

To:	Environment Agency	From:	Envireau Water
Ref:	P:\TE KMA Monitoring 2018 (2335)\40 - Reporting\Duplicates\TN r2.docx	Pages:	9
Re:	KMA water quality results – review of blank and duplicate data	Date:	12/01/2018

## 1 Introduction

This technical note has been prepared by Envireau Water in response to comments raised by the Environment Agency in EPR Compliance Assessment Report 402444/0298598 [Ref. 1] and provides an update of the laboratory anomalies that have been noted in weekly surface water and groundwater monitoring at the KMA Wellsite. The anomalies concern reproducibility of the following blank and duplicate data:

14th Dec 17  
 blank sulphate 0.8 mg/L  
 blank anionic surfactants 0.4 mg/L  
 blank Petroleum hydrocarbons (EPH) 100 µg/L  
 blank boron in the blank 13 µg/L  
 S4 duplicate Nitrate 13 and 24 mg/L  
 S4 duplicate COD 20 and 38mg/L

5th to 6th Dec 17  
 blank total dissolved solids 116mg/L  
 blank sulphate 0.6 mg/L  
 blank boron 38 µg/L  
 blank Anionic surfactants 1.6 mg/L  
 G3 duplicate Anionic surfactants 0.3 and 1.2mg/L  
 G3 duplicate Arsenic <2.5 and 6.1 µg/L

29th Nov 17  
 blank dissolved methane 18 µg/L  
 blank total dissolved solids content 79 mg/L  
 blank boron 18 µg/L  
 S1 duplicate dissolved methane 1 µg/L and 12 µg/L

22nd Nov 17  
 blank Anionic surfactants 0.7mg/L

Duplicate samples comprise two separate samples from the same source of the “real” primary samples, whilst blank samples comprise distilled water that has been obtained from a single supplier, in two batches. There have been no changes to the sampling technique during the period of monitoring and all the above analysis is performed by Jones Environmental Laboratory (JEL).

The reproducibility of the above analytical parameters is considered in the following sections.

## 2 Boron

JEL's method statement notes that boron is analysed by ICP-OES methods, which is a robust analytical method for boron, although interferences with iron and chromium are known [Ref. 2].

Figure 1 shows the concentrations of boron detected in primary samples and in blanks since April 2017.

