GROUND TRUTHING A PFAS MODEL

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ABSTRACT

Understanding the fate and transport of PFAS in affected groundwater aquifers is fundamental to managing the risk associated with these contaminant plumes.

Pattle Delamore Partners Ltd has been involved in an ongoing assessment of the (likely) future behaviour of an existing, large scale PFAS groundwater plume. The initial project objectives were to predict, as far as reasonably practical, the existing extent and concentration distribution of the plume, and how the plume could evolve in the short to long-term future. Quantitative 3D numerical groundwater flow modelling (MODFLOW) and contaminant transport modelling (MT3DMS) was utilised to assist with these complex predictions.

The project has now moved into a validation phase. Additional drilling and groundwater monitoring has addressed areas of the aquifer/hydrological system with previous knowledge gaps, which posed key uncertainties for the regional groundwater resource. The additional data has provided a basis for further validation of the conceptual model, and the predictions of the plume and it's likely future behaviour. This paper will cover the relevant history of the plume, the original plume predictions, as well as presenting results and interpretations from the recent gap filling and validation work .e.g. have we got it *'right'* so far?, what are the ongoing risks?

KEYWORDS

PFAS, Groundwater Resources, Aquifer Management, Numerical Groundwater Modelling, Model Validation

PRESENTER PROFILE

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Aslan is an established hydrogeologist with over 13 years' experience working on large-scale mining, tailings, civil construction, and water resource focused projects. Aslan has specialist groundwater qualifications and skills; including 3D & 2D numerical flow and contaminant/solute transport modelling.

1 INTRODUCTION

Aqueous Film Forming Foams containing Per- and Poly-fluoroalkyl Substances (PFAS) were used for firefighting, fire prevention and firefighting training at a large site in regional New Zealand from the 1980's until at least the early 2000's. The direct application of AFFF to bare soil can result in the contamination of soil and groundwater through leaching and surface water via runoff. PFAS compounds are known to leach from fire training pads over multiple decades (Baduel et al., 2015), and may extend for many 10's of kilometres (Awad et al., 2011; Kwadijk et al., 2014).

Pattle Delamore Partners Ltd has been involved in an ongoing assessment to predict, as far as reasonably practical, the existing extent and concentration distribution of a PFAS groundwater plume which has formed beneath and downgradient of the site. The study has also looked at how the plume could evolve in the short to long-term future. An initial comprehensive sampling programme including several rounds of groundwater and surface water monitoring, undertaken between 2015 and 2018. During the initial sampling programme 297 groundwater samples and 147 surface water samples were collected and analysed for PFAS compounds. This paper specifically focuses on the compounds Perfluorohexane sulfonate (PFHxS) and Perfluorooctane sulfonate (PFOS).

Results and interpretations from the sampling were used for quantitative 3D numerical groundwater flow modelling (MODFLOW) and contaminant transport modelling (MT3DMS) to assist with understanding the current plume, and to make future predictions. Further sampling has been undertaken between 2020 and 2021. The additional data has provided a basis for some validation of the conceptual model, and the predictions of the plume and its likely future behaviour.

2 GROUNDWATER PLUME MODELLING AND EVOLUTION PREDICTIONS

2.1 KEY STUDY OBJECTIVES / QUESTIONS

The questions this assessment sought to address are outlined below:

- How much contaminant mass (PFOS + PFHxS[1]) may be present in the existing plume?
- What is the likely shape of the existing plume?
- What size is the likely area of the plume at or above the current drinking water guideline (≥0.06 µg/L PFOS + PFHxS with Uncertainty of Measurement (UOM))?
- What is the likely size of the plume in the long-term future?
- How long before the plume may decay to be below drinking water guideline?
- What and where are the likely key receptors of the plume?
- How long may the plume take to deplete in area and mass, e.g. how long may it take to halve the current area and mass?

[1] Sum of total PFOS + total PFHxS

Groundwater flow and solute transport modelling (plume modelling), was employed to assist interpretations of how the existing PFOS + PFHxS groundwater plume (the plume) had evolved to present-day form. Simulations were set up within a 3D numerical groundwater flow and solute transport model. Model simulations were 'calibrated' to reasonably match the available observation data and conceptual hydrogeological understanding of the region and the plume.

2.2 APPROACH TO FUTURE PLUME PREDICTIONS

Three different scenarios were adopted for the future plume predictions, these encompassed:

- (A) 'best estimate' – which utilised an assumed 25-yr depletion rate for the soil source zones, run for 125-yrs into the future. This has been adopted arbitrarily as a 'best estimate', and based on case work undertaken by Baduel et al. (2015) in Queensland. PDP undertook a limited literature review to identify potential leaching rates in soils and did not identify any other suitable estimates at the time.
- (B)'instant source zone removal' – which assumes instantaneous removal of the soil source zones, run for 125-yrs into the future.
- (C) 'longer source depletion' scenario – which utilises an assumed 50-yr depletion rate for the soil source zones, run for 250-yrs into the future.

For each of these scenarios, both 'conservative' and 'retarded' transport were assessed – as both were deemed equally plausible with respect to the existing condition calibration. No contaminant decay was incorporated, due to the understanding from available literature that these particular contaminants would require many decades to breakdown, and hence it was not considered an important factor (ITRC, 2018a; ITRC, 2018b). The creation of 'daughter' molecules was also excluded from the simulations.

The sum of PFOS + PFHxS was modelled because of its applicability to the interim drinking water guidelines (HEPA, 2019).

This suite of scenarios was selected as it provided a range of perceived 'best case (B)', 'worst case (C)', and 'most likely case (A)' outcomes. The range of outcomes was required due to key uncertainties, and consequently to provide a basis for environmental management decisions.

As with any type of prediction modelling, and particularly cases where long-term predictions are required, numerous assumptions and uncertainties are inherent. These assumptions and uncertainties must be realised and taken into consideration when making technical interpretations and/or communicating the interpretations to stakeholders.

