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MICROPROOF
Micropollutants in Road Run-Off

Measurements of organic micropollutants, microplastics and associated substances from road transport

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1 Introduction

Road transport are responsible for a wide range of pollutants. Concentrations of suspended solids and metals in runoff are relatively well known and measured more frequently, but concentrations of other pollutants like microplastics and organic micropollutants is only measured sporadically.

Within work package 1 of the Microproof project, a list of potential pollutants from road transport is derived. D1.3 contains a list of pollutants that may be the most interesting. Since data on these pollutants are scarce, it was decided to do extra measurement on concentrations of these pollutants in runoff, surface water, sediment and soil.

This report provides a description of the methodology (chapter 2) and the results from the measurements.

2 Sampling sites

Tyre wear particles (as the main microplastic from roads) and organic micropollutants have been measured from 4 different sites in the Netherlands, Germany and Sweden. Table 1 shows the samples per site that have been gathered for measurement. Runoff is measured as direct runoff from the road edge. In Sweden, runoff water is gathered in a well next to the road. This well contains runoff water, but already a part of the pollutants in the runoff water has already deposited. Well sludge contains the deposited particles from the runoff, and this is similar to sludge from a treatment system. Solids from the road surface are collected with a wet dust sampler. Soil is sampled at three different distances from the road (1 meter, 5 meter and 10 meter distance from the road).

Table 1 Samples per site. S: Concentration in solids. W: Concentration in water. T: Total concentration

	Netherlands, A2	Netherlands, Rhine	Netherlands, Meuse	Germany, A61	Sweden, E18
Runoff				S, W, T	
Well water					S, W, T
Well sludge					S
Solids from road surface					S, W, T
Soil 1 m				S	S
Soil 5 m				S	S
Soil 10 m				S	S
Surface water	S, W, T	S	S		
Sediment waterway	S				

2.1 Netherlands, Highway A2

In the Netherlands, in a surface water body next to the A2, a sample has been taken of the surface water and the sediment. Figure 1 show the location of the surface water body. The A2 highway in the Netherlands is a busy highway with 5 lanes in each direction (10 lanes in total) and an emergency lane. The average traffic intensity in 2018 on a working day is 190,000 vehicles per day. The asphalt consists of porous asphalt, which reduces the amount of pollutants that could reach the surface water body. Next to the road a guardrail is present. The surrounding area is flat and does not contain any trees. The main wind direction is crosswise to the road. Based on the combination of wind crosswise to the road and no wind obstruction, it can be expected that spray of water and pollutants from the road is an important pathway. However, the porous asphalt and the presence of an emergency lane reduces the amount of spray.

Figure 1 Location of the surface water samples at the A2 highway in the Netherlands. Coordinates: 52.24 N, 4.98 E. Pictures from Google Maps.

2.2 Netherlands, Rhine

In the river Rhine, near Lobith (the border between the Netherlands and Germany), solids from surface water have been gathered by Rijkswaterstaat using a continuous centrifuge system. Samples from 31 January 2018 and from 15 July 2009 have been used in this study. The river Rhine is a large European river with an average flow of 2200 m^3 per second (near Lobith). Characteristics of the Rhine at the date of sampling are presented in Table 2.

Table 2 Flow and suspended matter concentration of the Rhine at the dates of sampling

	Flow (m3 per second)	Suspended matter concentration (mg/l)
31 January 2018	5469	36
15 July 2009	1816	6
Overall average	2200	16

Source: https://waterinfo.rws.nl

Due to the relatively large flow on 31 January 2018, resuspension occurred, and the concentration suspended matter was higher than average.

2.3 Netherlands, Meuse

In the river Meuse, near Eijsden (the border between the Netherlands and Belgium), solids from surface water have been gathered by Rijkswaterstaat using a continuous centrifuge system. Samples from 26 June 2018 and from 14 June 2005 have been used in this study. The river Meuse is a European river with an average flow of 200 m^3 per second (near Eijsden). Characteristics of the Meuse at the date of sampling are presented in Table 3.

Table 3 Flow and suspended matter concentration of the Meuse at the dates of sampling

	Flow (m3 per second)	Suspended matter concentration (mg/l)
26 June 2018	63.3	5.5
14 June 2005	35.4	4
Overall average	200	13

Source: https://waterinfo.rws.nl

2.4 Germany, Highway A61

In Germany, samples have been gathered of runoff and soil from the highway A61 between Kreuz Meckenheim and Dreieck Bad Neuenahr-Ahrweiler (at the parking place 'Goldene Meile'). See Figure 2. The samples have been collected on 18 March 2019. On the sampling day, it was cloudy and there was some precipitation (0.4 mm in Köln-Bonn Flughafen). There was more precipitation on the days before the sampling day (2.3-18.2 mm per day in the five days before the samples were gathered).

The highway A61 in Germany is a busy highway with five lanes (three on the northern side and two at the southern side of the road) and an emergency lane at both sides. The average traffic intensity is 73,310 vehicles per day and the asphalt consists of normal asphalt. Traffic signs are present next to the road, but no guardrail is present here. There is no separate treatment system available, but runoff is infiltrated in the road shoulder and embankments. The surrounding area is flat and does not contain any trees, but there are some bushes. The main wind direction is crosswise to the road. Based on the combination of normal asphalt, wind crosswise to the road and no wind obstruction, it can be expected that spray of water and pollutants from the road is an important pathway.

Figure 2 Location of the surface water samples at the E18 testsite in Sweden. Coordinates: 50.58 N, 7.06 E. Picture from Google Maps.

2.5 Sweden, Highway E18

In Sweden, samples have been gathered from the VTI testsite located at the highway E18. See Figure 3 for the exact location of the testsite. The collected samples include soil samples (from the southern side of the road), water and sediment samples (collected in the well) and west dust samples from the road surface (close to the kerb). The samples have been collected on 14 June 2019. On the sampling day, it was cloudy at first (no rain), and later sunny, with a temperature of 18-21 degrees Celsius. In the days before the sampling, there was some rain measured at weather station Enköping Mo (0-13 mm per day in the five days before the sampling).

Figure 3 Location of the surface water samples at the E18 testsite in Sweden. Coordinates: 59.63 N, 16.86 E. Picture from Google Maps.

The water and sediment samples were taken from a well where runoff is collected. This well is a storm water well which contains road runoff water. The well is made of concrete (ca 90 cm in diameter) and has different measuring devices in it made of different materials. It is also separated by a divider, which causes the water depth to differ giving higher levels in the inlet part and lower levels in the outlet part. From this well, samples of water and sediment have been collected.

The soil samples have been taken at 1, 5 and 8-9 meter distance from the road. Due to a high fence, it was not possible to sample at 10 distance from the road. The sampling sites at 1 meter from the road was a gravel strip at the same level as the asphalt road. The sampling sites at 5 meter from the road were at a steep slope overgrown with grass. The sampling sites at 8-9 meter from the road were on a gentle slope with grass. The height difference between the road and sampling sites at 8-9 meter from the road was 3 meter. At each distance from the asphalt road edge six samples were taken at 0 m (starting point), 20 m, 40 m, 60 m, 80 m and 100 m. These were either put in a separate can or together with the previous sample (depending on space). The sampling depth ranged between 2 and 5 cm because of grass and roots.

Figure 4 Sampling site at the E18 testsite in Sweden. Location of soil samples at 1, 5 and 8-9 meter from the road. Water and sediment samples taken from the well. Photos: Mats Gustafsson, VTI

The highway E18 in Sweden is a highway with 2 lanes in each direction (4 lanes in total) and no emergency lane. The average traffic intensity is 21,300 vehicles per day and the asphalt consists of stone mastic asphalt. A guardrail is located next to the road.
The surrounding area is flat. The main wind direction is crosswise to the road. Based on the combination of stone mastic asphalt, wind crosswise to the road, no wind obstruction and no emergency lane, it can be expected that spray of water and pollutants from the road is an important pathway.

3 Analysis

3.1 Introduction

Table 4 provides an overview of the pollutants that are measured for each sample. This chapter contain more detailed information on the analysis of TWP (tyre wear particles), organic micropollutants and metals.

In Microproof report 1.3, a first selection of potentially important organic micropollutants is made, and most of these pollutants have been measured. Table 5 provides an overview of the pollutants from Microproof report 1.3 that have been measured. Also other organic micropollutants have been measured in cases where the measurement of additional pollutants could be performed together with the selected list of pollutants. The complete list of measured pollutants in included in Annex A.

Table 4 Overview of the pollutants that are measured for each sample.