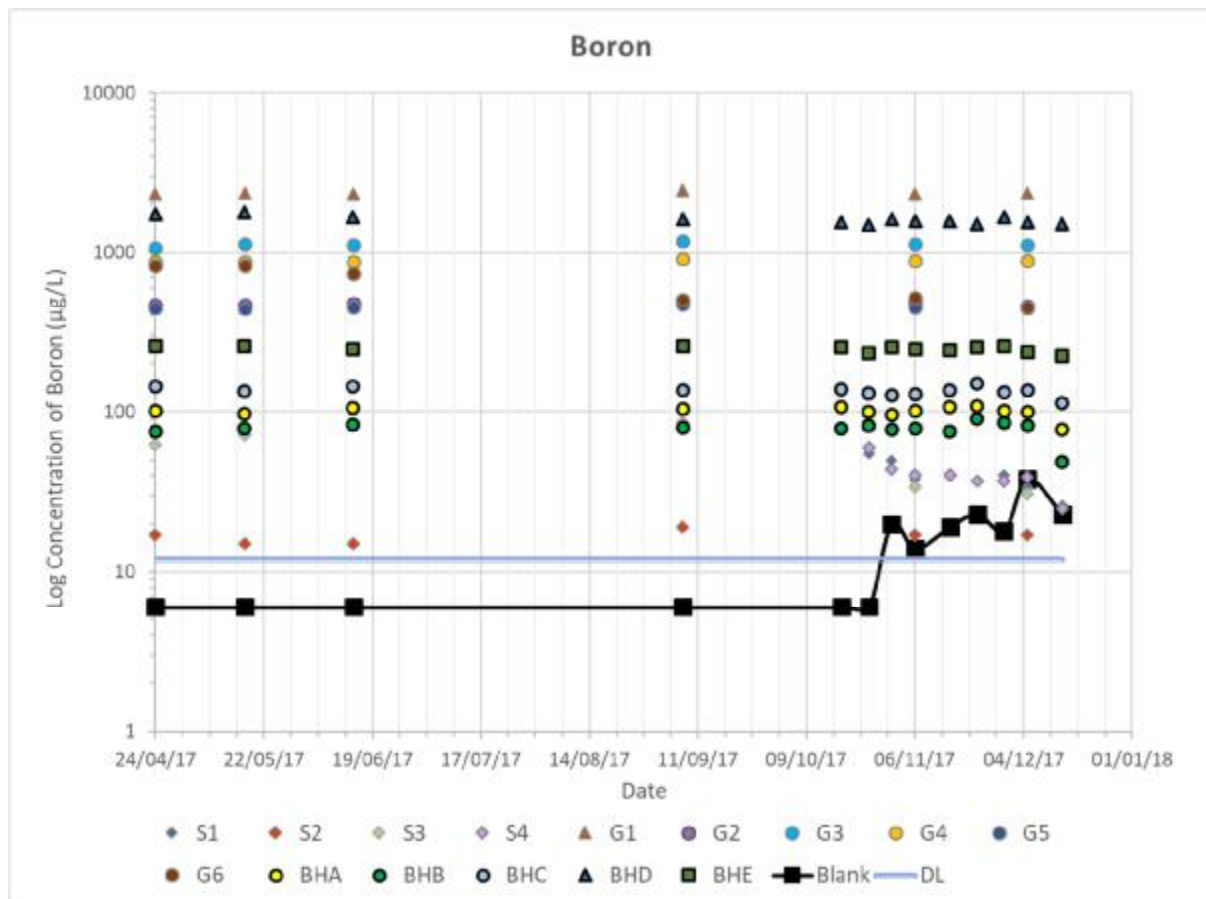


Figure 1. Concentrations of boron reported for KMA water samples (excluding duplicates) from April – December 2017. Values < detection limit are plotted at  $\frac{1}{2} \times$  detection limit.

Figure 1 shows that until 31 October 2017, the blank samples returned values below the analytical detection limit and from 31 October onwards, the blank samples returned values above the analytical detection limit (varying from 14 to 38 µg/L). Two possibilities to explain this are:

- That the nature of the laboratory sample preparation or analysis has changed since 31 October 2017.
- That the nature of the distilled water submitted as the laboratory blank has changed since 31 October 2017.

Note that there is no sign of the “real” samples having experienced a systematic rise in boron concentrations since October 2017 (rather the opposite, in fact), and therefore there is no suspicion of the groundwater samples having been “contaminated” with boron or the analysis method being substantially compromised.

Due to the increase to weekly monitoring in October 2017, Envireau Water obtained a second batch of distilled water from the supplier, which has been used for the preparation of blank samples since 31 October onwards. Envireau Water has asked the supplier to confirm whether there have been any known changes in

the method of production of the distilled water between the first and second batch of distilled water but is still awaiting a response.

It would appear that the second batch of distilled water may be different from the first, or that the second batch has become lightly contaminated. It is noted that the following are possible sources of contamination:

- 1) Boron is present in some detergents.
- 2) Boron may possibly be leached into water in small quantities by storage in, or passage through, borosilicate glass (which is common in laboratory / chemical ware).
- 3) Boric acid (a potent source of boron) is used in other analyses, notably in standard analytical procedures for determination of anionic surfactants (see below).

JEL has confirmed that the samples were received in the correct containers and their own internal QA/QC data (for replicate samples of known concentration) is within acceptable limits. JEL run their own blank samples alongside the real samples in the laboratory and these do not show positive detects.

Envireau Water still has samples from both the first and second batches of distilled water. It is therefore proposed to submit these to JEL for analysis, with the expectation that the sample of the first batch of distilled water will be below limit of detection and that the sample from the second batch will be above this. Duplicate samples will also be submitted to another laboratory for analysis. The findings will be reported to the Environment Agency.

### 3 Anionic Surfactants

JEL's method statement notes that anionic surfactants are analysed by the methylene blue assay. This is a colorimetric method which returns the concentration of methylene blue active substances (MBAS) in water. These substances include carboxylates, organic sulphates (e.g. lauryl sulphate), sulphonates and phosphates.

