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Test and development of a new model for the dispersion and impact assessment of PUR foams in alpine environment

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Alla mia famiglia: grazie al loro sostegno e al loro incoraggiamento oggi sono riuscita a raggiungere questo traguardo.

ABSTRACT

This master's thesis presents the design, implementation, and evaluation of a dispersion model tailored for assessing the environmental impact of *polyurethane foams* in alpine environment.

Polyurethane foams, defined also as *PUR*, are widely used in various applications, ranging from insulation to packaging, yet their environmental footprint remains a concern, especially in sensitive mountain ecosystems.

The aim of this project is to focus on the dispersion of this kind of organic polymer as a consequence of its usage in the sole of trekking shoes.
The proposed model integrates data on foam production, usage, and disposal, accounting for the unique characteristics of alpine environments, such as temperature fluctuations, altitude effects, and ecosystem vulnerabilities.

Through a comprehensive life cycle assessment (*LCA*) framework, the model evaluates the emissions, and potential ecological consequences associated with *polyurethane foam* utilization across its entire life cycle. By simulating dispersion patterns and environmental interactions specific to alpine settings, but also associated to other different morphologies, this research aims to provide stakeholders with valuable insights into the sustainability implications of *polyurethane foam* usage in mountainous regions.

The findings contribute to the advancement of *LCA* methodologies tailored for complex environmental contexts, facilitating informed decision - making towards more environmentally responsible material choices in alpine environments.

RIASSUNTO ESTESO

La dispersione di plastica nell'ambiente è, al giorno d'oggi, una delle sfide ambientali più urgenti e complesse. Ogni anno, *milioni di tonnellate* di plastica vengono disperse negli ecosistemi terrestri e marini, causando danni a lungo termine a flora, fauna e persino alla salute umana. La plastica ha un'elevata resistenza alla degradazione, ciò significa che, una volta rilasciata nell'ambiente, può persistere per decenni o addirittura secoli. In particolare, i materiali plastici utilizzati per l'imballaggio e i componenti industriali, come quelli nelle suole delle scarpe da trekking, rappresentano una fonte rilevante di inquinamento da micro e macro-plastiche.

Il seguente studio si focalizza sull'analisi della dispersione di poliuretano (*PUR*) in forma di particolato, materiale che viene più ampiamente utilizzato negli ultimi anni anche nelle suole delle scarpe da trekking.

L'obiettivo principale di questo lavoro è lo sviluppo e la validazione di un modello innovativo per la valutazione della dispersione delle schiume poliuretaniche nell'ambiente alpino, il quale deve essere concorde e rispettare le linee guida di *ARPA*. L'attenzione è rivolta in particolare alla fase di utilizzo delle suole, durante la quale vengono rilasciate microplastiche che si disperdono nel suolo, nelle acque superficiali e nell'atmosfera. Il modello proposto tiene conto delle caratteristiche uniche degli ecosistemi montani, come l'altitudine, le variazioni climatiche stagionali e la topografia complessa, che possono influenzare notevolmente i percorsi di trasporto e l'accumulo di microplastiche.

Attraverso un'analisi del ciclo di vita (*LCA*), viene valutato quindi l'intero ciclo di vita delle suole, dall'estrazione delle materie prime fino allo smaltimento finale, inclusa la fase di utilizzo. La metodologia *LCA* fornisce una valutazione quantitativa dei carichi ambientali associati alla produzione, all'utilizzo e alla dispersione delle schiume poliuretaniche, fornendo i dati necessari per identificare i principali punti critici e le potenziali aree di intervento per mitigare gli impatti ambientali.

Il modello di dispersione sviluppato integra diversi fattori ambientali e operativi per simulare il trasporto e l'accumulo di particelle di poliuretano, valutandone la dispersione anche in funzione della durata di utilizzo, del tipo di terreno e delle condizioni atmosferiche. I risultati mostrano che una percentuale significativa di particelle di poliuretano può essere trasportata su lunghe distanze attraverso l'acqua piovana, il vento e i corsi d'acqua, raggiungendo così il mare.

Il modello considera anche le diverse vie di rilascio delle microplastiche: una parte di esse viene direttamente rilasciata nel suolo durante l'uso delle scarpe, mentre una frazione significativa viene dispersa nell'atmosfera e può successivamente depositarsi in corpi idrici o su superfici vegetali. Si è inoltre osservato che le microplastiche con un diametro inferiore a *10 micrometri* hanno una maggiore probabilità di essere trasportate nell'aria e successivamente depositate nel suolo o nell'acqua, aumentando il rischio di inquinamento diffuso.

Il modello ha evidenziato che l'inquinamento da microplastiche durante la fase di utilizzo rappresenta una sfida critica. Le microplastiche, una volta rilasciate, possono rimanere nell'ambiente per anni, causando potenziali danni agli ecosistemi e alla biodiversità.

I risultati di questo studio forniscono un contributo significativo alla comprensione della dispersione e dell'impatto delle microplastiche in ambienti alpini, offrendo informazioni preziose per lo sviluppo di politiche e strategie di mitigazione. La modellazione della dispersione delle particelle di poliuretano in diversi scenari ambientali rappresenta un passo importante verso una maggiore consapevolezza delle implicazioni ambientali legate all'uso di materiali plastici in ecosistemi delicati.

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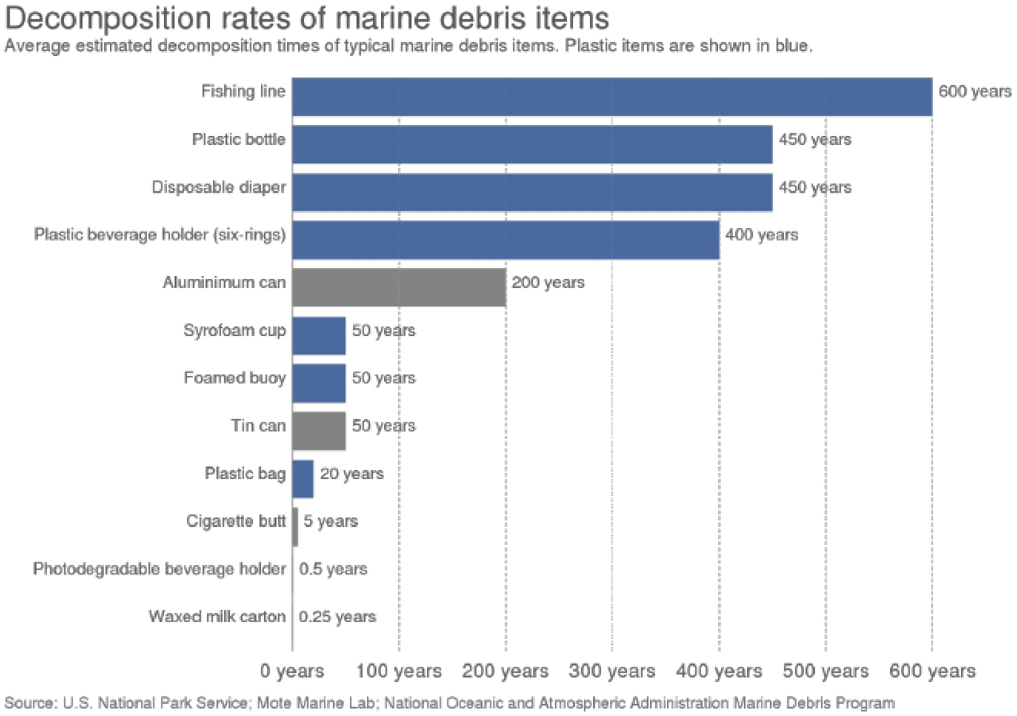
Chapter 1

Microplastics

1.1 Introduction

We often hear about microplastics, usually in reference to seas and oceans. But what exactly are microplastics?

Plastic pollution refers to the dispersion and accumulation of plastic materials in the environment, resulting in serious consequences for wildlife habitats, ecosystems, and even humans. The severity of this issue stems from the global plastic economy, its widespread use, and the material's high persistence over time.



Source: U.S. National Park Service; Mote Marine Lab; National Oceanic and Atmospheric Administration Marine Debris Program

Figure 1.1: Decomposition rates of marine debris items over years, US National Park Service, 12th February 2020

Plastic pollution represents one of the most serious and pressing environmental problems of our time, with widespread impacts on terrestrial, aquatic, and marine ecosystems from a global perspective. This type of pollution results from the accumulation of plastic products and waste which are not properly managed or recycled. According to the *OECD*[1], an international organization for cooperation and development based in *Paris*, less than *10%* of the plastic produced in the worldwide is recycled. The versatility and durability of plastic, which have made it extremely popular in almost every aspect of modern life, paradoxically contributes to the severity of the problem when these materials become waste.

The statistics on plastic pollution are alarming: every year, *millions of tons o*f plastic end up in the oceans, causing the death of *millions* of marine animals due to ingestion or entanglement. Microplastics, fragments of plastic less than *5 millimeters* in size, have been found in almost every corner of the planet, from the *Arctic* to the ocean depths, and even in drinking water and the human food chain, with consequences still not fully understood.

Since *1950*, plastic production has grown exponentially, and it is projected to increase further. Plastic production has doubled in the last *20 years*, now exceeding *300 million tons annually*, with a significant percentage intended for single use. These products, often used for just a few minutes, can persist in the environment for *hundreds of years*, slowly breaking down into smaller particles without ever fully degrading.

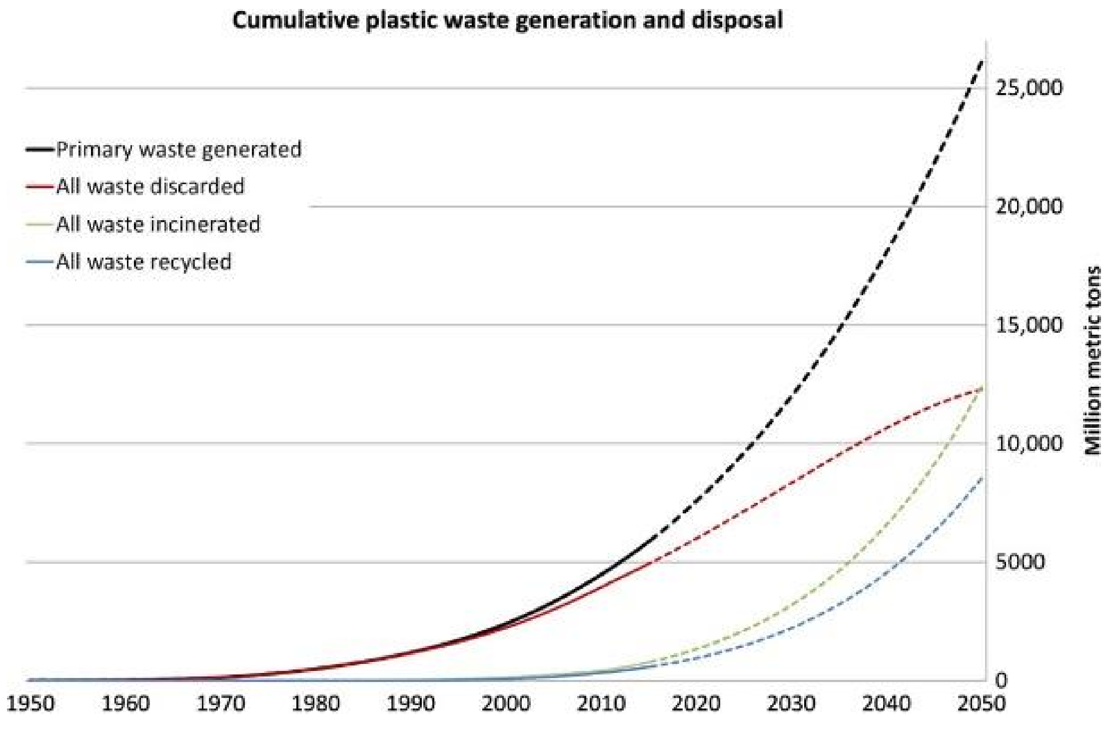


Figure 1.2: Cumulative plastic waste generation over years

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[1] OECD: Organization for Economic Co-operation and Development

Plastic waste management varies significantly around the world, with some countries having implemented efficient recycling and waste management systems, while others rely on open landfills or, even worse, uncontrolled disposal into the environment. Even when plastic is collected for recycling, only a small percentage is transformed into new products due to the technical and economic challenges associated with the recycling process.

1.2 Plastic pollution

Plastic pollution is a complex problem that reflects the challenges of environmental sustainability in the *modern era*. Addressing it requires a significant shift in how we produce, use, and perceive plastic, moving towards a future where the health of the environment and the wellbeing of future generations are central to our decision making.

Solutions to plastic pollution exist, but they require a comprehensive and multidisciplinary approach. This includes reducing the production and consumption of *single – use plastics*, improving waste management infrastructure, innovative material design and recycling processes, and increasing public awareness about the consequences of plastic pollution. Furthermore, more stringent policies and regulations are essential to steering industrial production towards more sustainable materials and promoting responsible consumer behavior.

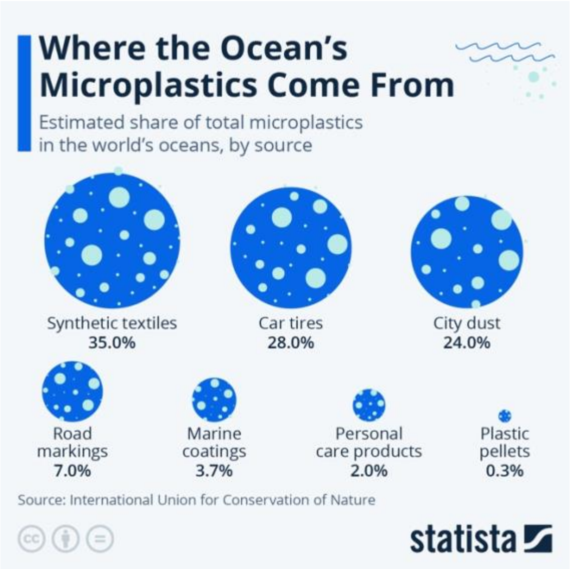
Recently, particular attention has been paid to *microplastics*: fragments of organic plastic material smaller than *5 millimeters*. This definition, widely accepted by researchers and environmental institutions, encompasses a variety of particles with different shapes, sizes, colors, and chemical compositions. Microplastics can result from the breakdown of larger pieces of plastic following exposure to environmental factors such as sunlight, mechanical wear, and biological processes, or they can be directly produced at these small sizes for specific uses, such as microgranules found in some cosmetics, cleaning products, and paints.

Microplastics represent a significant environmental challenge due to their persistence in the environment and their ability to be transported long distances via waterways and the atmosphere. Their small size makes them easily ingestible by a wide range of organisms, with potentially harmful effects on ecosystem and human health.

