Microplastics and Contaminants of Concern in the Strategic Road Network

Appendix B: Initial assessment to identify future contaminants of concern

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Table of Contents

Appendix B. Initial assessment to identify future contaminants of concern 6
B.1. Task aim 6
B.2. Sample details 7
B.3. Presence and concentrations of contaminants found 8
B.4. Relationships between contaminants and microplastics 11
B.5. Comparison of sample results with HEWRAT 13
B.6. Recommendations for improvements to HEWRAT 14
B.7. Recommendations for future research 15
B.8. Summary 15
B.9. References 18
B.10. Supplementary Information 19

Tables

Table B.1 Date and location of successful samples collected and analysed................................... 7
Table B.2 Contaminants detected at a lower average concentration in the samples than the associated LOD, and had positive samples collected... 9
Table B.3 Contaminants detected at a higher average concentration in the samples than the associated LOD, and below the relevant EQS/PNEC where available. 9
Table B.4 Contaminants detected at a higher average concentration than the associated EQS/PNEC and sorted by ratio of average concentration to EQS/PNEC value............................ 10
Table B.5 Presence count of contaminants with TWPs per sample... 13
Table B.6 : Contaminants recorded with positive sample results without a comparative EQS/PNEC value.. 15
Table B.7: Contaminants worthy of further investigation.. 16
Table B.8 List of determinands and pollutants analysed from the 15 samples.............................. 19
Table B.9 EQS/PNEC values used in project, with reference to source country if not England. 21
Table B.10 Input data for HEWRAT models. 30

Figures

Figure B.1 TWP vs all contaminants sampled with positive results. All contaminant concentrations are presented in µg/l, except total suspended solids in mg/l... 12
Figure B.2 TWP vs total suspended solids concentrations labelled with the rainfall depth prior to sample collection (mm). 12
Figure B.3 Comparison of average soluble copper measured v HEWRAT outputs. 14
Figure B.4 Comparison of average soluble zinc measured v HEWRAT outputs........................... 14
Figure B.5 TWP vs total suspended solids concentrations labelled with the rainfall depth prior to sample collection (mm) 23
Figure B.6 TWP vs total metals concentrations... 23
Figure B.7 TWP vs total copper concentrations 23
Figure B.8 TWP vs total zinc concentrations... 24
Figure B.9 TWP vs dissolved copper concentrations 24
Figure B.10 TWP vs dissolved zinc concentrations.. 24
Figure B.11 TWP vs total antimony concentrations... 25
Figure B.12 TWP vs total manganese concentrations.. 25
Figure B.13 TWP vs fluoranthene concentrations 25
Figure B.14 TWP vs phenanthrene concentrations 26
Figure B.15 TWP vs pyrene concentrations 26
Figure B.16 TWP vs 4-tert-octylphenol (4t-OP) concentrations 26

Figure B.17 TWP vs N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) concentrations 27
Figure B.18 TWP vs 1,3-diphenylguanidine (DPG) concentrations 27
Figure B.19 TWP vs Benzothiazole-2-sulfonic acid (BTSA) concentrations........ 27
Figure B.20 TWP vs Hexa(methoxymethyl)melamine (HMMM) concentrations........ 28
Figure B.21 TWP vs Hydroxy benzothiazole (HOBt) concentrations 28
Figure B.22 TWP vs benzo(ghi)perylene concentrations........ 28
Figure B.23 TWP vs benzo(b)fluoranthene concentrations 29
Figure B.24 TWP vs glyphosate concentrations........ 29

Appendix B. Initial assessment to identify future contaminants of concern

B.1. Task aim

This task of the project, Task 3c, looks to identify future contaminants of concern, as well as, explore the benefits and options of reviewing and supplementing the dataset of chemicals monitored within road runoff that underpins design and assessment tools such as the Highways England Water Risk Assessment Tool (HEWRAT). As part of the scope, Task 3c has one primary objective which is, 'Identification and contextualisation of new pollutants of concern'. This will provide a list of target pollutants for consideration by National Highways for the future with commentary of scenarios when these pollutants are prominent.

B.1.1. Objectives

To complete the aim, 15 runoff samples were collected and analysed for the complete list of pollutants of concern identified in Microplastics Phase 1 (Highways England, 2020). Analysis was completed at two United Kingdom Accreditation Service (UKAS) accredited labs: Element and RPS.

To achieve the objective of this task, the following items were actioned:

- Review of the list of contaminants for analysis. This list was based on contaminants identified during Phase 1 and updated through consultation with the Project Steering Group (PSG), the Environment Agency, the client (Mike Whitehead / National Highways) and the Consultant (Atkins and Jacobs).

- A suitable laboratory[1] was sourced to undertake the prescribed suite of analysis. A laboratory was selected based on reviewed analytical methodologies and associated limits of detection (LODs) and limits of quantification (LOQs) proposed including applicable UKAS accreditations. A total of 15 samples were analysed due to the availability of laboratory analysis and project timeline constraints[2][3]. However, these samples still give an indication of the range of concentrations for the contaminants found in road runoff.

- Project sampling was completed by staff at the University of Plymouth, aligned with the collection of samples for microplastics.

Analysis of the samples covered a broad initial set of aims, which are directly answered in the following sections. The initial set of report aims was to:

- Detail the presence and concentrations of contaminants found, providing context for these concentrations. Due to the relatively small sample size the context assumptions and limitations are outlined (Section B.3).

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[1] It was necessary for some of the contaminants to be analysed by a second sub-contracted laboratory as not all analyses were available at one lab.
[2] During the project, some of the analysis was not UKAS accredited. The laboratory provided caution ahead of the project that "some chemicals which would be analysed on the basis of 'best endeavours' and would be dependent on recoveries from the samples, assuming little/no interference from the samples themselves.
[3] Despite the intention to collect 15 sediment samples at the same time as water samples, this was not possible. Accessibility issues and challenges with collecting sufficient volume of sample meant that this part of the monitoring was not feasible based on the existing sites selected to collect water samples for microplastic analysis.

- Investigate and highlight the possible relationships between specific contaminants and concentrations of microplastics found from the University of Plymouth analysis (Section B.4).

- Compare and contrast some sample results with concentrations generated by HEWRAT (a water quality model developed to quantify road runoff from highways) based on specific site characteristics where samples were collected. This will focus on the accuracy of modelling of concentrations and the treatment efficiencies used for different types of highways drainage assets or SuDS (sustainable drainage system) (Section B.5)

- Recommend any general improvements to HEWRAT user interface, if required (Section B.6).

- Recommend any areas of future research for consideration by National Highways (and perhaps the Environment Agency (EA)). This could include future pollutants of concern to target over longer-term monitoring/sampling (Section B.7).

It should be recognised that the limited number of samples taken does not provide a statistically robust dataset. However, they do provide an indication of the range of concentrations for the contaminants found in road runoff. This research does not replace the need for a specifically designed programme of research to investigate chemicals in road runoff.

To complete the aim, 15 runoff samples were collected (as part of Task 2) and analysed for the complete list of contaminants or pollutants of concern identified in Microplastics Phase 1 (Highways England, 2020). Analysis was completed at two UKAS accredited labs: Element and RPS. Following review of the contaminants identified during Phase 1, and consultation with commercial laboratories, the following updates to the analysis list were made:

- BOD removed – due to the potential lag in sample collection leading to instability.

- 2-benzothiazolesulfenamide removed – not available at a commercial laboratory.

- Steranes replaced with stearic acid.

- Extended monitoring of Perfluorooctanoic acid (PFOA) and Perfluorooctane sulfonate (PFOS) to include a wider per- and polyfluoroalkyl substances (PFAS) suite – as requested by the EA.

- Included a full acid herbicides suite – as requested by the EA.

- Replaced mineral oil with speciated Total Petroleum Hydrocarbons (TPH) – as requested by the EA.

B.2. Sample details

A total of 15 successful samples were collected during wet weather conditions between 23rd May 2022 and 30th September 2022 across seven different locations (**Error! Reference source not f ound.**).

Table B.1 Date and location of successful samples collected and analysed.

Sample number	Date	Location (Abv.)	Road	Outfall/road section	AADT*
1	23/05/2022	Chudleigh (Chud)	A38	Curved	41,000
2	23/05/2022	Chudleigh (Chud)	A38	Straight	41,000
3	18/06/2022	Donnington Park (Don)	A453	A	30,000
4	18/06/2022	Donnington Park(Don)	A453	B	30,000
5	18/06/2022	Kegworth (Keg)	M1, J24a	A	>100,000
6	18/06/2022	Kegworth (Keg)	M1, J24a	B	>100,000
7	18/06/2022	Kegworth (Keg)	M1, J24a	C	>100,000
8	28/06/2022	Chudleigh (Chud)	A38	Curved	41,000

Sample number	Date	Location (Abv.)	Road	Outfall/road section	AADT*
9	16/08/2022	P.B. North (P.B.N.)	A43 & M40 slip road	n/a	35,000
10	22/08/2022	Cornwall Services (Corn)	A30 & slip road	n/a	36,000
11	22/08/2022	Pond 12 (P12)	A30	n/a	35,000
12	24/08/2022	Bodmin (Bod)	A38	n/a	17,500
13	24/08/2022	Cornwall Services (Corn)	A30 & slip road	n/a	36,000
14	24/08/2022	Pond 12 (P12)	A30	n/a	35,000
15	30/09/2022	P.B. North (P.B.N.)	A43 & M40 slip road	n/a	35,000

*AADT = annual average daily traffic

B.3. Presence and concentrations of contaminants found

To better understand the context of the concentrations of contaminants found in the sampling, available environmental quality standard / predicted no effect concentration (EQS/PNEC) values were sought for each one. A desk-based study of European environmental agencies and European government departments was completed, searching for annual averaged values. Only 33 of the 241 determinands had EQS/PNEC values relevant to this study (B.10). To clarify the outcome that so few EQS/PNEC values were available, a meeting was held with the EA on the 22nd September 2022 for comment. Feedback from the EA was that there is currently not enough known data to generate appropriate EQS/PNEC values for each contaminant, but this research could help contribute to the current data shortage.

A total of 241 contaminants were tested for in the monitoring (B.10). Of the 241 contaminants tested for, 199 had an average concentration below the LOD which included 19 positive samples with concentrations above the LOD (Table B.2). Sample results below the LOD were represented within the analysis as half of the LOD value. Further comment on these contaminants cannot be made in this study and further analysis should be completed with a lower LOD. This is important for this study as Cyclohexyl-3-phenylurea (CPU), N, N'-dicyclohexylurea (DHU), hexa(methoxymethyl)melamine, and 2-methylthiobenzothiazole are known chemicals from tyres. For some contaminants, such as perfluorooctanesulfonic acid (PFOS), chrysene, pyrene and dibenzo(ah)anthracene, the EQS/PNEC value was below the LOD offered by the contracted lab[4]. Without more sensitive detection methods, it is not possible to comment on whether these contaminants should be of concern at this time.

[4] In some instances, LOD was higher than EQS/PNEC due to laboratory assessment methods and updated EQS/PNEC discovered after the contract award to the laboratory.

Table B.2 Contaminants detected at a lower average concentration in the samples than the associated LOD, and had positive samples collected.

Contaminant	Number of samples above LOD	LOD (µg/l)	EQS/PNEC (µg/l)*	Average concentration (µg/l)**
Dibenzo(ah)anthracene	4	0.005	0.0014	0.0045
PFOS	1	0.05	0.00065	0.0267
Cyclohexyl-3-phenylurea (CPU)	4	1	NA	0.853
N, N'-dicyclohexylurea (DHU)	4	1	NA	0.82
hexa(methoxymethyl)melamine	4	10	NA	7.267
2-methylthiobenzothiazole	2	1	NA	0.691

**Where no EQS/PNEC information is available, 'NA' is used.*

***Average concentration calculated from all samples. If the concentration for a sample was <LOD, this has been assigned a concentration equivalent to 50% of the LOD.*

The other 42 contaminants tested for (B.10) were present with average concentrations above the LOD. Although these contaminants have been detected, 29 of these are below the relevant EQS/PNEC information or there is no EQS/PNEC information available. These 29 contaminants are detailed in Table B.3.

Table B.3 Contaminants detected at a higher average concentration in the samples than the associated LOD, and below the relevant EQS/PNEC where available.

