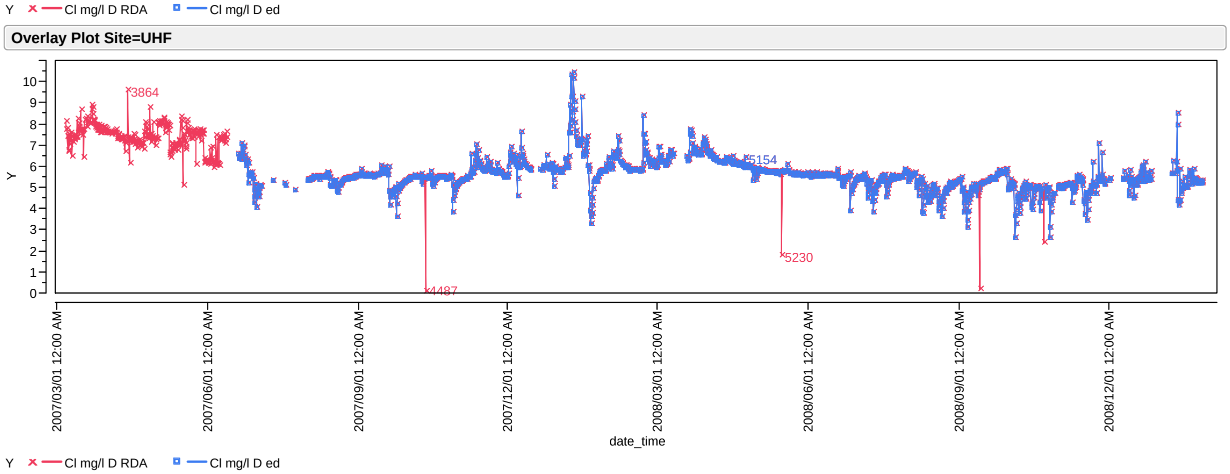




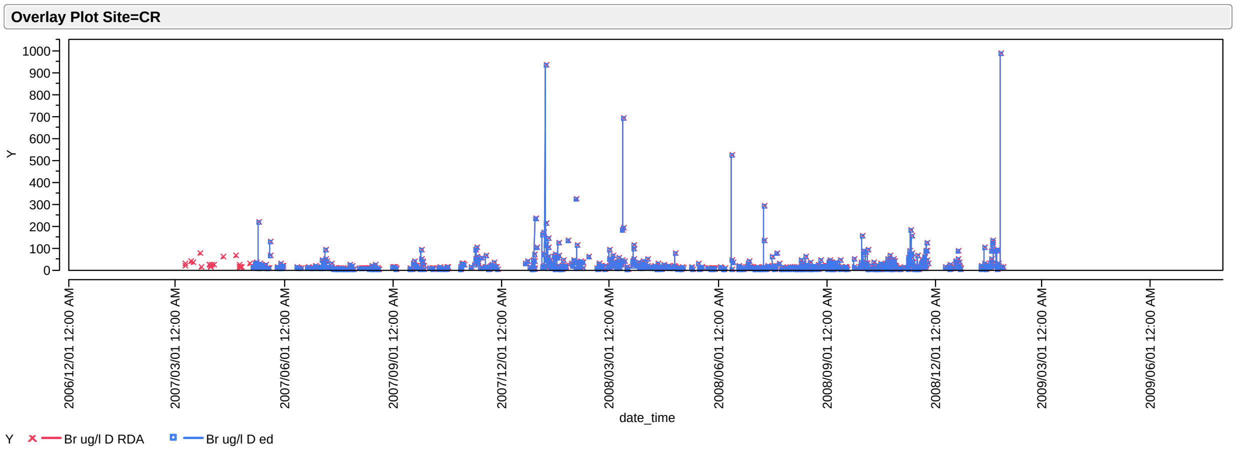
SO_4_by_ICP: This variable is calculated as mg/l of sulfate ion, using edited values of S as analyzed by ICP-OES. Because they are based on edited data, there are no Raw Data Archive values for this variable.

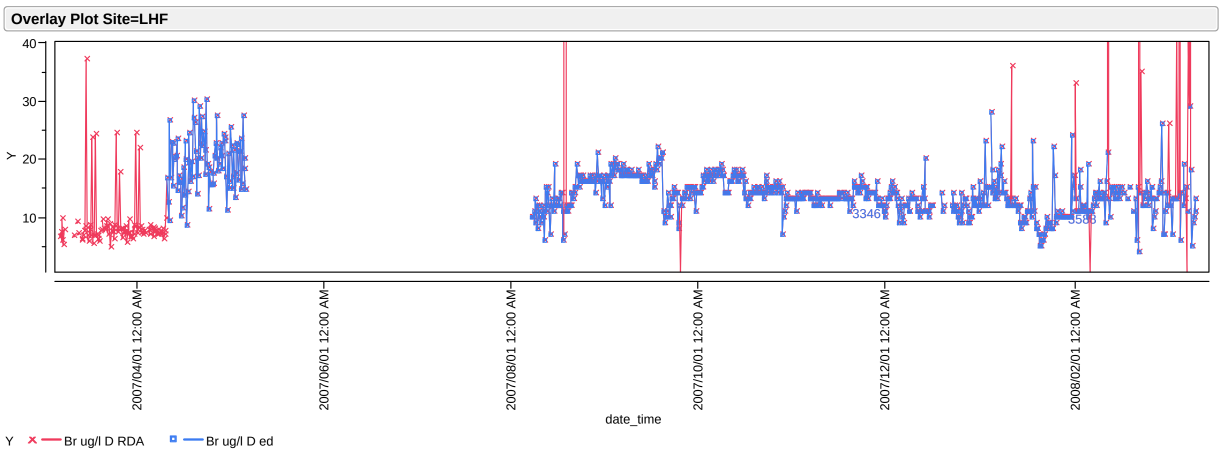


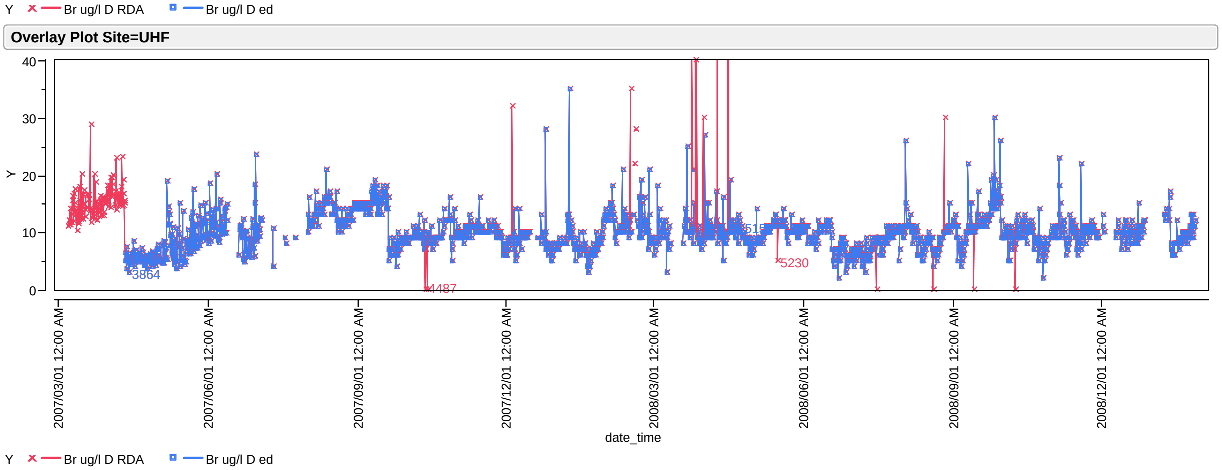




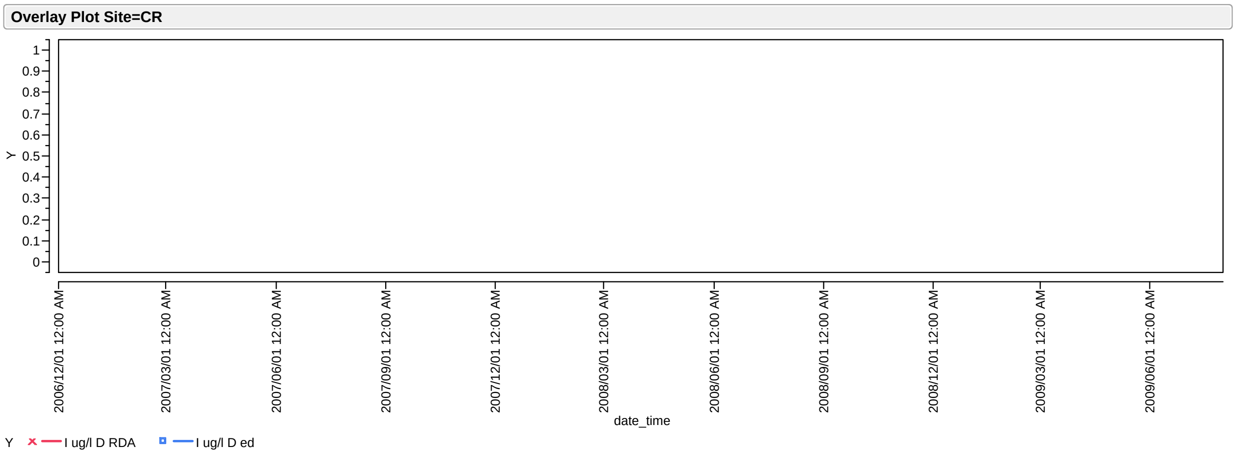
Cl: Chloride singleton flyers and drop-outs were deleted. Cl analyses done at CEH Wallingford (up to July 2007) were also omitted, because they alternate high and low blocks, in a pattern that suggests calibration problems and is inconsistent with the rest of the time series.

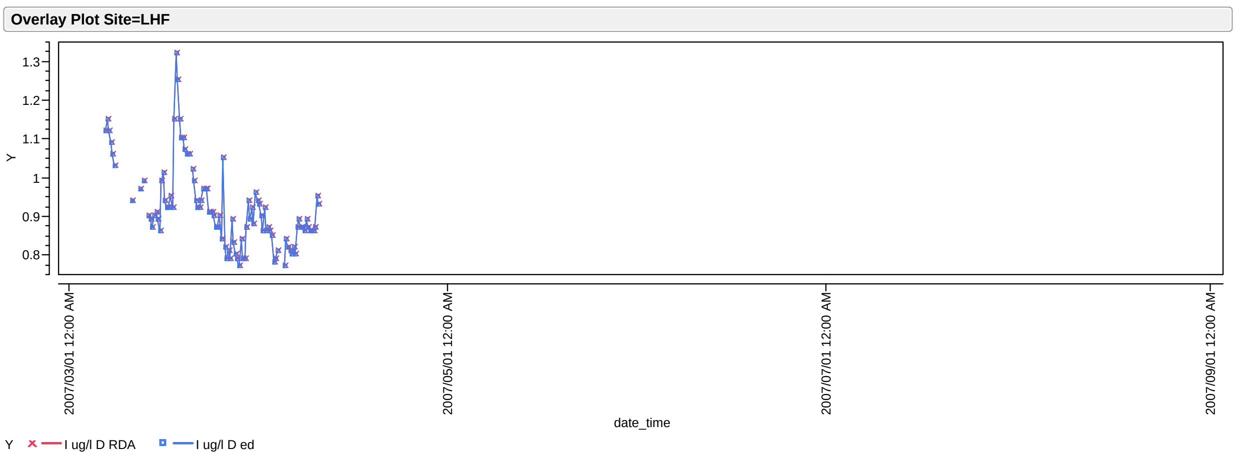


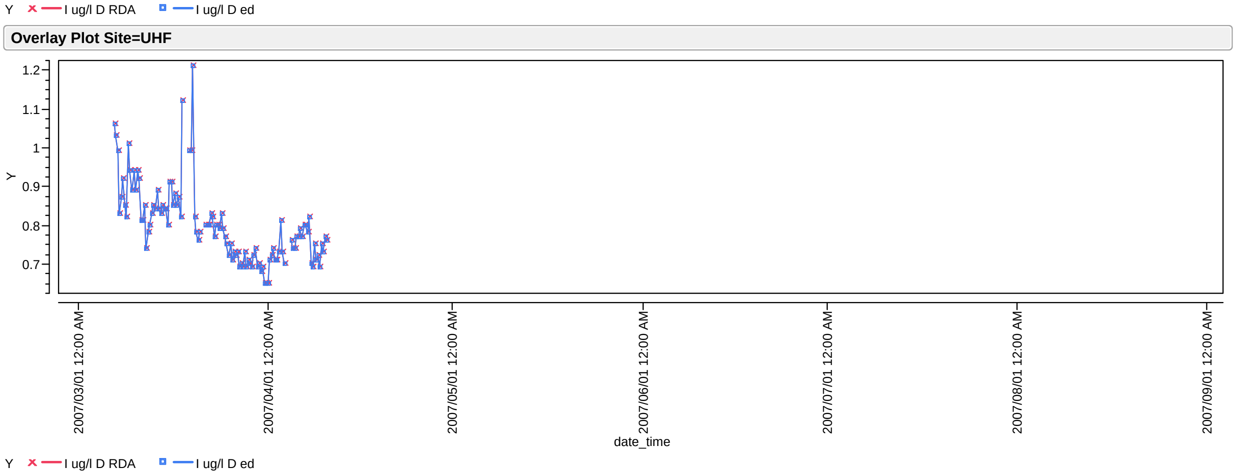




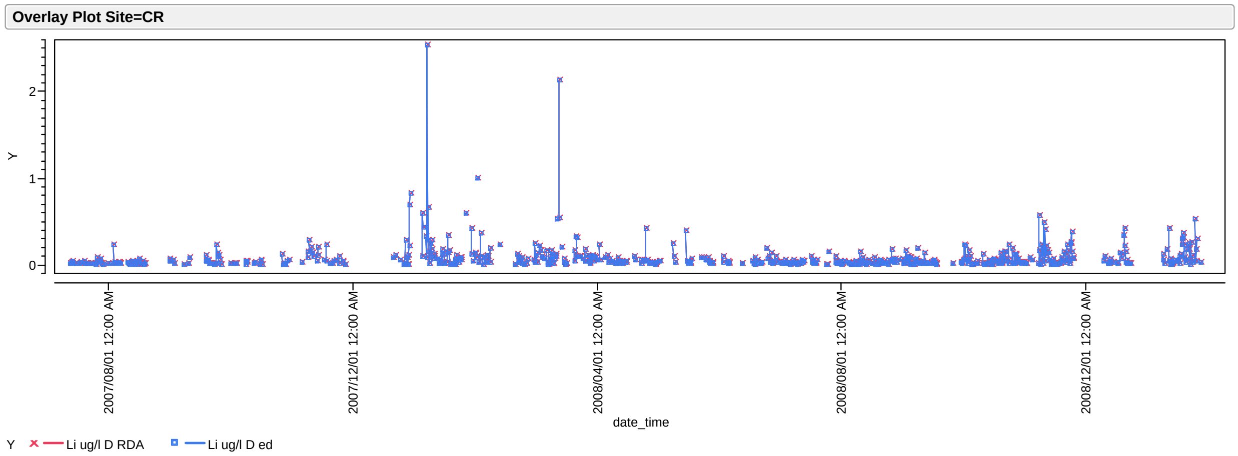
Br: We dropped bromide values from the first five sampling trips at both LHF and UHF, due to suspected calibration problems and a large number of flyers. We also culled numerous individual flyers and drop-outs in the rest of the time series.

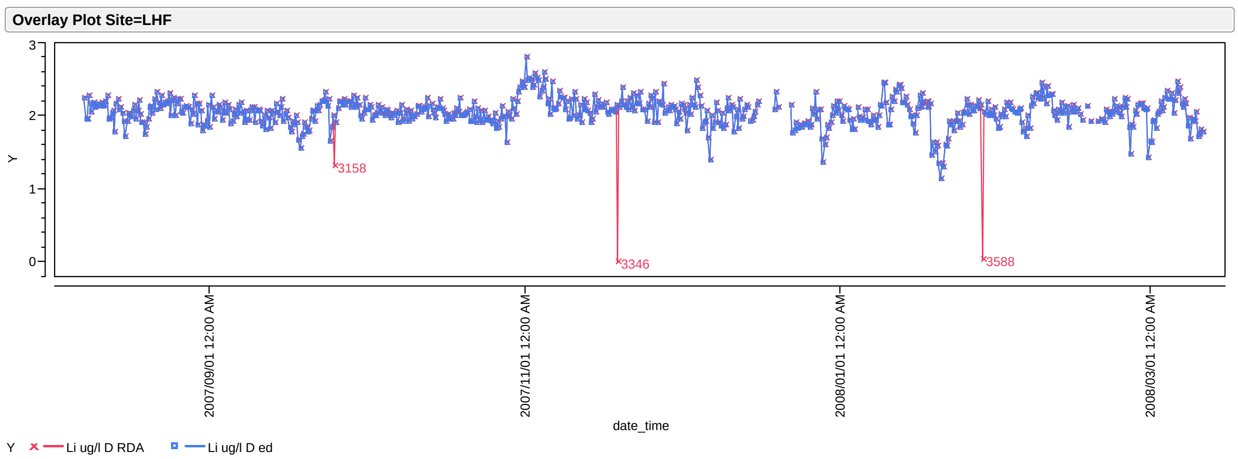


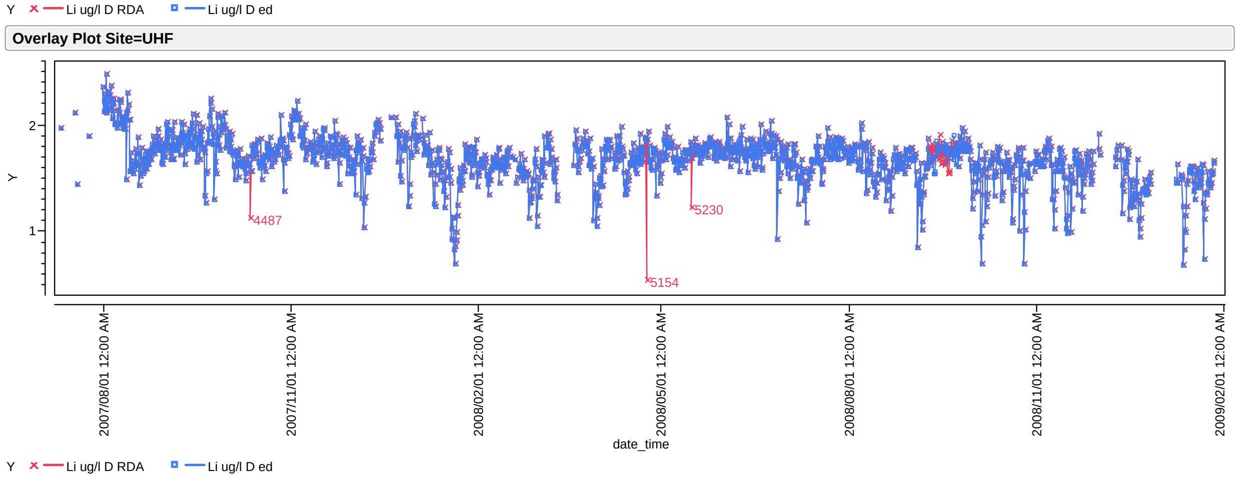




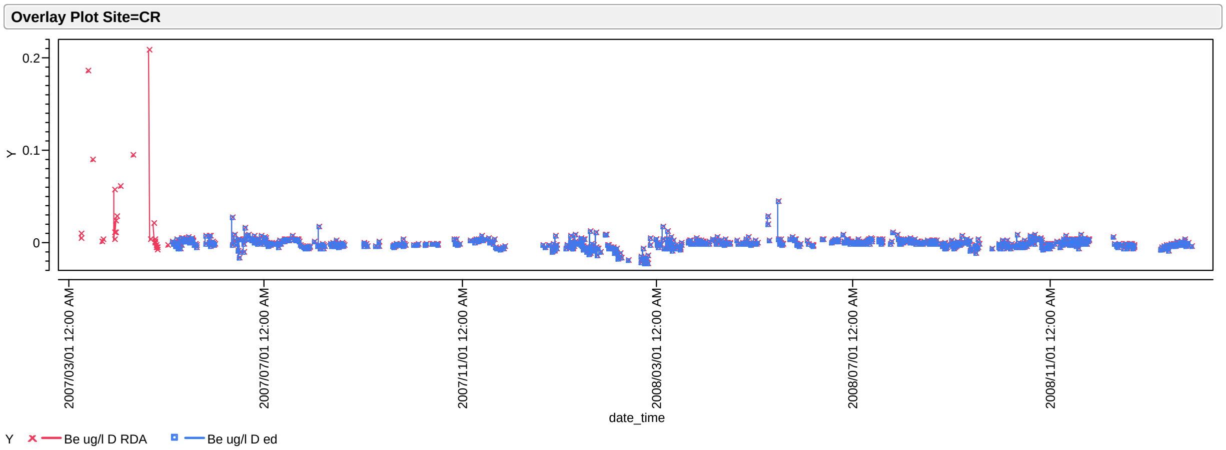
I: Analyses of iodine are only available for a short period at the beginning of the study. We have not edited the I values because the record is too short to provide a basis for separating signal and noise.

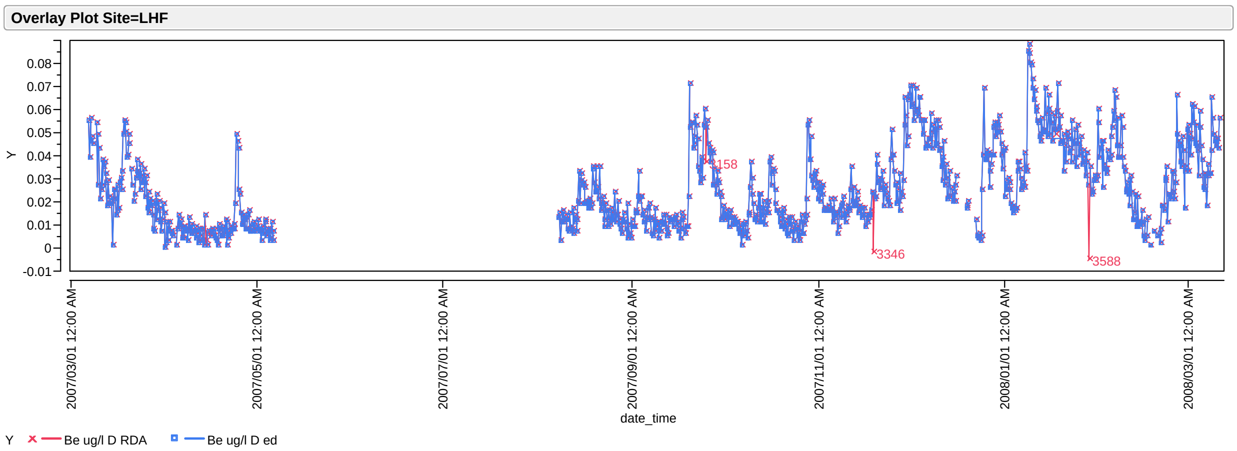


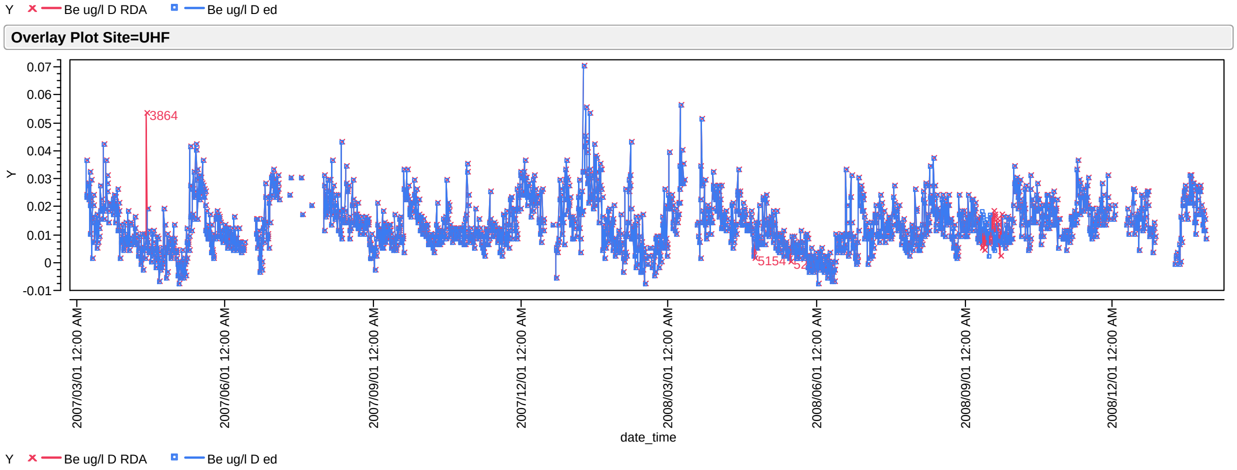




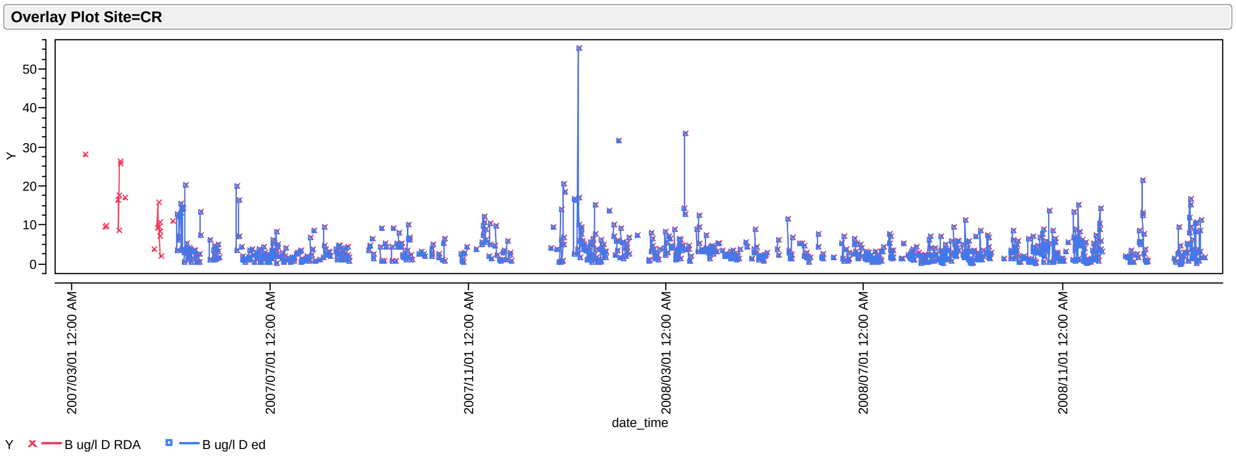
Li: Several anomalous lithium samples were culled; because the same samples have anomalous values of many analytes, they probably represent sample mix-ups, rather than analytical problems.

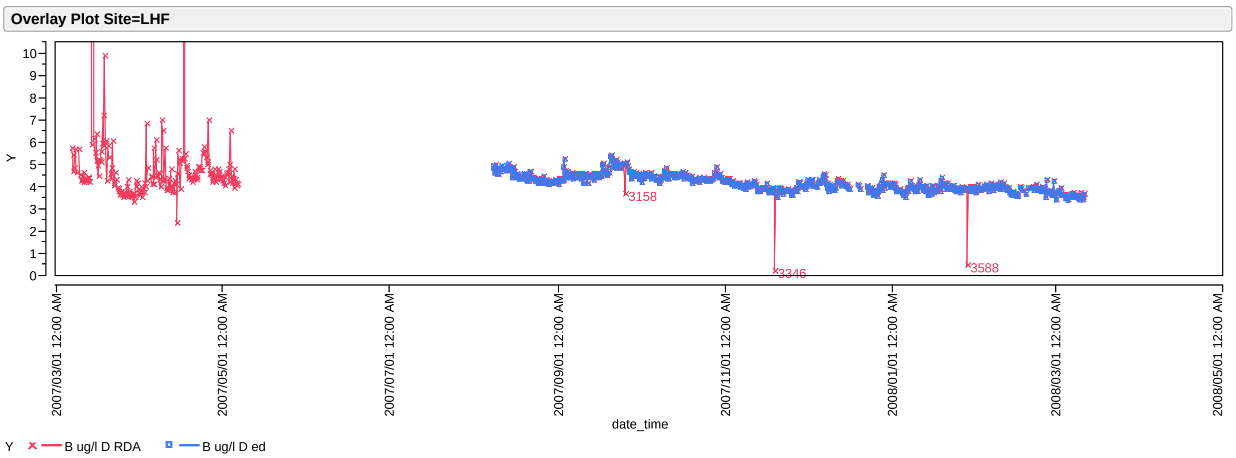


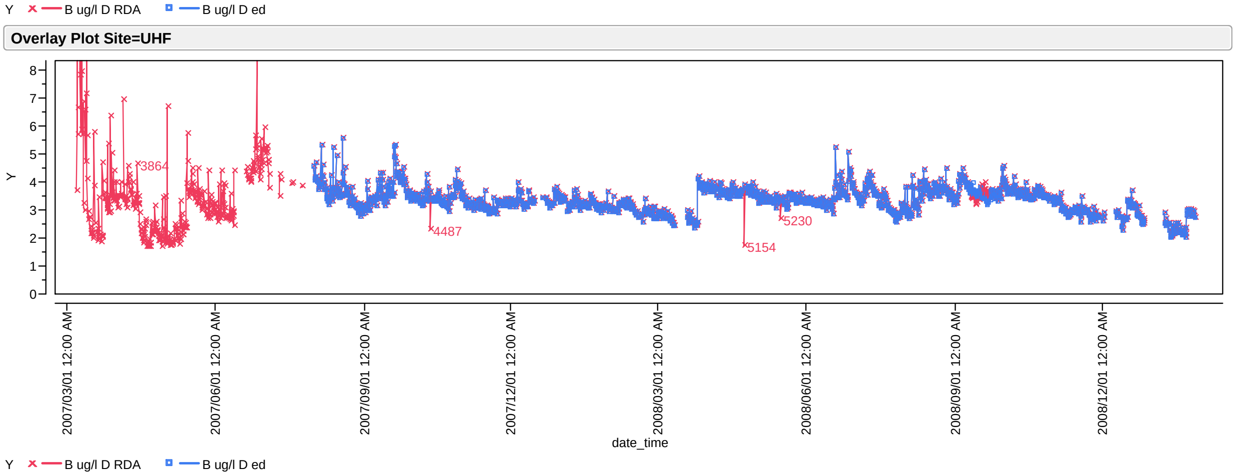




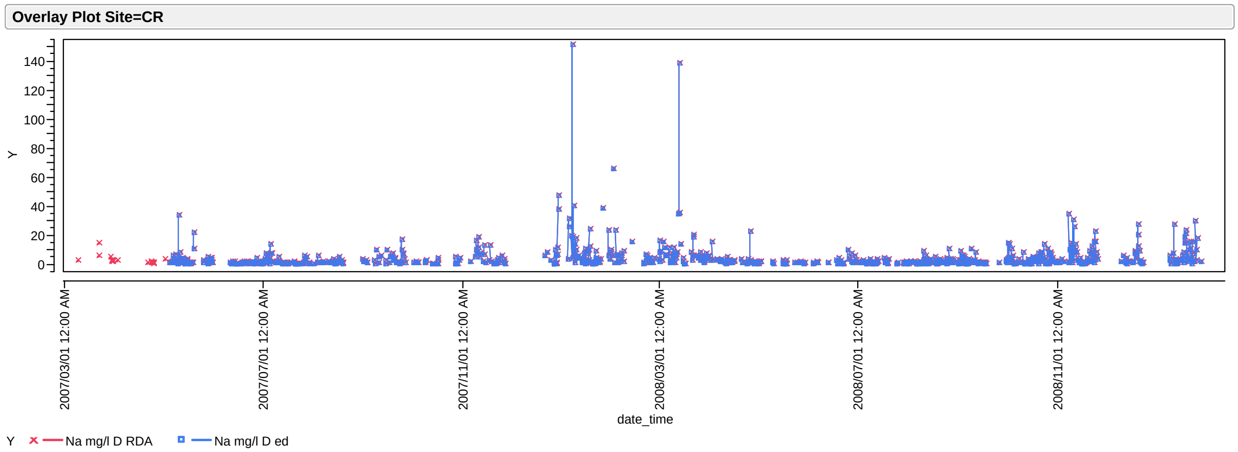
Be: Only a few beryllium flyers were culled; the others were correlated with, e.g., high values in Al, and were retained.