Growing concern about the *environmental impact* of microplastics has led to an increase in scientific research and regulatory initiatives aimed at reducing their presence in the environment.
Based on their origin, microplastics are categorized into *two* main types: primary microplastics and secondary microplastics. *Primary microplastics* are released directly into the environment in the form of particles and represent *15-31%* of all microplastics. They often result from tire wear on roads or from microplastics intentionally added to cosmetics.
Secondary microplastics, on the other hand, are produced from the degradation of larger plastic objects and represent approximately *68 – 81%* of the microplastics present in the marine environment.

The amount of microplastics in marine environments is increasing, and these can be ingested by marine organisms, eventually making their way to humans through the food chain. Microplastics can end up in seas and lakes through several mechanisms:

- *Wastewater discharges*: from homes, industries, and water treatment plants. If water is not adequately treated, microplastics can end up directly in the surrounding water basins.
- *Direct release*: through the usage of products which contain it, such as cosmetics, detergents and so on.
- *Degradation of larger waste*: these can undergo fragmentation processes following exposure to the sunlight, the mechanical action of water or deterioration, causing serious damage to the ecosystem.
- *Runoff or rainwater runoff*: microplastics present on roads can be transported away thanks to the rainwater, reaching the drainage systems which, in turn, reach rivers, lakes or oceans.


Where the Ocean's Microplastics Come From

Estimated share of total microplastics in the world's oceans, by source

Source: International Union for Conservation of Nature

Figure 1.3: Origin of microplastics, International Union for Conservation of Nature

Once microplastics enter seas and lakes, they accumulate in the aquatic ecosystem. Marine organisms not only ingest them, but they can also absorb toxic chemicals released by the plastic degradation contained in the water. In addition to direct effects on marine organisms, impacts on aquatic ecosystems are also observed.

Among the impacts on the marine environment, we find:

- *Ingestion and Accumulation*: marine organisms can ingest microplastics directly from the water or through the food chain. Once ingested, these particles can accumulate in tissues, potentially causing physical injuries, digestive obstructions, reduced nutrient intake, and alterations in feeding behavior and reproduction.
- *Vectors of Contaminants*: microplastics can absorb and carry environmental contaminants, such as *PCBs*[2], heavy metals, and other persistent organic compounds, which can then be released into the organisms that ingest them, increasing the risk of toxicity.
- *Altered Habitats*: the accumulation of microplastics can alter the physical characteristics of marine habitats, such as the seabed and beaches, affecting the flora and fauna that depend on these environments.
- *Impacts on Human Health*: through the consumption of seafood and fish that have ingested microplastics, these contaminants can enter the human food chain, with potential health risks that are not yet fully understood.

Managing microplastic pollution in marine environments presents considerable challenges, mainly due to the vastness and complexity of the oceans, the persistence of plastics in the environment, and the continuous production and use of plastic materials in daily life. However, various solutions have been proposed and, in some cases, implemented:

- *Source Reduction*: limit the production and use of products containing microplastics, such as microbeads in cosmetics, and promote sustainable alternatives.
- *Waste Management Improvement*: optimize collection, recycling, and disposal systems to reduce the amount of plastic reaching the marine environment.
- *Cleanup and Remediation*: develop and implement technologies to remove microplastics from the water, especially in coastal areas and estuaries.

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[2] PCBs: polychlorinated biphenyls

- *Education and Awareness*: increase public awareness of the consequences of microplastic pollution and encourage responsible behavior.

Effectively addressing microplastic pollution requires a global approach involving governments, industries, scientific communities, and the public, working together to reduce the introduction of new microplastics into marine environments and mitigate the impacts of those already present.

1.3 Diffusion of microplastics

It is known that microplastics can diffuse in the marine environment in several ways. One of the most significant is through the food chain.
In fact, *plankton*, which forms the base of the marine food chain, can ingest microplastics, influencing the entire food chain and the availability of food for all animals. Consequently, the photosynthesis of aquatic plants also suffers harmful effects, impacting microbial communities. The entire ecosystem, along with its biodiversity and the functionality of aquatic habitats, is therefore affected in a cascading manner by the phenomenon of microplastics.

A study conducted in the *North Pacific* found plastic particles in the stomachs of *8* out of *11* seabird species caught as bycatch[3]. The list of affected species indicates that marine debris is impacting a significant number of species. It affects at least *267* species worldwide, including *86%* of all sea turtle species, *44%* of all seabird species, and *43%* of all marine mammal species.

The problem may be greatly underestimated, as most victims are likely to remain hidden in large areas of the ocean, either sinking or being consumed by predators.

There is also a potential danger to marine ecosystems from the accumulation of plastic debris on the seabed. According to *Kanehiro et al., 1995*, plastic made up *80-85%* of the seafloor debris in *Tokyo Bay*, an impressive figure considering that most plastic debris float. The accumulation of such debris can inhibit the exchange of gases between the overlying waters and the interstitial waters of the

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[3] Bycatch: unintended catch

sediments, leading to hypoxia[4] or anoxia[5] in the benthos[6]. This can interfere with the normal functioning of the ecosystem and alter the composition of life on the seafloor. Furthermore, like pelagic organisms, benthic biota is also at risk of entanglement and ingestion.

Microplastics are not biodegradable, and for this reason, once present in the environment, they accumulate and persist. In the oceans alone, it is estimated that annual pollution from plastics and microplastics ranges between *4* and *14 million tons*. In *2018*, microplastics were found in *114* different aquatic species, particularly in the digestive tracts and tissues of many invertebrates that inhabit our seas, including crustaceans and crabs. Fish and birds are especially prone to ingesting microplastics, which can be mistaken for food. In fact, microplastics are suspected to have entered marine food chains, from *zooplankton* to small fish to large marine predators.

1.4 MariLCA project

A study analyzing the *LCA* impact in marine environments on microplastics is *MariLCA*: a project aimed at integrating the potential environmental impacts of marine waste, particularly plastic, into *LCA* results. The project will be carried out in *three* phases from *2019* to *2025*:

- *Phase 1* provides an initial document that allows for the development of various impact pathways associated with marine waste and identifies any gaps (*2019*).
- *Phase 2* coordinates and initiates different research projects aimed at filling the identified gaps and serves as a central scientific reference on the topic to avoid overlaps (*2019 – 2022*).
- *Phase 3* focuses on building consensus by providing harmonized, consensus – based impact pathways and methods that address the impacts of plastic waste in *LCA*.

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[4] Hypoxia: oxygen deficiency

[5] Anoxia: total lack of oxygen

[6] Benthos: ecological category that includes aquatic organisms, both freshwater and marine, that live in close contact with the bottom or are fixed to solid substrates

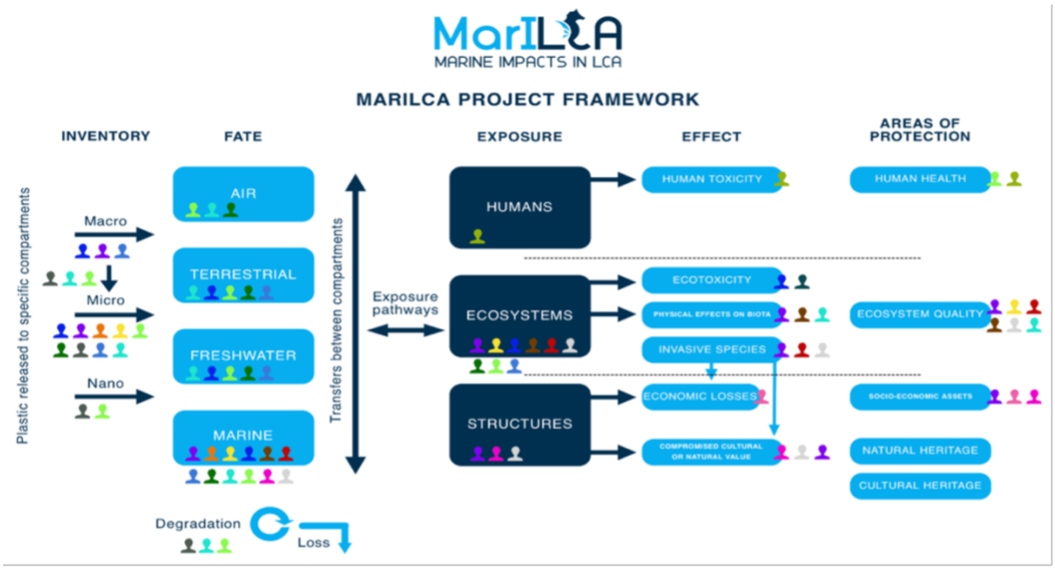

Figure 1.4: MariLCA project framework

The project specifically explores how these small plastic fragments, which are persistent in the environment, influence marine ecosystems throughout their "*life cycle*".
It aims to quantify the release using various methodologies, assess exposure and impacts (developing models to evaluate these in marine ecosystems), and provide tools and guidelines for assessing and managing the risks associated with microplastics, along with sustainability criteria.

Like any project, it is possible to individuate different pros and cons related to this project. As concern pros:

- *Enhanced Environmental Knowledge*: it provides a detailed understanding of the impact of microplastics on marine ecosystems, contributing to scientific research and public awareness.
- *Tools for Policy Decision-Making*: it offers stakeholders, including policymakers and industries, data-driven tools to make informed decisions regarding microplastic management.
- *Promotion of Sustainability*: it encourages the development and adoption of more sustainable practices and products, reducing reliance on single-use plastics and improving waste management.
- *Methodological Innovation*: it develops new *LCA* methodologies that can be applied to other pollutants and environmental issues, broadening the field of environmental analysis.
- *Long - Term Impact*: it contributes to mitigating the long – term effects of microplastics on ocean health, marine biodiversity, and consequently human health.

As regards cons, instead:

- *Complexity and Costs*: the research and development of *LCA* methods specific to microplastics can be complex and costly, requiring significant investments in time and resources.
- *Challenges in Data Collection*: obtaining accurate and comprehensive data on the emission and spread of microplastics can be difficult due to their pervasiveness and the variety of sources. All studies on microplastics emphasize that data collection is extremely challenging, as we are dealing with particles measuring just a few microns in diameter.
- *Limitations of the LCA Model*: despite being a powerful tool, it may still have limitations in capturing all environmental impacts, especially indirect or long – term ones.
- *Possible Conflicts of Interest*: industries involved in plastic production may oppose or attempt to influence research outcomes, hindering mitigation efforts.
- *Implementation of Recommendations*: even with clear and reliable guidelines, implementing recommendations to reduce the impact of microplastics requires political will and adoption by industries, which can be slow or face resistance.

Microplastics were also found in some soil particles, which may have been transported to the ocean following dispersion thanks to the rivers. In this regard, reference is made to a study called "*GripAlp: high performance soles for the alpine environment*".

1.5 GripAlp project

In the *Alpine environment*, shoes, whose sole is made of plastic, are used: during the wear of the shoes, the sole wears out producing microplastics, *i.e.*, plastics whose diameter is in the order of *millimeters* up to the order of *micrometers*. Microplastic pollution, caused by very small waste, infiltrates the ground causing serious damages to the ecosystem/environment and also to the human health.

Polyurethane soles, instead of vulcanized rubber ones, were therefore studied and resistance and abrasion tests have been carried out.
Vibram TRONT Fourà vulcanized rubber was analyzed from the point of view of *LCA* from the supply of raw materials to post – treatment, then to stabilization.

Polyurethane soles have a different production process via injection molding with reaction: *polyol* and *isocyanate* are used for the mold and heated up to *50°C*, even in the presence of catalysts. What makes the production of *polyurethane* vary is the origin of the *polyol* (natural or fossil?), the *isocyanate/polyol* ratio and the addition of fillers, including zirconia, cellulose fibers, microcrystalline cellulose.

Two functional units were used for the study: *one* on a mass basis and *the other one* as the mass needed for the sole production for a duration of *10* years.

The product system to which it is referred is the "*cradle to grave*" one, applying a "*cut-off*[7]" to the transportation from the production plant to the customer. The function is to constitute a material that can be used in the sole of the trekking shoe, while the declared unit for the *LCA* is *1 kg*, sole number *42 EU* for a duration of *10* years. The *end – of – life* phase is not included in the analysis. For this purpose, *six* impact categories were considered.

The first formulation used in the study is the fossil one, with the addition of additives, and the *isocyanate/polyol* ratio is different.
For the *bio – based* formulation, the *polyol* is of *bio – based* origin, while the *isocyanate* is of fossil origin (only the unfilled formulations were produced during the study).
The recycled *polyol* formulation, instead, involves the combination of *polyol* from fossil sources and recycled *polyol*, together with isocyanate from fossil sources[8].

The study revealed that the more the *isocyanate/polyol* ratio increases, the more the environmental impact decreases: this is due to *isocyanate* production, which has a greater impact than the production of *polyol*. *PUR*, compared to vulcanized rubber, has the potential to reduce the environmental impact for *three* impact categories analyzed: *GWP*[9]*, abiotic depletion potential – elements* and *fossil fuels*. The *three* most critical impact categories are: *acidification potential*, *photochemical oxidant formation potential* and *eutrophication potential*.

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[7] "Cut – off" method : material flows which contribute to less than *1%* of the inputs by mass may not be considered
[8] The isocyanate used is virgin
[9] GWP: Global Warming Potential

A first conclusion deriving from the study is that the usage of *polyurethane* compared to *vulcanized rubber* presents a lower reduction in volume, which means a longer sole lifespan and therefore fewer soles used. At this point, environmental impacts improve on *five* categories out of *six* analyzed.

After the release of microplastics, they are transferred through *three* pathways:

- For microplastics with a diameter below *10 μm*, the hypothesis is that they are dispersed in the air. After a certain amount of time, these tend to settle: *3%* in fresh water, *97%* in other terrestrial environments.
- For microplastics above *10 μm*, *83%* is deposited in the soil and remains there.
- Again, for microplastics above *10 μm*, *90%* is deposited in freshwater, while the remaining *10%* reaches the ocean.

Basing the study on the functional unit of *1 kg*, decreasing *isocyanate/polyol* ratio, also the environmental impact decreases due to *isocyanate*, which is more impacting.
In the series without *MEG*[10], formulations with *recycled polyol* allow to reach less environmental impact than the fossil equivalents; with the addition of *MEG*, the improvements previously reached vanish.

For the second functional unit, however, the various filled formulations appear to have a lower environmental impact compared to the unfilled formulations and it can be noticed that the volumetric loss is considerably lower for *PUR* compared to soles with vulcanized rubber. Regarding potential environmental impacts, recycled formulations are better than fossil ones, but they still show worse environmental impacts than vulcanized rubber due to the high abrasion rate.

Another characteristic noticed is that for the formulation with a higher *isocyanate/polyol* ratio there is a lower environmental impact if *recycled polyol* is used compared to fossil formulations. For a lower ratio, instead, there are no improvements in environmental impacts.
The one with the least impact is the formulation with a ratio of *0.6*, with *4%* cellulose fibers.

From the study, it was possible to notice that for the *bio – based* formulation *A* (higher *polyol/isocyanate* ratio), the release of microplastics is already lower compared to the fossil formulations and therefore it will remain so over the time, with the addition of better biodegradation compared to the fossil formulation.

