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technical memorandum

TO	Nigel Donovan	FROM	Graeme Proffitt, Natalie Webster
	Ministry for the Environment	DATE	14 May 2021
RE	Derivation of Class 3 TPH WAC using BTEX and PAH Proxies		

1.0 Introduction

Pattle Delamore Partners Limited (PDP) previously proposed Class 3 landfill waste acceptance criteria (WAC) for total petroleum hydrocarbons (TPH) in the C_7-C_9 and C_{10}-C_{14} carbon ranges of 1,000 mg/kg and no limit[1], respectively, based on parameters taken from the Ministry for the Environment petroleum hydrocarbon soil guideline document[2]. It was acknowledged that soils impacted by C_7-C_9 hydrocarbons at a concentration of 1,000 mg/kg are likely to have hydrocarbon odours, and it was suggested that the WAC for individual BTEX compounds (benzene, toluene, ethylbenzene, and total xylenes) should also be applied to assess the suitability of disposal at a Class 3 site for such soil.

The WAC working group were uncomfortable with this approach. Given that, at elevated total petroleum hydrocarbon concentrations one or more of the BTEX compound WAC could be exceeded, it was decided to use these compounds as proxies to determine whether a better C_7-C_9 TPH WAC could be arrived at. To do this, a large, anonymised dataset of TPH and BTEX results for the same soil samples was obtained from Hill Laboratories. It was also decided to look at whether a similar approach could be taken comparing C_{10}-C_{14} TPH results with PAH results for the same samples to arrive at a C_{10}-C_{14} WAC.

This memorandum describes the process and results and is a revision of an initial version dated 18 December 2020.

2.0 C_7-C_9 TPH

The purpose of the TPH C_7-C_9 - BTEX data pairs comparison was to determine if there was a concentration for TPH in the C_7-C_9 range which, if set as a Class 3 WAC, would ensure that BTEX compounds would not exceed the individual BTEX WAC.

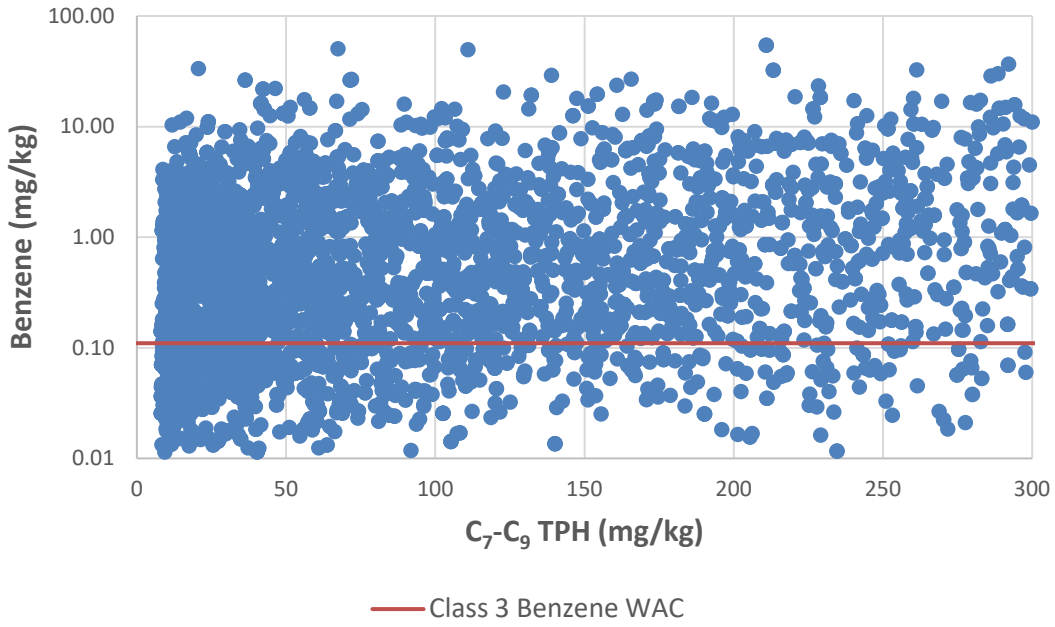
Using the individual BTEX compounds as the proxy for TPH in the C_7-C_9 carbon range is considered to be a reasonable (if conservative) approach as, although there are other hydrocarbons present in the C_7-C_9 range which are measured by the TPH test, the mono-aromatic (ring-shaped) BTEX hydrocarbons are similarly or more toxic than the light, volatile aliphatic (straight chain and branched) hydrocarbons such as hexane and octane.