	TWP particles	Suspended particles	Organic micropollutants	Metals
Runoff	X	X	X	X
Well water	X	X	X	X
Well sludge	X		X	X
Solids from road surface	X	X	X	X
Soil 1 m	X		X	X
Soil 5 m	X			
Soil 10 m	X			
Surface water	X	X	X	
Sediment waterway	X		X	

Table 5 Relevant organic micropollutants from Microproof report 1.3. This table indicates whether the pollutant is a priority substance within the Water Framework Directive (WFD), whether this pollutant is included in the risk assessment (Microproof report 3.1) and whether concentrations of these pollutants have been measured

Source	Substance	Short name	CAS number	Priority substance in WFD	Included in the risk assessment	Measured
Tyres	Benzothiazole	BT	95-16-9			X
	Mercaptobenzothiazole	MBT	149-30-4		X	X
	Benzothiazolone	BTON	934-34-9			X
	Hydroxybenzothiazole	OHBT	934-34-9			X
	Cyclohexylamine	CHA	108-91-8			X [3)]
	Dicyclohexylamine	DCHA	101-83-7			X [3)]
	Hydroxydiphenylamine	4-HDPA	122-37-2			X
	Aminodiphenylamine	4-ADPA	101-54-2			X [3)]
	Aniline		62-53-3			X
	PAH			X	X [1)]	X [2)]
Brakes and brake fluid	Tributylphosphate		126-73-8			X
	Triethanolamine		102-71-6			X [3)]
	PAH			X	X [1)]	X [2)]
Car coatings	Hexa(methoxymethyl)melamine	HMMM	3089-11-0		X	X
	Nonylphenol ethoxylates	NP1EO, NP2EO	9016-45-9, 20427-84-3			X
	Octylphenolethoxylates	OP2EO, OP2EO	51437-89-9, 2315-61-9			X
	Bisphenol A	BPA	80-05-7		X	X
Coolants	Benzotriazole		95-14-7			X
	Tolyltriazole	TT	29385-43-1		X	X
	Mercapto benzothiazole	MBT	149-30-4			X
Other	Diisodecyl phthalate	DIDP	26761-40-0		X	X
	Di(2-ethylhexyl)phthalate	DEHP	117-81-7	X	X	X
	Nonylphenol	NP	104-40-5	X	X	X
	4-tert-octylphenol	OP	140-66-9	X	X	X

[1)] In the risk assessment, the PAH benzo(a)pyrene and fluoranthene are used.
[2)] The 16 PAH are measured separately (acenaphthene, acenaphthylene, anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene, chrysene, dibenzo(a,h)anthracene, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene, naphthalene, phenanthrene, pyrene)
[3)] Measured concentration of this pollutant is uncertain.

3.2 Sample pre-treatment

Water samples (runoff, surface water, road water and well water and sludge) were filtered through a glass fiber filter, to separate the non-soluble fraction (solids) from the water fraction. The resulting filter samples together with the soil and sediment samples were frieze-dried to remove residual water. The soil and sediment samples were cryogenically ground with a rotor mill to particle sizes below 0.25mm. For TWP the solids were dried in a laboratory oven for 24 h at 105 °C.

3.2.1 Benzothiazoles, benzotriazoles and amines

Prior to extraction, labelled internal standards were added to the samples; for the amines no suitable labelled standards were available. The water samples were directly extracted via a liquid-liquid extraction with dichloromethane. Solid samples (filters, soil and sediment) were extracted via an accelerated solvent extraction method (ASE) with 0.05M Na2-EDTA in MQ, buffered at pH 7.0 with ammonium acetate and sodium hydroxide. Subsequently, with the resulting MQ extracts liquid-liquid extraction (LLE) was performed with dichloromethane.

3.2.2 Phenols, octylphenolethoxylates (OPEO) and nonylphenolethoxylates (NPEO)

Prior to extraction, labelled internal standards were added to the samples. The water samples were directly extracted via a solid phase extraction (SPE) with an OASIS HLB extraction cartridge. The cartridge was eluted with a mixture of methanol/acetone/ethylacetate (2:2:1) and 0.1% formic acid. Solid samples (filters, soil and sediment) were extracted via an accelerated solvent extraction method (ASE) with methanol. A clean-up was performed on a 15% deactivated alumina column with 10% acetic acid in methanol.

3.2.3 Polycyclic aromatic hydrocarbons (PAH), organophosphate esters (OPE), hopanes/steranes and phthalates.

Prior to extraction, labelled internal standards were added to the samples. The water samples were directly extracted via a liquid-liquid extraction with hexane. Solid samples (filters, soil and sediment) were extracted via an accelerated solvent extraction method (ASE) with hexane. Half of the extracts is used for the analysis of PAH and hopanes/steranes. These extracts were fractioned into two fractions via an activated silica column. The first fraction (10 mL hexane) contains hopanes/steranes and the second fraction (12 mL hexane/dichloromethane (50:50) contains PAH. The other half of the extracts was used for the analysis of OPE and phthalates. A clean-up is performed on a 3% deactivated florisil column with 10 mL diethyl ether/hexane (1:1) and 10 mL acetone/hexane (1:1).

3.2.4 Metals

Solid samples (filters, soil and sediment) were first digested with aqua regia (mixture of concentrated hydrochloric acid and nitric acid 3:1) in a Microwave Digestion System; water samples were directly analysed.

3.3 Analysis

3.3.1 GCMS analysis

PAH, hopanes/steranes, OPE and phthalates were analysed by gas chromatography in combination with mass spectrometry (GCMS) in selected ion mode (SIM) using electron impact ionization (Agilent 6890/5973N) with a semi-polar capillary GC-column (DB-5ms-UI, 30m x 0.25mm i.d. 0.25µm film thickness; Agilent) using multiple reaction monitoring (MRM) with two ion transitions for each compound. The identification of target compounds was accomplished by comparing the retention time and two optimized ion pairs with corresponding standard compounds. Quantification was based on external multiple point calibration lines with required components and associated internal standards. The internal standards were used to monitor the quality of the determination; results for individual samples were corrected based on the recoveries of the internal standards.

3.3.2 LCMSMS analysis

Benzothiazoles, benzotriazoles, amines, phenols and OPEO/NPEO were analyzed with liquid chromatography in combination with tandem mass spectrometry (LCMSMS). Benzothiazoles and benzotriazoles were analysed with an Electron Spray Ion source (ESI) in the positive multi mode source (MMI-ESI-POS) with an Agilent HP1100 Series LC and Agilent 6410 triple Quad LCMS selective detective detector). Amines and OPEO/NPEO were analysed in the ESI Jetstream positive mode (AJT-ESI-POS) with an Agilent HP1100 Series LC and Agilent 6410 triple Quad LCMS selective detective detector. Phenols were analysed in the ESI Jetstream negative mode (AJT-ESI-NEG). In both cases multiple reaction monitoring (MRM) was applied using two ion transitions for each compound. For benzothiazoles, benzotriazoles, amines and NPEO/OPEO a biphenyl reversed phase column (Kinetex 2.6 µm, Biphenyl 100A, 2.1 mm i.d. × 100 mm, Phenomenex, USA) was used and for phenols a Gemini NX-C18 110 A column (length: 100 mm, IS: 2.0 mm, film thickness: 3.0 µm) was used.

For benzothiazoles and benzotriazoles separation was performed using a gradient from two different mixtures of water in methanol. One mixture with 5 mM ammonium formiate and a second mixture with 100 µl formic acid. For amines a mixture of milli-Q water (pH 2.5) and methanol both with 0.1% formic acid was used. For phenols a mixture of pure milli-Q water and methanol was used and finally for NPEO/OPEO a mixture of milli-Q water and methanol with 100 µl formic acid was used. The identification of target compounds was accomplished by comparing the retention time and two optimized ion pairs with corresponding standard compounds. Quantification was based on external multiple point calibration lines with required components and associated internal standards. The internal standards were used to monitor the quality of the determination; results for individual samples were corrected based on the recoveries of the internal standards.

3.3.3 TED-GCMS analysis

Pyrolysis-GC/MS analysis of characteristic thermal decomposition fragments of rubber (styrene, 4-vinylcyclohexene (4-VCH) and dipentene) has been previously published (Unice et al., 2012). We used an adapted method using thermal extraction and desorption GCMS (TED-GCMS) (Duemichen et al., 2017). This technique combines thermal extraction and solid-phase adsorption with automated thermal desorption GCMS (ATD-GCMS). Solid samples (filters, soil and sediment) were pyrolyzed with the combustion furnace of a TOC analyser (C-MAT 5500, Stroehlein instruments). The samples were heated at a temperature of 475°C during a period of 10 minutes. During the heating a nitrogen flow was passed over the sample. The pyrolysis compounds (4-VCH, styrene, dipentene) were collected by a stainless thermal desorption tube (6 mm O.D. × 90 mm long, 5 mm I.D., Perkin-Elmer) containing 300 mg of Tenax® GR (Supelco). After sampling, the sorbent tubes were immediately analysed with an automatic thermal desorption unit (ATD Turbomatrix 400, Perkin-Elmer) coupled with a capillary gas chromatograph (HP 6890, Hewlett-Packard) and a mass spectrometer as detector (Agilent 5973, Agilent technologies). The thermal desorbed compounds were introduced onto a GC-column (VF624MS, 30-m x 0.25-mm i.d. 1.4µm film thickness; Agilent). Identification and quantification of components was achieved via a comparison of retention times, qualifier ion ratios and mass spectra with those of an external standard mixture.

The calculation to convert the characteristic thermal decomposition fragments to TWP concentration is based on the average concentration of these fragments in 30 analyzed car tires in the Netherlands. The conversion factor takes into account the most used car tires in the Netherlands and the percentage of freight traffic (6%). For 4-VCH, styrene and dipentene conversion factors of 970, 3303 en 1181 mg/kg in TWP are used.