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[10] MEG: ethylene glycol, additive

For a ratio of *0.6*, however, the *bio – based* formulation releases more microplastics than fossil formulations: only after a *few years*, with biodegradation, there will be fewer microplastics in the soil.

The impact of the choice of electricity is limited and it does not influence the conclusions of the study.

Through the uncertainty analysis with the *Monte Carlo method*[11], it is noted that vulcanized rubber has an impact well outside the confidence interval of *polyurethanes* with regards to *GWP*, *acidification and photochemical oxidant formation potential*, as well as *ADP – fossil fuels and elements*. No differences are noticed in the case of *eutrophication potential*.

In conclusion:

- On a mass basis, formulations with *recycled polyol* make possible to reduce environmental impacts if the *MEG* additive is not used. If *MEG* is added for performance enhancement, the benefit of using this formulation is nullified.
- In the second functional unit (mass of material necessary to produce the number of pairs of *42EU* soles to walk for *10* years), the use of *PUR* is advantageous compared to vulcanized rubber, as the abrasion coefficient of *PUR* compared to rubber is found to be *2 – 2.5* times lower and therefore a longer lifespan is reported. The best *PUR* formulation is the one that has an *isocyanate/polyol* ratio of *0.6*, with *4%* cellulose fibers, allowing a notable reduction of the impact.
- The mass loss associated to abrasion tests was considered as representative of the release of microplastics during the usage phase.

1.6 Effects and dispersion

1.6.1 Effects on human beings

As previously argued, in recent years, microplastic pollution has emerged as one of the major environmental concerns globally. While initial studies focused on the ecological impacts of these persistent particles, research is now extending to their potential effects on human health.

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[11] Monte Carlo method: a broad class of computational algorithm that relies on repeated random sampling to obtain numerical results

Microplastics have entered the human environment through various channels, including the consumption of marine foods, drinking water, and even the air we breathe.

The primary route by which microplastics can enter the human body is through ingestion. Marine foods, such as fish and shellfish, can accumulate microplastics throughout their lives, introducing these particles into the human food chain. Recently, studies have also revealed the presence of microplastics in freshwater products, table salt, beer, and even in agricultural products due to the use of sewage sludge as fertilizer, which may contain microplastics. Furthermore, inhaling air particles containing microplastics represents another route of exposure, particularly in highly polluted environments or during the use of synthetic fabrics.

A recent study, whose article was published on 7*th* *March 2024*, has demonstrated how microplastics can also cause damages and dysfunctions in the cardiovascular system.
A total of *304* patients from the *Cardarelli hospital, Ospedale del Mare* and the *University of Salerno* were enrolled in the study and followed for a total of approximately *35* months. Patients in whom *micro-* and *nano – plastics* have been detected inside the *atheroma*[12] were at higher risk of a primary "end – point" event[13] compared to those in whom micro- and nano – plastics were not detected. The visualization and transmission of the images occurred thanks to the usage of an electron microscope. *MNPs*[14] have been found in several tissues, including placenta, lungs, and spleen, but also in urine and blood. According to the *World Health Organization*, particles larger than *150* µ*m* or *10* µ*m* in diameter are not absorbed by blood and do not penetrate the walls of the arteries. What was discovered instead is that nano – plastics, more than microplastics, could accumulate in sites of atherosclerosis. It is important to underline that exposure levels to *PM2.5* and *PM10* were not considered.
Patients in whom *MNPs* were detected had a higher composite risk of myocardial infarction, stroke, or death for any cause at *34* months of follow – up than those in whom *MNPs* were not detected.

The discovery of microplastics in the human placenta is a topic of growing concern and interest in the scientific community. This phenomenon raises important questions regarding potential fetal exposure to microplastics and their effects on human health.

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[12] Atheroma: plaque made up of fats, proteins and fibrous tissue, which is formed in the walls of the arteries, configuring the picture of atherosclerosis; layers of fibrin can be deposited on the surface of the atheroma, facilitating the formation of thrombi

[13] End – point event: clinical event of major interest, which can cover a vast range of problems; in this case myocardial infarction

[14] MNPs: micro- and nano – plastics

Recent studies have documented the presence of microplastics in the human placenta, suggesting that these particles can cross the placental barrier and reach the fetus during development. However, the scope and impact of this exposure are not yet fully understood.

According to an article published on 12th *December 2020*, the presence of microplastics in the human placenta was proven for the first time thanks to a study carried out in the *Fatebene – fratelli Hospital* in *Rome* and by the *Polytechnic of Marche*.
It has been demonstrated that the immune system recognizes even what is not organic as "*self* ": the study has analyzed the placentas of *6* healthy women, between *18* and *40* years old, dividing the analysis into *5* phases and identifying *12* fragments in the placentas of artificial material, particles between *5* and *10* µ*m*, *i.e.*, as large as a red blood cell or a bacterium (*3* fragments identified as *polypropylene* and *9* of painted synthetic material).
The entry route of microplastics is currently unknown, but it is assumed through the respiratory system or through nutrition and skin absorption of products which contain microplastics. Once in the placenta, microplastics can potentially interact with fetal cells and affect the development and health of the fetus.

However, it is important to underline that the research in this field is still at a preliminary stage and there are many open questions to be addressed.
For example, there is a need to better understand the mechanisms by which microplastics cross the placental barrier and whether there are differences in their distribution and impact depending on the type and size of the particles.
Furthermore, longitudinal studies are needed to evaluate the potential long – term effects of fetal exposure to microplastics on child health and development.

Ultimately, the presence of microplastics in the human placenta raises important questions regarding the protection of maternal and fetal health and it highlights the importance of reducing human exposure to microplastics through prevention measures and reduction of plastic pollution in the environment.

In laboratory tests, microplastics have been shown to cause damages to human cells, including both allergic reactions and cell death, but epidemiological studies have not yet been conducted to document the linkage between exposure to microplastics and the impact on health. However, there are considerable research on the toxins found in plastic materials, as well as on lung diseases, from asthma to the cancer: the "*American Lung Association*" has declared that *COPD*[15] is the fourth leading cause of death in the *United States*.

1.6.2 Ways of diffusion

Microplastic presence and resulting contamination is still poorly evaluated in underground water systems. Most of the time, studies on plastic microparticle pollution focus only on surface ecosystems. As a result, only a few authors have examined microplastic pollution in caves and underground.

Once deposited on the ground, plastic microparticles can be transferred horizontally by surface carriage, or vertically, through *percolation*[16] through soil particles, moving across long distances, passing through unconsolidated sediments, rock pores, or fractures, until they reach an aquifer and accumulate.

Some authors focused on the downward percolation movement of microparticles through soil. Microplastic particles can diffuse downward to deeper layers in a soil profile with percolating water. This migration process is limited and dependent on the size and shape of microplastics as well as the soil grain size and resulting porosity and permeability. Transport downward is easier through cracks, faults, or macropores.

Where the macropores density decreases, the microplastic particles will likely again be blocked in their further *downward leaching* by the porosity characteristics distribution of the matrix. Although migration of microplastic particles to deeper soil layers is relatively limited and deterioration of buried microplastic particles in soils is considered slow, after the natural degradation process and resulting decrease in particle size to the nano plastics category, the transport of the particles to deeper layers and groundwater becomes faster.

Estuarine ecosystems consist of transitional sites between land and oceanic waters. As a result, drastic variation in the water column happens because of the different densities of the water contacts. The mixture and resulting stratification processes between the saline and freshwater could potentially impact the migration of buoyant microplastic particles. Still, the strong tidal currents may impact their residence time and transport processes between high and low tides.

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[15] COPD: chronic obstructive pulmonary disease

[16] Percolation: slow movement of a fluid through a porous media

Once present in estuarine waters, the particles may be dispersed throughout all compartments. Through the saline wedge, low – density plastics generally tend to submerge, while smaller particles are carried by the flow of water and settle where water movements are less intense.

The previous explained study tried to detect a diffusion and accumulation pattern in the varied aquatic ecosystems present on Earth.

On the other hand, the scarcity of data still does not allow for projecting a clear behavior pattern of plastic microparticles. So, more detailed research is necessary for the understanding and possible projection of the dispersion of plastic particles and their deposition rates, in view of the innumerable variables that the environment offers and the specific characteristics of these contaminants. The production of a global database becomes essential for a more effective projection of patterns of different types of microplastics and their respective responses to environmental variants.

A study called "*multiscale dynamics of colloidal deposition and erosion in porous media*" from *Princeton University* has revealed the mechanism by which microplastics are transported for long distances through soil and other porous media, leading to the accumulation of contaminants in sources of food and water.

In this study, the knowledge of the diffusion of microplastics in porous media was recognized as fundamental, noticing that not only the tortuosity of the porous media can alter the transportation of the particles, but also the deposition in the solid matrix, producing coupled dynamics, which are difficult to interpret.

For example, in many cases colloids have been found to enhance the transportation of chemicals through a porous medium, while other studies have reported the opposite, supporting that colloids suppress the transportation by reducing the permeability of the medium. This discrepancy is therefore believed to be established in the flow conditions and in the colloid chemistries studied, which can strongly influence the interactions between the flowing fluid, the particles and the medium.

From this study it has emerged that there is a connection between the pore scale and the macroscopic deposition behavior. While the characteristics of the deposition on the pore scale depend on the interactions between particles and the solid matrix, the macroscopic characteristics of the deposition are tuned by the pressure imposed in a similar way for particles of different surface properties, highlighting the importance of the hydrodynamic interactions related to the transportation and colloidal deposition.

The research group has analyzed *two* types of fluids: viscous and non – viscous, which correspond to the types of microplastics present in the environment. In this regard, the pressure mentioned above is capable of removing any occlusions that may form from the deposit of particles considered. Non–viscous particles tend to get stuck in the narrowest passages anyway, while the viscous ones stick to every surface they encounter. This "*stop and start*" process is new, and it helps to better understand the spread of microplastics.

The objective at this point, knowing the diffusion mechanism of the particles, is to study more in detail how these particles, which highlight the behavior of microplastics, behave by changing the porous medium, the chemistry and the size of the particles.

Chapter 2

LCA inventory

2.1 Introduction to PLP methodology

The *Plastic Leak Project* (*PLP*) provides the first science – based methodology, industry – specific guidance, and metrics to help manage the sustainability by identifying and inventorying plastic leaks along the value chain[17].
The *PLP* guidelines provide companies a robust calculation method for estimating plastic and microplastic losses at the production level.

Every manufacturing company must first identify plastic leaks along the supply chain in or- der to effectively track and address environmental pollution on a global scale.
This methodology enables companies to minimize risk, enhance business resilience, strengthen brand reputation, and explore opportunities for product innovation and supply chain management.

A case study of *Arla Food* highlights this approach: its sustainability strategy begins with defining an effective action plan, starting with an assessment to determine how much plastic is leaking, where it occurs and during which stage of the supply chain. The study found that *4%* of the *100,000* tons of plastic used annually is dispersed into the environment, with *23%* of this dispersed plastic ending up in the oceans and *77%* in other natural ecosystems. The loss occurs primarily at the end-of-life cycle (*96%*), especially in countries like *Nigeria* and *Bangladesh*.

A similar study was conducted for the company "*Sympatex Technologies*", revealing that *122 grams* out of *400 grams* of plastic used are dispersed into the environment, with *5%* reaching the oceans and *95%* affecting terrestrial areas. The study showed that over *99%* of plastic dispersion occurs at the product's *end – of – life stage*.

There are different steps for releasing *micro* and *macro – plastic*.
Between these:

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[17] Value chain: the set of activities and business processes needed to create and sell a product or a service

- *Leakage*: this occurs during transportation, washing, unintentional spillage during production and poor waste management.
- *Transfer*: the main routes through which plastic is released into the environment are wastewater, road runoff, air, uncollected waste, or poorly managed waste.
- *Initial release*: the natural systems into which they are released are ocean, fresh water, soil, terrestrial environment (other than soil), air.
- *Redistribution*: the mechanism of transfer of plastic in the natural environment, from initial release to final release, are transport by river, redistribution from air to fresh water or soil, from soil to fresh water and oceans.
- *Final release*: the natural systems in which dispersed plastic ends up are oceans, fresh water, soils, terrestrial environment.

Plastic is generally produced as pellets, resins, textile fibers and others. The intrinsic properties of plastic, such as *low density* and *high durability* over time, mean that plastic is one of the most used polymers in various everyday applications.

Usually, plastic with a lower molecular weight, *MW*, has lower *GHG*[18] emissions throughout its life cycle than other packaging made of other materials. Thermoplastic materials can be easily recycled and reprocessed making them promising materials in the context of the circular economy.

2.2 The methodology

To stop the leakage of plastic into the environment, it is essential to identify the hotspot where the actual loss occurs. The *PLP* methodology is used for this purpose, which is able to evaluate the actual loss of plastic throughout the product's life cycle, helping to develop a "*close the tap*" strategy.

It is known that plastic re-enters the natural environment in *two ways*: through *visible macro – plastic* or, more commonly, through *invisible microplastic*. In addition to macro – plastics and microplastics, different classes of plastic can be distinguished.

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[18] GHG: Green House Gas

These include:

- *Primary microplastic*: plastic particles lost from the techno – sphere[19] and released into various environments as small particles. Some are added directly as additives in products like cosmetics, while others result from tire abrasion on asphalt.
- *Secondary microplastics*: these are generated by the degradation of larger plastics after exposure to environmental factors.

It is important to note that atmospheric exposure not only degrades macro – plastics into smaller fragments, but also breaks down *primary microplastics* into even smaller particles.

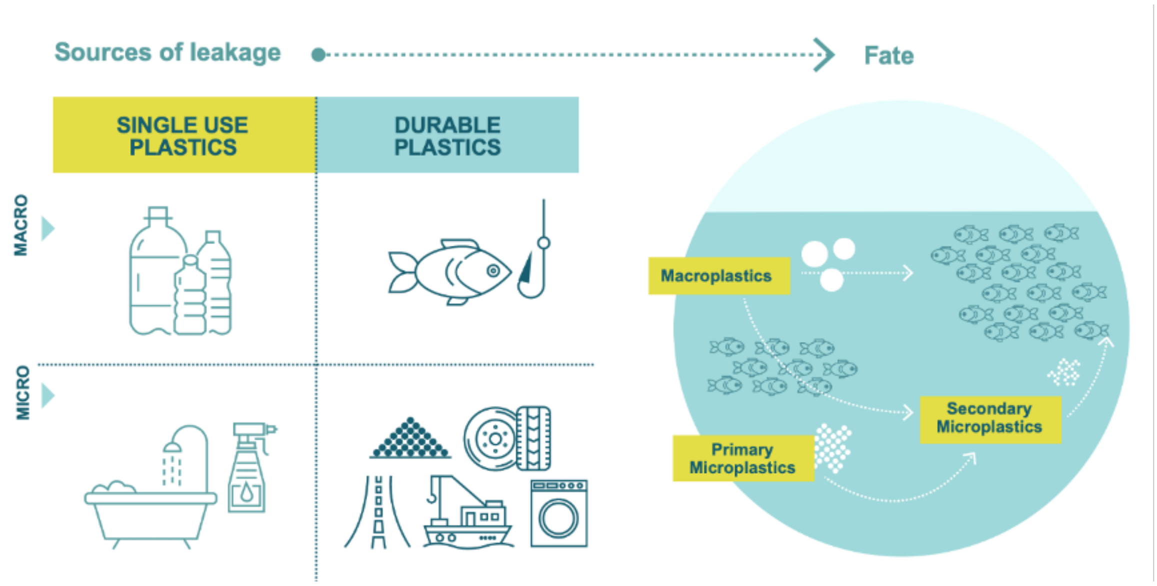

Figure 2.1: Different sources of leakage: macro- and microplastics (Boucher et al., 2019)

Figure 2.1 explains how plastics spread into the environment, and this is summarized below:

- *Poorly managed waste in the coasts (macro – MPW)*: *8 Mt/year*. *Jambeck et al., 2015*, focuses on the amount of plastic dispersed in the environment and generated by coastal populations in *192* countries.
- *Poor waste management in the hinterland (macro)*: *1 Mt/year*. Poorly managed inland (*macro*) plastic waste represents the addition of river (macro) plastic to global plastic losses, which can vary by season and location. *Lebreton et al., 2017*, uses *1 Mt* as a preliminary estimation for the mismanagement of plastic in the hinterland without considering the one produced by the coastal population, to avoid the "*double counting*" phenomenon.