Contaminant	Number of samples above LOD	LOD (µg/l)	EQS/PNEC (µg/l)*	Average concentration (µg/l)**
Dissolved Antimony	12	2	5	3.53
Dissolved Arsenic	8	0.9	50	1.18
Dissolved Cadmium	10	0.03	0.45	0.044
Dissolved Lead	9	0.4	14	0.83
Dissolved Manganese	11	1.5	123	26.91
Total Arsenic	15	0.9	50	3.49
Total Cadmium	12	0.03	0.45	0.16
Total Lead	15	0.4	14	12.77
Total Mercury	8	0.01	NA	0.015
Acenaphthylene	10	0.005	1.3	0.006
Acenaphthene	9	0.005	3.7	0.007
Fluorene	9	0.005	0.25	0.006
Phenanthrene	11	0.005	0.5	0.039
Anthracene	9	0.005	0.1	0.009
Benzo(a)anthracene	11	0.005	NA	0.045
Benzo(bk)fluoranthene	11	0.008	NA	0.48
Benzo(a)pyrene	11	0.005	0.27	0.046
Indeno(123cd)pyrene	10	0.005	0.27	0.032
Polycyclic aromatic hydrocarbon (PAH) 16 Total	10	0.173	NA	0.032
Benzo(k)fluoranthene	10	0.008	NA	0.029

Contaminant	Number of samples above LOD	LOD (µg/l)	EQS/PNEC (µg/l)*	Average concentration (µg/l)**
Orthophosphate as P	5	0.01	NA	0.032
6:2 FTS	4	0.2	NA	0.78
Total Suspended Solids	13	10000	NA	98467
4-n-octylphenol	3	0.02	0.1	0.027
N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine	15	0.1	NA	1.16
Glyphosate	13	0.1	196	0.74
Benzothiazole-2-sulfonic acid (BTSA)	13	1	NA	28.25
Cyclohexylamine	4	0.1	NA	0.14
Hydroxy benzothiazole	6	1	NA	1.93
1-indanone	15	1	NA	2.67

**Where no EQS/PNEC information is available, 'NA' is used.*

***Average concentration calculated from all samples. If the concentration for a sample was <LOD, this has been assigned a concentration equivalent to 50% of the LOD.*

For some detectable contaminants, no EQS/PNEC information was available. Information within the literature suggests that some of these contaminants are toxic to aquatic organisms, such as N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD), which is toxic to coho salmon (a Pacific salmon species) in concentrations of 0.8-1.2 µg/l (Challis *et al.*, 2021), whilst 6:2 Fluorotelomer sulfonic acid (6:2 FTS) is known to be toxic to humans (Hamid *et al.*, 2019), although the toxicity of 6:2 FTS to the aquatic environment is yet to be determined. Bioaccumulation of these contaminants and the risk that poses to human health is also a concern (Waring and Harris, 2005), and has led to octyl phenols, for example, being identified as Water Framework Directive (WFD) priority substances (Díaz-González *et al.*, 2016). However, without known toxicity levels and associated EQS/PNEC information, it is difficult to determine if the concentration of these contaminants within the samples should be cause for concern. It is recommended that further investigation is needed for National Highways to understand the potential risks associated with these contaminants.

Where available, comparisons have been made between the data received and EQS/PNEC information. This has identified 13 pollutants where the average concentration, across the 15 samples collected, is greater than the associated EQS/PNEC; see Table B.4 for details.

Table B.4 Contaminants detected at a higher average concentration than the associated EQS/PNEC and sorted by ratio of average concentration to EQS/PNEC value.

Contaminant	Number of samples above LOD	Number of positive samples > EQS/PNEC	EQS/PNEC (µg/l)	Average concentration (µg/l)*	Ratio of concentration to EQS/PNEC
Total Copper	15	15	1	74.53	75:1
Pyrene	14	14	0.0046	0.146	32:1
Total Zinc	15	15	10.9	267.89	25:1
Chrysene	13	13	0.0029	0.07	24:1
Dissolved Copper	15	15	1	22.93	23:1
1,3-diphenylguanidine (DPG)	13	13	0.14	2.24	16:1
Dissolved Zinc	15	15	10.9	62.16	6:1
Benzo(b)fluoranthene	11	10	0.017	0.074	4:1

Contaminant	Number of samples above LOD	Number of positive samples > EQS/PNEC	EQS/PNEC (µg/l)	Average concentration (µg/l)*	Ratio of concentration to EQS/PNEC
Benzo(ghi)perylene	10	10	0.0082	0.032	4:1
Total Antimony	14	9	5	11.2	2:1
4-tert-octylphenol	11	10	0.1	0.13	1:1
Total Manganese	15	4	123	144.55	1:1
Fluoranthene	14	9	0.12	0.139	1:1

Average concentration calculated from all samples. If the concentration for a sample was <LOD, this has been assigned a concentration equivalent to 50% of the LOD.

NOTE: Dibenzo(ah)anthracene and PFOS are not included in this table due to lack on the number of positive samples above LOD (4 and 1, respectively). Based on data and analysis the respective ratio of concentration to EQS/PNEC would be 3:1 and 410:1. Further sampling with a lower LOD is required to better determine concern to the environment.

There was no clear relationship identified between contaminant concentration and AADT for the sample locations. Some contaminants were found to be present in similar concentration in the lowest and highest AADT areas. Other contaminants were seen in higher concentrations where the AADT was lowest, such as at Donnington Park, suggesting that vehicle behaviour and/or local land use may have influence at some locations. From the data available, no conclusion could be made regarding the impact of the shape of the road section, i.e., the difference between contaminant concentration at straight or curved sections.

The comparison of copper and zinc to the outputs of HEWRAT are made in Section B.5. Pyrene and Fluoranthene can also be compared to event mean concentrations within the HEWRAT Manual (Highways England, 2015). This shows that the average concentrations found in this study were below the total values in Table A.1 in the HEWRAT Manual (Pyrene: 0.146 µg/l in this study versus 1.03 µg/l in HEWRAT; Fluoranthene: 0.139 µg/l in this study versus 1.02 µg/l in HEWRAT).

B.4. Relationships between contaminants and microplastics

This section of the report focuses solely on the microplastic data from tyre wear particles (TWPs). The influent TWPs concentrations, along with the other influent contaminant concentrations from the same sample have been compared to see if there are any correlations with the TWPs concentrations. This could provide an indication if the contaminants have originated from the same source, or the TWPs have contributed to the pollution.

Comparable samples were collected at seven sites and any contaminants lower than the LOD were assigned as half of the LOD. The considerably higher concentrations of total suspended solids (656 mg/l), total zinc (1,645 ug/l) and total copper (315 ug/l), for example, from P.B. North (Sample 9) are suspected as outliers, which would skew the average concentrations. Therefore, this sample was removed, so there are only six sites that are suitable. The TWPs concentrations were plotted against detected contaminants of concern, example shown in Figure B.1 for all the contaminants, Figure B.2 for TSS, with full outputs shown in B.10.4. Total suspended solid concentrations were taken into consideration due to many contaminants having an affinity with sediment. The contaminants of interest were plotted against TWPs influent concentrations as shown and visually assessed for correlations. Figure B.1 shows a decreasing spread in contaminant concentrations as the amount of TWP increases. This could be due to the contaminants becoming bound to the TWPs.

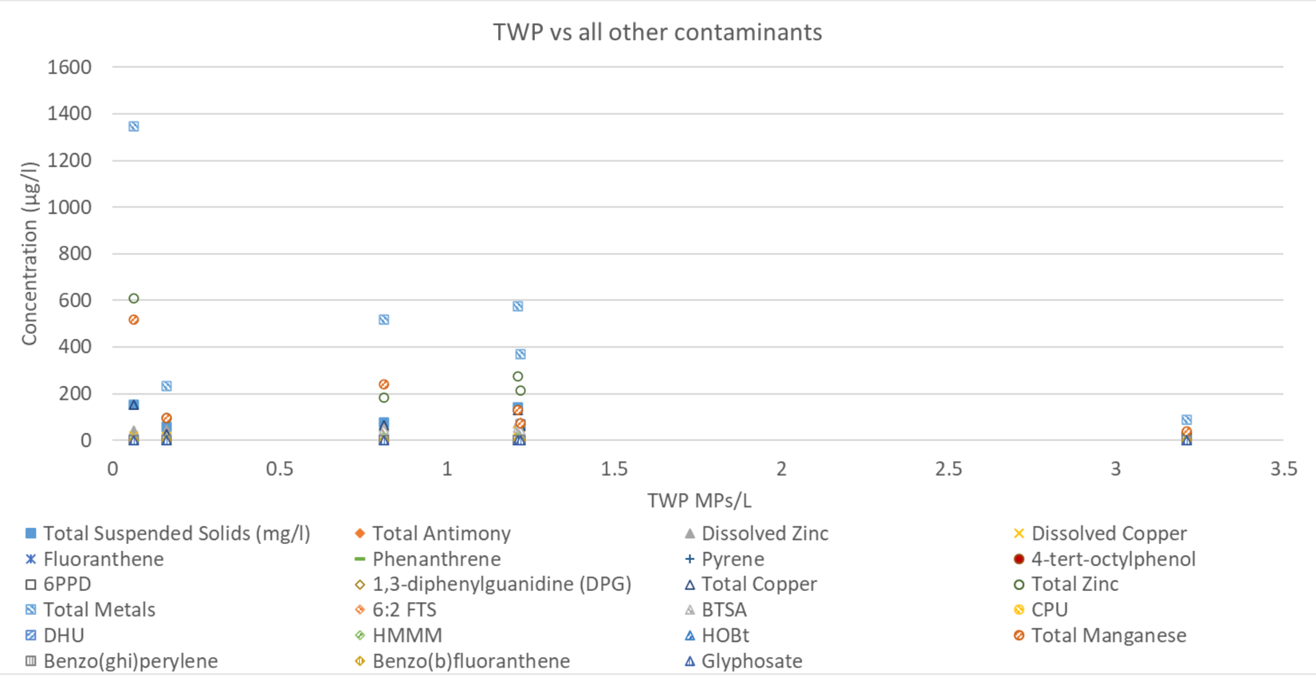

Figure B.1 TWP vs all contaminants sampled with positive results. All contaminant concentrations are presented in µg/l, except total suspended solids in mg/l.

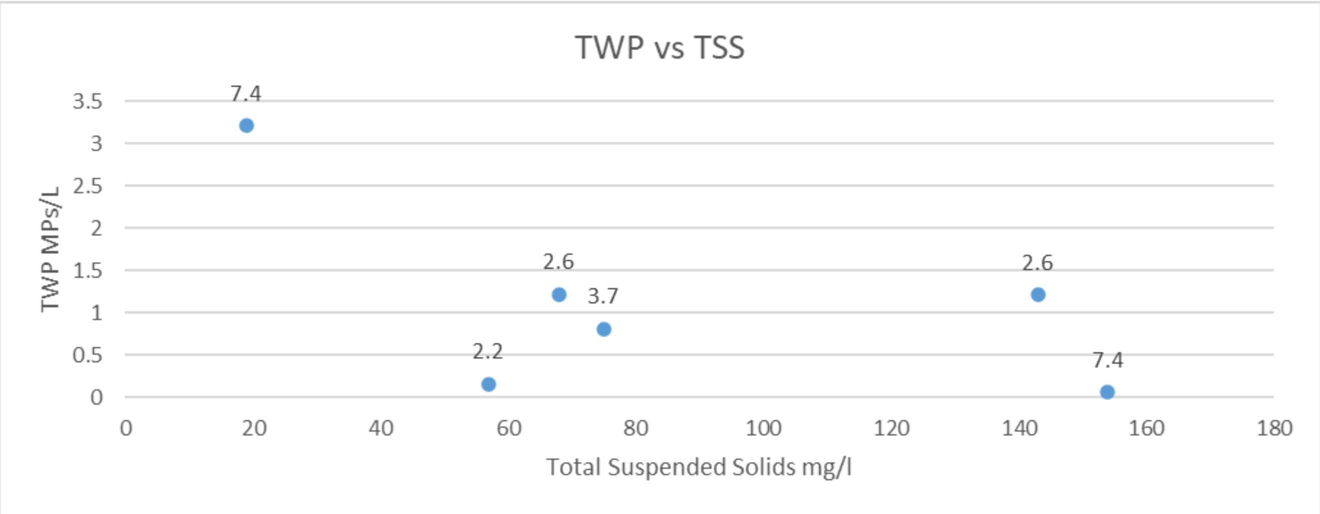

Figure B.2 TWP vs total suspended solids concentrations labelled with the rainfall depth prior to sample collection (mm).

