

Clariant, Llantwit Fardre, Post-Remediation – Technical Note: Groundwater / Surface Water Trend Analysis

Between September and December 2015, remedial excavation works were undertaken to remove identified areas of soil contamination at the Clariant Llantwit Fardre site. The remediation works were required to reduce the contaminant mass associated with former production areas, effluent drainage systems and the effluent treatment / storage area and to allow Clariant to surrender two Environmental Permits relating to the former speciality chemical manufacturing operation.

Groundwater and surface water monitoring was undertaken during the remedial works, at selected downgradient pathway and receptor monitoring locations. The agreed Remediation Strategy included a six-month period of post-remediation monitoring to assess contaminant concentration trends following the removal of the main source areas. The Remediation Strategy identified a risk that a six-month period may not be sufficient for trends to stabilise and decrease following the ground disturbance associated with the remediation excavation works, and therefore included an option to extend monitoring to up-to 12 months and / or to provide additional in-situ remediation for any pockets of groundwater within the shallow Boulder Clay that were continuing to exhibit high contaminant concentrations (i.e. residual contamination mass resulting in exceedance of the off-site surface water Environmental Quality Standards (EQS values).

This Technical Note provides a review of the six-month groundwater and surface water monitoring data, in order to allow an informed discussion of the key contaminant trends and a decision on further monitoring.

All of the source areas targeted by the remediation works were located beneath areas of concrete hardstanding or roadways, which had effectively isolated the shallow soil contamination from rainfall infiltration. Removal of the hardstandings and excavation / disturbance of the underlying soils exposed each of the source areas to rainfall, infiltration and potential leaching / mobilisation. Additionally, the soils deemed suitable for re-use as excavation backfill also contained elevated concentrations of the key contaminants of concern, although at significantly lower concentrations than those removed off-site for disposal.

Monitoring undertaken during the remediation phase identified some concentration spikes for primary contaminants within groundwater/surface water. A degree of mobilisation was anticipated due to the disturbance of the ground and the significant increase in rainwater infiltration resulting from the removal of hardstandings and opening up of the excavation areas.

To remove the effects of any upwards concentration trends associated with the active excavation works, this trend analysis covers the period 24th November 2015 to 8th June 2016, i.e. from the post-excavation peak readings and includes the backfill/disposal phase (November-December 2015), plus six rounds of monthly post remedial monitoring for the months January to June 2016. Trends have been assessed using the Mann-Kendall statistical analysis tool within AECOM's ESdat environmental data management application.

The following table shows only those analytes where an Up / Down Mann-Kendal trend has been identified from elevated levels recorded in November 2015 over the six month post-excavation monitoring period from January to June 2016.

Trend Analysis using Mann Kendal Trend with Confidence = 0.1 (90%) Nov 2015 to June 2016			
Location Code	Analyte	Max Value Last	Mann Kendal Trend
Groundwater (GW) Wells			
BH504	Tert-butyl Alcohol	No	Up
	Phenol	No	Up
	Vinyl Chloride	No	Down
BH519	Vinyl Chloride	Yes	Up
	Ethane	No	Up
BH522	Tetrachloroethene	No	Down
	Trichloroethene	No	Down
	cis-1,2-dichloroethene	No	Down
BH523	cis-1,2-dichloroethene	No	Down
Surface water (SW) locations			
SS02	Tetrachloroethene	Yes	Up
	cis-1,2-dichloroethene	Yes	Up
SS05	Tetrachloroethene	No	Down
	Trichloroethene	No	Down
	cis-1,2-dichloroethene	No	Down
SS06	Tetrachloroethene	No	Down
	Trichloroethene	No	Down
	cis-1,2-dichloroethene	No	Down

Groundwater Observations and Trends

Note: No sample was recovered from BH519 during the April 2016 monitoring. During the June 2016 round samples were recovered from only BH504, BH519 and BH523 as remaining locations were dry.

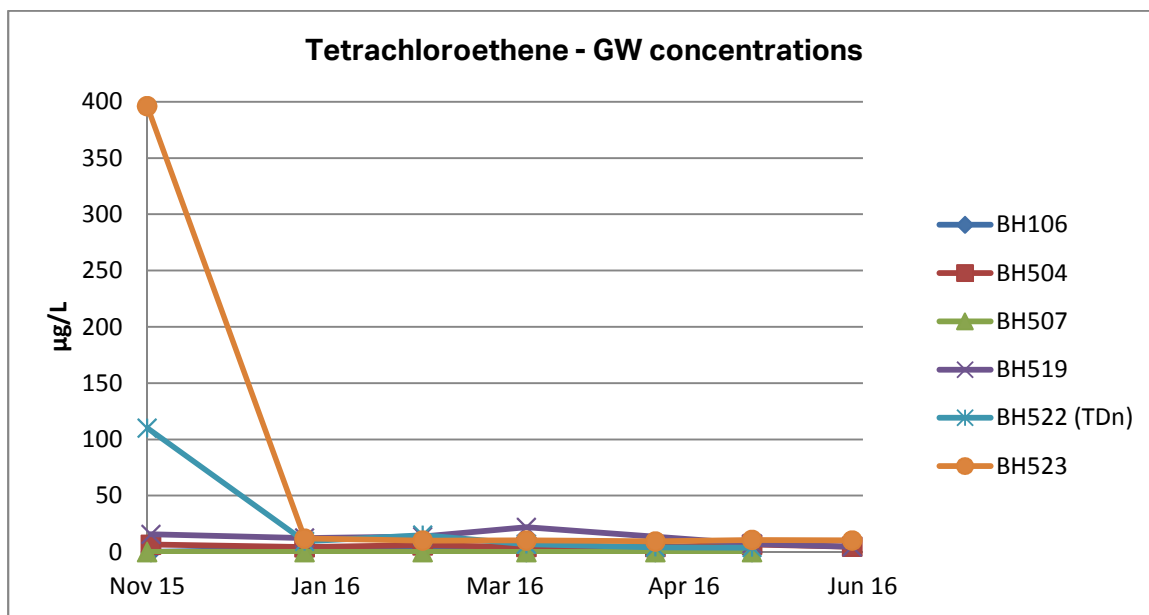
Note: The Remedial Target Values (RTVs) and Freshwater EQS (where available) are referred to below for reference and will apply to the off-site surface water locations for final validation purposes.

The remediation areas and monitoring locations are shown on the attached figure.