[1] See PDP memorandum W01820600M007 *WasteMINZ Landfill Guidelines – Proposed Class 3 and 4 WAC for Organic Compounds*, dated 1 July 2020

[2] *Guidelines for Assessing and Managing Petroleum Hydrocarbon Contaminated Sites in New Zealand* (updated 2011), Ministry for the Environment, Wellington, 2011

It is noted that the Class 3 and Class 4 WAC for all of the BTEX compounds are the same. This is because the leaching pathway was found to be limiting for these compounds. Therefore, whatever TPH WAC is derived must aim to prevent the leaching of BTEX compounds at concentrations which would exceed either the drinking water or aquatic guidelines, whichever was the applicable limiting guideline value (once the dilution and attenuation factor – DAF – has been taken into account to model the attenuation between the contaminant in the landfill and the groundwater use or aquatic environment receptor).

A data set for nearly 7,000 soil samples was obtained from the laboratory. Plotting the relationship between TPH C_7-C_9 and each of the BTEX data found that even samples with low concentrations of TPH in the C_7-C_9 range can have concentrations of BTEX compounds which exceed the WAC for those compounds; and hence are theoretically capable of producing leachate that would exceed the applied guideline values. As an example, the plot of C_7-C_9 TPH against benzene is shown below, limited to TPH less than 300 mg/kg (which represents only a small part of the dataset; the maximum TPH measured was 77,000 mg/kg) and benzene on a logarithmic scale.



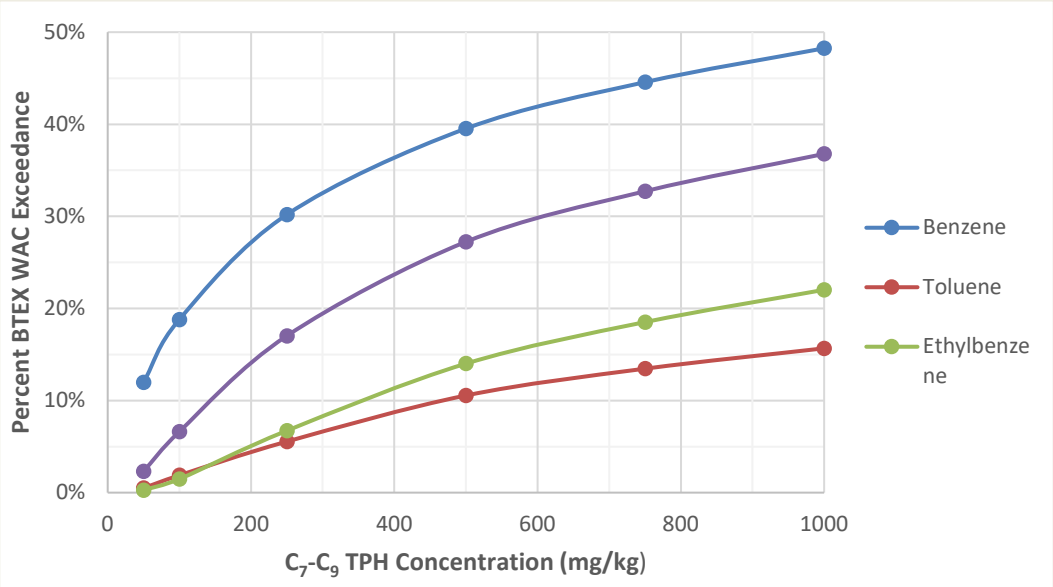
In summary, soils which contain TPH in the C_7-C_9 range as low as 9 mg/kg may contain concentrations of benzene which exceed the benzene WAC of 0.11 mg/kg; for toluene, TPH as low as 18 mg/kg may exceed the toluene WAC of 19 mg/kg; for ethylbenzene, TPH as low as 23 mg/kg may exceed the ethylbenzene WAC of 10 mg/kg; and for total xylenes, TPH as low as 12 mg/kg may exceed the total xylenes WAC of 25 mg/kg. This means setting a C_7-C_9 TPH WAC that would prevent all soils which contain BTEX concentrations above the respective BTEX WAC being placed in a Class 3 facility would result in an impractically low TPH WAC (particularly as natural TPH could be higher than these concentrations).