3 EXISTING PLUME ASSESSMENT & SIMULATION

A general description of the interpreted existing plume (present-day simulation) is provided below:

- The majority of the existing PFOS + PFHxS groundwater plume is likely to have formed from contaminants which have leached through the soil profile and into the groundwater system.

- Area of the plume (PFOS + PFHxS ≥0.06 ug/L) is estimated at 1100 ha to 1600 ha.

- Total PFOS + PFHxS mass of the existing plume (in solution) is estimated between 50 kg to 70 kg. This is considered a best estimate, and realistic estimate with respect to plausible quantities used on-site, however significant uncertainty remains.

- Even though PFOS + PFHxS containing product is no longer used on site, a significant mass of contaminant is still likely to be contained within the surface soils/unsaturated zone from historic use. These areas are termed 'Soil Source Zones' and their presence is expected to provide continued leaching of contaminants to groundwater.

- At least 13 individual onsite Soil Source Zones are either known or suspected and are contributing to the overall plume (the model assumes these are the primary sources of PFAS and therefore assumes the historical information regarding use and storage of AFFF is reliable and complete). In theory, each Soil Source Zone is likely to be producing an individual plume, but due to the geographical spread and nature of the groundwater flow system beneath the wider site, these individual plumes have coalesced into essentially a single plume e.g. a greater plume comprised of a number of smaller plumes. The contour plot on Diagram 4 enables some differentiation of the individual plumes within the greater plume.

- Selected surface water drains that originate on-site and drain off-site were also set as input sources to the plume. These have been incorporated in an attempt to simulate the effect of PFOS + PFHxS being transported from the site via the surface water route, and then discharging from surface water into the adjacent shallow groundwater/aquifer.

- Additional Soil Source Zones may also be present that are yet to be identified. If present, these may be producing additional plumes.

- Surface water has been identified as another key pathway for PFOS + PFHxS contaminant to migrate from site and into groundwater. Surface water flow can move contaminants much faster than groundwater flow, and due to the strong connection between groundwater-surface water within the region, contaminant transport via surface water is a key influencing factor for the groundwater plume. There are three key conceptual methods for this:

    - Run-off containing PFOS + PFHxS that flows into streams/drains which exit the site e.g. run-off from the Soil Source Zones, or from contaminated concrete, etc. Further along the streams/drains, contaminant may discharge into the adjacent shallow groundwater system; where the stream is losing flow and/or during losing conditions.

- Some areas of the groundwater plume are likely to discharge groundwater into streams/drains which are connected to groundwater e.g. are cut below the water table. This moves contaminant from the groundwater system into the surface water system, which can then re-discharge back into the shallow groundwater system further downstream.

- Sediments within the streams/drains may adsorb PFOS + PFHxS (from either of the abovementioned methods), and then these sediments can effectively become off-site Soil Source Zones. These sediments may continue to leach contaminant to both the groundwater and surface water system.

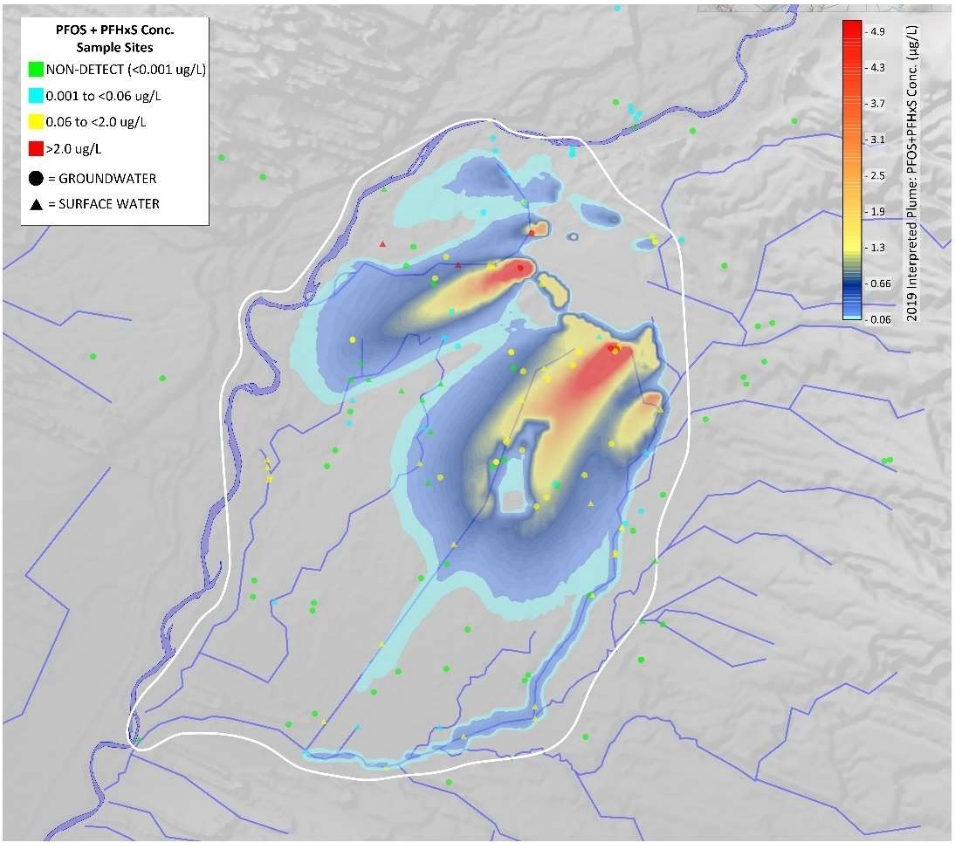
- From the more southern Soil Source Zones, the plume migrates in a generally SSE direction, and is interpreted to extend approximately 3 km from the site boundary in this direction (to the 0.06 ug/L limit).

