Reviewer's New Comment:

While there are two ways in which figures R1 and R2 should be modified (as described below), let me first discuss the current versions. A reasonable interpretation of the close agreement between the measured and metal-calculated DTT rates in Figure R1 is that copper and manganese are very important in the measured DTT responses. As the authors point out, there are cases where the calculated values are up to ~ 2 times higher than the measured rates. But given all of the uncertainties in these calculations - and the fact that the Cu and Mn concentration-response curves were determined in our lab with a static method while the authors used the new flow system in their lab for the sample measurements - this level of agreement is very good.

The authors bring up the point that HULIS are active in the DTT assay and I agree that these species could be important. Dr. Verma's 2012 paper describes a clever use of separation to determine the DTT activity of hydrophobic organics and hydrophilic compounds. But of course the separation was not perfect (as no separation is) and there were significant amounts of metals in the hydrophobic fraction, including approximately half of the initial Mn and Fe. They achieved better separation for Cu, with (113 ± 46)% of the copper from the original water extract being present in the hydrophilic fraction, but there is sufficient noise in this average to indicate that Cu likely made a contribution to the DTT result in at least some of the "HULIS" samples. So I don't consider this HULIS work conclusive evidence that Cu and Mn are not major contributors to the DTT loss in the SCAPE samples.

(As an aside, it should be possible to examine the 2012 HULIS sample DTT results on a case-by- case basis to remove the metals contributions to DTT loss and estimate a concentration-response curve for HULIS, analogous to what we have done for metals and quinones. This curve could then be used to estimate the contribution of HULIS to DTT activity in the current SCAPE

samples. But I am not suggesting this be done as part of the current manuscript.)

As for the issue of our concentration-response curves being based on “pure metals”, in our lab solutions the metals are not present as free ions (as the authors suggest), but probably rather as complexes with DTT and possibly phosphate. As a dithiol, DTT likely binds very strongly to copper and manganese. It is possible that organic ligands in the PM extracts compete with DTT as a ligand for the metals, but it’s unlikely that a given ligand has a higher concentration than DTT in the extract solution and so the ligand would need to have a stronger binding constant than DTT. This is possible, but not a sure bet. So, while I agree that organic ligands from the PM might alter the metal reactivity, it is not clear if this is a minor or major issue.

As for Figure R2, I agree that the poor correlation weakens the case for metals, but there are some important caveats. First, the range of measured (and predicted) values is very small – a factor of approximately two – which makes it difficult for the signal to be clearly above the noise. Second, the uncertainties (for both the x and y values) need to be shown on each point to give a sense of this “noise”.

This brings me to the two (important) details I mentioned in the first paragraph of this new comment. The first is that the authors need to show the propagated errors for both the measured and calculated DTT rates on both Figures R1 and R2. The errors are likely to be significant (as they are in our work) because there are many components that go into the measured and/or calculated rates, including uncertainties in mass (especially for their samples without mass measurements), DTT sample and blank rates, air volumes, and metal concentrations. The second detail is that the results in Figures R1 and R2 are shown as monthly averages at a given site. But because the Cu and Mn responses are non-linear, one cannot use the average Cu for the month and compare it to the

monthly average DTT rate. Unfortunately, each sample has to be examined individually. This might, or might not, change the results in Figures R1 and R2 significantly; it depends on the spread of values in the average.

Recommendation

I recommend that the paper be accepted once a new version of Figure R1 is included in the main text. This figure should show results for each individual sample and should include propagated uncertainties for each measured and calculated result. While the authors and I might disagree on the interpretation of the results in this figure, at least if it is in the main text then the reader can make his or her own assessment.

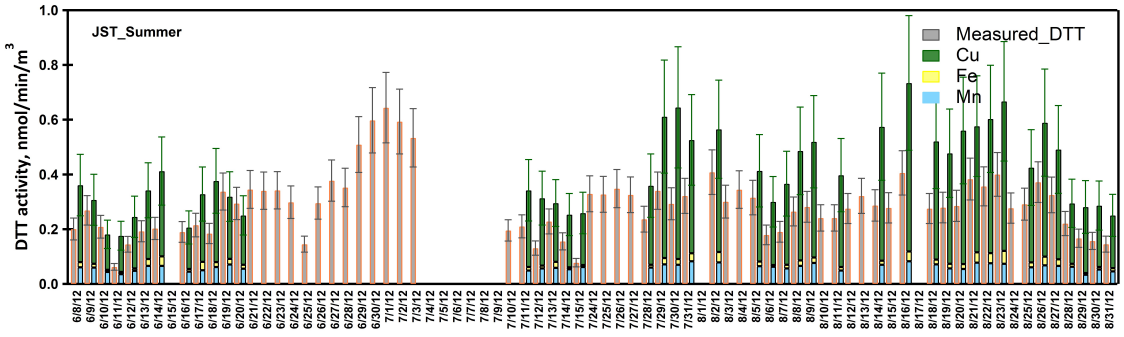
It would also be good to include a similarly new version of Figure R2 in the main text, but I leave this up to the authors.