The following table and graph (Table 1 and Figure 2) shows the concentrations of anionic surfactants returned in primary samples and in blanks. It also shows the "reproducibility" for replicate samples, where:

$$\text{Reproducibility} = \frac{\text{Concentration in primary sample}}{\text{Concentration in duplicate sample}}$$

Where one or both of the samples is below the JEL detection limit (<0.2 mg/L), the value has arbitrarily been set to half the detection limit (i.e. to 0.1 mg/L). From Table 1 and Figure 2, it can be seen that:

- The results show very little consistency between sampling rounds.
- Detects at >1 mg/L have been noted in all sampling rounds in samples from various sampling points, although higher levels of detection are typically reported after c. 31 October 2017. This can be clearly seen in the median value returned from all samples during the sampling round. The reproducibility is typically around 1 (which it should be) but does on occasion vary from 0.25 to 4.
- After 15 November 2017, the blank sample has consistently returned a detect between 0.7 and 1.6 mg/L.
- Anionic surfactants are detected even in the deep boreholes samples from BHD and BHE, which would be the least likely to contain anthropogenic chemicals.

Table 1 Concentrations of anionic surfactants reported for KMA water samples, together with reproducibility for duplicate samples, from April – December 2017. Values < detection limit (0.2 mg/L) are set at ½ × detection limit (0.1 mg/L).

Anionic Surfactants mg/L	24/04/17	17/05/17	14/06/17	07/09/17	18/10/17	25/10/17	31/10/17	06/11/17	15/11/17	22/11/17	29/11/17	05/12/17	14/12/17
<b>S1</b>						0.4 (<0.2)	0.4	0.7	0.9	1.7	1.8 (1.4)	0.3	0.2
<b>S2</b>	0.5	0.8	0.7	0.1				0.4				1.1	
<b>S3</b>	0.7	0.9		0.1				0.1				0.7	
<b>S4</b>						0.5	0.7	0.3	1.2 (1.3)	0.6	1.1	1.9	1.5 (1)
<b>G1</b>	1	0.4	1.1	0.1				0.1				1.3	
<b>G2</b>	1	0.5	0.7	0.1				0.4				0.4	
<b>G3</b>	0.7	0.3	1.3	0.1 (0.1)				0.1 (0.1)				0.3 (1.2)	
<b>G4</b>	0.2	0.1	1 (1.2)	0.1				0.1				0.3	
<b>G5</b>	0.6	0.7	0.7	0.1				0.3				0.9	
<b>G6</b>	0.5	0.9	1.1	0.5				0.6				1.9	
<b>BHA</b>	0.1	0.3	1.1	0.1	0.1	0.2	1.4	0.3	0.3	1 (0.7)	1.1	1	1.2
<b>BHB</b>	0.2 (<0.2)	0.4	1.1	0.1	0.1	0.1	1	0.6	1.4	0.4	0.8	1.4	0.5
<b>BHC</b>	0.2	0.1	0.4	0.1	0.1	0.3	0.8	0.4	0.3	0.2	0.5	0.8	1.5
<b>BHD</b>	0.1	0.4	1.3	0.1	0.1 (0.2)	0.2	0.7	0.5	0.3	1.2	1.2	1.1	1.6
<b>BHE</b>	0.3	1.4 (1)	1	0.1	0.4	0.2	0.9 (0.7)	0.4	0.4	0.4	0.6	1.2	1.6
<b>Blank</b>	0.1	0.1	1.1	0.1	0.1	0.1	0.1	0.1	0.8	0.7	1.2	1.6	0.7
<b>LOD</b>	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
<b>Reproducibility</b>	2.00	1.40	0.83	1.00	0.50	4.00	1.29	1.00	0.92	1.43	1.29	0.25	1.50

Note: Values reported in brackets (xx) represent duplicate sample analysis result