- From the remaining western and northern Soil Source Zones – the plume migrates in a generally SW to W direction, and is interpreted to extend to the river located approximately 3 km away.

- The thickness (e.g. the depth) of the groundwater plume to the 0.06 ug/L limit is generally not expected to extend greater than approximately 50 m below ground surface. This is primarily due to the interpretation that on a regional scale, deeper groundwater is generally upwelling e.g. deeper groundwater is moving upwards and into the shallow portion of the groundwater system. It is stressed that PFOS + PFHxS sampling from a range of depths has been limited, which to date, has prevented further validation of this concept.

- In locations where significant groundwater abstraction is occurring from deep boreholes, the action of pumping may pull the plume deeper than it would otherwise have migrated.

Graphical interpretation of the existing plume (PFOS + PFHxS ≥0.06 ug/L) is provided in Diagram 2 below, which contains both the non-retarded and retarded estimates. Both of these present-day estimates are considered equally likely; from a conceptual probability and statistical calibration standpoint. Hence the 'best estimate' of the existing plume is interpreted to lie within the range displayed on Diagram 2.



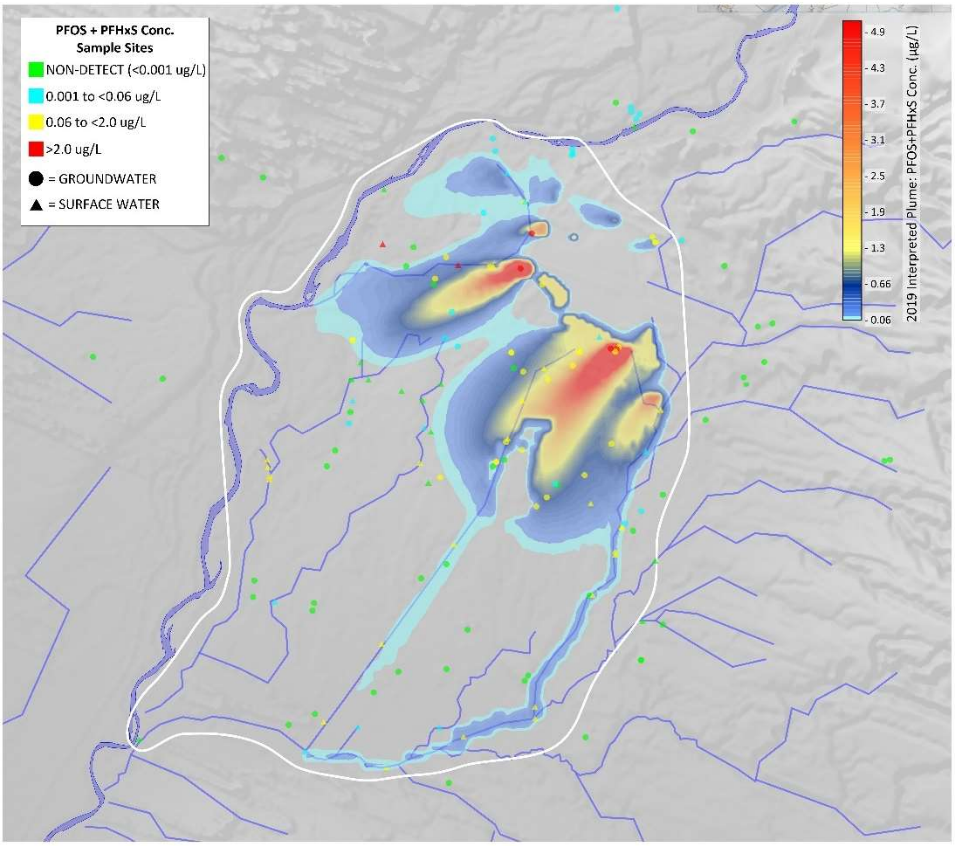


Diagram 2: Existing Plume Prediction – no retardation (Top), and Existing Plume Prediction – with retardation (bottom)

3.1 (A) BEST ESTIMATE FUTURE PLUME PREDICTIONS

Predictive modelling indicates that the three key processes which influence the evolution of the plume are:

- Groundwater flow direction and gradients. In general, the plume is predicted to evolve and migrate in agreement with groundwater flow.
- Groundwater flow boundaries. The plume is generally halted at groundwater flow boundaries e.g. major surface water features, groundwater flow divides, geological and topographical controls.
- Rate of contaminant input (from source zones to groundwater) vs rate of contaminant outflow (form groundwater to sinks). These assumptions, particularly the rate of source input, are influential to how large the plume evolves within the adopted timeframe e.g. if a greater rate of source input is adopted, a larger plume prediction would eventuate within the same time period, vice versa for a lesser rate.

With regards to the vertical thickness of the plume, within approximately 2 km from site, the maximum vertical thickness is generally expected to remain at approximately 40 m or less. This can however be influenced by groundwater abstraction, which can locally 'drag' the plume downwards. An example is shown below from a borehole approximately 55 m depth with a 1200 m^3/day take (annualised).