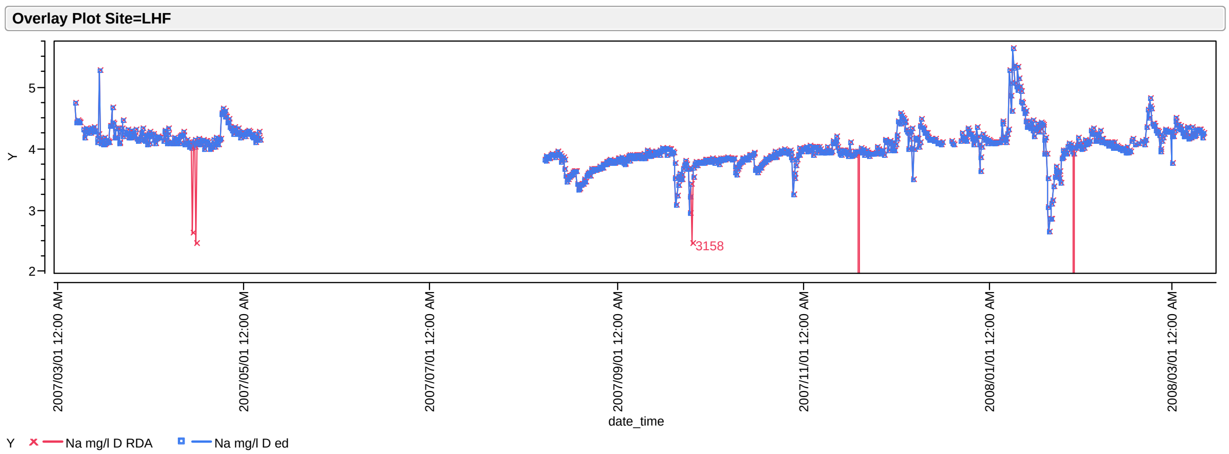


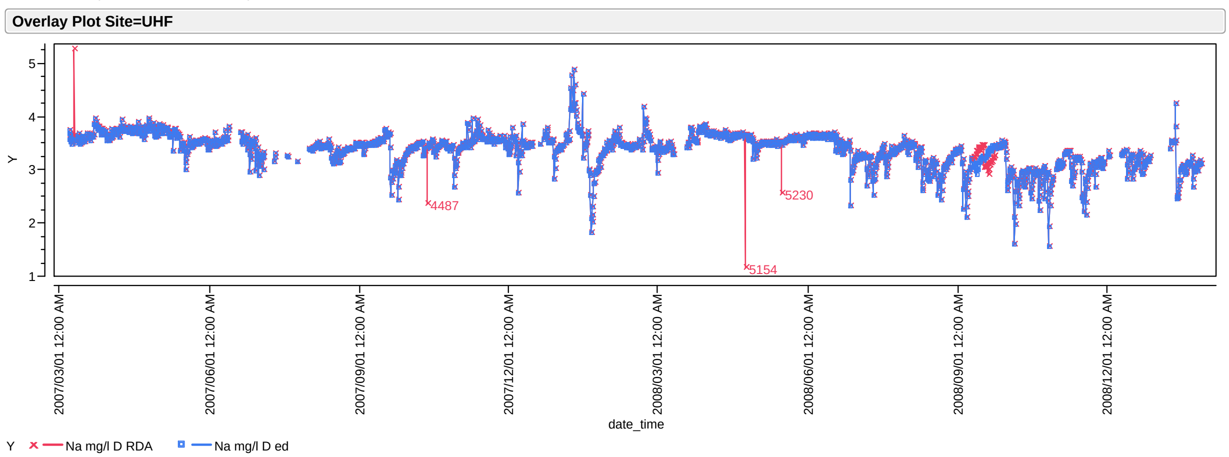




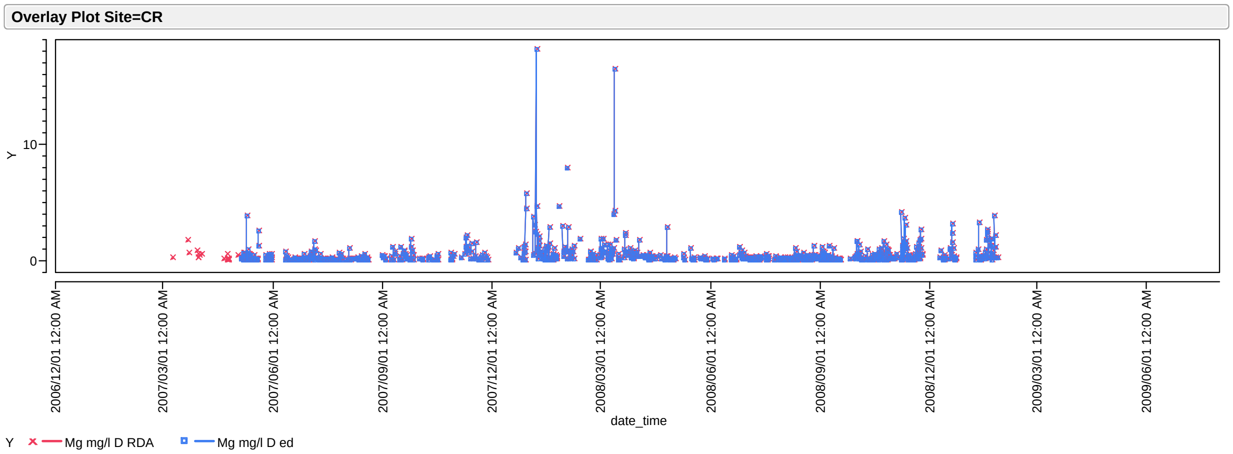
B: The early boron values at both streams have been culled, because of evident background correction "baseline" problems and many flyers.

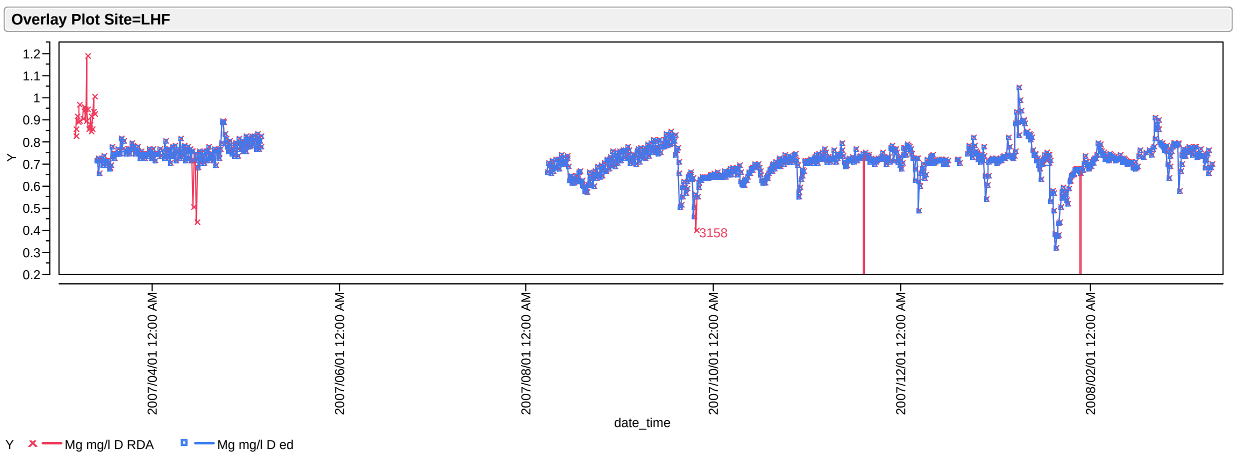


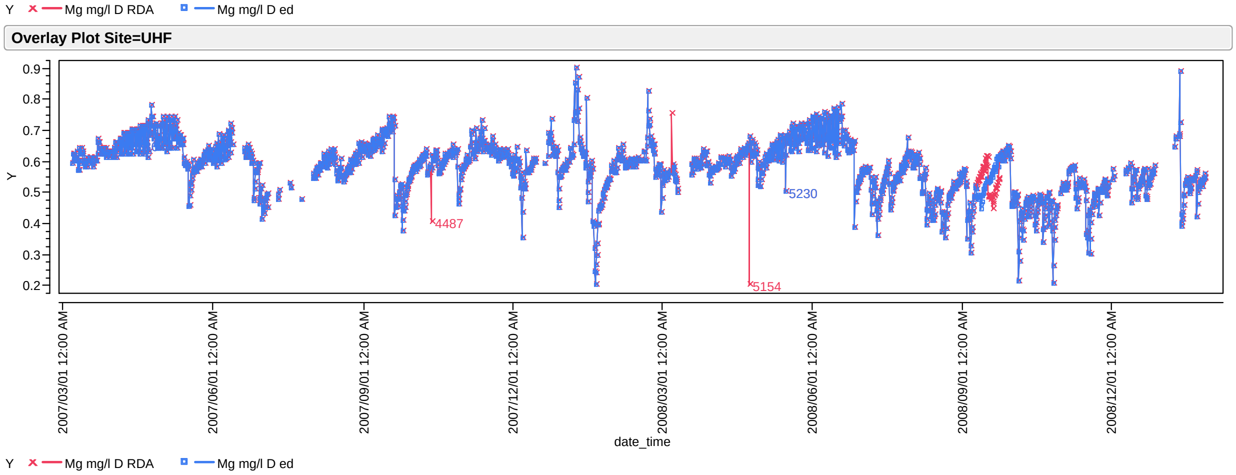




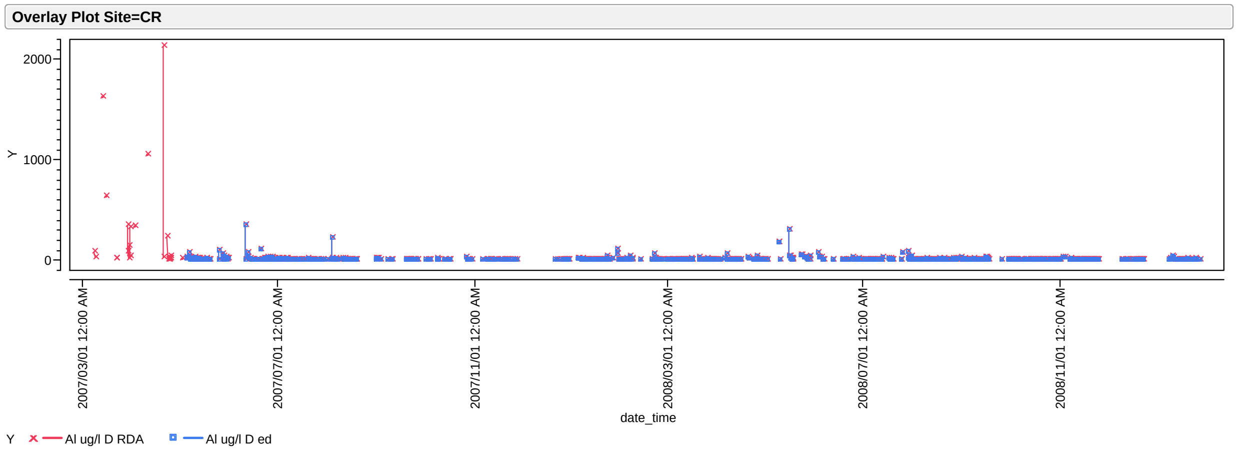
Na: A few sodium flyers and drop-outs were culled. Note the unusual appearance of the time series in September of 2008, with RDA and edited values appearing to move in parallel. This results from the fix that we applied to the accidental swap of Trips 80 and 81 in the ICP-OES and ICP-MS data. This will be seen in every element analyzed by the ICP-OES or ICP-MS, but is particularly obvious where there is a steep trend in the data.

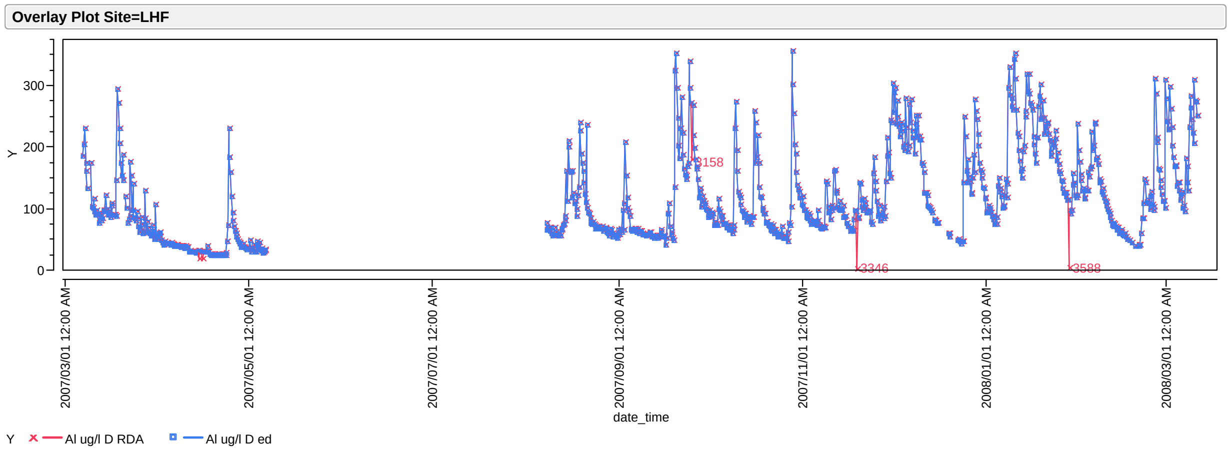


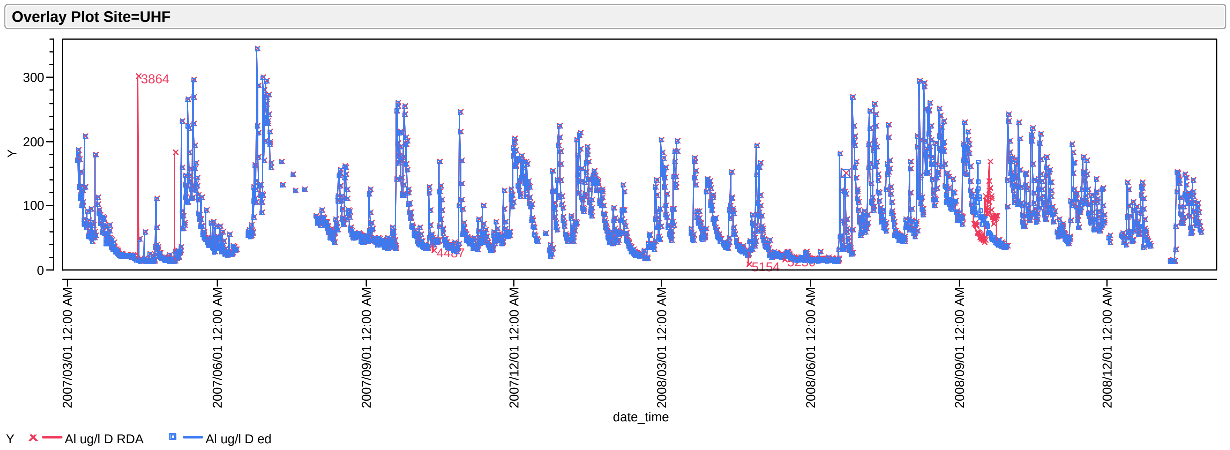




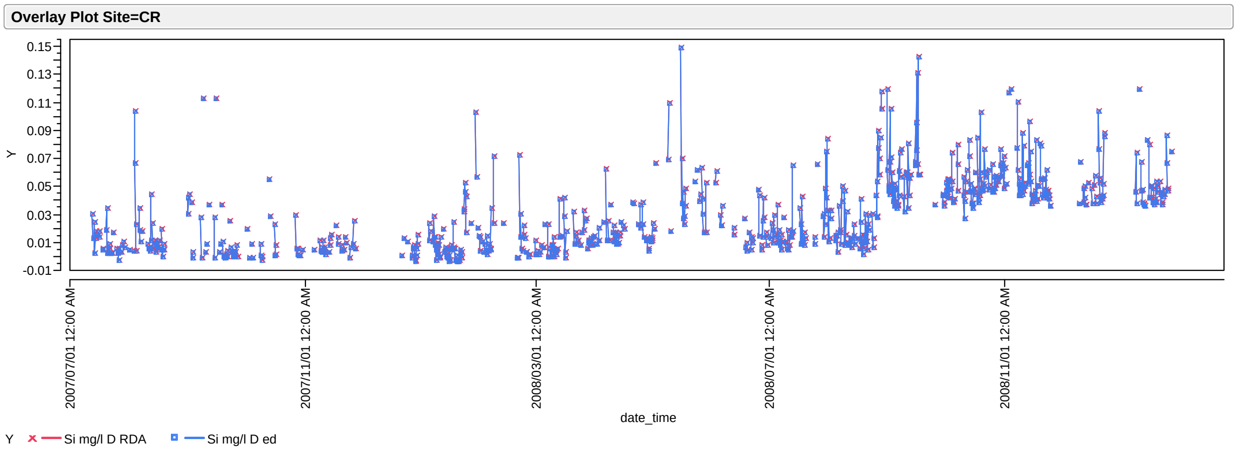
Mg: A few magnesium flyers and drop-outs were culled. Note the unusual appearance of the time series in September of 2008, with RDA and edited values appearing to move in parallel. This results from the fix that we applied to the accidental swap of Trips 80 and 81 in the ICP-OES and ICP-MS data. This will be seen in every element analyzed by the ICP-OES or ICP-MS, but is particularly obvious where there is a steep trend in the data.

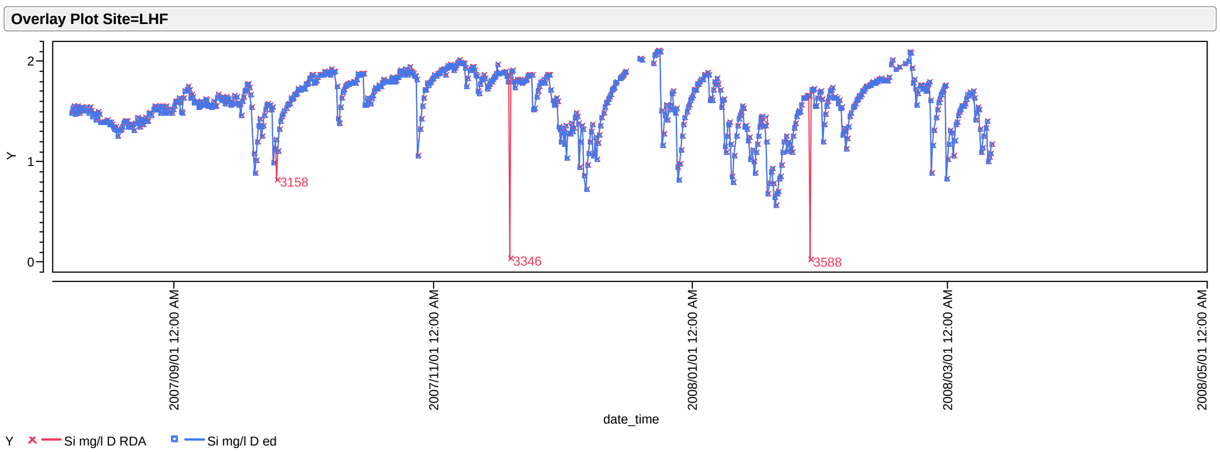


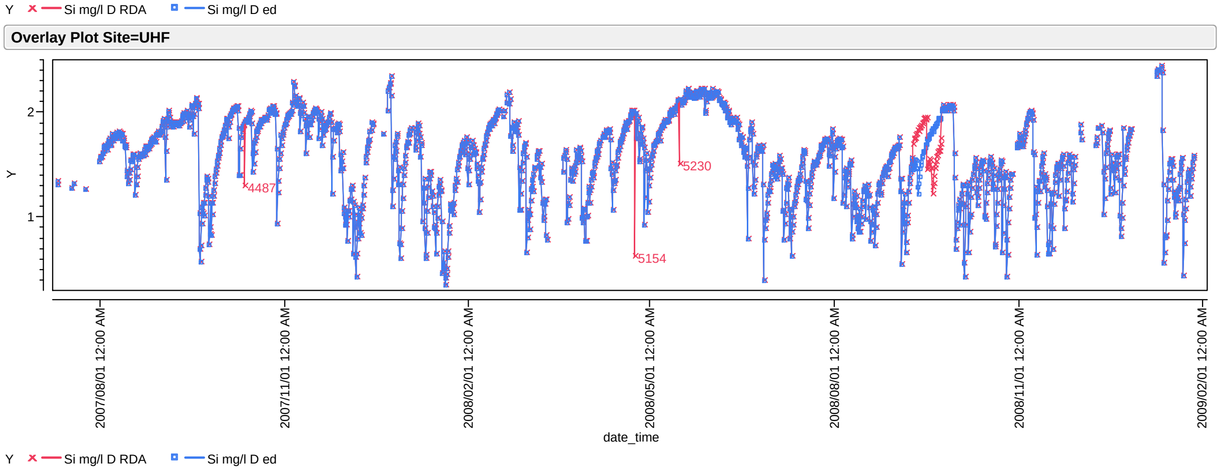




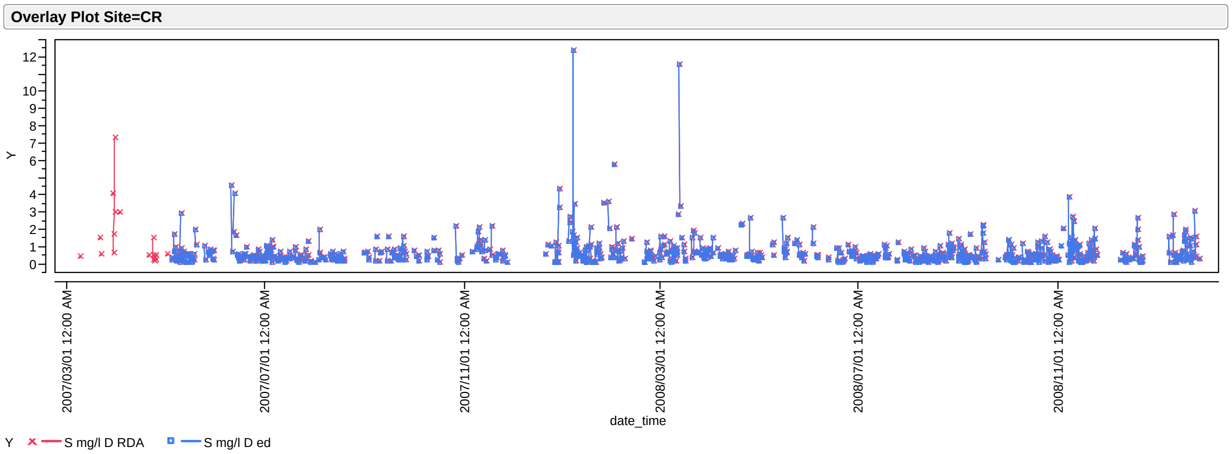
Al: Just a few aluminum flyers were culled (and the flip of Trips 80 and 81 is evident in the UHF time series).

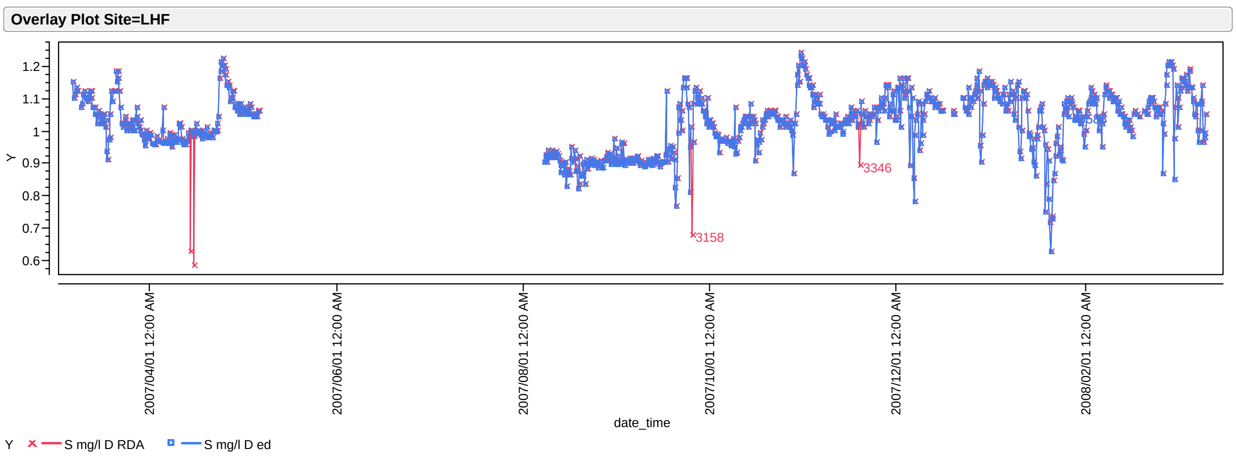


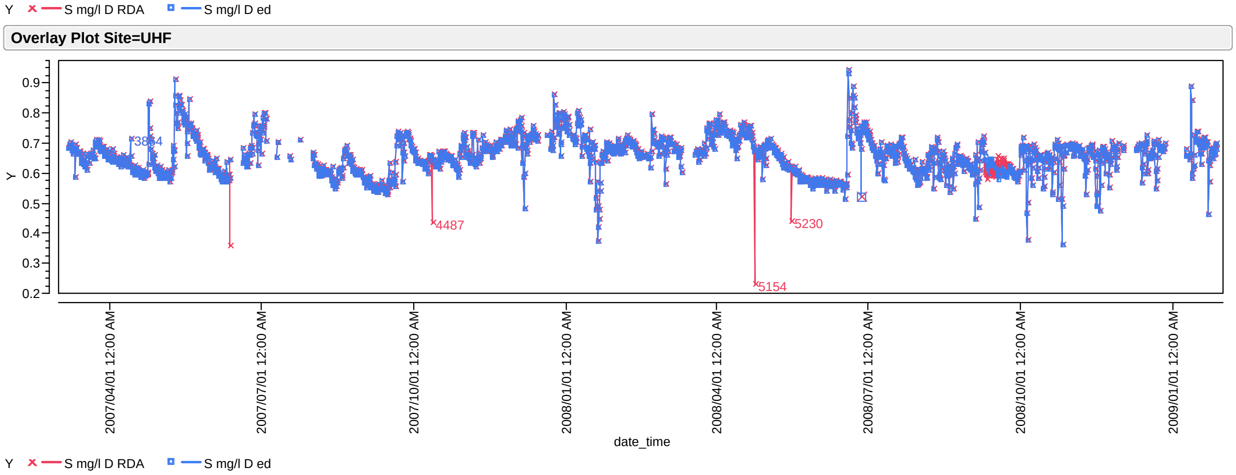




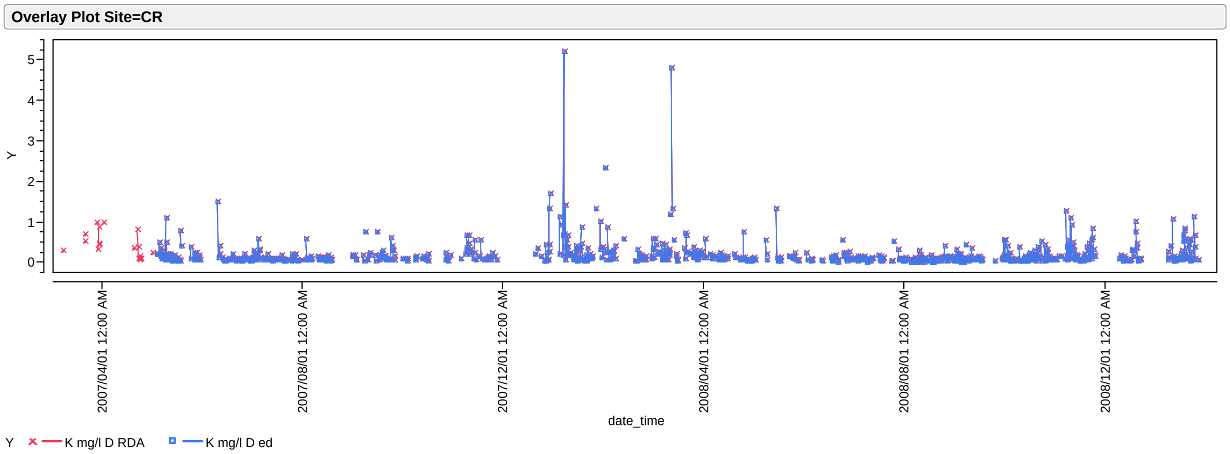
Si: Just a few silicon drop-outs were culled from the stream time series. We did not edit the precipitation Si values at all; the concentrations are tiny and thus noisy, with evident background correction "baseline" problems (for example, the step increase in the lower bound of measured values in September 2008).