The graphs show chemicals are weakly negatively correlated with TWPs; however, the strength of the correlations (R^2) and the significance (p value (two tier)) have not been included due to the small number of samples preventing statistical analysis. Therefore, a presence count is recorded within *Table B.5*. Most of the selected contaminants are present along with the TWPs having recorded sample values above LOD. This includes the metals, which corresponds with the two pollutants (copper and zinc) focused on in the HEWRAT assessment tool. Other emerging contaminants of concern that are consistently present are 6PPD, benzo(b)fluoranthene, polycyclic aromatic hydrocarbon (PAHs - phenanthrene, fluoranthene and pyrene), 1,3-diphenylguanidine (DPG) and benzothiazole-2-sulfonic acid (BTSA). This could indicate that they originate from the same source, or tyre particles have contributed to the pollution. However further sampling and analysis is needed to increase confidence in the conclusions, including further sampling in locations where types and usage of highways are similar, so variance is minimised to find common trends in the highway network.

Table B.5 Presence count of contaminants with TWPs per sample.

Contaminant	Number of positive samples out of 6 samples identified (samples that include microplastic concentrations) (excluding below LOD)
Total Suspended Solids (TSS)	6
Total Zinc	6
Total Metals	6
Total Manganese	6
Total Copper	6
Total Antimony	6
Pyrene	6
Phenanthrene	6
6PPD	6
Fluoranthene	6
Dissolved Zinc	6
Dissolved Copper	6
BTSA	6
Benzo(b)fluoranthene	6
DPG	6
Benzo(ghi)perylene	5
Glyphosate	5
HOBt	2
HMMM	2
4-tert-octylphenol	2
DHU	1
CPU	1
6:2 FTS	1
4-n-octylphenol	1
2-methylthiobenzothiazole	1

B.5. Comparison of sample results with HEWRAT

A comparison has been made between the 15 samples collected in the project against the outputs from HEWRAT v2.0.4. These focused on soluble copper, soluble zinc, soluble cadmium, phenanthrene, anthracene, fluoranthene, pyrene and total PAH as outputs are provided from HEWRAT. The HEWRAT input data for each of the respective sites is presented in B.10.5. Input data into HEWRAT was provided by the University of Plymouth and issues with the site data have been discussed in Appendix B.10.4. The mean and 99%ile HEWRAT outputs have been plotted against the concentration of copper and zinc at each sample site (Figure B.3, Figure B.4). For sites with multiple pollutant samples collected (all sample locations excluding Bodmin), a mean value was used to compare to its corresponding HEWRAT output, and individual sample values measuring below LOD were included as 50% of LOD value.

Outputs for copper and zinc present similar graphs with the P.B. North site greatly exceeding both the mean and 99%ile HEWRAT outputs (Figure B.3, Figure B.4). Only Donnington Park was above the mean predictions and remaining sites all below the mean predictions. For both copper and zinc, the HEWRAT outputs are shown to be in range of the samples collected.

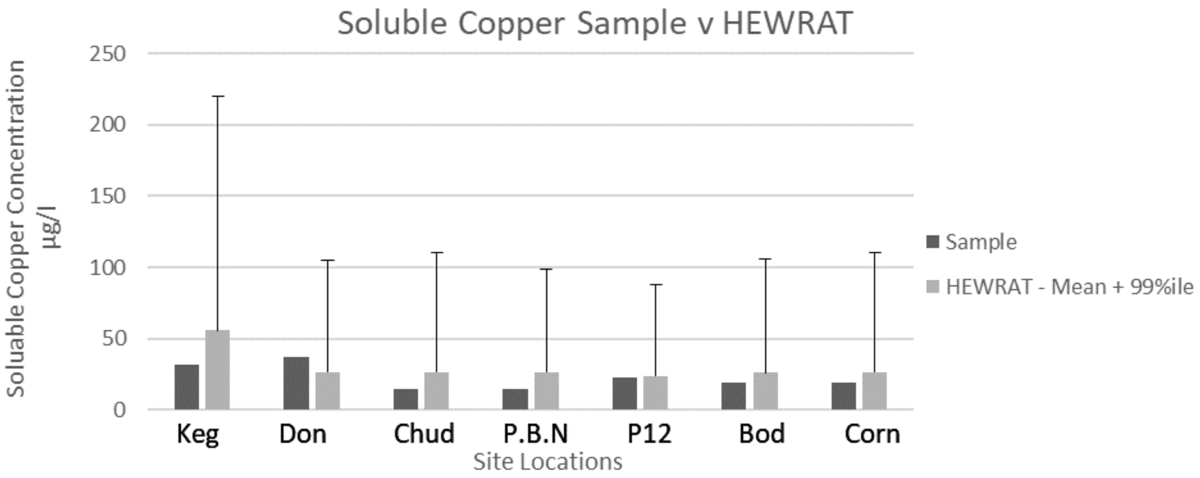

Figure B.3 Comparison of average soluble copper measured v HEWRAT outputs.

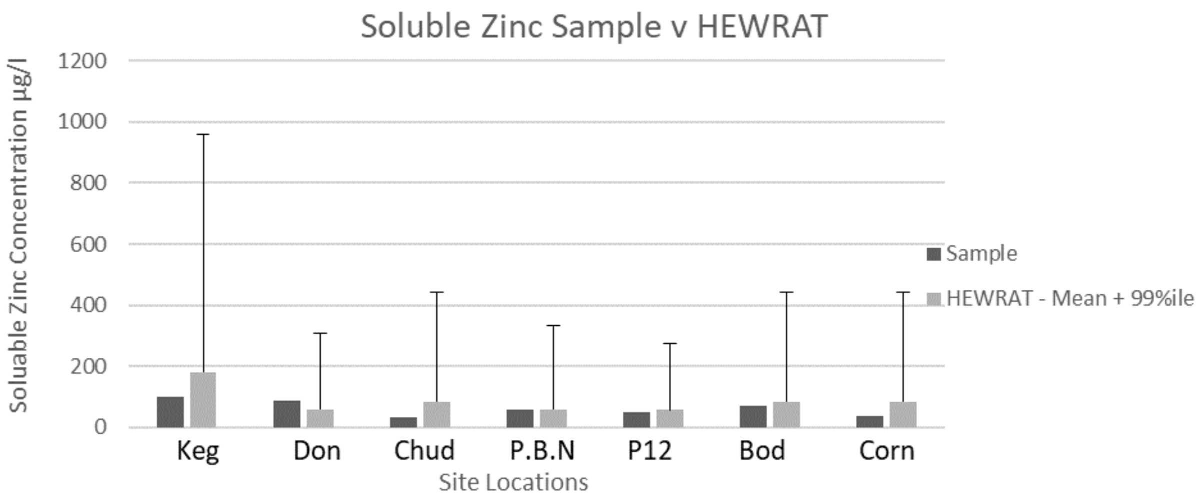

Figure B.4 Comparison of average soluble zinc measured v HEWRAT outputs.

From the sample comparisons to HEWRAT outputs, there is no evidence to suggest that the HEWRAT model is outputting incorrect data. That said, this investigation only intended to give an indication of the range of concentrations of pollutants in road runoff whilst focusing on monitoring for microplastics. Therefore, only a limited sample set has been used in this study with each sampling site having different characteristics, designs and expected driving styles from the traffic. Further assessment of HEWRAT should be undertaken with a wider, targeted sampling programme and contaminant sampling within the sediment to better understand confidence levels of HEWRAT base data.

An assessment of SuDS treatment efficiencies has not been possible in this project as samples were either collected from direct runoff (Chudleigh) or at inlets to receiving ponds. No water samples were taken at the outlets of the ponds.

B.6. Recommendations for improvements to HEWRAT

HEWRAT v2.0.4 was used in this study. The tool is currently a macro-enabled Microsoft Excel spreadsheet, which is 13 MB in size. It is recommended that HEWRAT be updated to be housed in an online digital user environment to improve user experience, efficiency of working and ability to work collaboratively with other project partners and stakeholders. Housing HEWRAT in an online digital environment would also enable better update capabilities for general user updates and updates to contaminant reference data, better localised rainfall data to be included, and the ability for National Highways to interrogate and understand usage of the tool for future updates and updating regulations.

B.7. Recommendations for future research

Future research is required to develop EQS/PNEC concentrations for contaminants that are commonly present within runoff samples. A total of 17 contaminants had recorded 139 positive samples and no EQS or PNEC values were available (Table B.6). Nine of these contaminants are known to be included in tyres. This is essential for understanding the range of contaminants of concern, their potential impacts, and how prevalent they are within the environment.

Table B.6 : Contaminants recorded with positive sample results without a comparative EQS/PNEC value.

Contaminant	LOD (µg/l)	Number of positive samples	Mean sample concentration (µg/l)	Maximum concentration (µg/l)
Mercury Total by CVAF	<0.01	8	0.015	0.09
Benzo(a)anthracene	<0.005	11	0.045	0.20
Benzo(bk)fluoranthene	<0.008	11	0.102	0.48
PAH-16 Total	<0.173	10	0.6909	2.79
Benzo(k)fluoranthene	<0.008	10	0.0293	0.13
Ortho Phosphate as P	<30	5	0.032	0.17
6:2 FTS	<0.2	4	0.780	7.00
Total Suspended Solids	<10,000	13	98,466.67	656,000.00
N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine	<0.1	15	1.157	4.36
Benzothiazole-2-sulfonic acid (BTSA)	<1	13	28.247	75.10
Cyclohexyl-3-phenylurea (CPU)	<1	4	0.853	2.50
Cyclohexylamine	<0.1	4	0.145	0.50
N, N'-dicyclohexylurea (DHU)	<1	4	0.820	2.10
Hexa(methoxymethyl)melamine	<10	4	7.267	20.00
Hydroxybenzothiazole	<1	6	1.935	10.40
1-indanone	<1	15	2.667	5.00
2-methylthiobenzothiazole	<1	2	0.690666667	2.57

Where EQS/PNEC values are below the LOD, methods will need to be improved to ensure detection of those contaminants to concentrations below toxicity levels. Without this, the extent to which these contaminants are present and the risk they pose cannot be assessed.

To better compare contaminant concentrations with other factors, such as AADT, dilution effects should be explored. This could not only be achieved through a greater amount of samples, but could also involve the installation of rain gauges at the sampling locations, allowing sample concentrations to be normalised and quantitatively compared to each other.

Further research is needed regarding the relationship between TWPs, and other contaminants commonly found in road runoff. The data presented here potentially demonstrates multiple positive correlations between TWPs and other contaminants, however, a larger sample size is required before the significance of these relationships can be determined.

B.8. Summary

- This study has been completed on a very limited number of samples and a wider and more thorough sampling study should be conducted to collect more robust data to inform decisions by National Highways. However, some early insights have been identified for contaminants of concern.

- A wide range of contaminants have been sampled within road runoff, of the 42 contaminants which were present in concentrations greater than the LOD, 30 of these contaminants have an established EQS/PNEC and 13 of these were found to be present in concentrations greater than the associated EQS/PNEC values (Table B.7). Six other contaminants also had positive samples, but the mean concentrations were below LOD values. Based on this limited dataset these contaminants should be considered worthy of further investigation as they have the potential to be at concentrations of concern in road runoff.

- Other potential contaminants of concern have been highlighted but further research is needed to identify the risk to the aquatic systems that their presence in road runoff may have.

