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SOS-ZEROPOL2030

M4.1 Assessment of primary emissions: per- and polyfluoroalkyl substances (PFAS) and Tyre Wear Particles (TWPs)

Public

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1. Executive Summary

The SOS-ZEROPOL2030 project aims to deliver a stakeholder led European Seas zero-pollution framework. In this framework, the so-called Integrated Assessment provides factual data for two case study pollutants to the stakeholders. SOS-ZEROPOL2030 focuses on two exemplary types of pollution, being per- and polyfluoroalkyl substances (PFAS) and tyre wear particles (TWPs). This report is intended to share the results of Task 4.1: Mapping of primary emission sources of PFAS and TWPs along the value chain.

In this report information is collated in thematic areas. For each of the case study pollutants, concise highlights are listed in a table. Background information and comments from analysis of data are provided in the Annexes, one for each case study pollutant. The main conclusions for each pollutant are listed below.

PFAS

- PFAS emissions are currently largely unknown, both in terms of molecular profile and emission volume; only very few monitoring programmes are in place.
- Using data sourced from literature and large-scale stakeholder interviews, the submitters of the PFAS restriction proposal estimated emissions. For the few PFASs for which emissions are monitored, the emissions are in the same order of magnitude as the estimations. Continuous monitoring and sampling from natural environments is necessary to gain an insight into the spatial concentrations and potential emission sources, which are important for policymaking.
- Diffuse emission sources (small-scale industrial use and end product use) represent far larger emission volumes than point emission sources. Effective monitoring is highly challenging for diffuse emissions. Import of PFAS-containing products into the EU could continue to cause PFAS emissions.
- Use categories with the largest total PFAS emissions are textiles and the use of fluorinated gases (especially for heating and cooling applications),
- The largest part of the scientific literature focuses on water-soluble, low molecular weight PFAS chemicals. Less information is available on the transport and fate of highly persistent, but likely less toxic, fluoropolymers.
- PFAS gases are almost always not managed, production volumes therefore largely translate in emission volumes. Most fluorinated gases with high production and use volumes do not fit the PFAS definition. After emission, however, atmospheric degradation takes place which will (partially) transform the gases into trifluoroacetic acid (TFA), which is a PFAS.
- No exhaustive quantitative data are available for PFAS volumes that reach the marine environment. While surface water seems to carry the largest volume of PFAS, aerial transportation likely also moves a large volume of PFAS into seas and oceans. Given that PFAS chemicals are typically both mobile and persistent, banning the production, use, and import of PFAS in the EU is considered unlikely to lead to a quick decrease in emissions and pollution on a global scale.
- Despite the relatively low concentrations of water-soluble low molecular weight PFAS chemicals in deep oceanic water that are typically measured as compared to more superficial seawater concentrations, it is anticipated that the deeper layers

of the global seas and oceans will be the main sink for most water-soluble PFAS chemicals over time.

TWPs

- TWPs are primarily produced through the friction and wear of tyres upon driving vehicles (cars, buses, lorries etc). Although the production phase and the processing of end-of-life tyres can also generate particles (e.g., crumb rubber used on artificial sports fields, playground surfaces and as an additive material to asphalt), these waste products are not considered to be TWPs as no wear takes place.
- TWPs are considered an important source of microplastics, representing a high proportion of total microplastic emissions globally.
- A wide variety of chemicals is used in tyres, with >800 different chemicals detected in one reported study. Some of these tyre wear chemicals (TWCs) can leach into the environment from both the tyres and the emitted TWPs. Pollution by TWPs therefore occurs both at the particle and chemical levels.
- Soils and freshwater bodies located a few meters from roads are the major sinks for TWPs. However, most TWPs are relatively small (<100 µm), which makes them prone to longer-range transport and accumulation in areas further away from the emission location. This transport of TPWs can occur through aqueous environments as well as through the atmosphere.
- In marine environments, TWPs are expected to settle due to having a higher density than seawater. Marine ecosystems adjacent to coastal towns and cities with significant vehicle volumes are expected to receive the highest TWP emissions.

2. Introduction

This document provides an overview of findings from literature study efforts in relation to emissions of tyre wear particles (TWPs) and per- and polyfluoroalkyl substances (PFAS). As a part of Work Package 4 within the SOS-ZEROPOL2030 project, this document aims to provide factual information to project partners and other work packages.

Chapter 3 and 4 contain brief summaries of the data on PFAS and TWPs, respectively. In-depth analysis of available and relevant information, descriptions of the used methodology, and references to data sources can be found for PFAS and TWPs in Chapter 5 and 6 (or Annex I and II), respectively.

3. Per- and polyfluorinated alkyl substances (PFAS): Case Study results

3.1. General introduction on the proliferation of PFAS over the planet

PFAS are persistent environmental pollutants as microorganisms cannot break them down and sunlight cannot degrade them in the atmosphere below the ozone layer. The carbon-fluorine bond is so stable that it can only be broken by incineration at elevated temperatures (roughly in excess of 1000 °C)² or exposure to UV irradiation³ as is present in the upper atmosphere. Some PFAS contain weak bonds such as ester or ether linkages, and these PFAS will typically degrade into smaller fragments. As these smaller fragments are typically also classified as PFAS, this degradation process does not reduce the amount of PFAS, it only helps to disperse them further over the planet. For instance, some common refrigerants are so-called unsaturated hydrofluoroolefins (HFOs), which are photodegraded into trifluoroacetic acid (TFA) in the upper atmosphere. This TFA subsequently undergoes wet and dry deposition into soils, rivers and the oceans.⁴ Both HFOs and TFA are PFAS and hence overall the total amount of accumulated PFAS on the planet doesn't change, but the distribution over the environmental compartments has changed.

After use, PFAS are often discarded and, depending on their physicochemical properties and end-of-life processing methods, they are either recycled, treated as solid waste, released into the air or discharged into the surface water. Only incineration results in the partial destruction of PFAS first to hydrofluoric acid and subsequently to calcium fluoride.² All other end-of-life treatment processes do not affect the PFAS. As only 11% of the solid waste is globally incinerated⁵ and this results only in a partial destruction of PFAS, the net result is the accumulation of PFAS on the planet. Some types of discarded PFAS will accumulate in fixed locations, such as for instance PFAS polymers in landfill sites⁶, whereas small PFAS molecules in the aqueous compartment can "accumulate" in a far more dynamical manner. These molecules can swiftly change their presence between sea, fish, humans, sea spray, ground water, plants, foods, etc., causing a complicated equilibrium and quick proliferation of their presence in multiple organisms and environmental compartments.

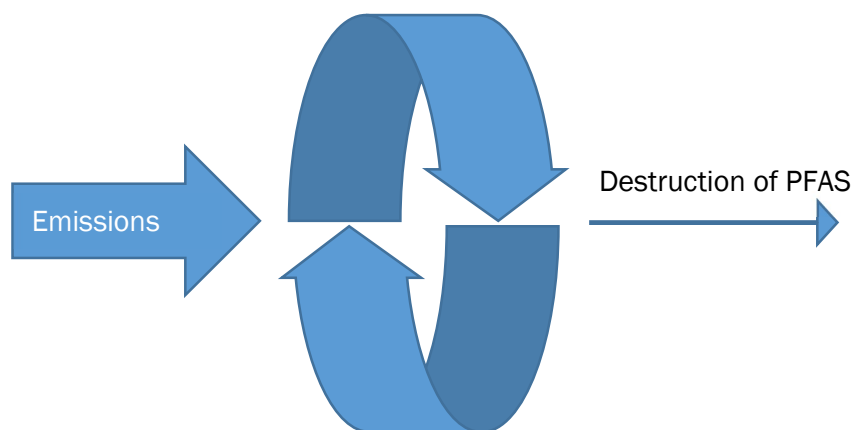


Figure 1. PFAS accumulate on our planet as the annual emissions exceed the annual amounts that are destroyed via incineration and photodegradation.

With a higher rate PFAS release into the environment than of natural degradation, the concentration of PFAS is constantly increasing in all environmental compartments. PFAS have various negative impacts on the environment, which vary from greenhouse gas activity to ecotoxicity and adverse effects on the human health.⁷ Some well-known PFAS, such as PFOS and PFOA, are also known to be carcinogenic. For these reasons, the manufacturing and use of these two PFASs (and a few others) is no longer allowed in the EU. Nevertheless, these two PFAS are already widely dispersed over the planet and are still being produced in some countries outside the EU. While the measured concentration may decrease at some highly polluted areas, the chemicals are still accumulating in the global environment. Only a global ban on the production and use of these chemicals can cause the accumulation to level off. But this will only happen after many years, since there are large PFAS stocks in many consumer products and waste materials that will be released in the coming decades. Therefore, even when these PFAS are banned and become a “legacy chemical”, they will stick with us for many years to come due to their persistence. That is the irony of PFAS; they have been promoted for their superior non-stick properties and will stick around with us for decades to come.

3.2. Data availability and data quality

Although much knowledge on PFAS pollution has been gathered over the last decades, the knowledge is still fragmented and incomplete. The data on production volumes within the EEA is reliable, other data usually show large margins or are incomplete. Data on the export and import of PFAS is much less reliable, as often products that contain PFAS are not registered as such. PFAS concentrations in seawater, surface water, soils and air are often measured only at a few locations and only at or during a few points in time. Furthermore, many studies use different analytical techniques and focus on a different selection of PFAS chemicals, making a meaningful comparison of data sets challenging. Moreover, the available data shows that measured concentrations of PFASs in the environment vary substantially, both spatially and temporally, and these variations are not always understood.

In this document, we aim to answer the technical questions raised in relation to the emission of PFAS into the environment. As the SOS-ZEROPOL2030 project focuses on the marine environment, we will aim to answer these questions both in relation to the total emissions and the emissions entering the marine environment. Nevertheless, most of the questions on PFAS emissions can only be answered with approximations and extrapolations given the paucity and fragmented nature of the data available.

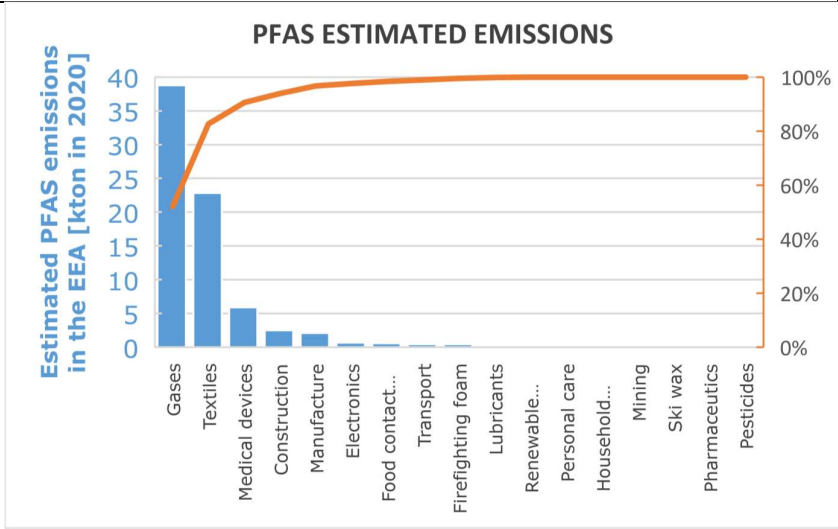
Environmental agencies from five EU countries (Denmark, Germany, the Netherlands, Norway, and Sweden) collaborated on a document that proposes to restrict the manufacture, placing on the market and use of PFASs in the EU. It was published [online](#) at the ECHA website in March 2023.⁸ In this report we will refer to this document as the ‘PFAS restriction proposal’. This document and its annexes were used as the main data source for this report, owing to its useful overviews, comprehensive data, and information from stakeholder surveys that is not available anywhere else. Where possible, information was cross-checked with other data sources.