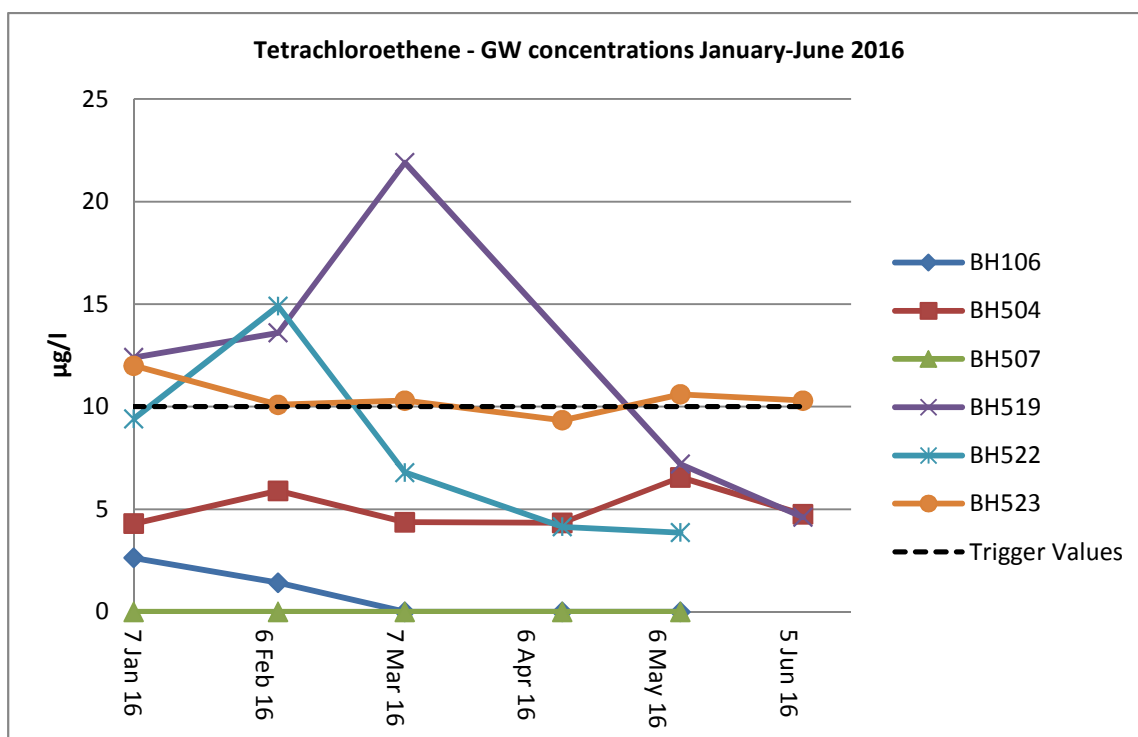
Tetrachloroethene (PCE):

PCE is considered to be the principal "primary contaminant" for the chlorinated hydrocarbon contamination that has been identified at the site. PCE was used as a solvent by Nipa Laboratories during the 1970s-1990s (prior to Clariant's purchase of the site). Trichloroethene (TCE), cis 1,2-Dichloroethene (cis1,2-DCE) and Vinyl Chloride (VC) are all breakdown products derived from this primary contaminant (although TCE may also have been used on site and could therefore be present as a primary contaminant and / or as a breakdown product of PCE).

Groundwater concentration trends for PCE in the downgradient pathway monitoring wells are therefore considered to provide a good indication of the effectiveness of the contaminant source removal works.



TDn = Trend Down (Mann Kendal 90%)

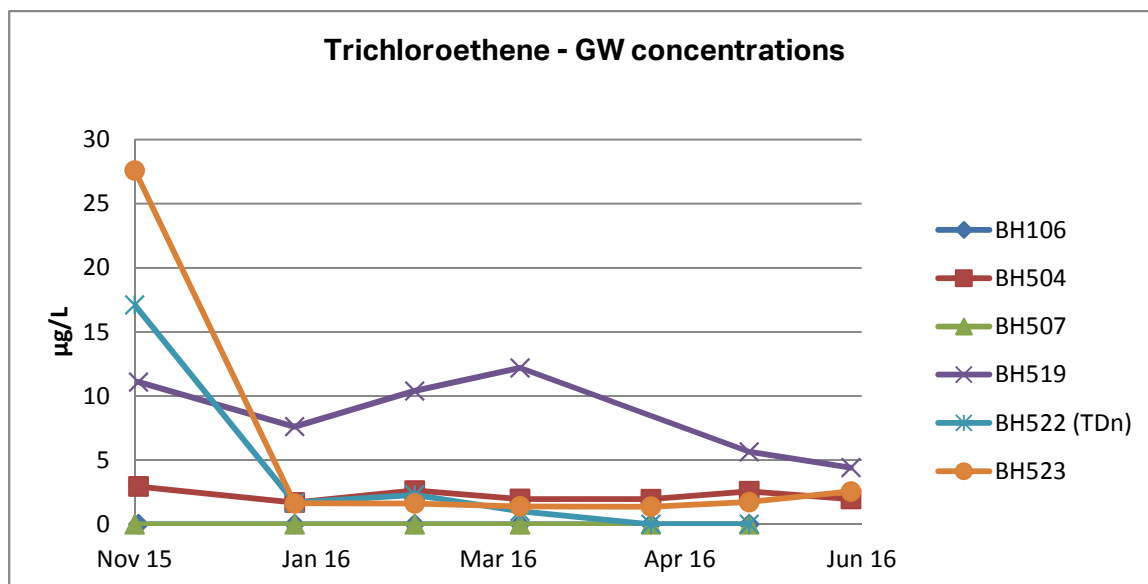


- A significant decrease (statistical trend down - TDn) is reported for BH522 from November 2015 (110µg/l) to May 2016 (3.86µg/l). No sampling was possible in June 2016 as the well was dry.
- A significant decrease is reported for BH523 from November at 396µg/l to June at 10.3µg/l (including a statistical trend down from November 2015 to April 2016). Concentrations between January and June 2016 range between 12µg/l to 9.34µg/l, fluctuating around the RTV of 10µg/l.
- Concentrations at BH519 (downgradient of former P1 production area) were above the RTV of 10µg/l throughout January to April 2016, with a maximum value of 21.9µg/l in March 2016. No sample was recovered in April 2016 as the well was dry. Samples recovered in May and June 2016 indicate a decrease in concentration to below the RTV at 7.2µg/l and 4.61µg/l respectively.

Trichloroethene (TCE):

TCE could be present as either a primary contaminant (i.e. derived from operational usage / release), or as a secondary breakdown product of PCE. Increasing / decreasing trends within groundwater could therefore represent a balance between contaminant mass reduction from source removal, primary contaminant mobilisation from ground disturbance and production of secondary TCE through the degradation of PCE.