On this basis, and in a similar way as was done as part of the derivation of WAC for inorganic elements using SPLP[3] / total concentration data pairs, the data was assessed to determine the percentage of BTEX exceedances that may occur at nominated TPH concentrations. The following table summarises this analysis.

[3] Synthetic Precipitation Leaching Procedure, a testing method which simulates the leaching that may occur from a soil as a result of water infiltrating through the soil profile, as occurs following rainfall.

Table 1: Percent Exceedance Over Respective WAC				
C_7-C_9 TPH (mg/kg)	Benzene	Toluene	Ethylbenzene	Total Xylenes
50	11.97%	0.49%	0.27%	2.30%
100	18.80%	1.88%	1.48%	6.62%
250	30.19%	5.54%	6.72%	17.02%
500	39.53%	10.55%	14.01%	27.23%
750	44.57%	13.46%	18.52%	32.72%
1000	48.25%	15.67%	22.02%	36.78%

A graph of this data is shown below:



As can be seen from the data and graph presented above, the BTEX WAC which are exceeded the most frequently are benzene and total xylenes. For benzene, even at a TPH concentration of 50 mg/kg approximately 12% of samples will contain benzene at concentrations which exceed the benzene WAC (0.11 mg/kg). At a TPH concentration of 100 mg/kg, approximately 19% of samples will contain benzene at concentrations which exceed the benzene WAC, and 6% of samples will contain total xylenes at concentrations which exceed the total xylenes WAC (25 mg/kg).

As discussed above, setting a TPH WAC at a low enough concentration to prevent a reasonably high percentage of the soils for disposal from exceeding the benzene WAC (in particular) will result in an impractically low TPH WAC, rendering it somewhat pointless.

It is also worth noting that the C_7-C_9 TPH WAC for Class 4 landfills (110 mg/kg) has been set at a concentration which is protective of ecological receptors in soils for agricultural land use; but which according to the TPH/BTEX data received from the laboratory, would result in soils being disposed of into Class 4 landfills which exceed the BTEX WAC (which are the same for both Class 3 and 4 landfills).

However, mitigating factors exist when considering BTEX compounds and the likelihood of soils containing these chemicals to cause a discharge to either drinking water or ecological receptors (which is what the

BTEX WAC have been derived to protect). All BTEX compounds are highly volatile and will volatilise to some degree on exposure to air. In addition, all the BTEX compounds will biodegrade relatively quickly under aerobic conditions, particularly benzene. A study by Landcare Research[4] showed that for soil samples individually spiked with 2,000 mg/kg of xylene, ethylbenzene and toluene, the following losses were recorded with time in an open test vessel:

- Xylene: up to 50% loss after 30 minutes, up to 89% loss after 6 hours
- Ethylbenzene: up to 65% loss after 30 minutes, up to 98% loss after 6 hours
- Toluene: up to 83% loss after 30 minutes, up to 99% loss after 6 hours

The action of excavating soils containing BTEX compounds from the source site, loading them into trucks, then unloading them at the landfill is expected to encourage attenuation through volatilisation and biodegradation; and further attenuation will occur if deposited soils are placed in a location with aerobic conditions at the landfill.