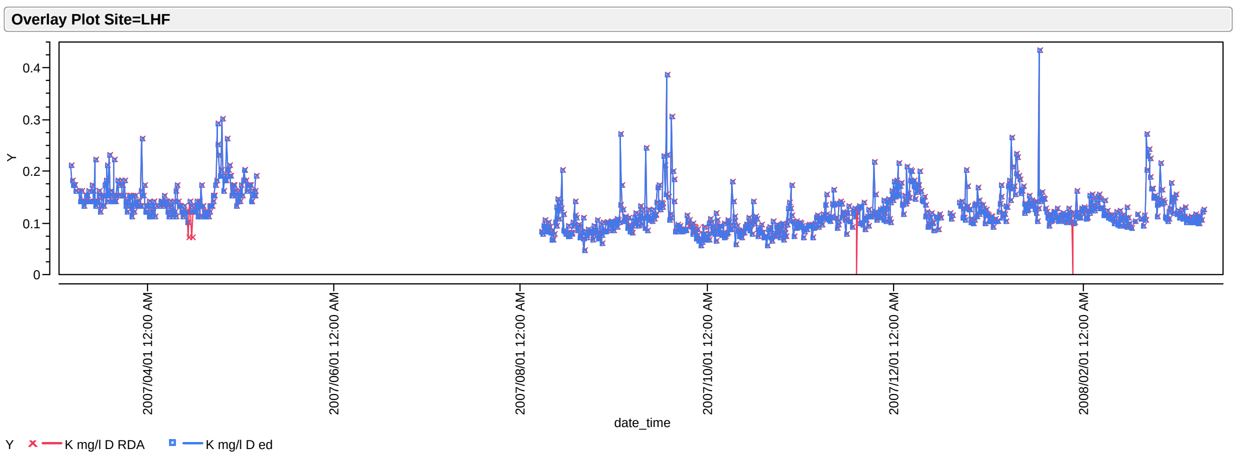


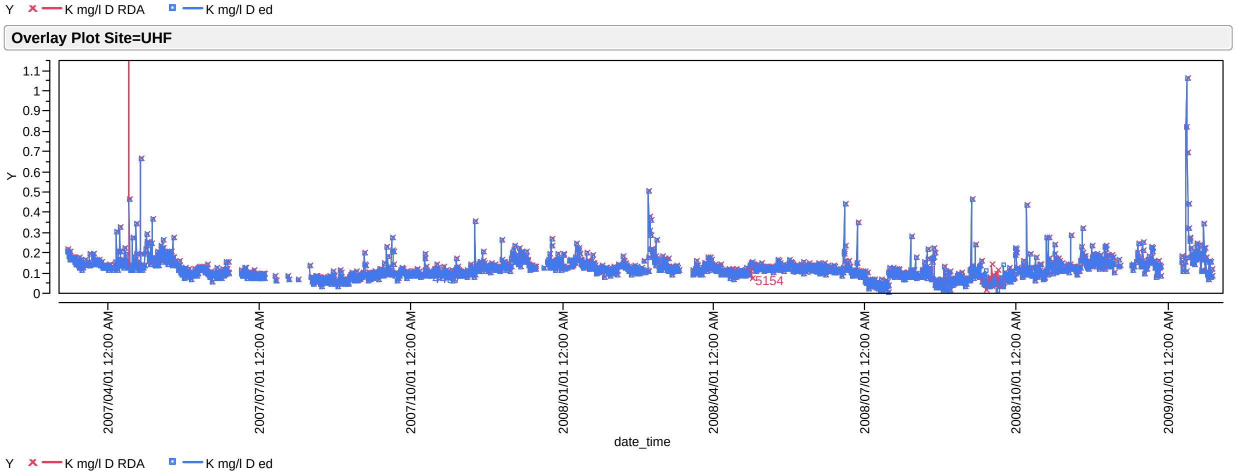




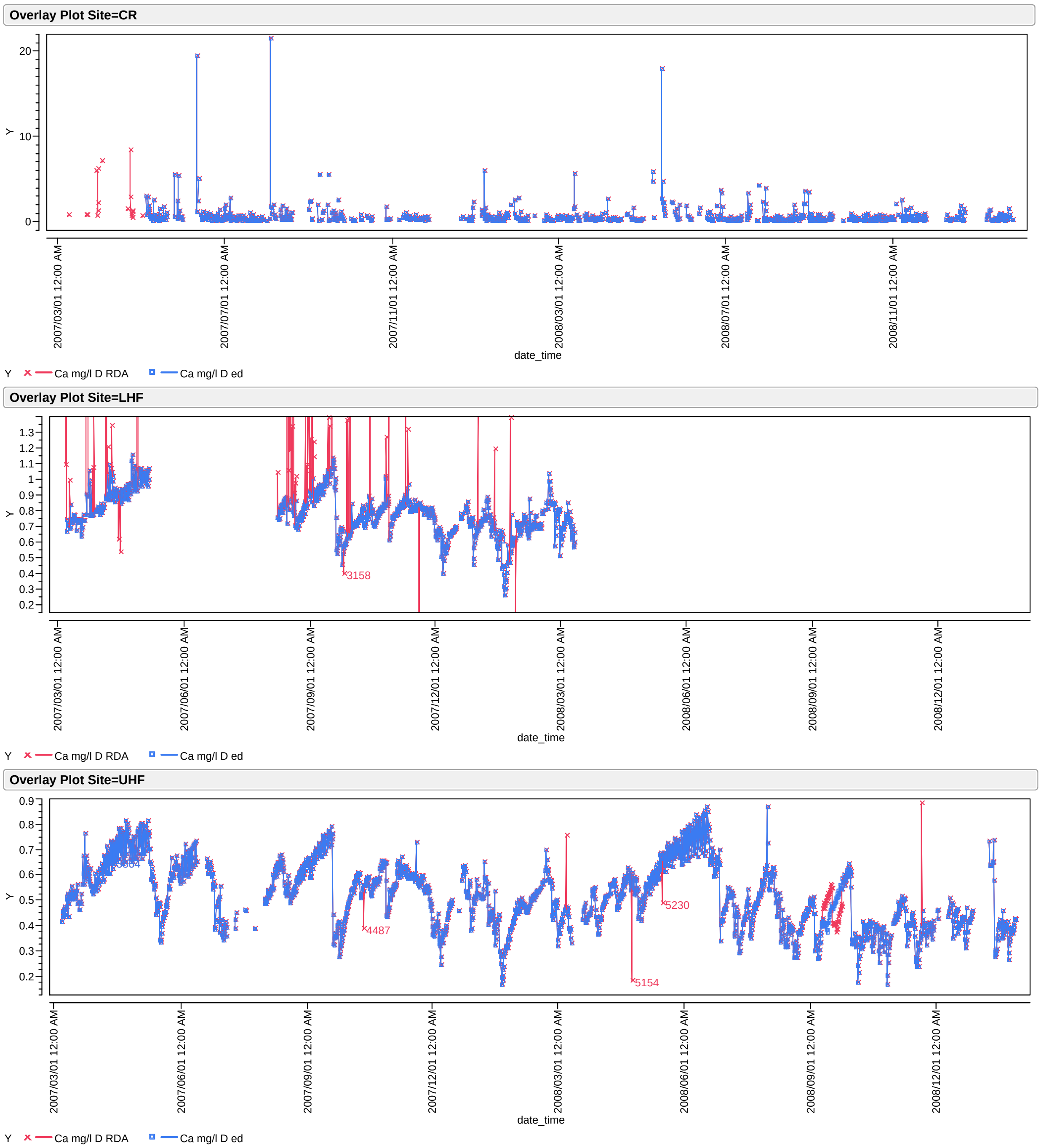
S: A few anomalously low sulfur values were culled where they were not matched by similar extremes in SO_4 as measured by ion chromatography. One exception is CR1051, in which there is a flyer in SO4_by_ICP that is well matched by flyers in Cl, Mg, and conductivity and therefore has been retained.



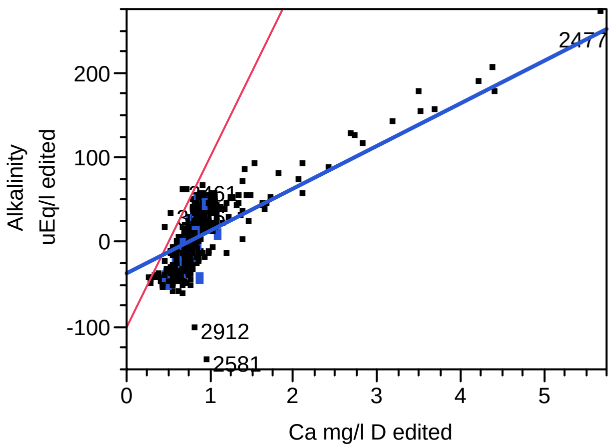




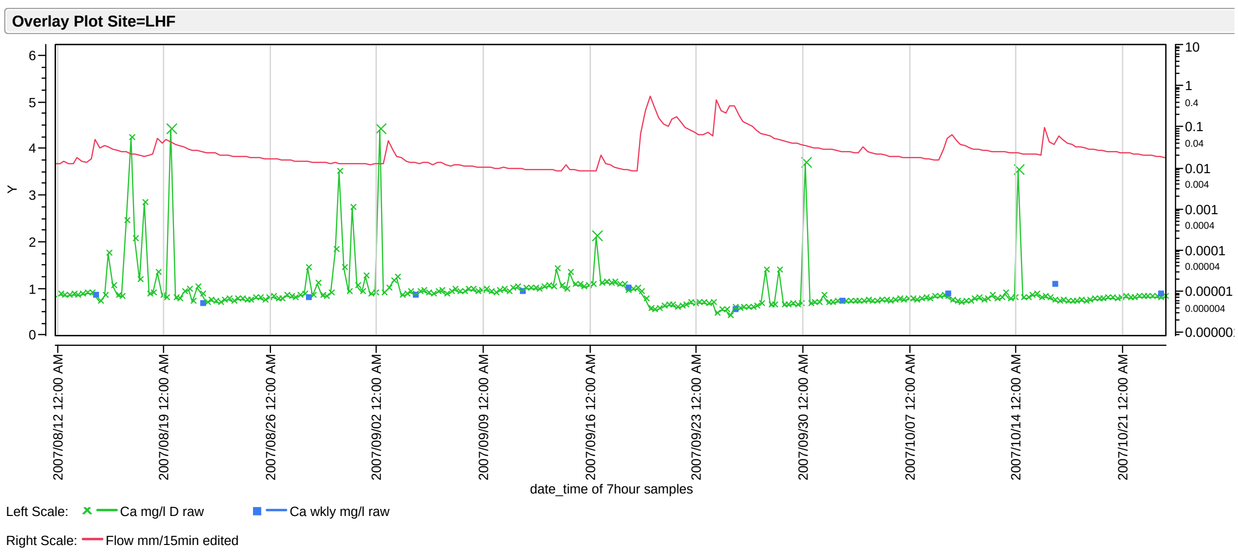
K: A few potassium flyers were culled. Many others were kept because they correspond to flow peaks, and/or because they are mirrored in Rb.



Ca: Multiple flyers in calcium at LHF were culled. These are correlated with spikes in Gran alkalinity and pH, and therefore do not plausibly arise from analytical issues, but they are not correlated with other analytes that typically correlate with Ca. The correlation between Ca and Gran alkalinity falls along a line corresponding to $CaCO_3$ (the blue line in the plot below), following a different trend than the rest of the data. Likewise the relationship between Ca and Sr in these spikes differs markedly from the rest of the data.

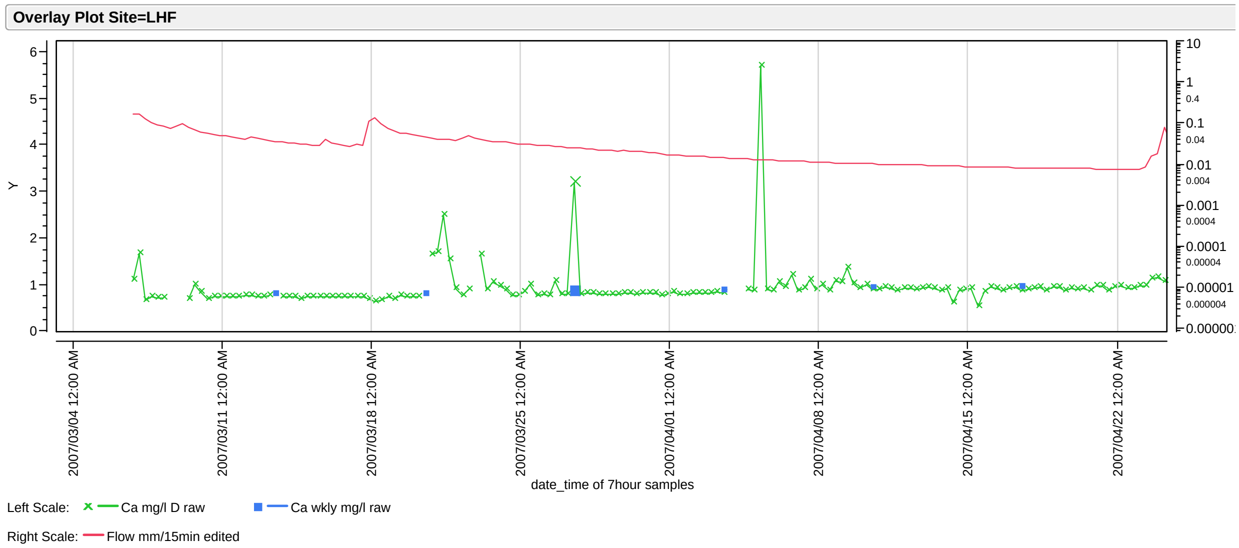


Note also that the flyers have an unusual temporal pattern. Many of the largest spikes occur at 4AM on Sunday, or in one case at 11AM on Sunday -- note the large X's in the plot below (the gridlines are midnight between Saturday and Sunday):

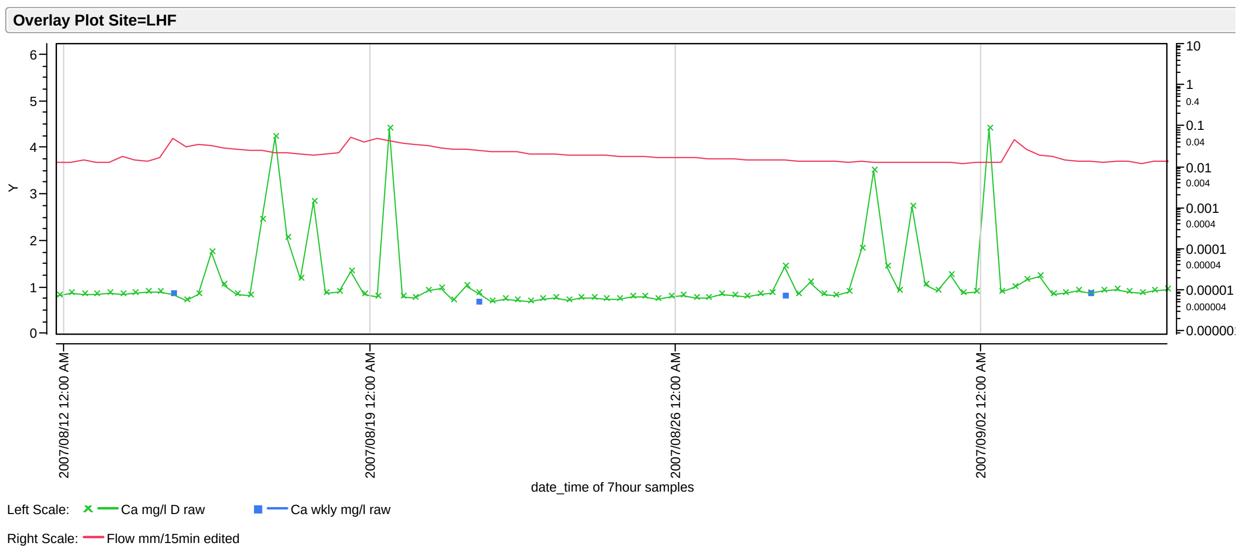


Note further that the spikes occur exactly every two weeks, suggesting that the cause is carryover contamination in one of the two sample carousels.

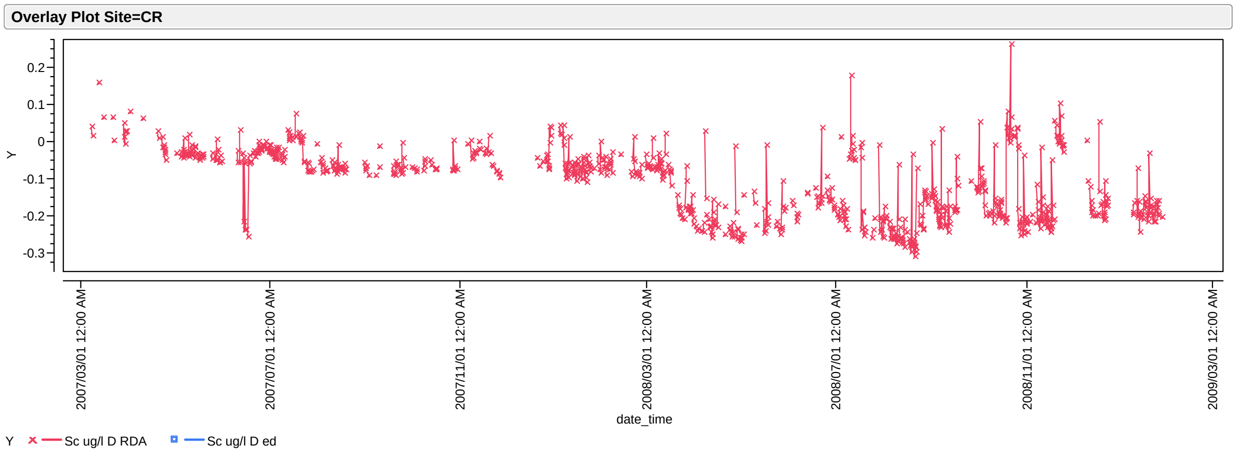
Similar spikes do not occur in the weekly data (the blue dots in the plot above above), even when the weekly samples are collected almost simultaneously. For example, in the highlighted sample below, the 7-hourly sample (collected at 12 Noon) has a value of 3.19 mg/l whereas the weekly sample (collected at 12:40 PM) has a value of 0.83 mg/L:

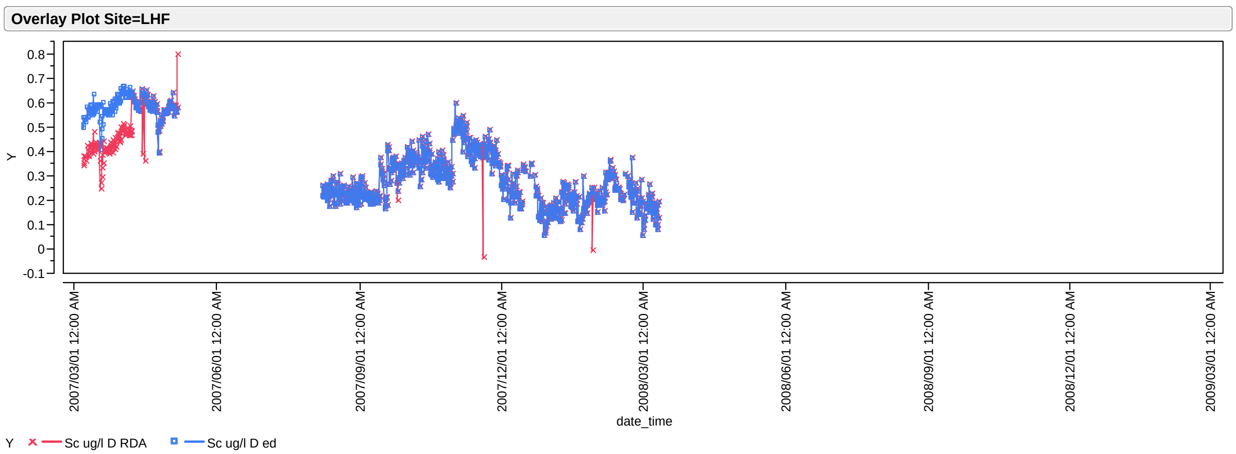


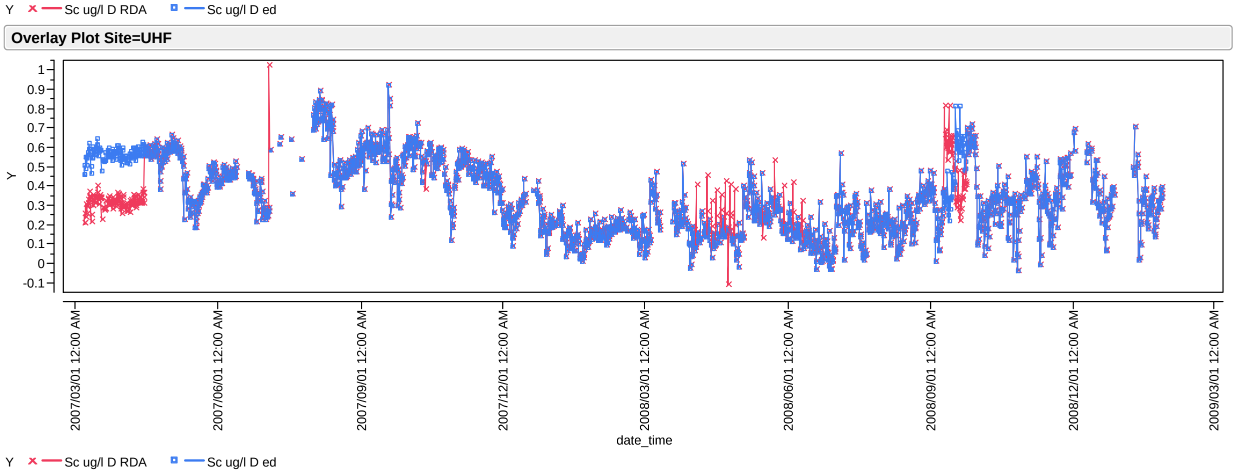
We believe that these spikes are most plausibly attributed to contamination in one of the two sample carousels used at LHF. This view is supported by the repeating pattern that occurs in the middle of August 2007, and again two weeks later at the end of August (see the figure below).



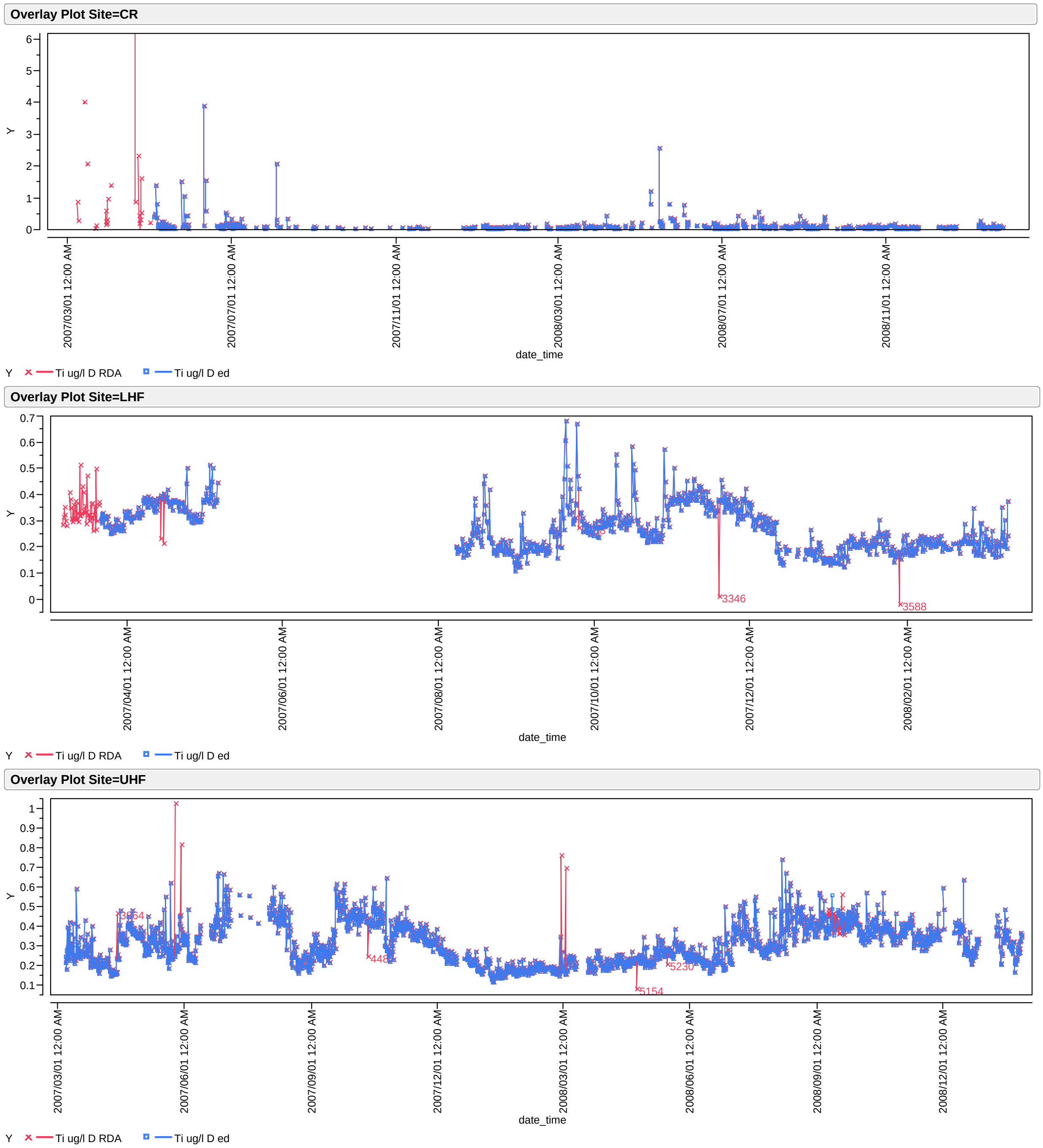
On this basis we have culled these spikes from the edited data. Users should be aware that high-alkalinity groundwaters do occur in the Plynlimon catchment (Neal, C., A.J. Robson, P. Shand, W.M. Edmunds, A.J. Dixon, D.K. Buckley, S. Hill, M. Harrow, M. Neal, J. Wilkinson, and B. Reynolds, The occurrence of groundwater in the Lower Paleozoic rocks of upland Central Wales, Hydrology and Earth System Sciences 1, 3-18, 1997), and intermittent high values of Ca and alkalinity could conceivably arise due to discharge of chalky groundwaters from the gravels in the streambed. However, we believe that the occurrence of the spikes in a repeating pattern every other week makes this explanation implausible.



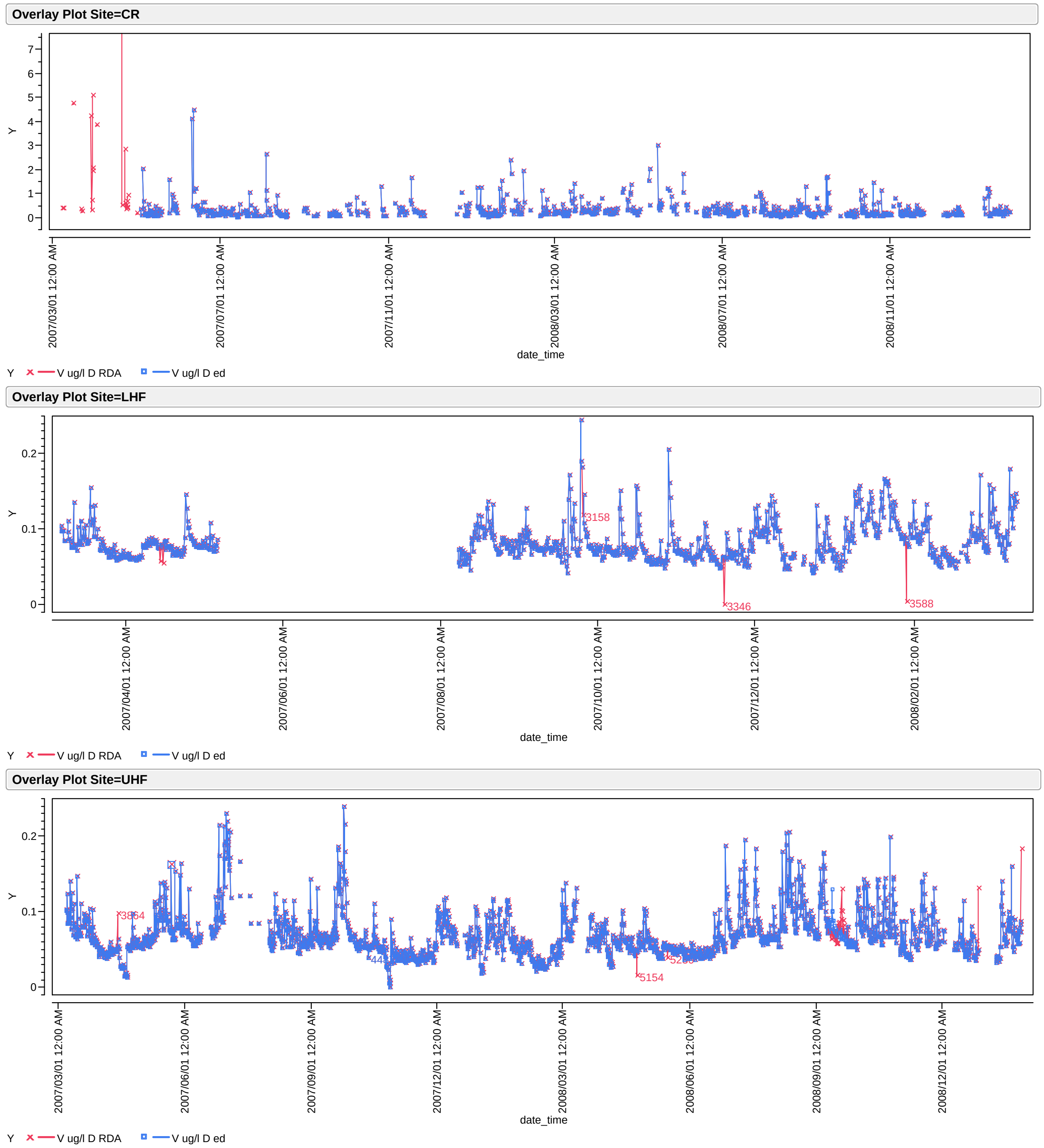




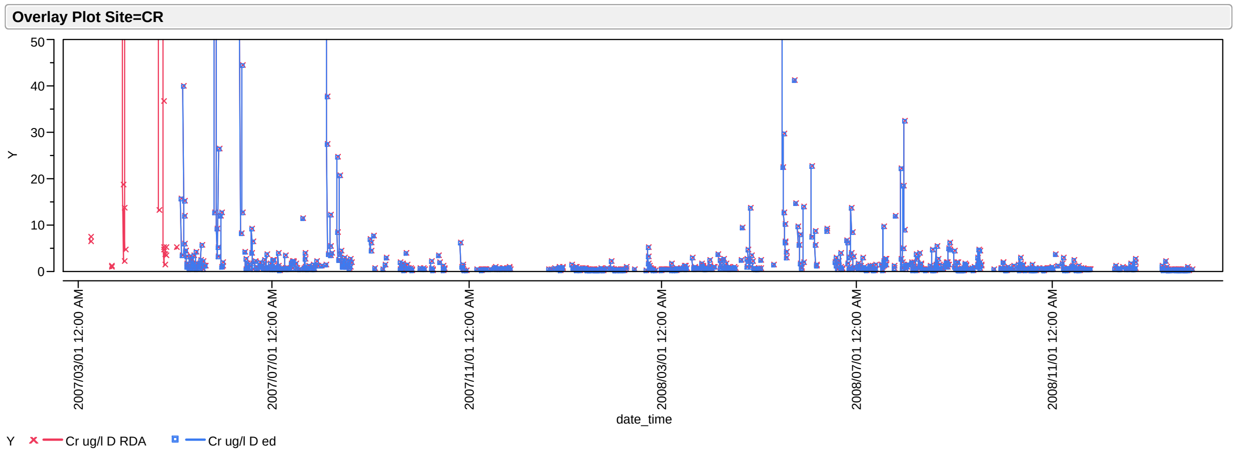
Sc: We culled the repeating "picket fence" of high scandium values at UHF resulting from carryover from the check standards. There are also obvious steps at LHF107 and UHF134, corresponding to the boundaries between analytical blocks (blocks EE196-EE197 at UHF, and EE210-EE211 at LHF). These are not simultaneous; they correspond to a one-week difference in sampling dates. We eliminated these steps by applying an ad hoc shift of 0.16 ug/L (LHF) and 0.25 ug/L (UHF) to Sc values before LHF107 and UHF134. All precipitation Sc values have been culled because of obvious calibration issues.