Contaminants detected above the LOD in multiple samples have been presented in Table B.7 The contaminants that have not been investigated in previous National Highways runoff research undertaken by WRC (Moy et al., 2003), the availability of an EQS or PNEC and if the average concentrations exceed this standard are also presented. This list can be used to identify contaminants that are "new" to National Highways runoff research and if they have been detected in concentrations above the relevant standard. Table B.7: Contaminants worthy of further investigation

Contaminant	Included in WRc report?	Has an EQS/PNEC?	Average concentration > EQS/PNEC?
1,3-diphenylguanidine (DPG)	No	Yes	Yes
4-tert-octylphenol	No	Yes	Yes
Benzo(b)fluoranthene	Yes	Yes	Yes
Benzo(ghi)perylene	Yes	Yes	Yes
Chrysene	No	Yes	Yes
*Dibenzo(ah)anthracene**	*No*	*Yes*	*Yes*
Dissolved Copper	Yes	Yes	Yes
Dissolved Zinc	Yes	Yes	Yes
Fluoranthene	No	Yes	Yes
*PFOS**	*No*	*Yes*	*Yes*
Pyrene	No	Yes	Yes
Total Antimony	No	Yes	Yes
Total Copper	Yes	Yes	Yes
Total Manganese	No	Yes	Yes
Total Zinc	Yes	Yes	Yes
1-indanone	No	No	N/A
2-methylthiobenzothiazole	No	No	N/A
6:2 FTS	No	No	N/A
Benzo(a)anthracene	No	No	N/A
Benzo(bk)fluoranthene	No	No	N/A
Benzothiazole-2-sulfonic acid (BTSA)	No	No	N/A
Cyclohexyl-3-phenylurea (CPU)	No	No	N/A
Cyclohexylamine	No	No	N/A
Hexa(methoxymethyl)melamine	No	No	N/A
Hydroxybenzothiazole	No	No	N/A
Mercury Total by CVAF	No	No	N/A
N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine	No	No	N/A
N, N'-dicyclohexylurea (DHU)	No	No	N/A
Ortho Phosphate as P	No	No	N/A
PAH-16 Total	No	No	N/A

* Dibenzo(ah)anthracene and PFOS are included but there was a limited number of positive samples above LOD (4 and 1, respectively) – see Table B.4. Further sampling with a lower LOD is required to better determine concern to the environment from these determinands.

- Analysis has shown a decreasing spread in contaminant concentrations as the amount of TWP increases. This could be due to the contaminants becoming bound to the TWPs and no longer soluble within the water samples. Further sampling and analysis is needed to understand this observation.

- In all instances in this study, using specific metrics for each outfall studies, HEWRAT was found to generate copper and zinc concentrations that are comparable to the sample data, however, a wider study would be beneficial to analyse the robustness of this claim.

- It is recommended that HEWRAT be updated to be housed in a digital user environment to improve user experience, efficiency, and ability to work collaboratively, better localised rainfall data, and to help with future updates and changes to regulations.

- This work has highlighted the need for future research to provide confidence in the conclusions and recommendations made. Further research is also necessary to improve understanding of the risk of the presence and prevalence of different contaminants, and how these interact with the aquatic ecosystem both the short and long-term and how they interact with each other that could increase toxicity on the aquatic ecosystem.

B.9. References

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B.10. Supplementary Information

B.10.1. Contaminants analysed

Within the project, 241 contaminants were analysed from the 15 samples taken. Table B.8 lists the contaminants and pollutants being measured.

Table B.8 List of determinands and pollutants analysed from the 15 samples

Determinands Category	Pollutants	
Metals	Dissolved and total Antimony Dissolved and total Arsenic Dissolved and total Cadmium Dissolved and total Copper Dissolved and total Lead Dissolved and total Manganese Dissolved and total Zinc	Mercury Dissolved by cold vapor atomic fluorescence (CVAF) Total Hardness Dissolved (as $CaCO_3$) Mercury Total by CVAF
PAH	Naphthalene Acenaphthylene Acenaphthene Fluorene Phenanthrene Anthracene Fluoranthene Pyrene Benzo(a)anthracene Chrysene	Benzo(bk)fluoranthene Benzo(a)pyrene Indeno(123cd)pyrene Dibenzo(ah)anthracene Benzo(ghi)perylene PAH 16 Total Benzo(b)fluoranthene Benzo(k)fluoranthene PAH Surrogate % Recovery
Volatile Organic Compounds Toxic Industrial Chemical (VOC TICs)	Methyl Tertiary Butyl Ether Benzene Toluene Ethylbenzene	m/p-Xylene o-Xylene Surrogate Recovery Toluene D8 Surrogate Recovery 4-Bromofluorobenzene
Semi-Volatile Organic Compound (SVOC) TICs	Benzothiazole 2-Methylbenzothiazole Mercaptobenzothiazole Hydroxybenzothiazole	Aniline Stearic acid Bisphenol A
Acid Herbicides	Benazolin Bentazone Bromoxynil Clopyralid 4-Chlorophenoxyacetic acid 2,4-Dichlorophenoxyacetic acid 4-(2,4-dichlorophenoxy)butyric acid Dicamba Dichloroprop Diclofop Fenoprop Flamprop	Flamprop-isopropyl Ioxynil 2-methyl-4-chlorophenoxyacetic acid 4-(4-chloro-2-methylphenoxy)butanoic acid Mecoprop Picloram Pentachlorophenol 2,4,5-Trichlorophenoxyacetic acid 2,3,6-Trichlorobenzoic acid Triclopyr
Total Petroleum Hydrocarbons Clean Water Group (TPH CWG) – Aliphatics	>C5-C6 >C6-C8 >C8-C10 >C10-C12 >C12-C16	>C16-C21 >C21-C35 >C35-C44 Total aliphatics C5-44
TPH CWG – Aromatics	>C5-EC7 >EC7-EC8 >EC8-EC10 >EC10-EC12	>EC16-EC21 >EC21-EC35 >EC35-EC44 Total aromatics C5-44

Determinands Category	Pollutants	
	>EC12-EC16	Total aliphatics and aromatics(C5-44)
Other	Ortho Phosphate as P Total Suspended Solids	Sulphide
Perfluoroalkyl Acids (PFAAS)	Perfluorobutanoic acid Perfluoropentanoic Acid Hexafluoropropylene oxide-dimer acid Perfluorobutanesulfonic acid Perfluorohexanoic acid 4:2 Fluorotelomer sulfonic acid 3-perfluoropentyl propanoic acid Perfluoropentanesulfonic acid Perfluoroheptanoic acid Dodecafluoro-3H-4, 8-dioxanonanoatePFHxS Perfluorooctanoic acid 6:2 FTS Perfluoroheptanesulfonic acid 2H-Perfluoro-2-decenoic Acid Perfluorononanoic acid Perfluorooctane sulfonamide PFOS N-Methyl-perfluorooctanesulfonamide	perfluorodecanoic acid N-Ethyl-perfluorooctane sulfonamide 8:2 Fluorotelomer sulfonic acid 9-Chlorohexadecafluoro-3-Oxanone-1-Sulfonic Acid Perfluorononane sulfonic acid Perfluoroundecanoic acid N-methyl perfluorooctanesulfonamidoacetic acid N-Ethylperfluorooctanesulfonamidoacetic acid Perfluorodecane sulfonatePFDoA Perfluoroundecane sulfonic acid Perfluorotridecanoic acid Perfluorododecane sulfonic acid Perfluorotetradecanoic acid Perfluorotridecane sulfonic acid Perfluorohexadecanoic acid Perfluorooctadecanoic acid 8:2 Fluorotelomer phosphate diester
SVOC – Phenols	2-Chlorophenol 2-Methylphenol 2-Nitrophenol 2,4-Dichlorophenol 2,4-Dimethylphenol 2,4,5-Trichlorophenol	2,4,6-Trichlorophenol 4-Chloro-3-methylphenol 4-Methylphenol 4-Nitrophenol Pentachlorophenol Phenol
SVOC - PAHs	2-Chloronaphthalene	2-Methylnaphthalene
SVOC – Phthalates	Bis(2-ethylhexyl) phthalate Butylbenzyl phthalate Di-n-butyl phthalate	Di-n-Octyl phthalate Diethyl phthalate Dimethyl phthalate
SVOC - Other	1,2-Dichlorobenzene 1,2,4-Trichlorobenzene 1,3-Dichlorobenzene 1,4-Dichlorobenzene 2-Nitroaniline 2,4-Dinitrotoluene 2,6-Dinitrotoluene 3-Nitroaniline 4-Bromophenylphenylether 4-Chloroaniline 4-Chlorophenylphenylether 4-Nitroaniline Azobenzene Bis(2-chloroethoxy)methane	Bis(2-chloroethyl)ether Carbazole Dibenzofuran Hexachlorobenzene Hexachlorobutadiene Hexachlorocyclopentadiene Hexachloroethane Isophorone N-nitrosodi-n-propylamine Nitrobenzene Surrogate Recovery 2-Fluorobiphenyl Surrogate Recovery p-Terphenyl-d14
VOC	Dichlorodifluoromethane Methyl Tertiary Butyl Ether Chloromethane Vinyl Chloride Bromomethane Chloroethane Trichlorofluoromethane 1,1-Dichloroethene (1,1 DCE) Dichloromethane (DCM) trans-1-2-Dichloroethene 1,1-Dichloroethane	Chlorobenzene 1,1,1,2-Tetrachloroethane Ethylbenzene m/p-Xylene o-Xylene Styrene Bromoform Isopropylbenzene 1,1,2,2-Tetrachloroethane Bromobenzene 1,2,3-Trichloropropane

Determinands Category	Pollutants	
	cis-1-2-Dichloroethene 2,2-Dichloropropane Bromochloromethane Chloroform 1,1,1-Trichloroethane 1,1-Dichloropropene Carbon tetrachloride 1,2-Dichloroethane Benzene Trichloroethene (TCE) 1,2-Dichloropropane Dibromomethane Bromodichloromethane cis-1-3-Dichloropropene Toluene trans-1-3-Dichloropropene 1,1,2-Trichloroethane Tetrachloroethene (PCE) 1,3-Dichloropropane Dibromochloromethane 1,2-Dibromoethane	Propylbenzene 2-Chlorotoluene 1,3,5-Trimethylbenzene 4-Chlorotoluene tert-Butylbenzene 1,2,4-Trimethylbenzene sec-Butylbenzene 4-Isopropyltoluene 1,3-Dichlorobenzene 1,4-Dichlorobenzene n-Butylbenzene 1,2-Dichlorobenzene 1,2-Dibromo-3-chloropropane 1,2,4-Trichlorobenzene Hexachlorobutadiene Naphthalene 1,2,3-Trichlorobenzene Surrogate Recovery Toluene D8 Surrogate Recovery 4-Bromofluorobenzene
Other Determinands	4-n-octylphenol 4-tert-octylphenol N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine Glyphosate Aminobenzothiazole Benzothiazole-2-sulfonic acid (BTSA) Cyclohexyl-3-phenylurea (CPU) Cyclohexylamine	N, N'-dicyclohexylurea (DHU) N,N'-diphenylurea (DPU) 1,3-diphenylguanidine (DPG) hexa(methoxymethyl)melamine hydroxybenzothiazole 1-indanone 2-methylthiobenzothiazole Mercaptobenzothiazole octyl mercaptan dicyclohexylamine nitrite

B.10.2. EQS/PNEC values obtained from desk study

Table B.9 EQS/PNEC values used in project, with reference to source country if not England.

Contaminant	LOD (µg/l)	EQS* (µg/l)	PNEC* (µg/l)	Source Country, if not England
Dissolved Antimony	2	5		
Dissolved Arsenic	0.9	50		
Dissolved Cadmium	0.03	0.45		
Dissolved Copper	15	1		
Dissolved Lead	0.4	14		
Dissolved Manganese	1.5	123		
Dissolved Zinc	15	10.9		
Total Antimony	9	5		
Total Arsenic	0.9	50		
Total Cadmium	0.03	0.45		
Total Copper	15	1		
Total Lead	0.4	14		
Total Manganese	4	123		
Total Zinc	15	10.9		
Dissolved Mercury	0.01	0.07		

Contaminant	LOD (µg/l)	EQS* (µg/l)	PNEC* (µg/l)	Source Country, if not England
Acenaphthylene	0.005	1.3		Ministry of Environment and Food of Denmark
Acenaphthene	0.005		3.7	Institut national de l'environnement industriel et des risques (France)
Fluorene	0.005		0.25	Institut national de l'environnement industriel et des risques (France)
Phenanthrene	0.005		0.5	Umweltbundesamt (Germany)
Anthracene	0.005	0.1		
Benzo(a)pyrene	0.005	0.27		
Dibenzo(ah)anthracene	0.005	0.0014		Ministry of Environment and Food of Denmark
Indeno(123cd)pyrene	0.005	0.27		
4-n-octylphenol	0.02	0.1		
Glyphosate	0.1	196		
Fluoranthene	9	0.12		
Pyrene	14	0.0046		Ministry of Environment and Food of Denmark
Naphthalene	0.1	2		
Chrysene	13		0.0029	National Institute for Public Health and the Environment (Netherlands)
Benzo(ghi)perylene	10	0.0082		
Benzo(b)fluoranthene	10	0.017		
4-tert-octylphenol	10	0.1		
1,3-diphenylguanidine (DPG)	13	0.14		
N Diphenylurea (DPU)	1	0.00014		
PFOS	0.05	0.00065		
PFBS	0.05		4.08	
PFPeA	0.05		3.91	
PFHpA	0.05		0.5	
PFHxA	0.05		1.09	
PFHxS	0.05		0.87	

**Values obtained from previous literature review and Norman Database (https://www.norman-network.com/nds/ecotox/).*

B.10.3. Sampling results

Available as a separate Excel file. (Data for Appendix B.10.3.xls).