Taking the various mitigating factors into account, we consider that a reasonably high percentage of exceedances for benzene and total xylenes can be tolerated, and propose that a concentration of 200 mg/kg for C_7-C_9 TPH would represent an acceptable WAC, on the basis that:

- It represents a reasonable increase from the Class 4 WAC (110 mg/kg), consistent with the general application of higher WAC for other contaminants for Class 3 landfills.
- At 200 mg/kg TPH the lab results indicate that approximately:
  - 27% of benzene results may exceed the benzene WAC
  - 4% of toluene results may exceed the toluene WAC
  - 5% of ethylbenzene results may exceed the ethylbenzene WAC
  - 14% of total xylenes results may exceed the total xylenes WAC
- This level of potential exceedances is considered acceptable in the context of the volatility and biodegradability of BTEX compounds, both of which are expected to reduce the concentration of the various BTEX compounds in the soil when it is disposed of in a landfill.
- Not all of the soil received into the landfill will be contaminated with petroleum hydrocarbons, so the actual BTEX-leaching potential of the quantum of deposited soils will be much less than has been assumed during this assessment (e.g. soil mixing with non-TPH/BTEX contaminated soils will result in lower concentrations and lower leaching potential).
- There are likely to be other procedures in place at the landfill, and / or consent conditions, that will aid in preventing the acceptance of soils which contain unacceptable concentrations of BTEX compounds, such as waste acceptance procedures that preclude the acceptance of stained or odorous soils.

3.0 TPH C_{10}-C_{14}

The purpose of the TPH C_{10}-C_{14}/PAH data pairs comparison was to determine if there was a concentration for TPH in the C_{10}-C_{14} range which, if set as a Class 3 WAC, would ensure that PAH compounds would not cause a discharge via leaching. Naphthalene has been selected as the key compound for comparison because it is the most soluble of the PAH compounds and therefore poses the greatest risk of leaching from a waste soil that contains a mixture of PAHs.

As an intermediate step, a naphthalene WAC must be calculated. There is no intention to actually have a new naphthalene WAC, but this enables determining where the WAC sits within the TPH – naphthalene

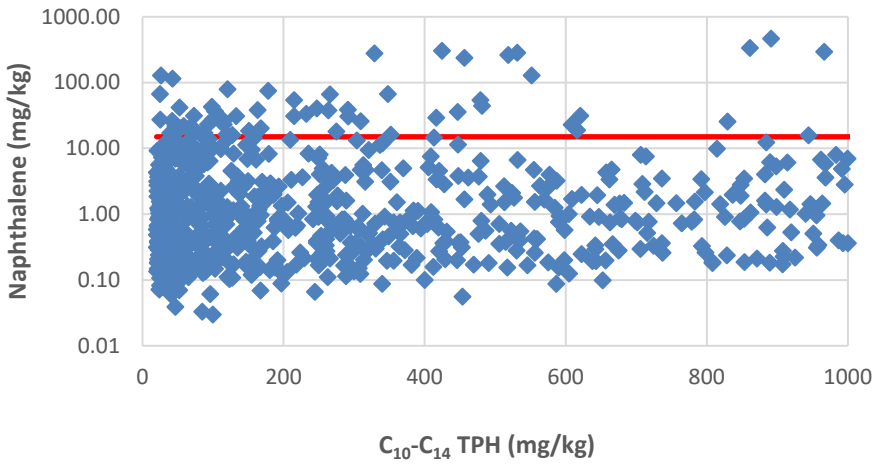
[4] https://contamsites.landcareresearch.co.nz/btex_details.htm

concentration comparison and therefore arrive at a TPH C_{10}-C_{14} WAC that is less than the previous "no limit" proposal. To calculate the WAC requires consideration of both the aquatic protection pathway (for which an Australian and New Zealand freshwater 95% species protection guideline is available) and the drinking water pathway. No New Zealand or World Health Organization drinking-water guidelines for naphthalene exist, and a search of other jurisdictions failed to find a value. Instead, a notional drinking-water guideline must be calculated using the standard calculation method.