Response

Following the reviewer's suggestion, we have applied his approach in all of our individual samples (N~500!) and a new version of the figure R1 is shown below (Figure RR1). This figure, as expected by the reviewer, gives a similar picture as that of the previous Figure R1 in our first response.

We feel the figure does not fit within the scope of our manuscript, which is on identifying the sources of DTT and not on attributing to specific chemical species. We leave that topic to a different manuscript where we will include metals and organic species.

Note that all replies to the reviewers are published if the paper will be accepted for final publication in ACP, so the figure would still be accessible to the interested readers. We appreciate the reviewer's comments.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Cu
Fe
Mn
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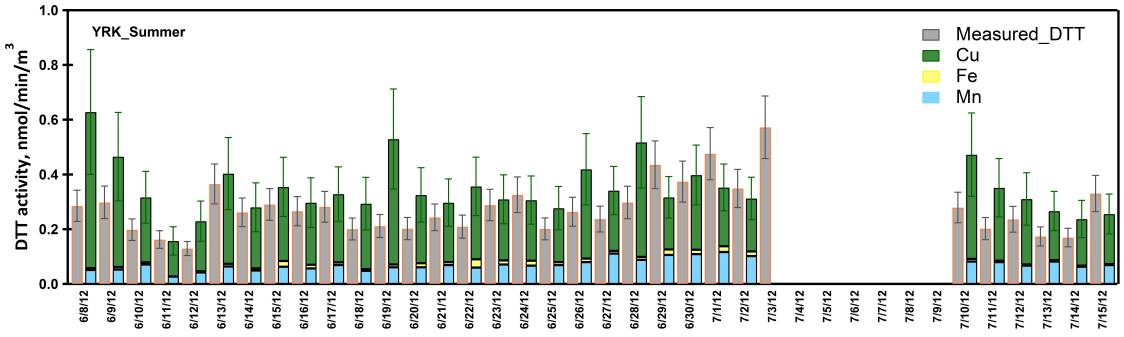
0.6
0.4
0.2
0.0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Cu
Fe
Mn
DTT activity, nmol/min/m3