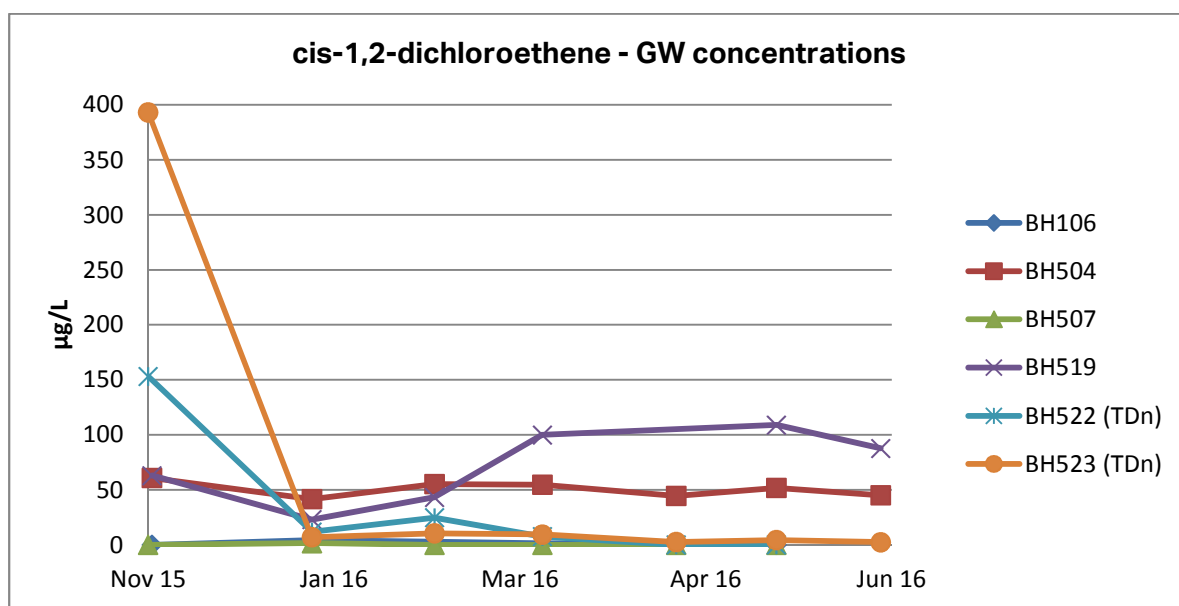
Cis1,2-DCE and VC are further breakdown products on the PCE > TCE > cis1,2-DCE > VC > ethane / ethane / Cl⁻ degradation chain.



- At BH504 (one of two downgradient wells close to the site boundary) concentrations decreased from a peak in November 2015 of 2.94µg/l to 1.97µg/l in June 2016, though given slight increases in February and May no statistical downwards trend is reported.
- No Detection was reported for all samples from BH106 (the second downgradient well close to the site boundary) and BH507 (downgradient of the Effluent Treatment Plant, (ETP)) from January to May 2016 (no sampling was possible in June 2016 as the well was dry).
- At BH519 concentrations ranged from 7.62µg/l to 12.2µg/l between November 2015 to March 2016, close to or exceeding the RTV of 10µg/l.
- A decrease is noted in BH519 from above the RTV at 12.2µg/l in March to below the RTV at a concentration of 4.42µg/l in June 2016.
- A Mann-Kendal decreasing trend is reported for BH522 from a maximum concentration of 17.1µg/l in late November with concentrations an order of magnitude lower for January to March 2016 and less than the Method Detection Limit (MDL) in April and May 2016.
- A decrease in concentration is evident at BH523 from a maximum concentration of 27.6µg/l in late November to within a range of between 1.37µg/l to 2.56µg/l for the period January to June 2016, though the maximum of this range was reported for the sample from June 2016.

Cis-1,2-dichloroethene (Cis-1,2-DCE):

Cis1,2-DCE is only likely to be present in groundwater as a degradation product from the breakdown of TCE (and the precursor primary contaminant, PCE). Therefore, any increases in cis1,2-DCE concentrations will reflect suitable conditions for natural attenuation (NA) processes and the ongoing degradation of TCE; whereas decreases in cis1,2-DCE could reflect an overall reduction of contaminant mass within the groundwater system or a change (can be seasonal) in groundwater conditions to less favourable NA conditions.