3.3. Template input for PFAS

Question	Answer
<p>What are the main <u>point source emissions</u> for PFAS in Europe?</p>	<p>The largest point emission sources of PFAS in Europe are PFAS production locations, with emissions in the order of 400-4000 tonnes per annum. The majority of the direct emissions are to the air (~98%) and only a small amount to the surface water. Hence, production locations are estimated to emit about 8-80 tonnes per annum to surface waters in Europe.</p> <p>The second largest point emission sources are waste management facilities, such as wastewater treatment plants (WWTPs; mostly to the surface water) and waste incinerators (mostly to the air; the leachates of landfill sites for bottom ashes are also treated by waste water treatment facilities).</p> <p>Extrapolations of Flemish emission data suggest that the European emission of point sources to surface water is approximately 26 tonnes per annum. These data relate to emissions from point sources to surface waters; industrial manufacturers, industrial and commercial PFAS users, and waste treatment facilities are all obliged to report on PFAS emissions.</p>
<p>What are considered the most relevant <u>diffuse sources</u> of PFAS emissions in Europe?</p>	<p>Diffuse emissions of PFAS occur predominantly in the use-phase. The emissions during use have been estimated in the restriction proposal, which is based upon a long list of defined assumptions. This estimation process indicated that applications within the TULAC (Textiles, Upholstery, Leather, Apparel, Carpets) domain cause the largest diffuse PFAS emissions of roughly 10-35 kilotonnes per annum in the EEA, followed by emissions in the medical application sector of roughly 4-8 kilotonnes per annum. In addition, there are many other PFAS applications with emissions of less than 1 kilotonne per annum. Fluorinated gases have a direct emission volume of roughly 1.5 kilotonnes per annum for the amount introduced to the market in the same year. Taking stocks also into account, the emission volume is estimated to be 31 kilotonnes.</p> <p>Three general remarks are highlighted here:</p> <ol style="list-style-type: none"> 1. There is substantial data uncertainty in relation to the fluorinated gases. It is inherently difficult to measure emissions related to leakage of gases from diffuse sources and data about collection at end-of-life are scarce. 2. Diffuse emissions are more important than the point emissions. 3. Although it is challenging to relate specific PFAS uses to emissions into specific environmental compartments, the

largest diffuse emissions of PFAS appears to be in the TULAC domain. Since this usage-domain encompasses textiles that are washed, it can be safely assumed that this diffuse source is also the largest emitter of PFAS to surface waters.

Which sources of PFAS are the largest contributors to overall PFAS emissions?



This graph shows PFAS emissions in the European Economic Area (EEA) in 2020, broken down into the contributions of industrial sectors. Data are retrieved from ECHA⁸. Assuming that the stakeholder information used in the restriction proposal is the most accurate data that is available, it can be concluded that:

- A small number of application groups (gases, textiles/TULAC, medical devices, construction, manufacturing) are accountable for the largest share of diffuse PFAS emissions in the EEA.
- Diffuse PFAS emissions are likely higher in total volume than emissions from point sources. As no measurements can be done at the source of diffuse emissions, tracing back to products or use cases is therefore very challenging.
- Manufacturing sites of PFAS chemicals are currently important point sources for emissions into air and wastewater. They may also be the origin of a large share of PFAS emissions from chemical waste incinerators.
- Usage of PFOS and PFOA have been prohibited in the EU in 2009 and 2019. In 2022 however, they still form a significant share of PFAS volumes in Flemish wastewater. This may be related to the slow release of PFAS chemicals from firefighting foam or end-of-life consumer products, import of products that still contain these chemicals, or degradation of fluorotelomer alcohols (in the case of PFOA). These emissions

	<p>are not taken into account in the graph above, as this only considers PFAS-containing products that were still in use or that were being manufactured in the year 2020.</p>																																								
<p>Provide details about the most relevant PFAS chemicals in terms of their <u>production/usage volumes</u>. Same for <u>emissions</u>.</p>	<p>PFAS chemicals can be categorised in many ways. Based on differences in physical appearance and transport pathways of emissions, here we propose the following categories: fluorinated polymers, fluorinated gases, and low molecular weight PFAS.</p> <table border="1" data-bbox="542 583 1357 1556"> <thead> <tr> <th>Main category</th> <th>Sub category</th> <th>Production volume [ktonne/y]</th> <th>Estimated emissions volume [ktonne/y]</th> </tr> </thead> <tbody> <tr> <td>Low mol. wt. PFAS</td> <td></td> <td></td> <td></td> </tr> <tr> <td></td> <td></td> <td></td> <td></td> </tr> <tr> <td>Fluorinated polymers</td> <td>Fluoropolymers [FP]</td> <td></td> <td></td> </tr> <tr> <td></td> <td>Perfluoropolyethers [PFPE]</td> <td></td> <td></td> </tr> <tr> <td></td> <td>Side-chain fluorinated polymers (SFP / SCFP)</td> <td></td> <td></td> </tr> <tr> <td>Fluorinated gases</td> <td>Emissive</td> <td></td> <td></td> </tr> <tr> <td></td> <td>Non-emissive / FP feedstock</td> <td colspan="2">0: gases are already counted in FP category</td> </tr> <tr> <td></td> <td></td> <td></td> <td></td> </tr> <tr> <td></td> <td></td> <td></td> <td></td> </tr> </tbody> </table> <p>Key messages:</p> <ul style="list-style-type: none"> • Low molecular weight PFAS chemicals (not gaseous) are of the highest concern with regards to human health and environmental impacts. These PFAS chemicals are often detected in water and soil samples, and are probably the 	Main category	Sub category	Production volume [ktonne/y]	Estimated emissions volume [ktonne/y]	Low mol. wt. PFAS								Fluorinated polymers	Fluoropolymers [FP]				Perfluoropolyethers [PFPE]				Side-chain fluorinated polymers (SFP / SCFP)			Fluorinated gases	Emissive				Non-emissive / FP feedstock	0: gases are already counted in FP category									
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	<p>most relevant category for the SOS-ZEROPOL2030 project.</p> <ul style="list-style-type: none"> Emissions of fluorinated gases mainly occur into the air. In that environment, gases partially decompose into PFAS chemicals. Some of these are water-soluble and end up in water systems (freshwater and marine). Fluorinated polymers (FPs) by themselves are considered to be less of an environmental issue than the PFAS processing aids used during manufacturing of FPs. Not all fluorinated gases are classified as PFAS chemicals. 																																															
<p>Where in the <u>value chain</u> are the PFAS emissions most likely to occur today?</p> <p>In which environmental compartment(s) are primary PFAS emissions most likely to occur (air, surface water, groundwater, etc.)?</p>	<table border="1"> <thead> <tr> <th rowspan="2">Stage</th> <th colspan="3">Emissions to compartment [mid estimate, kton in 2020]</th> <th colspan="3">Total emissions [kton in 2020]</th> </tr> <tr> <th>Air</th> <th>Water</th> <th>Soil</th> <th>Low</th> <th>Mid</th> <th>High</th> </tr> </thead> <tbody> <tr> <td>PFAS manufacturing</td> <td>3.7</td> <td>0.06</td> <td>0</td> <td>0.4</td> <td>2.1</td> <td>3.7</td> </tr> <tr> <td>End product manufacturing</td> <td colspan="3">74</td> <td>56</td> <td>74</td> <td>92</td> </tr> <tr> <td>Usage</td> <td colspan="3"></td> <td></td> <td></td> <td></td> </tr> <tr> <td>End-of-life</td> <td colspan="3">n.a.</td> <td>3.7</td> <td>n.a.</td> <td>7.3</td> </tr> </tbody> </table>			Stage	Emissions to compartment [mid estimate, kton in 2020]			Total emissions [kton in 2020]			Air	Water	Soil	Low	Mid	High	PFAS manufacturing	3.7	0.06	0	0.4	2.1	3.7	End product manufacturing	74			56	74	92	Usage							End-of-life	n.a.			3.7	n.a.	7.3	<p>Data in the table above are compiled from estimations in the PFAS restriction proposal.^{7, 8} There is a lack of data to allow for categorising the ‘End product manufacturing’ and ‘Usage’ stages. These stages are related to the highest emission volumes in a generalized value chain. On a sector level, however, it could be very different. Insufficient data is available to assess the emissions in different parts of the value chain for the indicated sectors.</p>			
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<p>What transportation pathways represent the largest volumes of PFAS emissions when spreading through the environment to accumulation zones?</p>	<p>This strongly depends on the chemistry of the PFAS of interest, the place where the emission occurs, and many more factors. Some general remarks:</p> <ul style="list-style-type: none"> - Ionic PFAS chemicals dissolve well in water and are therefore more likely to be transported in aqueous media than non-charged PFAS chemicals. - PFAS gases and fluorotelomer alcohols are volatile, which makes atmospheric transport the most likely transportation route. - Long-chain PFAS molecules (>C₈) tend to adhere more strongly to sediment, soil, and other solids than short-chain analogues. <p>Most research has focused on the transportation of PFAS chemicals through aqueous systems. Known polluted areas typically attract more attention from researchers than areas which are more remote or considered more pristine. Although transport through air is not quantified, it is likely that the main transport takes place <i>via</i> rivers into marine environments. In marine environments, both horizontal and vertical transportation mechanisms affect further distribution.</p>
<p>Which marine environmental compartments are considered to be the primary <u>accumulation zones/environmental sinks</u> for PFAS?</p>	<p>Coastal waters, especially when close to estuaries or rivers with high PFAS concentrations, typically show the highest concentrations of PFAS in measurements of marine water samples. Furthermore, superficial water typically contains higher concentrations of PFAS than deeper water, and the interchange between superficial and deeper water is generally limited. Such exchange does take place, however. The concentration gradient slowly drives the water-soluble PFAS chemicals to deep seas and oceans. Due to the large volume of deep water compared to superficial water, deep water is considered to be the main final sink.</p>

Please refer to Chapter 5 for further information and in-depth analysis regarding the emission of PFAS.

4. Tyre wear particles (TWPs) – Case Study results

4.1. Introduction on tyre wear particles (TWPS)

Tyre wear particles (TWPs) have been identified as an important source of microplastics (MPs; <5 mm) but reported particulate emission volumes and environmental concentrations are highly variable, both spatially and temporally. Car tyres and the emitted TWPs are known to contain a high level and diversity of potentially hazardous chemicals, many of which have been shown to partition or leach into environmental matrices. Here, we have collated the available literature data with the aim of providing state of the art insights into (i) the chemical composition of TWPs, and (ii) the major emission sources of TWPs and TW chemicals (TWCs) across Europe.

4.2. Methodology

To address the thematic areas highlighted above, peer-reviewed literature was accessed using Web of Science in February 2023⁹. Formulated search strings (key terms combined by Boolean operators) were used to retrieve bibliographic data (with abstracts) from the databases. Collated peer-reviewed literature was screened using Rayyan^{10, 11}, applying a combination of soft and hard include/exclude criteria.