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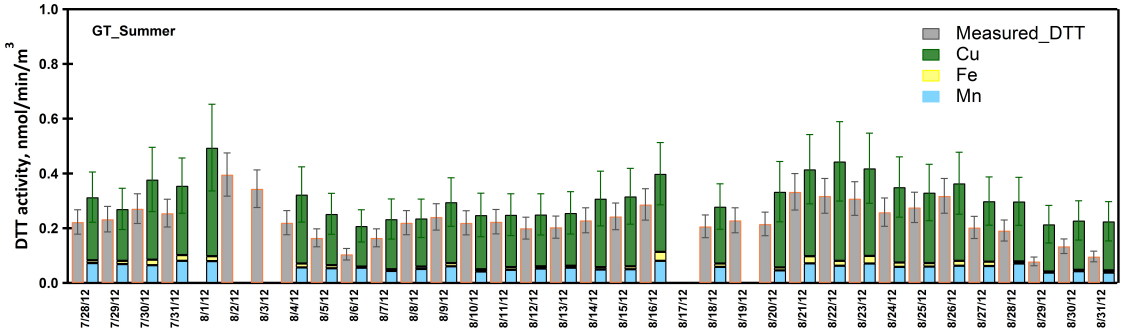
0.8
0.6
0.4
0.2
0.0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Cu
Fe
Mn
DTT activity, nmol/min/m3
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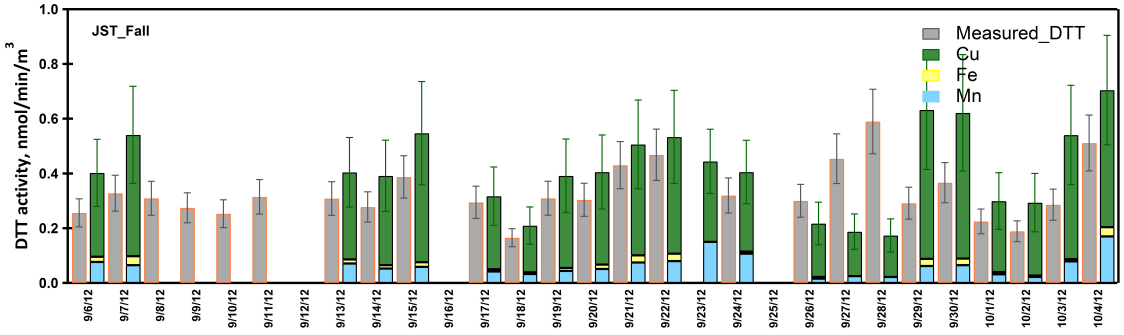
0.8
0.6
0.4
0.2
0.0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Cu
Fe
Mn
DTT activity, nmol/min/m3
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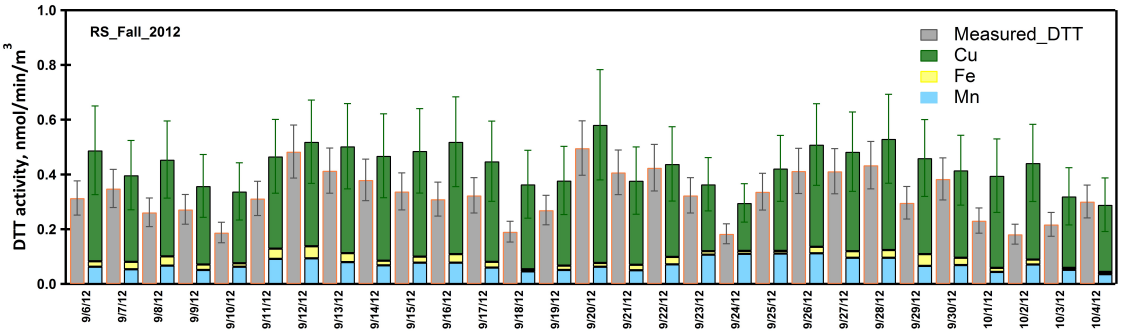
0.6
0.4
0.2
0.0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Measured_DTT
Cu
Fe
Mn
DTT activity, nmol/min/m3
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0.6
0.4
0.2
0.0
9/6/12
9/7/12
9/8/12
9/9/12
9/10/12
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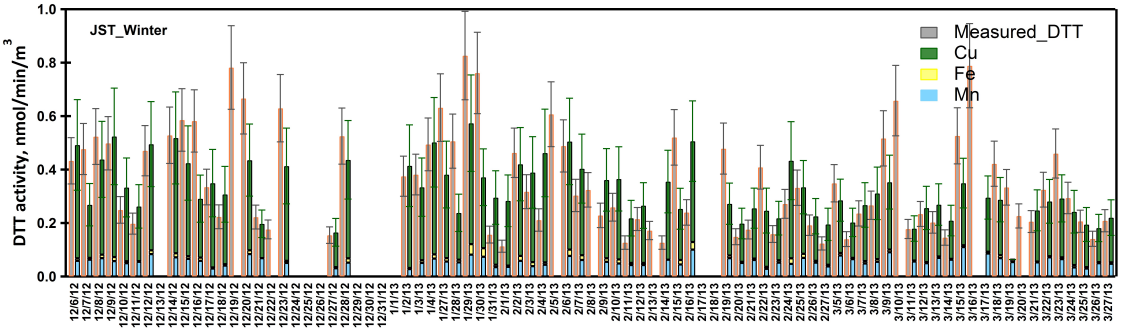
10/4/12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Measured_DTT
Cu
Fe
Mn
DTT activity, nmol/min/m3
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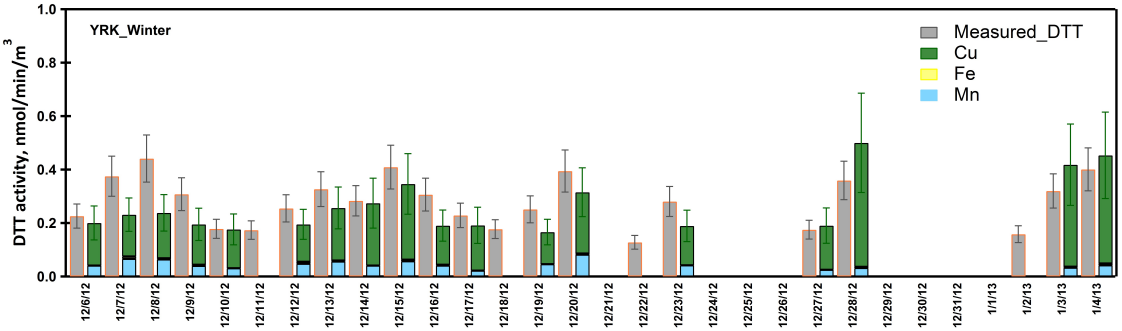
0.6
0.4
0.2
0.0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Measured_DTT