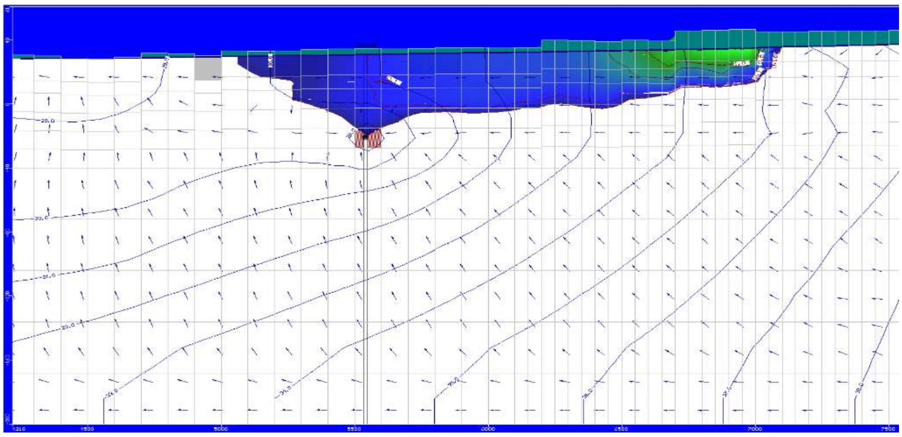


Diagram 3: Model output showing pulldown affect of groundwater abstraction on plume thickness

A summary table of the generalised plume evolution predictions over the short, medium, and long-term is provided in Table 1 below, outputs from the predictive modelling is shown in Diagram 4.

Table 1: Summary of Generalised 'Best Estimate' Plume Evolution Predictions and Interpretations			
Question	**Present Day to Short Term (0 yrs to approx. 10 yrs)**	**Medium Term (approx. 10 yrs to 50 yrs)**	**Long Term (approx. 50 yrs to 125 yrs)**
How much contaminant mass (PFOS + PFHxS) may be present in the plume?	50 to 70 kg (generally increasing)	65 k to 85 kg (likely contains peak)	85 kg to 20 kg (generally decreasing)
What is the likely area of the plume?	Max area generally increasing	Max area generally increasing (likely contains peak)	Max area generally decreasing
What size is the likely area at or above the current drinking water guideline (≥0.06 ug/L PFOS + PFHxS with UOM)?	1100 ha to 1400 ha (generally increasing)	1400 ha to 2200 ha (likely contains peak)	2000 ha to 100 ha (generally decreasing)
What and where are the likely key receptors of the plume?	Generally, all of the: Surface water bodies NW through SSW of the site, within 2 km to 3 km. Shallow wells/boreholes NW through SSW of the site, within 2 to 3 km.	Generally, all of the: Surface water bodies W through SSW of the site, within 6 km. Shallow wells/boreholes W through SSW of the site, within 6 km.	Some of the: Surface water bodies W through SSW of the site, within 6 km. Shallow wells/boreholes W through SSW of the site, within 6 km.
How fast is the leading edge of the plume advancing?	Maximum estimated at approximately 50 m/year to 100 m/year (likely contains peak advance rate)	Maximum estimated at approximately 50 m/year or less (advance of plume is generally slowing)	Plume edge has generally halted at the river and main stream. (plume is no longer advancing)
What is the likely shape of the plume?	Three primary plume 'arms'. Shape remaining generally similar to the present day prediction but beginning to elongate.	Evolving from three primary 'arms' towards only 'two' primary arms. The smaller northern arm is depleting, while the remaining southern and western arms continue to elongate.	Continued elongation of the two primary arms, until a maximum length is reached. Width of the plume arms begins to significantly decrease, and plume begins to break apart from the primary onsite source areas.
Comments on the expected level of uncertainty associated with the prediction	Likely to contain greater certainty.	Contains significant uncertainty.	Likely to contain the greatest level of uncertainty