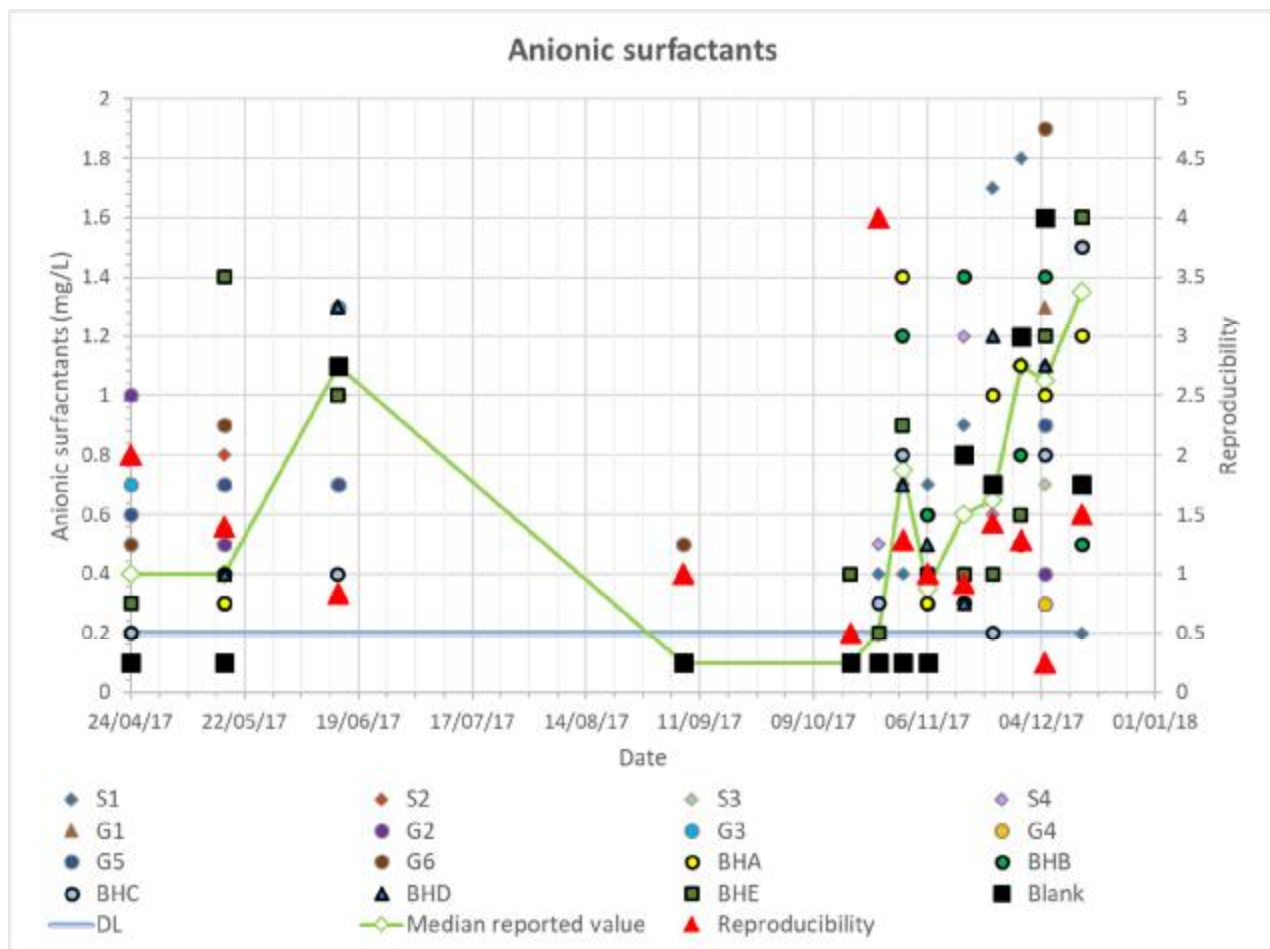


Figure 2. Concentrations of anionic surfactants reported for KMA water samples, together with reproducibility for duplicate samples, from April – December 2017. Values < detection limit are set at ½ × detection limit.