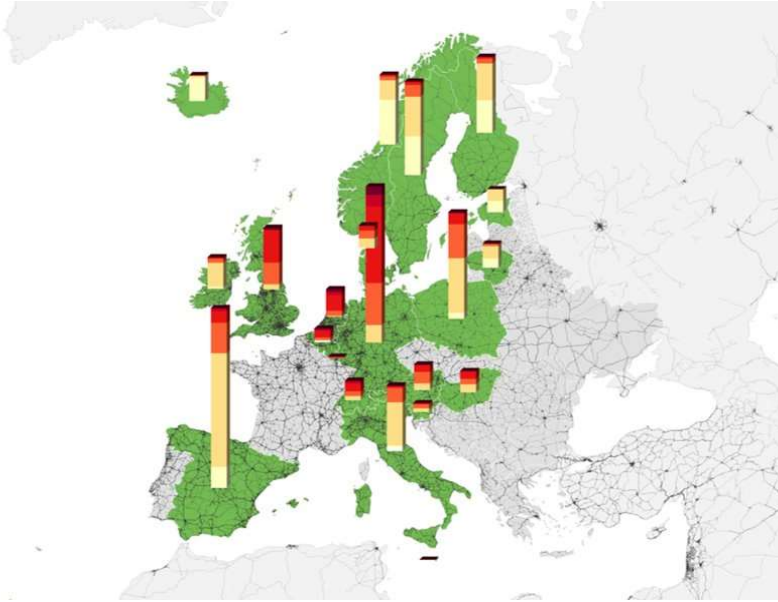
To address **chemical composition** of tyres and TWPs, the following search strings were used: care ti(y)re OR ti(y)re wear particle* OR TWP AND chemical composition OR reaction* OR composition OR chemical* OR element* OR byproduct OR vulcanization OR stabilizer* OR filler*. 415 unique articles were from the last 10 years were exported and subject to screening by two double-blind reviewers. Include criteria were: Rubber*, Zn, Metals, Cu, Carbon*, Metal*, Natural*, Zinc*, Reaction*, Hydrocarbons, Oil*, Additives, Copper*, Phenylenediamine, Synthetic*, Additive*, 6PPD*, filler*, PAH*, Carbon black*, Reactions, Steel*, Silica*, Elastomer*, Polyester*, Catalyst*, Sulphur*, Rubbers, Binder*, Agents, Amines, Hydrocarbon*, Cyclic amines, By-product*, Zinc oxide*, Phenylenediamines, Benzotriazoles, By-products, Phthalate*, Catalysts, Amine*, Nylon*, Resin*, Chlorinated paraffins, Natural and synthetic, Anti-oxidants, Carbon blacks, Aryl-amines, Binders, Resins, Steels.


Exclusion criteria were: titles and abstracts not mentioning either ti(y)res or TWP, articles only reporting concentration in the environment and not directly in tyres or tyre particles, articles only addressing particle emissions, articles only addressing toxicity without chemical characterisation or addressing toxicity of individual chemicals without a direct link to tyres. A total of 31 articles were left after inclusion/exclusion criteria were implemented, 25 of which were accessed and reviewed for information. Further information was also obtained from cascading literature, as well as overviews provided by tyre manufacturers.


To address **sources of TWP emissions**, the following search strings were used: ti(y)re wear particles OR AND emission sources OR emissions OR sources AND environment. Refinement of the search was performed to only include papers published from 2013 onwards, all in English language and from European countries. A total of 992 unique articles were exported and subject to screening by one reviewer. Include criteria were: Tyre wear, tyre wear, TWP.

Exclusion criteria were: non-European study area, articles only reporting method development or laboratory assessments without field sample demonstration. A total of 45 resulting articles were accessed and reviewed for information, two of which were deemed not relevant and subsequently omitted.

4.3. Template input for TWPs

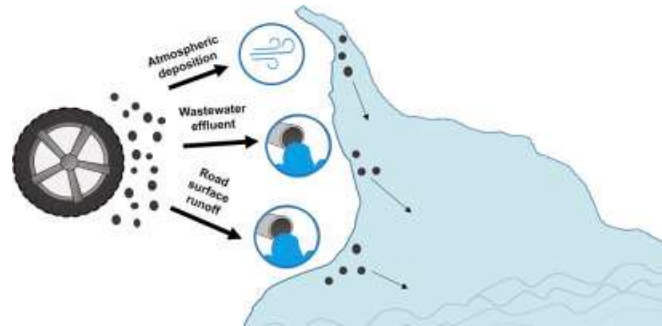
Question	Answer
<p>What are the main <u>point source emissions</u> for TWPs in Europe?</p>	<p>Urban, highway and rural roads are considered the main point sources of TWP emissions. There is a direct link between traffic volumes and TWP emissions, with higher emissions with increasing traffic loads. 'Heavier' traffic (e.g., vans, buses, and trucks) emit more particles by distance travelled. In particular, braking and accelerating, as well as turning, causes increased emissions for all vehicle types. Summer tyres release more TWP than winter tyres (while winter tyres, particularly studded tyres, cause road wear to a greater extent). Emissions per km travelled are largest in urban areas (due to increased braking, accelerating and turning), followed by highways and rural areas. Total TWP emissions from a few western European countries have been ranked in the following order: Germany > UK > Italy > Sweden > Netherlands > Norway > Denmark.</p>  <p>As a proxy, this map shows the road network in black, and per-country traffic intensity as stacked graphs where data is available. The total length of each bar represents the total road network length of the country (km). Each individual shade indicates a different traffic intensity class, expressed as average annual number of vehicles passing (light yellow = fraction of the total network that has less than 5,000 cars passing, dark red = above 100,000). The traffic intensity data stems from the CEDR annual pan-European road network report (2021).</p>

<p>What are considered the most relevant <u>diffuse sources</u> of TWP emissions in Europe?</p>	<p>Road run-off, atmospheric deposition of smaller TWPs, and re-distribution through WWTP may be considered relevant diffuse sources of TWPs. Re-purposing of roadside soil may also be a currently overlooked source of TWPs.</p>
<p>Which sources of TWPs are the <u>largest contributors</u> to overall TWP emissions?</p>	<p>The act of driving vehicles with tyres is by far the largest source of TWP emissions. It is estimated that through its usable lifetime, a tyre loses between 10-30% of its initial mass due to the abrasion of the tread in contact with the road. Considering an average initial mass of 8.2 kg for a passenger car tyre and of 70 kg for a truck tyre, this means that around 1.2 kg (passenger car) and 12.6 kg (truck) of rubber are lost in the environment during the working lifespan of the tyre¹². Due to their widespread use and higher vehicle numbers, passenger cars, followed by vans, lorries and trucks, are the largest contributors to TWP releases. In urban areas, mopeds, motorcycles and buses also contribute to overall TWP releases. Bikes and airplanes contribute minor, not vehicle-related, emissions.</p> <div data-bbox="545 993 1268 1434" data-label="Image">  </div> <p>Image reproduced from Tyroola: https://www.tyroola.com.au/guides/what-are-bald-tyres/</p>

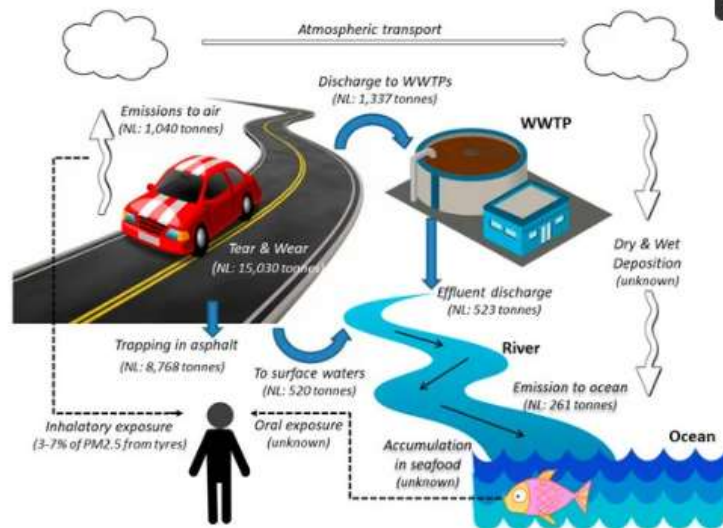
	 <p>Image reproduced from Oxford Indices: https://www.oxfordindices.com/news/2020/12/4/whats-in-a-tyre</p> <p>Tyres are also the primary sources of many tyre-related chemicals. However, many additive chemicals and non-intentionally added substances (NIAS) associated with tyres have other uses and sources. It is therefore difficult to distinguish the specific sources of these based on environmental concentration measurements, although the presence of multiple tyre-associated chemicals in a single sample could potentially increase the likelihood of tyres being a major source.</p>
<p>Provide details about the most relevant TWP chemicals (additives and NIAS) in terms of their <u>production/usage volumes</u>.</p>	<p>Both unreactive chemicals (e.g., polymers, oils, fillers, wax, resins and antioxidants) and reactive chemicals (e.g., sulphur compounds, retardants, accelerators, activators and glue) are used in the composition of the tyre tread (the part of the tyre where TWPs originate). Literature reviews have shown that nearly 800 chemicals are known to be used and/or present in tyres and tyre particles.</p> <p>Chemical groups in descending order by number of known chemicals: Vulcanisation accelerators, antioxidants and antiozonants, polymerisation agents, plasticiser, other protectants, adhesion agents, nitrosamine compounds, reaction products, mastication agents, blowing agents, vulcanisation agents, vulcanisation retarders, vulcanisation activators. Notably, decomposition products and 'other' chemicals represent some of the largest groups of chemicals.</p> <p>As the exact tyre formulation for each tyre on the market in Europe is subject to intellectual properties rights of the producers, there is limited transparency in terms of the use volumes of each of these chemicals in different tyres.</p>

<p>Where in the <u>value chain</u> are the TWP and TWP chemical emissions most likely to occur today?</p>	<p>It is the use phase of vehicle tyres (i.e., when driving) where TWPs are generated and emitted to the environment. As TWPs are formed through abrasion, other tyre-derived particles that might be produced in the production and end-of-life phases are not classified as TWPs but may contribute to chemical emissions. This is particularly the case for rubber granulates used as infill on artificial sports pitches and playgrounds. Similarly, chemical emissions from tyres can occur when the vehicle is stationary, but still in contact with the environment (especially under wet conditions).</p>
<p>Which <u>consumer products</u> are considered to be the primary sources of TWP and TWP chemical emissions?</p>	<p>Vehicle tyres are the key contributors to TWP emissions. Similar particle and chemical emissions may be expected from other sources where very similar materials are used in consumer products, such as airplane tyres, bikes, conveyor belts etc. Artificial turf infill material from end-of-life tyres is not fully representative of TWPs (larger particle sizes and possibly different chemical compositions) but are considered by some to be another consumer product that acts as a source of such emissions, especially chemicals.</p>
<p>In which <u>environmental compartment(s)</u> are TWP and TWP chemical emissions most likely to occur (air, surface water, ground water, etc.)?</p>	<p>Roadside soil is the main recipient of TWPs. European case studies have estimated 45-80% of TWP deposition occurs within the first few meters from the curb or roadside. Surface waters are the next largest recipient, receiving an estimated 6-26%. Smaller TWPs (low-micron and nanosized) remain airborne for longer and may be subject to long-range transport. Similarly, small TWPs and mobile TWCs may be subject to wash-out from soils and transfer to groundwaters. TWPs are not buoyant in natural waters (freshwater or seawater), and will sink, thus accumulating in freshwater and marine sediments. However, it should be noted that their small size (0.05-100 µm), means that sinking rates can be quite long as friction processes become more dominant.</p>
<p>What are the most likely <u>transportation routes</u> of the TWPs and TWP chemicals towards their accumulation zone(s)?</p>	<p>Most TWPs deposit directly onto the road or within a few metres of the roadside. Smaller TWPs may be airborne for longer and thus transported longer distances before deposition occurs. While limited data is available, some evidence of long-range transport of TWPs does exist.</p>

Water sources such as lakes, rivers and marine waters located close to main non-urban roads (e.g., highways) can act as accumulation zones and transport mechanisms for TWP and TWC to the marine environment. Similarly, coastal towns and cities may represent major point sources of emissions and transport of TWP and TWC to the marine environment via urban run-off bypassing or through WWTP systems.



Schematic reproduced from Parker-Jurd et al.¹³



Schematic reproduced from Kole et al.¹⁴

<p>Which marine environmental compartments are considered to be the primary <u>accumulation zones/environmental sinks</u> for TWPs and TWP chemicals?</p>	<p>For TWPs, estuaries and coastal zones are the primary accumulation zones, especially those closest to urban areas that act as a point source of TWPs. The sediments are expected to be the main marine environmental matrix in which the particles accumulate.</p> <p>For mobile TWPs, further transport by ocean currents will occur away from marine deposition areas. It is also important to note that some chemicals are also subject to biodegradation and photodegradation in the marine environment, although the degree of degradation depends strongly on their individual persistency.</p>
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Please refer to Chapter 0 for further information and in-depth analysis regarding the emission of TWPs.