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[19] Techno – sphere: all the artefacts and structures built over time by human, which testify the transformation of the planet by human beings

- *Microplastics*: approximately, *1.5 Mt/year* of plastic enter the marine environment annually as *primary microplastics*. The main sources of primary microplastics include marine coatings, road markings, tire wear, synthetic textile fibers, microspheres from personal care products, and dust from household materials and products containing synthetic polymers. For instance, *Boucher et al., 2017*, estimate that nearly two-thirds (*63%*) of the microplastics released into the oceans come from the abrasion of synthetic fabrics during washing (*35%*) and tire erosion during driving (*28%*). In terms of microplastics released into *European rivers*, *Siegfried et al., 2017*, calculate that tire abrasion accounts for *42%* of the total microplastic load transported from rivers to seas, followed by textiles based on plastic polymers (*29%*), synthetic polymers in household dust (*19%*), and personal care products (*10%*).
- *Fishing* and *aquaculture* are also a source of plastic losses.

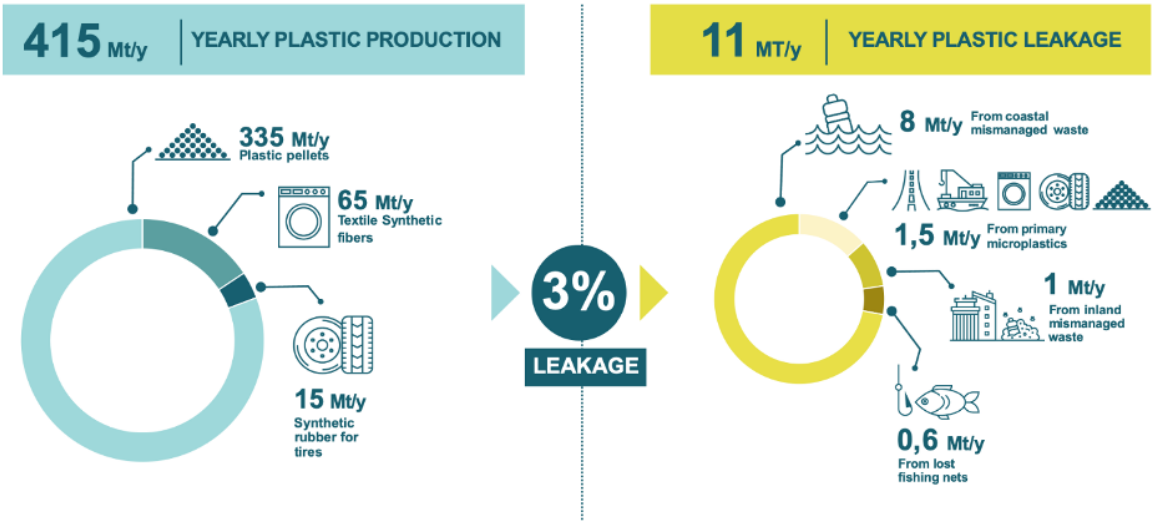

Figure 2.2: Plastic production and plastic leakage by source: current best estimates worldwide (Boucher et al., 2019b)

Currently, there are no precise metrics for evaluating plastic loss into the ocean. To fairly assess the environmental impacts of plastics within a comprehensive environmental framework and avoid trade – offs, life cycle methodologies need to be strengthened through standardized and widely accepted plastic loss accounting.

While no science – based metric yet exists to measure plastic losses, several recently developed methodologies assess the environmental impact of plastic use. These methodologies are classified by:

- *Output metrics*: quantity of plastic used, quantity of plastic released into the environment, etc.
- *Operativity*: actionability, such as differentiating plastics by polymer type and format
- *Purpose*: the focus of the methodology (*e.g.*, business, product life cycle)
- *Maturity level*: based on the year of release.

Additionally, there are initiatives working in collaboration with the *PLP project*, such as *MariLCA* (Marine impacts in *LCA*), which complements the *PLP* and serves as a starting point for assessing the environmental impact of plastic losses.

It is important to note that the *PLP* methodology does not take into account potential impacts on human health or biodiversity as a result of the plastic release into the environment.
In this context, the general term "*leakage*" refers to plastic that leaves the *techno – sphere* and ends up in the natural environment.
Leakage occurs through loss, transfer, and redistribution pathways.

Figure 2.3: Key stages of the plastic leakage modelling | overview

"*Loss*" refers to the amount of plastic that leaves a managed product or waste management system. In other words, it is the fraction of plastic material that detaches from the product during production, use, or transport (in the case of microplastics) or unmanaged waste (in the case of macro – plastics).

Regarding transfer pathways, there are different types that lead from loss to release. In the *PLP methodology*, *six* release routes are identified: *wastewater, road runoff (from tire abrasion), air, uncollected waste, waste mismanagement*, and *direct release routes*.

The initial release compartment refers to the environmental medium where plastic is released, either through a single route or a combination of multiple routes. The following initial release compartments are considered through this methodology:

- *Ocean release*, which represents release into the oceans.
- *Release into flowing water*, which represents release into rivers or lakes.
- *Release into the soil*.
- *Release into the terrestrial environment*, which represents the release into a terrestrial environment other than the soil.

- *Release in the air*.

The *PLP methodology* models *two* redistribution mechanisms:

- *Transport of plastic through rivers*, recognizing that microplastics can be partially transferred to oceans or deposited in river sediments.
- *The redistribution of microplastics emitted from air to running water and soil*, considering that all airborne microplastics eventually settle in either soil or water as their final release compartment.

Figure 2.4 provides a summary of the different distribution routes and release compartments included in the guidelines.

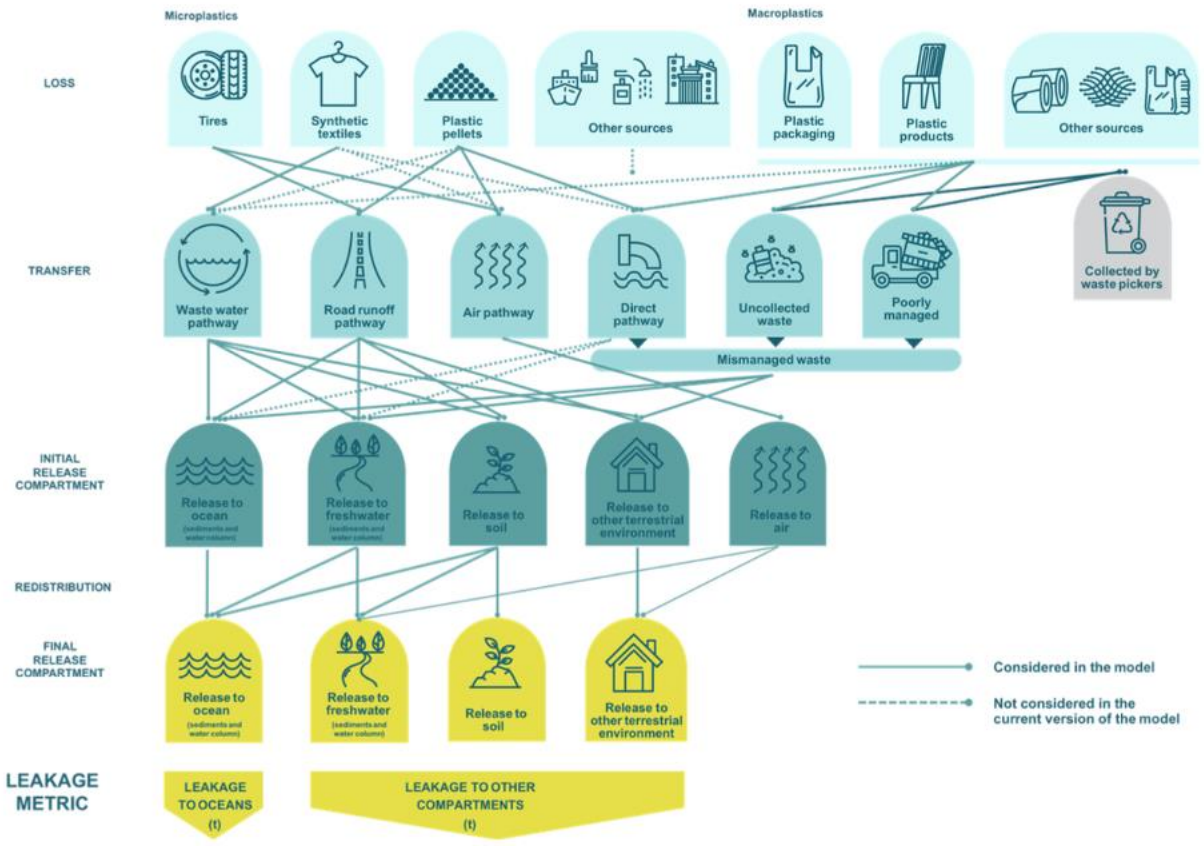

Figure 2.4: key stages of the leakage modelling | detailed view

The fate of plastic involves *three* key elements:

1 *Redistribution of plastic between environmental compartments*.

2 *Fragmentation of macro – plastics into secondary microplastics*: this is not considered in the *PLP methodology* due to a lack of data related on fragmentation rates.

3 *Degradation of plastics*: different polymers have different environmental impacts, depending on the rate of plastic degradation. For example, *1 kg* of plastic with a lifespan of *1 year* cannot be equated to *1 kg* of plastic with a lifespan of *100 years*. This distinction is crucial when comparing biodegradable plastics with conventional plastics, as they have different residence times[20].

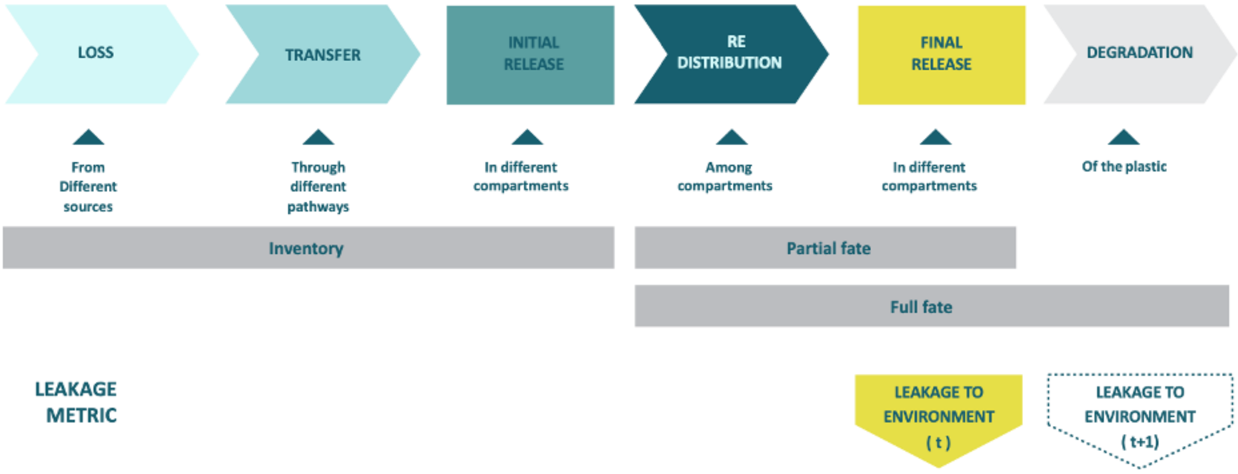

Figure 2.5: key stages of the plastic leakage modelling | fate integration

The measurement of the lifetime of plastic is defined including both the fragmentation of polymers into monomers and the conversion of those monomers into CO_2. In fact, plastic degradation is defined as a chemical change that drastically reduces the polymer's average molecular weight (*Andrady, 2011*). There are *four* mechanisms through which plastic degrades into the environment: *photodegradation* (the sun provides the energy needed to break molecular bonds), *thermo – oxidative degradation* (slow oxidation at moderate temperature breaks the polymer chain), *hydrolytic degradation* (breakdown of polymer chains by the action of water molecules) and *biodegradation by microorganisms* (microorganisms convert low molecular weight carbon chains into CO_2 or corporate them into biomolecules).

Some of these mechanisms may or may not occur simultaneously, depending on the properties of the polymer and environmental compartments in which the plastic is located.

Numerous factors influence the speed and rate of polymer degradation. These factors can be related to the inherent properties of the polymer itself or of the object, as well as environmental conditions.

Different time horizons can be considered in a plastic loss assessment.

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[20] Residence time is defined as the length of time that plastic remains in environmental medium such as soil, air, flowing water or seawater.