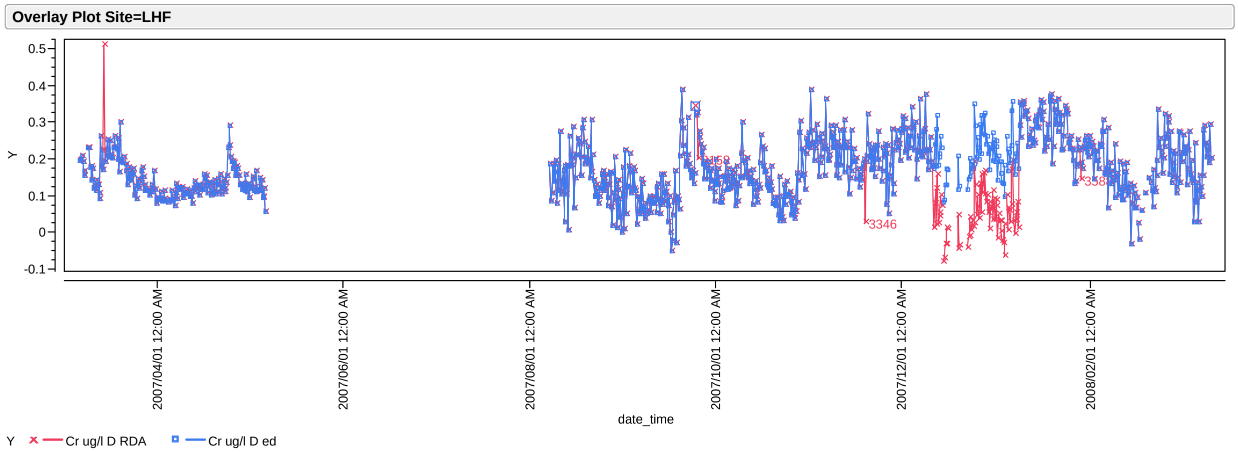


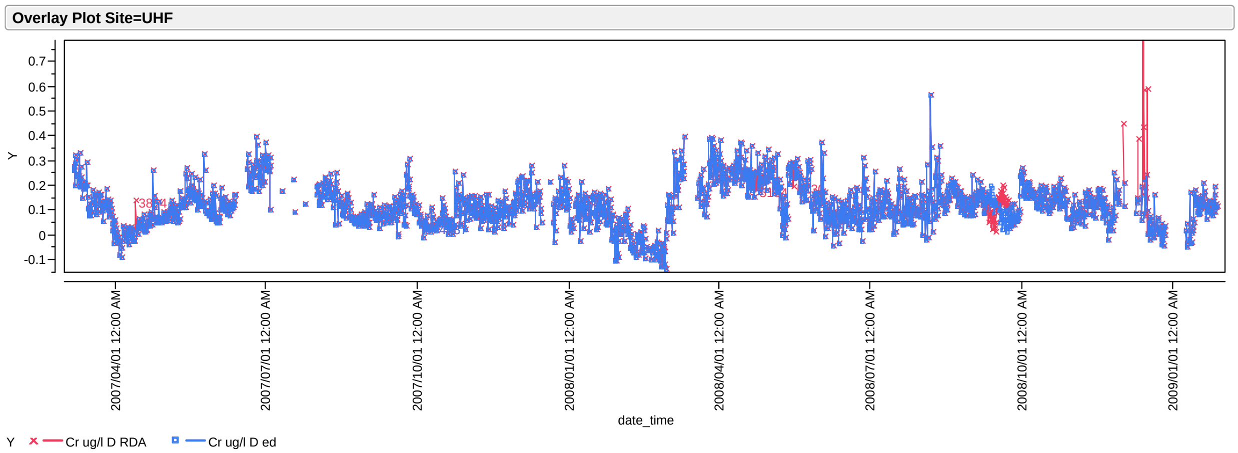
Ti: Several titanium flyers and drop-outs were culled, where they were inconsistent with correlations with As and DOC.



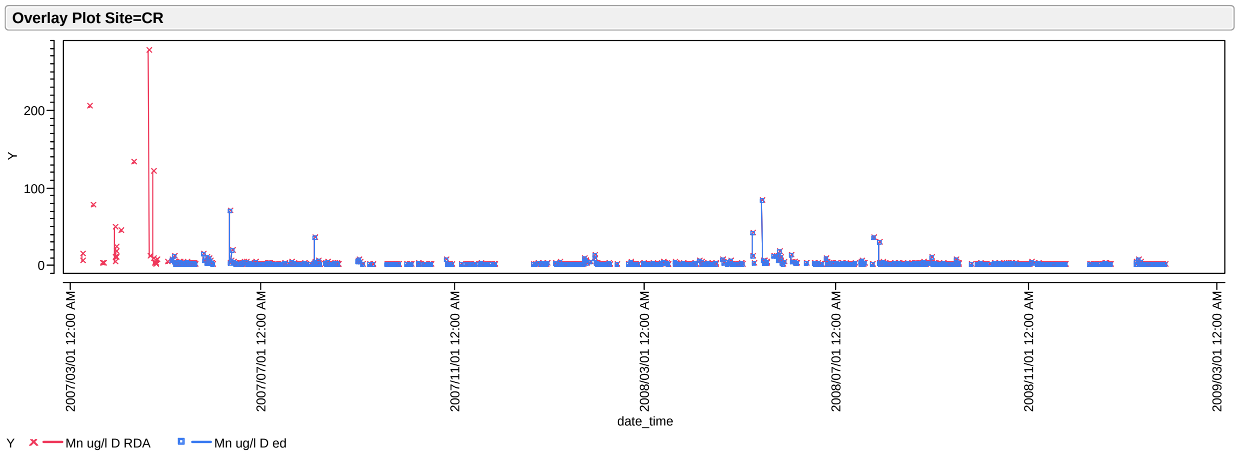
V: Several vanadium flyers were culled; other spikes, which were correlated with spikes in Al, Fe, and La, were not culled.

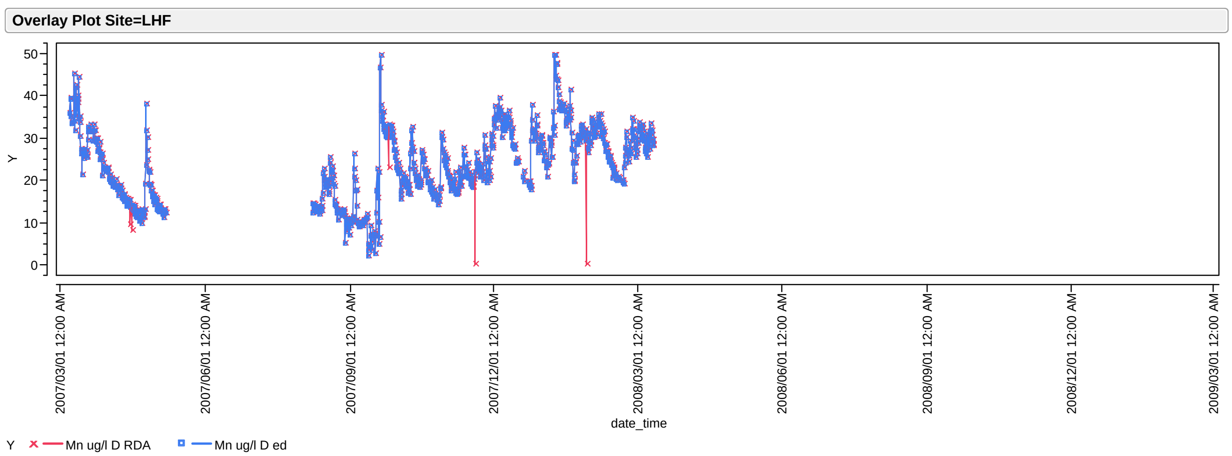


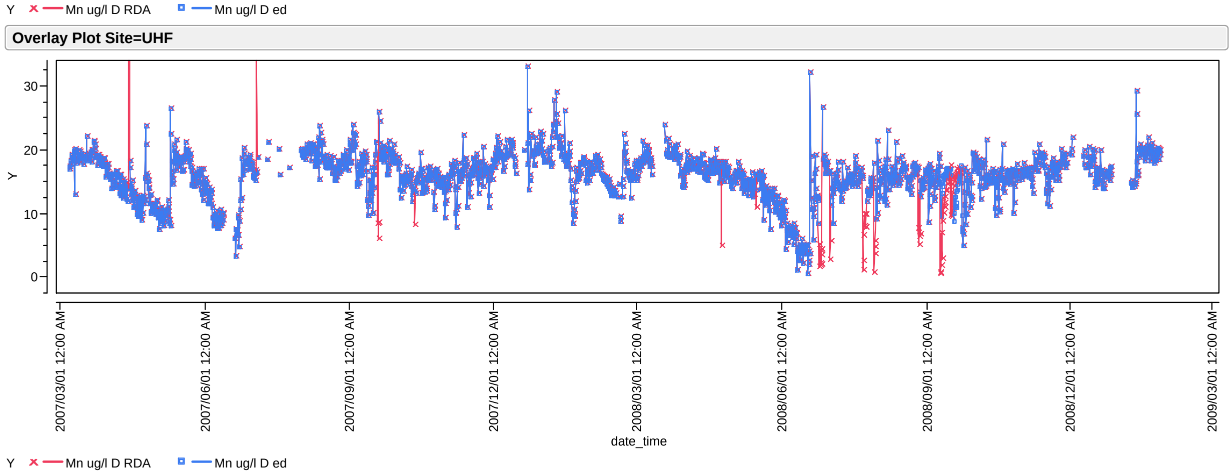




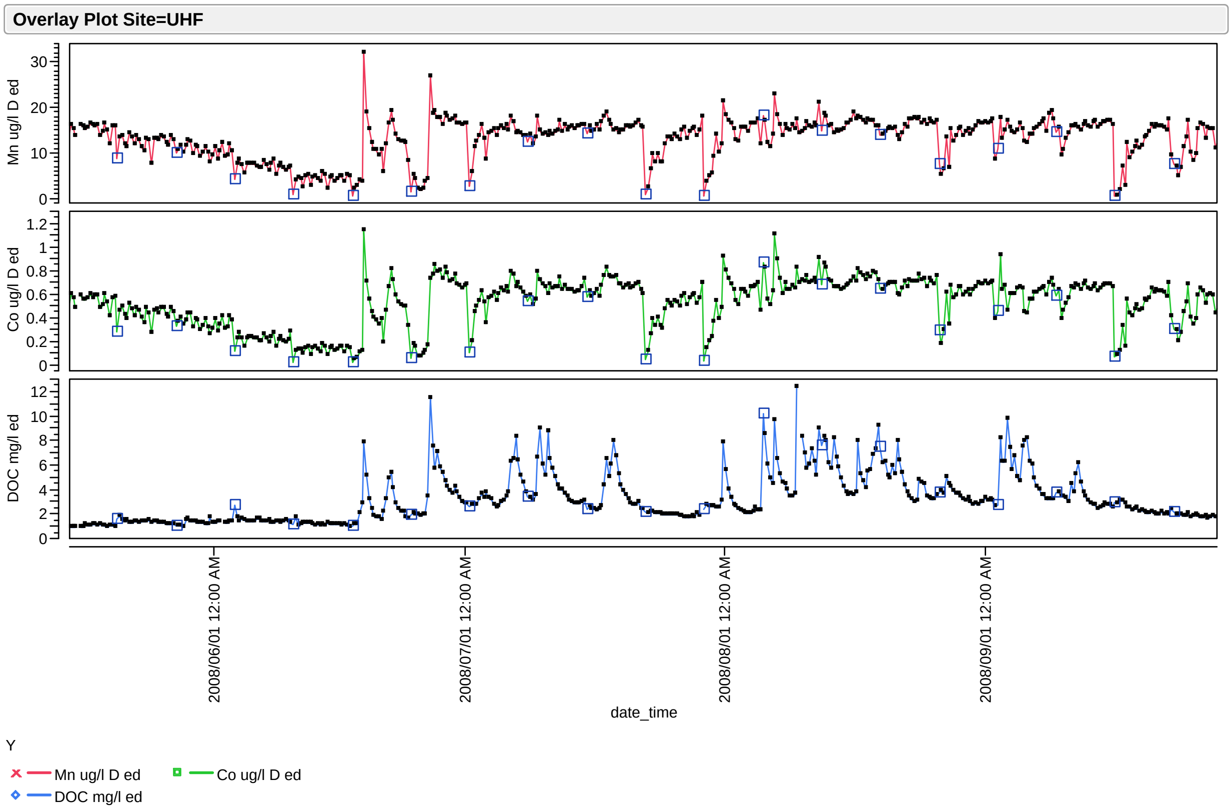
Cr: Chromium is problematic; the data are rather noisy at fine time scales, and there are evident background correction issues in some analytical blocks. In one case at LHF this has been handled with a constant offset of 0.16 ug/L. Several flyers were also culled.



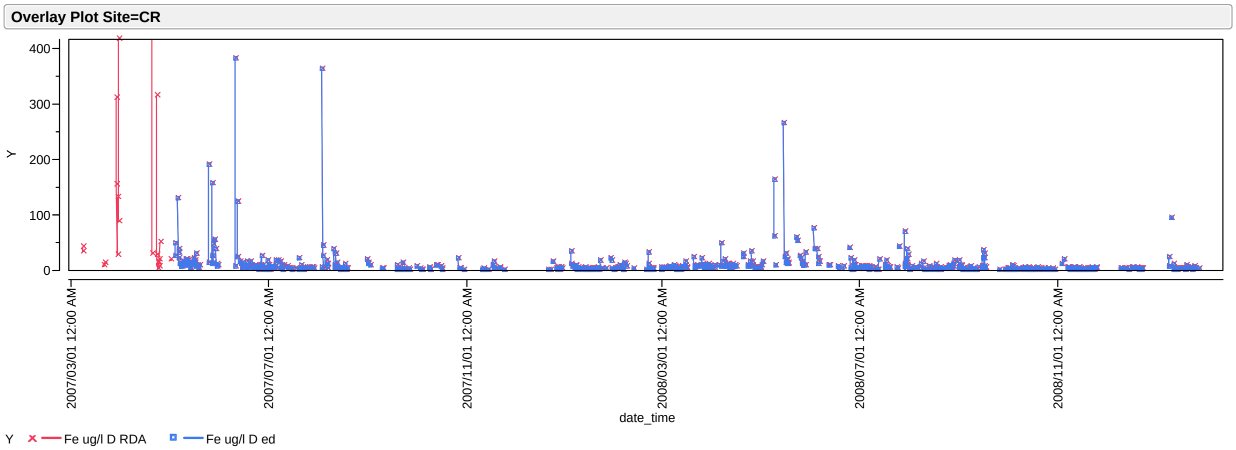


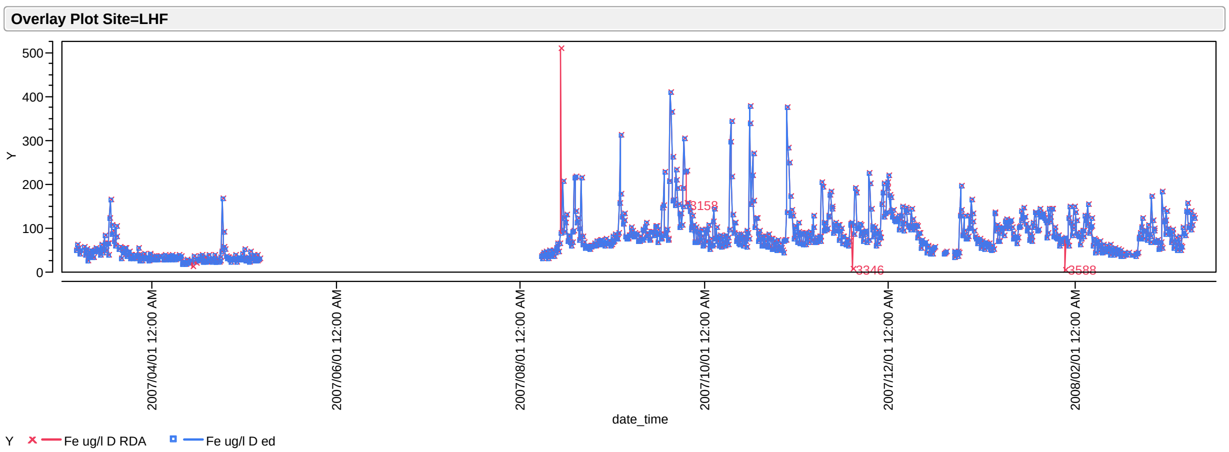


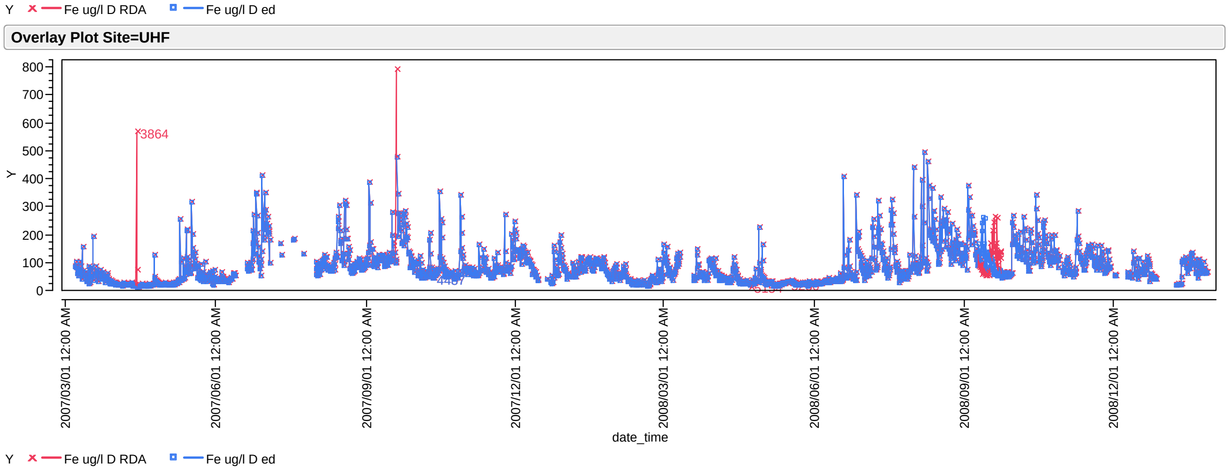
Mn: Note that manganese is more variable (and has less short-term noise) at LHF compared to UHF. The same is true for Co, with which Mn is strongly correlated. Both Mn and Co are problematic in the summer of 2008 at UHF, with unusually low values at the beginning of several analytical blocks. The figure below illustrates the issue (the big blue squares denote the beginning of each analytical block). It is unknown whether this arises from an analytical issue, or from a storage effect in the autosampler bottles, which for some reason is most evident in the summer/fall and which is more evident at UHF than at LHF. To minimize the effects of this issue, we have culled the early values of both Mn and Co in the affected blocks.



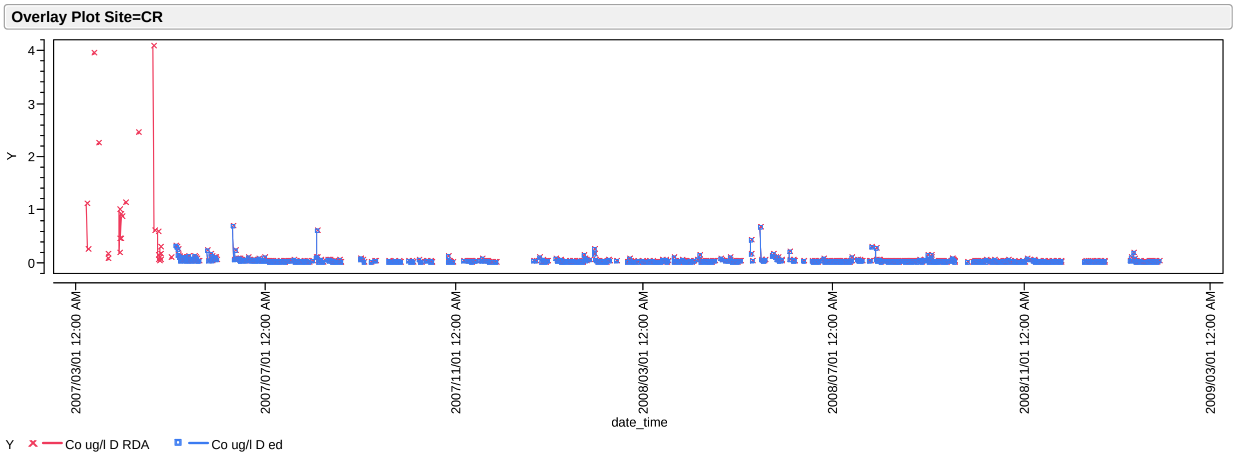
Overlay Plot Site=UHF
Mn ug/l D ed
Co ug/l D ed
DOC mg/l ed
0
10
20
30
0
0.2
0.4
0.6
0.8
1
1.2
0
2
4
6
8
10
12
2008/06/01 12:00 AM
2008/07/01 12:00 AM
2008/08/01 12:00 AM
2008/09/01 12:00 AM
date_time
Y
Mn ug/l D ed
Co ug/l D ed
DOC mg/l ed

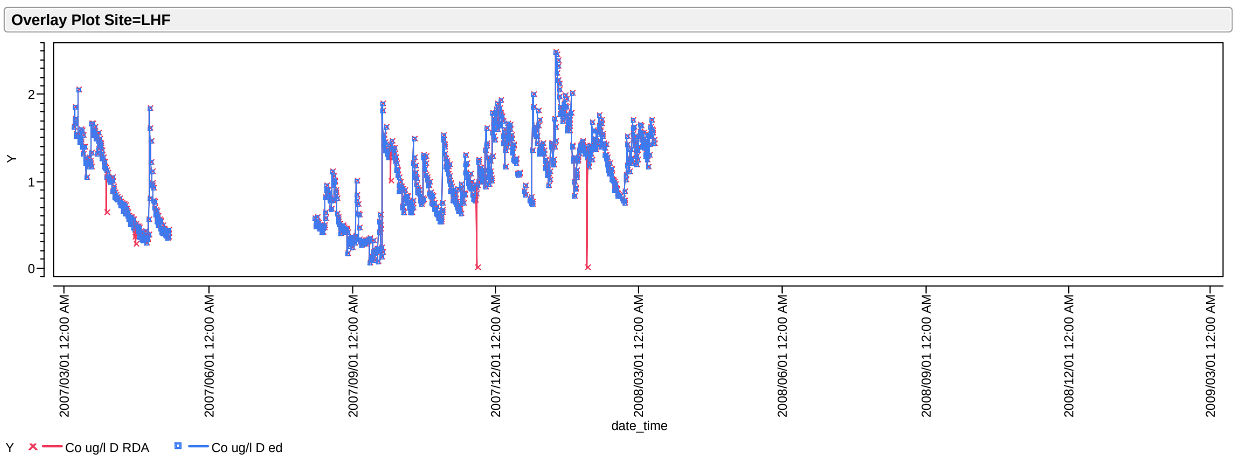


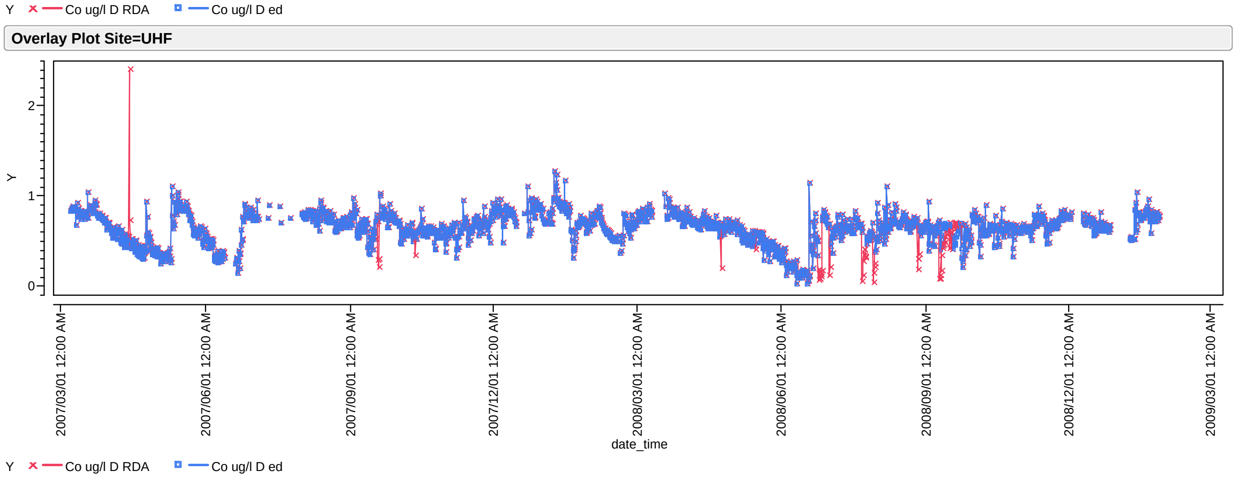




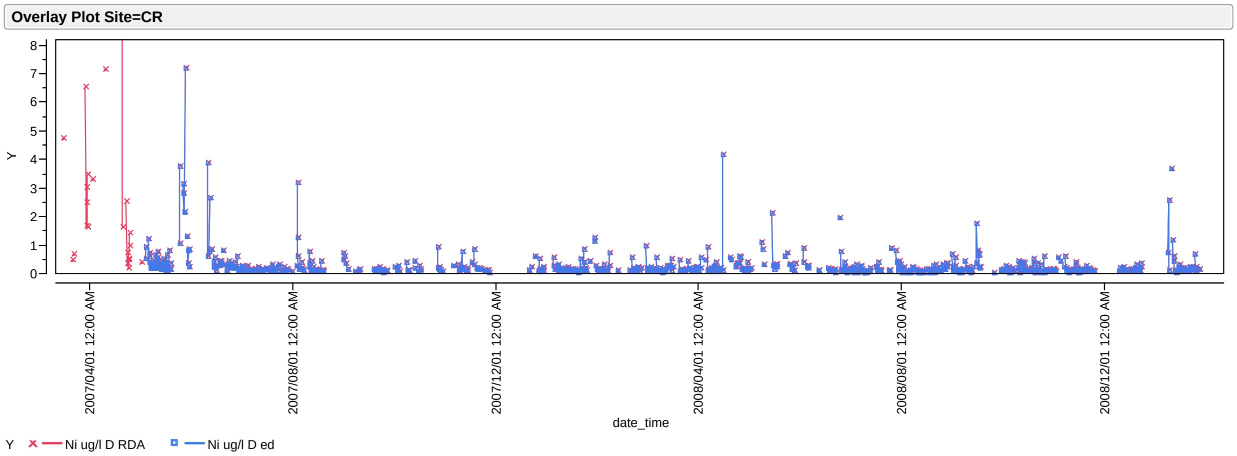
Fe: Just a few iron points were culled which were outliers from otherwise strong correlations between Fe and DOC, As, and the lanthanides.

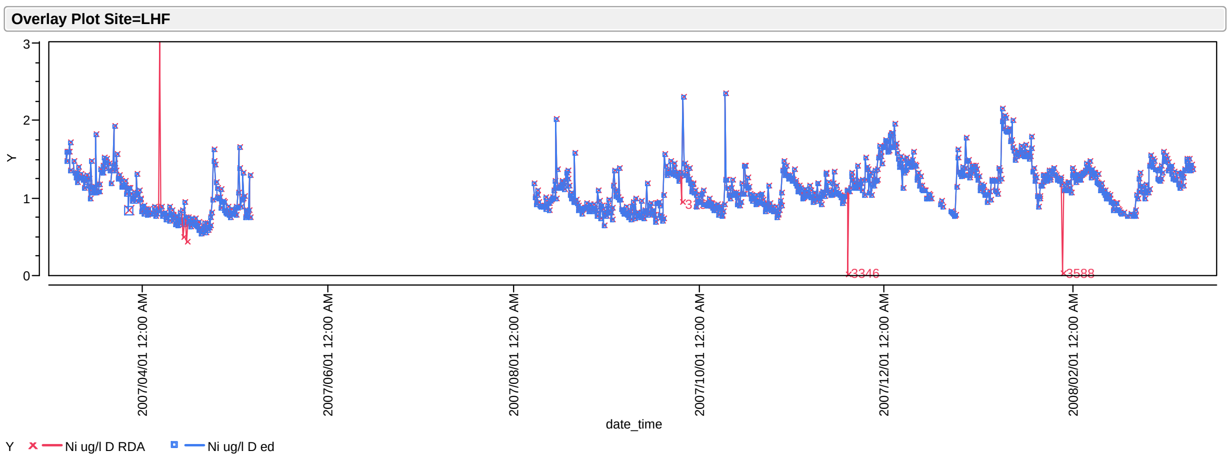


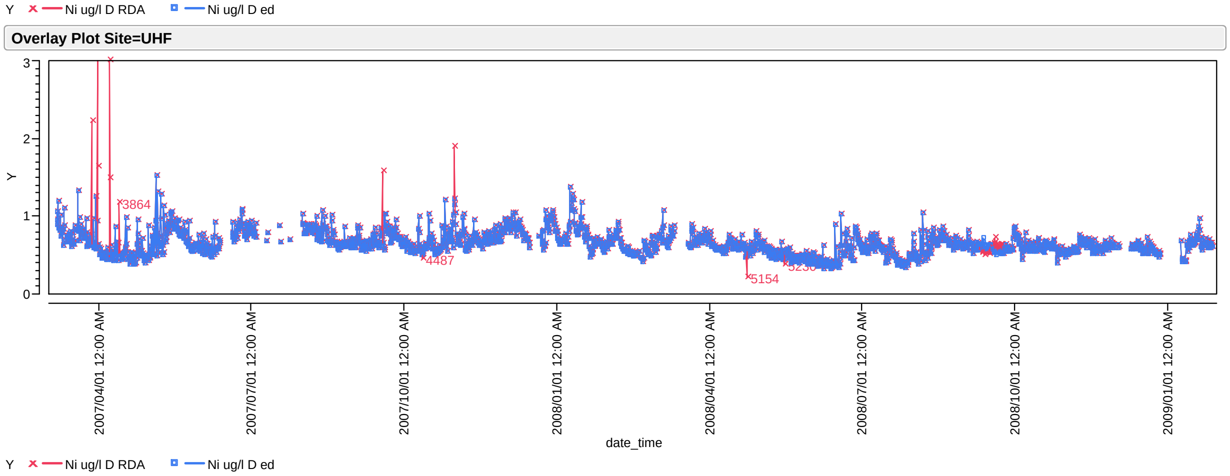




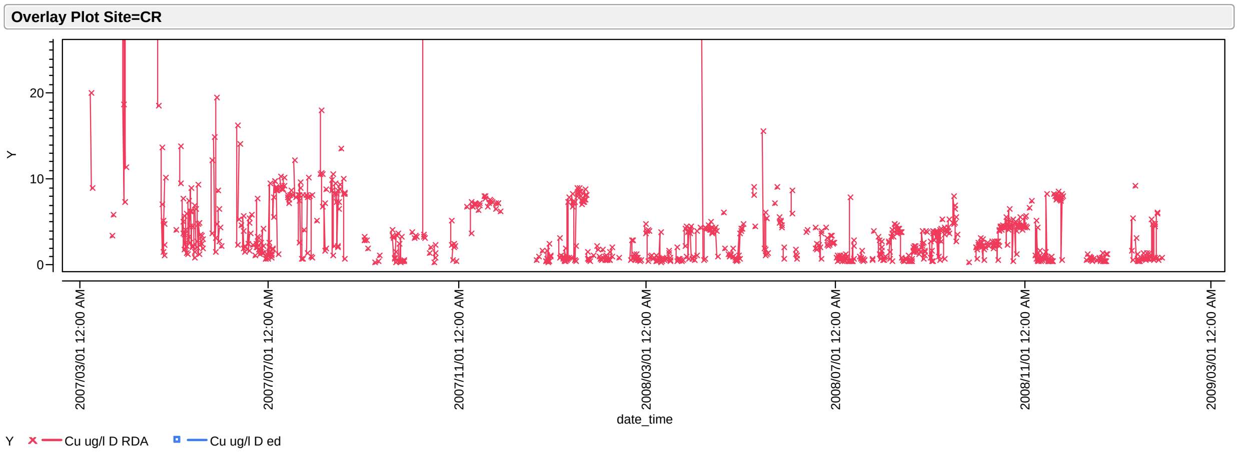
Co: As explained above for Mn, cobalt is problematic in the summer of 2008 at UHF, with unusually low values at the beginning of several analytical blocks. To minimize the effects of this issue, we have culled the early values of both Mn and Co in the affected blocks.