5. Annex I: PFAS emissions in detail

5.1. Main point source emissions of PFAS in Europe

Two approaches can be followed to answer this question. Firstly, the total emissions of point source emissions is listed in the restriction proposal and with the approximated share of these emissions to the surface water both the total point source emission emissions and the total point source emissions to the surface water can be estimated. Secondly, the Flemish database of point source emissions to the surface water in Flanders can be extrapolated to the European level.

5.1.1. First approach: using data of the restriction proposal

The prime point emission sources of PFAS in Europe are production locations of PFAS with emissions in the order of 400-4000 tonnes per annum. At the PFAS production locations most emissions are to the air compartment and only a small fraction to the surface water. Secondary point emission sources are waste management facilities, such as waste water treatment facilities (mostly to the surface water) and waste incinerators (mostly to the air; the bottom ashes of incinerators are land-filled and the leachates of these landfill sites that contain PFAS are also treated by waste water treatment facilities).

The total emission of the 20 PFAS manufacturing locations in the EEA is estimated to be between 400 and 4000 tonnes per annum⁷ [Annex B, section B9.2.2], of which the direct emissions to air are dominant (~98%) and the direct emissions to surface water are far less (~2%). This would imply that roughly between 8 and 80 tonnes PFAS per annum is directly discharged to the surface water in the EEA at the manufacturing sites. The indirect emissions of these production manufacturing sites via their solid waste to mostly the water and soil compartments are substantial, but accounted for at the waste management sites.

The following waste treatment facilities emit PFAS to the environment: landfill sites, incinerators and waste water treatment facilities. The total PFAS emission of European landfill sites for solid wastes via leachate to the water compartment is crudely estimated to be 1-5 ton per annum⁷ [Annex B, B9.18.2.3].

The total PFAS emission at waste incinerators cannot be estimated as the PFAS is partially converted into smaller break down products which behave like fluorinated gases and will be emitted into the air. The rest will remain in the bottom ash and the fly ash. The loads of PFAS entering the incinerators are only crudely known and the fates of the PFAS after the incineration process are unknown. Hence, only very crude estimations are available based on the analysis of ashes from a few incinerators. When these measured concentrations are extrapolated, the amounts of PFAS in European bottom ashes are approximately 26 kg per annum and in the fly ashes 46 kg per annum⁷ [Annex B, B9.18.2.4]. These ashes are typically landfilled. In most European countries the landfill sites are well-managed and leachates are collected for treatment at waste water treatment facilities. This indirectly results in the emission to the surface water. Furthermore, it should be noted that the gaseous emissions of small PFAS molecules to the air, can indirectly cause emissions to the aqueous compartment. Due to photochemical degradation in the stratosphere some of these PFAS molecules are converted into trifluoroacetic acid that will precipitate into the rivers and the seas. These emissions cannot be approximated yet.

The total PFAS emission at waste water treatment facilities in the EU is estimated to be 5-10 ton per annum via the effluent and crudely 0.5 ton per annum via the sludge⁷ [Annex B, section B9.18.2.5]. A second estimation was made by extrapolating the Dutch data of waste water treatment facilities¹⁵ over the whole EU using the population (17.5m in NL and 745m in EU in 2021) as weighing factor. In this way, we estimate that 5 tonne per annum of PFAS is discharged with the effluent and 1.3 ton per annum in the sludge.

5.1.2. Second approach: using the Flemish data of point emission sources to surface water

The Flemish database of point-source emissions to the surface water is particularly detailed. It shows that in the time period of 2007 to 2020 8 tonnes of PFAS have been discarded in Flanders to the surface water (both direct and indirect). The lion share of the emissions (66%) occurred at manufacturing sites, followed by 32% at various waste treatment facilities and 1% for a long list of miscellaneous point sources. If we extrapolate this data to the whole European Union with the GDP as weighing factor we can crudely estimate that 26 tonnes of PFAS is discharged to the surface water in the EU per annum. This would crudely imply 17 tonnes from manufacturing sites and 9 tonnes from waste treatment facilities. The 17 tonnes per annum discharged at manufacturing facilities to the surface water corresponds reasonably well with the estimation in the restriction proposal: between 8 and 80 tonnes per annum. Moreover, the 9 tonnes at waste treatment facilities compares reasonably well with the numbers estimated in the restriction proposal (between 6 and 16 tonnes annum).

5.2. Main diffuse sources of PFAS emissions in Europe

Diffuse emissions of PFAS occur predominantly in the use-phase. The emissions during use have been estimated in the restriction proposal with a long list of assumptions. This renders the picture that applications within the textile (TULAC) domain cause the largest emissions of roughly 10-35 kilotonne per annum in the EEA, followed by emissions in the medical application sector of roughly 4-8 kilotonne per annum, emissions due to construction products is 1.5-3.5 kilotonnes per annum, fluorinated gases with an emission of roughly 1.5 kilotonne per annum and then many applications with less than 1 kton per annum. The emission of the fluorinated gases is clouded by a large uncertainty as the stock levels of these gases is much larger, crudely estimated 39 kilotonnes, hence the actual emissions can be much larger.

Several points are important here. First of all, the diffuse emissions are much larger than the point emissions and also the uncertainty is larger. Secondly, when we focus on potential emissions to the surface water, the TULAC domain is not only overall the largest, but also the largest net discharger to the surface water.

5.3. Emissions in the PFAS value chain

PFAS emissions stem from

- Production of base (PFAS) chemicals;
- (industrial) Usage of the chemicals in end product manufacturing;
- Usage of PFAS-containing end products;
- End-of-life treatment of discarded objects containing PFAS.

The most complete and reliable data source for PFAS emissions in the EU is the overview in the restriction proposal for PFAS under REACH and its annexes.^{7, 8, 16, 17} This proposal estimates emissions to all environmental compartments and considers many different angles.

Since most EU countries do not obligate companies to measure and register of PFAS emissions, no dataset is available that gives a reliable overview of the real emissions based on monitoring data. The best available dataset about PFAS emissions in the EU contains information about PFAS loads in Flemish wastewater, which is publicly available.¹⁸ The number of chemicals that need to be registered and the concentration limit above which reporting is obligatory have been made more strict over the years in which registration has taken place (from 2007 onwards). Nevertheless, the registered volume of emissions covers < 0.1% of the emissions in 2021 which could be expected to occur in Flanders, based on the average emissions in the EU mentioned in the restriction proposal.

Potential PFAS **point sources** encompass manufacturing sites of PFAS (20 in EEA), industrial processing and application sites (>100 000 facilities in EEA where such activities may take place has been estimated⁸) and waste treatment facilities (~500 incinerators, ~30000 waste water treatment sites and ~300.000 landfill sites in EU). In many of these facilities, it is unknown which types and quantities of PFAS emissions occur and to which environmental compartment. It could be argued that these should be seen as **diffuse sources** instead. **The combined emissions from PFAS application and end products usage represent about 90% of the total PFAS emissions**, as shown in Table 1.

Table 1. Breakdown of emissions into stages and environmental compartments, data are from Annex B of the PFAS restriction proposal⁷.

Stage	Emissions to compartment [mid estimate, kton in 2020]			Total emissions [kton in 2020]		
	Air	Water	Soil	Low	Mid	High
PFAS manufacturing	3.7	0.06	0	0.4	2.1	3.7
End product manufacturing	74			56	74	92
Usage						
End-of-life	n.a.			3.7	n.a.	7.3

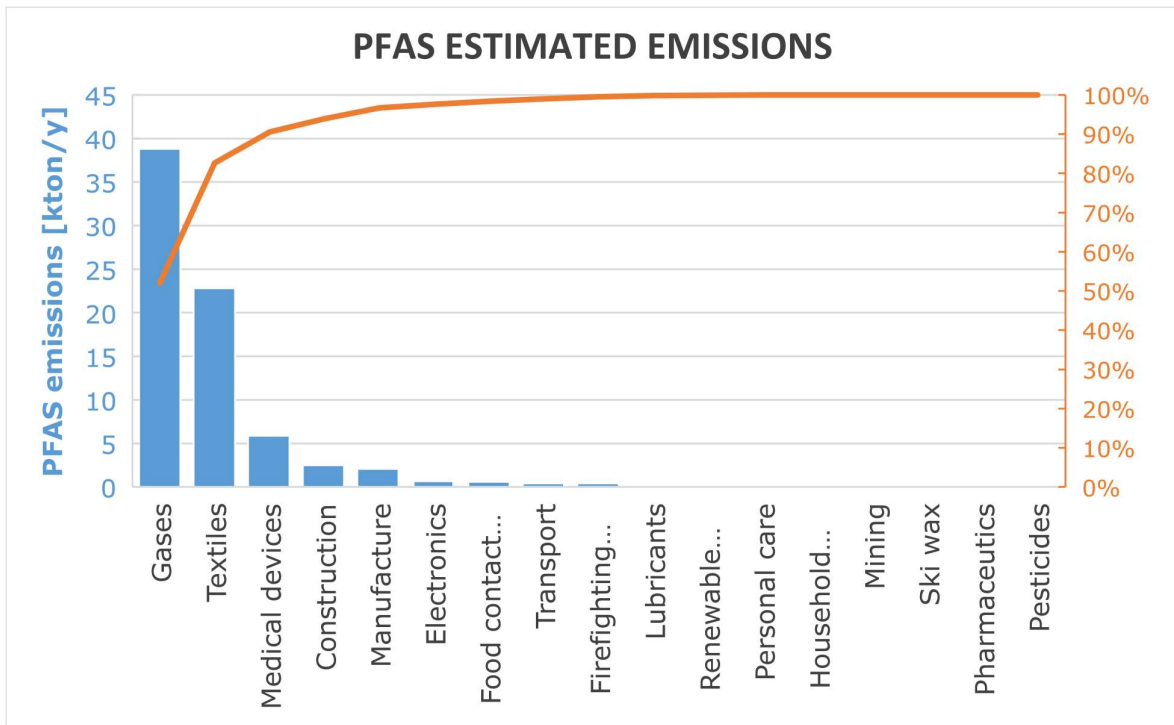
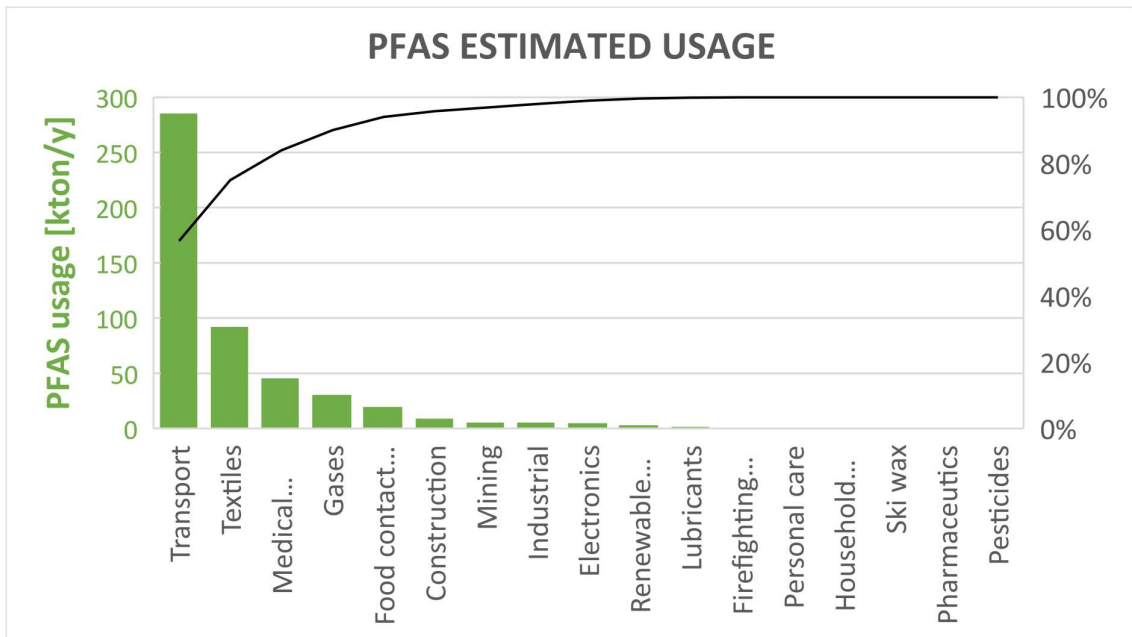


Figure 2. Sectors with the highest estimated usage of PFAS in the EU (top) and highest estimated emissions of PFAS in the EU (bottom). Data are from the main document of the PFAS restriction proposal⁸.