3.3.4 HR-ICP-MS analysis

An Element XR High Resolution Inductively Coupled Plasma Mass Spectrometer (HR-ICP-MS; Thermo, Bremen, Germany) was used for the analysis of metals (Li, Be, Zn, Si, Cd, Ba, Pt, Pb, Mo, Na, Mg, Al, P, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Ag, Sb, B, Sn, W, Zr, S, Au, K, Ca, As, Se, Ce, Pd and Rh). All data acquisitions were carried out in high resolution mode, to avoid the influence of spectral interferences on the results. As an internal standard the element Ge (Germanium) was used. The quantification was carried out by external three-point-calibration. Recovery of heavy metals was determined with reference material (NIST R1648a).

3.4 Quality control

TNO Earth, Life and Social Sciences operates in compliance with the Quality System standard ISO-9001 (certificate no. 00680-97-AQ-ROT-RvA). This study was performed in compliance with that Quality System standard. Quality of the analysis was assessed following the Dutch norm NEN 7777 Environment - Performance characteristics of measurement methods. Samples were spiked with deuterated and 13C-labeled compounds as recovery internal standards to determine extraction efficiencies. Results for individual samples were corrected based on the recoveries of the internal standards. All results were blank corrected. Efficiencies of the total analytical methods were assessed with standard addition experiments. The limit of detection (LOD) was calculated as three times the standard deviation of blank samples.

3.5 Uncertainty

Standard addition tests are performed to test the accuracy of the analysis. The recovery of the substances is measured and Table 6 shows how much of the added substances are recovered. The standard deviation is calculated from at least six standard addition samples. Table 6 shows the relative standard deviation (expressed as the ratio between the standard deviation and the mean (%)).

For TWP analysis, also the variability in tyre markers causes an uncertainty in the TWP analysis. The relative standard deviation of TED-GCMS, determined with six samples from the same tyre is 6%, while the relative standard deviation in duplicate samples from road surface and runoff is 10%. The relative standard deviation in the concentration in tyre pyrolysis markers is 28%. Combined, this results in a relative standard deviation of 30%.

Table 6 Recovery of standard addition tests (%) and relative standard deviation from these standard addition tests, expressed as the ratio between the standard deviation and the mean (%)

Substance group	Recovery (%) [1)]	Relative standard deviation (%) [1)]
PAH	51 [2)] – 90	7 - 11
hopanes/steranes	64 – 84	4 - 6
OPE (tributylphosphate)	34 – 123 (72)	5 - 29
phthlates	81 – 142	6 - 16
benzothiazoles / triazoles	55 [3)] – 113	3 - 26
phenols	84 – 106	8 - 22
amines	46 – 79 [4)] (0.1 – 5)	11 - 21
OPEO/NPEO	85 – 111	4 - 25
Metals	60 - 115	7

1) range within substance group
2) low recovery for the volatile naphthalene
3) low recovery for 2-mercaptobenzothiazole
4) only 4-hydroxydiphenylamine, aniline and hexa(methoxymethyl)melamine, between parenthesis the recovery for 4-aminodiphenylamine, cyclohexylamine, dicyclohexylamine and triethanolamine

4 Results

4.1 Microplastics (tyre wear)

TWP particles have been measured with 4-vinylcyclohexene as a marker, but the concentrations have also been checked by calculating tyre wear concentrations based on measured ZnO, sulphur and black carbon concentrations. Table 7 and Table 8 show the measured TWP concentrations, as measured with 4-vinylcyclohexene as a marker.

Table 7 Concentration of TWP in runoff, solids from the road surface, soil and well sludge in the sampling sites in Germany and Sweden.

	Suspended matter concentration (mg/l)		Concentration in suspended matter (g/kg)		Total concentration in water (mg/l)	
	Germany (A61)	Sweden (E18)	Germany (A61)	Sweden (E18)	Germany (A61)	Sweden (E18)
Runoff from road side [1)]	390		150 / 130		59 / 51	
Runoff from well		25		39		1.0
Solids from road surface				6.0		
Soil 1 m			5.9	3.0		
Soil 5 m			0.7	1.1		
Soil 10 m			0.7	0.5		
Well sludge				13		

[1)] The TWP concentration in the runoff sample from Germany has been measured in duplo

Table 8 Concentration of TWP in surface water and sediment of the waterway

		Suspended matter concentration (mg/l)	Concentration in suspended matter (g/kg)	Total concentration in water (mg/l)
Surface water	NL (A2)	7.5	0.8 / 0.4 [2)]	0.006 / 0.003
	NL (Rhine 31/1/2018)	36 [1)]	0.3 / 0.2 [2)]	0.011 / 0.007
	NL (Rhine 15/7/2008)	6	0.2	0.001
	NL (Meuse 26/6/2018)	5.5	0.3	0.002
	NL (Meuse 14/6/2005)	4	0.2	0.001
Sediment waterway	NL (A2)		0.3	

[1)] The suspended matter concentration in the Rhine is not measured by TNO, but is analysed by Rijkswaterstaat. This is the concentration on 31 January 2018, which is higher than the average concentration in the Rhine of 16 mg/l.
2) The TWP concentration at the A2 and in the Rhine sample of 31/1/2018 have been measured in duplo.

The TWP concentration in the runoff sample from Germany has been measured in duplo.

Table 9 Comparison of the measured TWP concentration (measured with 4-vinylcyclohexene as a marker), with the possible TWP concentration that could be calculated from ZnO, sulphur and black carbon. Please note that the concentrations calculated from ZnO, sulphur and black carbon are less accurate, because these substances could also be released from other sources and could be removed by other processes.

	Tyre wear (based on 4-VCH) g/kg	Tyre wear (based on ZnO) g/kg	Tyre wear (based on sulphur) g/kg	Tyre wear (based on black carbon) g/kg
Suspended matter in runoff from road side, Germany (A61)	150 / 130	92	170	340
Suspended matter in runoff from well, Sweden (E18)	39	33	320	60
Soil 1 meter from the road, Germany (A61)	5.9	29	60	not measured
Soil 1 meter from the road, Sweden (E18)	3.0	13	58	not measured
Solids from road surface, Sweden (E18)	6.0	10	53	not measured

Runoff

The highest measured TWP concentration is measured in runoff from highway A61 in Germany, with an average concentration of 140 g per kg suspended matter (55 mg/l). The tyre wear concentration that could be calculated from ZnO, sulphur and black carbon in this location (see Table 9) are in the same order of magnitude (92 – 340 g/kg), which provides confidence that the actual TWP concentration in this location is in fact measured correctly. The concentration measured in runoff from highway E18 in Sweden (39 g per kg suspended matter and 1.0 mg/l) is much lower, which is due to the sampling method. In this test site, the runoff was sampled from a well where runoff was gathered, and part of the pollutants may have sedimented to the bottom of the well.

The measured concentration can also be compared to a potential concentration (based on estimated emissions and precipitation). This potential concentration can be calculated from the road width, average daily traffic (ADT), average emission factors (EF) and the average yearly precipitation with the following formula:

Potential concentration based on emission and precipitation =
(ADT x 365 x EF) / (road width x road length x precipitation)

The average daily traffic (ADT), road width and precipitation are site specific characteristics (see chapter 2). An average emission factor of 150 mg/km is used (see Microproof report 1.1). A large part of the precipitation will be evaporated and not result in runoff and taking that into account would result in higher potential concentrations. Also, part of the tyre wear particles will be removed by drift and will not end up in the runoff and taking that into account would result in lower potential concentrations. These two effects have not been taken into account for this first comparison between potential concentrations in runoff and the actual concentrations.

For Germany, this calculation results in a potential TWP concentration of (73310 x 365 x 150) / (20 x 1000 x 700) = 287 mg/l, which is higher than the measured concentration of 55 mg/l. For Sweden, this results in a potential TWP concentration of (21300 x 365 x 150) / (20 x 1000 x 400) = 145 mg/l, which is much higher than the measured concentration of 1 mg/l.

Surface water

The TWP concentration in surface water is measured in a small water body next to the busy highway A2 in the Netherlands, in the river Rhine at the border between the Netherlands and Germany and in the river Meuse at the border between the Netherlands and Belgium. The measured concentrations are 4.5 µg/l in the A2 water body, 1.2 µg/l and 11 µg/l in the river Rhine on 15/7/2009 and 31/1/2018 respectively, and 0.8 µg/l and 1.7 µg/l in the river Meuse in 14/6/2005 and 26/6/2018 respectively. The measured concentrations were between 0.2 and 0.8 g/kg and were close to the level of detection of 0.5 g/kg. Therefore, these concentrations are more uncertain than the other measurements.

Unice et al (2019) predicted (based on a mass balance model) a daily average concentration of TRWP in Seine subcatchments between 3.7 and 120 µg/l with an annual average of approximately 27 µg/l. The concentrations measured in the water body next to the A2 and in the river Rhine are on the lower end of the predictions from the mass balance model from Unice et al. (2019).

For the river Rhine, a concentration of 1.2 and 11 µg/l was measured on 15/7/2009 and 31/1/2018 respectively. Combined with an average flow of 2200 m^3 per second, this would result in an amount of 83 - 750 ton TWP per year. During the sampling in 2018, resuspension occurred due to the relatively high flow (5469 m^3 per second), resulting in a higher concentration of suspended matter. If the amount is calculated with a TWP concentration of 0.2 g/kg, a solid particles concentration of 16 mg/l and an average flow of 2200 m^3 per second, this would result in an amount of 222 ton TWP per year.