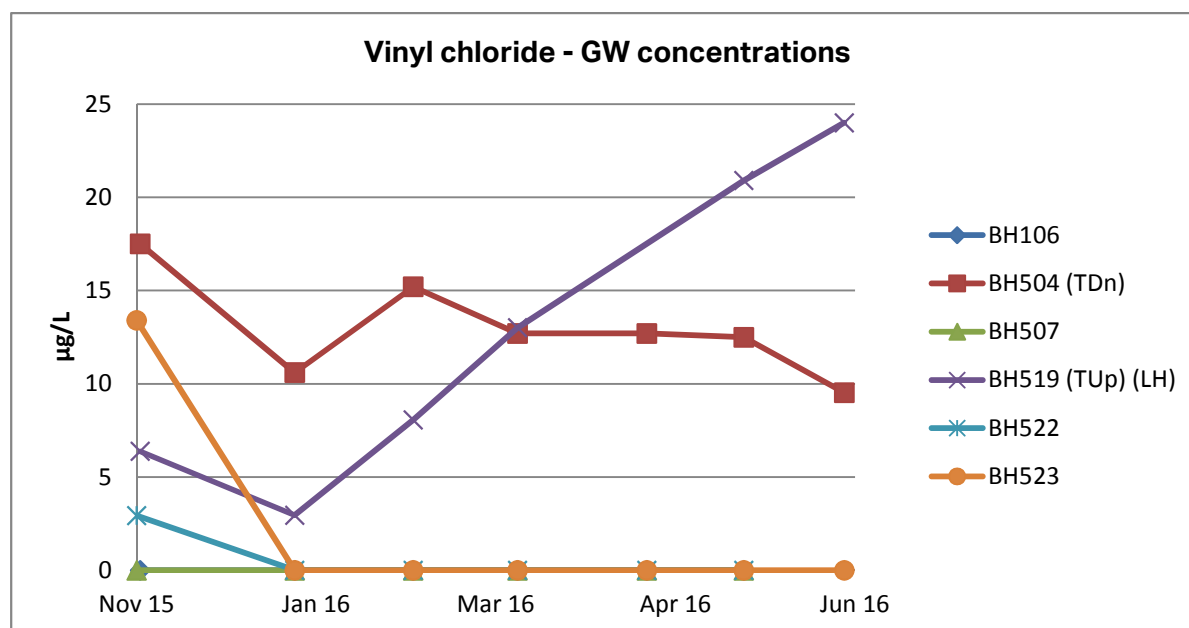


- Concentrations of cis1,2-DCE have been decreasing in samples from all locations with the exception of those from BH519.
- At BH519 the November 2015 peak was 63µg/l decreasing to 23µg/l in January 2016. However, an increase was reported from January to May 2016 at a maximum concentration of 109µg/l in May 2016. In June 2016 the concentration had decreased marginally to 87.8µg/l though still above the RTV value of 70µg/l.
- It is notable that the increases in cis1,2-DCE at BH519 mirror (but are higher than) the increases in TCE and PCE at the same location and timeframe. BH519 is downgradient of P1 and these trends suggest that the disturbance / mobilisation of PCE (and TCE) within the source area has resulted in an increase in NA.
- At BH522 a downward trend has been reported from a maximum concentration of 153µg/l in November 2015 to less than the MDL in April and May 2016 (no sampling was possible in June 2016 as the well was dry).
- At BH523 a downward trend of two orders of magnitude has been reported from a maximum concentration of 393µg/l in November 2015 to 2.49µg/l in June 2016.

Vinyl Chloride:

VC is the final chlorinated hydrocarbon species on the PCE > TCE > cis1,2-DCE > VC > ethene / ethane / Cl⁻ degradation chain.

The presence and concentration of VC is therefore an indicator of NA processes. As with cis1,2-DCE, any increases in VC concentrations will reflect suitable conditions for natural attenuation (NA) processes and the ongoing degradation of PCE > TCE > cis1,2-DCE; whereas decreases in VC could reflect an overall reduction of contaminant mass within the groundwater system or a change in groundwater conditions to less favourable NA conditions.



Note: LH = Last value highest

TUp = Trend Up (Mann Kendal 90%)

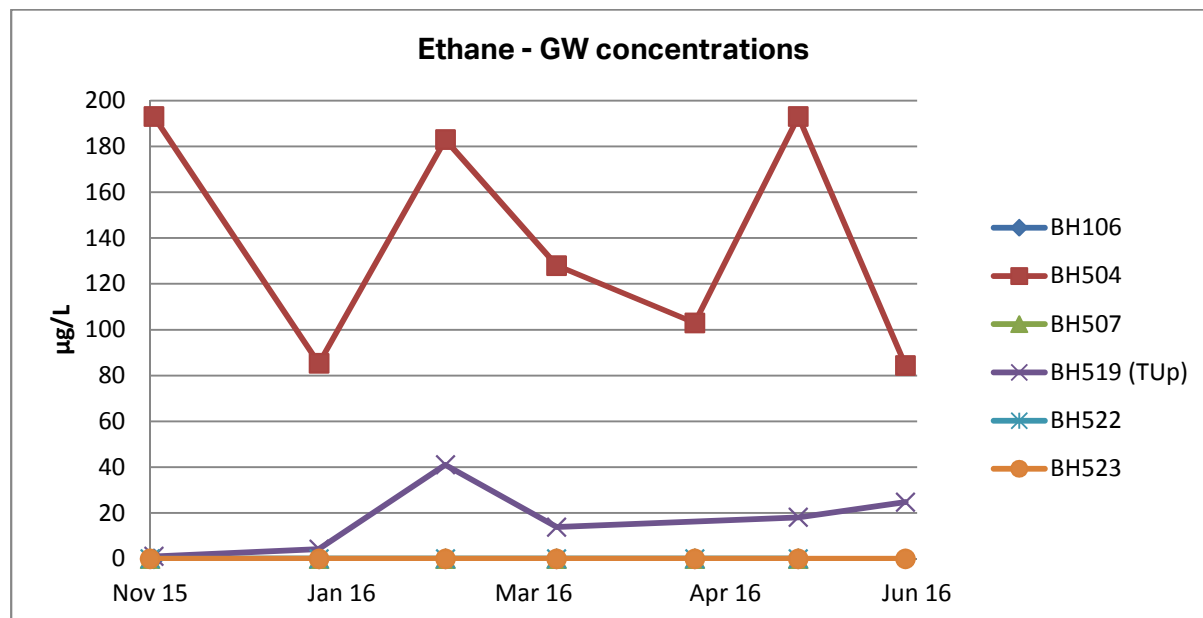
- No concentrations above the MDL have been reported in samples from BH106, BH507, BH522 or BH523 between January 2016 and May 2016 (June 2016 for BH523).
- At BH519 an increasing trend (TUp) is identified at a maximum concentration of 24µg/l (exceeding the RTV of 10µg/l) in the sample for June 2016. In this case the maximum concentration reported is the most recent (Last value highest – LH).
- As for cis1,2-DCE, the increase in VC concentration at BH519 is interpreted as a positive indication that the chloroethene species are being naturally attenuated through reductive dechlorination – i.e in-situ bioremediation is naturally occurring at this location.
- At BH504 a decreasing trend is identified from a concentration of 17.5µg/l in November 2015 to 9.53µg/l in June 2016.

Ethene and Ethane:

Ethene and ethane are the final products of the natural reductive dechlorination of the PCE > TCE > cis1,2-DCE > VC > ethene / ethane / Cl⁻ degradation chain.

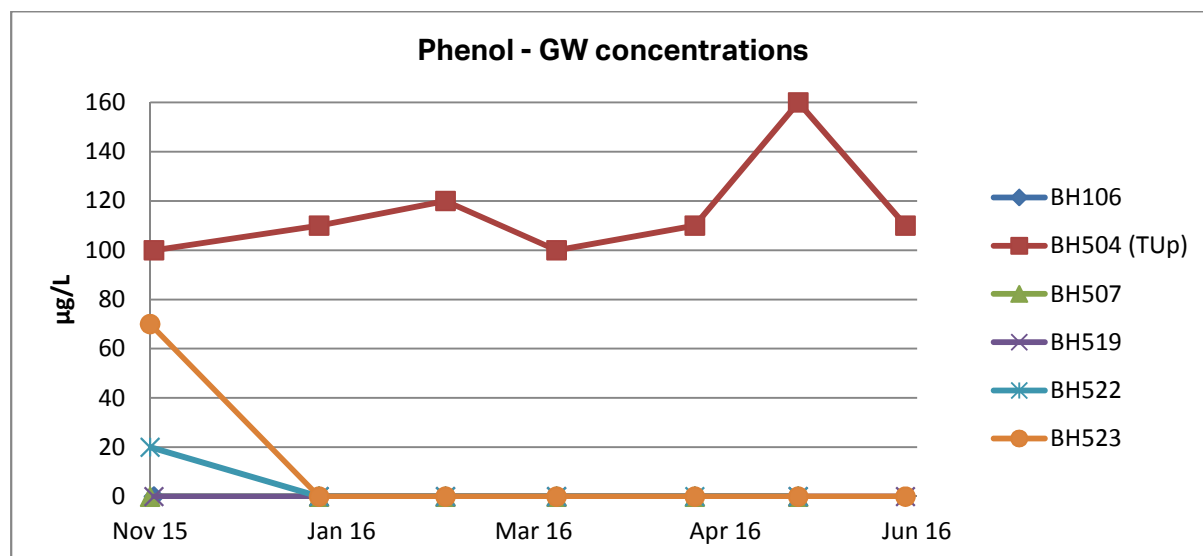
Ethene: All samples were reported as <MDL with the exception of two detections reported for the March and May 2016 samples from BH519 at concentrations of 1.44µg/l and 1.36µg/l respectively.