5.4. PFAS chemicals categories: production, usage and emissions.

This section is still to be populated.

5.5. Where in the value chain are the PFAS emissions most likely to occur today?

Comments relating to this question can be found in Section 5.3.

5.6. PFAS emissions in relation to consumer products

In the PFAS restriction proposal, end product manufacturing and usage of that product together govern the PFAS emission volumes. Emissions from PFAS chemical production and product end-of-life treatments are not taken into account. While it should theoretically be possible to estimate PFAS emissions from all product lifecycle stages for single products, in practice this is not common practice. This implies that products with high emissions during PFAS chemicals manufacturing or during end-of-life are likely underrepresented in this overview. Some examples include emissions from the use of PFAS to prevent mist formation during metal plating, the use of PFAS as lubricant in plastic processing, and the use of fluorinated gases as solvent for cleaning in semiconductor manufacturing. Nevertheless, the emission volumes of these applications are estimated to be negligible in comparison to the amounts of fluorinated gases produced and the amounts used in TULAC.

Figure 2 shows estimates of PFAS usage and emissions per sector; the relation to consumer products is discussed in the next section. Two sectors clearly stand out: ‘**Textiles**’, which includes Textiles, Upholstery, Leather, Apparel and Carpets (TULAC) and ‘**Gases**’, which relates to the application of fluorinated gases and includes the usage in other sectors. Emissions from **medical devices** are expected to grow significantly and it is likely that this sector will be given derogations that allow continued PFAS use. Other sectors that emit >500 t/y of PFASs include **construction, PFAS chemicals manufacturing, electronics & semiconductors, and food contact materials.**

Consumer products that within these sectors were estimated to cause the highest emission volumes are listed in Table 2.

Table 2. Top 3 of consumer products per sector with highest estimated emission volumes.

Sector	Top 3 of (consumer) product groups per sector with highest estimated PFAS emissions		
Textiles [Annex A]	Consumer apparel (water-resistant clothes and shoes)	Home textiles (stain-resistant carpets and furniture)	Technical textiles (various coatings)
Gases [Annex A]	Air conditioning (stationary & mobile)	Refrigeration (commercial, industrial, transport)	Closed-cell foams (polyurethane, for insulation)

Medical devices [2nd stakeholder consultation]	Propellants in metered dose inhalers	Other propellants ()	Anaesthetics
Construction [Annex A]	Architectural paints and coatings	Coil coating (metal parts, e.g. for facades)	Wind turbine and solar panel coatings
Electronics & semiconductors *	Wires and cables	Printed circuit boards	Capacitors
Food contact materials [Annex A]	Parts in industrial lines for food & feed production	Consumer cook & bakeware with anti-stick coatings	Beverage can coatings

Where possible, the selection of products in Table 2 was made based on direct emissions from a product category. Data for attributing emissions to consumer product groups were taken from Annex A of the restriction proposal.¹⁶ For the ‘medical devices’ and ‘electronics and semiconductors’, no quantification was found. For these sectors, the top 3 of products was selected based on information from other sources, of which the references are given in the table.

5.7. Transportation of PFAS in the environment

Transportation pathways are strongly dependent on physiochemical properties of the chemical and the environmental compartment into which the emission has taken place.¹⁹ Several schemes have been drawn that provide a visual clue as an answer to this question, although reality is always more complex. A good example is shown in Figure 3, as cited from Panieri *et al.*²⁰. In this scheme, the volumes of the streams are not taken into account. An important remark is that long-range atmospheric transport is not shown in this figure, while it is known to be an important pathway in the distribution of certain PFASs.^{21, 22} Furthermore, this scheme suggests that uptake into aquatic and terrestrial ecosystems and humans mainly takes place from sediment. Whereas this is true for aquatic plants²³, the general consensus is that the uptake of PFAS by the general populations is mainly through drinking water and dietary exposure, although many potential exposure routes have not been investigated in detail.¹⁹

Given that PFAS chemicals are typically both mobile and persistent, banning the production, use, and import of PFAS in the EU is considered unlikely to lead to a quick decrease in emissions and pollution on a global scale.

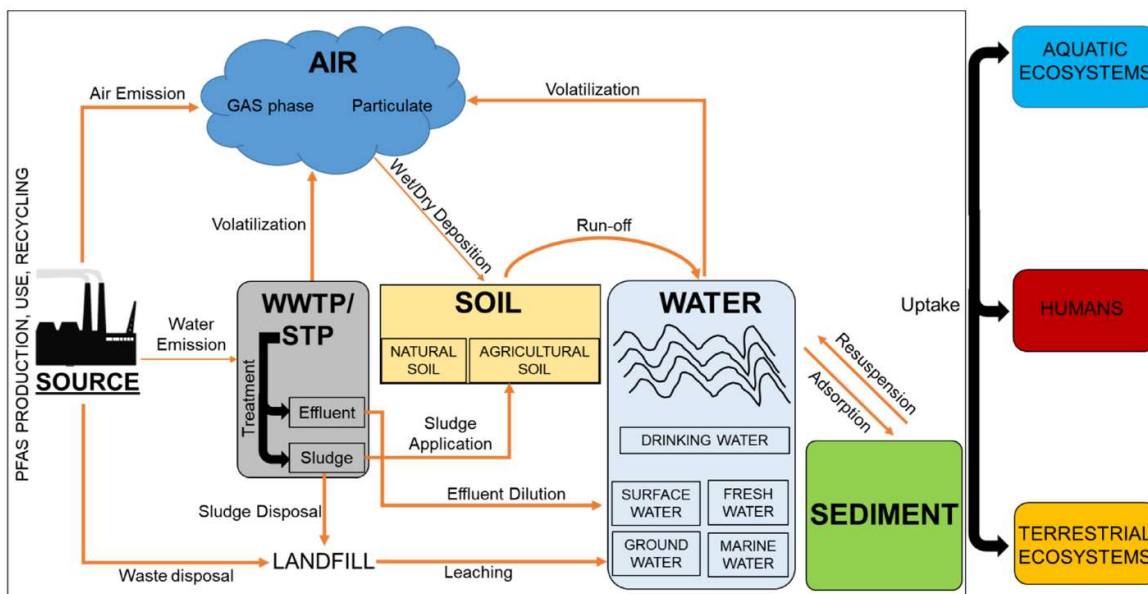


Figure 3. Schematic overview of transportation routes for PFASs after primary emission has occurred, reused from Panieri et al.²⁰. Note that the blocks represent potential accumulation zones and the arrows represent transportation pathways.

Another scheme, designed by Evich et al.²², is shown in Figure 4. This scheme clearly points out that emissions occur in each of the steps in the PFAS lifecycle. Alike Figure 3, many more emission and transportation routes exist in reality.

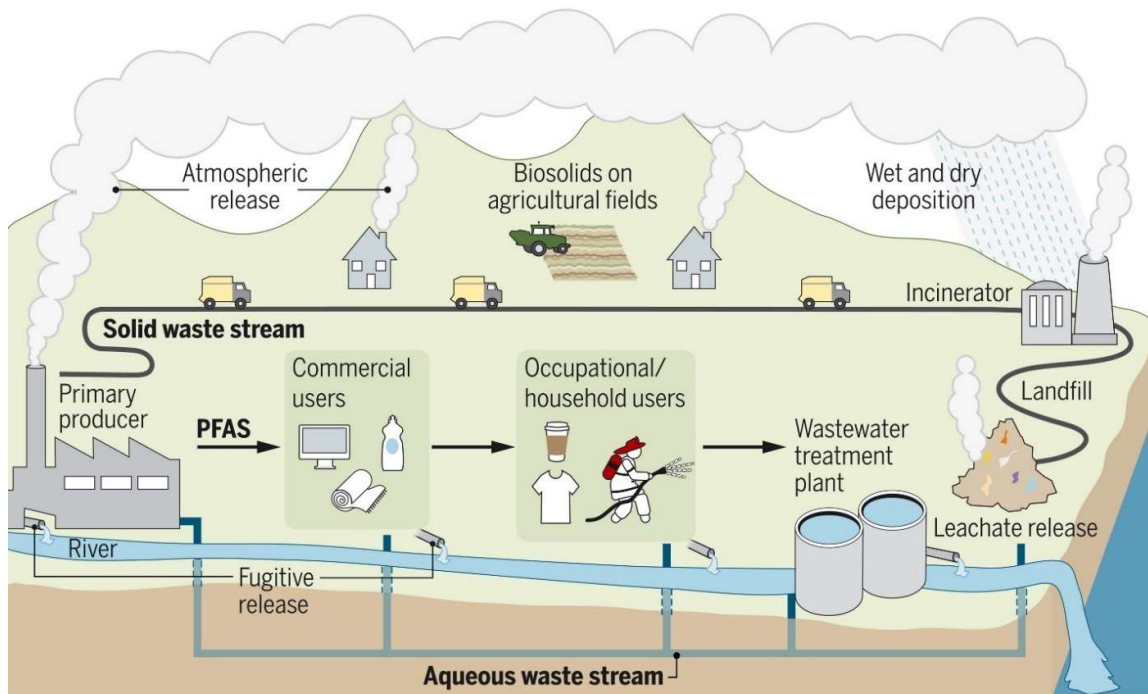


Figure 4. PFAS lifecycle and emissions from each of the steps, reused from Evich et al.²²

5.7.1. Water

PFAS emissions to water take place at many locations; both point sources and diffuse sources contribute significantly. Many groups of PFAS molecules are charged, giving rise to water-solubility. They will likely accumulate in surface water, groundwater and marine water.²¹ Transportation towards an accumulation zone may be severely slowed down due to interaction with sediments or soil, especially for cationic and zwitterionic chemicals.²²

Transportation routes of PFASs emitted into water bodies vary widely, depending on among others partition coefficients, chemical structure of the molecule, presence of currents and flow, water temperatures and ionic strength, presence of objects in the water to absorb onto, and etc. Considering that diffuse sources are the most relevant primary source of PFAS emissions into water (see Section 5.3), the transportation routes with highest estimated volumes are shown in Figure 5.

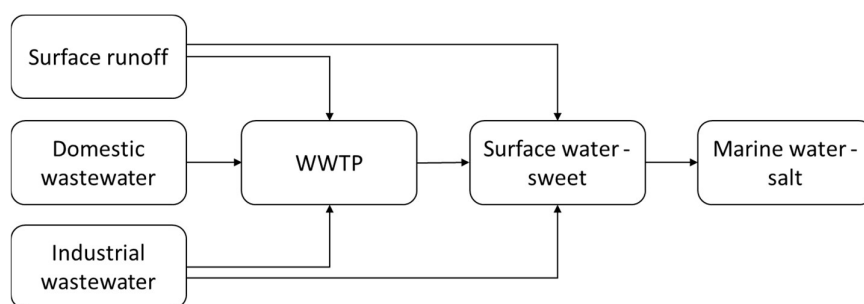


Figure 5. Scheme indicating the PFAS transportation routes in water with likely the largest PFAS fluxes.