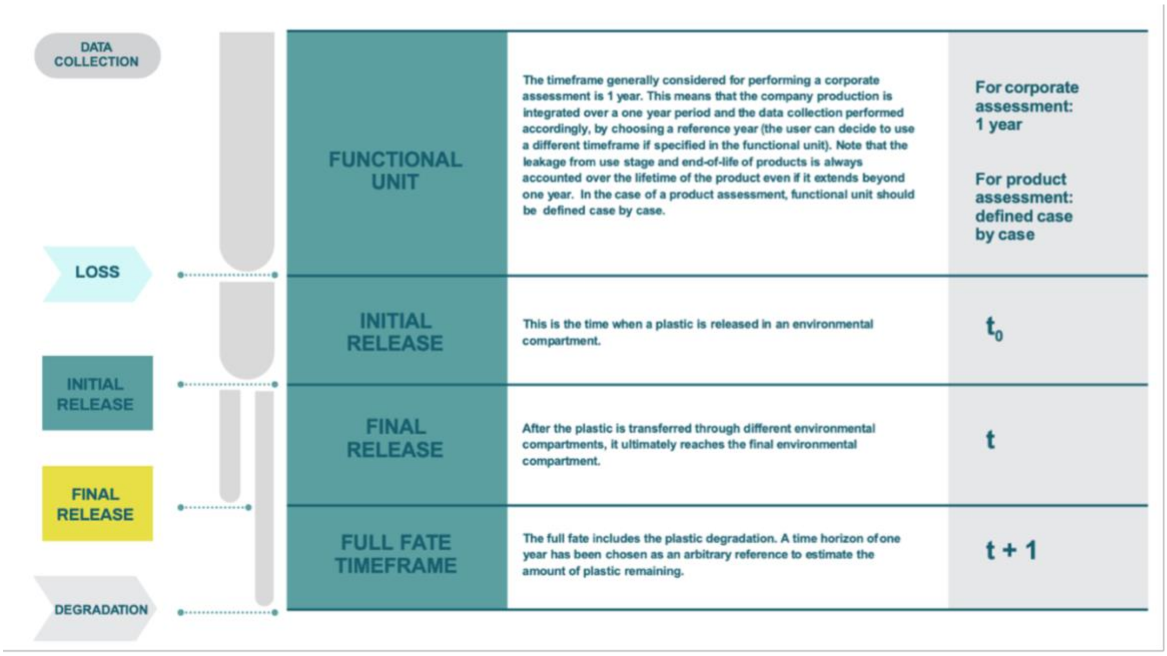
First, the functional unit[21] can be linked to a specific time horizon in business evaluations, such as considering the loss over *1 year*. While this does not have a direct influence on the modeling, it defines how data should be collected.

Additionally, loss, initial release, and final release do not happen simultaneously. Furthermore, the transfer between loss and initial release is not instantaneous. When the transfer occurs and the initial release begins, this is considered as $t_0 = 0$.

Redistribution of plastic between the initial release compartment and the final release compartment may occur over an undefined time horizon considered for this redistribution (t). Although impacts from plastic in various sectors should be integrated over time, but this is beyond the scope of the *PLP methodology*.

In this case, the fate of the plastic includes its complete degradation. A time horizon of *1 year* has been selected as an arbitrary reference point to estimate the amount of plastic remaining after this period. The time horizon for complete degradation is therefore represented as $t + 1$.

In summary, the initial version is represented by t_0 within the framework. The final release occurs after an indefinite time t. The full fate begins after the initial release at time t_0 and is evaluated *1 year* after the final release at time $t + 1$.



FUNCTIONAL UNIT	The timeframe generally considered for performing a corporate assessment is 1 year. This means that the company production is integrated over a one year period and the data collection performed accordingly, by choosing a reference year (the user can decide to use a different timeframe if specified in the functional unit). Note that the leakage from use stage and end-of-life of products is always accounted over the lifetime of the product even if it extends beyond one year. In the case of a product assessment, functional unit should be defined case by case.	For corporate assessment: 1 year For product assessment: defined case by case
INITIAL RELEASE	This is the time when a plastic is released in an environmental compartment.	t_0
FINAL RELEASE	After the plastic is transferred through different environmental compartments, it ultimately reaches the final environmental compartment.	t
FULL FATE TIMEFRAME	The full fate includes the plastic degradation. A time horizon of one year has been chosen as an arbitrary reference to estimate the amount of plastic remaining.	$t + 1$

Figure 2.6: plastic leakage time horizons

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[21] Functional unit describes a quantity of a product or product system based on the performance it delivers in its end – use application

The metric for evaluating plastic leaks takes into account different perspectives to identify hotspots. These hotspots are defined as a country, product, polymer, or chain step that significantly contributes, directly or indirectly, to plastic leakage.

Each perspective contains mandatory and optional elements.

Below are the mandatory ones.

Key results answer the following questions:

- What is the spill about?
- In which environmental compartment?
- Key results include total loss, loss to the ocean and other environmental compartments, with a distinction between *macro*- and *microplastics* as the indicator of loss intensity.

The value chain answers the following questions:

- Where does the loss occur along the chain?
- In which environmental compartment?
- Where are the hotspots?

The country perspective answers the following questions:

- In which country does the loss occur?
- What is the intensity of plastic loss?
- It provides a nation loss hotspot analysis for each final release compartment.

The optional perspective are the following ones:

- The market perspective answers the following questions:
  – Which market is responsible for plastic loss?
  – What is the intensity of plastic loss?
  – Provides insight into the market responsible for the loss.
- The product perspective answers the following questions:
  – Which product is contributing to the loss?
- The polymer perspective answers the following questions:
  – Which polymer contributes to the loss?
  – Only relevant if several polymer types are included.
- The fate perspective answers the following questions:
  – How much plastic remains after a year?

– Relevant if different polymers have different degradation rates.

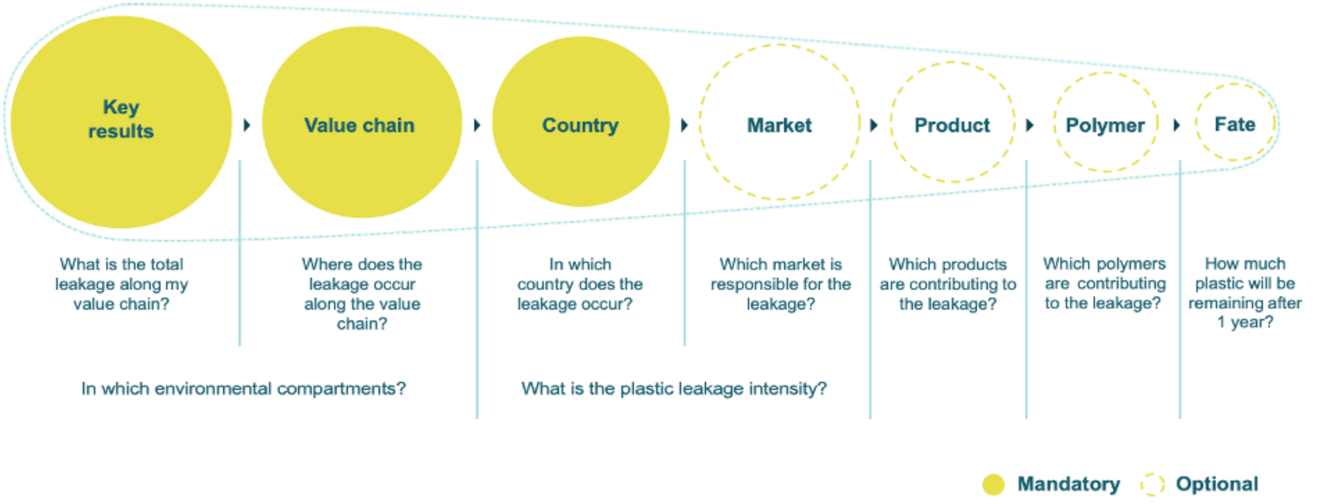


Figure 2.7: different perspectives on plastic leakage

As any life cycle assessment, this methodology is structured as represented in the figure below:

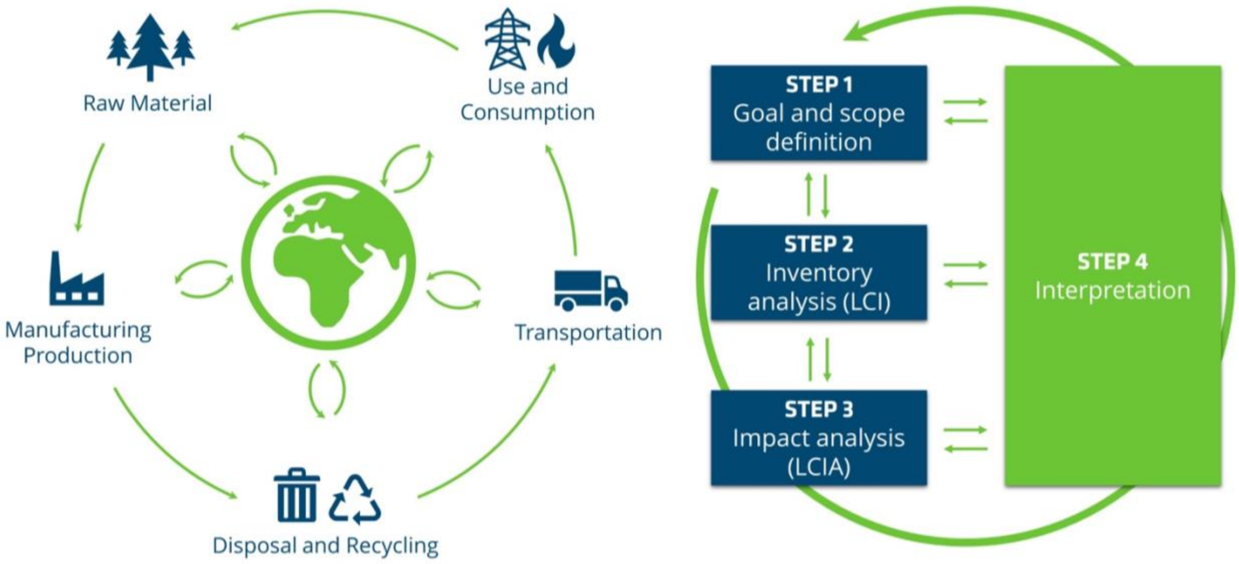


Figure 2.8: Structure of the life cycle assessment

2.3 Key results

Key results represent aggregate metrics of all plastic losses generated across a product’s lifecycle or the lifecycle of an embedded business.

These results should be expressed either as a single metric or divided into two metric divisions: *loss to the ocean* and *loss to other environmental compartments*.

An indicator of the intensity of plastic loss should be provided in case macro – plastic loss is a significant hotspot of plastic loss.

An indicator of the intensity of plastic loss can be calculated as the ratio between the mass of macro – plastic leaked and the mass of macro – plastic used to provide preliminary information on the extent of plastic loss at the product or company level.

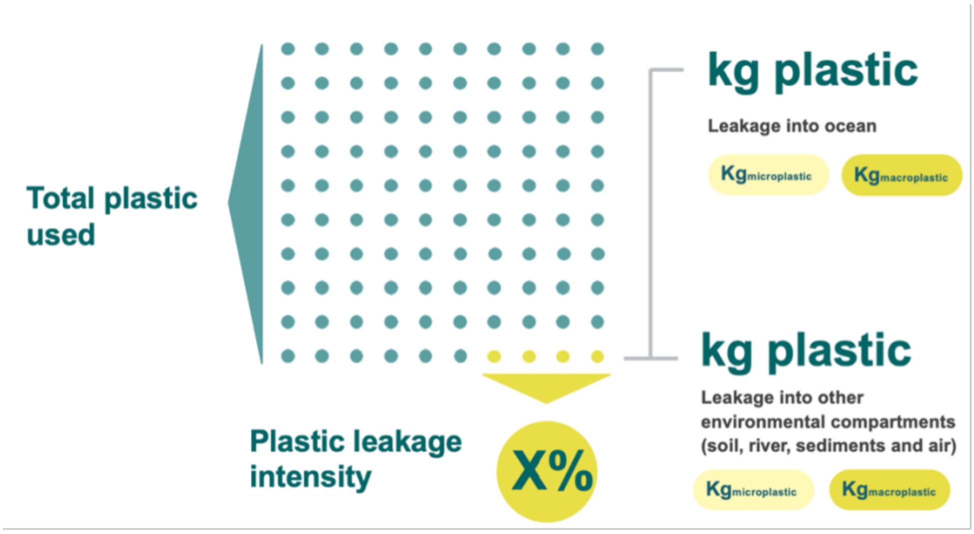


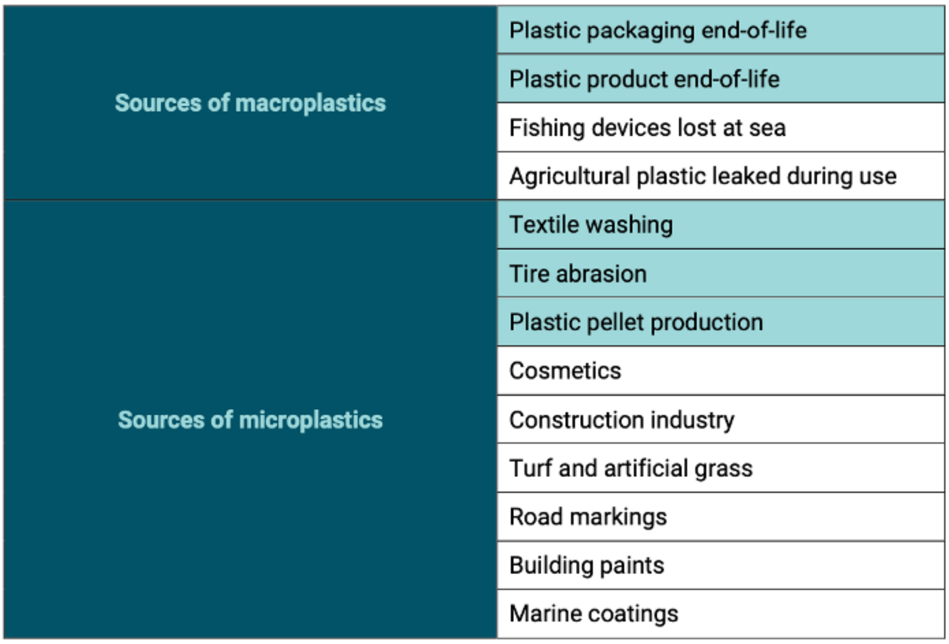
Figure 2.9: example of display for a plastic leakage assessment key result

The structure considered by this guideline follows *ISO 14040/44*:

1. Purpose and objective of the plastic loss assessment, including the definition of system boundaries.
2. The inventory of plastic loss, which starts from the evaluation of the quantity of micro and macro – plastic.
3. Impact assessment.
4. Interpretation.

2.4 Goal and scope

The objective of this study is to analyze the quantity of plastic lost throughout the various steps of the product life cycle of a *PUR sole*, with the aim of documenting and raising awareness about the different environmental compartments affected by the spread of plastic.



Sources of macroplastics	Plastic packaging end-of-life
	Plastic product end-of-life
	Fishing devices lost at sea
	Agricultural plastic leaked during use
Sources of microplastics	Textile washing
	Tire abrasion
	Plastic pellet production
	Cosmetics
	Construction industry
	Turf and artificial grass
	Road markings
	Building paints
	Marine coatings

Figure 2.10: Main sources of macro – plastics and microplastics. Highlighted in blue are the sources included in the guidelines (Lassen et al., 2015)

An *LCA analysis* is generally carried out for the duration of *1 year* conventionally.

The functional unit used for this purpose is the sole of a *42 EU* trekking shoe weighing *200 grams*, for *1 year* of activity.

2.5 Inventory of plastic leakage

To draw up a plastic loss inventory, there are *two steps*:

1. Map of the loss of micro and macro – plastics: identify the area where the loss occurs.
2. Data collection: they are divided into primary and secondary ones.

When assessing plastic loss, the first step is to create a map identifying where losses occur throughout the entire life cycle of the product.

For this purpose, it is necessary to determine the region where the loss takes place and the nature of the leak itself.