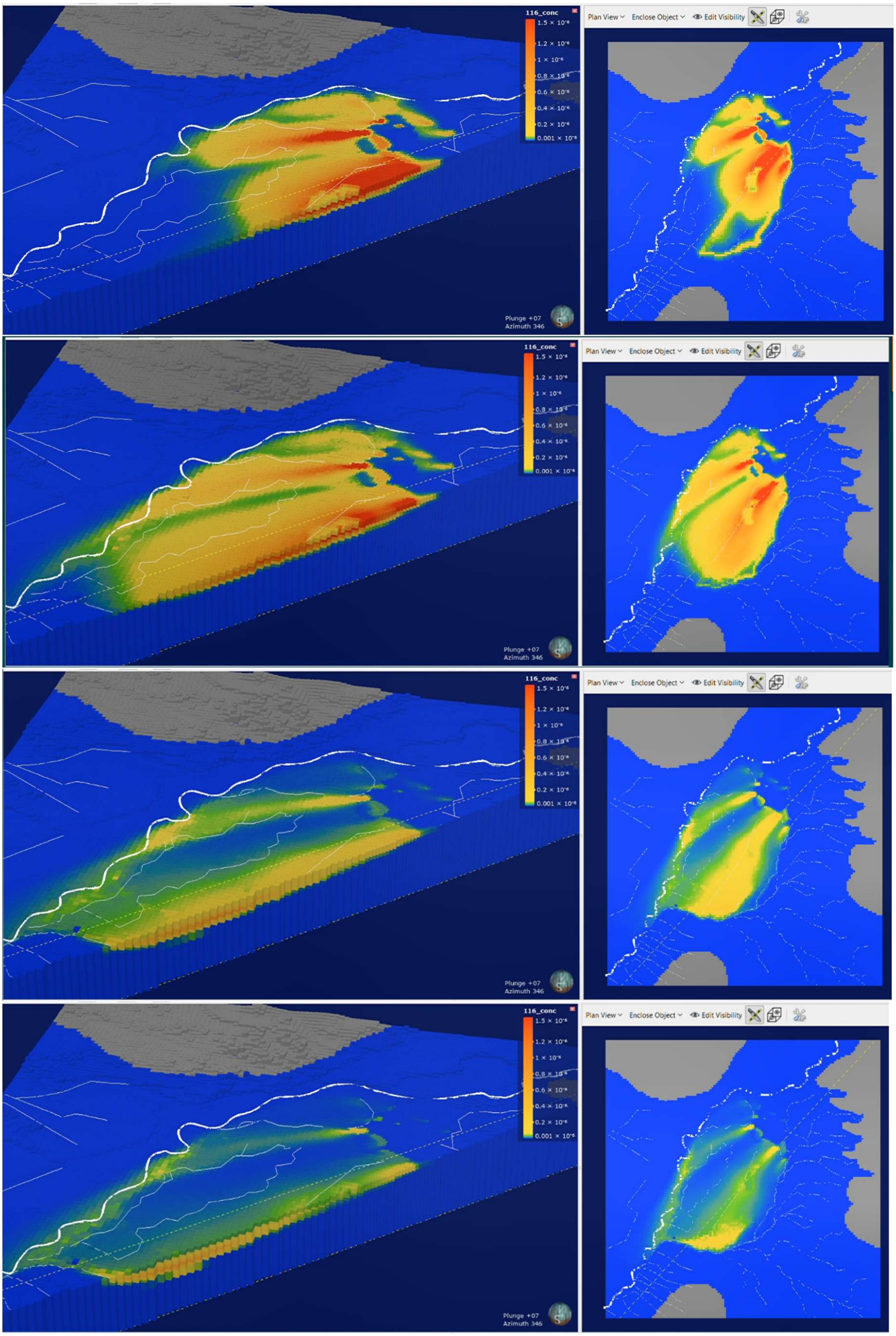


Diagram 4: (A) ‘Best Estimate’ Future Plume Prediction model output

3.2 (B) INSTANT SOURCE REMOVE SCENARIO

A prediction was also completed whereby the existing Soil Source Zones and Surface Water Source Zones were assumed to have instantaneously removed/remediated e.g. prediction starts with the existing plume prediction, the modelled source zones are instantaneously removed, and the model is run into the future for 125 years. This scenario is considered analogous to a 'Best Possible Case' estimate and its purpose is to provide a prediction which tends towards the fastest perceivable (but unlikely) plume depletion.

General description of the 'source removed' future plume predictions and interpretations are outlined below. The predicted plume evolution over the adopted 125-year time period is displayed graphically on Diagram 5.

- Plume is expected to continue migration, but the plume is likely to 'disconnect' from source zones e.g. the three primary 'arms' of the existing plume break off from their respective source zone areas.

- Plume depletion is likely to be significantly more rapid than for the 'A' scenario, however plume depletion is still on the multiple decade scale. It is estimated at approximately 20 to 50 years for the plume (PFOS + PFHxS >0.06 ug/L) to have decreased in area from the present day prediction, and estimated at approximately 55 to 80 years for the plume area to halve.

- The individual 'arms' of the plume are generally expected to continue advancing in their current direction of travel until they encounter a major groundwater discharge boundary.

- The leading edge of the plume (e.g. the PFOS + PFHxS 0.06 ug/L contour), is expected to advance at a similar velocity to that of the 'best estimate' prediction e.g. maximum advance velocity of approximately 50 m/year to 100 m/year in the primary direction of travel (e.g. longitudinal axis).

- The trailing edge of the plume is predicted to move away from the onsite source areas at varying rates, which are primarily controlled by the interpreted geology immediately beneath or downgradient of the source areas i.e. onsite source areas dominated by shallow gravels are likely to experience rapid plume disconnect, and then the trailing edge migrating off-site at a similar velocity to the respective leading edge advance. Areas containing silt/clay dominated geology are likely to require much longer timeframes before the plume disconnects, and slower trailing edge migration.

- The maximum width of 'flanks' of the plume (PFOS + PFHxS >0.06 ug/L) are generally expected to remain similar to the 'A' prediction. However, due to the plume disconnect and more rapid depletion in this scenario, the plume is not predicted to elongate into the medium- and longer-term future.

- The behaviour of the plume in the vertical direction is generally similar to that described for the 'best estimate' scenario.

- The overall mass of PFOS + PFHxS within the plume is expected to decrease at approximately twice the rate (faster) than for the 'best estimate' scenario. The time to halve the existing plume mass (PFOS + PFHxS) is estimated to be in the order of 50 to 70 years+.