Deriving a notional drinking-water guideline requires a tolerable daily intake (TDI) value. A search of North American and European authorities found a range of TDI values from 0.02 – 0.1 mg/kg bw/day, the lower value being from what is acknowledged as a low reliability TDI value from the United States Environmental Protection Agency (US EPA) IRIS database[5] and the higher value from a later study by the US EPA[6]. This range of values results in a drinking-water guideline range of 0.07 – 0.7 mg/L using the World Health Organisation (WHO) calculation methodology[7] (which the Ministry of Health follows with an adjustment for a heavier body weight) with both 10% and 20% as the proportion of the TDI assigned to water.

At the lower end of the calculated range the drinking-water pathway proves to be critical with the calculated naphthalene WAC being 13 mg/kg, compared with 15 mg/kg for the aquatic protection pathway. However, if any of the three other calculated drinking-water values[8] are chosen, the aquatic protection pathway is critical. Given the lowest drinking-water value uses a low reliability TDI and a percentage of TDI assigned to water no longer recommended by the WHO, it is considered appropriate to select the aquatic protection pathway as critical. However, whether the lowest drinking water pathway or the aquatic pathway is used gives essentially the same C_{10}-C_{14} TPH WAC, taking into account the various uncertainties involved in the calculation.

A dataset of approximately 1,350 TPH and PAH sample results was obtained from Hill Laboratories. A comparison of the C_{10}-C_{14} TPH results to naphthalene results shows that a significant proportion of the naphthalene concentrations (e.g. approximately 85%) are below the naphthalene WAC. A plot of the data for naphthalene concentrations that are <1,000 mg/kg is presented below.



[5] US EPA 1998 from IRIS database: https://cfpub.epa.gov/ncea/iris2/chemicalLanding.cfm?substance_nmbr=436

[6] Reregistration Eligibility Decision for Naphthalene, EPA 738-R-07-010, United States Environmental Protection Agency, Office of Pesticide Programs, Washington DC, 8 September 2008. https://www3.epa.gov/pesticides/chem_search/reg_actions/reregistration/red_PC-055801_12-Sep-08.pdf

[7] *Guidelines for drinking-water quality: fourth edition incorporating the first addendum*, World Health Organization, Geneva, 2017. The MoH follows this method except uses a 70 kg body weight and by default assigns 10% of the TDI to water whereas WHO has more recently changed to using 20% of the TDI assigned to water, advising 10% is too conservative.

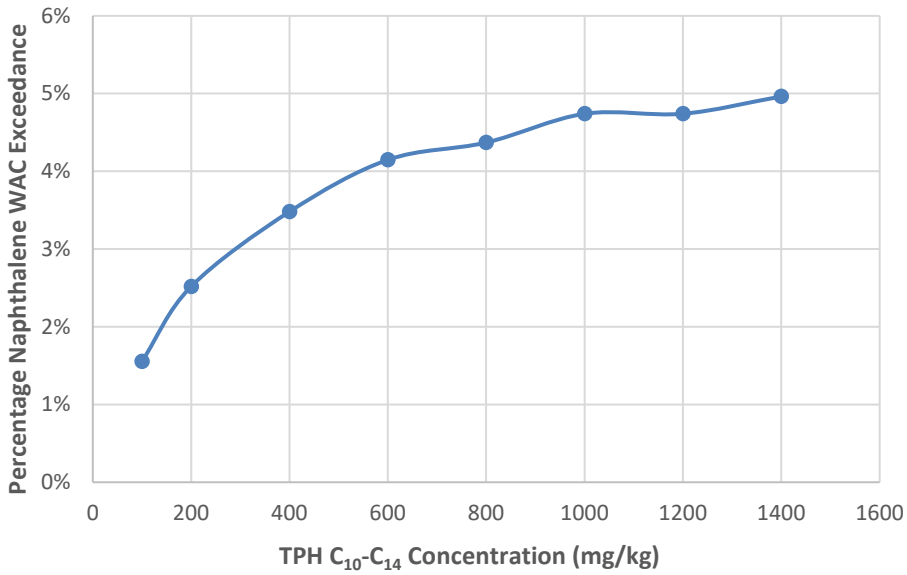
[8] Total of four calculated values, from two TDI values and two percentages of these values assigned to water.