B.10.4. Tyre wear particle concentrations against detected contaminants

Contaminants that have only one detectable sample have been excluded from the comparison.

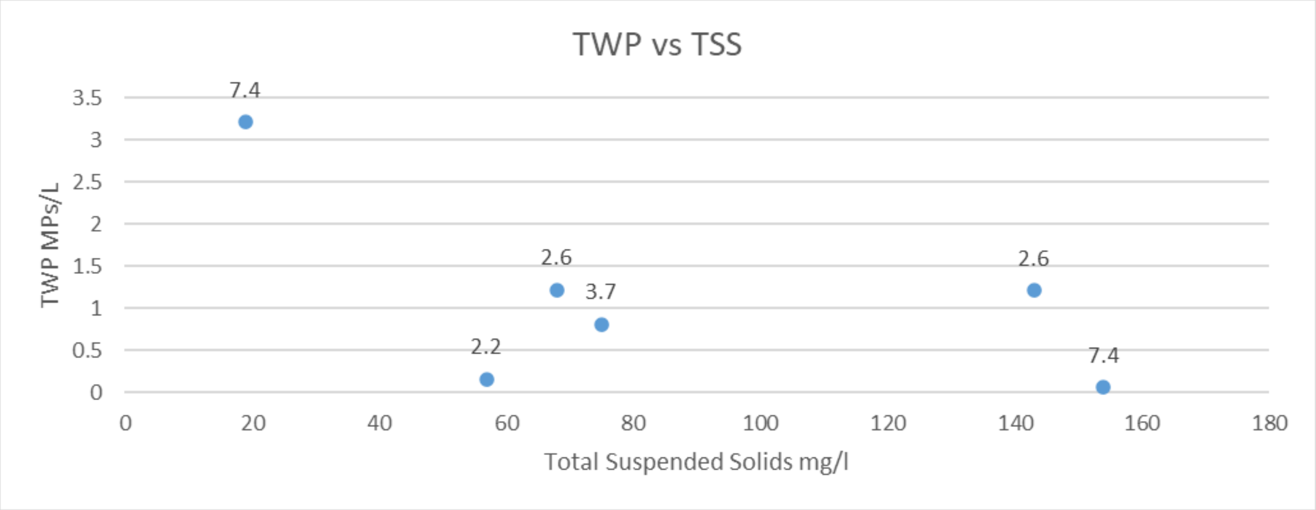

Figure B.5 TWP vs total suspended solids concentrations labelled with the rainfall depth prior to sample collection (mm)