Ethane:



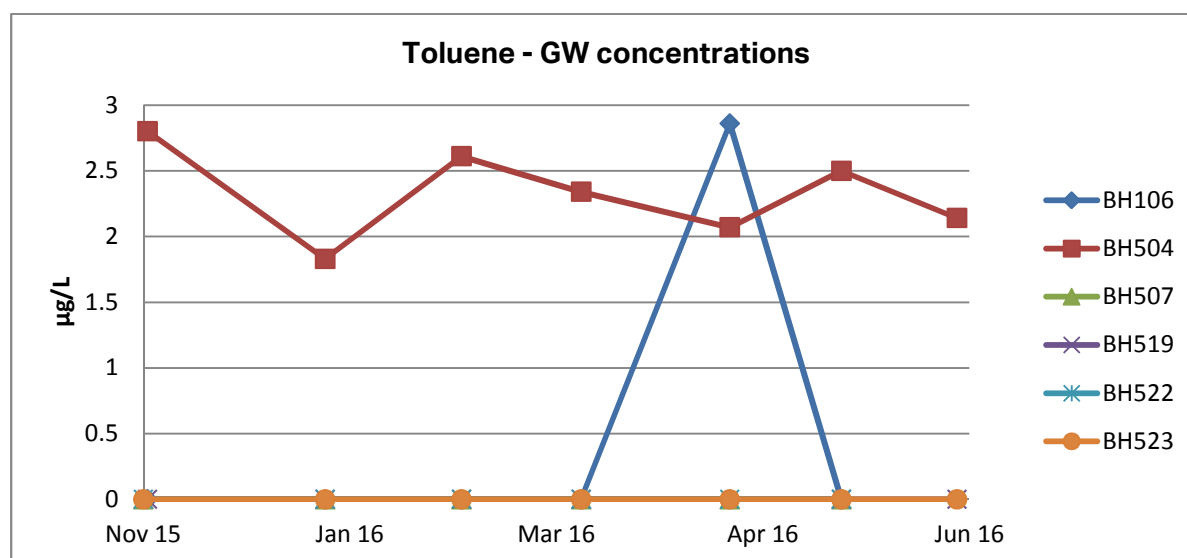
- No concentrations above the MDL have been reported in samples from BH106, BH507, BH522 and BH523.
- At BH519 an increasing trend is identified at a maximum concentration of 41µg/l (exceeding the RTV of 10µg/l) in the sample for February 2016. Concentrations for March to June 2016 are marginally lower and range from 13.8µg/l in March to 24.7µg/l in June. As with cis 1,2-DCE and VC, this data indicates that NA is occurring in the vicinity of BH519.
- An elevated fluctuating concentration is evident in samples from BH504 with a maximum concentration of 193µg/l reported for samples from both November 2015 and May 2016. No clear trend is evident. However, the concentration reported for June 2016 is the lowest of the range at 84.3µg/l. The high ethane and reducing cis 1,2-DCE and VC concentrations at BH504 suggest that the final dechlorination step is occurring in the vicinity of BH504.

Phenol:



- An upwards trend is reported for BH504 with elevated concentrations ranging from 100µg/l (November 2015 and March 2016) to 160µg/l (May 2016) against an EQS of 7.7µg/l.
- At BH522 and BH523 concentrations decreased from excavation peaks of 20µg/l and 70µg/l respectively in November 2015 to <MDL in January 2016.

Toluene:

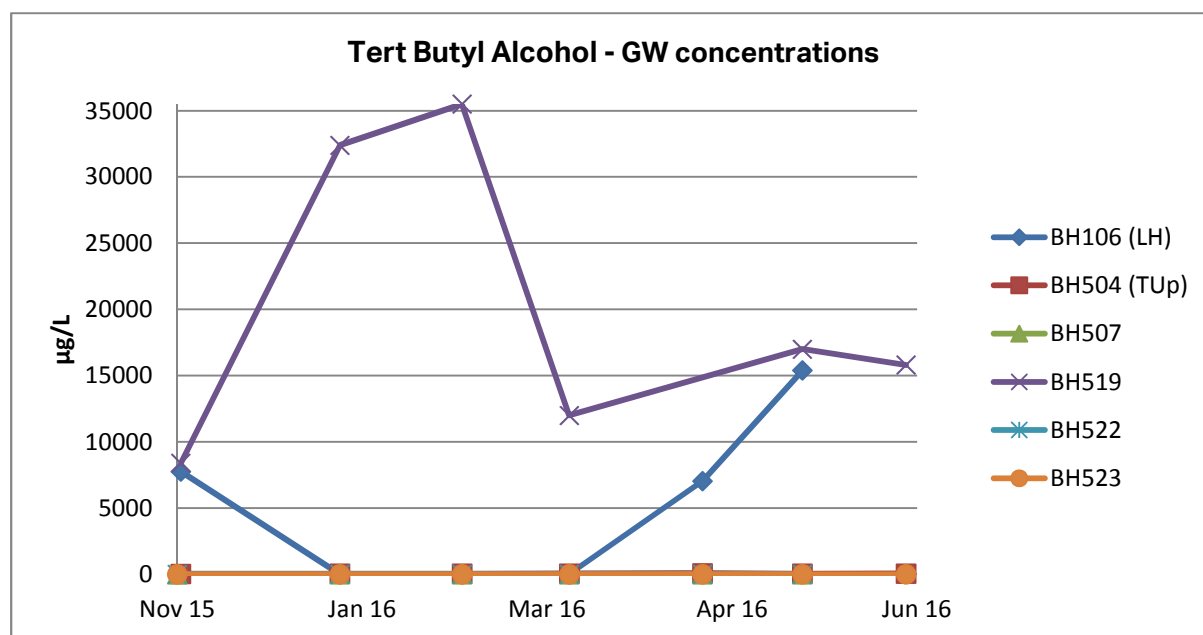


- No concentrations above the MDL have been reported in samples from BH507, BH519, BH522 and BH523
- In samples from BH504 toluene is consistently reported, ranging from 1.83µg/l to 2.8µg/l. In general a slight decrease is noted from the excavation phase concentration of 2.8µg/l (November 2015) to 2.14µg/l in June 2016 (RTV 50µg/l) though no statistical trend is reported.
- At BH106, one concentration was reported above the MDL in April 2016 at 2.86µg/l.