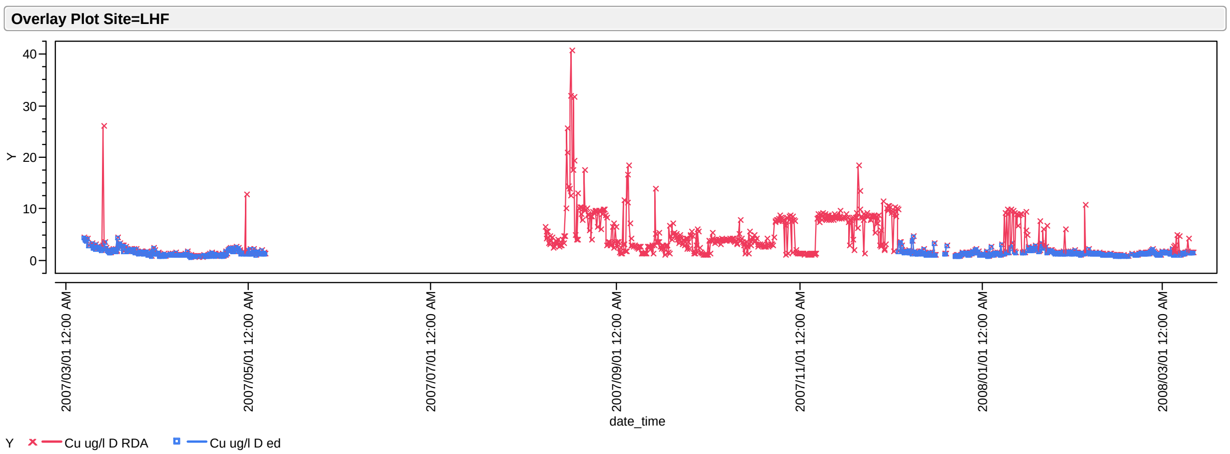


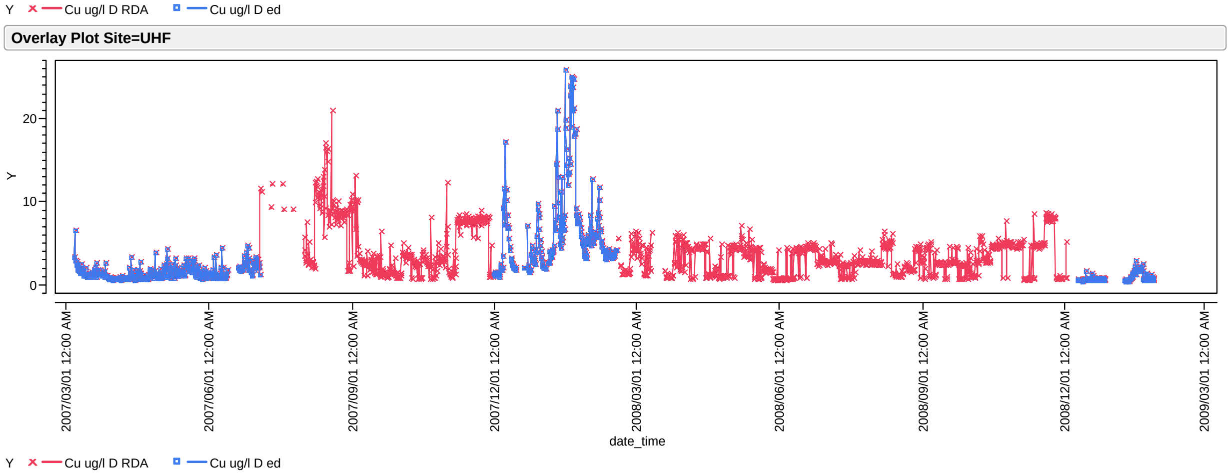




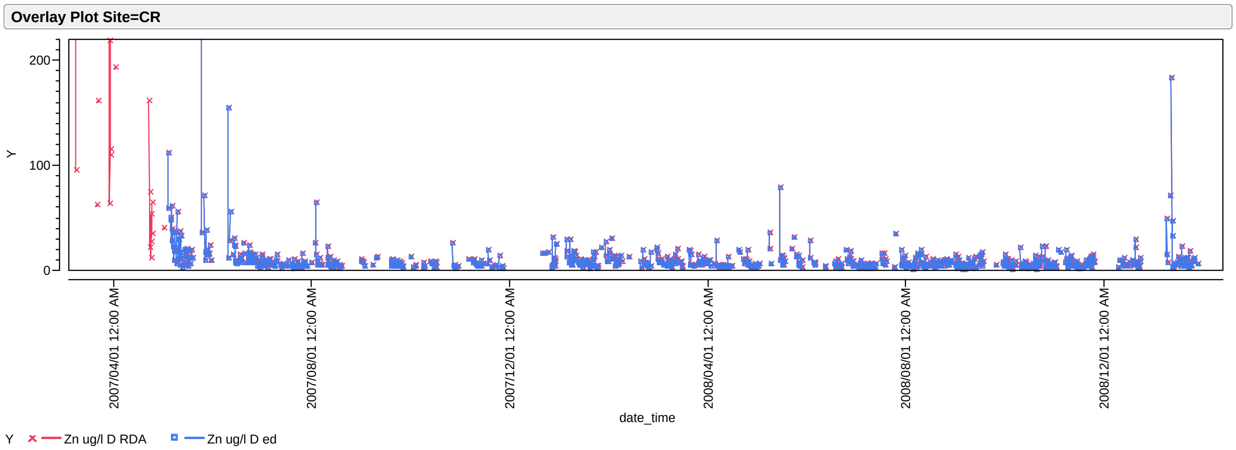
Ni: Several nickel flyers were culled, where they were inconsistent with correlations with Mn, Be, and Zn.

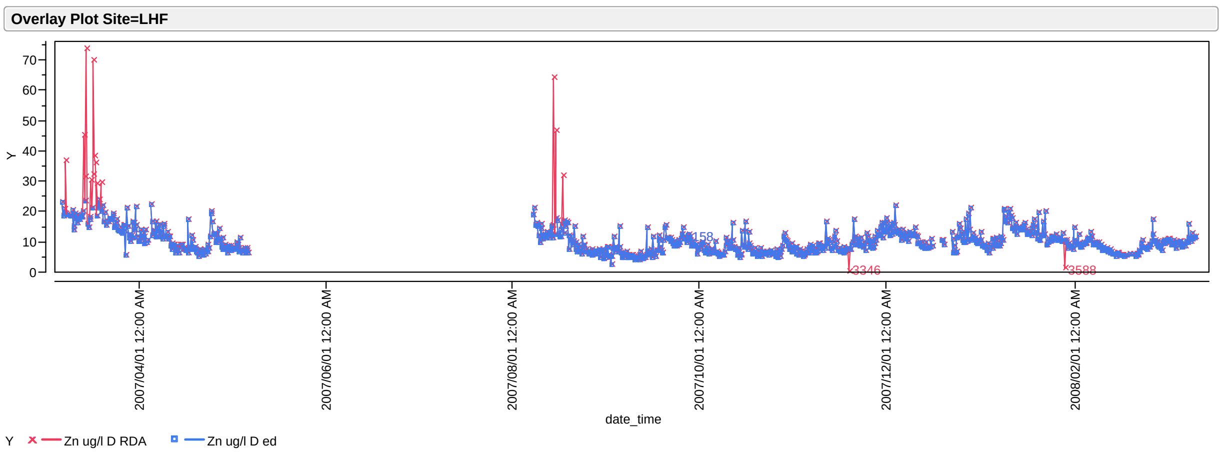


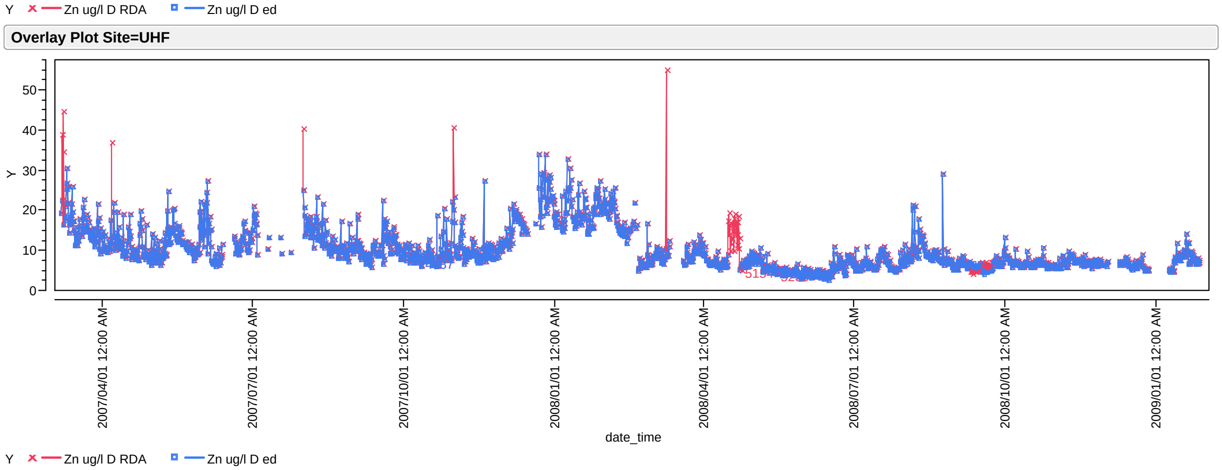




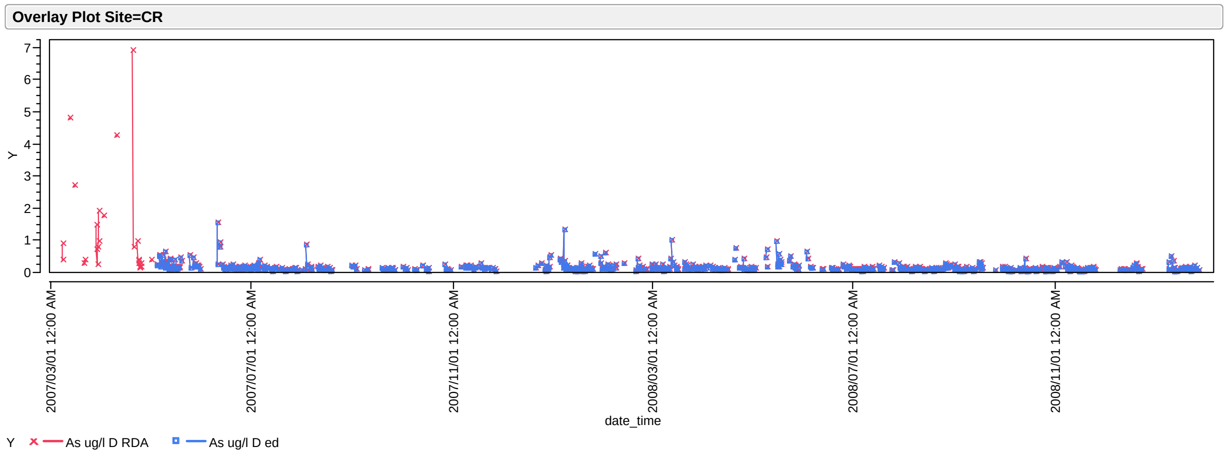
Cu: We have had to cull copper values from long stretches of the time series where calibration problems are evident. Cu analyses at CEH Lancaster are also known to be susceptible to laboratory contamination. We have culled the entire precipitation time series, because there are evident calibration problems throughout.

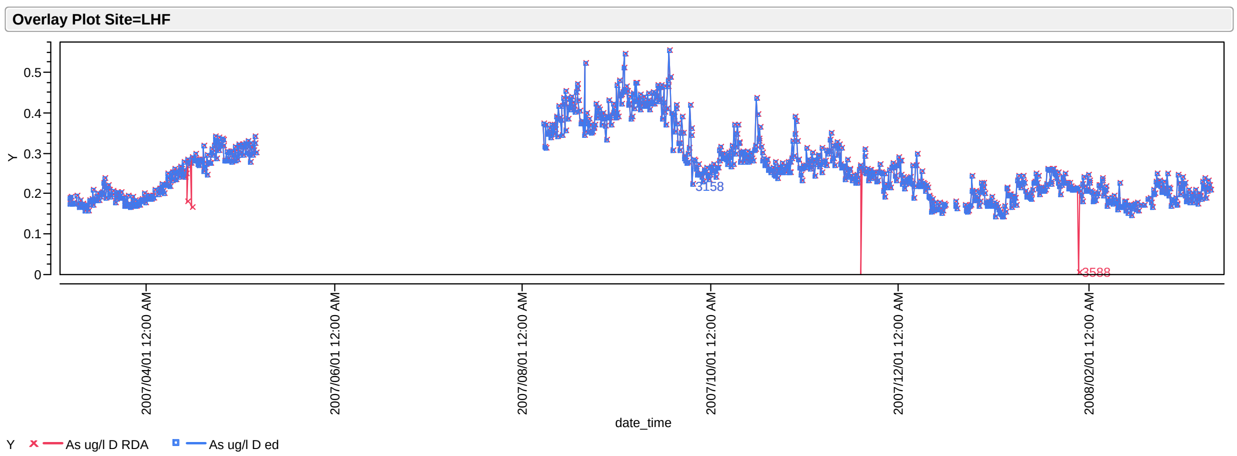


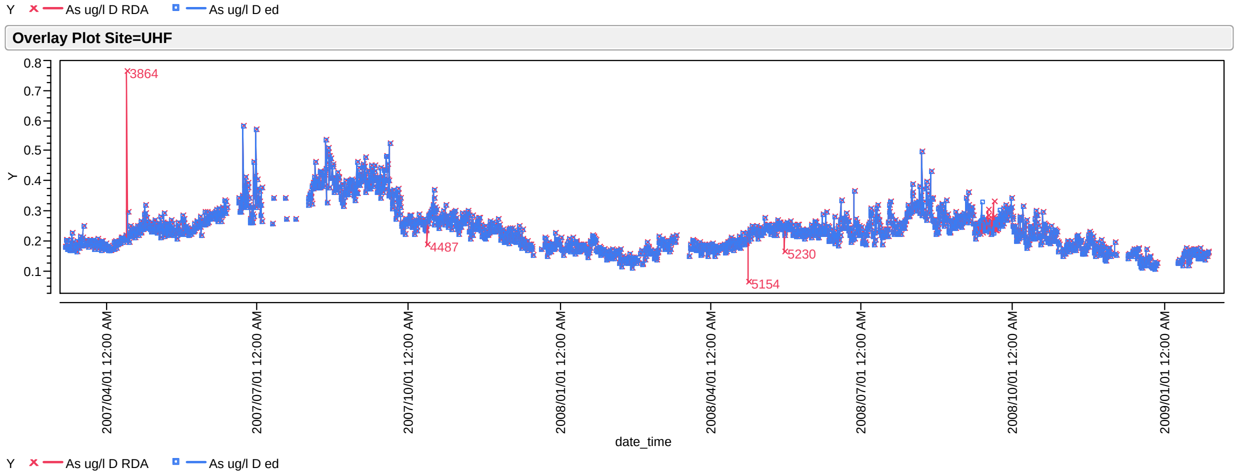




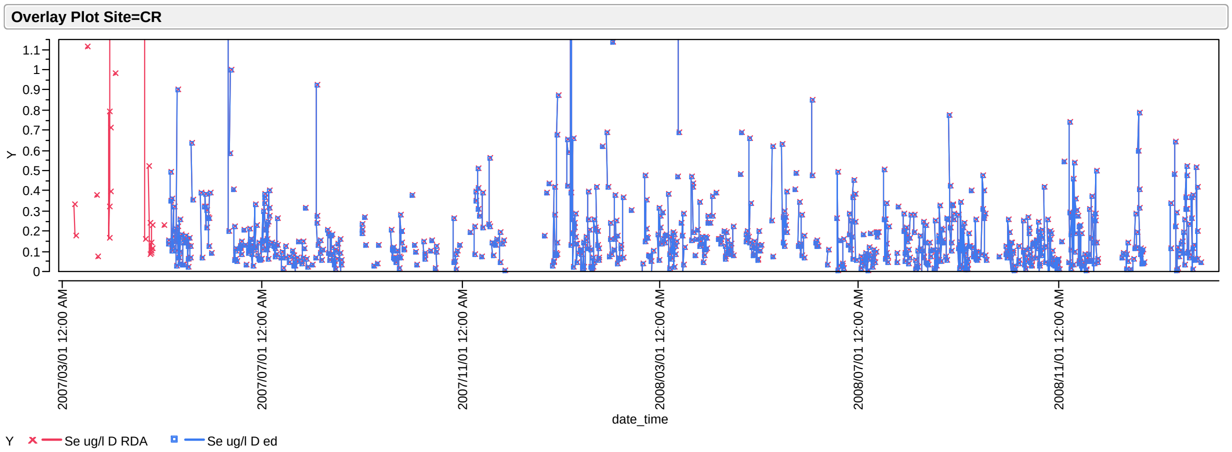
Zn: We have culled several zinc flyers, as well as an analytical block at UHF with obvious calibration problems.

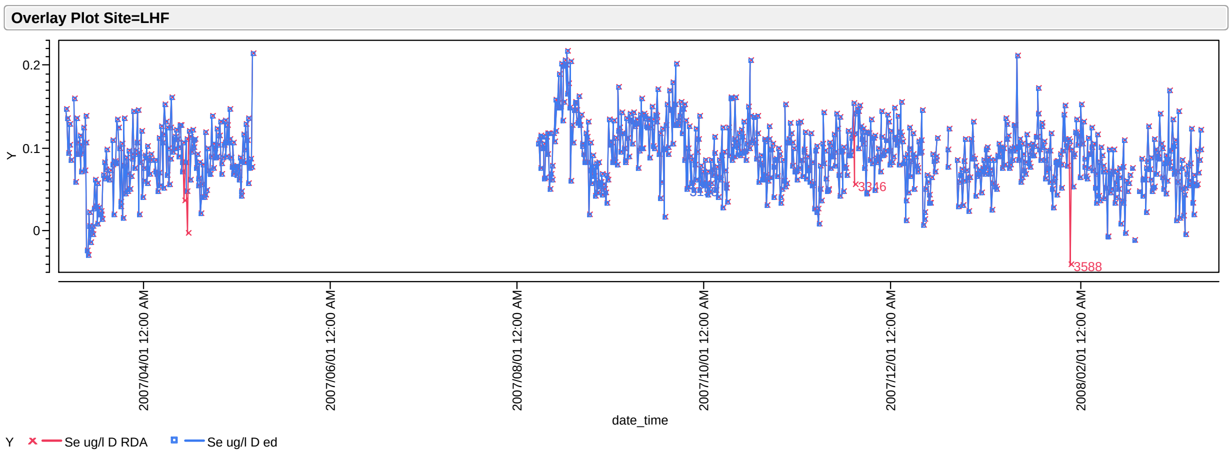


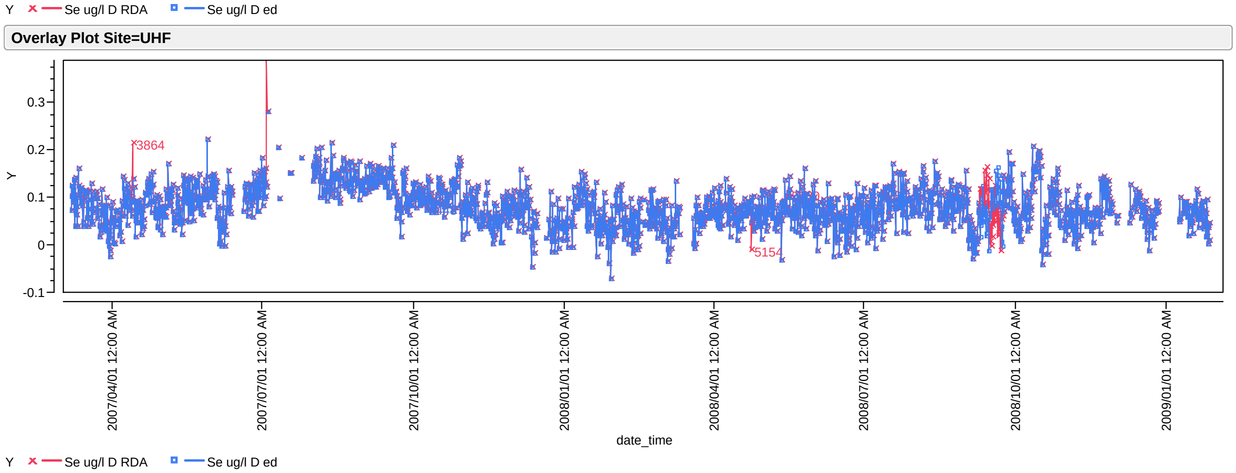




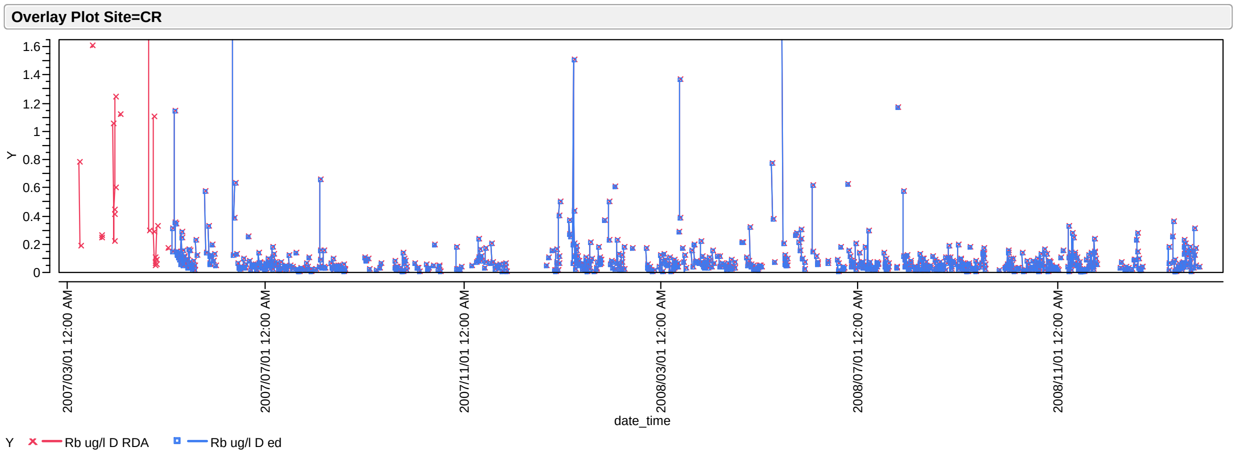
As: We have culled several anomalous values of arsenic, where these are not associated with similar extremes in Fe, V, or Sr.

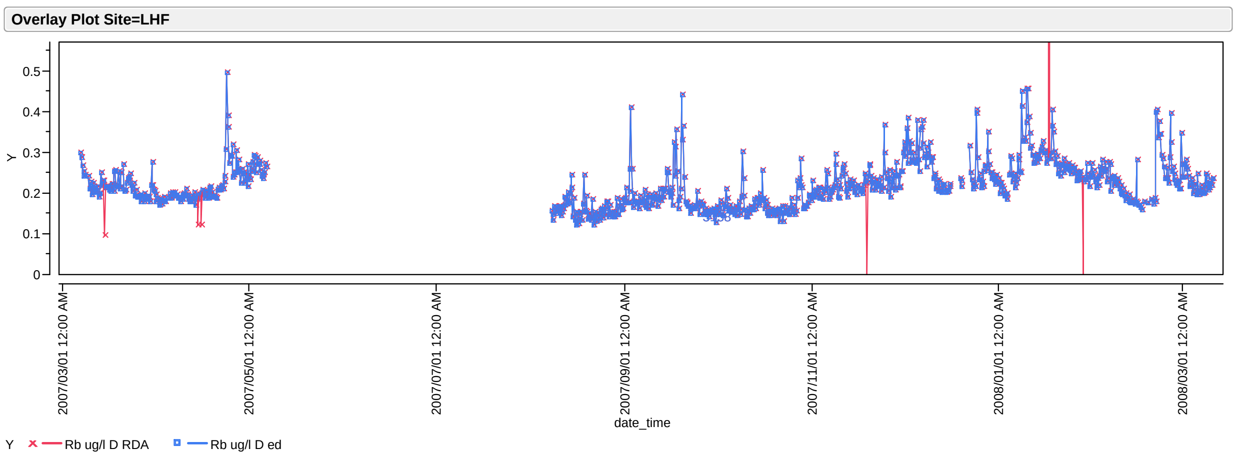


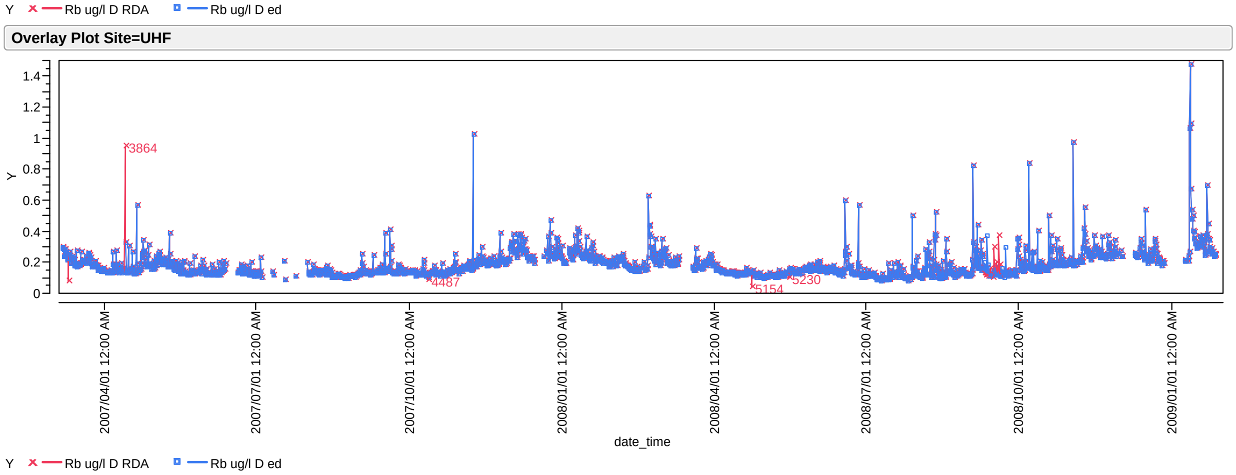




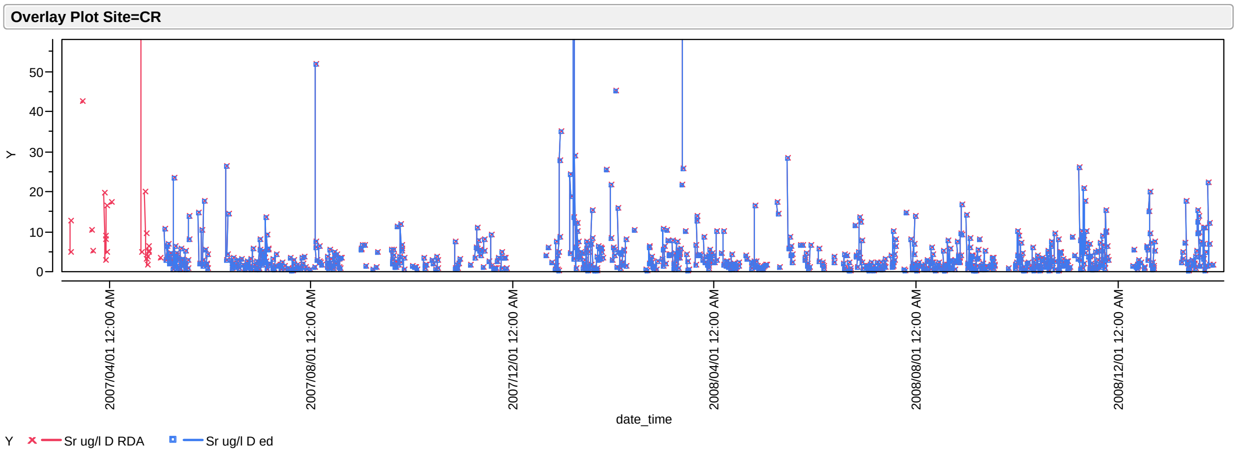
Se: Selenium is rather noisy, making identification of anomalous points tricky. We have not culled out values below zero, since these appear to arise from statistical fluctuations around a near-zero mean value, and do not correspond with individual analytical blocks (there does not appear to be an "offset" to correct for).