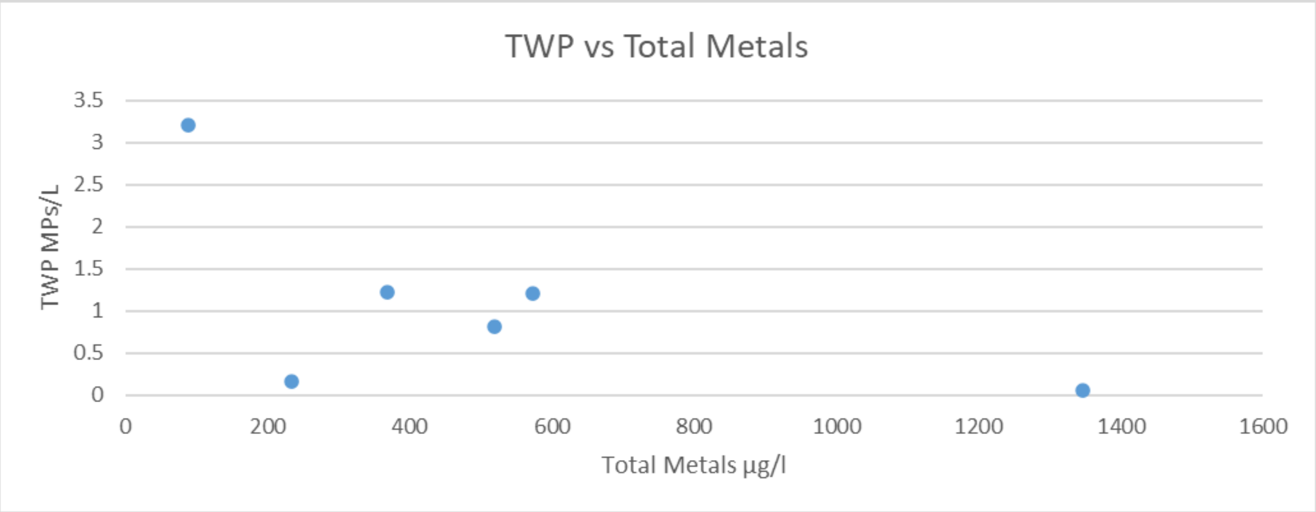

Figure B.6 TWP vs total metals concentrations

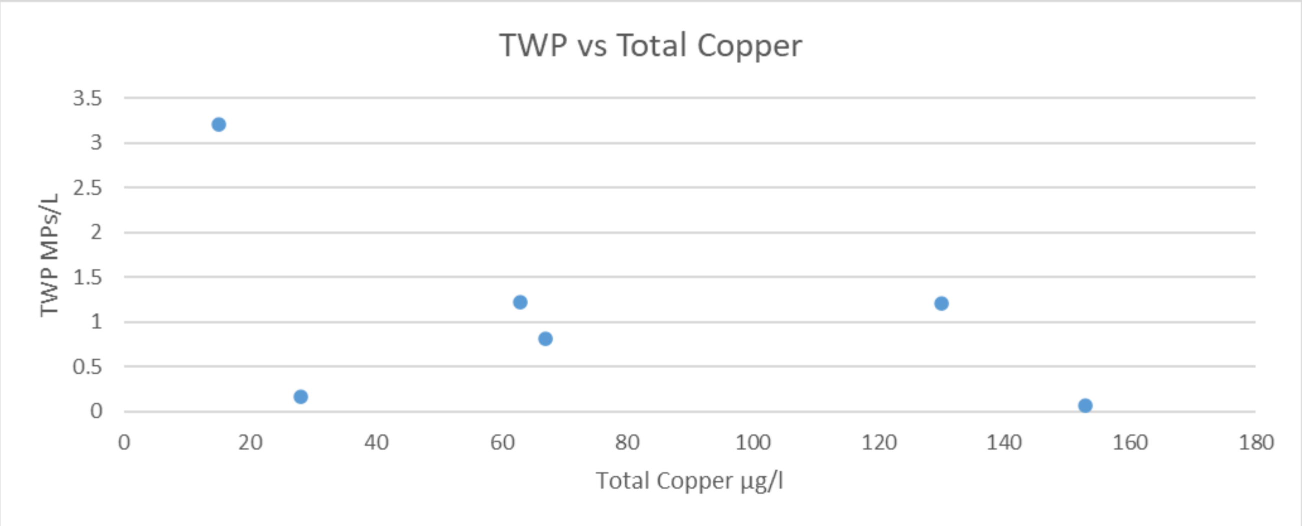

Figure B.7 TWP vs total copper concentrations

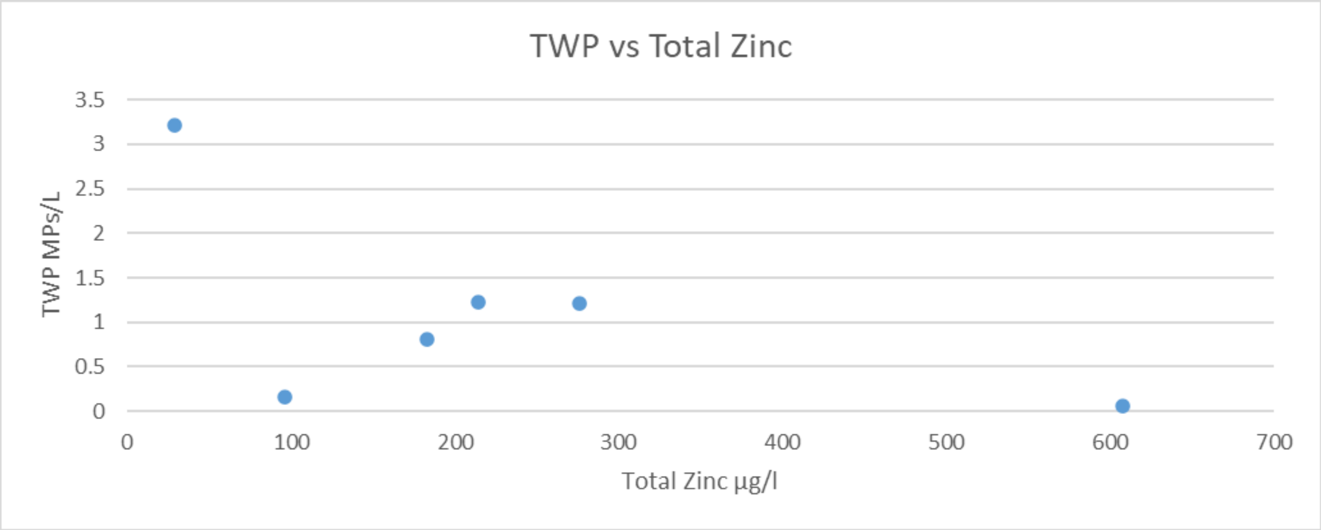

Figure B.8 TWP vs total zinc concentrations

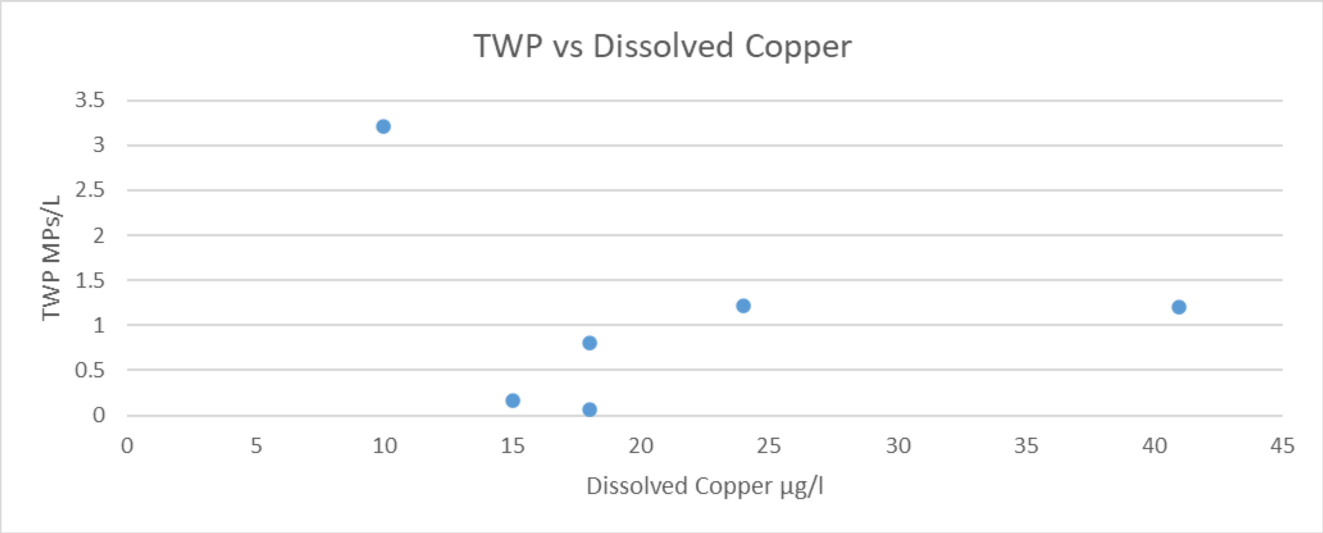

Figure B.9 TWP vs dissolved copper concentrations

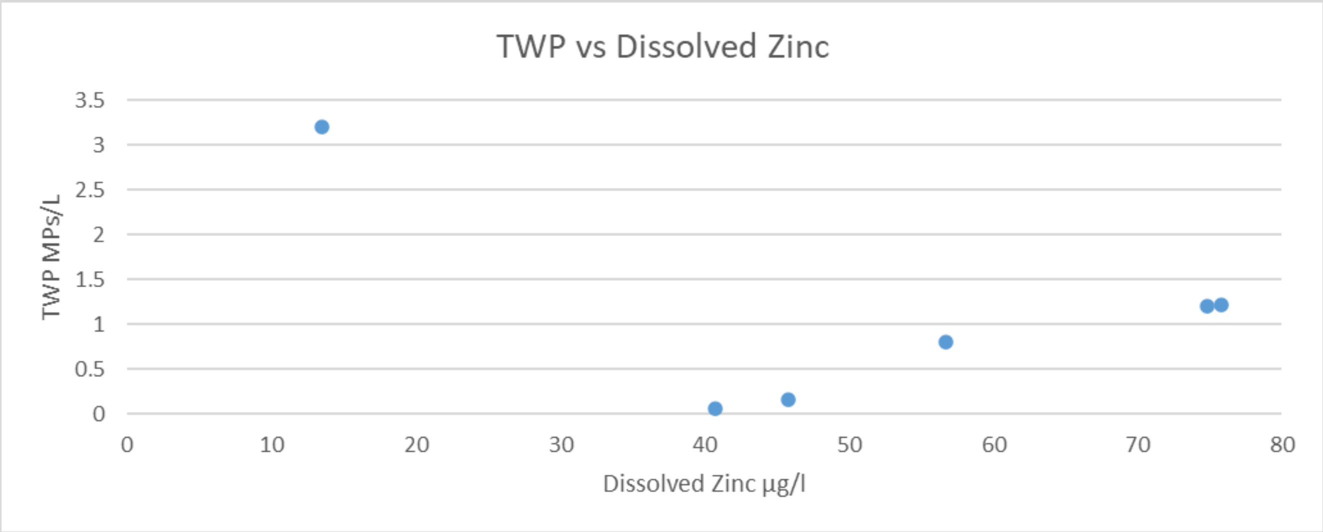

Figure B.10 TWP vs dissolved zinc concentrations

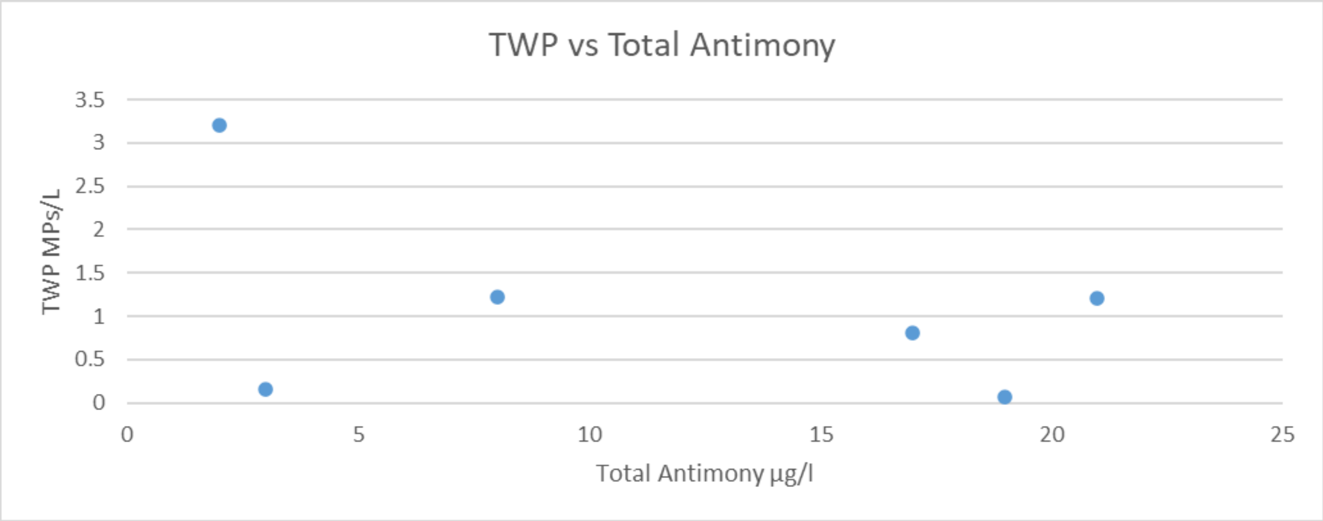

Figure B.11 TWP vs total antimony concentrations

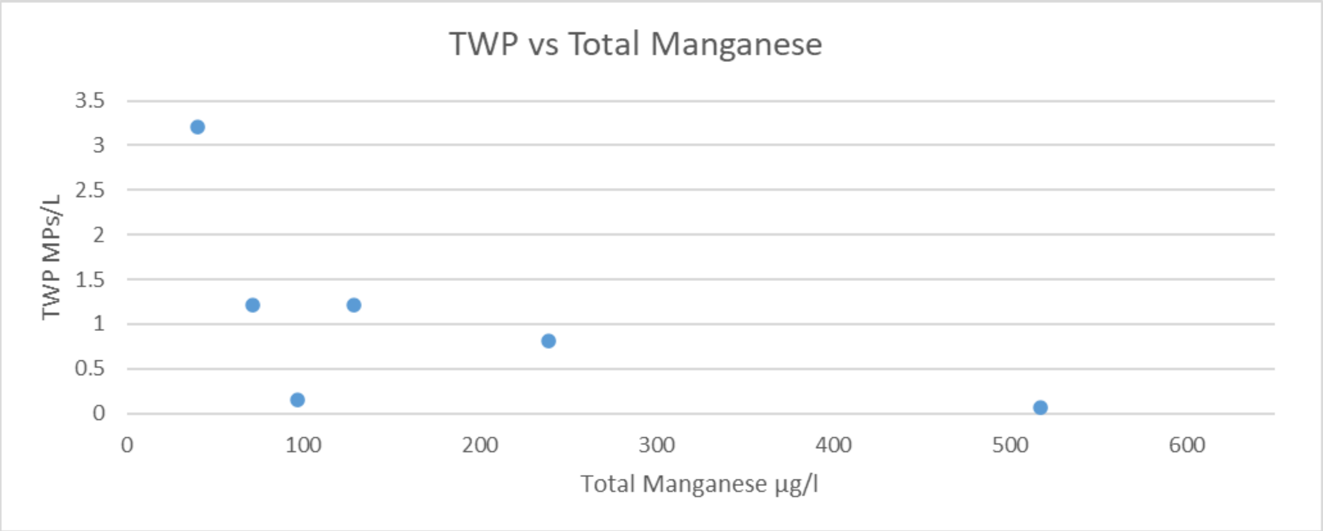