Methanol:

Methanol was not reported above the MDL during the monitoring period.

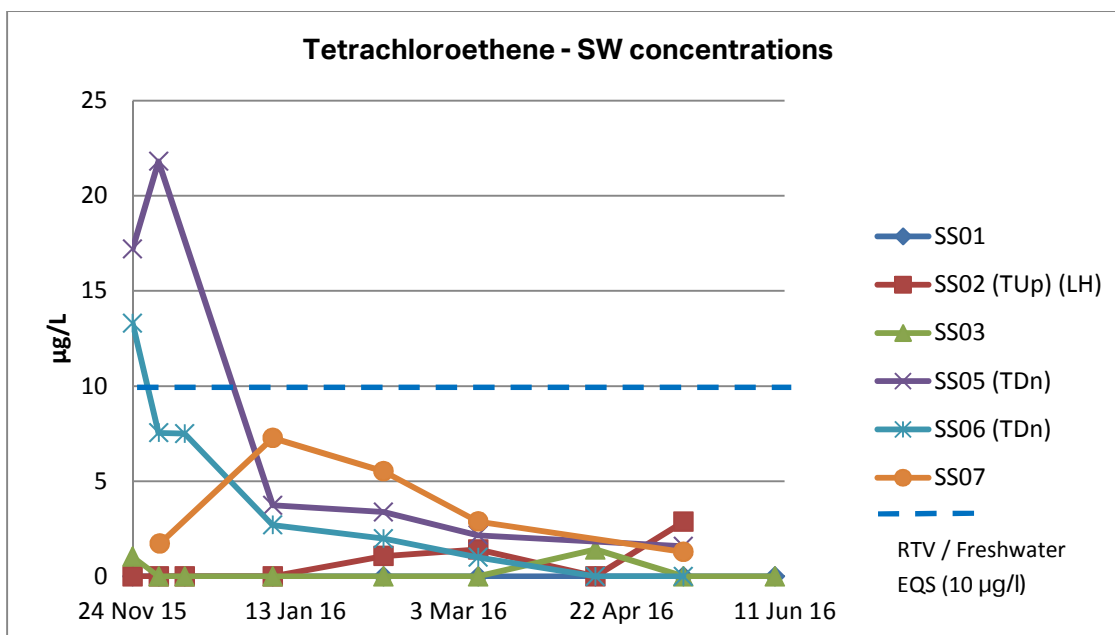
Tert-butyl Alcohol (TBA):



- No concentrations above the MDL have been reported in samples from BH507, BH522 and BH523.
- At BH519 no clear trend is reported though concentrations are highest at this location with a sharp increase from 8,400µg/l in November 2015 to 35,500µg/l in February 2016, reducing sharply to 12,000µg/l in March 2016. Concentrations again increased in May to 17,000µg/l, reducing slightly in June to 15,800µg/l (no sample could be collected in April). The concentration reported for June 2016 is nearly twice that reported in November 2015.
- The concentration reported in the sample from BH106 was greater than the Freshwater EQS (6,640µg/l) and the site RTV (40µg/l) at 7,760µg/l in November 2015 decreasing to <MDL in January 2016. However, April and May's results report a sharp increase to 7,040µg/l and 15,400µg/l respectively.
- At BH504 an upwards trend is reported with concentrations generally increasing since November 2015 from 31.5µg/l to 88.4µg/l in April. Concentrations for May and June are lower at 46.2µg/l and 65.1µg/l respectively.

Surface Water Observations and Trends

PCE:



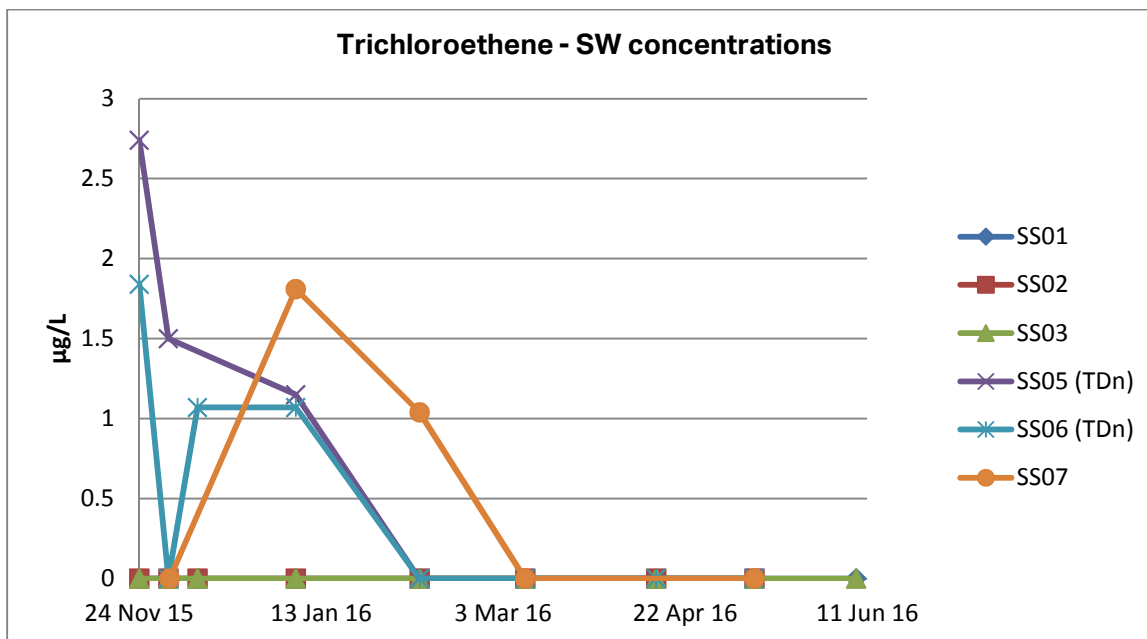
Note: LH = Last value highest

TDn = Trend Down (Mann Kendal 90%)

TUp = Trend Up (Mann Kendal 90%)

- A slight increase was reported at SS02 (beyond the eastern site boundary) from <MDL to 1.07µg/l in February and 1.41µg/l in March, reducing to <MDL in April. However, a concentration of 2.87µg/l was reported in the sample from May 2016 resulting in a statistical upwards trend at this location. Concentrations are currently below the RTV of 10µg/l. SS02 is adjacent to the former P1 / P6 / P5 production areas.
- A slight increase from <MDL to 1.4µg/l from March to April was reported for SS03. No concentration was reported above the MDL in May and June 2016.
- A clear downward trend is reported for both SS05 and SS06. Concentrations during the remedial works had briefly peaked above the RTV of 10µg/l at a maximum of 21.8µg/l on the 2nd December 2015 at SS05. In June 2016 the reported concentrations were 1.58µg/l and <MDL respectively.
- At SS07 the concentration increased from 1.72µg/l in December 2015 to a peak of 7.27µg/l in January 2016. Concentrations have been decreasing since to 1.29µg/l in May 2016.
- No sample was collected in June 2016 as the location was dry.