Some remarks concerning transportation of PFAS in the environment:

- Sectors with the highest estimated emissions, as discussed in Section 5.3 are not directly associated with the marine environment. Direct emissions of PFAS into seawater (from the use of aqueous film forming foam (AFFF)) likely represent relatively little emission volumes compared to emissions from terrestrial sources, but may be impactful in or close to navy harbours or in warzones.²⁴
- Surface runoff relates to PFAS which are present at terrestrial grounds, typically in areas in which a PFAS spillage has occurred and in urban areas. After solubilization by rain or snow or , the PFAS chemicals typically flow into surface water.²⁵ The EU proposed to introduce new regulations for the treatment of wastewater in 2022, which still have to be agreed upon. These regulations would oblige to treat rainwater from urban areas in WWTPs, in order to decrease direct emissions of pollutants into surface water.
- High concentrations of various PFAS molecules have been found in various environmental compartments close to airports, military sites and fire stations.²⁶⁻²⁸ These are likely related to the use of aqueous film-forming foam (AFFF). According to literature, currently available models are not able to accurately predict the transportation routes of PFAS chemicals in such a real-world contamination site or require more diverse and specific input values than what is usually available.²⁹

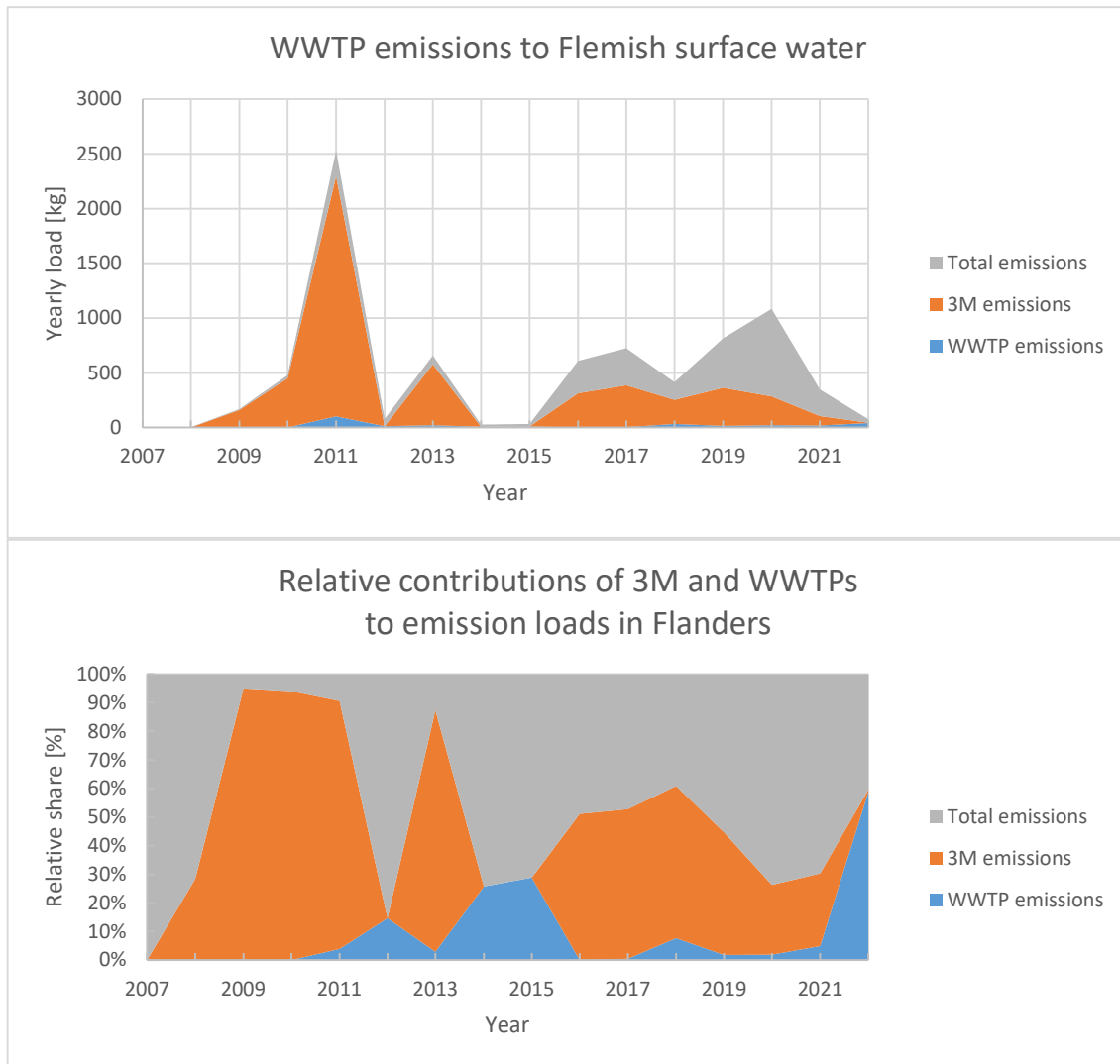


Figure 6. Yearly loads of PFAS emissions into Flemish wastewater and relative contributions of the 3M manufacturing plant in Zwijndrecht and that of all Flemish wastewater treatment plants to the total yearly loads, in the period 2007-2022. Data were retrieved from a publicly available database¹⁸; categorization and data analysis has been performed for the current report.

- Yearly loads of PFASs in emissions from government-owned wastewater treatment plants (WWTPs) to surface water in Flanders have shown strong fluctuations¹⁸; without further investigation the reason for this fluctuation remains unknown. Temporal fluctuations in emissions from the 3M plant in Zwijndrecht dominate the input of PFASs into wastewater in Flanders, as indicated in Figure 6. Emission volumes from diffuse sources do not depend on production schemes or treatment plant efficiencies and hence are expected to provide a stable baseline of emissions into water. The role of WWTPs in the transportation routes varies with, among others, region, plant layout and wastewater input composition. Industrial wastewater may, in some cases, be directly disposed into surface water. Some

WWTPs concentrate most of the PFAS in the influent into the sludge, while in others the total PFAS concentration in the effluent water is higher than in the influent. WWTPs and waste incinerators are interconnected. Sludge from WWTPs is often incinerated. As discussed in the introduction of this document, thermal destruction of PFAS materials is likely incomplete in most combustion processes.³⁰ In a study on PFAS waste from municipal waste incinerators in China, it was found that the yearly load of PFAS decreased in the order leachate > bottom ash > fly ash.³¹ The leachate is likely sent to the WWTP again, completing the cycle.

- In Romania, a recent study shows that PFAS emissions from WWTPs into surface water represent a small fraction of the total presence of PFAS in riverine water. The authors conclude that the largest share of PFAS in surface water could be linked to improper disposal of PFAS-containing products or the use of firefighting foam.³²
- For example in Italy it was observed that the concentration of PFAS in effluent water can often be higher than in influent³³. In WWTPs showing this phenomena, biotransformation processes such as the formation of PFAS molecules from precursors produce more PFAS than the amount that is removed by the sludge in the same period of time. A review article suggests that this is the case for the majority of WWTPs globally.³⁴
- The effluent of an industrial wastewater treatment plant close to Leverkusen was in 2010 found to be the main point source for PFAS emissions into the Rhine. Mitigation actions have been taken and were found to reduce the emissions of the plant to a level that is indistinguishable from that of the river sections just before the plant.³⁵

Once arrived in a sea or ocean, the high persistence of PFAS chemicals allow for distribution over the water body, mainly driven by currents. This aspect is further discussed in Section 5.8.1.

5.7.2. Air

A large share of emissions from manufacturing of PFAS chemicals is into the air compartment. The most likely transportation route is the following:

PFAS chemical production facility -> deposition to soil and dust at a concentration level decreasing with distance to the source -> dissolution in water phases related to precipitation -> surface water & sea.

Depending on the products and processes used in the production facility, the chemical profiles in the emissions can vary.^{36, 37} In the Chemours plant in Fayetteville, North Carolina, a thermal oxidizer has been installed and operations have started in 2019. A sampling campaign took place in the close vicinity of this plant before and after the commissioning of the plant. The significantly lower emissions of emerging PFAS after commissioning may indicate that effective measures to mitigate emissions to air can be designed.³⁶ Fluorotelomer alcohols form an example of a group of PFAS chemicals that are volatile, ubiquitous, have a lifetime long enough (20 days) to enable long-range transport, and are known to degrade in the atmosphere.³⁸

Further important mechanisms related to emissions into air are:

- Certain hydrofluorocarbons and hydrofluoroolefins in the atmosphere are known to degrade into trifluoroacetic acid (TFA). This molecule is miscible with water and does not adsorb onto sediment nor bioaccumulate significantly.³⁹ Once present in the atmosphere, TFA will partition entirely into water droplets, leading to wet deposition⁴⁰. Together with direct TFA emissions into water, the molecule will flow towards the lowest point. Oceans, seas and lakes are the likely accumulation zones for TFA.^{41, 42}
- Several industrial end product manufacturing processes are known to generate PFAS emissions into air. Examples include the thermal application of fluoropolymer dispersions on fabrics⁴³, the use of volatile PFASs as surfactants in semiconductor manufacturing, and the application of paints⁴⁴
- A long list can be composed of end products that directly emit PFAS into air. Some examples include propellants in inhalers and aerosols in the field of cosmetics⁴⁵, sulphur hexafluoride (SF₆) used as dielectric gas in the power industry⁴⁶, and certain cleaning agents⁴⁵.
- The formation of sea spray aerosols (SSAs) from surfactants in superficial seawater causes PFAS deposition from the sea onto terrestrial grounds.⁴⁷ In Europe, this effect is the strongest in countries that are close to the Atlantic Ocean and often have relatively high wind speeds (most notably Ireland, Iceland, Norway, Great-Britain, the north-western part of Spain and the western part of France). This process shows that the marine environment should not be seen as a sink for all PFAS chemicals. It is, however, an important accumulation zone for long-chain PFAS.

5.7.3. Sediment and suspended particulate matter

The continuous interaction between water and sediment and the fact that PFAS can be present in/at both matrices contribute to the role of sediment in transport of PFAS chemicals. In rivers and estuaries it was found that concentrations of PFAS in water were higher than those in sand on the beach and sediment in the water.⁴⁸⁻⁵¹ Higher concentrations of PFAS in sediment than in the corresponding water body have however also been reported.^{51, 52} This is likely related to the molecular structure of the PFAS (the longer the chain and the more hydrophobic the molecule, the stronger the partitioning towards sediment and suspended particles^{50, 51}). A trend of substituting long-chain PFAS chemicals by short-chain analogues is ongoing⁵³, hence it could be expected that in the near future the concentration of PFAS in water environments will increase compared to the concentration adhered onto particles. The magnitude of PFAS transport via particles in water has not been quantified in literature. In rivers, suspended particulate matter can be up to 36 kg m⁻³.⁵⁴ It could therefore be considered as a minor transport route.

More specific for Europe, in Austrian and Hungarian sections of the Danube, it has been shown that the sediment mostly consists out of sand and has a low carbon content. As expected, PFAS adsorption to this type of sediment is minor and transport of PFAS is expected to occur mainly through the water phase.⁵⁵ The same conclusion was drawn for the Rhine.⁵⁶ The opposite situation, in which sediment brings along major amounts of PFAS and contributes significantly to pollution levels, has been reported in rivers that flow into the Great Lakes.⁵⁷

PFAS transportation in marine environments can also take place through adsorption of the chemicals onto particulate matter. This can be either sediment or biological matter.^{58, 59} For most PFAS chemicals, transport in the water phase (advective transport) is a more important mechanism. However, for perfluorodecanoic acid (PFDA) and precursor compounds to perfluorooctane sulfonate (PFOS), transport via particles was found to be responsible for 35% and up to 86% of the chemicals' vertical flux, respectively.⁶⁰

5.7.4. Man-made environments

Microplastics have been shown to preferentially adsorb certain PFAS chemicals⁶¹, hence they could act as PFAS carriers (transport) and concentrators (accumulation). The scale at which this mechanism takes place and affects the distribution of PFASs in surface water and seawater seems to be largely unknown to date.