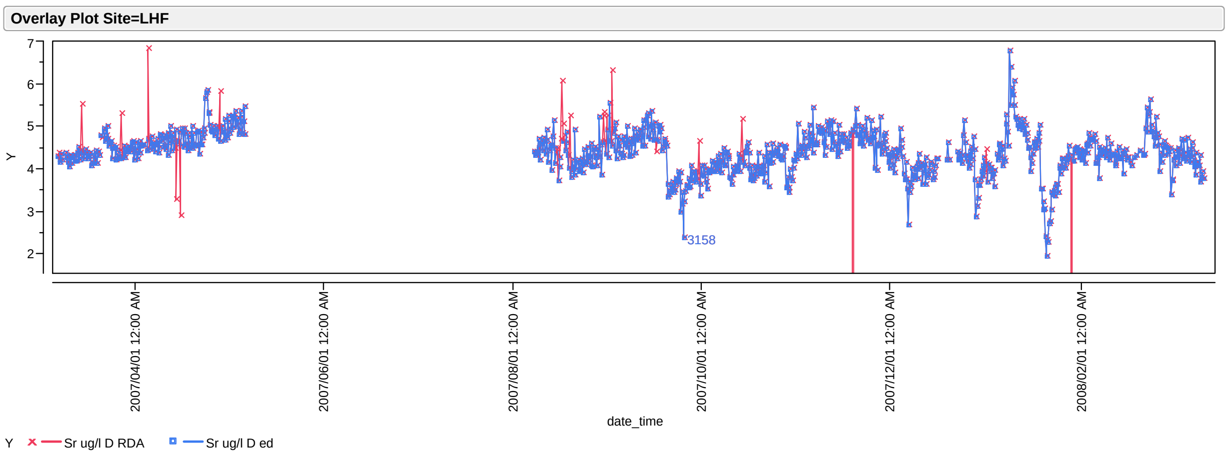


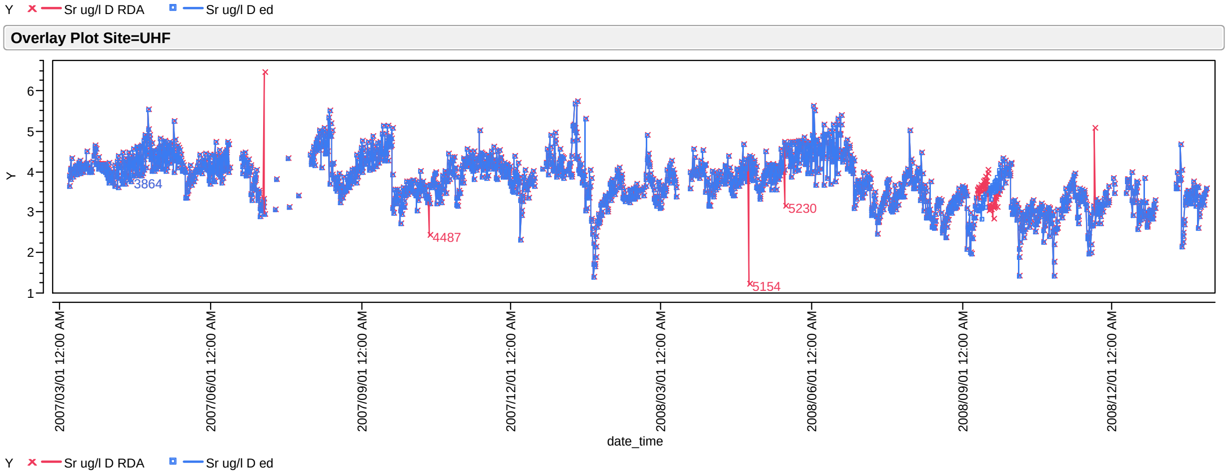




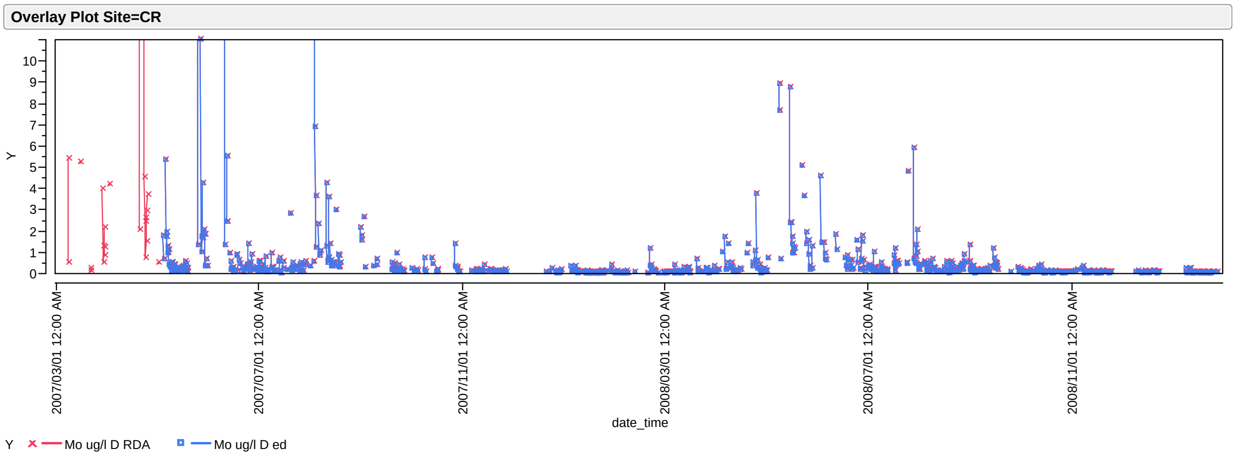
Rb: Only a few rubidium flyers were culled; the rest were kept because they were correlated with K flyers. Most of the K/Rb spikes correspond to flow peaks (or the last sample before a flow peak). However, a few are singletons in the middle of long recessions. Nonetheless, these were kept unless there was a substantial deviation from the usual correlation between Rb and K.

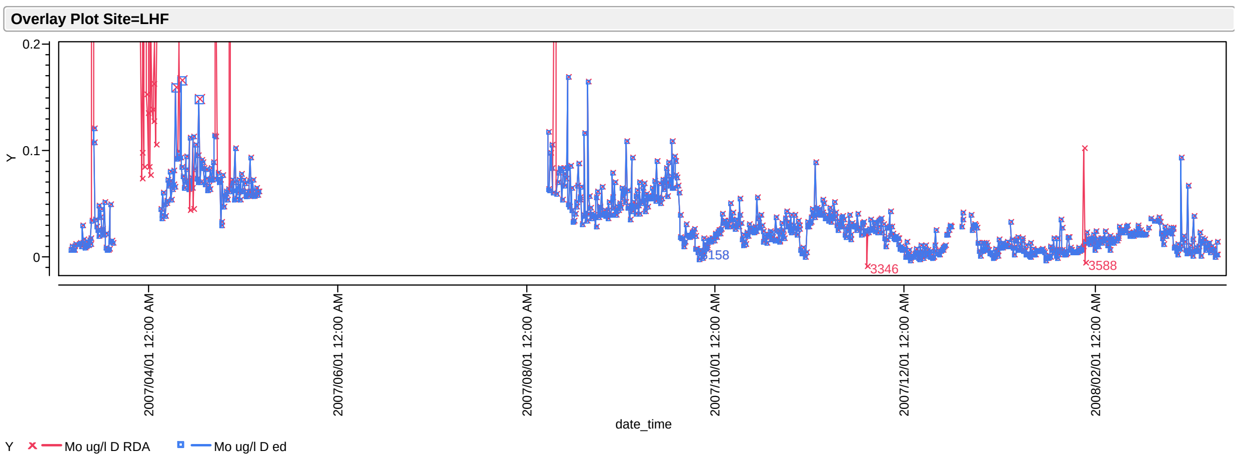


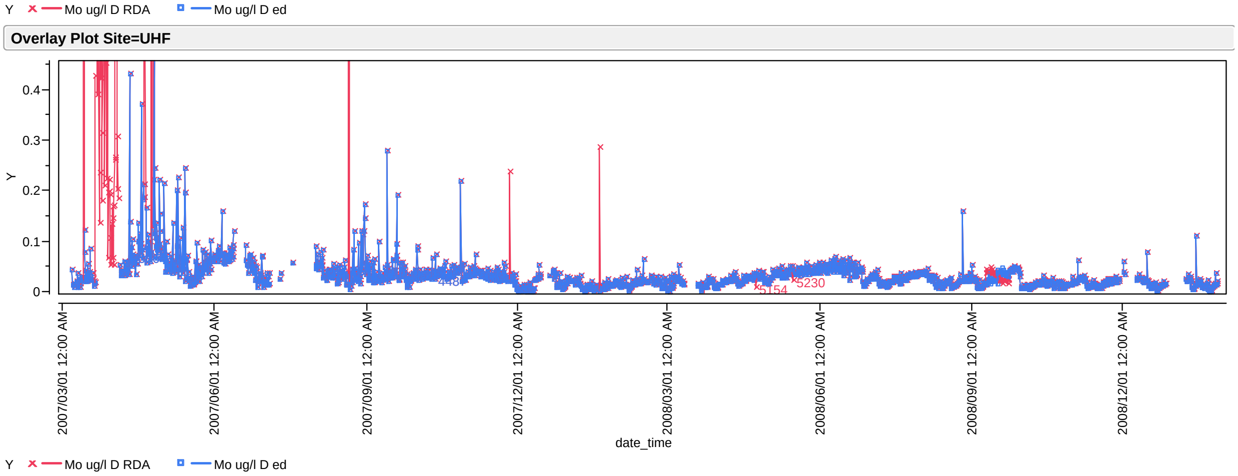




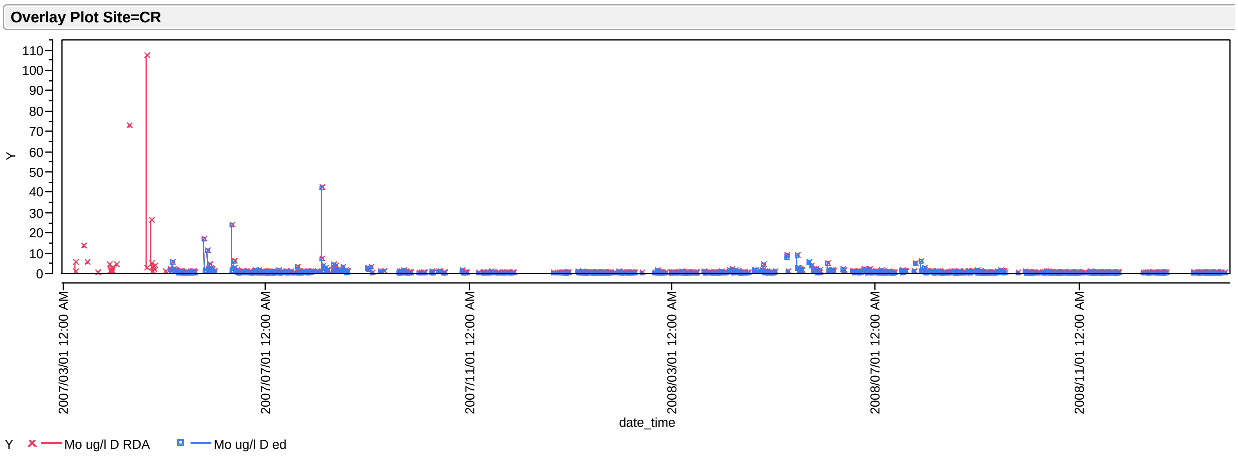
Sr: A few strontium flyers were culled; the rest showed correlations with other analytes including Ca, Cs, Mg, and Cl.







Mo: The most extreme molybdenum flyers have been culled, but some spikes have been kept, even though they occur during featureless recessions and are not well correlated with other analytes (Mo correlates poorly with almost everything). To appreciate the scale of the flyers that have been culled, see the figure below:



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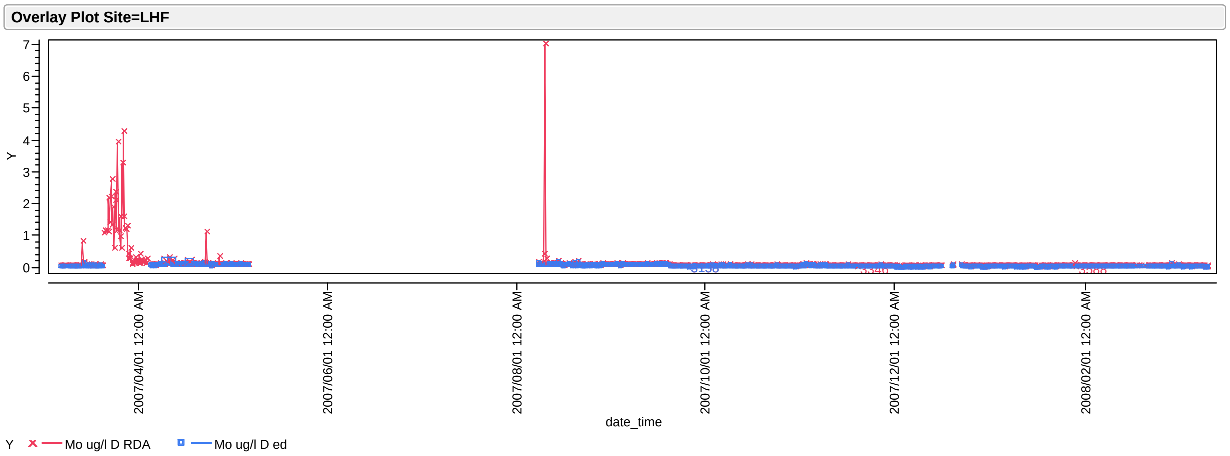

Overlay Plot Site=LHF
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Mo ug/l D RDA
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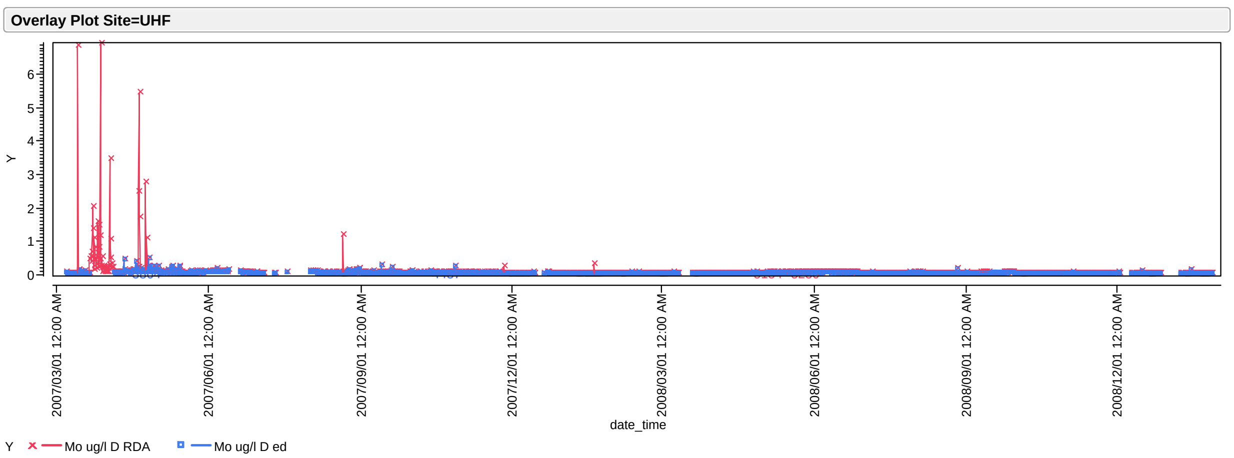

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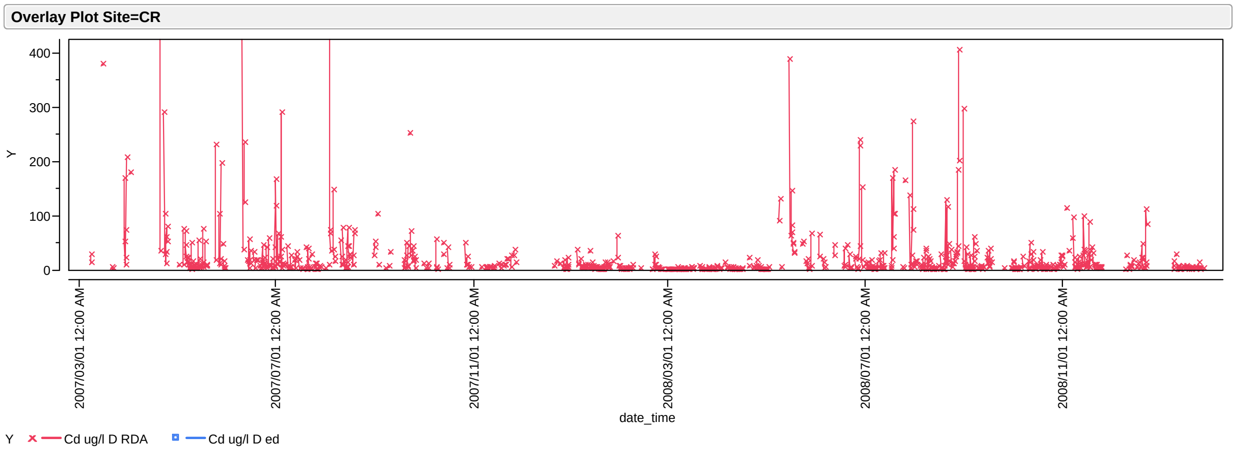
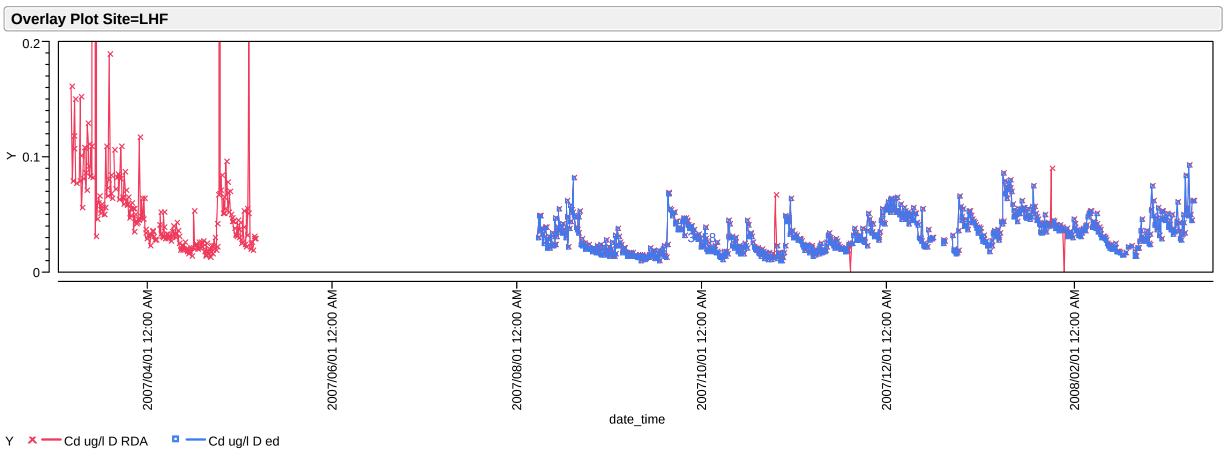
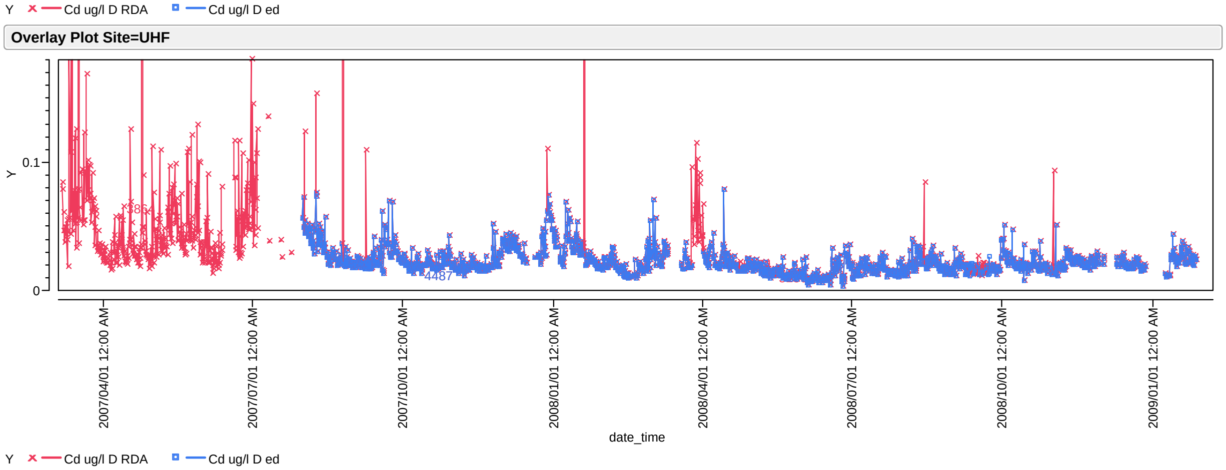
Mo ug/l D RDA
Mo ug/l D ed

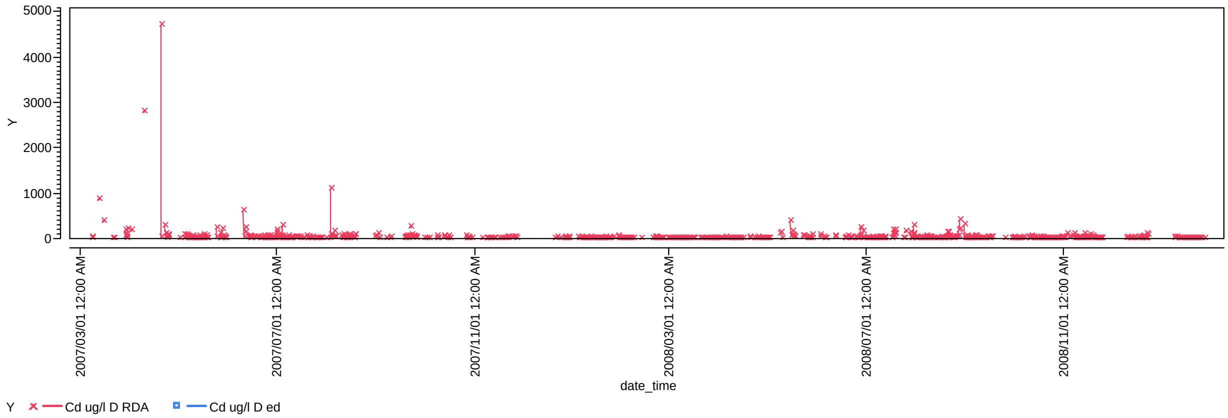




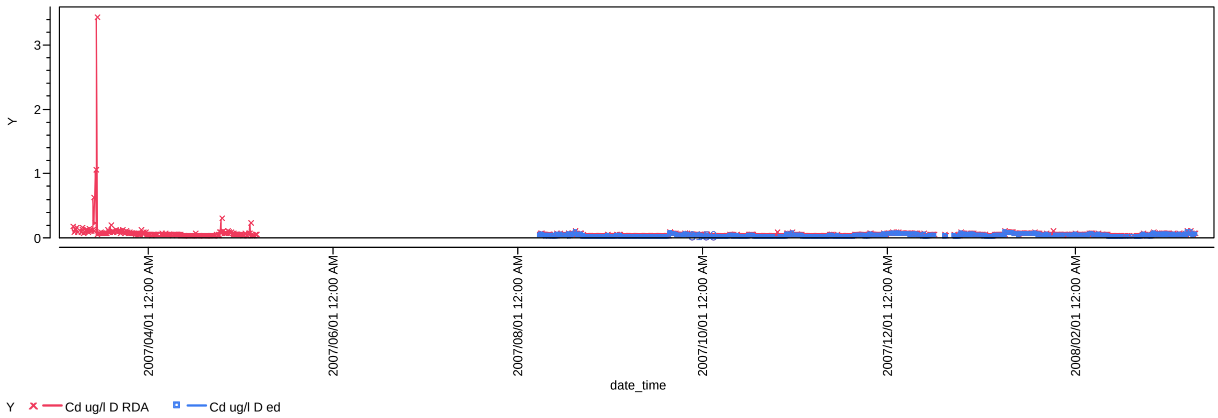


Cd: All precipitation cadmium data have been culled, because the 7-hourly concentrations are many times greater than those in the weekly sampling. The early stream Cd values have also been culled, since they are noisy with many flyers. Individual flyers have been culled from the remaining series, where they are inconsistent with the strong correlations with other metals (Ba, Ni, Co, Be, Al). Below the same plots are shown, but with the full range displayed.