In a master thesis from the Dutch Open University (Urgert, 2015), the concentration microplastics (excluding TWP) has been measured in the Rhine at the same location in 2014. A microplastic concentration of 0.56 mg/m^3 (0.56 µg/l), which would result in an annual load of 40 ton per year (for microplastics without TWP). The TWP measurements indicate that the TWP load in the river Rhine is higher than the microplastics load (without TWP) in this river.

Soil

Both at the site at highway A61 in Germany and highway E18 in Sweden, TWP particles have been measured in the soil, with concentrations of 5.9 and 3.0 g/kg at 1 meter from the road and 0.7 and 0.5 g/kg at 10 meters from the road. A weighted average of 2.0 and 1.4 g/kg soil can be calculated from these measurements.

For the soil samples, approximately 2 cm of soil was gathered. With an average density of soil of 1500-2000 kg/m^3, these two centimetres of soil equals 30-40 kg per m^3. With an average of 2 grams TWP per kg in Germany and 1.4 grams TWP per kg in Sweden, this means that 60-80 grams of TWP is available on the soil per m^2 in Germany and 42-56 grams of TWP is available on the soil per m^2 in Sweden (in the top layer of 2 centimetres).

The total amount in the verge in a 1 km stretch of 10 meters wide, would be 600-800 kg in Germany and 420-560 kg in Sweden. This is lower than the potential yearly emission of 4014 kg per km length of the road for Germany and 1166 kg per km length of the road for Sweden (based on average daily traffic and an average emission factor of 150 mg/km). It is unknown for how long these tyre wear particles have been accumulated in the soil. If the top layer of the soil is removed once in a while, this would reduce the time that the particles have accumulated in the soil. As long as we do not know the accumulation time, it is difficult to say whether the soil is an important sink for tyre wear or not.

4.2 Organic micropollutants

Measured concentrations of organic micropollutants (excluding PAH) in runoff and in surface water is presented in Table 10. As expected (due to dilution), the concentrations in surface water are lower than the concentrations in runoff. Only the concentration of Bisphenol A in surface water is higher than the concentration of this pollutant in runoff from highway A61 (Germany) and highway E18 (Sweden). Probably, part of the Bisphenol A load is released from other emission sources.

Based on the difference in average daily traffic in Germany (73310) and Sweden (21300), it could be expected that the runoff concentrations in Germany would be higher. For about half of the pollutants, a higher concentration can be observed in the runoff samples from Germany, while the concentrations in Sweden are higher for only two pollutants (Benzothiazole and Benzothiazolone). Benzothiazole and Benzothiazolone are released from tyre wear. While aging, Benzothiazole and Benzothiazolone are leached from the tyre wear tread and are prone to degradation, thus resulting in a reduced concentration in water (Unice et al, 2015). Maybe, the tyre wear in the sample from Germany is older than the tyre wear sample from Sweden.

Another explanation is that the Swedish runoff sample is taken from the well. Benzothiazole and Benzothiazolone concentrations in Sweden are mainly measured in the water phase (dissolved substances), while Benzothiazole and Benzothiazolone concentrations in Germany are mainly measured in suspended matter. Possibly, a larger part of the Benzothiazole and Benzothiazolone concentrations is leached from the tyre wear particles and while the tyre wear particles itself were deposited on the bottom of the well, a part of the Benzothiazole and Benzothiazolone pollutants remained in the water.

In Table 11, a comparison between the measured concentrations and concentrations reported in literature has been made. The results from the measurements are in the same order of magnitude as the concentrations reported in literature. Differences can most likely be explained by the differences between the different sites.

Table 10 Concentration of organic micropollutants in runoff and surface water (µg/l)

Substance	Short	CAS	Runoff, Germany (highway A61)	Runoff Sweden (highway E18)	Surface water (Netherlands, A2)
Benzothiazole	BT	95-16-9	0.34	1.9	0.026
Mercaptobenzothiazole	MBT	149-30-4	0.40	0.11	0.0008
Benzothiazolone / Hydroxybenzothiazole	BTON / OHBT	934-34-9	0.25	2.9	0.028
Benzotriazole		95-14-7	0.26	0.22	<
Tolyltriazole	TT	29385-43-1	0.43	0.41	<
Di(2-ethylhexyl)phthalate	DEHP	117-81-7	26	3.1	0.98
Diisodecyl phthalate	DIDP	26761-40-0	57	4.5	<
Nonylphenol	NP	104-40-5	<	<	<
4-tert-octylphenol	OP	140-66-9	0.76	0.038	<
Nonylphenol ethoxylates	NP1EO - NP16EO		2.8	0.56	0.0041
Octylphenolethoxylates	OP1EO - OP15EO		<	0.12	0.0097
Bisphenol A	BPA	80-05-7	0.12	0.10	0.46
Hydroxydiphenylamine	4-HDPA	122-37-2	0.88	0.067	0.0011
Aniline		62-53-3	1.8	0.44	0.0004
Hexa(methoxymethyl)melamine	HMMM	3089-11-0	3.9	2.2	0.071
Tributylphosphate		126-73-8	0.29	0.28	0.013

< The concentrations of the pollutants marked with < are below the limit of detection

Table 11 Concentration of organic micropollutants in runoff, compared to earlier reported concentrations of organic micropollutants in runoff and storm water (µg/l)

Substance	Short	CAS	Runoff, Germany (A61)	Runoff Sweden (E18)	Runoff, reported in literature	References
Benzothiazole	BT	95-16-9	0.34	1.9	0.4 – 11.8	2), 3), 6), 10)
Mercaptobenzothiazole	MBT	149-30-4	0.40	0.11	0.11	1)
Benzothiazolone / Hydroxybenzothiazole	BTON / OHBT	934-34-9	0.25	2.9	0.16 - 22	1), 2), 3), 4), 10)
Benzotriazole		95-14-7	0.26	0.22	0.10	1)
Tolyltriazole	TT	29385-43-1	0.43	0.41	2.30	1)
Di(2-ethylhexyl)phthalate	DEHP	117-81-7	26	3.1	2.27 – 11.3	4), 10)
Diisodecyl phthalate	DIDP	26761-40-0	57	4.5	8.60	4)
Nonylphenol	NP	104-40-5	<	<	0.17 - 0.36	5), 10)
4-tert-octylphenol	OP	140-66-9	0.76	0.038	0.04 – 0.07	5), 10)
Nonylphenol ethoxylates	NP1EO - NP16EO		2.8	0.56	0.51	5), 8)
Octylphenolethoxylates	OP1EO - OP15EO		<	0.12	0.03	5), 9)
Bisphenol A	BPA	80-05-7	0.12	0.10	0.08 - 0.55	5), 10)
Hydroxydiphenylamine	4-HDPA	122-37-2	0.88	0.067	-	-
Aniline		62-53-3	1.8	0.44	-	-
Hexa(methoxymethyl)melamine	HMMM	3089-11-0	3.9	2.2	0.01 – 0.88	1), 7)
Tributylphosphate		126-73-8	0.29	0.28	-	-

1) Seitz & Winzenbacher, 2017
2) Kloepfer et al., 2005
3) Reddy & Quinn, 1997
4) Holsteijn, 2014
5) Gasperi et al., 2014
6) Baumann & Ismeier, 1998
7) Dsikowitsky & Schwarzbauer, 2015
8) Note: Only NP1EO and NP2EO
9) Note: Only OP1EO and OP2EO
10) Grotehusmann, et al., 2017
< The concentrations of the pollutants marked with < are below the limit of detection

Measured concentrations of polycyclic aromatic hydrocarbons (PAH) in runoff and in surface water is presented in Table 12. Highest concentrations are measured for pyrene, fluoranthene, benzo(b)fluoranthene and benzo(g,h,i)perylene. The main part of the PAH is adsorbed to the suspended matter, while a relatively small part is dissolved in the water.

PAH concentrations in runoff reported in literature are also presented in Table 12. The upper range of the runoff concentrations reported in literature are for most pollutants (much) higher than the measured concentrations in runoff in Germany and Sweden. This can partly be explained by the fact that the reported concentrations in literature are for a large part from before 2010, when Directive 2005/69/EC came into force.

According to Directive 2005/69/EC it is prohibited to place on the market, tyres (and treads for rethreading), containing extender oils, exceeding the limits of 1 ppm for benzo(a)pyrene and/or 10 ppm total of 8 PAHs (Benzo(a)pyrene, Benzo(e)pyrene, Benzo(a)anthracene, Chrysene, Benzo(b)fluoranthene, Benzo(j)fluoranthene, Benzo(k)fluoranthene, Dibenzo(a,h)anthracene). Even though some authors (Favraux, 2013 and Pan et al., 2016) are in doubt whether the effect of Directive 2005/69/EC was as expected, the PAH content of most tyres have reduced, and therefore a lower PAH concentration in runoff water can be expected.

Table 12 Concentration of polycyclic aromatic hydrocarbons (PAH) in runoff and surface water compared to concentrations reported in (a selection of) literature (µg/).