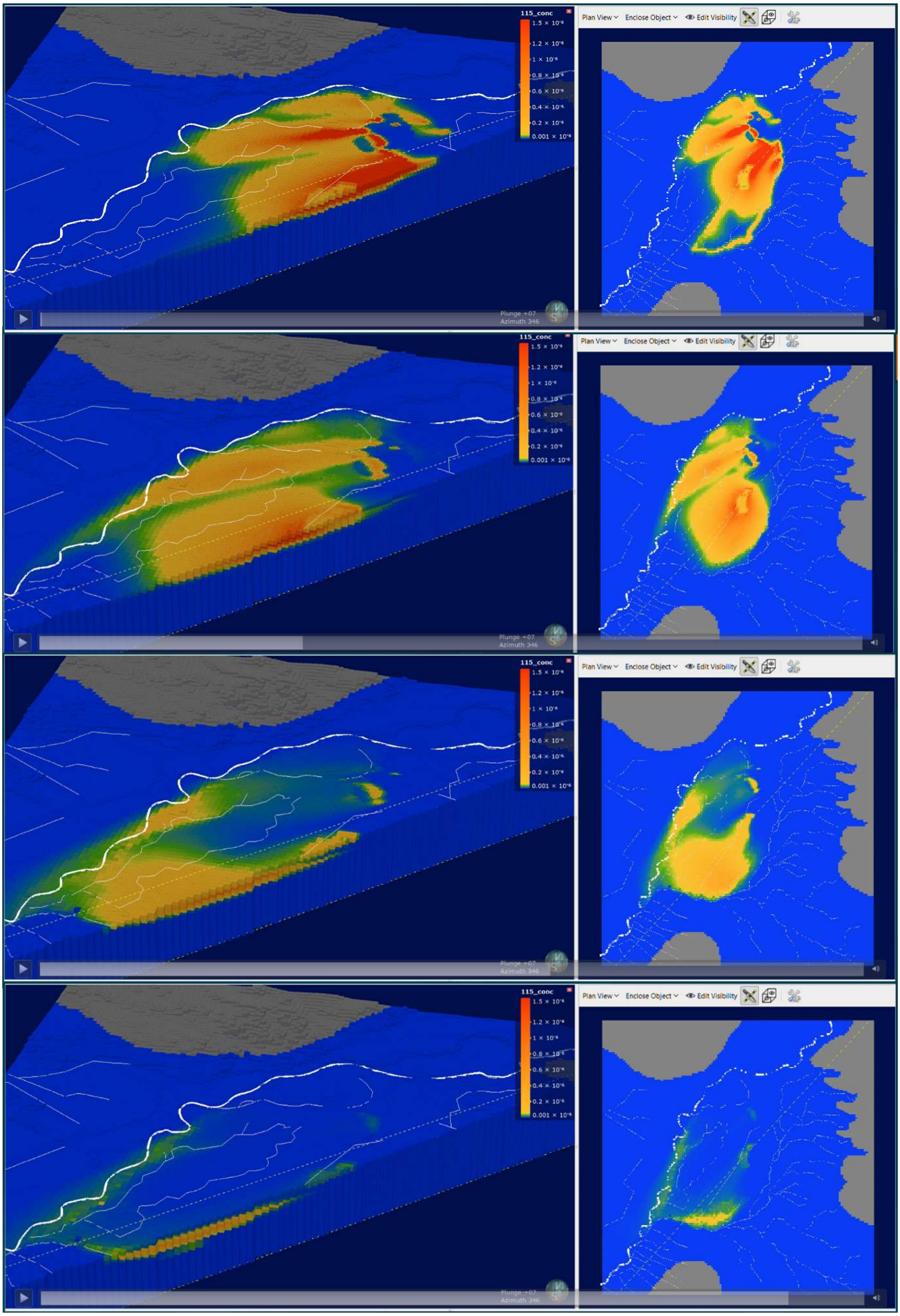


Diagram 5: Existing Plume Prediction (Top), and predicted plume migration (expansion and then depletion) over time under instant source removal scenario

3.3 (C) LONGER SOURCE DEPLETION SCENARIO

An alternative scenario which adopts an even longer source depletion was completed. Under this scenario, the soil source zones and surface water source zones were set at a depletion rate which took twice as long than that adopted for the 'Best Estimate' scenario. This equates to a depletion which halves the concentration every 50-years rather than 25-years.

The purpose of this scenario is to provide a prediction which tends towards the slower end of possible source zone depletion, and to evaluate what effect this could have on the predicted plume. Inherently, the assumptions of this scenario require that a greater source mass is available for leaching e.g. more mass in the soil zone to supply contaminant leaching over a longer time period.

A general description of the 'longer source depletion' future plume predictions and interpretations are outlined below. The predicted plume evolution was run out to a 250-year time period and is displayed graphically on Diagram 6.

- The plume is generally predicted to take on a similar overall shape and aerial extent - to scenario (A) - however the depletion of the plume is likely to be significantly slower.
- The maximum width or 'flanks' of the plume (PFOS + PFHxS >0.06 µg/L) are generally expected to be similar. The width of the plume is expected to start contracting near the 80-year time mark. Contraction is expected to be slow and to gradually reduce over the subsequent 80-100 years.
- It is estimated at 80 to 140 years for the plume to have decreased in mass to below the present-day mass estimate. The time to halve the existing plume mass (PFOS + PFHxS) is estimated to be 170 years to greater than 230 years.
- The PFOS + PFHxS >0.06 µg/L extent is predicted to have largely depleted by approximately 200-years future, however, detectable concentrations are predicted to remain.