Landfills are a known accumulation zone for PFAS-containing products.²² In the US it was estimated that most of these products are from municipal solid waste and biosolids (sewage sludge), and that the annual PFAS outflow is around 16% of the PFAS mass.⁶²

5.8. PFAS sinks in the marine environment

Literature does not provide an exhaustive overview of PFAS volumes that are accumulated or will accumulate in certain environmental compartments. A review paper from 2006, written by Prevedouros *et al.*⁶³, is one of the few that explore the concept of environmental inventories with regards to PFAS in detail. The inventories calculated in this paper are limited to the Northern Hemisphere, due to limits in data availability. The spread in the estimations is too large to draw solid conclusions on the magnitude of accumulation zones or environmental sinks. For as far as we have found, more recent literature does not provide better estimations.

Table 3. Estimated inventory of PFCAs in the Northern Hemisphere, listed per environmental compartment. Data was retrieved from Prevedouros *et al.*⁶³.

Environmental compartment	Estimated inventory [tonnes]
Sea & ocean	110 – 10 000
Freshwater	4 - 800
Sediments	3 – 340
Air	n.a.
Other media	n.a.

Marine waters are in the scientific literature considered to be the main sink for water-soluble PFASs.^{59, 63} Examples of PFASs that are water-soluble and thought to accumulate in marine environments are perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), which are two of the most extensively researched PFAS molecules in literature. In the Arctic seas it was shown that although the concentration of PFOS decreases with decreasing depth, the total mass of PFAS stored in deep layers is significantly higher than that in superficial and intermediate waters. Furthermore, the concentration of PFOS is predicted to increase in deep water and to decrease in more superficial water at least until 2038.⁶⁴

Lakes have also been shown to accumulate perfluoroalkyl acids (PFAAs)⁴². Lakes which are not connected to an open sea are however scarce and are likely of minor importance for the total environmental inventory.

5.8.1. Effect of currents and vertical mixing

In general, literature reports higher concentrations of water-soluble PFASs at the surface of seas and oceans than in deeper waters.⁶⁴⁻⁶⁶ The main horizontal transportation routes in seas and oceans are large-scale currents.

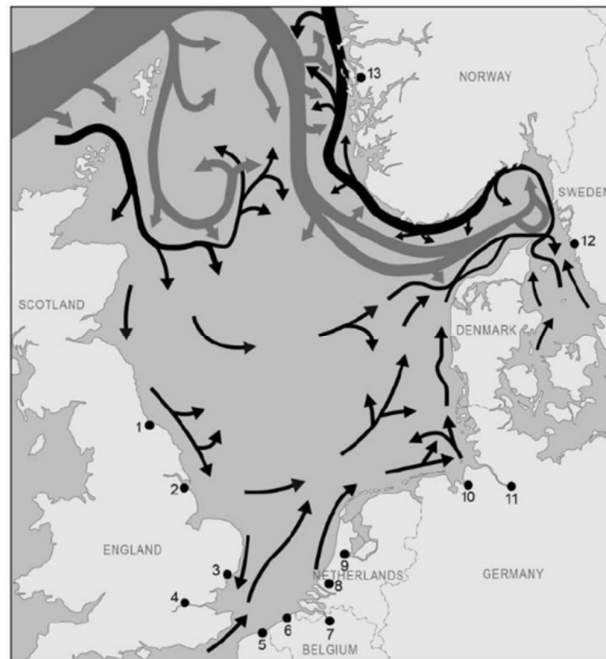


Figure 7. General circulation pattern in the North Sea, image taken from¹. The width of the arrows is a broad indication for the volume of the currents.

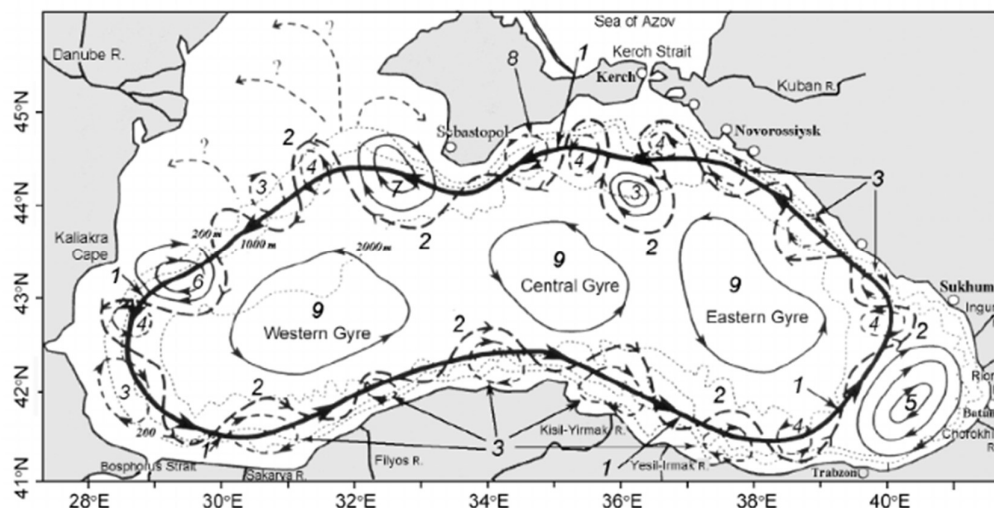


Figure 8. General circulation pattern in the Black Sea, image taken from Korotenko et al.

Figure 7 shows the system of currents in the North Sea. Grey arrows indicate the inflow from the Atlantic Ocean, black arrows relate to the more superficial currents that bring water back to the ocean. The width of the arrows relates to the volume of the current. PFAS substances from rivers such as the Scheldt and Rhine have been shown to be transported towards Germany and Denmark, likely due to these currents.^{35, 67} Effects like the outflow of PFAS from the North Sea into the Atlantic Ocean and the partitioning between seawater and sediment have not been studied, for as far as we know.

In the Black Sea, a main cyclonic circulation (known as the Rim Current) exists, which is surrounded by smaller vortices (‘coastal eddies’) which flow in the opposite direction. These were considered important for transportation of oil spills from the coastal areas onto the open sea⁶⁸; the same argument might be used for PFAS surfactants since their concentration is also highest at the air-water interface.

The almost complete absence of vertical mixing is a particular feature of the Black Sea. In oceans, vertical mixing is an important driving force for redistribution of PFAS.⁵⁹ Considering the patterns in the Black Sea, it could be imagined that most of the PFAS will remain relatively close to its surface.

5.8.2. Surface enrichment

Sea spray and aerosols play an important role in long-range transportation of PFAS with surfactant properties.⁴⁷ Transport of PFASs from the sea to terrestrial grounds affects the bigger picture: seas and oceans are not only a sink for PFAS but can also act as pathway towards other environmental compartments.

5.8.3. Coastal areas vs mid-ocean

Several papers have reported that concentrations of PFAS in seawater generally decrease with increasing distance to the coast.^{35, 49, 63} This could well be a temporal effect, the high persistence of typical PFAS chemicals would allow further distribution into deeper water and oceans.

5.8.4. Soil

Soil is an important sink for long-chain PFCA, especially if the soil is carbon-rich.^{22, 69} Short-chain PFAS molecules and especially surfactants are more likely to remain in the water phase and end up in surface water or groundwater than fluoropolymers and long-chain PFASs. It has been shown that PFOS and PFOA can migrate with precipitation into underlying aquifer systems, although the topmost few meters of soil typically contains the highest concentration of PFAS.²²

5.8.5. Sediment and suspended particulate matter

Alike in soil, partition coefficients mainly relate to the carbon content of the solid and the molecular structure of the pollutant. In riverine systems, partition of pollutants can take place between water, sediment, and suspended particulate matter. The dynamics of such exchange processes can vary significantly among different PFAS chemicals.

5.8.6. Macro and microplastics

Many plastics derived from fossil feedstocks have a density lower than that of seawater. This causes plastic particles to accumulate preferentially at the sea surface and in ocean gyres. Microplastics were however also shown to be present at high concentrations in deeper water layers.⁷⁰ This effect may also be present for PFAS, which could either become microplastics themselves or be present in or at other plastics that become microplastics. It should be noted that:

- Fluoropolymers such as PTFE, ETFE, and FKM rubbers have significantly higher densities than non-fluorine containing polymers or than seawater, in the range of 1700 – 2200 kg m⁻³.⁷¹ This could increase the sinking velocity compared to other particles of similar size and shape. Studies focusing on PFAS typically analyse low molecular weight PFASs and disregard fluoropolymers, potentially overlooking the deposition of fluoropolymer PFAS at the bottom of seas and oceans.
- Concentrations of PFAAs in the Northern Atlantic Subtropical Gyre were shown to be higher than in surrounding seawater⁶⁶, indicating that there may be similarities between the fate of microplastics and that of PFASs in marine environments.

The input of microplastics input to the Black Sea is known to be dominated by riverine input. The three largest rivers – Danube, Dniepr and Don – are responsible for over 50% of the current microplastics input into the Black Sea.⁷² Considering the limited exchange between the Black Sea and the Mediterranean Sea, together with the fact that eddies are a typical sink for microplastics, one could expect that these eddies are also a sink for certain PFAS. Quantification of the volume of PFAS concerned with this mechanism is yet to be reported.

5.8.7. Biota

Uptake of PFAS into plants happens mostly through the roots and is typically faster with short-chain PFAS.^{37, 73} The application of contaminated sludge as fertilizer ('biosolids') is one of the main drivers for the concentration of PFAS chemicals on agricultural land. Both agricultural soils and the plants on top are currently not considered as a main reservoir for PFAS in the literature. Literature research shows that higher levels of PFAS are typically observed in tissues in species higher in the trophic level, but also that a large bandwidth exists. Figure 9 (adapted from Khan *et al.*⁷⁴) graphically represents this trend.

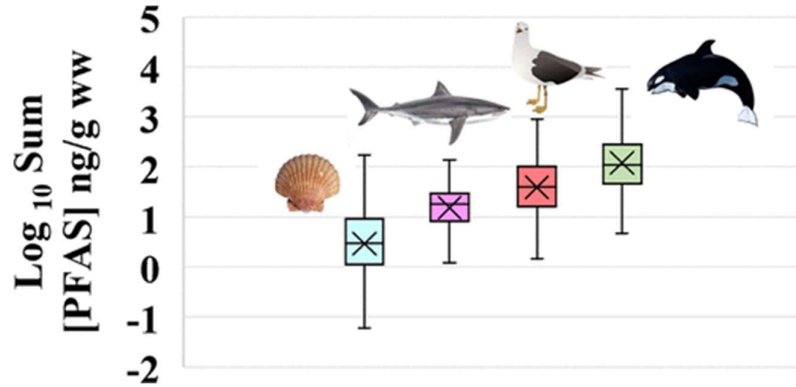


Figure 9. PFAS concentration levels in invertebrates, fish, birds, and mammals; adapted from⁷⁴.

6. Annex II: Analysis of TWP emissions

6.1. Tyre wear particles

Every year, almost 2 billion new vehicle tyres are produced world-wide. At the same time >1 billion tyres reach their end-of-life. During use, millions of TWPs form from each tyre through abrasion of the rubber material in contact with the road surface. Friction between vehicle tyres and the road surface causes tiny particles of the tyre to wear off, forming so-called TWPs. TWPs have many definitions, depending on the perspective they are studied in, but the following may be the most generic and easy to understand: **TWPs are small particles abraded from tyres during driving due to friction between the tyres and the (road) surface**^{75, 76}. In terms of vehicle emissions, TWPs are defined as *non-exhaust particles that are transported to and through the environment primarily through run-off and via air*. It is important to distinguish TWPs from 'tyre particles' generated through shredding, milling and grinding of tyre tread in the laboratory or as part of repurposing of end-of-life tyres^{77, 78}. Other types of microplastics or microparticles may be released from vehicle use on roads, including road wear particles and microplastics from road markings⁶. TWPs and road wear particles are often grouped together and defined as 'tyre and road wear particles (TRWPs).

TWPs have been identified as being 'roundish', 'kidney'-shaped' or elongated⁷⁹. They are chemically and physically affected by the interaction with the road surface and friction energy, changing shapes and inclusion of road wear and mineral particles on the TWP surface^{79, 80}. The most commonly detected size ranges of TWPs are 0.05-100 µm, with most of the particles being below 2.5 µm^{14, 81-83}.