Substance	**CAS**	**Runoff, Germany (highway 61)**	**Runoff Sweden (highway E18)**	**Surface water (Netherlands, A2)**	**Runoff, reported in literature**	**References**
Naphthalene	91-20-3	0.095	0.03	0.029	0 – 0.214	1), 2)
Acenaphthylene	208-96-8	0.049	0.005	0.0003	0 – 0.079	1), 2)
Acenaphthene	83-32-9	0.011	<	0.0023	0 – 0.171	1), 2)
Fluorene	86-73-7	0.021	<	0.0051	0 – 0.061	1), 2)
Phenanthrene	85-01-8	0.36	0.025	0.016	0 – 0.769	1), 2), 3)
Anthracene	120-12-7	0.058	0.0041	0.0096	0 – 0.08	1), 2), 3)
Fluoranthene	206-44-0	0.94	0.048	0.045	0 – 3.649	1), 2), 3)
Pyrene	129-00-0	1.2	0.11	0.0095	0 – 2.47	1), 2), 3)
Benzo(a)anthracene	56-55-3	0.27	<	<	0 – 0.891	1), 2), 3)
Chrysene	218-01-9	0.58	0.089	0.0012	0 – 2.169	1), 2), 3)
Benzo(b)fluoranthene	205-99-2	0.98	0.082	0.0033	0 – 1.084	1), 3),
Benzo(k)fluoranthene	207-08-9	0.31	<	0.0015	0 – 0.456	1), 2), 3)
Benzo(a)pyrene	50-32-8	0.37	0.022	0.0013	0 – 0.829	1), 2), 3)
Indeno(1,2,3-cd)pyrene	193-39-5	0.29	0.019	0.0015	0 – 0.25	1), 2)
Dibenzo(a,h)anthracene	53-70-3	0.098	0.0084	0.0031	0 – 0.118	1), 2), 3)
Benzo(g,h,i)perylene	191-24-2	0.70	0.056	0.0014	0 – 1.271	1), 3)
sum PAH16		6.3	0.50	0.13	0 – 62.19	4), 5), 6), 7), 8), 9)

1) Brongers, 2010
2) Schipper et al., 2003
3) Tromp, 2005
4) van den Berg, 2009
5) Holsteijn, 2014
6) Schipper et al., 2003
7) Meland et al., 2016
8) van Velsen, 1997
9) Grotehusmann, et al., 2017
< The concentrations of the pollutants marked with < are below the limit of detection

5 Conclusion

Release of tyre wear particles and organic micropollutants from road transport were discussed in Microproof report 1.3, based on literature. For most pollutants, no or only a few measurements were reported in literature. To improve the results of the Microproof study, concentrations of tyre wear particles and several organic micropollutants were measured in runoff, soil and surface water in different sites in Europe.

Tyre wear particles were measured in all the samples. The marker 4-vinylcyclohexene was used to measure and calculate the tyre wear concentration. As a check, the tyre wear concentration was also calculated with ZnO, sulphur and black carbon as markers. Concentrations calculated from ZnO, sulphur and black carbon are less accurate, because these substances could also be released from other sources and could be removed by other processes. However, these checks show that the measured concentrations are in the correct order of magnitude.

Measured tyre wear concentrations in runoff are 1.0 and 55 mg/l for the Swedish and German site respectively, while measured tyre wear concentrations in surface water are 0.011 and 0.006 mg/l for the river Rhine and the water body next to the A2 respectively. The concentration in the surface water is in the lower end of the modelled concentration of TRWP in Seine subcatchments by Unice et al. (2019) who modelled a concentration between 0.0037 and 0.12 mg/l with an annual average of approximately 0.027 mg/l.

Most organic micropollutants were detected in runoff and in surface water. The average daily traffic in Germany was higher than the average daily traffic in Sweden, and this is also visible in the concentrations of most pollutants. The concentrations in the German samples are most often higher than the concentrations in the Swedish samples. This can also partly be explained by the sampling method.

The results from the measurements of organic micropollutants (excluding PAH) are in the same order of magnitude as the concentrations reported in literature. Differences can most likely be explained by the differences between the different sites. For PAH, the upper range of the runoff concentrations reported in literature are for most pollutants (much) higher than the measured concentrations in runoff in Germany and Sweden. This can partly be explained by the fact that the reported concentrations in literature are for a large part from before 2010, when Directive 2005/69/EC came into force.

As expected (due to dilution), the concentrations in surface water (A2 in the Netherlands) are lower than the concentrations in runoff (A61 in Germany and E18 in Sweden). The difference between surface water and runoff is approximately a factor 10-1000.

The measured concentrations in runoff, surface water and sediment are used in the risk assessment (Microproof report 3.1) to calculate the risk of a selection of pollutants. Part of the TWP analysis was performed after the risk assessment. This includes the analysis of the TWP concentrations in both samples of the Meuse, the 2009 sample of the Rhine and the duplo values of the A2 and the Rhine. Therefore, these data have not been included in the risk assessment. Table 13 shows the concentrations that were used in the risk assessment.

Table 13 Predicted environmental concentrations that were used in the risk assessment (see Microproof report 3.1)

	Runoff				Surface water		
	Water (µg/l)		Suspended solids (mg/kg)		Water (µg/l)	Suspended solids (mg/kg)	
Location	**DE A61**	**SE E18**	**DE A61**	**SE E18**	**NL A2**	**NL A2**	**NL Rhine**
TWP (tyre wear)	59000	980	150000	13000	6.0	300	300
Benzo(a)pyrene	0.0012	0.00081	0.94	0.21	0.00011	0.073	0.24
Fluoranthene	0.0030	0.0031	2.4	0.30	0.0011	0.17	0.45
Nonylphenol	<0.01	<0.01	<0.001	<0.001	<0.01	0.021	0.0011
4-tert-octylphenol	0.20	0.016	1.5	0.53	<0.01	<0.001	0.0042
Di(2-ethylhexyl)phthalate	0.66	0.72	65	2.4	0.98	10	14
Bisphenol A	0.028	0.10	0.24	0.056	<0.01	<0.001	0.0053
Mercapto benzothiazole	<0.01	<0.01	1.0	0.19	<0.01	0.0023	<0.0001
Tolyltriazole	<0.01	0.40	1.1	0.039	<0.01	0.0058	0.0064
Diisodecyl phthalate	2.6	0.60	140	4.6	<0.001	2.0	0.65
Hexa(methoxymethyl)melamine	3.9	2.2	0.032	0.0017	0.071	<0.001	<0.001

5.1 Recommendations

To further enhance the understanding of the distribution of tyre wear particles in the environment, it is recommended to measure the TWP concentrations and loads in one site for a longer period. With this data, a mass balance could be made, which will improve the understanding if and how tyre wear particles are released to the environment.

In this study, TWP particles have only been measured in three surface water bodies. It is recommended to measure tyre wear particles in other surface water bodies as well, preferably using different measurement methods.

A large set of organic micropollutants have been measured in the runoff from two highways. If certain pollutants appear to be a potential risk for surface water quality (as discussed in Microproof report 3.1), it is recommended to perform extra measurements on these pollutants (in other sites) and to determine how much of these pollutants are released from road transport.

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Annex A: Measurement data

This Annex provides an overview of all of the measured data in the following tables:

- Table 14: Germany (A61) and Sweden (E18)
- Table 15: the Netherlands (A2) and the Netherlands (Rhine)

Table 14 Measured concentration in runoff, soil, road surface and sludge from Germany (A61) and Sweden (E18). In runoff, the concentration in the water phase and in the solids is measured separately

	Runoff						Soil. road surface solids and sludge			
	Germany			Sweden			Germany	Sweden		
Description	Solids	Water	Total	Solids	Water	Total	Soil (1m)	Soil (1m)	road surface	sludge well
Solids (mg/L)	390	-	-	25	-	-	-	-	-	-
PAH	µg/kg	ng/L	ng/L	µg/kg	ng/L	ng/L	µg/kg	µg/kg	µg/kg	µg/kg
Level of detection	0.1	0.1		0.1	0.1		0.1	0.1	0.1	0.1
naphthalene	220	9.5	95	960	5.7	30	24	12	25	21
acenaphthylene	120	0.19	49	200	<	5	14	3	5	12
acenaphthene	29	<	11	<	<	<	9	<	<	<
fluorene	50	0.90	21	<	<	<	9	2	4	25
phenanthrene	920	2.0	360	970	0.9	25	130	23	45	210
anthracene	140	2.4	58	160	<	4	25	5	9	49
fluoranthene	2400	3.0	940	1800	3.1	48	330	48	150	300
pyrene	2900	3.3	1200	4000	11.0	110	300	110	250	600
benzo(a)anthracene	680	<	270	<	<	<	160	<	<	<
chrysene	1500	<	580	3300	5.7	89	270	170	390	970

	Runoff						Soil. road surface solids and sludge			
	Germany			Sweden			Germany	Sweden		
Description	Solids	Water	Total	Solids	Water	Total	Soil (1m)	Soil (1m)	road surface	sludge well
benzo(b)fluoranthene	2500	3.4	980	3200	2.9	82	550	150	330	580
benzo(k)fluoranthene	800	1.2	310	<	<	<	160	<	<	<
benzo(a)pyrene	940	1.2	370	850	0.80	22	210	44	61	210
indeno(1.2.3-cd)pyrene	740	0.91	290	720	0.62	19	160	42	60	150
dibenzo(a.h)anthracene	250	0.34	98	340	<	8.0	55	32	45	160
benzo(g.h.i)perylene	1800	1.9	700	2200	1.6	56	340	140	200	520
sum PAH	16000	30	6300	19000	32	500	2700	780	1600	3800
Organophosphate ester	µg/kg	ng/L	ng/L	µg/kg	ng/L	ng/L	µg/kg	µg/kg	µg/kg	µg/kg
Level of detection	2	2		2	2		2	2	2	2
TMP	190	160	230	9500	160	400	<	210	410	150
TEP	34	20	33	24	18	18	<	<	38	12
TiPP	<	<	<	<	11	11	<	4.2	<	4.0
TPP	17	<	<	27	27	28	<	<	53	13
TBP	220	200	290	240	270	280	6.0	6.0	11	<
TCEP	20	<	7.7	<	<	<	<	<	<	<
TCPP-1	500	2000	2200	1000	10000	11000	40	42	34	28
TCPP-2	180	380	450	190	2400	2400	9.0	9.0	7.9	18
TMPP	37	13	28	<	<	<	<	<	<	29
TCPP-3	5.8	<	2.3	<	97	97	2.6	<	<	23
DBPP	<	<	<	1100	140	170	<	<	46	21
BDPP	2.9	<	1.1	<	<	<	<	<	<	170
TDCPP	<	13	13	29000	1000	1800	<	360	690	1100