Cu
Fe
Mn
DTT activity, nmol/min/m3
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0.6
0.4
0.2
0.0
12/6/12
12/7/12
12/8/12
12/9/12
12/10/12
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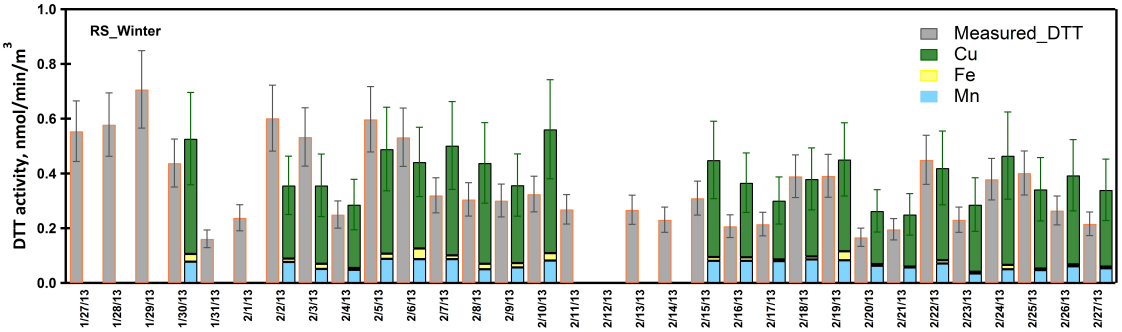
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Cu
Fe
Mn
DTT activity, nmol/min/m3
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0.8
0.6
0.4
0.2
0.0
1/27/13
1/28/13
1/29/13
1/30/13
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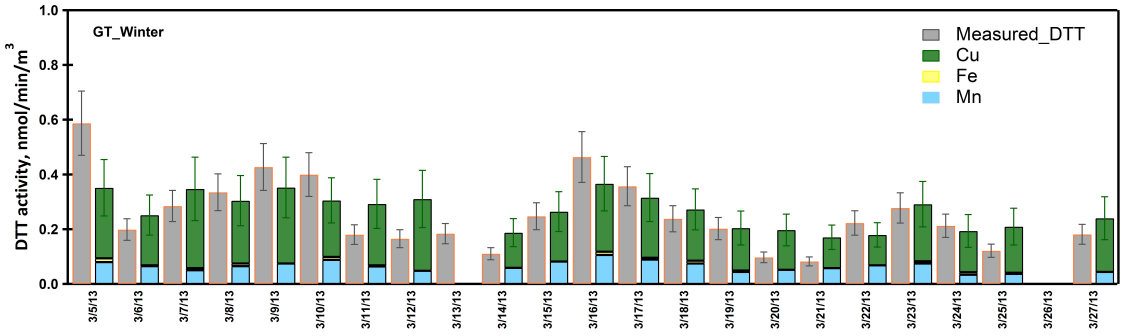
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Measured_DTT
Cu
Fe
Mn
DTT activity, nmol/min/m3
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0.8
0.6
0.4
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0.0
3/5/13
3/6/13
3/7/13
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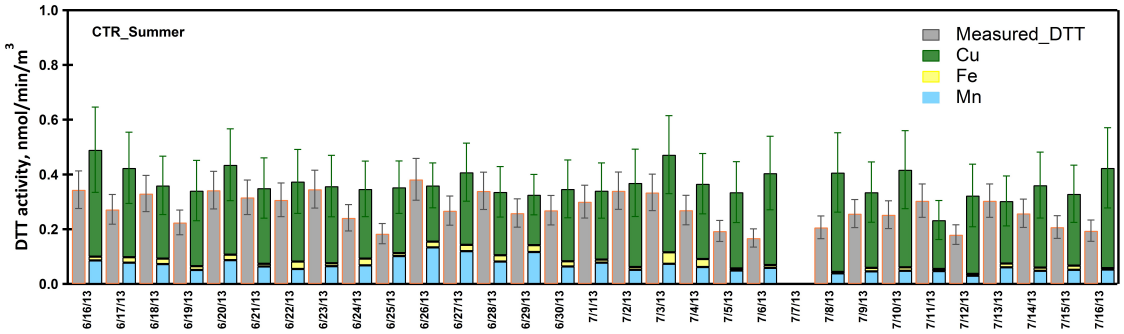
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Cu
Fe
Mn
DTT activity, nmol/min/m3
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0.6
0.4
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0.0