Life cycle steps	Nature of plastic leakage	Data quality
Suppliers	PUR microplastic pellet	Low
Production	Packaging macro – plastics	Medium

Product usage	Loss of plastic during show wear and washing	Good
End of product life	Microplastics from landfills	Low, not included in this guideline
	Macro – plastics from the product and end of life of the packaging	Medium
Transport	Microplastics from tire abrasion	Good
	Microplastics from road signs	Low, not included in this guideline

Table 2.1: different compartments of leakage

At this stage, the identification of *primary* and *secondary data* can proceed. Primary data refers to data collected specifically for the study, while secondary data is used when primary data is unavailable, with assumptions applied accordingly.

2.6 Inventory of microplastic loss from plastic waste

Once the inventory has been identified, *three* calculation steps are outlined for each direction of loss.

Loss rate (LR) is a measure of the amount of plastic which leaves a well – managed product or waste management system.

The *release*, instead, identified with the *release rate* (*RelR*), is a measure of the transported plastic through an initial environmental compartment, including:

- Running water
- Ocean

  Other land compartments (different than those already listed above)

Redistribution rate, RedR, is a measure of the redistribution of plastic through final environmental compartments.

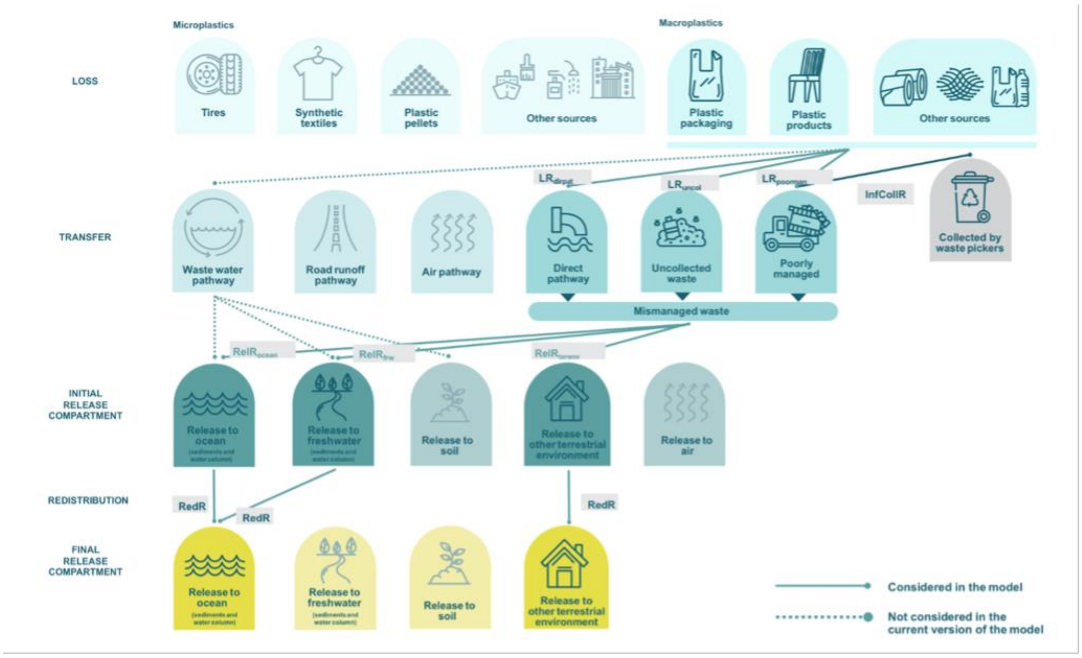
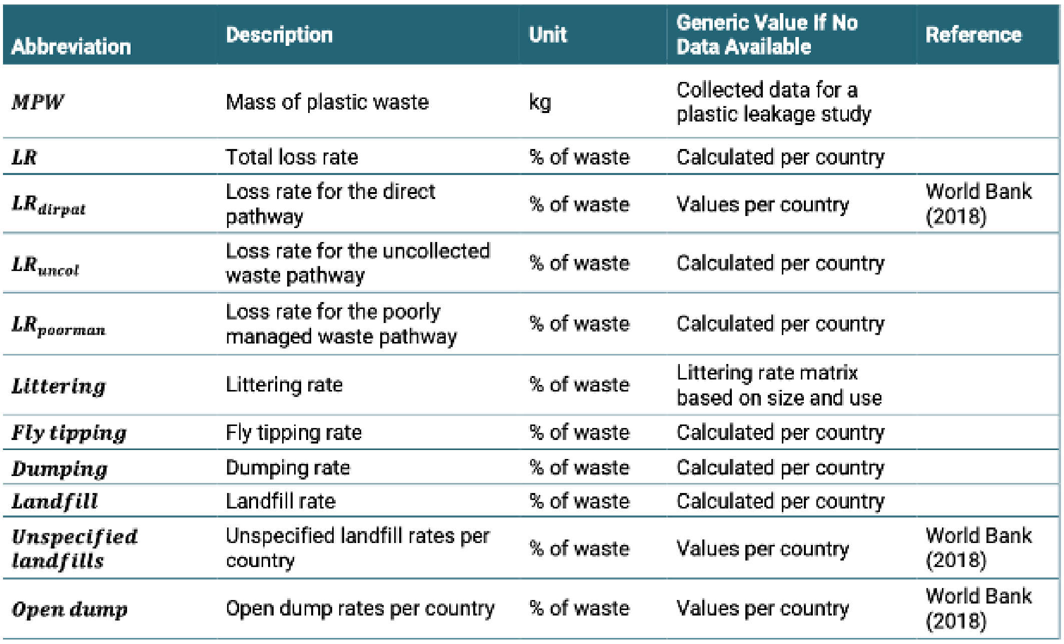


Figure 2.11: Losses, transfer pathways and plastic release compartments for macro – plastics

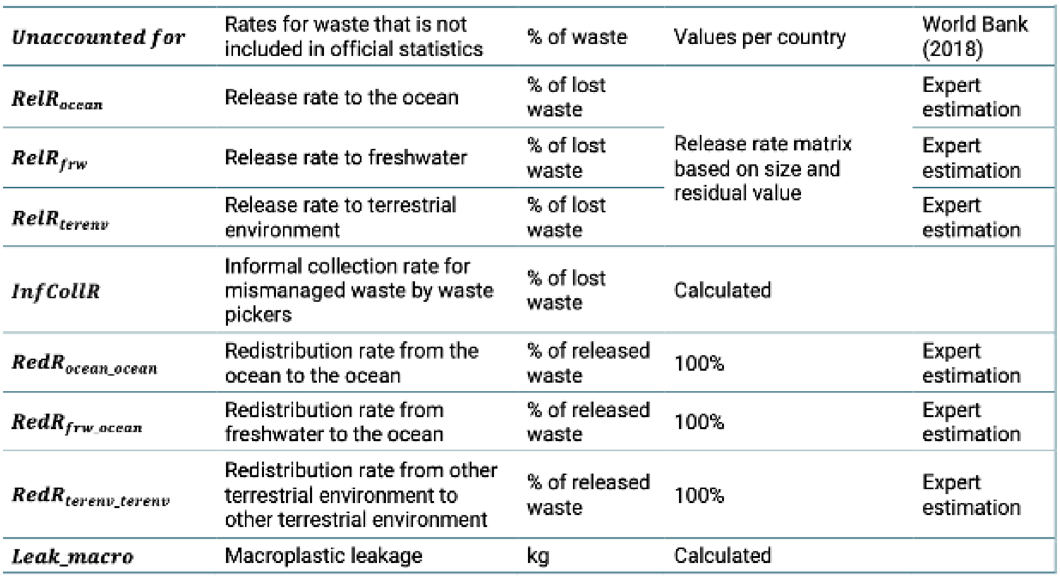
It is considered that the macro – plastics released into the environmental compartments, once reached, they remain there.

2.6 Data collection

The first step of an analysis of plastic leakage into environmental compartments is to collect data on the mass of plastic released, differentiating the various polymers if possible. In this case, there is only *one* polymer, namely *polyurethane*.



Abbreviation	Description	Unit	Generic Value If No Data Available	Reference
MPW	Mass of plastic waste	kg	Collected data for a plastic leakage study	
LR	Total loss rate	% of waste	Calculated per country	
LR_{dirpat}	Loss rate for the direct pathway	% of waste	Values per country	World Bank (2018)
LR_{uncol}	Loss rate for the uncollected waste pathway	% of waste	Calculated per country	
$LR_{poorman}$	Loss rate for the poorly managed waste pathway	% of waste	Calculated per country	
Littering	Littering rate	% of waste	Littering rate matrix based on size and use	
Fly tipping	Fly tipping rate	% of waste	Calculated per country	
Dumping	Dumping rate	% of waste	Calculated per country	
Landfill	Landfill rate	% of waste	Calculated per country	
Unspecified landfills	Unspecified landfill rates per country	% of waste	Values per country	World Bank (2018)
Open dump	Open dump rates per country	% of waste	Values per country	World Bank (2018)



$\boldsymbol{Unaccounted\ for}$	Rates for waste that is not included in official statistics	% of waste	Values per country	World Bank (2018)
$\boldsymbol{RelR_{ocean}}$	Release rate to the ocean	% of lost waste	Release rate matrix based on size and residual value	Expert estimation
$\boldsymbol{RelR_{frw}}$	Release rate to freshwater	% of lost waste		Expert estimation
$\boldsymbol{RelR_{terenv}}$	Release rate to terrestrial environment	% of lost waste		Expert estimation
$\boldsymbol{InfCollR}$	Informal collection rate for mismanaged waste by waste pickers	% of lost waste	Calculated	
$\boldsymbol{RedR_{ocean\_ocean}}$	Redistribution rate from the ocean to the ocean	% of released waste	100%	Expert estimation
$\boldsymbol{RedR_{frw\_ocean}}$	Redistribution rate from freshwater to the ocean	% of released waste	100%	Expert estimation
$\boldsymbol{RedR_{terenv\_terenv}}$	Redistribution rate from other terrestrial environment to other terrestrial environment	% of released waste	100%	Expert estimation
$\boldsymbol{Leak\_macro}$	Macroplastic leakage	kg	Calculated	

Figure 2.12: parameters used to calculate the amount of plastic leaked to the ocean

The evaluation of the *LR loss rate* is performed considering the following expression:

$$LR = LR_{dirpat} + LR_{uncol} + LR_{poorman} \tag{2.1}$$

$$\begin{aligned} LR &= Littering + (1 - Littering) \cdot \left(LR_{dirpat} + Fly\ tipping + Dumping + Landfill\right) \\ &= Littering + (1 - Littering) \cdot (Unspecified\ landiflls \\ &\quad + open\ dump + unaccounted\ for) \end{aligned} \tag{2.2}$$

Where:

- *LR_{dirpat}*

- LR_{dirpat} represents the dispersion loss rate of the plastic packaging and products transferred through a direct direction. Due to the lack of specific data on this, statistics from the World Bank[22] are used.
- LR_{uncol} represents the loss rate for plastic packaging and products transferred through uncollected waste.
- $LR_{poorman}$ represents the loss rate for plastic packaging and products transferred through poorly managed waste.

As regards macro – plastics, in this case, you are considering *polyethylene* (*LDPE*) films which cover the cardboard boxes containing the soles. Therefore, according to *Jambeck et al., 2015*, the littering rate for single-use plastics is *2%*; "*fly tipping + damping + landfill*" is counted in *Italy* as *20.9%*, *26%* as "*unspecified landfills*", "*open dump*" as *0%*, "*unaccounted for*" as *11%.*

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[22] Kaza et al., 2018

Using these data, it is possible to evaluate the LR factor using *Equation 2.2* as:

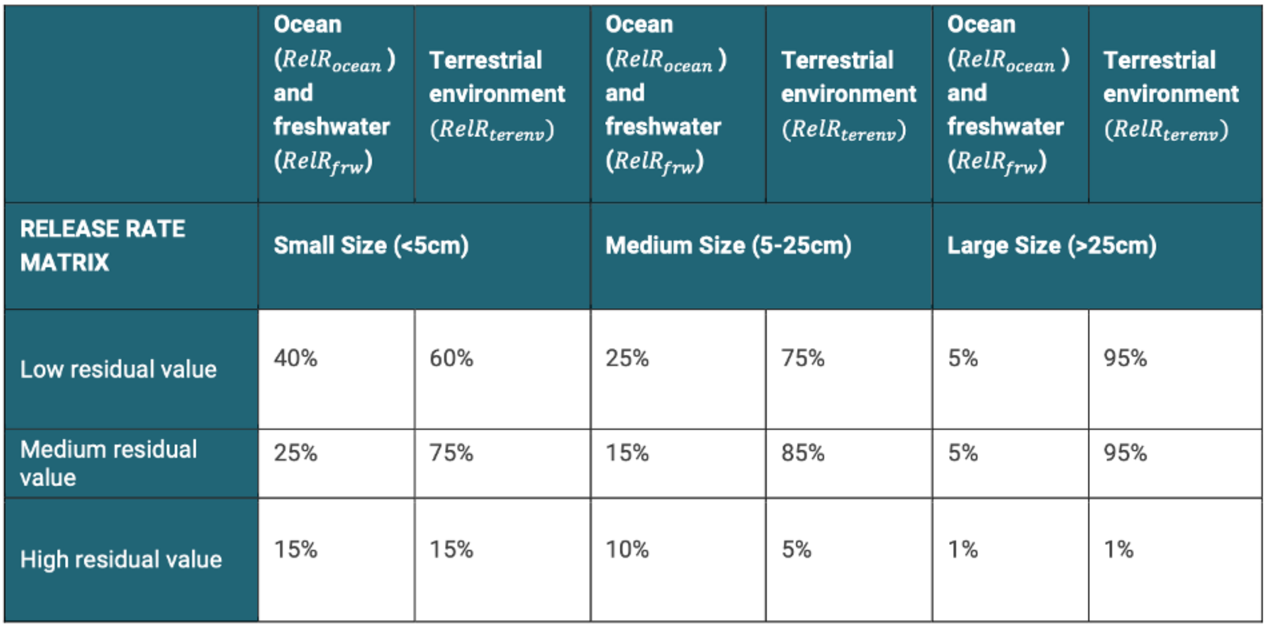
$$LR = 0.02 + (1 - 0.02) \cdot (0.26 + 0 + 0.11) = 0.3826 = 38.26\%$$

An important limitation of this loss rate is inherent to the import and export of waste between various countries, since this is not considered.

The release rate represents the percentage of waste released into a compartment relative to the generation of unmanaged waste.

In this case, *three* parameters are used to estimate the release in the various compartments. These include $RelR_{ocean}$ which considers the release into the ocean, $RelR_{frw}$ which considers the release into flowing water, and $RelR_{terrenv}$ for the release into other terrestrial compartments. Since the behavior of macro – plastic is analyzed, it is assumed that the film wrapping is made of *LDPE*, which is easy to recycle and marketable. Consequently, this guideline considers *LDPE* as a high value product, according to a classification that distinguishes it in the following manner:

- *Low residual value*: polymers with low recycling potential in each market.
- *Medium residual value*: polymers with recycling potential but associated with an application that does not allow the easy recovery of plastic.
- *High residual value*: polymers that are easily collected and then recycled in each market.