	Runoff						**Soil. road surface solids and sludge**			
	Germany			**Sweden**			**Germany**	**Sweden**		
Description	**Solids**	**Water**	**Total**	**Solids**	**Water**	**Total**	**Soil (1m)**	**Soil (1m)**	**road surface**	**sludge well**
TBEP	400	<	150	<	<	<	<	<	<	71
TPhP	120	7.6	56	<	36	36	8.5	<	<	120
diphenyl EHP	540	14	230	7700	470	660	12	140	230	190
TEHP	3400	15	1300	12000	41	340	34	87	180	430
CDP-1	160	<	63	<	<	<	<	<	<	92
CDP-2	97	<	38	<	<	<	<	<	<	<
DCP-1	97	<	38	<	<	<	<	<	<	<
ToCP	8.7	<	3.4	<	<	<	<	<	<	<
DCP-2	87	<	34	<	<	<	<	<	<	<
DCP-3	14	<	5.6	<	<	<	<	<	<	<
TmCP	95	<	37	<	<	<	<	<	<	<
T(m.m.p)CP	130	<	50	<	<	<	<	<	<	<
T(m.p.p)CP	68	<	27	<	<	<	<	<	<	<
TpCP	15	<	5.9	<	<	<	<	<	<	<
sum OPE	6500	2900	5400	61000	15000	17000	110	860	1700	2500
Hopanes and steranes	µg/kg	ng/L	ng/L	µg/kg	ng/L	ng/L	µg/kg	µg/kg	µg/kg	µg/kg
Level of detection	1	0.5		1	0.5		1	1	1	1
Ts	2600	21	1000	510	16	28	120	210	800	1300
Tm	1900	12	770	300	9.0	16	75	150	580	850
H29ab	5700	48	2300	990	32	57	21	330	1300	2200
H29aa/ba	440	3.2	180	71	1.9	4.0	40	45	160	280
H30ab	7100	51	2800	1200	37	67	330	440	1900	2800

	Runoff						Soil. road surface solids and sludge			
	Germany			Sweden			Germany	Sweden		
Description	**Solids**	**Water**	**Total**	**Solids**	**Water**	**Total**	**Soil (1m)**	**Soil (1m)**	**road surface**	**sludge well**
H30ba	820	4.8	320	130	3.8	7	42	71	270	420
H30bb	830	0.31	320	<	<	<	4.6	<	<	480
H31S	6500	44	2600	1100	36	63	370	490	1900	2900
H31R	3000	22	1200	570	18	32	190	210	790	1300
C27abbR	1300	15	520	410	12	22	74	76	500	960
C27aaaR	960	7.2	380	180	5.9	10	9.5	21	190	440
C28abbR	1100	9.1	420	250	7.9	14	56	82	370	670
C29abbR	1900	16	750	470	15	27	120	160	550	1000
C29abbS	1600	16	660	420	14	24	140	160	550	1000
Hopanes	29000	210	11000	4900	150	270	1200	1900	7700	13000
Steranes	6900	64	2700	1700	54	98	400	490	2200	4100
Total hopanes+steranes	36000	270	14000	6600	210	370	1600	2400	9900	17000
Phthalates	µg/kg	ng/L	ng/L	µg/kg	ng/L	ng/L	µg/kg	µg/kg	µg/kg	µg/kg
Level of detection	1	1		1	1		1	1	1	1
dimethyl phthalate	290	<	110	<	29	29	<	17	54	83
diethyl phthalate	1000	<	390	<	110	110	<	<	660	310
diisobutyl phthalate	1200	130	580	1200	66	96	18	20	6.0	36
dibutyl phthalate	1000	1.3	400	3600	31	120	26	110	<	9.0
1diisopentyl phthalate	43	<	17	<	<	<	<	<	<	<
1dihexyl phthalate	170	<	68	<	<	<	<	2	<	<
butylbenzyl phthalate	420	4.4	170	<	2.6	3	160	14	50	110
bis (2-ethylhexyl) adipate	3600	140	1500	2000	46	97	280	59	58	78

	Runoff						Soil. road surface solids and sludge			
	Germany			Sweden			Germany	Sweden		
Description	Solids	Water	Total	Solids	Water	Total	Soil (1m)	Soil (1m)	road surface	sludge well
dicyclohexyl phthalate	500	17	210	2600	5.0	70	96	7.0	16	27
bis(2-n-ethylhexyl) phthalate	65000	660	26000	95000	720	3100	17000	280	2300	2400
difenyl phthalate	<	1.7	1.7	<	<	<	<	<	<	<
di-n-octyl phthalate	10000	28	3900	13000	10	350	86	15	260	360
diisononyl phthalate (isomers)	1230000	320	480000	1180000	2600	32000	18000	2700	26000	54000
diisodecyl phthalate (isomers)	140000	2600	57000	160000	600	4500	<	360	1300	4600
di-n-nonyl phthalate	1300	46	540	3200	9.0	88	99	8.0	58	100
Sum phthalates	1450000	3900	570000	1460000	4300	41000	36000	3600	30000	62000

Benzothiazoles	µg/kg	µg/L	µg/L	µg/kg	µg/L	µg/L	µg/kg	µg/kg	µg/kg	µg/kg
Level of detection	0.1	0.01		0.1	0.01		0.1	0.1	0.1	0.1
benzothiazole	740	0.05	0.34	4400	1.8	1.9	19	23	170	140
N-cyclohexyl-2-benzothiazolesulfenamide *	<	<	<	<	<	<	<	<	<	<
2-mercaptobenzothiazole	1000	<	0.39	4400	<	0.11	<	<	6	190
2.2-dithiobis(benzothiazole)	620	<	0.24	<	<	<	<	<	<	1.1
2-methoxybenzothiazole	52	0.01	0.03	370	0.27	0.28	5.5	5.2	10	8.5
2-hydroxybenzothiazole (=benzothiazolone)	490	0.06	0.25	760	2.9	2.9	32.0	58	41	1200
5.6-dimethyl-1H-benzotriazole	0.27	0.07	0.07	<	<	<	0.10	<	4.3	<
2-aminobenzothiazole	93	0.48	0.52	140	0.08	0.08	7.1	5	4.8	22
benzotriazole	600	0.03	0.26	210	0.22	0.22	74	6	10	34
N-cyclohexyl-1.3-benzothiazol-2-amine	23	<	0.009	79	0.01	0.01	1.2	1.1	2.7	1.0
1-hydroxybenzotriazole *	<	0.60	0.60	<	<	<	<	<	<	<
tolyltriazole	1100	<	0.43	670	0.40	0.41	52.0	13	21	39

	Runoff						Soil. road surface solids and sludge			
	Germany			Sweden			Germany	Sweden		
Description	**Solids**	**Water**	**Total**	**Solids**	**Water**	**Total**	**Soil (1m)**	**Soil (1m)**	**road surface**	**sludge well**
benzothiazole-2-sulfonate	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Sum benzothiazoles	4700	1.3	3.1	11000	5.7	5.9	190	110	270	1600
Phenols	µg/kg	µg/L	µg/L	µg/kg	µg/L	µg/L	µg/kg	µg/kg	µg/kg	µg/kg
Level of detection	1	0.01		1	0.01		1	1	1	1
4-n-octylphenol	<	<	<	<	<	<	<	<	<	3.6
4-nonylphenol	<	<	<	<	<	<	<	<	<	<
4-tert-octylphenol	1500	0.20	0.76	880	0.02	0.04	8.4	37	42	530
bisphenol-A	240	0.03	0.12	<	0.10	0.10	73	12	10	56
tetrabromobisphenol-A	7.6	<	0.003	<	<	<	1.4	<	<	1.2
triclosan	<	<	<	<	<	<	<	<	<	<
Sum phenols	1700	0.2	0.9	880	0.1	0.14	82	49	52	590
Amines	µg/kg	µg/L	µg/L	µg/kg	µg/L	µg/L	µg/kg	µg/kg	µg/kg	µg/kg
Level of detection	1	0.005		1	0.005		1	1	1	1
4-aminodiphenylamine *	59	0.07	0.10	<	0.02	0.02	<	<	<	<
4-hydroxydiphenylamine	170	0.82	0.88	<	0.07	0.07	13	4.0	6.0	10
aniline	3600	0.44	1.8	6500	0.28	0.44	65	37	78	200
cyclohexylamine *	5.2	0.01	0.01	<	<	<	<	<	1.5	2.3
dicyclohexylamine *	110	<	0.04	140	<	0.004	15	3.0	62	110
hexa(methoxymethyl)melamine	32	3.9	3.9	<	2.2	2.2	2.2	<	<	1.7
triethanolamine *	1.0	0.09	0.09	200	<	0.01	5.7	5.1	5.2	6.6