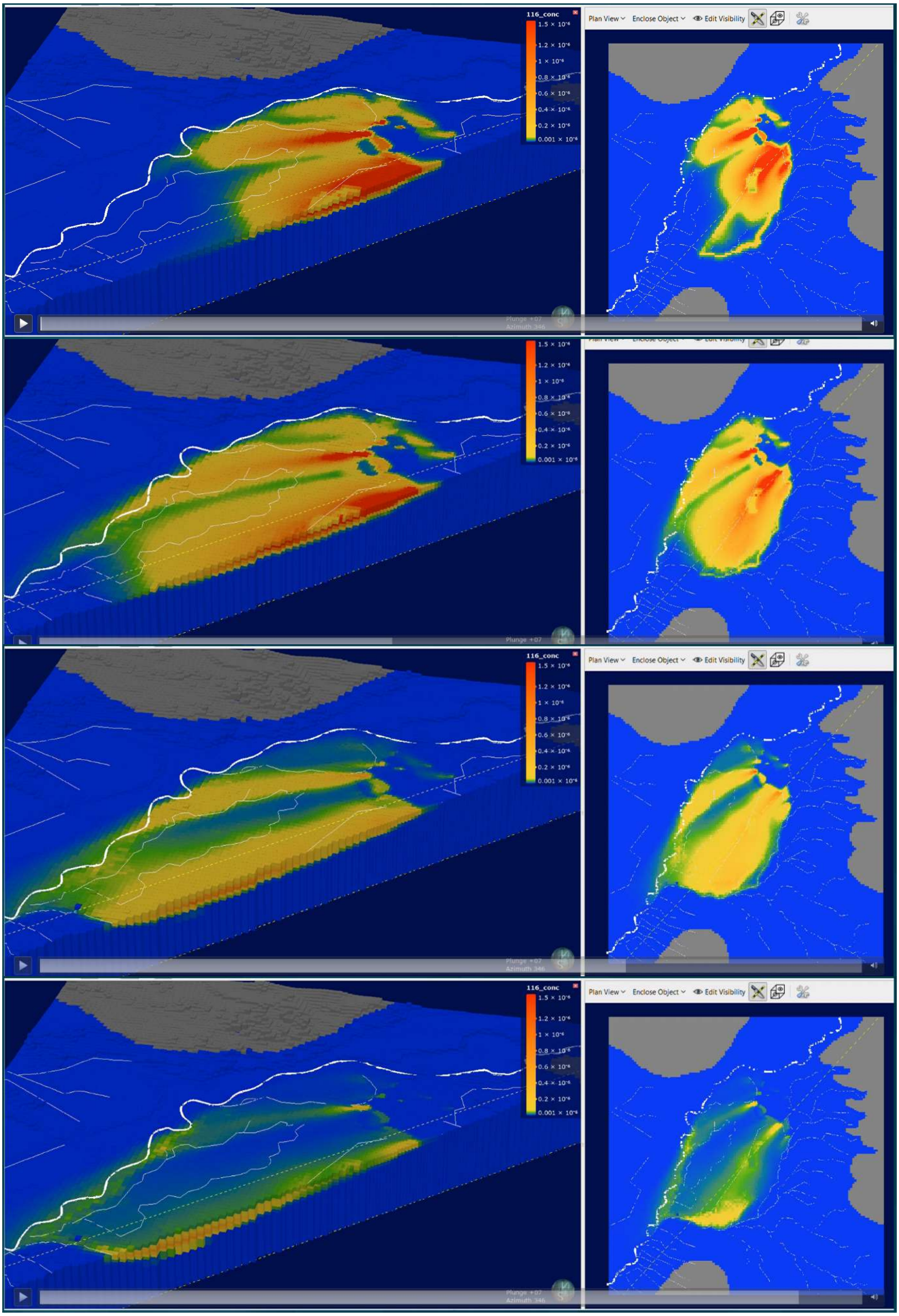


Diagram 6: Existing Plume Prediction (Top), and predicted plume migration (expansion and then depletion) over time under the long source depletion scenario

3.0 VALIDATION AND GAP FILLING

Additional drilling and groundwater monitoring carried out in 2020 and 2021 has addressed areas of the aquifer/hydrological system with previous knowledge gaps, which posed key uncertainties for the regional groundwater resource. The additional data also provides a basis for further validation of the conceptual model, and the predictions of the plume and it's likely future behaviour.

Overall, the recent surface and groundwater sites tested are considered generally in alignment with previous monitoring results and the 2019 predictions/interpretations.

Diagram 7 shows the results of the latest monitoring rounds against the predicted plume concentrations.

Of interest, the following samples have recorded notable changes in concentrations since the 2019 CSIR work:

- New downstream boreholes – which were installed within the shallow groundwater system, have all returned <0.001 ug/L observations. These results match with 2019 plume predictions of non-detection for these locations (at 2019 / 'present day').

- New nested boreholes at (~400m downstream from key soil source zone):
  - Shallow system borehole (screened from 5 to 11 m bgl) recorded concentrations slightly lower than expected (as per 2019 work), but well within the anticipated range of results.
  - Intermediate (~40 m depth/screened from 36.5 to 39.5 m bgl) and Deep (~80 m depth/screened from 78 to 84 m bgl) system boreholes both returned non-detection. These results generally agree with the 2019 predictions e.g. that plume migration was likely to be predominantly within the shallow groundwater system, although it was noted that detections within the upper ~50 m could be possible.

- New nested boreholes at ~1600 m downstream of the same source zone:
  - Shallow system borehole (screened from 3.5 to 9.5 m bgl) recorded non-detection in Q1 2021. The non-detection at this shallow depth was not expected. 2019 predictions for this location and depth were circa ~0.8 ug/L to 1.4 ug/L.
  - Intermediate (~50 m depth/screened from 51.28 to 54.28 m bgl) borehole recorded above detection in Q1 2021. This magnitude of detection was not expected at this depth, particularly given the non-detection within the shallow system borehole.

- It is not presently clear what is driving the vertical discrepancy in observed results at the downstream nest location – further sampling to confirm readings and situation has been recommended.

