ALS Environmental

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# Variation of Naphthalene Results and its Significance when reporting F2 in Waters

## BACKGROUND

In 2011 ALS moved to TRH/BTEXN reporting in preparation for the NEPM. The addition of Naphthalene would facilitate the calculation of F2, when TRH only was requested. This avoided additional costs for the industry. This also presented a conundrum when two Naphthalene results were reported – one with BTEX and one with PAHs.

Soon after, ALS began to field questions about discrepancies between Naphthalene from volatiles analysis (purge and trap GC/MS analysis) and semi-volatile analysis (solvent extraction, GC/MS) and which was correct.

## DIFFERENCES BETWEEN METHODS

Typically, where results for waters were sufficiently different, the volatile Naphthalene number tended to be higher than that from the semi-volatile method. This might suggest some problem with the semi-volatile analysis however ALS quality control procedures (surrogates and LCS) did not support this. Further investigation was warranted to understand the root cause of the variations in waters.

## INVESTIGATIONS

ALS used its extensive database of results to look for patterns indicating the cause of the trend. Findings were that the bias was statistically significant for waters (only) and that little of the discrepancy could be associated with laboratory aspects.

## CONCLUSIONS

*ALS has concluded that the lack of preservation of waters (other than chilling), may be the leading cause for the low bias in Naphthalene results (from SVOC bottles). ALS also noted a possible benefit from superior VOC vial seals vs. SVOC bottle seals.* As a result ALS will use the volatile Naphthalene result for F2 calculation for waters.

For consistency and due to there being no discernible difference for soil data, ALS will use the volatile Naphthalene data for the computation of F2 in both soils and waters

## SUPPORTING INFORMATION

### Re-analysis

Investigations on individual cases, where a difference was observed, included ALS going back and performing SVOC analysis for PAHs using a VOC vial (a benefit of ALS miniaturisation). This typically yielded a Naphthalene result closer to the volatile result than the original extraction of the 100 mL semi-volatile sample.

### Microbiological and Spiking Tests

One particular sample indicated a very large discrepancy and still had sufficient unpreserved sample available post analysis and reporting. This sample was used in a study which also included testing for Hydrocarbon Utilising Bacteria (HUB). The trial was performed in duplicate, spiking 20µg/L of BTEX and Naphthalene into the sample in preserved and unpreserved VOC vials. Unpreserved vials were analysed immediately as a 'Zero hour control'. The remaining pairs of preserved and unpreserved vials were incubated at 21 degrees for eight days and then analysed.

**The results were unequivocal.** Unpreserved samples returned results <LOR for all but Benzene i.e. 90% of Benzene was lost and >95% of TEX and Naphthalene. For the preserved controls, BTEX and Naphthalene recovered fully post incubation period. Importantly, this sample recorded positive HUB results.

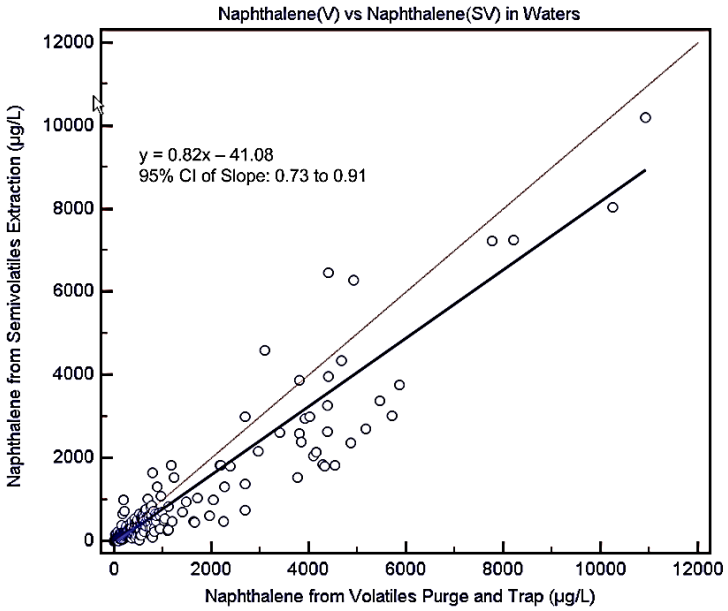
This data supports preservation and clearly shows why the volatile analysis is more appropriate for Naphthalene and F2 calculation particularly when biological degradation is actually occurring (Natural attenuation or otherwise) at your site.

### Data Mining

ALS also queried a large population of samples where volatile and semi-volatile Naphthalene's were both performed. This proved that lower surrogate recoveries were not associated with lower Naphthalene results in semi-volatile analyses.

## RESULTS AND DATA - WATERS

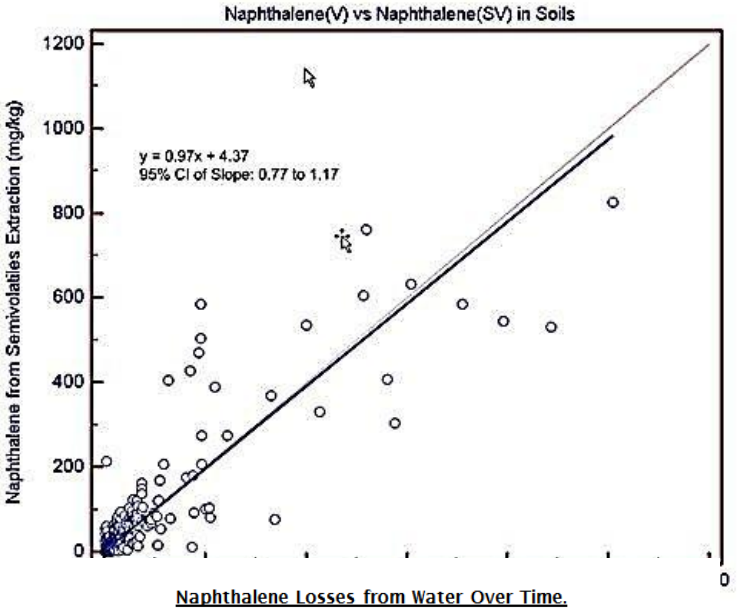
A plot of Naphthalene results obtained by volatile and semi-volatile techniques show the trend of a low bias for semi-volatile results compared to volatile results in Water (see adjacent with the brown line indicating method equivalence i.e. no bias). This was based upon a random population of approximately 700 water samples across all ALS Australian Laboratories.




## RESULTS AND DATA - SOILS

A plot of Naphthalene results obtained by volatile and semi-volatile techniques for soils shows no significant trend or bias for semi-volatile results compared to volatile results (see adjacent with the fine line indicating method equivalence i.e. no bias). This was based upon a random population of approximately 700 soil samples across all ALS Australian Laboratories.

It should be noted that for soils the identical container of sample is used for volatile and semi-volatile analysis. Key differences in analysis are primarily due to the use of Methanol for the volatile Naphthalene extraction and DCM/Acetone for the semi-volatile extraction of PAHs.




## Losses over time from Preserved VOC vials

ALS has conducted a number of studies on losses of VOCs from real samples in preserved vials over the years. The adjacent graph measures losses for samples chilled to 4.3ºC, 7.7ºC and a room temperature of 24.1ºC. These results are uncorrected for surrogate recoveries and include analytical variation. The key points to note are the trend for gradual VOC losses over 14 days and no significant different between temperatures. This supports earlier findings and indicates that preservation (in VOC vials) for Naphthalene is robust.