6/16/13
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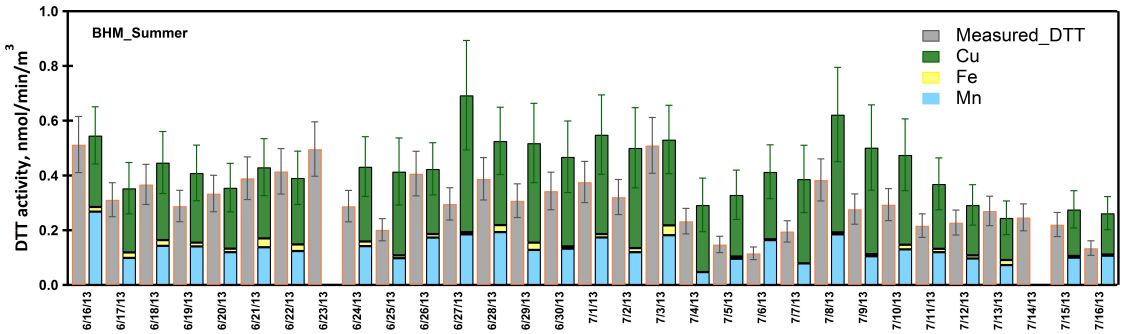
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Measured_DTT
Cu
Fe
Mn
DTT activity, nmol/min/m3
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0.6
0.4
0.2
0.0
6/16/13
6/17/13
6/18/13
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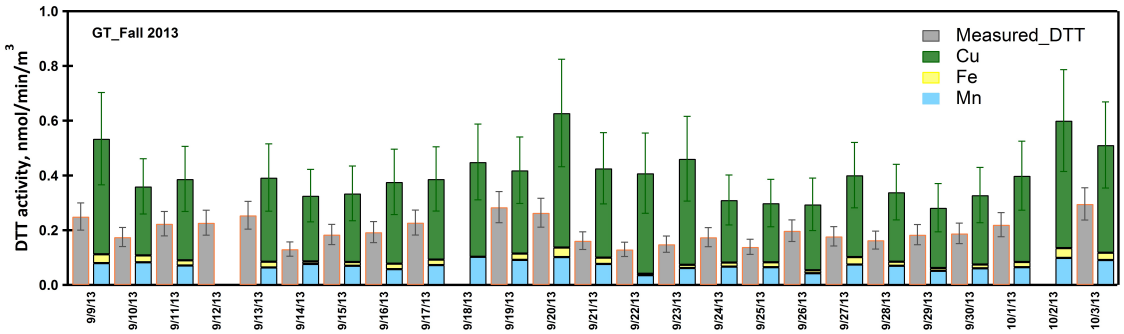
GT_Fall 2013
Measured_DTT
Cu
Fe
Mn
DTT activity, nmol/min/m3
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0.6
0.4
0.2
0.0
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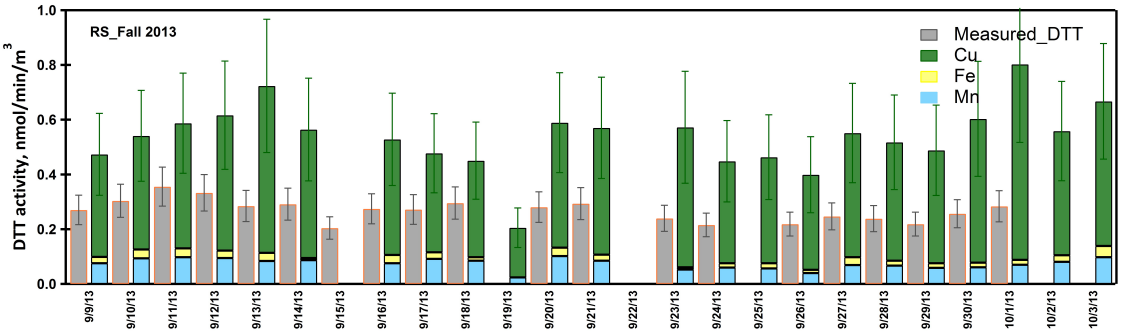

Figure RR1: Comparison of Measured DTT activity and the estimated DTT activity from Cu, Mn and Fe based on the equations derived in Charrier and Anastasio, 2012 in all of the SCAPE samples.

Notes:

1. Uncertainties in the estimated activity (shown as the error bars) have been propagated from the individual measurements
2. No bars have been shown in samples where metals or DTT couldn't be measured due to analytical problem in the system