Figure B.12 TWP vs total manganese concentrations

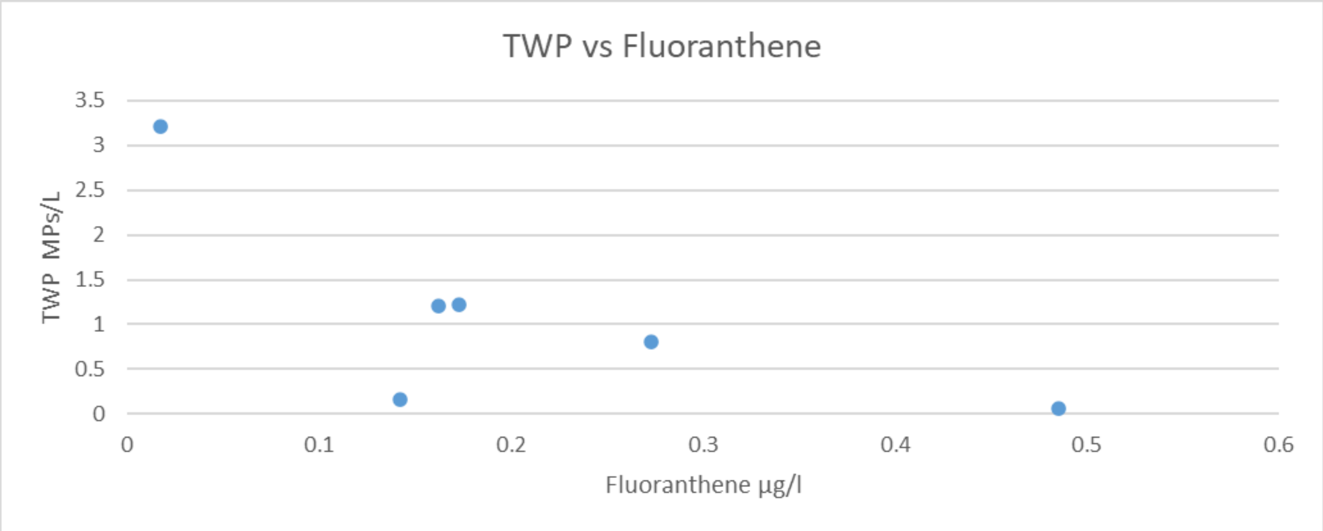

Figure B.13 TWP vs fluoranthene concentrations

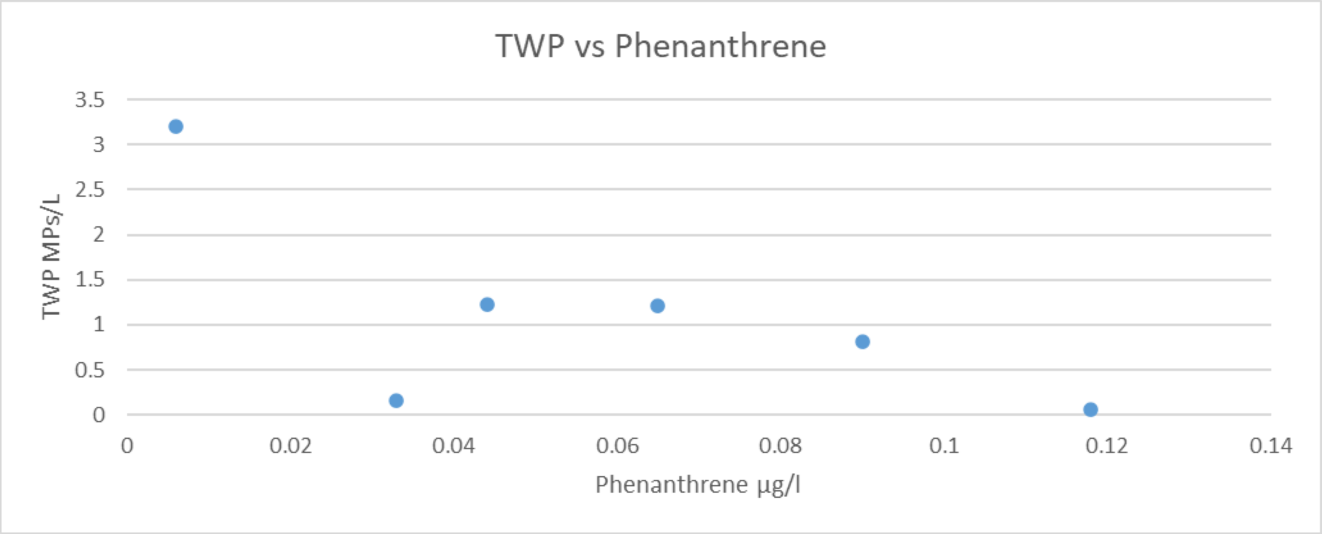

Figure B.14 TWP vs phenanthrene concentrations

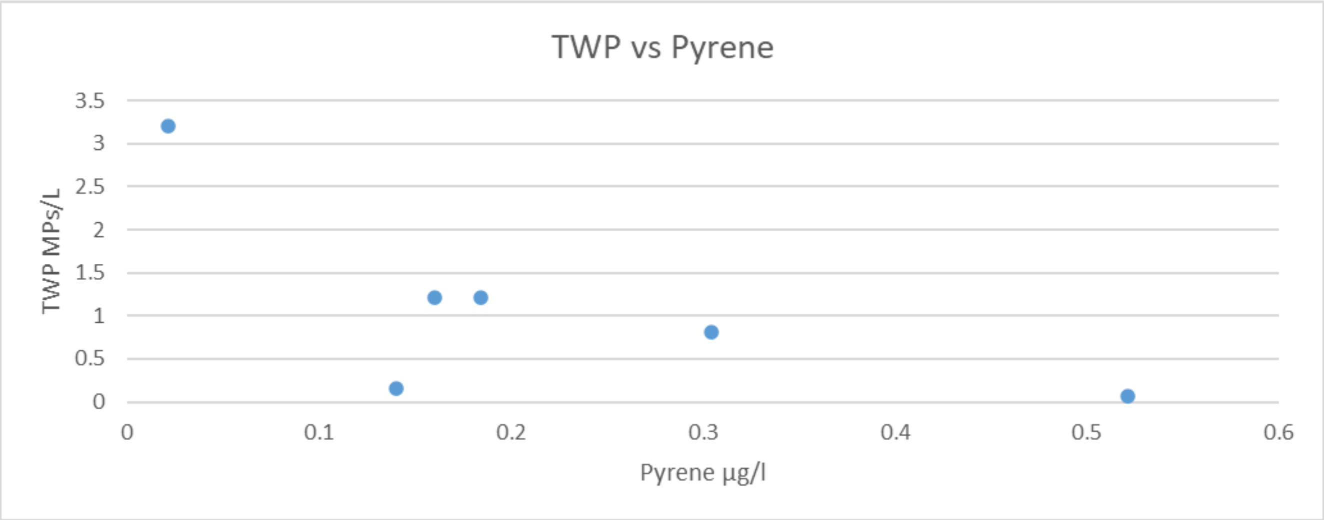

Figure B.15 TWP vs pyrene concentrations

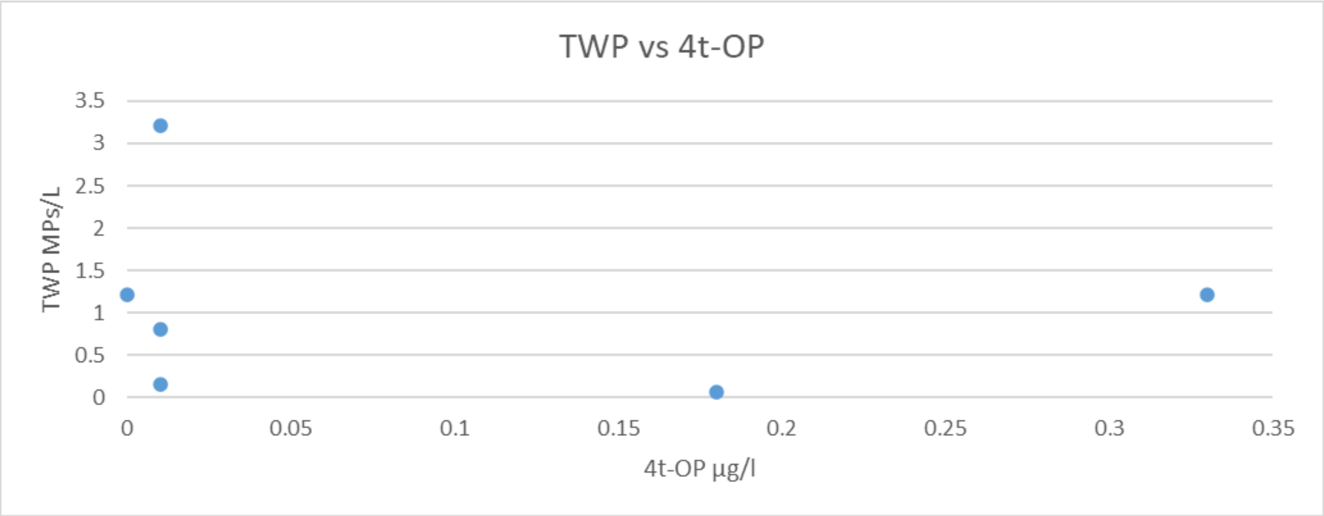

Figure B.16 TWP vs 4-tert-octylphenol (4t-OP) concentrations

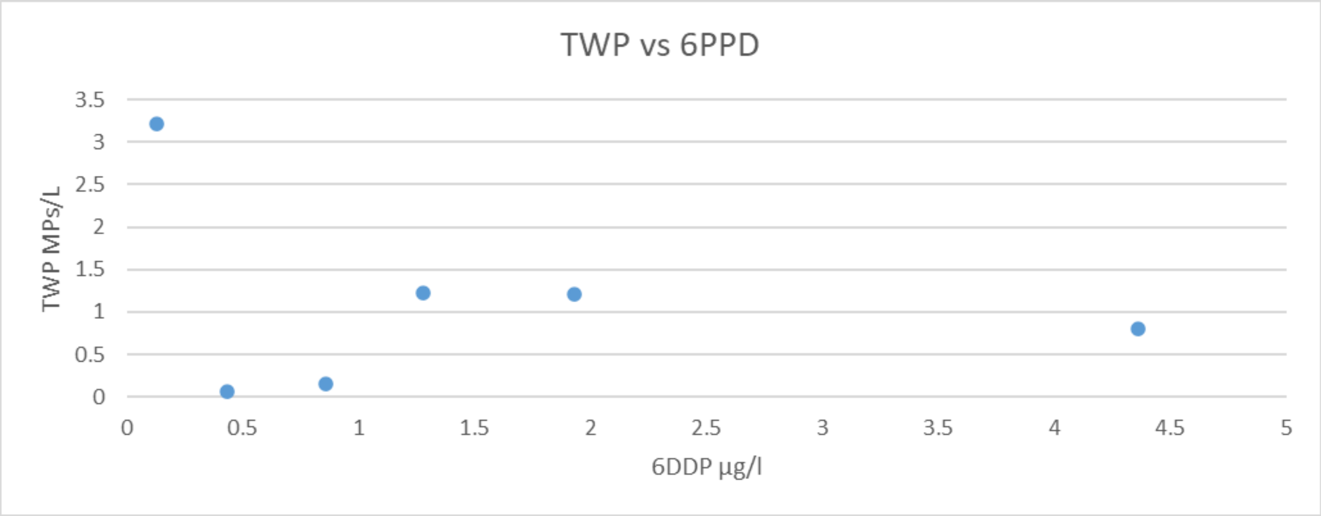

Figure B.17 TWP vs N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) concentrations