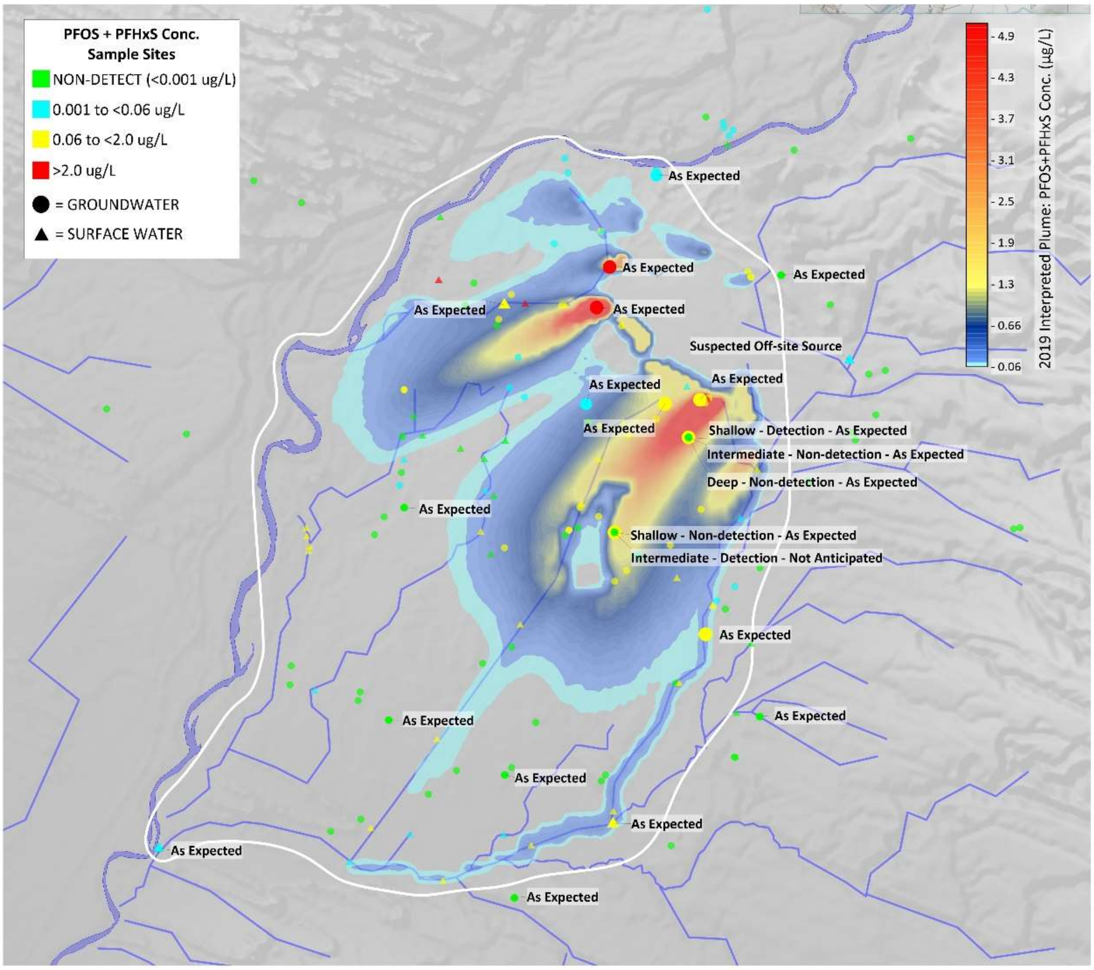


Diagram 7: Result of recent sampling results against the predicted 2019 current plume

CONCLUSIONS

The existing plume (PFOS + PFHxS ≥0.06 ug/L) has an estimated area of 1,100 ha to 1,600 ha, and has an estimated total PFOS + PFHxS mass (in solution) between 50 kg to 70 kg. An estimated 'above detection'[2] extent has also been developed for the existing plume, with an estimated area of approximately 3,600 ha. Whilst these are considered best estimates, there are gaps in data and knowledge on the plume extent, concentration distribution, and geochemical processes. Consequently, there is significant uncertainty associated with the aforementioned estimates.

However, despite the uncertainties, the general plume extent is reasonably well covered spatially by physical observation data, and the present-day plume is interpreted to be well constrained in the northern and eastern direction (and in the western direction to a lesser extent). This has enabled development of a predictive assessment which is considered 'fit for purpose' with respect to the project objectives.

Into the future, the plume is expected to continue migration and expansion before beginning a slow process of depletion. This is primarily because while the source

[2] Above the limit of reporting

is not being added to (i.e. AFFF containing PFOS + PFHxS is no longer used) ongoing leaching from soil is occurring. The individual 'arms' of the plume are generally expected to continue advancing in their current direction of travel – generally west through south-southwest from the site until they encounter a major groundwater discharge boundary. Surface water, particularly the surrounding river and main stream, are the primary receptors of the plume. The plume discharges to these receptors (and their tributaries) as baseflow.

The hydrogeological setting in which the plume resides is interpreted to provide control on the fate and form of the plume into the future. In general, higher topography and groundwater pressures exist north, east and south of the existing plume. This effectively bounds the plume from migrating much further afield in these directions. Rather, the plume is expected to migrate north-west through south-southwest towards and into the river and main stream (the regional groundwater sinks). It must be noted that plume migration/transport under and beyond these surface water bodies is possible, but as these are the regional groundwater sinks, they are the ultimate receivers, and migration back into these surface water bodies would ultimately occur, albeit slightly further downgradient.

Shallow wells (i.e. <50 m depth) which abstract groundwater from within the extent of the plume and the plumes predicted future migration path are also likely to be receptors. Deep wells e.g. >100 m depth, are less likely to be receptors of the plume. This is because the plume is generally predicted to be present and remain in the top portion of the groundwater system e.g. top 40 m to 60 m of saturation. Significant groundwater abstraction and/or poorly sealed boreholes do however have the potential to locally 'drag' the plume to greater depths.

The 'best estimate' of the likely time period for the existing plume (PFOS + PFHxS >0.06 ug/L) to decrease below its current area is estimated at approximately 75 years (no retardation) to 100 years (with retardation). The time to halve the existing plume area (PFOS + PFHxS >0.06 ug/L) is estimated at approximately 95 years (no retardation) to 125 years (with retardation). Even in a theoretical scenario where all source zones are instantaneously removed, it is expected that the plume (PFOS + PFHxS ≥0.06 ug/L) would remain approximately the same area (as the existing plume) for at least the next 25 years (approximately). Consequently, all predictions and interpretations point towards the existing plume having a significant presence for time periods on the multi-decade scale.

A maximum future extent of 'above detection' or ≥0.001ug/L (PFOS + PFHxS) is estimated at approximately 4300 ha. This extent should be considered as a probability extent e.g. PFOS + PFHxS detection outside of this extent is considered unlikely, but not impossible. The timing of when this maximum extent could be reached is likely to be in the long-term future i.e. >50 years.

Validation and gap filling works completed in 2020 and 2021 have generally matched the interpretations and simulations for the 'existing plume' e.g. the plume does not appear to have migrated further than predicted in the lateral direction. Questions over the vertical extent of the plume still remain, and further sampling/works would be required to confirm initial results and address these gaps – which could pose key implications if the reality is different from what has previously been interpreted and modelled. Additionally, preliminary soil leachability testing conducted within some of the Soil Source Zones has confirmed that leachate concentrations, including from soils with relatively low total PFOS + PFHxS concentrations, are above the interim drinking water guidelines. More assessment is required on this aspect, but it could indicate that the conservative scenarios regarding source zone depletion are more applicable.

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