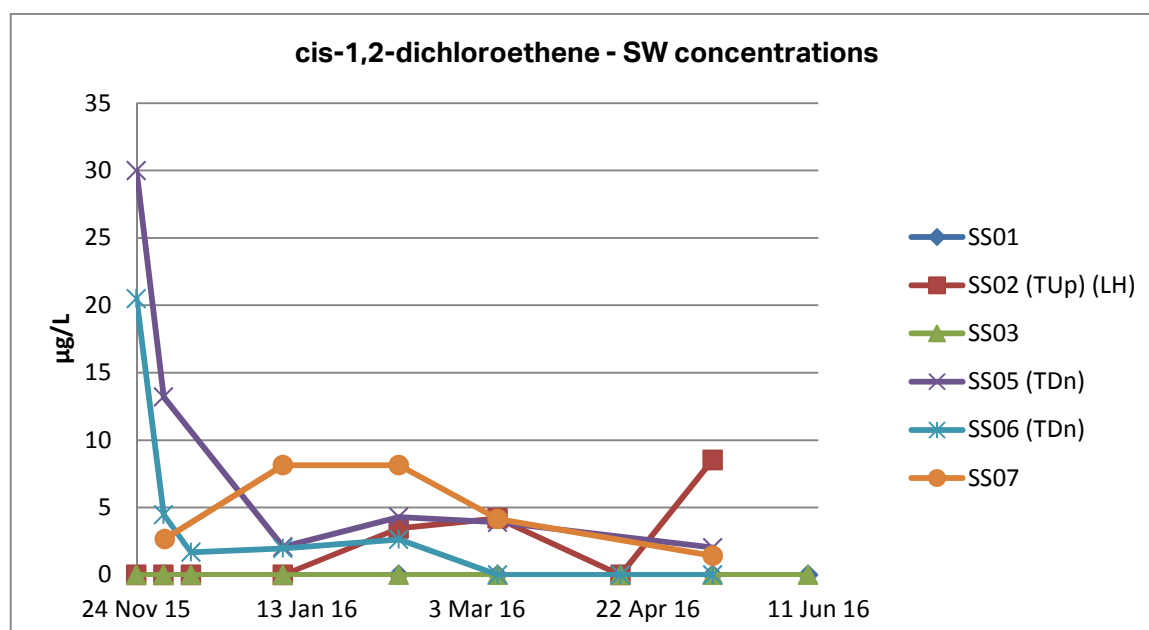
TCE:



Note: RTV / Freshwater EQS = 10µg/l

- No concentrations above the MDL have been reported in samples from SS01, SS02 and SS03.
- A downward trend is reported for SS05 from 2.74µg/l in November 2015 to <MDL (1µg/l) between February to May 2016.
- A downward trend is reported for SS06 from 1.84µg/l in November 2015 to <MDL between February to May 2016.
- At SS07 two detections were reported above the MDL in January and February 2016 at concentrations of 1.81µg/l and 1.04µg/l respectively, reducing to <MDL in March and May 2016.
- The concentrations reported are below the RTV of 10µg/l.

Cis-1,2-DCE:

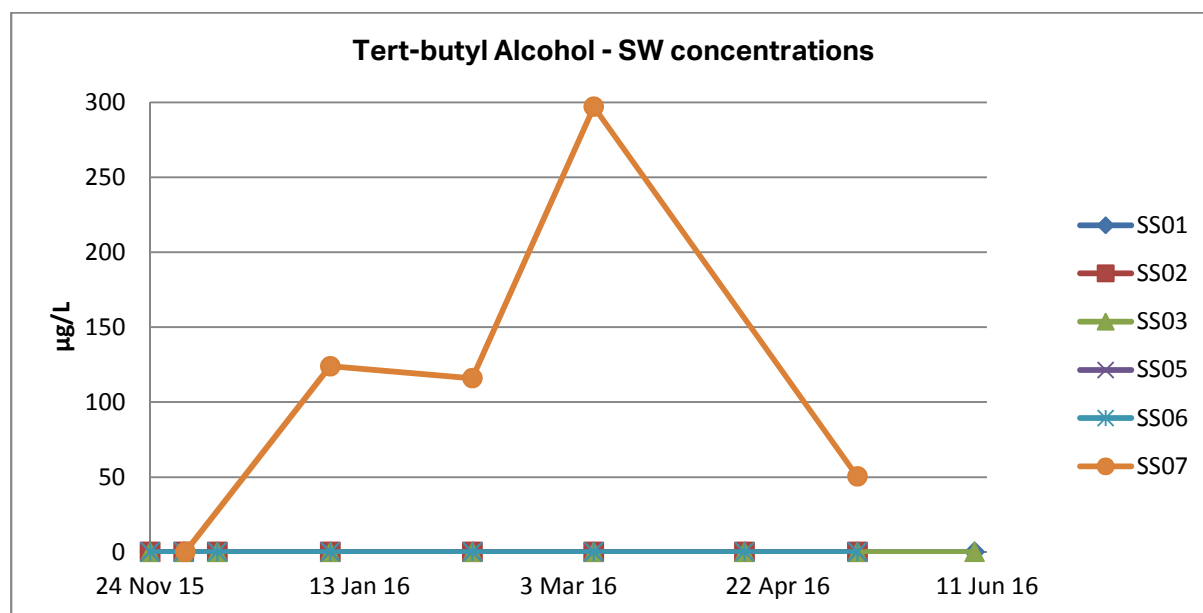


Note: RTV = 70µg/l (Freshwater EQS not available)

- No concentrations were reported above the MDL of 1µg/l in the samples from SS01 and SS03.
- At SS02, after an increase in February and March 2016, Cis-1,2-DCE reduced from 4.2µg/l to <MDL in April. However, in May 2016 a peak of 8.53µg/l was reported, resulting in a statistical upwards trend for this location and maximum value most recent.
- A clear downwards trend is identified at SS05 with a reduction in concentration from 30µg/l in November 2015 to 2.03µg/l in May 2016.
- A clear downwards trend is identified at SS06 with a reduction in concentration from 20.5µg/l in November 2015 to 2.63µg/l in February, reducing to <MDL for March to May 2016.
- The concentration at SS07 appears to be decreasing from a peak of 8.14µg/l recorded in samples from January and February 2016 to 1.42µg/l in May 2016.
- None of the detections reported above the MDL have approached the RTV of 70µg/l.