The data was assessed to determine the percentage of naphthalene exceedances that may occur at nominated TPH concentrations. The following was determined for a range of TPH C_{10}-C_{14} concentrations.

Table 2: Percent Exceedance Over Naphthalene WAC

C_{10}-C_{14} TPH (mg/kg)	Naphthalene
100	1.6%
200	2.5%
400	3.5%
600	4.1%
800	4.4%
1,000	4.7%

A graph of this data is shown below:



As can be seen for the data presented above, the WAC for naphthalene is not frequently exceeded even at relatively high concentrations of TPH in the C_{10}-C_{14} range. This finding, along with the knowledge that all PAH compounds are relatively insoluble in soils, leads to the conclusion that a C_{10}-C_{14} TPH WAC could be set at a concentration of up to, nominally, 800 mg/kg without creating a significant risk from the leaching of PAHs. However, it is accepted that this concentration represents a significant increase in comparison to the Class 4 WAC of 58 mg/kg, and therefore a lower concentration may be considered to be more acceptable to stakeholders. A concentration of 500-600 mg/kg is proposed.

4.0 Conclusion

On the basis of the data comparisons undertaken between TPH and BTEX, and TPH and PAH laboratory analysis data pairs; and taking into consideration the behaviour of the various compounds in the environment, WAC have been proposed for TPH in the C7-C9, and the C10-C14 carbon ranges. The proposed WAC are:

- TPH C_7-C_9 – 200 mg/kg
- TPH C_{10}-C_{14} – 500 – 600 mg/kg

These WAC are presented in a revised Class 3 and 4 WAC comparison table, appended.

5.0 Limitations

This memorandum has been prepared by PDP on the specific instructions of Ministry for the Environment for the limited purposes described in the memorandum. PDP accepts no liability if the memorandum is used for a different purpose or if it is used or relied on by any other person. Any such use or reliance will be solely at their own risk.

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Appendix A – Revised Class 3 and 4 WAC Comparison Table

Table 3: Class 3 and 4 WAC as per Guidelines and Proposed Revised (mg/kg)

Contaminant	Class 3 using Guideline Class 4 Derivation	Proposed Class 3	Class 4 from Guidelines	Proposed Class 4
Arsenic	310[1]	140	17[3]	17
Cadmium	10[2]	10[5]	0.8	0.8
Chromium	630	150	290	150
Copper	>44 or soil background	280	>44 or soil background	220[4]
Lead	1,000	460	>60 or soil background	160
Mercury	160	3[5]	0.7	0.7
Nickel	310	320[5]	310	320[5]
Zinc	400	2,700	400	190
TPH $C_7 – C_9$	No Practical Limit[6]	200[7]	120	110
TPH $C_{10} – C_{14}$	No Practical Limit[6]	500-600[8]	58	58
Benzene	0.2	0.11	0.2	0.11
Ethylbenzene	66	10	59	10
Toluene	50	19	50	19
Total Xylene	29	25	30	25
Benzo(a)pyrene (eq)[9]	54	125	Interim based on soil background = 2	2.8
Dieldrin	0.2	0.10	0.2	0.10
Total DDTs[10]	26	2.0	0.7	1.9

Notes:

1. *Blue shading indicates drinking water pathway is limiting.*
2. *Green shading indicates aquatic pathway is limiting.*
3. *Grey shading indicates human health agricultural land use or rural residential land use is limiting.*
4. *Orange shading indicates soil quality for protection of ecological receptors (minimal risk / protective of agricultural land use) is limiting.*
5. *Not calculated. Based on SPLP – total concentration dataset comparison and professional judgement.*
6. *Not calculated in the Guidelines but if calculated using the Guidelines parameters, value very large and unlikely to be encountered on real world sites (no practical limit).*
7. *Based on TPH – BTEX dataset comparison and professional judgement.*
8. *Based on TPH – PAH dataset comparison and professional judgement.*
9. *Equivalent benzo(a)pyrene concentrations calculated as a toxicity-weighted sum of the nine carcinogenic PAHs in the standard PAH analytical suite.*
10. *Sum of the concentrations of the six DDT, DDD and DDE isomers.*