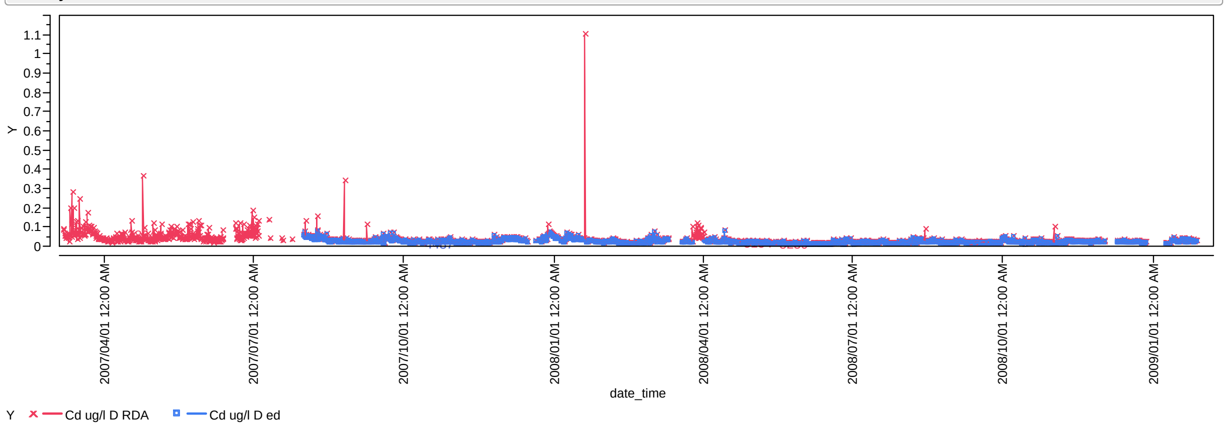
Overlay Plot Site=CR

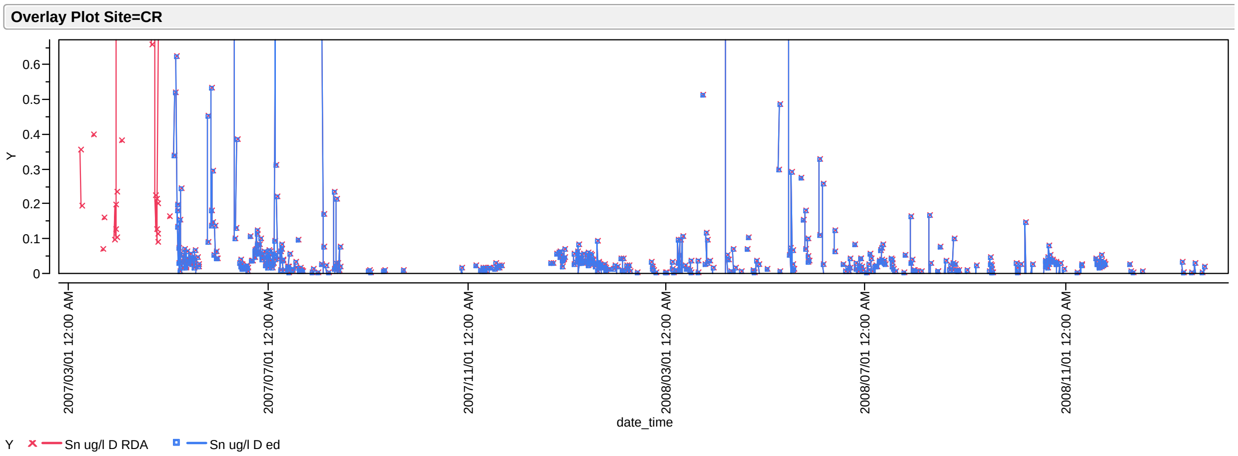


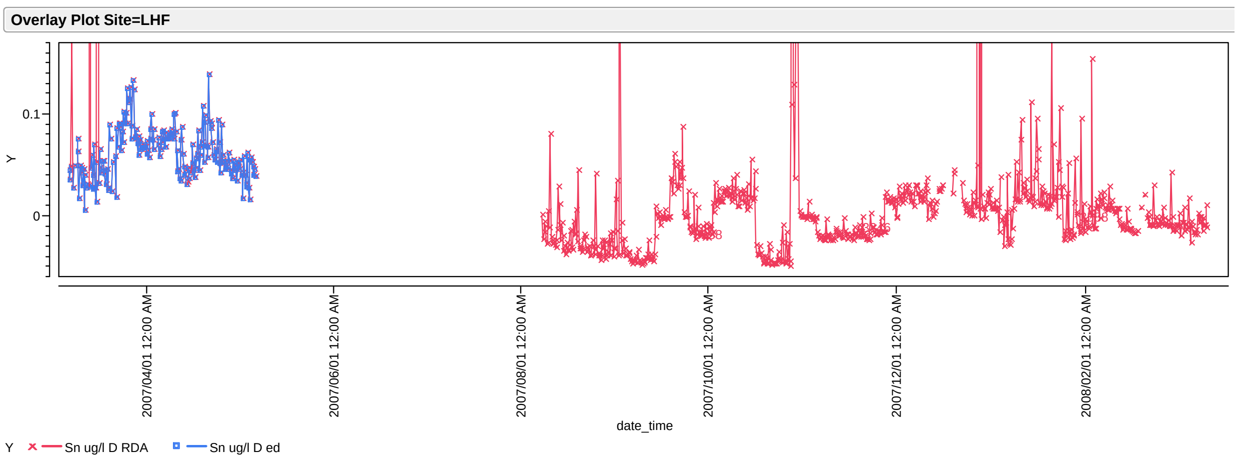
Overlay Plot Site=LHF

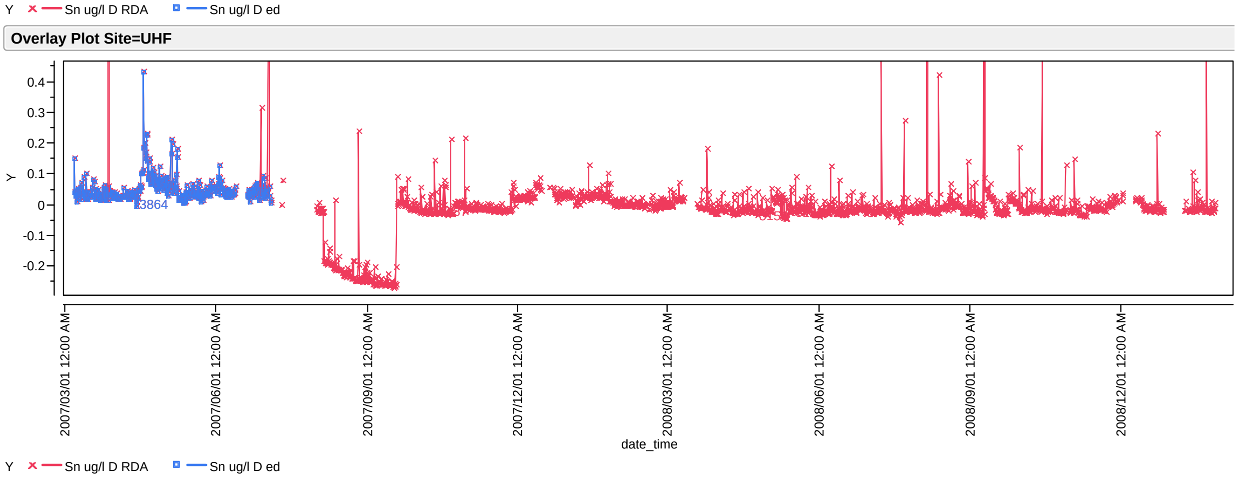


Overlay Plot Site=UHF

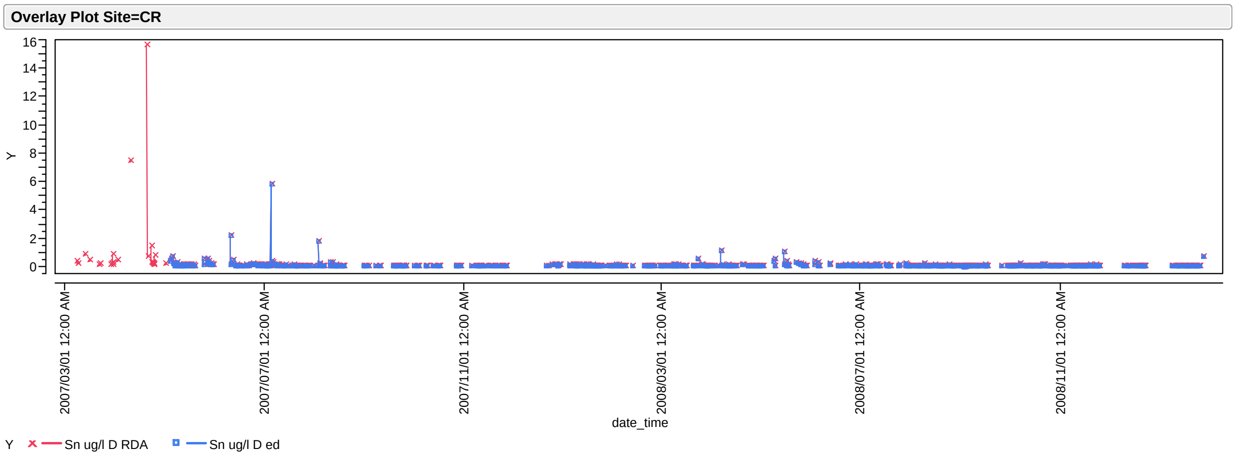








Sn: We have removed almost all the stream tin values, except for the early data (March-June 2007). The later data hovers around zero, with many negative values, and is badly corrupted by background correction problems and the "picket fence" effect of the check standards (with a general decline in values within each set of 10 following each check standard). The figure below shows the full ranges of the data: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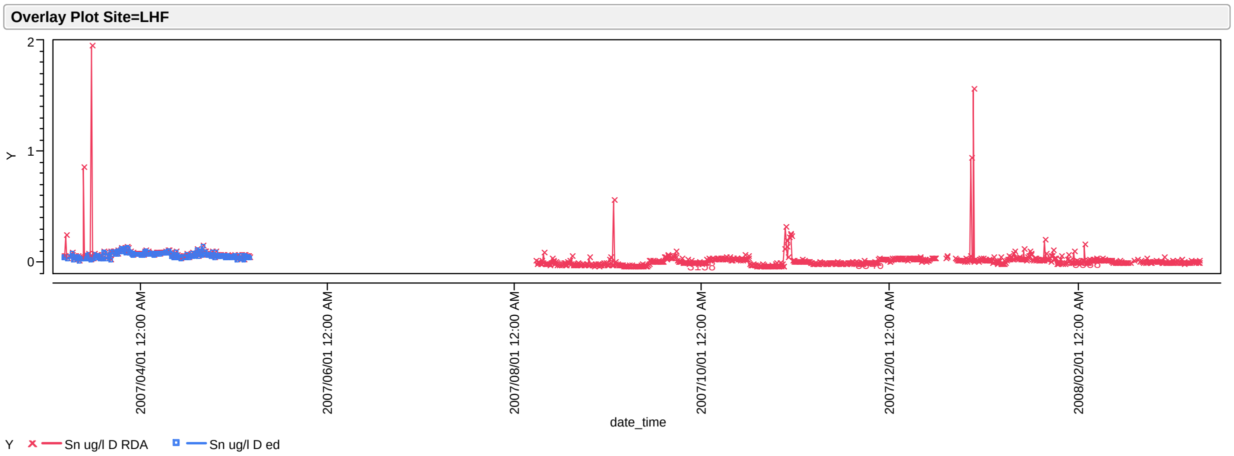
Y Sn ug/l D RDA Sn ug/l D ed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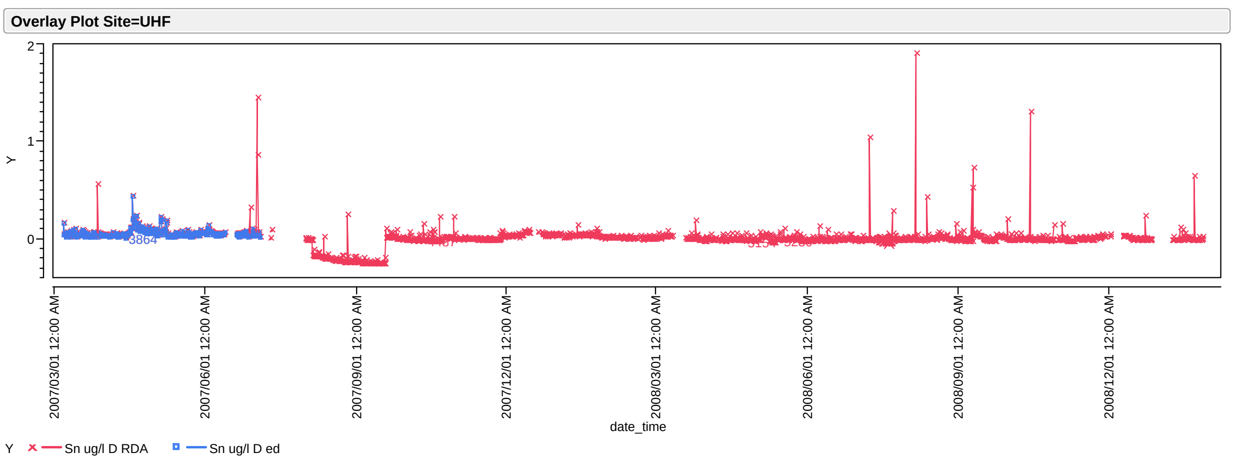
Y Sn ug/l D RDA Sn ug/l D ed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date_time
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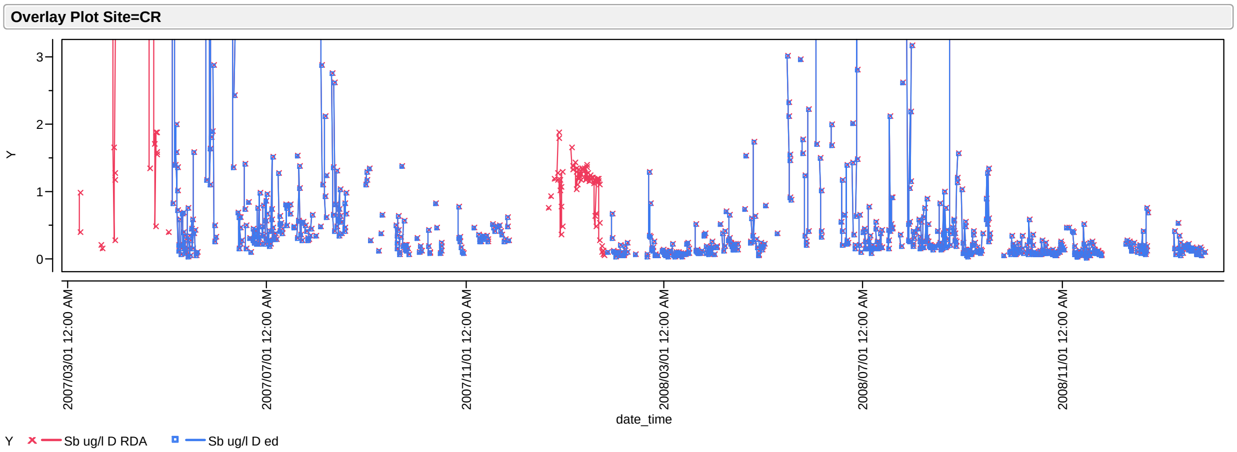
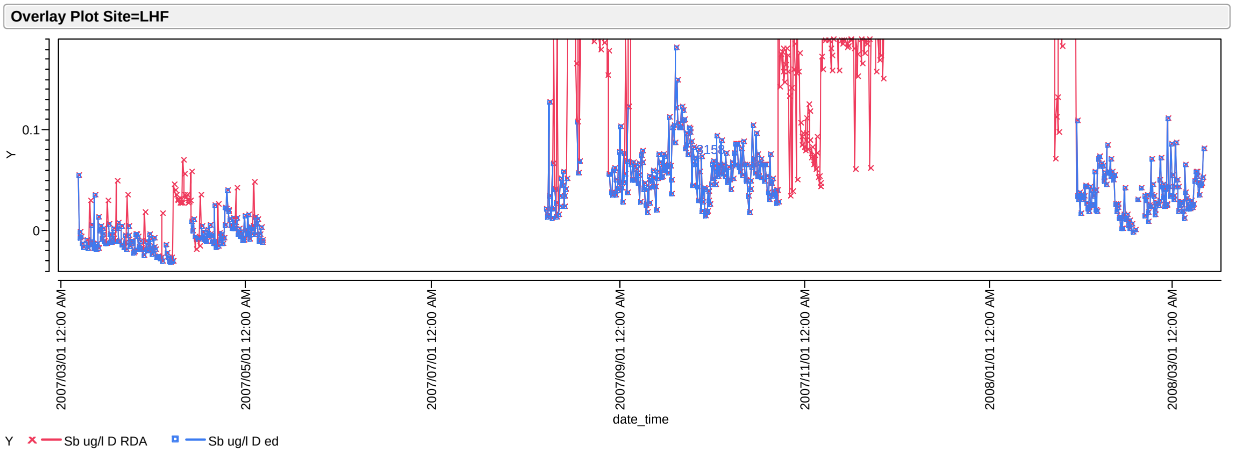
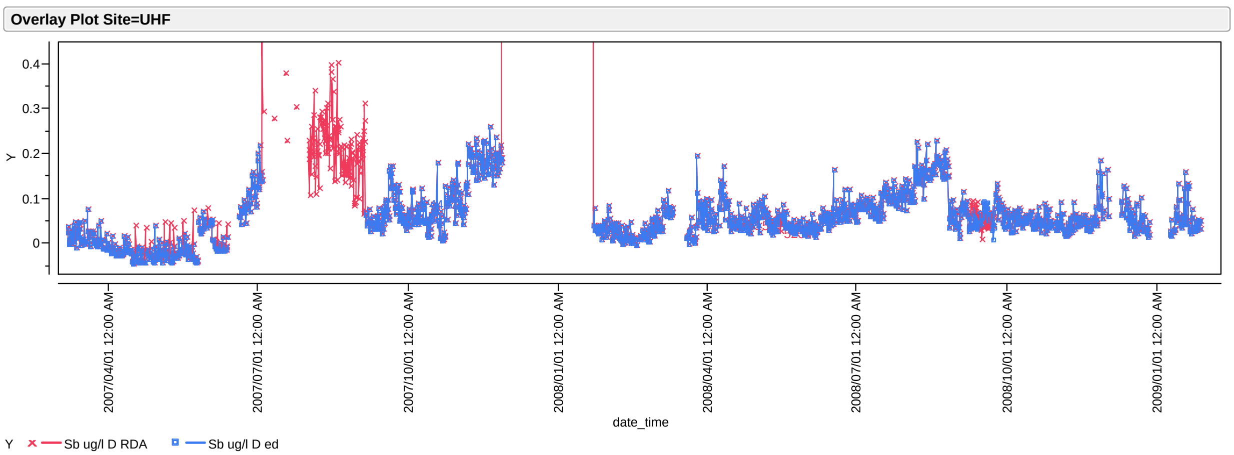
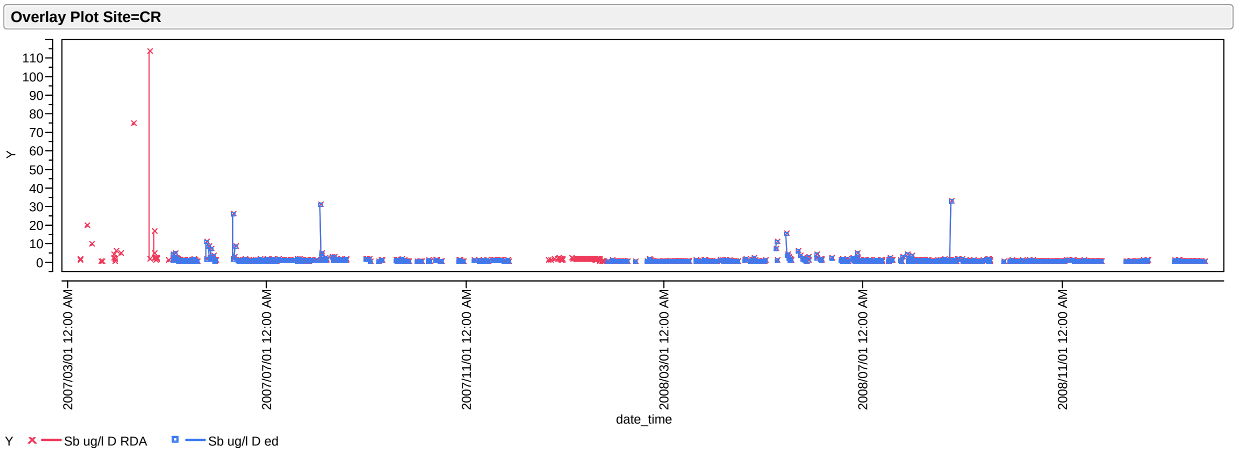
Y Sn ug/l D RDA Sn ug/l D ed







Sb: There are obvious calibration issues in antimony, requiring several large blocks to be culled. There are also several flyers and apparent carryovers from the check standards that were individually culled. The figure below shows the full range of the data, and shows more clearly several large blocks that were culled.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date_time
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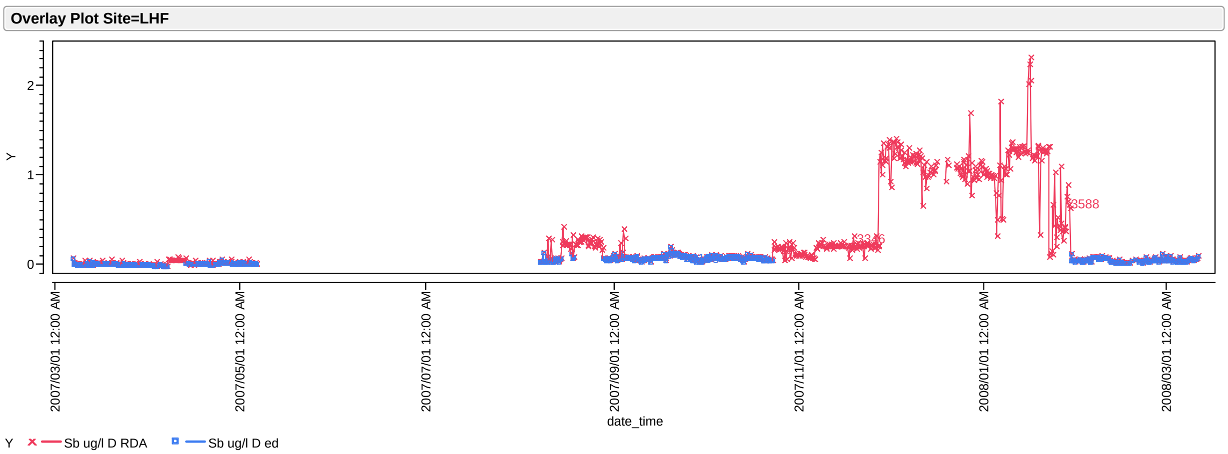
Sb ug/l D RDA
Sb ug/l D ed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2007/05/01 12:00 AM
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date_time
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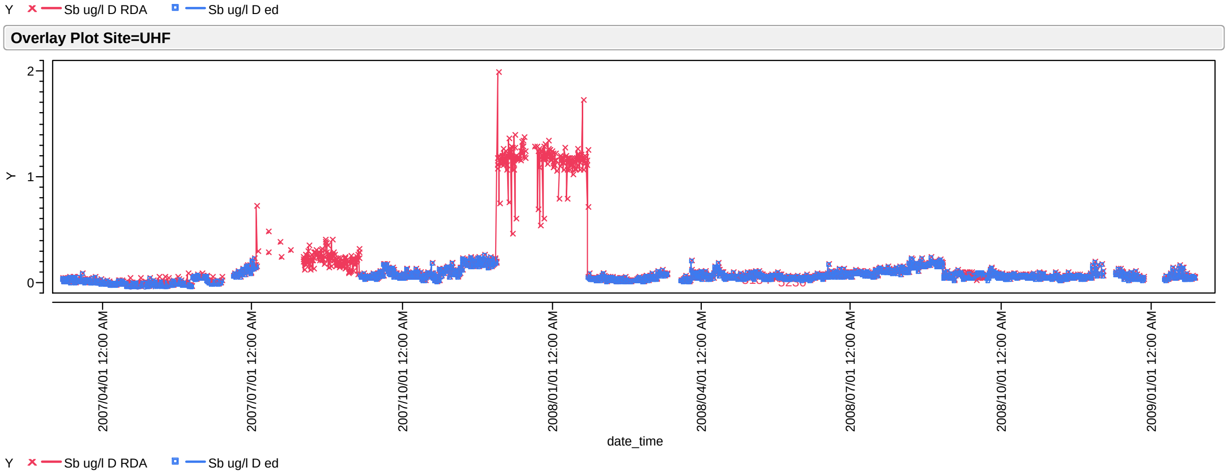
Sb ug/l D RDA
Sb ug/l D ed


Overlay Plot Site=UHF
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2008/01/01 12:00 AM
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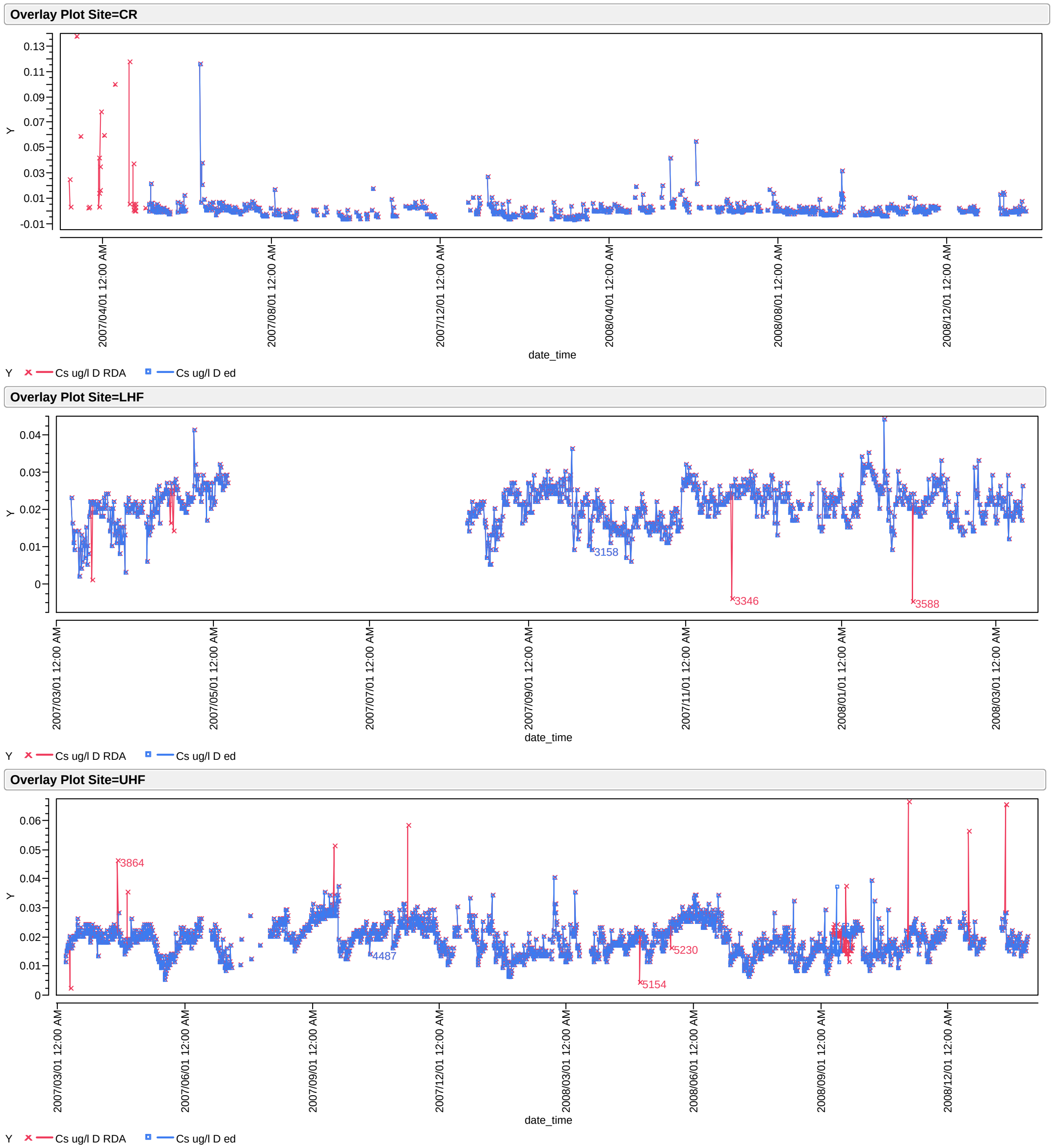
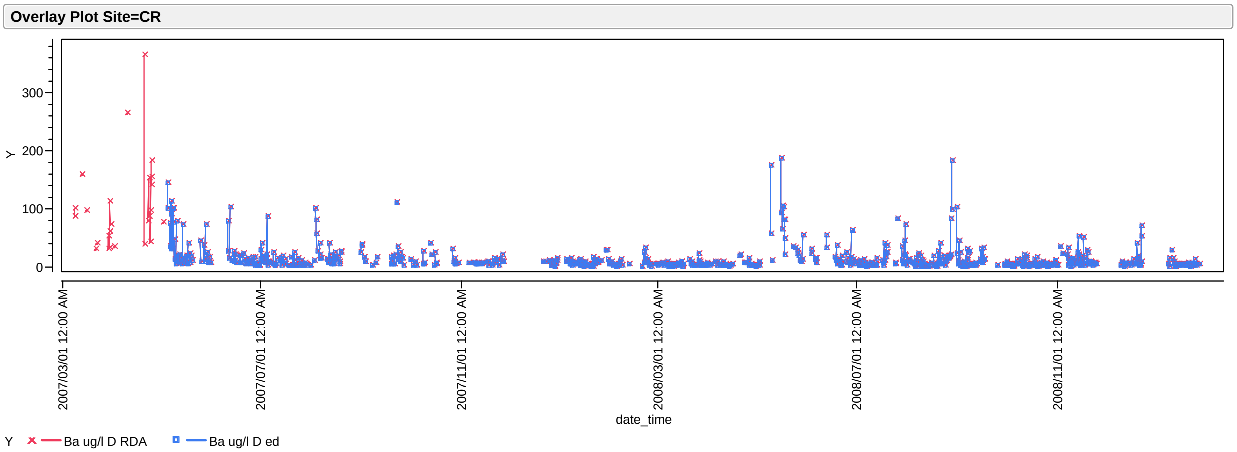
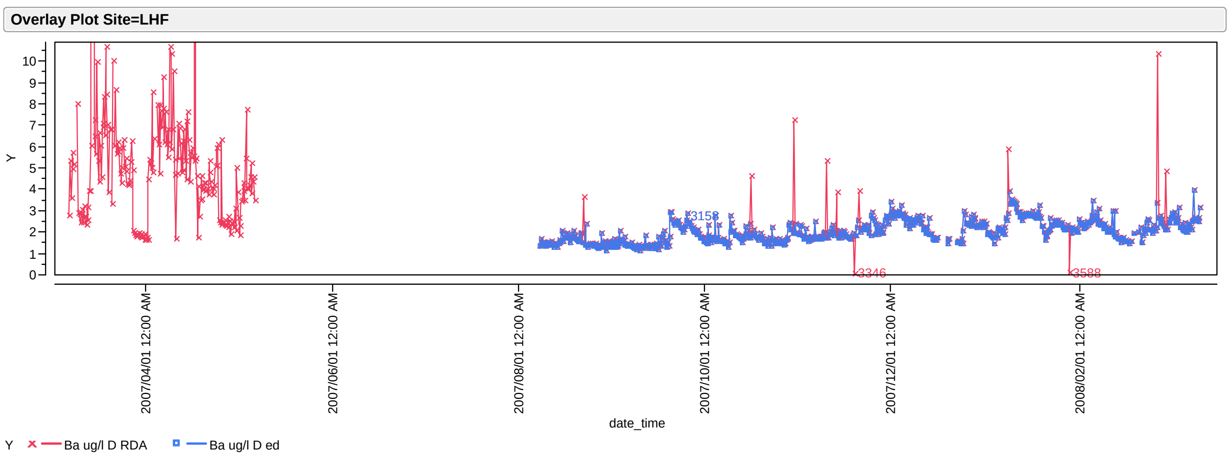
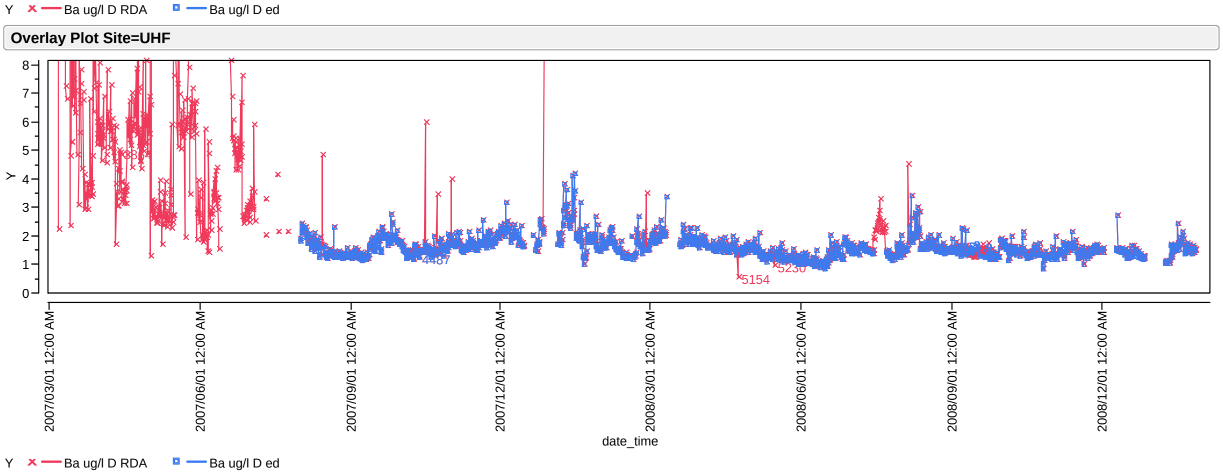
Sb ug/l D RDA
Sb ug/l D ed



Cs: Just a few singleton cesium flyers were culled.

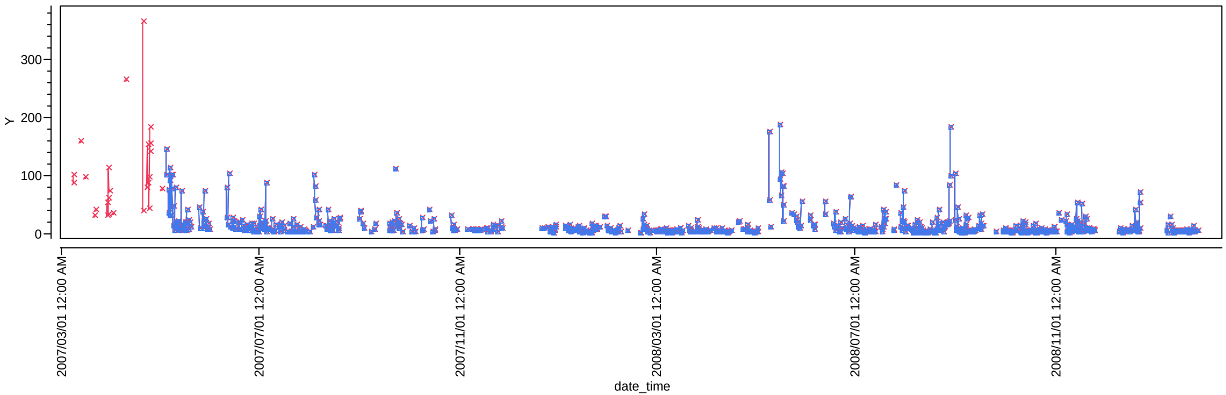






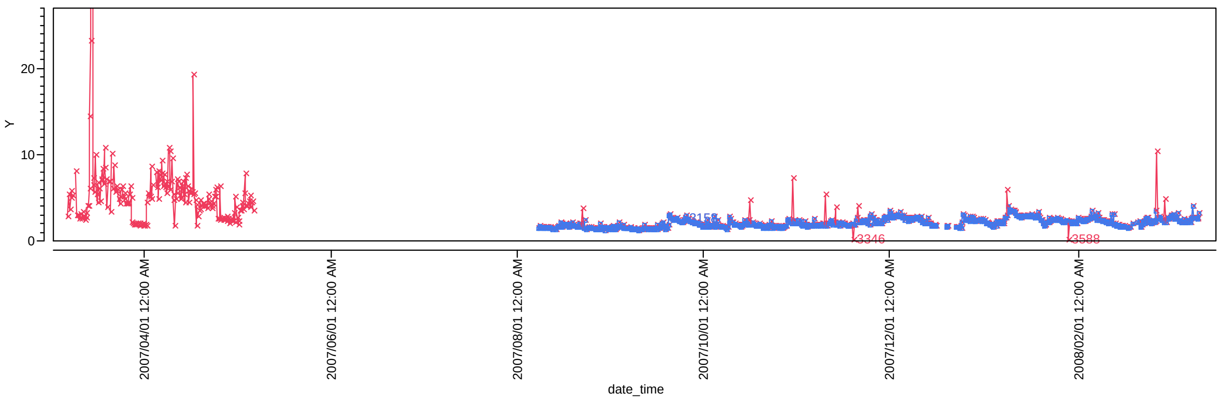
Ba: Early barium values were culled because of obvious background correction problems. Likewise two later analytical blocks at UHF were culled for similar reasons. These are more visible in the figure below.