The following should be noted:

- The ASTM has, in fact, withdrawn the MBAS assay (ASTM D2330-02) as a standard method, pending review [Ref. 3].
- NATA (Australian accreditation authority) identified risks of false positives for MBAS analyses and recommended an additional sublation step to avoid these [Ref. 4]. JEL has confirmed that they have not adopted this recommendation.
- The method is subject to some interferences (including with chloride in high concentrations, although this should not affect the blank or shallow groundwater samples [Ref. 5]).
- The method does not distinguish between artificial surfactants and natural carboxylic acid anions (e.g. palmitic or stearic acids).

The reproducibility of the anionic surfactant data could therefore be attributed to:

- A fundamental problem with the reproducibility of the laboratory method and an issue with false positive detects. JEL has confirmed that their own internal QA/QC data (for replicate samples of known concentration) is within acceptable limits, but they have not analysed their own blank samples alongside the real samples.
- As regards the issue of false detects in blanks, it is possible that the blank samples (or the flasks in which they are submitted) have become contaminated (e.g. with detergents). It is interesting that

the worst blank “detects” for anionic surfactants coincides with the period of positive boron detects in blanks. There is potentially a link here to the distilled water used as part of the sampling programme.

- It is also possible that some of the detects in the groundwater samples could be ascribed to the occurrence of natural carboxylic acids, rather than artificial surfactants or detergents. Ref. 6 confirms the ubiquity of natural carboxylic acids in groundwater, although typically at the µg/L rather than mg/L range.

To investigate this further, Envireau Water proposes to submit a set of duplicate samples from the next sampling round to an alternative laboratory that has adopted the NATA recommendations.

#### 4 Sulphate

The Environment Agency has noted the reporting of a blank determination of 0.6 mg/L sulphate from the sampling round conducted on 05 – 06 December and 0.8 mg/L on 14 December. These two occurrences are isolated and marginally above the analytical detection limit of 0.5 mg/L. The sample from 14 December was reanalysed and the result was found to be <0.5 mg/L.

Such a low level of sulphate is well below the several tens of mg/L recorded in all other groundwater samples (except BHE), and thus arguably has little practical implication for the veracity of the results. Envireau Water will however monitor the future concentrations of sulphate in blanks to evaluate whether this detect represents more than an isolated minor false positive.

#### 5 Arsenic, Dissolved Methane, COD

The Environment Agency has noted isolated occurrences where duplicate samples exhibited a poor degree of reproducibility for these three parameters. Figure 3 shows the reproducibility with time, where

$$\text{Reproducibility} = \frac{\text{Concentration in primary sample}}{\text{Concentration in duplicate sample}}$$

and also, concentrations below the detection limit are arbitrarily set to a value of  $\frac{1}{2} \times$  detection limit.

Figure 3 shows that the reproducibility for *arsenic* is rather good (most values close to 1). There are discrepancies on two occasions:

- On 31 October 2017, when the duplicates returned 2.6 and <2.5 µg/L.
- On 05 – 06 December, when the duplicates returned 6.1 and <2.5 µg/L.

The first occurrence provides a result that is just in excess of the limit of detection. The latter discrepancy is a more notable issue and is essentially an isolated instance of poor reproducibility. Envireau Water will therefore continue to monitor this parameter for further instances of poor analytical reproducibility.

The graph shows that the reproducibility for *COD* is also rather good (most values close to 1), especially given that COD is a multi-stage “wet chemical” hot digestion technique. There are notable discrepancies on two occasions:

- On 24 – 25 April, when the duplicates returned 13 and 23 mg/L.
- On 15 November, when the duplicates returned 12 and <7 mg/L.

Given the inherently tricky nature of the COD analysis and that the discrepancies are around 50%, rather than orders of magnitude, these discrepancies do not impact the overall veracity of the analyses. However, Envireau Water will continue to monitor this parameter for further instances of poor analytical reproducibility.