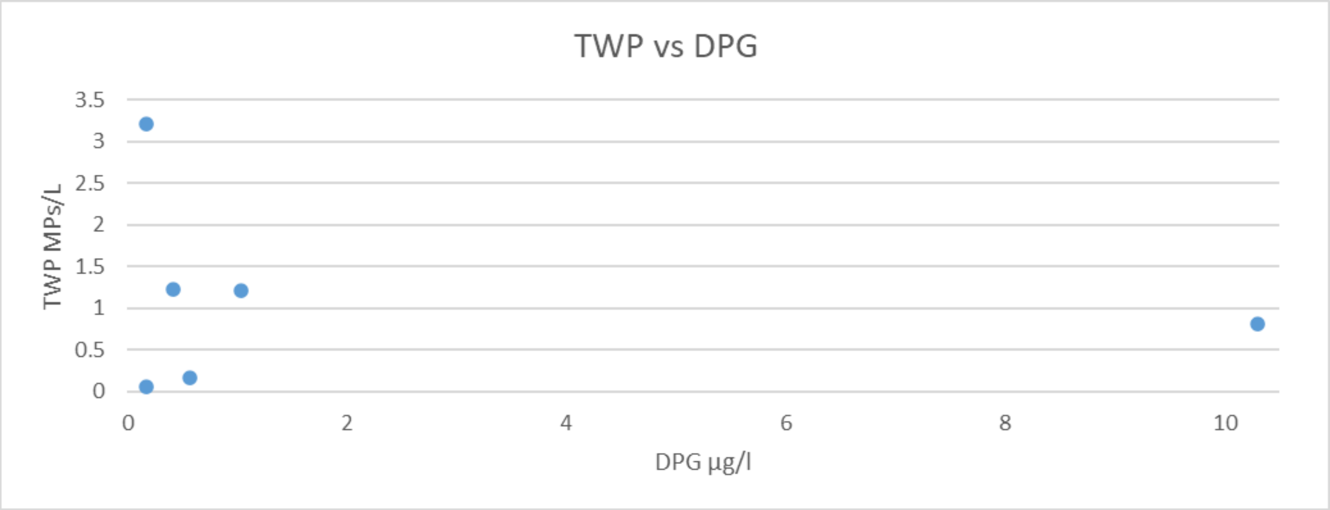

Figure B.18 TWP vs 1,3-diphenylguanidine (DPG) concentrations

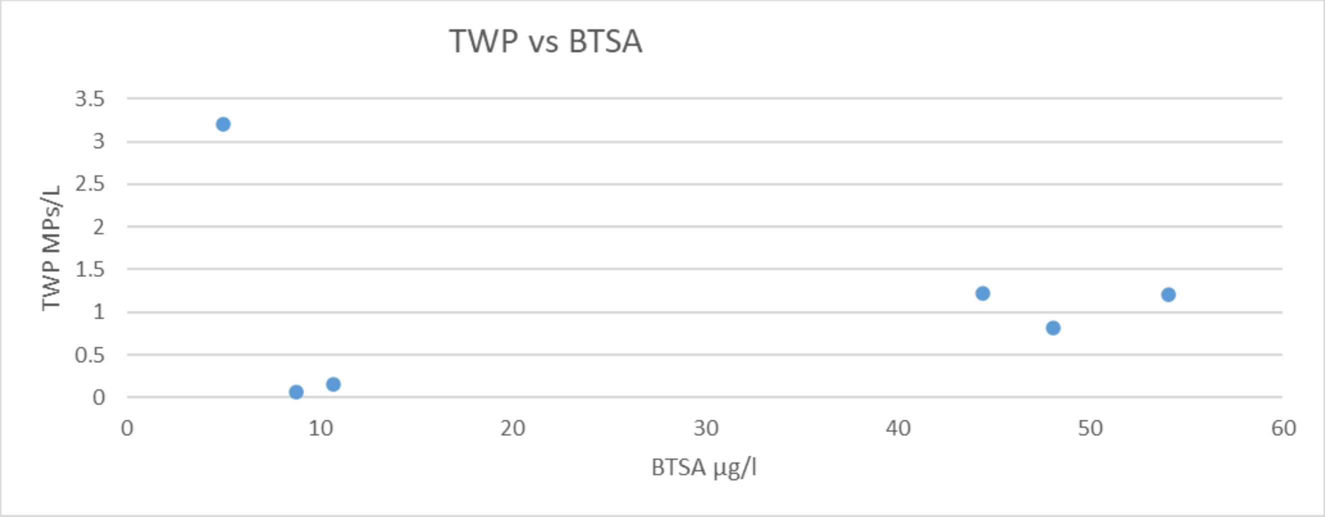

Figure B.19 TWP vs Benzothiazole-2-sulfonic acid (BTSA) concentrations

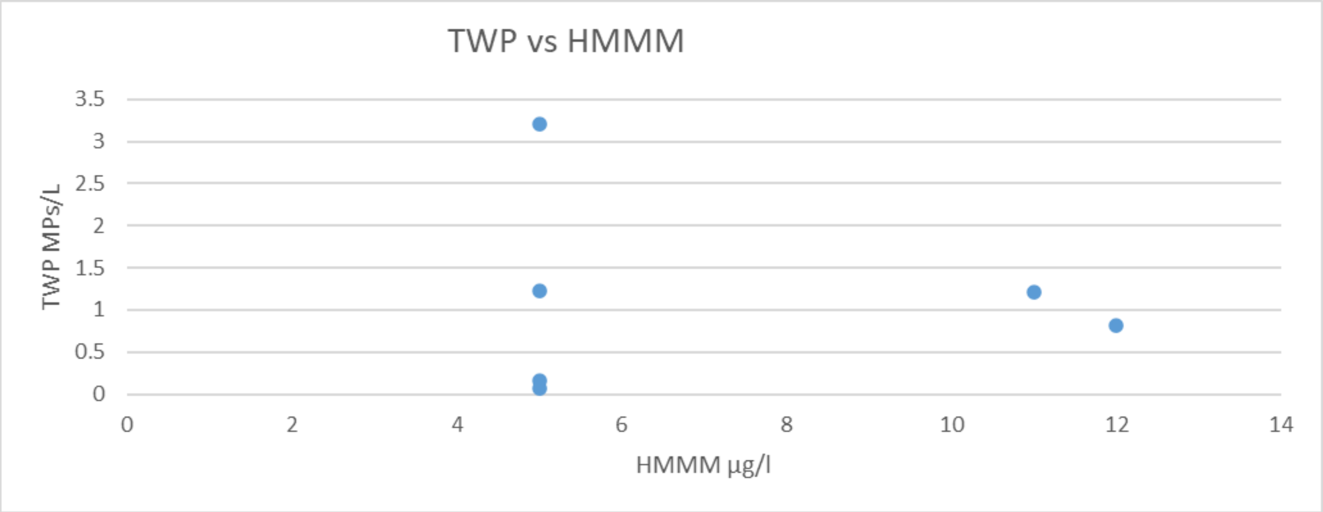

Figure B.20 TWP vs Hexa(methoxymethyl)melamine (HMMM) concentrations

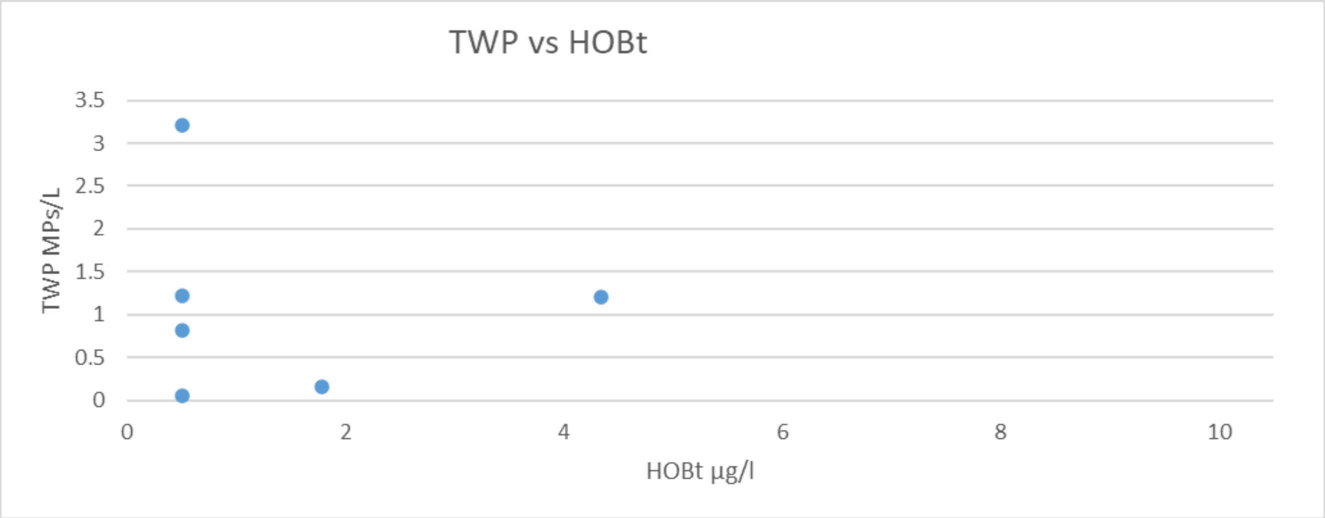

Figure B.21 TWP vs Hydroxy benzothiazole (HOBt) concentrations

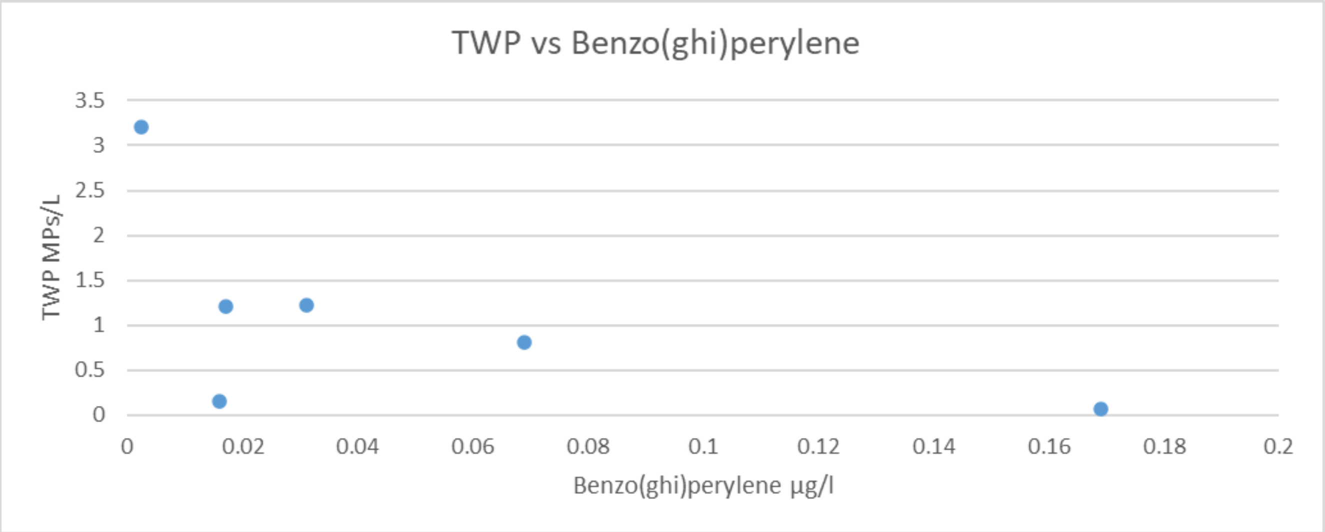

Figure B.22 TWP vs benzo(ghi)perylene concentrations

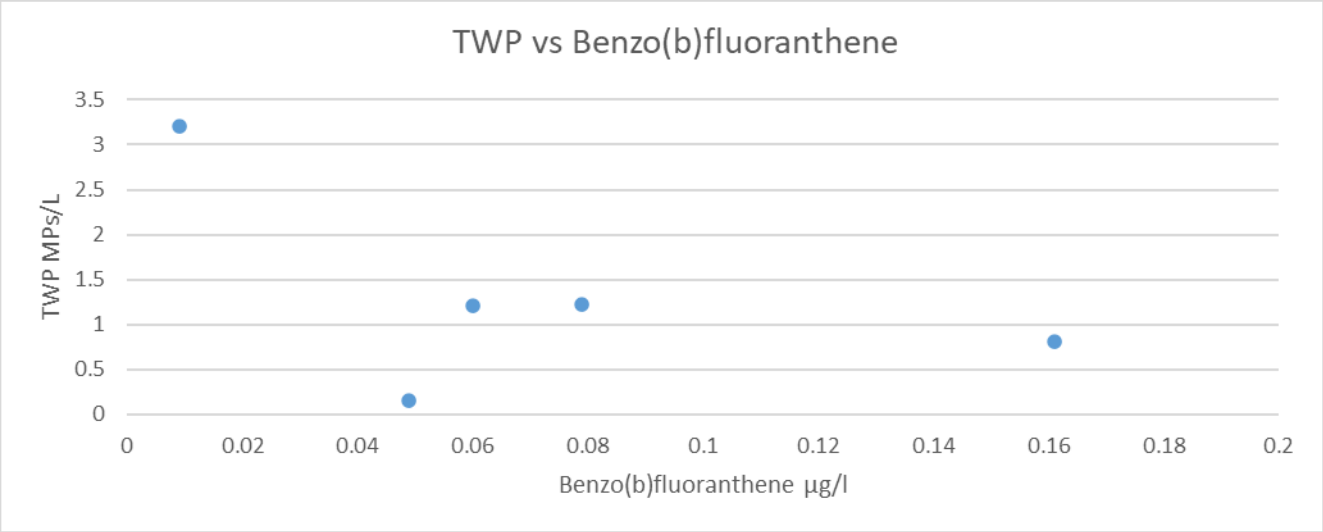

Figure B.23 TWP vs benzo(b)fluoranthene concentrations

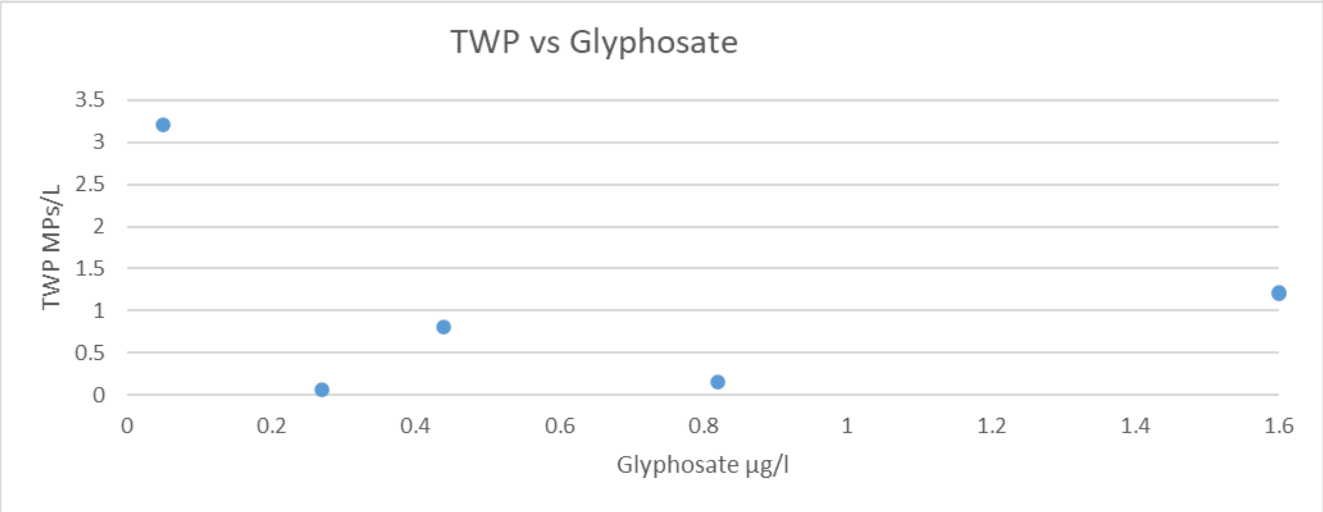

Figure B.24 TWP vs glyphosate concentrations

B.10.5. Input data to HEWRAT

Table B.10 Input data for HEWRAT models.

Parameters*	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7
Site name	Kegworth	Donnington Park	Chudleigh	Bicester	Pond 12	Bodmin	Cornwall Services
Site Data							
Road number	M1, J24a, slip road	A453	A38	M40, J9	A30	A38	A30, slip road
Assessment type	Single outfall	Single outfall	Single outfall	Single outfall	Single outfall	Single outfall	Single outfall
Receiving water course	Trib. of River Soar	Trib. of River Soar	Kate Brook - River Teign	Trib. of River Cherwell/RSPB Otmoor	Trib. of Upper River Ruthern	Trib. of River Fowey	Trib. of Par River
Step 1 - Runoff Quality							
AADT	>=100k	10-50k	10-50k	10-50k	10-50k	10-50k	10-50k
Climate region	Warm Dry	Warm Dry	Warm Wet	Warm Dry	Warm Wet	Warm Wet	Warm Wet
Rainfall site	Birmingham	Birmingham	Exeter	London	Bodmin	Bodmin	Bodmin
Step 2 - River Impacts							
Annual Q95 river flow (m^3/s)**	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Impermeable area (ha)	1.892	9.5237	9.3564	4.0955	0.65	1.3706	2.2
Permeable area (ha)							
Base Flow Index							
Bioavailable dissolved copper (µg/l)	1	1	1	1	1	1	1
Bioavailable dissolved zinc (µg/l)	10.9	10.9	10.9	10.9	10.9	10.9	10.9
Discharge within 1km upstream of protected site?	No	No	No	Yes	No	No	No
Water hardness	Low	Low	Medium	Medium	Low	Low	Low
Ambient background copper concentration (µg/l)							
Sediment impact - Tier 1:							

Parameters*	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7
Estimated river width (m)	2	2	4	2	3	5	3
Sediment impact - Tier 2***:							
Bed width (m)							
Manning's n							
Side slope (m/m)							
Long slope (m/m)							

*Parameters with no data input into table were left blank in HEWRAT assessment.

**Annual Q95 flow rates all set at minimum flow-rates as discharge locations are at end of minor tributaries and not near monitoring stations with available data.

*** Sediment impact - Tier 2 not undertaken due to not available data on watercourse.

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