Vinyl Chloride, Ethene / Ethane, Phenol, Toluene and Methanol were not reported above the MDL.

TBA:



No detection at all locations except for a marked increase at SS07 from ND in December 2015 to 297µg/l in March 2016. The reason for this increase is currently unclear. Sampling of the adjacent discharge manhole prior to remediation reported TBA in groundwater/infiltrated water from the surrounding surface at a concentration of 297µg/l (RTV value is 40µg/l) suggesting a relatively high background level. A sample could not be collected in April or June 2016. The sample for May 2016 reported a concentration of 50.4µg/l, a significant reduction, though still above the RTV of 40µg/l.

Summary

The monitoring so far suggests that concentrations of the primary contaminants are broadly decreasing following some sharp increases resulting from the excavation works. The breakout of extensive areas of concrete, disturbance of ground and of the groundwater levels and increased recharge, resulted in the anticipated mobilisation of some contaminants at that time. Whilst the levels are apparently decreasing (based on six months initial post excavation monitoring), concentrations of some primary contaminants are still elevated compared to the baseline conditions prior to excavation.

Downwards trends for PCE have been identified from excavation peaks for BH522 and downgradient surface water locations SS05 and SS06. SS05 exceeded the RTV of 10µg/l on two occasions at a maximum concentration of 21.8µg/l in December 2015. SS06 marginally exceeded the RTV on one occasion at a concentration of 13.3µg/l in November 2015. In June 2016 concentrations in the on-site wells were below the RTV of 10µg/l with the exception of BH523 at a concentration of 10.3µg/l. One upwards trend has been identified in June 2016 at SS02 to the east of the site at a maximum concentration of 2.87µg/l, below the RTV of 10µg/l.

TCE concentrations within on-site wells in June 2016 are below the RTV of 10µg/l at a maximum concentration of 4.42µg/l in the sample from BH519 (lower than the July 2015 baseline of 5.66µg/l). The maximum detection reported for surface water is 2.74µg/l at SS05 in November 2015. TCE has not been reported in any surface water samples since March 2016. Statistical downward trends are identified for SS05 and SS06, suggesting that up-gradient Natural Attenuation (NA) is taking place.

Statistical downward trends are identified for cis-1,2-DCE at BH522 and BH523. Concentrations in BH519 were increasing to May 2016 but have decreased slightly in June 2016 to 87.8µg/l. This concentration is above the RTV of 70µg/l and higher than the July 2015 baseline of 41.4µg/l, suggesting that a degree of PCE/TCE NA has taken place. At the surface water locations a statistical trend down for cis-1,2-DCE is identified at SS05 (2.03µg/l in May 2016) and SS06 (<MDL in May 2016) whilst the concentration at SS07 also appears to be declining (1.42µg/l in May 2016). An increase has been reported at SS02 (8.53µg/l in May 2016), though the RTV has not been exceeded at any surface water locations based on the monitoring results.

No concentrations of vinyl chloride have been reported above the MDL for samples from BH106, BH507, BH522 or BH523 between January 2016 to May 2016 (June 2016 for BH523). At BH519 an increasing trend is identified at a maximum concentration of 24µg/l (exceeding the RTV of 10µg/l) in the sample for June 2016. In this case the maximum concentration reported is the most recent. This increase in vinyl chloride, coupled with the corresponding decrease in cis-1,2-DCE suggests that natural reductive dechlorination of the primary contaminants is taking place as the baseline concentration was <MDL. At BH504 a decreasing trend in vinyl chloride is identified (9.53µg/l in June 2016) from excavation peaks, and concentrations are comparable with baseline conditions (9.66µg/l). Vinyl chloride has not been reported above the MDL in any of the surface water samples.

At BH519 ethane (as for vinyl chloride) is statistically trending upwards at a maximum concentration of 24.7µg/l in June 2016, supporting the case for ongoing NA. Ethane has only been reported above the MDL in samples from BH519 and BH504. The maximum ethane detections are reported for samples from BH504 though no clear trend is evident (maximum 193µg/l in both November 2015 and May 2016). However, coupled with the decreasing trend in vinyl chloride this further supports the case for active NA. The lowest concentration reported for BH504 was 84.3µg/l in June 2016, lower than the baseline concentration of 136µg/l. This reduction at BH504 may reflect

that more attenuation is taking place at up- hydraulic gradient locations (supported by increases at BH519) as a result of the removal of hardstanding and rain / surface water infiltration. The only detections of ethene were reported at BH519 in March and May at a maximum of 1.44µg/l, again providing evidence of NA. Ethene and ethane have not been reported above the MDL in any of the surface water samples.

Detections of vinyl chloride and ethene/ethane suggests that NA is taking place as these compounds are the degradation breakdown products of PCE, TCE and cis-1,2-DCE. The PCE concentration at BH519 is generally decreasing whilst cis-1,2-DCE increased between February and May 2016 and began to decrease in June 2016. In support of this, concentrations of PCE, TCE and cis-1,2-DCE at downgradient location BH522 are all statistically trending downwards, however, a corresponding increase in breakdown products has not been detected at this location.

A high concentration of TBA is reported in samples from BH519 at 15,800µg/l in June 2016 decreasing from a maximum of 35,500µg/l in February 2016. At BH106, a location in close proximity to SS07, the May 2016 sample was the maximum reported for that location at a concentration of 15,400µg/l (comparable to up-gradient concentrations at BH519). These borehole concentrations exceed the Freshwater EQS of 6,640µg/l (EQS source is the EU probable no effect concentration – PNEC). A concentration increase of TBA is also noted at BH504 (though at far lower levels to 65.1µg/l, exceeding the RTV of 40µg/l). Of the surface water locations, TBA has only been reported at SS07 with an increase from December 2015 (<MDL) to March 2016 (297µg/l). The sample from May 2016 was lower at 50.4µg/l though marginally exceeds the RTV. These concentrations of TBA suggest that further monitoring may be required.

An upward trend in phenol in BH519 at a concentration of 110µg/l in June 2016 (exceeding the RTV of 7.7µg/l) suggests a potential for future impact on the downgradient validation locations SS05/SS06, which may require additional monitoring. However, as of June 2016 no phenol has been reported above the MDL in any of the surface water locations.