	Runoff						**Soil. road surface solids and sludge**			
	Germany			**Sweden**			**Germany**	**Sweden**		
Description	**Solids**	**Water**	**Total**	**Solids**	**Water**	**Total**	**Soil (1m)**	**Soil (1m)**	**road surface**	**sludge well**
Sum amines	4000	5.3	6.9	6800	2.6	2.7	100	49	150	330
Octylphenol ethoxylates and nonylphenol ethoxylates	µg/kg	µg/L	µg/L	µg/kg	µg/L	µg/L	µg/kg	µg/kg	µg/kg	µg/kg
Level of detection	5	0.01		5	0.01		5	5	5	5
OPEO1	<	<	<	<	<	<	<	<	<	<
OPEO2	<	<	<	<	<	<	<	<	<	<
OPEO3	<	<	<	<	<	<	<	<	<	5.7
OPEO4	<	<	<	<	0.01	0.01	<	<	<	<
OPEO5	<	<	<	<	0.04	0.04	<	<	<	7.8
OPEO6	<	<	<	<	0.02	0.02	<	<	<	<
OPEO7	<	<	<	<	0.01	0.01	<	<	<	<
OPEO8	<	<	<	<	<	<	<	<	<	<
OPEO9	<	<	<	<	0.01	0.01	<	<	<	<
OPEO10	<	<	<	<	<	<	<	<	<	<
OPEO11	<	<	<	<	<	<	<	<	<	<
OPEO12	<	<	<	<	<	<	<	<	<	<
OPEO13	<	<	<	<	<	<	<	<	<	<
OPEO14	<	<	<	<	0.02	0.02	<	<	<	<
OPEO15	<	<	<	<	<	<	<	<	<	<
NPEO1	<	<	<	<	<	<	<	<	<	<
NPEO2	24	<	0.009	<	<	<	<	<	<	<
NPEO3	1700	0.17	0.90	<	0.20	0.20	64	<	<	670

	Runoff						Soil. road surface solids and sludge			
	Germany			Sweden			Germany	Sweden		
Description	Solids	Water	Total	Solids	Water	Total	Soil (1m)	Soil (1m)	road surface	sludge well
NPEO4	1500	0.12	0.69	<	0.18	0.18	67	<	<	330
NPEO5	780	0.05	0.35	<	0.08	0.08	29	<	<	210
NPEO6	840	<	0.33	<	0.05	0.05	84	<	<	240
NPEO7	400	<	0.16	<	0.02	0.02	46	<	<	260
NPEO8	120	<	0.05	<	0.02	0.02	<	<	<	240
NPEO9	89	<	0.04	<	0.01	0.01	<	<	<	180
NPEO10	210	<	0.08	<	<	<	11	<	<	170
NPEO11	150	<	0.06	<	<	<	<	<	<	84
NPEO12	170	<	0.07	<	<	<	7.0	<	<	57
NPEO13	110	<	0.04	<	<	<	5.7	<	<	<
NPEO14	80	<	0.03	<	<	<	<	<	<	<
NPEO15	39	<	0.02	<	<	<	<	<	<	<
NPEO16	32	<	0.01	<	<	<	6.3	<	<	<
Octylphenol ethoxylates (OPEO)	<	<	<	<	0.12	0.12	<	<	<	13
Nonylphenol ethoxylates (NPEO)	6200	0.35	2.8	<	0.56	0.60	320	<	<	2400
Sum OPEO + NPEO	6200	0.35	2.8	<	0.68	0.70	320	<	<	2400
Metals	mg/kg	µg/L	µg/L	mg/kg	µg/L	µg/L	mg/kg	mg/kg	mg/kg	mg/kg
Level of detection	0.005	0.001		0.005	0.001		0.005	0.005	0.005	0.005
Li	24	1.0	11	41	1.3	2.3	15	36	16	22
Be	1.0	0.006	0.44	3.3	0.004	0.09	1.0	1.3	1.4	1.9
B	36	14	28	18	12	13	15	9.0	6.9	50
Na	3600	61000	62000	2000	9700	9800	4600	1100	580	1100

	Runoff						Soil. road surface solids and sludge			
	Germany			Sweden			Germany	Sweden		
Description	Solids	Water	Total	Solids	Water	Total	Soil (1m)	Soil (1m)	road surface	sludge well
Mg	11000	700	4800	14000	410	760	8200	11000	5100	5400
Al	34000	9.0	13000	57000	17	1400	29000	29000	16000	17000
Si	2500	1900	2900	4700	1400	1500	890	870	800	2100
P	1100	3.4	410	1800	2.3	47	860	480	280	240
S	2500	1900	2900	4700	1400	1500	890	870	800	2100
K	7700	1400	4400	9400	880	1100	7200	6100	3700	5600
Ca	15000	15000	21000	19000	5900	6300	18000	15000	9400	11000
Ti	1900	0.04	740	3800	0.09	95	2300	3200	1500	1300
V	85	0.08	33	230	2.3	8.2	72	96	52	72
Cr	160	0.30	65	260	1.5	8.0	200	150	77	220
Mn	550	93	310	600	47	62	700	530	500	330
Fe	52000	27	20000	69000	41	1800	38000	47000	30000	23000
Co	12	0.15	5.0	23	1.5	2.1	14	15	11	14
Ni	59	2.2	25	43	1.6	2.7	85	49	16	77
Cu	620	9.1	250	390	8.3	18	210	33	61	54
Zn	1900	230	980	690	72	89	600	270	200	580
As	10	0.09	3.9	14	0.27	0.63	5.3	1.6	3.3	1.6
Se	14	0.11	5.5	1.7	0.16	0.20	2.5	1.0	7.6	71
Zr	57	0.02	22	58	0.09	1.6	41	50	79	57
Mo	15	1.9	7.8	23	1.2	1.8	14	9.0	3.7	15
Cd	1.0	0.05	0.35	0.30	0.04	0.04	0.72	0.12	0.16	0.10
Sn	110	0.04	45	200	0.19	5.1	17	8.0	12	15
Sb	110	4.4	48	53	1.3	2.7	25	2.6	3.8	4.4

Description	Runoff						Soil. road surface solids and sludge			
	Germany			Sweden			Germany	Sweden		
	Solids	Water	Total	Solids	Water	Total	Soil (1m)	Soil (1m)	road surface	sludge well
Ba	350	33	170	130	22	25	250	130	58	79
Pb	65	0.04	26	35	0.05	0.93	64	10	10	10
W	2.8	0.02	1.1	100	2.4	5.0	1.7	32	49	64
Ag	0.74	0.001	0.3	0.7	0.002	0.02	0.41	0.64	0.51	0.39
Au	0.01	0.01	0.02	<	0.01	0.01	0.009	<	0.002	<
Ce	51	0.01	20	130	0.13	3.5	52	88	120	82
Pt	0.05	0.001	0.02	0.03	0.003	0.004	0.05	0.02	0.04	0.02
Pd	0.42	0.14	0.30	1.6	0.06	0.10	0.48	0.13	0.11	0.42
Rh	0.02	0.002	0.009	0.02	0.001	0.001	0.01	0.002	0.002	0.007

* The concentrations of the pollutants in red are very uncertain due to a low recovery in the measurements
< The concentrations of the pollutants marked with < are below the limit of detection

Table 15 Measured concentration in surface water from the Netherlands (A2) and from the Rhine (border of Germany and the Netherlands) In surface water from the A2. the concentration in the water phase and in the solids is measured separately. In the surface water from the Rhine. only the concentration in the solids have been measured. The concentration in the Rhine water only includes the solid phase and not the water phase. The suspended matter concentration in the Rhine is not measured by TNO but is provided by Rijkswaterstaat.

	Surface water					Sediment
	Rhine		the Netherlands (A2)			NL (A2)
Description	**Solids**	**Solids**	**Solids**	**Water**	**Total**	**Sediment**
Solids (mg/L)	36	-	7.5	-	-	-
PAH	µg/kg	ng/L	µg/kg	ng/L	ng/L	µg/kg
Level of detection	0.1		1	0.1		0.1
naphthalene	49	730	2500	11	29	15
acenaphthylene	30	440	<	0.32	0.32	8.6
acenaphthene	15	220	140	1.3	2.3	6.5
fluorene	24	350	390	2.2	5.1	12
phenanthrene	200	3000	1700	2.5	16	65
anthracene	45	680	1100	1.7	9.6	15
fluoranthene	450	6800	5900	1.1	45	170
pyrene	360	5400	1200	0.53	9.5	120
benzo(a)anthracene	210	3100	<	<	<	82
chrysene	290	4400	160	<	1.200	92
benzo(b)fluoranthene	570	8500	360	0.62	3.3	190
benzo(k)fluoranthene	170	2500	170	0.22	1.5	65
benzo(a)pyrene	240	3600	150	0.10	1.3	73
indeno(1.2.3-cd)pyrene	150	2200	200	<	1.5	43