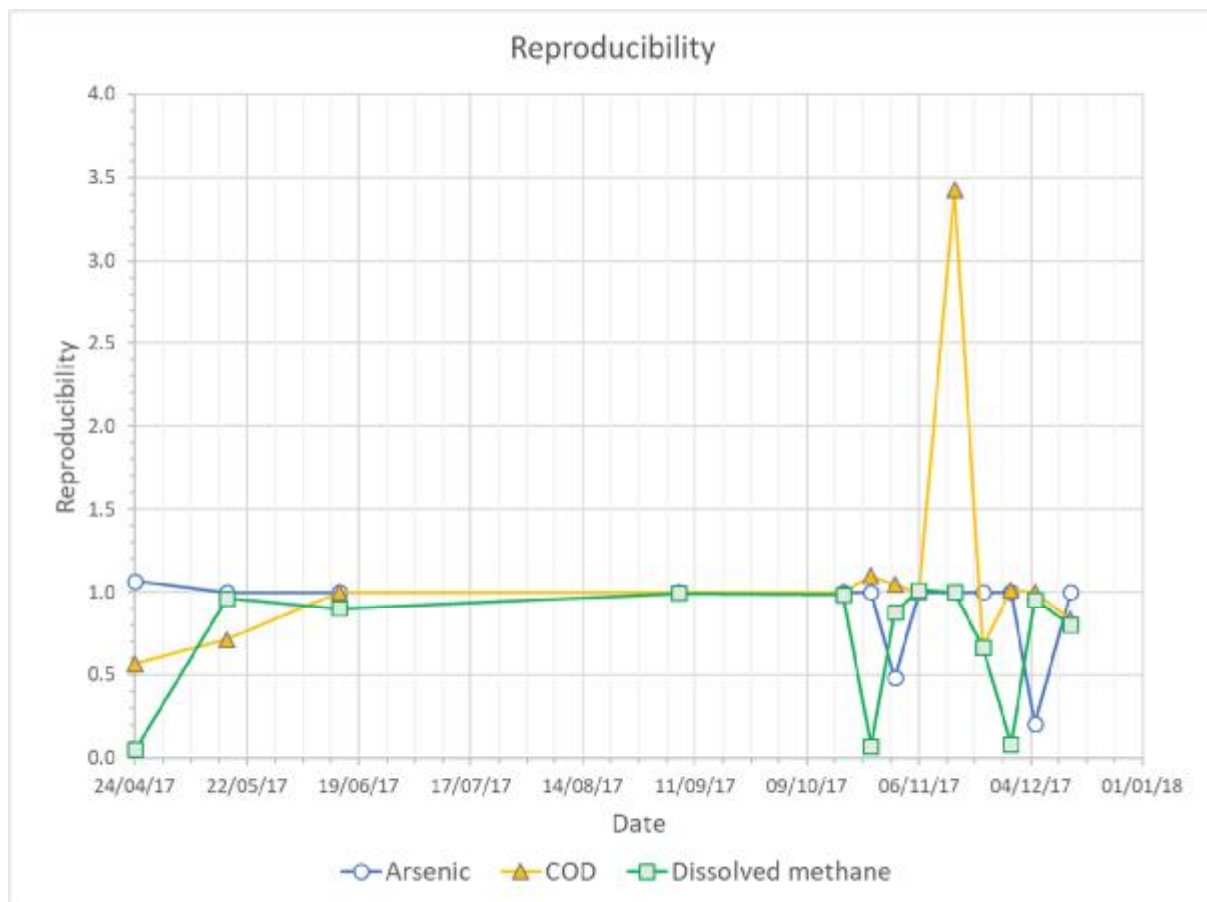


Figure 3. Reproducibility for duplicate samples for methane, COD and arsenic in KMA samples, from April – December 2017. Values < detection limit are set at ½ × detection limit.

Figure 3 also shows that the reproducibility for *dissolved methane* is also rather good (most values close to 1), especially given that the sampling and analysis must be done without any loss of dissolved gas or gas exchange with the atmosphere. There are discrepancies on three occasions and all of these involve methane concentrations at low levels:

- On 24 – 25 April 2017, when the duplicates returned 10 and <1 µg/L. On the same date, the blank returned a value of 13 µg/L, suggesting that, on this date, the issue may have been with false low-level methane detects rather than poor reproducibility in itself.
- On 25 October 2017, when the duplicates returned 7 and <1 µg/L. On the same date, the blank returned a value of 11 µg/L, suggesting that, on this date, the issue may have been with false low-level methane detects rather than poor reproducibility in itself.
- On 29 November, when the duplicates returned 12 and 1 µg/L. On the same date, the blank returned a value of 18 µg/L, suggesting that, on this date, the issue may have been with false low level methane detects rather than poor reproducibility in itself.