6.2. Tyre and TWP chemical composition

Car tyres contain a complex mixture of components ('ingredients'). The production of car tyres is a multi-step process, with a multitude of materials, chemicals and processes involved. As a basis for the tyre tread, synthetic and natural rubber, as well as a multitude of other chemicals are used. Steel for cords and bead cores, and textiles for reinforcement are also used. The key ingredient groups of tyres and their weight contribution to a new tyre are summarised in Table 1.

Table 1: Main components in a general tyre formulation^{76, 77}

Group	Content	Function	Wt.%
Natural and synthetic rubbers	Poly-butadiene (BR), styrene-butadiene (SBR), neoprene-isoprene, polysulphide	Main components that give elastic properties providing force, friction and comfort.	40-60
Fillers	Carbon black, silicon dioxide, precipitated calcium carbonate (PCC), calcium and aluminium silicates, clay, resins	Strengthens the rubber by improving resistance to strain and wear and tear.	20-35

Oils	Mineral oils	Lubrication.	12-15
Reinforcement materials	Textile (rayon, nylon, polyester and aramid fibres) or metal nets.	Reinforcement to provide strength and resistance.	5-10
Additives	Preservatives, antioxidants, drying agents, plasticisers, processing aids.	Various.	5-10
Vulcanisation agents	ZnO, ZnS, S, Se, Te, thiazoles, organic peroxides, nitro compounds	Transforms rubber to a solid product through vulcanisation (hardening of the rubber) by forming cross-links between polymer chains.	1-2

6.3. Tyre tread composition

Tyre tread composition varies depending on the purpose or intended use of the specific tyre and the area of use, for example summer and winter tyres. For winter tyres, the tread pattern is aligned across the tyre to provide a good grip on snow and ice, while summer tyres have a tread pattern that runs around the tyre to reduce the risk and effect of hydroplaning/aquaplaning. Non-studded winter tyres have a type of tread called sipes, which contributes to providing the best possible grip. To optimise the desired properties for each tyre category, tyre manufacturers use different combinations of compounds in different tyres. In winter tyres, the rubber mixture is softer than that used in summer tyres, to ensure that winter tyres remain soft at low temperatures. In contrast, a harder mix of rubber is used in summer tyres to prevent them from becoming too soft in very warm conditions⁷⁷. An example of the difference in composition of three different types of summer tyres is shown in the table below (reproduced from ⁸⁴).

Table 2: Example of composition of summer tyre samples from different producers (wt.%)⁸⁴

Component	Tyre A	Tyre B	Tyre C
SBR	39.0	-	20.0
NR	-	41.3	45.0
BR	-	22.3	25.0
Carbon black	36.9	23.2	-
Oil	19.5	4.1	-
Other	4.5	9.1	10.0

6.3.1. Rubber

Rubber is an elastic substance either gathered from natural latex through exudation or collected from certain tropical plants ('natural rubber') or derived from petroleum and natural gas ('synthetic rubber'). The elastic and tough properties of rubber make it extremely suited as a main component in vehicle tyres. The rubber used in vehicle tyres is a mixture of different compounds, where the most important are elastomers – large, long-chained molecules that can be stretched and still retain their original shape once tension is removed. These elastomers contribute largely to the strength of rubber and its ability to be stretched repeatedly without tearing or breaking. Synthetic rubber does not have all the properties of natural rubber, and in many cases synthetic rubber cannot substitute natural rubber. For instance, natural rubber provides better resistance to tears and fatigue cracks in tyres. A mixture of natural and synthetic rubber is therefore often used to make vehicle tyres.

6.3.2. Synthetic rubber production

Synthetic rubber is produced via different methods, including polymerisation, mixing and latex treatment. Further chemical steps to modify the rubber polymer may involve treatments such as churning (mastication), extrusion, calendaring, and vulcanisation. The two most important synthetically produced rubber polymers used in vehicle tyres are butadiene rubber (BR, made from 1,3-butadiene monomers) and styrene-butadiene rubber (SBR, made from styrene and butadiene monomers).

6.3.3. Natural rubber production

Natural rubber is flexible, a natural electrical isolator and resistant to many corrosive chemicals. It is obtained from latex, a white fluid consisting of proteins, starch, and alkaloids produced by certain plants. Approximately 20,000 different plants produce latex, but only about 2500 of these produce latex with natural rubber. The main monomer that makes the polymer in natural rubber is *cis*-1,4-polyisoprene. The processing of natural rubber starts with the harvesting of latex from the plant. Acid is added to the latex to cause the material to coagulate from lumps, before water is removed by a mill, simultaneously as the remaining components (lumps) are turned into sheets. After this the sheets undergo pre-vulcanisation through specific chemical reactions at low temperatures. Subsequent heating after this step hardens the rubber and finalises the vulcanisation process.

6.3.4. Chemicals in tyres

Both unreactive chemicals (e.g., polymers, oils, fillers, wax, resins, and antioxidants) and reactive chemicals (e.g., sulphur compounds, retardants, accelerators, activators and glue) are used in the composition of the tyre tread. Most of these reactive chemicals are used in tyre production during the vulcanisation and hardening processes. The tyre tread usually consists of natural rubber and polybutadiene rubber in specific ratios, as these components provide resistance to low heat build-up, as well as resistance to cracks and wear and tear. Natural rubber composites are preferred over conventional metals as they have favourable mechanic and chemical properties when fillers are added⁸⁵⁻⁸⁷.

Table 3: Examples of tyre compound groups, typical chemicals and their function⁷⁷

Compound	Examples of chemicals	Function
Vulcanising agents	Sulphur	Transforms rubber to a solid product through vulcanisation (hardening of the rubber) by forming cross-links between polymer chains.
Activators	ZnO and stearic acid, resins.	Activates hardening during vulcanisation.
Accelerators	Sulphenamides (N-cyclohexyl-2-benzothiazolsulphenamide, CBS)	Speeds up the vulcanisation process.
Inhibitors	Nitrosodiphenylamine, salicylic acid, benzoic acids.	Prevents too rapid/early vulcanisation.
Antioxidants	Trimethyl quinoline (TMQ), amines, phenols, quinoline, phosphites	Prevents deterioration of rubber due to temperature or oxygen.
Antiozonants	Monocrystalline wax and chemical antiozonants. Phenylenediamines (DPPD), Paraphenylenediamines (PPDA)	Prevents weathering caused by exposure to ozone.
Peptisation agents	Zinc salt of pentachlorophenol	Accelerates the churning process (when viscosity is reduced to aid the mixture).
Softeners	Aromatic petroleum process oils (containing polycyclic aromatic hydrocarbons; PAHs), MES-oils (mild extracted solvate oil), rapeseed oil and resins.	Softens and aids the process by reducing viscosity during processing
Other process aids	Rosin, synthetic resins, process oils, pine tar, fatty acids, esters of fatty acids, low molecular weight resins.	Aids the mixing and processing.

Müller *et al*⁸⁸ compiled a list of 792 substances known to be used in car tyre formulations or previously detected in car tyre particles. The list included 163 vulcanisation accelerators, 10 vulcanisation activators, 15 vulcanisation agents, 14 vulcanisation retarders, 111 antioxidants and antiozonants, 91 polymerisation agents, 80 plasticiser, 46 other protectants, 53 decomposition products, 40 adhesion agents, 23 nitrosamine

compounds, 20 reaction products, 18 mastication agents, 17 blowing agents and 91 other agents.

6.3.5. Vulcanisation and the chemicals involved

During tyre production, vulcanisation occurs after 'building' the tyre and assembling the structure. Vulcanisation is a chemical reaction discovered in the first half of the 19th century. It involves a reaction between elementary sulphur and diene rubber; the rubber is mixed with activators (inorganic oxides), accelerators (such as sulphenamides), coactivators (fatty acids) and sulphur at high temperatures. Tensile strength and resistance to weathering is increased by cross-links between long rubber molecules. Cross-links between unsaturated rubber are initiated by vulcanisation using sulphur, the most widely used vulcanising agent. Using sulphur alone causes slow reaction rates and results in the rubber being susceptible to corrosion. To counter these negative effects, an accelerator is used that becomes a part of the rubber compound in the end²¹. Zinc oxide (ZnO) is often added in vulcanisation processes as an activator. It enhances the curing process and increase the density of cross-links between rubber composites. Quinones, amines, benzothiazoles, sulphenamides, thiurames and dithiocarbamates are among the most commonly used accelerators. Mercaptobenzothiazole (MBT), *N*-cyclohexyl-2-benzothiazole sulphonamide (CBS) and tetramethyl thiuram disulfide (TMTD) are examples of such accelerators^{89, 90}.

6.4. Emissions of TWPs

There is limited available data on TWP emissions from direct measurements of environmental compartments⁷⁵. Emissions are either estimated based on material flow analysis (MFA), applying the expected mass loss of tyres over their lifespan, or from the limited available data on TWP emissions from controlled road simulations^{75, 82}. Emission factors of 30-214 mg/km per passenger car are typically reported^{14, 75}. Release per km per vehicle type is reported to decrease in the order lorry > truck > bus > van > passenger car > motorcycle > moped, i.e. increasing with increasing vehicle weight¹⁴. Total TWP emissions from a few western European countries have been ranked in the following order: Germany > UK > Italy > Sweden > Netherlands > Norway > Denmark, with total emissions ranging from 6.7 (Denmark) to 92.6 (Germany) kTonnes/year¹⁴.

In addition to the vehicle tyre composition and environmental temperature in which it is being used, factors such as tyre dimensions, strain, tyre pressure, wheel adjustment, speed, driving behaviour and the properties of the road surface will all influence the wear of tyres (e.g., rate, particle type emitted). Tyres with air pressures that are lower than recommended will cause internal heat development and increase the damage, while simulations/modelling have shown that higher pressures reduce the wear. In general, the wrong pressure will decrease the lifespan of the tyre, as the tyre is worn down irregularly and thus more rapidly⁷⁷.

6.5. Transport and accumulation of TWPs and TWCs in the environment

Environmental monitoring data for TWPs is limited compared to other types of microplastics and chemical pollutants, mainly due to analytical challenges related to quantification. Only in recent years have methods that directly identify TWPs based on spectroscopic or mass spectrometry-based identification of NR/SBR been developed and reported^{79, 81, 91}. Earlier works have typically used the elemental composition fingerprint, focusing on the large content of Zn and sometimes sulphur or organic carbon, to distinguish 'TWP' contribution to particle loads⁹²⁻⁹⁷. Even today, there are challenges with the identification of TWPs in environmental matrices (waters, soils, sediments, biota), as rubber marker compounds are non-specific to vehicle tyres and are also often found in analytically challenging low concentrations^{80, 98-100}. Soils located within a few meters of the roadside are the main sink of TWPs, followed by surface waters and soil at greater distances^{78, 101, 102}. TWPs smaller than 100 µm (i.e. the majority of TWP emissions) are generally more prone to longer range transport, while small TWPs and mobile TWCs may also leach by rain and into groundwater and other receiving waters^{83, 103-105}. TWPs make up a significant fraction of airborne particulate matter in urban areas, mostly in the smaller (<2.5 µm) fractions^{93, 95, 96}. TWPs also make up a significant fraction of road dust^{92, 94}, making their way into street run-off⁸¹ and into WWTPs¹⁰⁶. Similarly, coastal towns and cities can represent major point sources of direct emissions of TWPs and TWCs to the marine environment, as well as their further transport within the marine ecosystem. However, there are very limited studies looking at direct TWP and TWC emissions to the marine environment, which represents a significant knowledge gap regarding their current exposure levels and potential for impacts. Both tyre tread and TWPs are denser than fresh and seawater, meaning they will mostly sink and accumulate in sediments⁷⁷. It should be noted that the small size of many TWPs (0.05-100 µm) means that sinking rates can be quite long as friction processes become more dominant for particles in water in this size range.

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