	Surface water					Sediment
	Rhine		the Netherlands (A2)			NL (A2)
Description	Solids	Solids	Solids	Water	Total	Sediment
dibenzo(a.h)anthracene	48	720	380	0.17	3.1	17
benzo(g.h.i)perylene	190	2800	170	0.18	1.4	59
sum PAH	3000	45000	14000	22	130	1000
Organophosphate ester	µg/kg	ng/L	µg/kg	ng/L	ng/L	µg/kg
Level of detection	2		50	2		2
TMP	55	820	6400	63	110	34
TEP	<	<	81	8.3	8.9	<
TiPP	23	340	1300	120	130	<
TPP	5.8	87	270	<	2.1	39
TBP	22	330	500	9.4	13	<
TCEP	<	<	950	<	7.2	<
TCPP-1	<	<	550	80	84	20
TCPP-2	<	<	1000	19	27	<
TMPP	<	<	1400	<	10	<
TCPP-3	<	<	150	<	1.1	7.8
DBPP	<	<	<	<	<	<
BDPP	<	<	<	<	<	<
TDCPP	<	<	290	<	2.2	<
TBEP	<	<	<	<	<	100
TPhP	<	<	58	<	0.43	4.3
diphenyl EHP	<	<	3400	23	49	10
TEHP	4.4	66	<	<	<	<

	Surface water					Sediment
	Rhine		the Netherlands (A2)			NL (A2)
Description	**Solids**	**Solids**	**Solids**	**Water**	**Total**	**Sediment**
CDP-1	<	<	<	<	<	<
CDP-2	<	<	<	<	<	<
DCP-1	<	<	<	<	<	<
ToCP	<	<	<	<	<	<
DCP-2	<	<	610	<	4.5	<
DCP-3	<	<	<	<	<	<
TmCP	<	<	<	<	<	<
T(m.m.p)CP	<	<	<	<	<	<
T(m.p.p)CP	<	<	<	<	<	<
TpCP	<	<	<	<	<	<
sum OPE	110	1600	17000	330	450	220
Hopanes and steranes	µg/kg	ng/L	µg/kg	ng/L	ng/L	µg/kg
Level of detection	1		50	0.5		1
Ts	34	510	370	2.0	4.8	12
Tm	22	330	110	0.66	1.5	10
H29ab	100	1500	970	4.1	11	42
H29aa/ba	5.7	86	54	0.25	0.66	16
H30ab	96	1400	1100	4.5	13	41
H30ba	19	290	190	0.66	2.1	38
H30bb	5.7	85	130	0.41	1.4	22
H31S	89	1300	1100	4.8	13	34
H31R	57	850	590	2.4	6.8	42

	Surface water					Sediment
	Rhine		the Netherlands (A2)			NL (A2)
Description	**Solids**	**Solids**	**Solids**	**Water**	**Total**	**Sediment**
C27abbR	20	300	200	1.1	2.5	7.1
C27aaaR	7.2	110	87	0.46	1.1	3.1
C28abbR	13	200	120	0.55	1.4	4.1
C29abbR	33	500	330	1.4	3.8	10
C29abbS	25	380	320	1.3	3.7	8.7
Hopanes	430	6400	4600	20	55	65
Steranes	99	1500	1000	4.8	13	15
Total hopanes+steranes	530	7900	5700	25	67	80
Phthalates	µg/kg	ng/L	µg/kg	ng/L	ng/L	µg/kg
Level of detection	1		100	1		1
dimethyl phthalate	<	<	<	6.5	6.5	<
diethyl phthalate	5000	75000	<	110	110	<
diisobutyl phthalate	930	14000	31000	15	250	41
dibutyl phthalate	610	9200	36000	1.5	270	22
1diisopentyl phthalate	<	<	<	<	<	<
1dihexyl phthalate	<	<	<	<	<	<
butylbenzyl phthalate	14	220	<	<	<	<
bis (2-ethylhexyl) adipate	59	880	8300	75	140	92
dicyclohexyl phthalate	9.4	140	<	<	<	6.4
bis(2-n-ethylhexyl) phthalate	14000	210000	600	980	980	10000
difenyl phthalate	<	<	<	<	<	<
di-n-octyl phthalate	10	150	<	<	<	230

	Surface water					Sediment
	Rhine		the Netherlands (A2)			NL (A2)
Description	Solids	Solids	Solids	Water	Total	Sediment
diisononyl phthalate (isomers)	3500	53000	<	<	<	4500
diisodecyl phthalate (isomers)	650	9800	<	<	<	2000
di-n-nonyl phthalate	20	300	<	<	<	15
Sum phthalates	25000	380000	75000	1200	1700	17000
Benzothiazoles	µg/kg	µg/L	µg/kg	µg/L	µg/L	µg/kg
Level of detection	0.1		10	0.01		0.1
benzothiazole	2.2	0.03	110	0.03	0.03	<
N-cyclohexyl-2-benzothiazolesulfenamide *	<	<	52	0.001	0.001	<
2-mercaptobenzothiazole	<	<	110	<	0.0008	2.3
2.2-dithiobis(benzothiazole)	<	<	<	<	<	<
2-methoxybenzothiazole	1.6	0.02	70	0.04	0.04	2.1
2-hydroxybenzothiazole (=benzothiazolone)	7.7	0.12	8.7	0.03	0.03	5.8
5.6-dimethyl-1H-benzotriazole	<	<	<	<	<	0.19
2-aminobenzothiazole	0.2	0.003	21	0.18	0.18	0.31
benzotriazole	17	0.26	<	<	<	8.9
N-cyclohexyl-1.3-benzothiazol-2-amine	0.2	0.003	26	<	0.0002	0.33
1-hydroxybenzotriazole *	<	<	<	0.06	0.06	<
tolyltriazole	6.4	0.10	<	<	<	5.8
benzothiazole-2-sulfonate	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Sum benzothiazoles	36	1	400	0.34	0.34	26
Phenols	µg/kg	µg/L	µg/kg	µg/L	µg/L	µg/kg

	Surface water					Sediment
	Rhine		the Netherlands (A2)			NL (A2)
Description	**Solids**	**Solids**	**Solids**	**Water**	**Total**	**Sediment**
Level of detection	1		100	0.01		1
4-n-octylphenol	<	<	<	<	<	<
4-nonylphenol	1.1	0.02	<	<	<	21
4-tert-octylphenol	4.2	0.06	<	<	<	<
bisphenol-A	5.3	0.08	62000	<	0.46	<
tetrabromobisphenol-A	1.0	0.02	<	<	<	3.5
triclosan	24	0.36	<	<	<	4.5
Sum phenols	36	0.54	62000	<	0.46	29
Amines	µg/kg	µg/L	µg/kg	µg/L	µg/L	µg/kg
Level of detection	1		50	0.005		1
4-aminodiphenylamine *	<	<	<	<	<	<
4-hydroxydiphenylamine	31	0.47	150	<	0.001	19
aniline	4.4	0.07	47	0.006	0.0004	4.9
cyclohexylamine *	<	<	<	<	<	<
dicyclohexylamine *	<	<	<	<	<	1.2
hexa(methoxymethyl)melamine	<	<	<	0.07	0.07	<
triethanolamine *	<	<	<	<	<	<
Sum amines	36	0.53	200	0.08	0.07	25
Octylphenol ethoxylates and nonylphenol ethoxylates	µg/kg	µg/L	µg/kg	µg/L	µg/L	µg/kg
Level of detection	5		100	0.01		5
OPEO1	<	<	<	<	<	<

	Surface water					Sediment
	Rhine		the Netherlands (A2)			NL (A2)
Description	Solids	Solids	Solids	Water	Total	Sediment
OPEO2	<	<	<	<	<	<
OPEO3	<	<	<	<	<	<
OPEO4	<	<	<	<	<	<
OPEO5	<	<	<	<	<	<
OPEO6	<	<	<	<	<	<
OPEO7	<	<	<	<	<	<
OPEO8	<	<	420	<	0.003	<
OPEO9	<	<	<	<	<	<
OPEO10	<	<	<	<	<	<
OPEO11	<	<	480	<	0.004	<
OPEO12	<	<	<	<	<	<
OPEO13	<	<	380	<	0.003	<
OPEO14	<	<	<	<	<	<
OPEO15	<	<	<	<	<	<
NPEO1	<	<	<	<	<	<
NPEO2	<	<	<	<	<	<
NPEO3	21	0.31	<	<	<	<
NPEO4	10	0.15	<	<	<	<
NPEO5	16	0.24	<	<	<	<
NPEO6	8.3	0.13	180	<	0.001	<
NPEO7	<	<	<	<	<	<
NPEO8	<	<	<	<	<	<
NPEO9	<	<	<	<	<	<

	Surface water					**Sediment**
	Rhine		**the Netherlands (A2)**			**NL (A2)**
Description	**Solids**	**Solids**	**Solids**	**Water**	**Total**	**Sediment**
NPEO10	<	<	<	<	<	<
NPEO11	<	<	<	<	<	<
NPEO12	<	<	<	<	<	<
NPEO13	<	<	<	<	<	<
NPEO14	<	<	<	<	<	<
NPEO15	<	<	170	<	0.001	<
NPEO16	<	<	200	<	0.002	<
Octylphenol ethoxylates (OPEO)	<	<	1300	<	0.01	<
Nonylphenol ethoxylates (NPEO)	55	0.82	550	<	0.004	<
Sum OPEO + NPEO	55	0.82	1800	<	0.01	<

* The concentrations of the pollutants in red are very uncertain due to a low recovery in the measurements
< The concentrations of the pollutants marked with < are below the limit of detection