Overlay Plot Site=CR



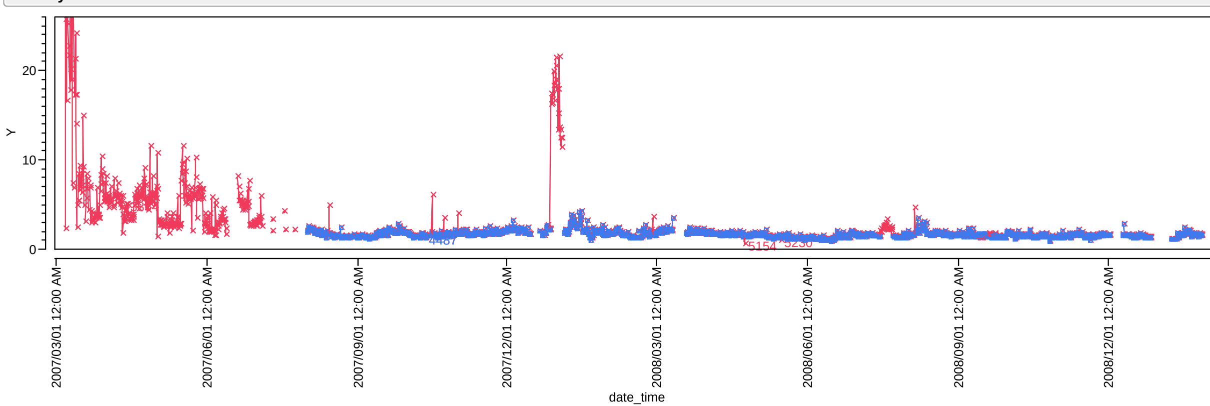
Y — Ba ug/l D RDA — Ba ug/l D ed

Overlay Plot Site=LHF

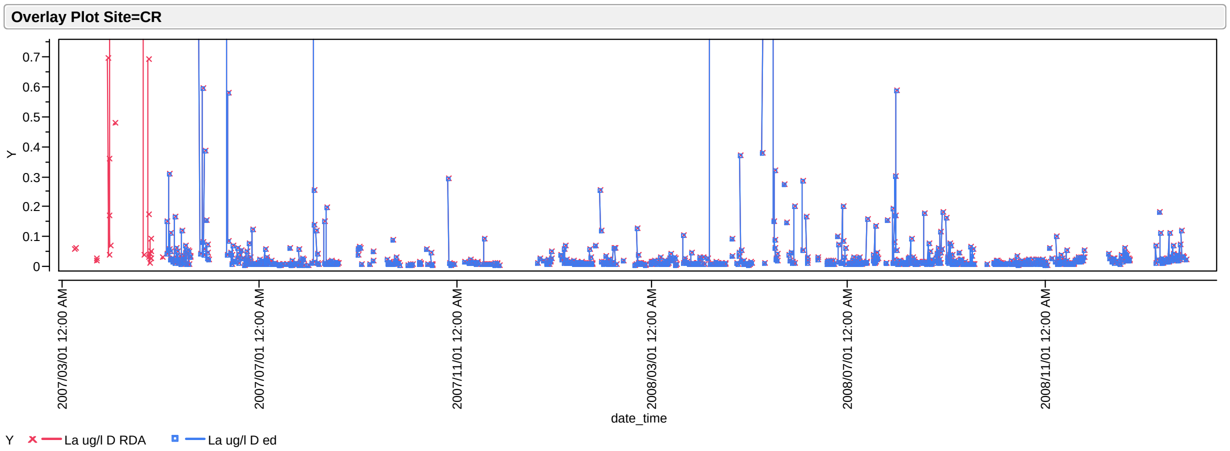


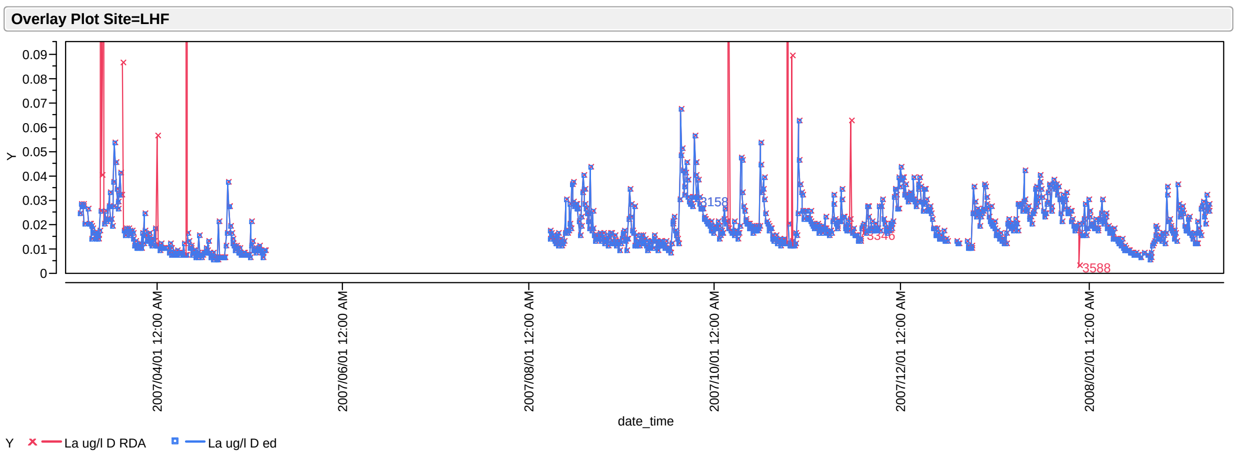
Y — Ba ug/l D RDA — Ba ug/l D ed

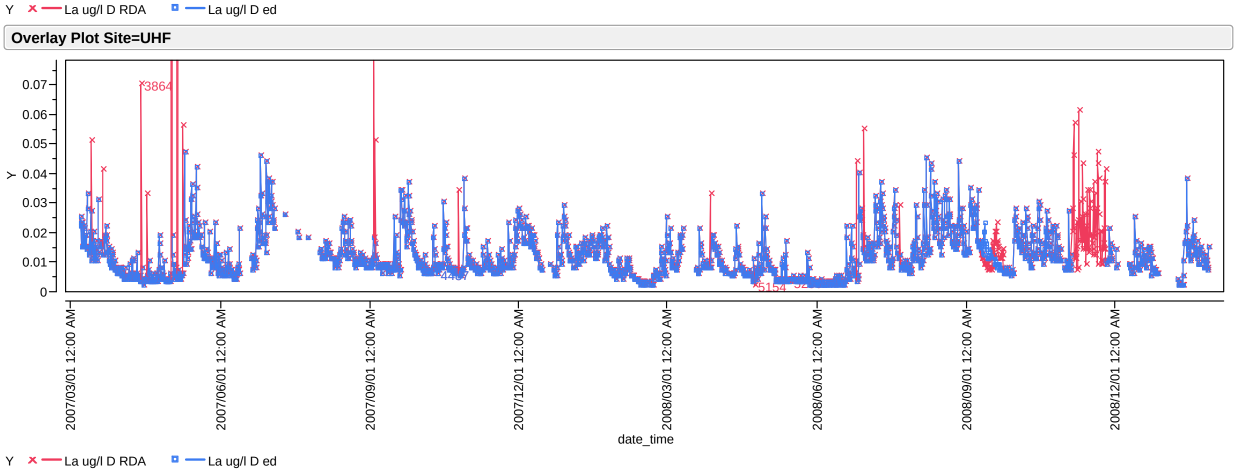
Overlay Plot Site=UHF



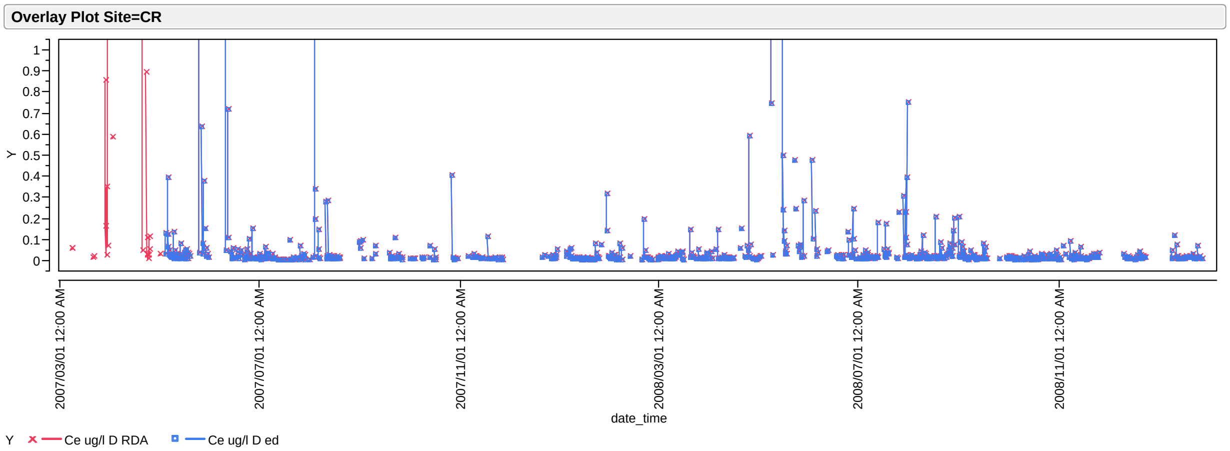
Y — Ba ug/l D RDA — Ba ug/l D ed

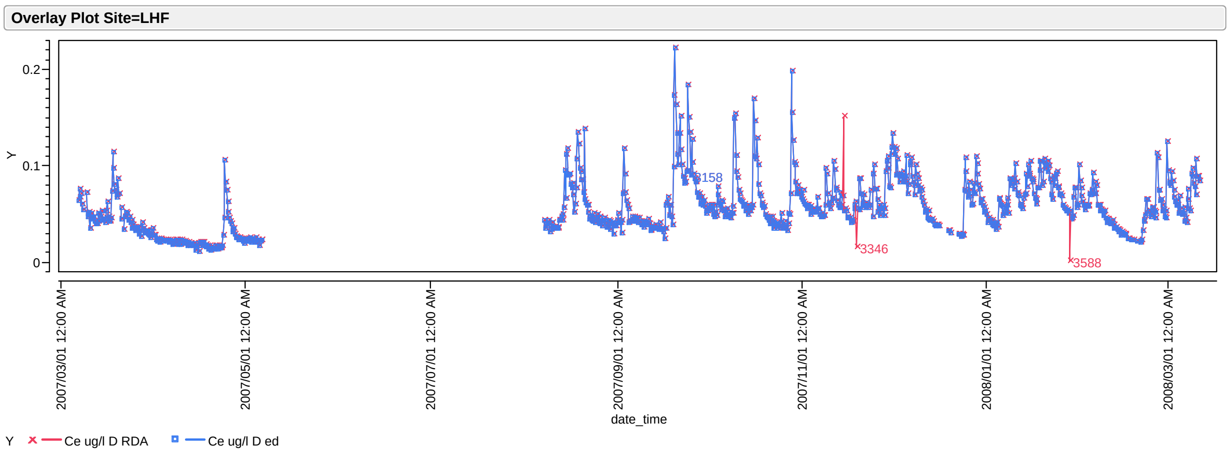


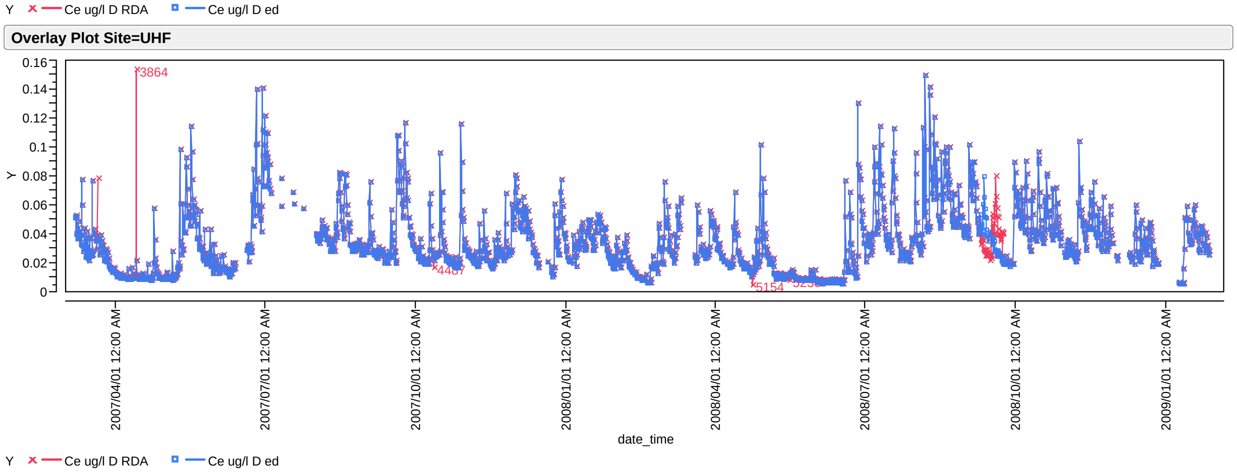




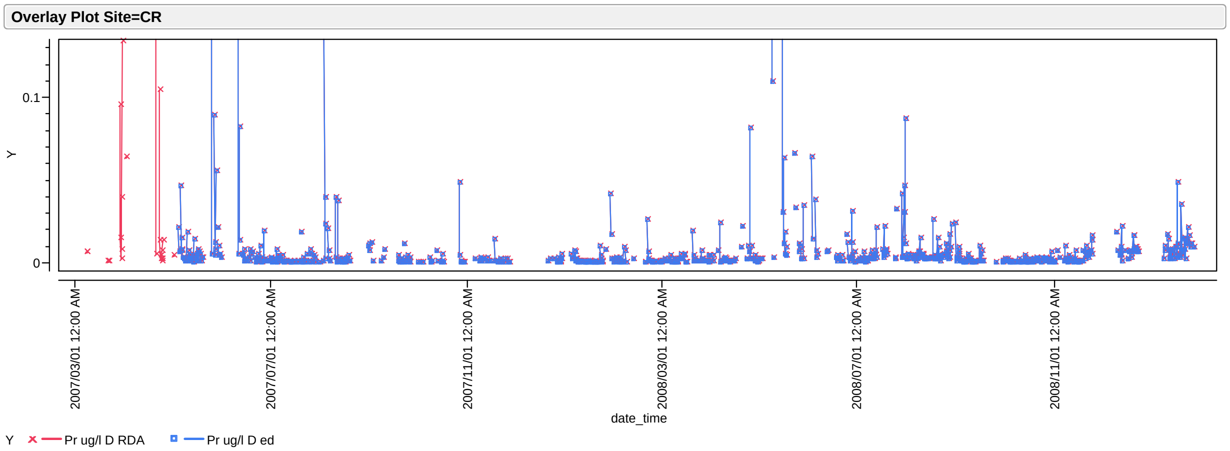
La: Some lanthanum flyers were culled from the stream samples, using correlations with the other lanthanide elements, DOC, and Al as a guide. Several contiguous analytical blocks were also culled at UHF because of apparent calibration problems.

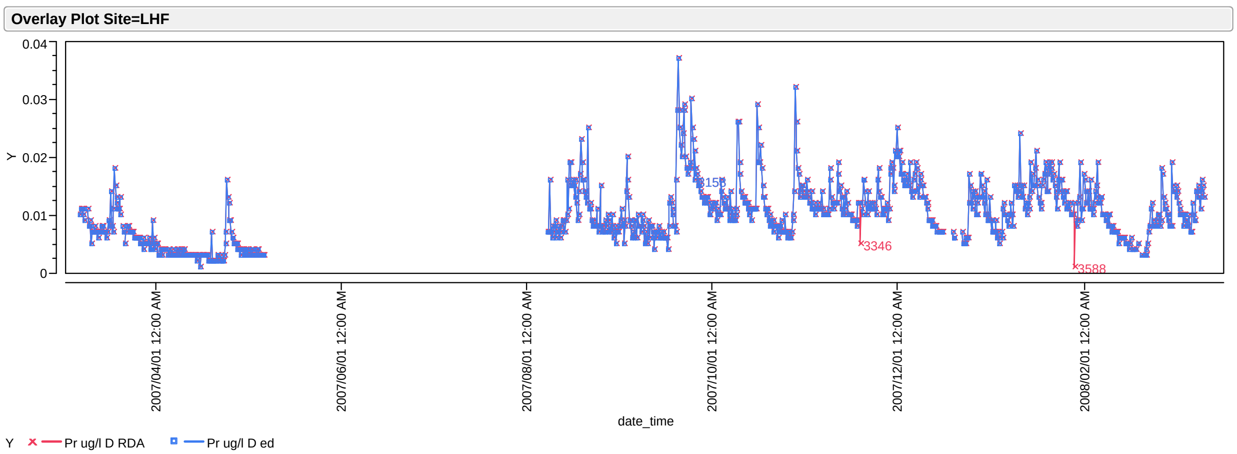


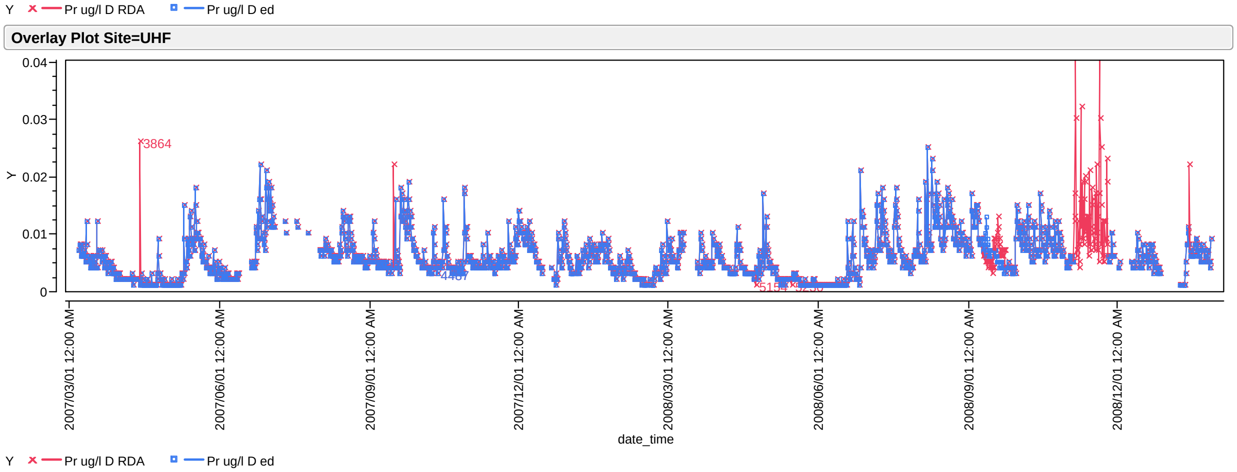




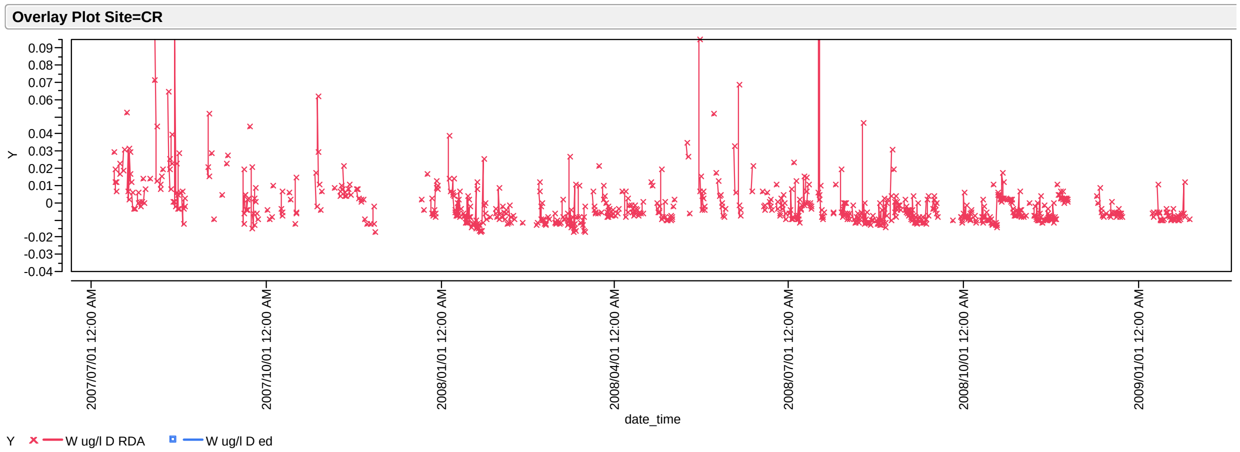
Ce: Relatively few cerium flyers needed to be culled (again using correlations with other lanthanide elements DOC, and Al as a guide)..

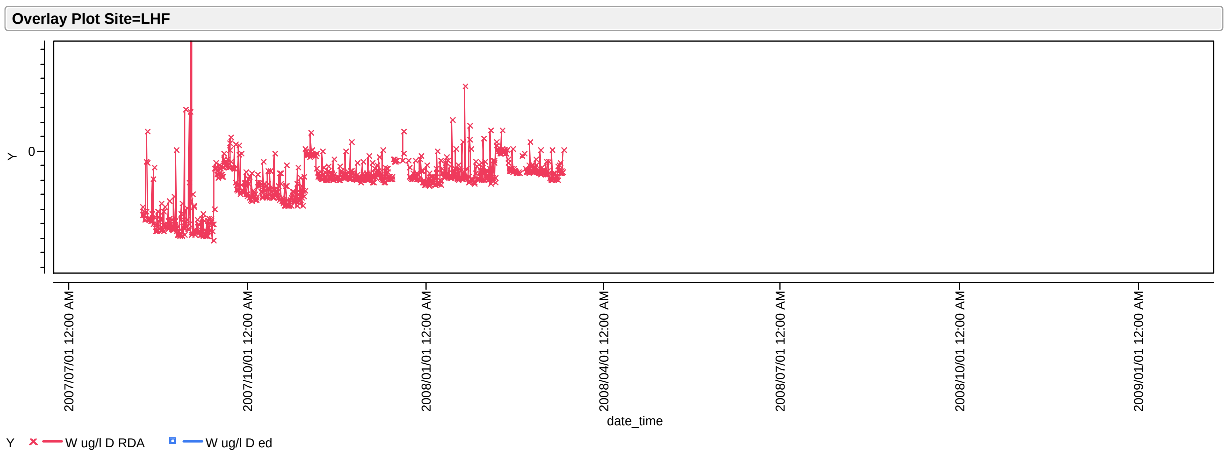


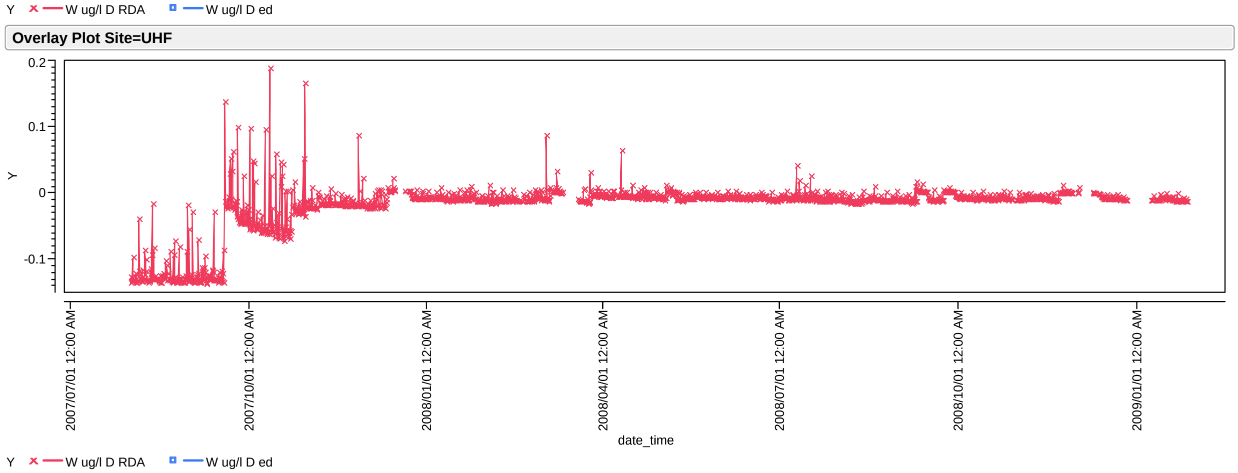




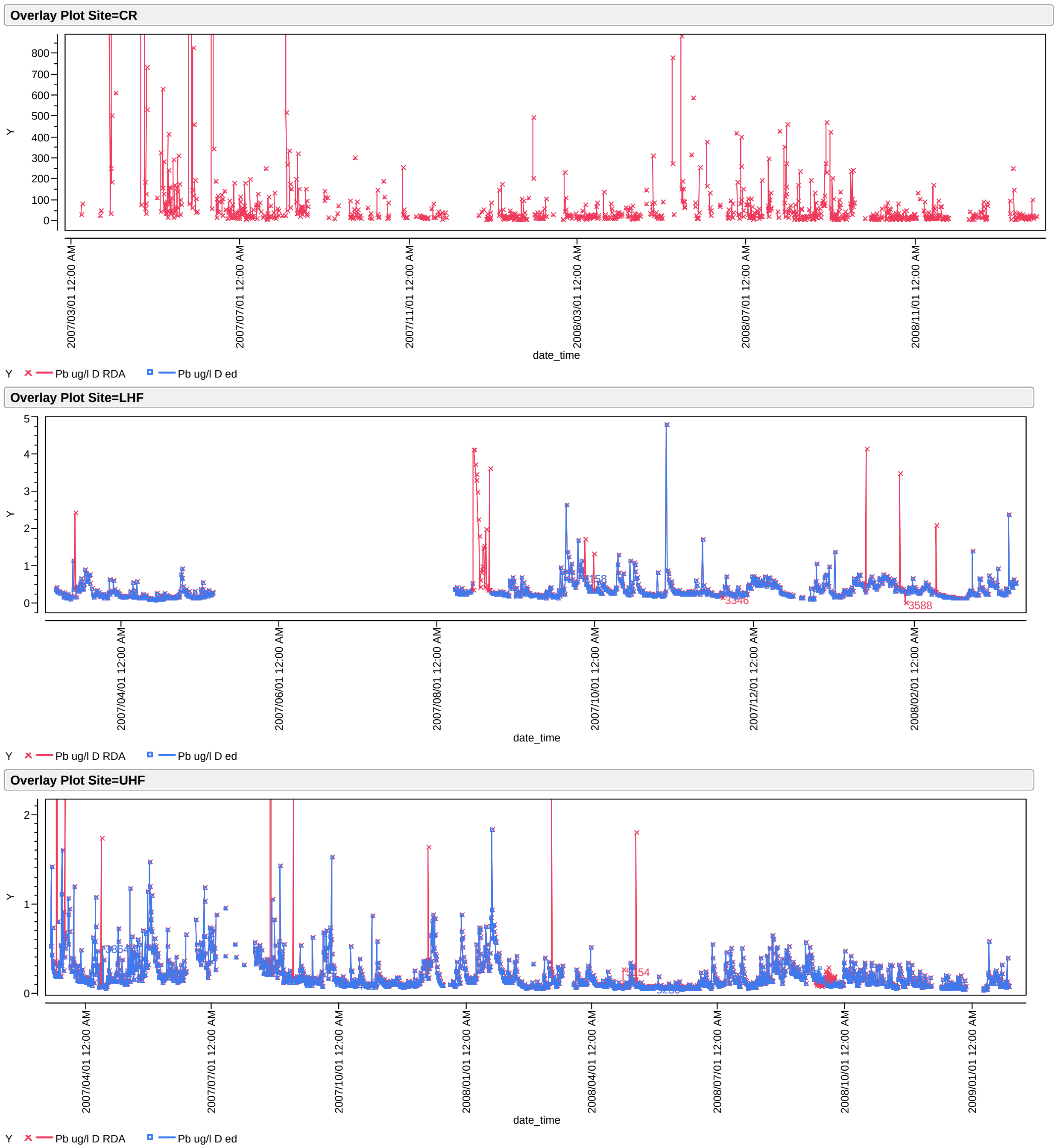
Pr: At UHF, several contiguous praseodymium analytical blocks needed to be culled because of apparent calibration issues (as with La). Concentrations are lower in Pr than in La or Ce, and the coarse-graining effect of the reporting interval (0.001 ug/l) is evident.



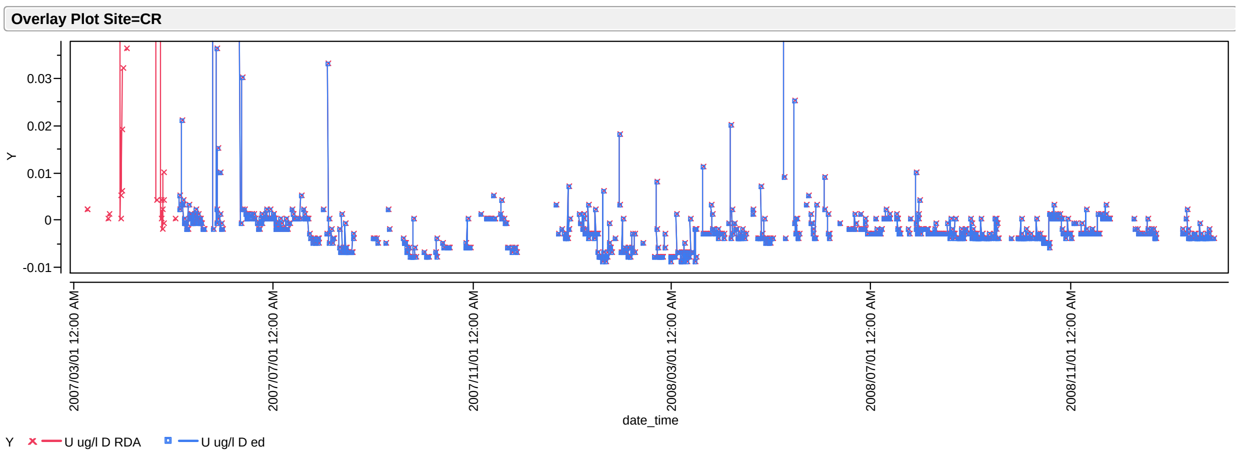


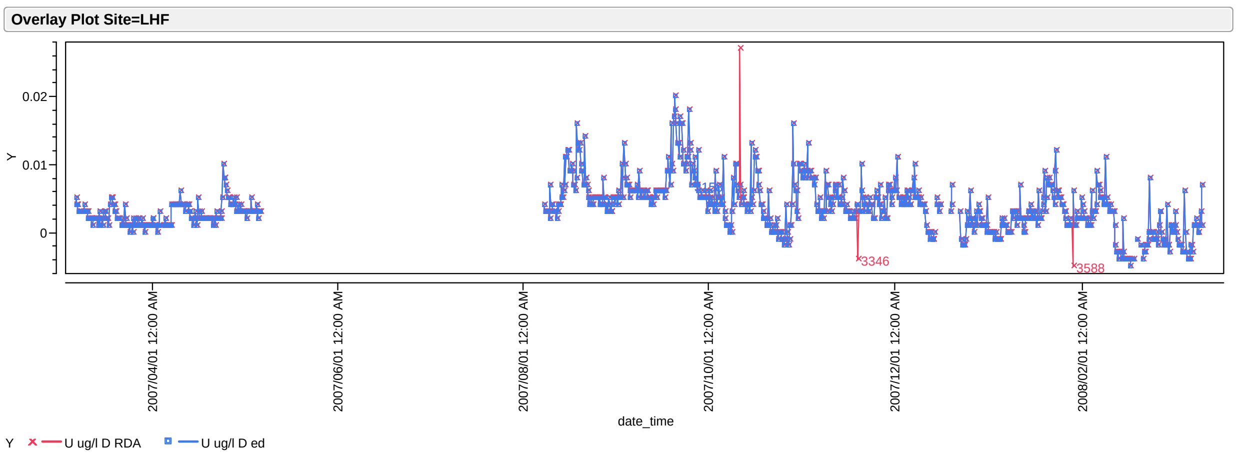


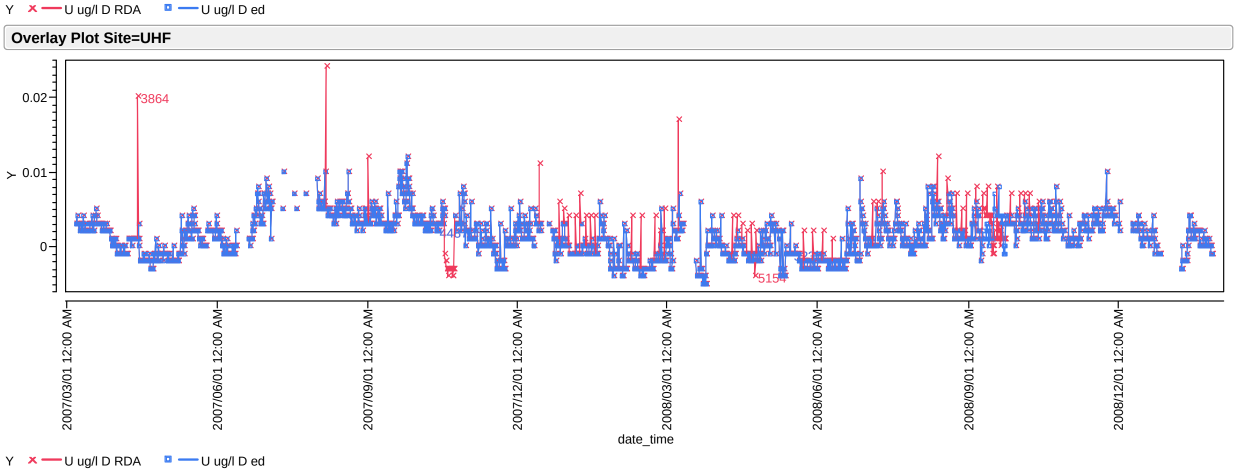
W: We omitted tungsten entirely from the edited data, because the great majority of the values are below zero, and the time series are badly corrupted by background correction problems and the picket fence effect of the check standards.



Pb: All precipitation lead data have been culled, because the 7-hourly concentrations are many times higher than those measured in the weekly sampling. One analytical block was culled from LHF, because its temporal pattern was highly anomalous. Several individual flyers were culled from LHF and UHF.







U: Uranium concentrations are very small, with evident coarse-graining due to the reporting interval of 0.001 ug/l. We culled many "picket fence" points, inferred to be lag effects of the check standards, in the UHF time series. Near-blank concentrations resulted in analytical results often below zero. These were retained, but users should note that at such low concentrations, at best only the relative values are meaningful. The absolute numbers should be interpreted with caution.