	Ocean ($RelR_{ocean}$) and freshwater ($RelR_{frw}$)	**Terrestrial environment ($RelR_{terenv}$)**	**Ocean ($RelR_{ocean}$) and freshwater ($RelR_{frw}$)**	**Terrestrial environment ($RelR_{terenv}$)**	**Ocean ($RelR_{ocean}$) and freshwater ($RelR_{frw}$)**	**Terrestrial environment ($RelR_{terenv}$)**
RELEASE RATE MATRIX	**Small Size (<5cm)**		**Medium Size (5-25cm)**		**Large Size (>25cm)**	
Low residual value	40%	60%	25%	75%	5%	95%
Medium residual value	25%	75%	15%	85%	5%	95%
High residual value	15%	15%	10%	5%	1%	1%

Figure 2.13: Release rate matrix

Since plastic films used to wrap pallets for goods trade are generally made of *LDPE* and are recyclable, they are considered to have a "*high residual value*" if their dimension exceeds *25 cm*.

Consequently, the release rates ($RelR_{ocean}$, $RelR_{frw}$ and $RelR_{terenv}$) are set at *1%*. The amount of waste that is poorly managed but not released into the environment represents the share of waste collected by waste management systems, which is ultimately recycled or reused:

$$InfCollR = 1 - \left(RelR_{ocean} + RelR_{frw} + RelR_{terenv}\right) \tag{2.3}$$

Through *Equation 2.3*, the following result has been obtained:

$$InfCollR = 1 - (0.01 + 0.01 + 0.01) = 0.97 \rightarrow 97\%$$

2.7.6 Rules for redistribution rate evaluation

A limitation of this methodology is the assumption regarding the path of plastic: it is assumed that the plastic distributed into the ocean remains there. Similarly, the same assumption is also made for plastic distributed into terrestrial compartment and remains there as well:

$$RedR = 100\% \tag{2.4}$$

2.7.2 Loss

Macro – plastic loss (denoted as *Leak_macro*) at life cycle stage *X*, through country *Y* and in the ocean or terrestrial environment is calculated as the sum of the plastic waste mass (*MPW*) during the life cycle of a product or of an activity at life cycle stage *X*, multiplied by the loss (LR) in country *Y*, the release into different environmental compartments (*RelR*) and the rate of redistribution (*RedR*).

In this case, it is not possible to estimate the macro – plastic loss due to the lack of detailed information on the distribution.

2.8 Microplastic inventory

Textile microplastics are considered a major cause of pollution in the marine environment. It is assumed that, within *1 year*, trekking shoes, and thus the sole itself, are washed once.

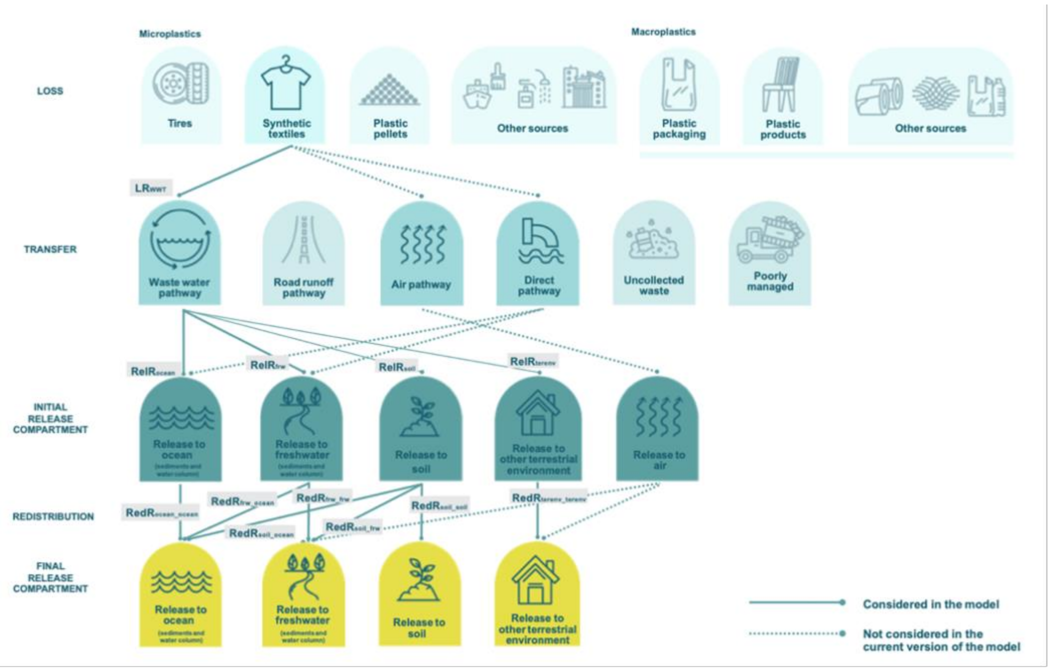


Figure 2.14: Losses, transfer pathways and plastic release compartments for synthetic microfibers from textiles

Microplastics that have settled in the soil are assumed to be transported to the oceans, flowing water, or captured in agricultural soils.

Figure 2.15: Fiber life cycle

Generally, the sole of a *42 EU* hiking shoe made of *PUR* weighs *200 grams*. Since there are no data on plastic loss during the production stage, it is suggested to assume the same rate of loss during the during usage stage.

It is assumed that the *polyurethane synthetic polymer* undergoes *one wash per year*, with *one cycle* at *30°C* using either solid or liquid detergent.

The following equation can be used to calculate the mass of synthetic microfiber loss, $LR_{textile}$, during the lifecycle of the textile (assuming an entire lifecycle of *10 years*, with $N_{wash} = 10$):

$$LR_{WWP} = N_{wash} \cdot LR_{perwash} = 10 \cdot 46\ {}^{mg}/_{kg\ textile\ wash} = 460\ {}^{mg}/_{kg_{textile\ wash}} \tag{2.5}$$

meaning that for one single cycle wash, 46 $mg/kg_{textile\ wash}$ are lost.

In *Equation 2.5*, $LR_{perwash}$ is the loss per kilogram of washed textiles per wash cycle; LR_{wwp} represents the rate of loss of textiles during pre-washing and processing in textile production, as well as during hand or machine washing in the use phase, assuming the wastewater is connected to a wastewater treatment plant.

Through the following expression (*Equation 2.6*), instead, it is possible to calculate the synthetic microfiber mass lost:

$$MiPL = N_{wash} \cdot LR_{perwash} \cdot M_{textile} = 10 \cdot 46 \ {}^{mg}/_{kg\ textile\ wash} \cdot 0.2\ kg = 92\ mg \qquad (2.6)$$

where $M_{textile}$ is the mass of textile used, assuming that a sole weighs *200 grams*. The value found refers to a duration of *10* years.

Therefore, it is assumed that the mass of synthetic microfibers lost in one year is equal to $MiPL = 9.2\ mg_{microfiber\ lost}$.

2.8.1 Release rate calculation

In this section, it is evaluated the release rate considering the release rate in the ocean and freshwater.

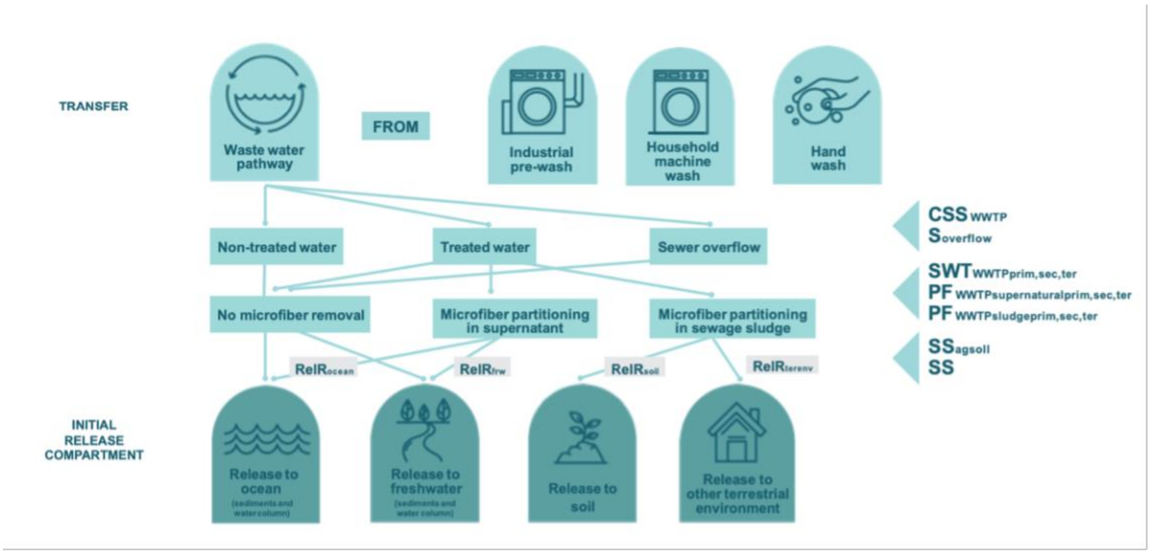


Figure 2.16: Release rates leading from the wastewater treatment pathway to the initial release compartment for synthetic microfibers

The release rate is evaluated considering the following expression:

$$\begin{aligned} RelR_{ocean} + RelR_{frw} &= 1 - CSS_{WWTP} \\ &\cdot (1 - S_{overflow} - SWT_{WWTPprim} \cdot PF_{WWTPsupernatantprim} - SWT_{WWTPsec} \\ &\cdot PF_{WWTPsupernatantsec} - SWT_{WWTPter} \cdot PF_{WWTPsupernatantter}) = \end{aligned}$$

$$1 - 0.63 \cdot (1 - 0.05 - 0.05 \cdot 0.19 - 0.3 \cdot 0.05 - 0.65 \cdot 0.02) = 0.4251 \rightarrow 42.51\% \qquad (2.7)$$

Where $RelR_{frw}$ is the release rate to freshwater; CSS_{WWTP} [%] is the connection to the sewer system, which varies by country; $S_{overflow}$ is the share of overflow (due to wet weather conditions), assumed to be 5% based on expert estimations; $SWT_{WWTP,prim}$ is the share of the treatment type for a given level of wastewater treatment, *e.g.*, primary, secondary, or tertiary; $PF_{wwtp,supernatantprim}$ is the distribution factor of synthetic microfibers in the supernatant in the *WWTP*[23] for a given level of final treatment, *e.g.*, primary (*19%*), secondary (*5%*), or tertiary (*2%*).

The release rate to freshwater instead is evaluated through the following expression:

$$RelR_{frw} = R_{f/_m} \cdot \left(RelR_{ocean} + RelR_{frw}\right) = 0.74 \cdot (0.42) = 0.3108 \rightarrow 31.8\% \tag{2.8}$$

where $R_{f/m}$ is the ratio of release into flowing water to the oceans, assumed to be *74%*.

The release rate to the ocean, instead:

$$RelR_{ocean} = \left(1 - R_{f/_m}\right) \cdot \left(RelR_{ocean} + RelR_{frw}\right) = \\ = (1 - 0.74) \cdot (0.42) = 0.1092 \rightarrow 10.92\% \tag{2.9}$$

The release rate to soil:

$$RelR_{soil} = \left(1 - \left(RelR_{ocean} + RelR_{frw}\right)\right) \cdot SS_{agsoil} = (1 - 0.42) \cdot 0.5 = 0.29 \rightarrow 29\% \tag{2.10}$$

where SS_{agsoil} is the share of sewage sludge deposited on agricultural soil and is assumed to be *50%.*

The release rate to other terrestrial compartments:

$$RelR_{terenv} = \left(1 - \left(RelR_{ocean} + RelR_{frw}\right)\right) \cdot SS_{mismanaged} \\ = (1 - 0.42) \cdot 0.11 = 0.0638 \rightarrow 6.38\% \tag{2.11}$$

where $RelR_{terenv}$ is the release rate to other terrestrial compartments; $SS_{mismanaged}$ is the share of sewage sludge mismanaged and it is assumed to be *11%.*

2.8.2 Redistribution rate calculation

It is assumed that all synthetic microfibers released into the oceans remain there:

$$RedR_{ocean_{ocean}} = 100\% \tag{2.12}$$

Synthetic microfibers released into freshwater are assumed to be partially released into the oceans and partially trapped in freshwater sediments. Several studies estimate the fraction of synthetic

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[23] WWTP: waste water treatment plant

microfibers that are captured in freshwater sediments. The ratio of synthetic microfibers captured in freshwater sediments, $R_{freshed}$, is used to calculate $RedR_{frw,ocean}$ and $RedR_{frw,frw}$.

$$RedR_{frw_{ocean}} = 1 - R_{freshed} = 0.7 \rightarrow 70\% \tag{2.13}$$

$$RedR_{frw\_frw} = R_{freshed} = 30\% \tag{2.14}$$

It is assumed that synthetic microfibers released into soil are either retained in the soil or transferred to oceans or freshwater. If transferred, they may become trapped in freshwater sediments.

$$RedR_{soil_{soil}} = R_{soil} = 27\%$$

$$RedR_{soil_{ocean}} = (1 - R_{soil}) \cdot (1 - R_{freshed}) = (1 - 0.27) \cdot (1 - 0.3) = 0.511 \rightarrow 51.1\%$$

$$RedR_{soil\_frw} = (1 - R_{soil}) \cdot R_{freshed} = (1 - 0.27) \cdot 0.3 = 0.219 \rightarrow 21.9\% \tag{2.15}$$

Synthetic microfibers released into other terrestrial environments are assumed to remain there:

$$RedR_{terenv\_terenv} = 100\% \tag{2.16}$$

2.8.3 Loss calculation

The leakage of synthetic microfibers, *Leakmicro*, into different environmental compartments, is ultimately calculated as the sum of the synthetic microfiber waste lost (*MiPL*) during the life cycle of a product or business activity, multiplied by the release (*RelR*) and redistribution rates (*RedR*) to the different environmental compartments:

$$Leak_{micro_{oceans}} = \sum (MiPL \cdot (RelR_{ocean} \cdot RedR_{ocean_{ocean}} + RelR_{frw} \cdot RedR_{frw_{ocean}} + RelR_{soil} \cdot RedR_{soil_{ocean}}) = 9.2\,mg \cdot (0.1092 \cdot 1 + 0.318 \cdot 0.7 + 0.29 \cdot 0.511) = 4.42\,mg \tag{2.17}$$

$$Leak_{micro_{freshwater}} = \sum \left(MiPL \cdot \left(RelR_{frw} \cdot RedR_{frw_{frw}} + RelR_{soil} \cdot RedR_{soil_{frw}} \right) \right) = 9.2\,mg \cdot (0.318 \cdot 0.30 + 0.29 \cdot 0.219) = 1.46\,mg \tag{2.18}$$

$$Leak_{micro_{soil}} = \sum (MiPL \cdot RelR_{soil} \cdot RedR_{soil_{soil}}) = 9.2\,mg \cdot 0.29 \cdot 0.27 = 0.72\,mg \tag{2.19}$$

$$Leak_{micro_{terenv}} = \sum \left(MiPL \cdot RelR_{terenv} \cdot RedR_{terenv_{terenv}} \right)$$
$$= 9.2\, mg \cdot 0.0638 \cdot 1 = 0.59\, mg \qquad (2.20)$$

2.8.4 Plastic loss during transportation

Since tires are prone to abrasion during transportation, microplastics are released onto the surface.