The reproducibility of the methane data is examined in more detail in Figure 4.

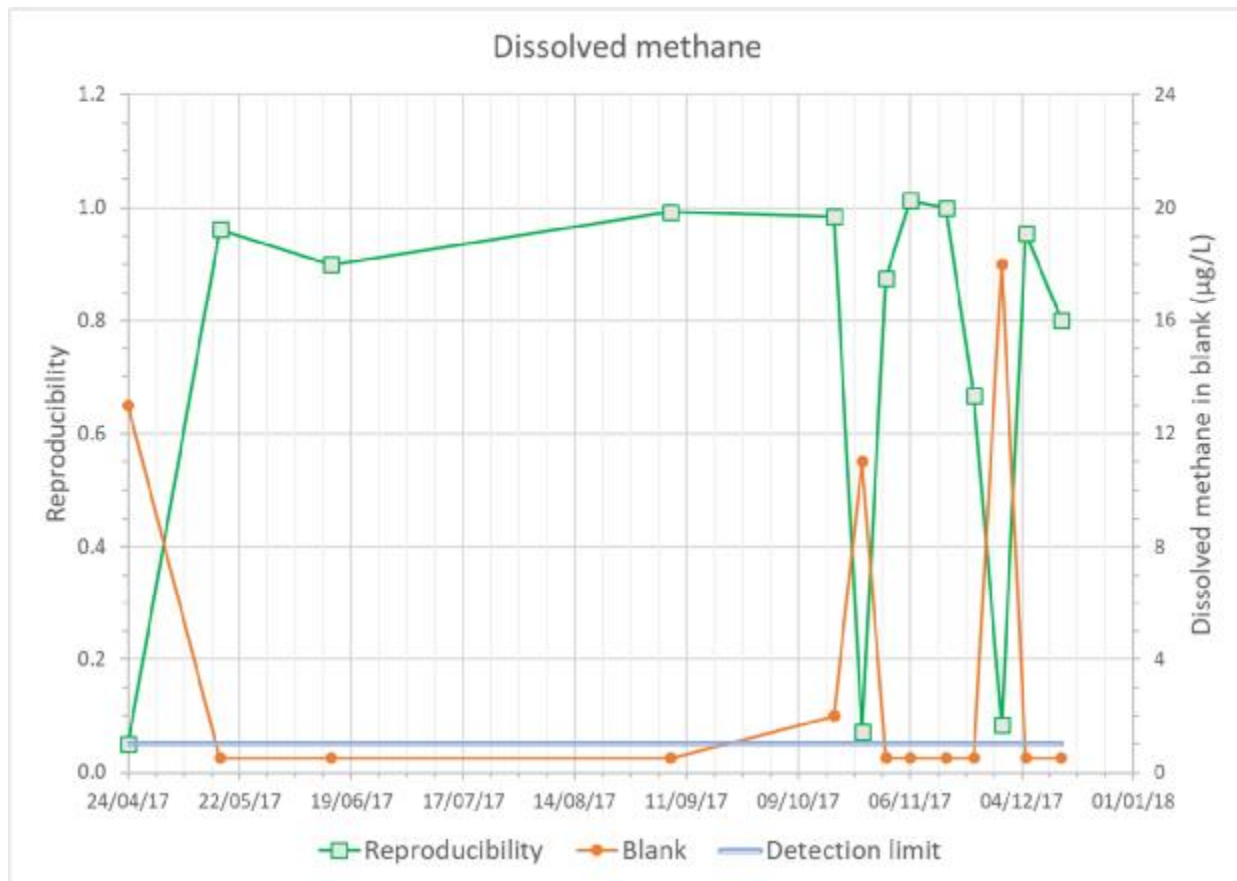


Figure 4. Concentrations of dissolved methane reported for KMA water samples, together with reproducibility for duplicate samples, from April – December 2017. Values < detection limit are set at ½ × detection limit.

Figure 4 suggests that, on certain dates, blank samples are subject to low (<20 µg/L) false positive detects of methane, and on these dates, poor reproducibility is also exhibited at low concentrations. This could be ascribed to either the presence of low methane concentrations in the laboratory air, or unflushed methane in the laboratory equipment (among other possible explanations). However, given the generally otherwise good reproducibility of methane at higher concentrations, this essentially represents an issue for very low concentrations of methane and does not affect the veracity of the detects at more significant concentrations.

## 6 Total Dissolved Solids (TDS)

The Environment Agency also notes the presence of unrealistically high TDS in two blank samples. Envireau Water also notes that the electrical conductivity of the water was considerably higher than would be expected for ultrapure water and, as discussed in the other sections above, is examining the source of the distilled water used for blanks.

## 7 Petroleum Hydrocarbons (EPH)

The Environment Agency also notes the presence of petroleum hydrocarbons (EPH) in the blank sample on 14 December 2017. This sample was reanalysed and the result confirmed. On the same date, EPH was not detected in any the “real” water samples. This is a relatively isolated instance (although a low-level EPH detect was also noted on 06 and 22 November 2017) and suggests an issue with the distilled water used for blanks.



## 8 Nitrate

The Environment Agency also notes a discrepancy between primary and duplicate samples for nitrate at one of the surface water monitoring locations on 14 December 2017. Reanalysis confirms that both the primary and duplicate samples contain approximately 21mg/l nitrate (as NO<sub>3</sub>).

## 9 Summary

The reproducibility of the KMA monitoring data is good, with the exception of the anionic surfactant data, where there is an identified risk of obtaining false positives with the analysis method. This will be investigated further by submitting a set of duplicate samples from the next sampling round to another laboratory that has adopted an additional sublation step in the method to try and avoid the issue.

The issues with false positives in blank samples appears to be related to a second batch of distilled water that has been used during sampling since 31 October 2017. This may also have a bearing on the reproducibility of the anionic surfactant data, which is generally poorer after this date. Envireau Water proposes to submit samples from the two batches of distilled water used during sampling for analysis at JEL and another laboratory. It is expected that this will confirm the issues with blank samples from the second batch of distilled water.

In any event, a new supply of distilled water will be obtained and a sample will be analysed in the laboratory to confirm suitability for use during future sampling rounds.

Envireau Water  
12/01/2018

## REFERENCES

- Ref. 1: EPR Compliance Assessment Report 402444/0298598. Environment Agency, 20/12/2017.
- Ref. 2: Kmiecik E., Tomaszewska B., Wątor K. & Bodzek M. (2016) Selected problems with boron determination in water treatment processes. Part I: comparison of the reference methods for ICP-MS and ICP-OES determinations. *Environ. Sci. Pollut. Res. Int.* 23: 11658–11667. doi: 10.1007/s11356-016-6328-7
- Ref. 3: <https://www.astm.org/Standards/D2330.htm>
- Ref. 4: [www.alsglobal.com%2F-%2Fmedia%2Fals%2Fresources%2Fservices-and-products%2Fenvironmental%2Fenviromails-au%2Fenviromail-105---the-differences-between-mbas-and-anionic-surfactants-as-mbas.pdf&usg=AOvVaw2u1cVrm3ho94V0z4FfSNBw](http://www.alsglobal.com%2F-%2Fmedia%2Fals%2Fresources%2Fservices-and-products%2Fenvironmental%2Fenviromails-au%2Fenviromail-105---the-differences-between-mbas-and-anionic-surfactants-as-mbas.pdf&usg=AOvVaw2u1cVrm3ho94V0z4FfSNBw)
- Ref. 5: George A.L. & White G.F. (1999) Optimization of the methylene blue assay for anionic surfactants added to estuarine and marine water. *Environmental Toxicology and Chemistry* 18: 2232–2236. doi:10.1002/etc.5620181016
- Ref. 6: Thurman E.M. (1985) Carboxylic acids and phenols. In: "Organic Geochemistry of Natural Waters". *Developments in Biogeochemistry, Vol 2.* Springer, Dordrecht. doi: 10.1007/978-94-009-5095-5\_6