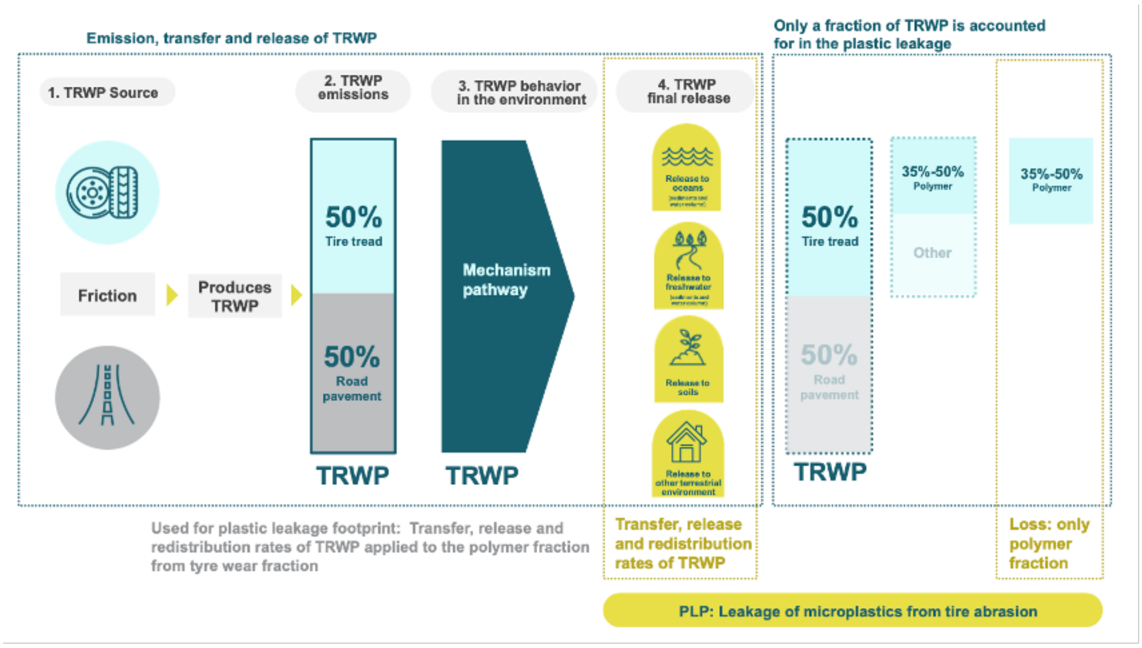

Figure 2.17: Tire and road wear particles (TRWP) and calculation of leakage of microplastics from tire abrasion; the behavior of TRWP (i.e., the transfer, release and redistribution) is considered, but applied only to the theoretical fraction of polymer from TRWP

There are *three* different transfer directions:

1. A small fraction, ranging from *1%* to *7%*, is emitted into the air as particles with a diameter of less than 10 μm.
2. The main portion of TRWP, with a diameter above 10 μm, is deposited on the soil near the road, accounting for *49%* to 85%, depending on the study.
3. The remaining portion is deposited on the road (asphalt),while the other fraction is transported by rainwater.

The release rate is defined as the fraction of loss that is released into different compartments. The distribution is as follows:

- *TRWP*[24] below 10 μm is emitted into the air.
- *TRWP* above 10 μm deposited near the road is then dispersed into the soil.

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[24] TRWP: Tire and Road Wear Particles

- *TRWP* above 10 μm transported by runoff water is released into the soil, water surfaces, oceans, or sewer systems, depending on the type of road.

TRWP released into the initial compartments can be redistributed into the final compartments.

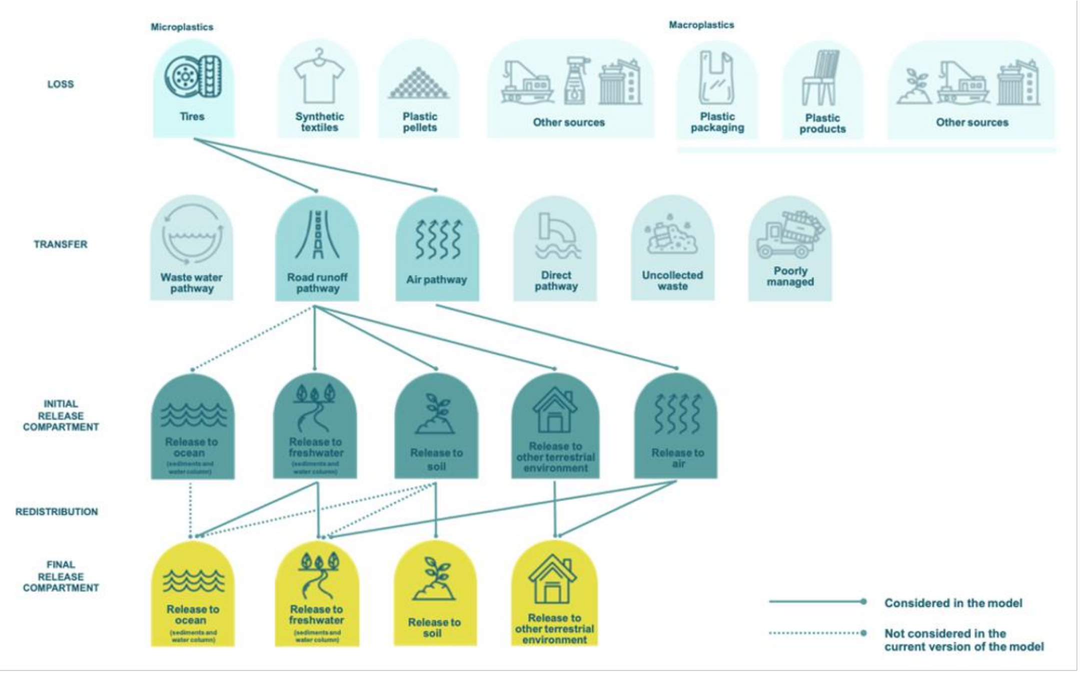

Figure 2.18: Different pathways of release

Some studies identify common key parameters that influence the loss of microplastics from tires. These include:

- Intrinsic characteristics of tire design.
- Vehicle characteristics.
- Road surface characteristics.
- Driving behavior.

Once *TRWP* is released, its dispersal depends on weather conditions and the type of water runoff collection systems. The location of the road also significantly influences the release, as coastal areas allow microplastics to enter the oceans more easily, or even directly.

There is no available data on the percentage of roads that discharge runoff into freshwater bodies versus the oceans.

At the time of this guideline's publication, no reliable data existed to assess the sedimentation rate in coastal areas (which are closer to the sea) or the retention rate in runoff water infrastructure.

Therefore, a sedimentation rate of *90%*[25] was assumed for both small and large watersheds, meaning that 90% of *TRWP* released into freshwater are deposited in freshwater sediments. This assumption is *one of the main limitations* of the guidelines.

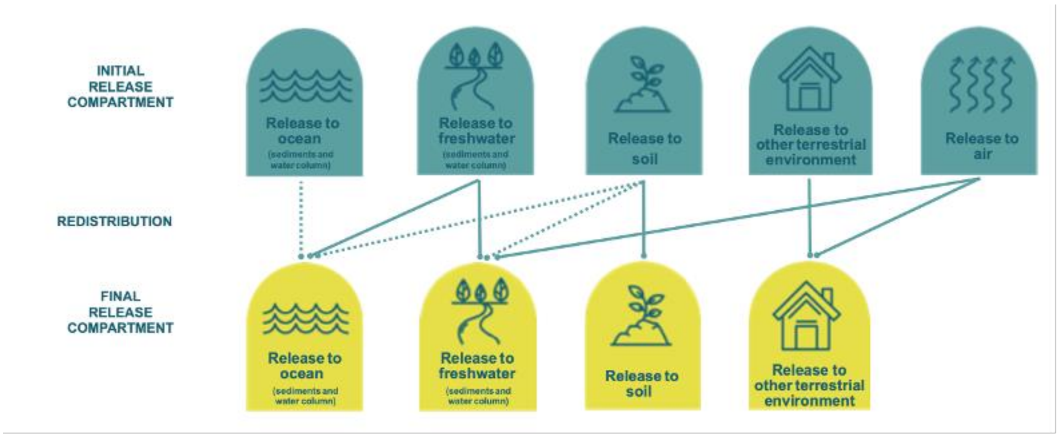

Figure 2.19: Redistribution rates and final release compartments

Regarding the calculation pathways for release, the data to be collected include:

- Number of passengers and corresponding distance traveled per vehicle type.
- Mass of goods and corresponding distance traveled per vehicle type.
- Number of passengers and number of flights for air transport.

In the following case study, it is assumed that the transportation of trekking soles is carried out by trucks used for freight transport (logistics) according to the expression below, where $D_{truck,vhc}$ is the average distance traveled by a truck, $Loss_{truck,tires}$ is the tire wear loss per kilometer traveled, and $ShPolymer_{truck,tires}$ is the share of polymer fraction in the tire tread.

If we consider that a truck can carry a maximum of *28 tons*, or *28,000 kg*, and assuming that one sole weighs *200 g*, the truck will be able to transport approximately *140,000* soles. Knowing the transported mass, the formulation becomes as follows:

$$TotTireLoss_{truck}[kg\ microplastics] = \frac{D_{truck,prod}[km]*M_{prod}[kg]}{Load_{av}[kg]} \cdot Loss_{truck_{tires}}\left[\frac{kg\ tread}{vhc*km}\right] \cdot ShPolymer_{truck_{tires}}\left[\frac{kg\ microplastics}{kg\ tread}\right] = \frac{400\ km \cdot 0.2\ kg}{12000\ kg} \cdot 517\frac{kg}{vhc \cdot km} \cdot 0.6\ \frac{kg\ microplastics}{kg\ tread} = 2.068\ kg \tag{2.21}$$

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[25] Unice et al., 2018

This result means that for the transportation of one sole, $1.5 \cdot 10^{-5}\ kg$ of microplastics is lost during the transport.

The number of kilometers that can be daily travelled have been estimated, along with the transportable mass by each truck, based on the current regulations. The $Load_{av}$ value expressed in kilograms have been extrapolated from the guideline *PLP* table, as the $ShPolymer_{truck,tires}$ and $Loss_{truck,tires}$ values.

Considering air freight in the case of internation commerce, the equation below accounts for the landing, take-off and taxiing cycle (including movement from the parking area):

$$\begin{aligned} TotTireLoss_{plane}[kg\ microplastics] \\ &= NbCycle\ [cycle] \cdot Loss_{aircraft_{tires}} \left[\frac{kg\ tread}{cycle}\right] \\ &\cdot ShPolymer_{aircraft_{tires}} \left[\frac{kg\ microplastics}{kg\ tread}\right] \\ &= 3\ cycle \cdot 2.278 \frac{kg\ tread}{vhc \cdot cycle} \cdot 0.53 \frac{kg\ microplastics}{kg\ tread} \\ &= 3.622\ \frac{kg\ microplastic}{vhc} \end{aligned} \tag{2.22}$$

where $Loss_{aircraft,tires}$ is assumed to be $0.278\ \frac{kg\ tread}{vhc \cdot cycle}$ and it is the loss of tread per "take-off, landing, taxiing" cycle; $ShPolymer_{aircraft,tires}$ is assumed to be $0.53\ \frac{kg\ microplastics}{kg\ tread}$ for this kind of aircraft and it is the amount of plastic (synthetic rubber + natural rubber) in the tires tread.

Initial release rate evaluation

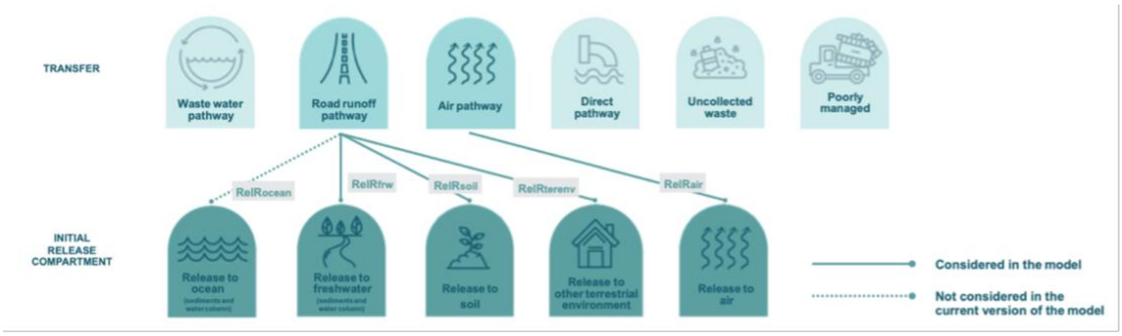
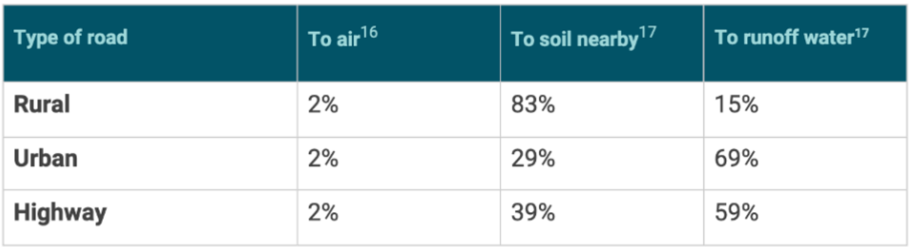


Figure 2.20: Release rates leading from the road runoff and air pathways to the initial release compartment for TRWP

The first *three* major directions that microplastics follow are the ones below:

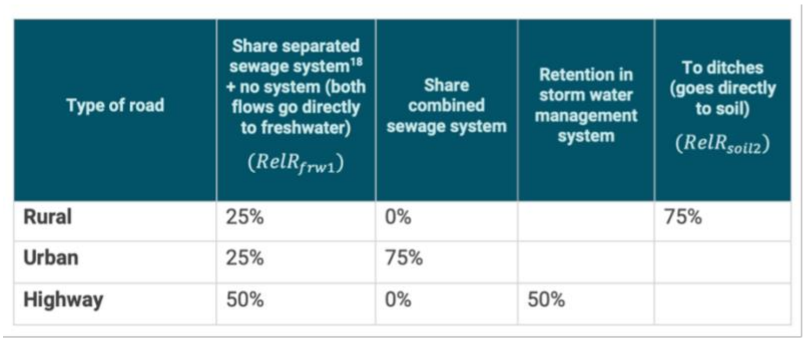


Type of road	To air[16]	To soil nearby[17]	To runoff water[17]
Rural	2%	83%	15%
Urban	2%	29%	69%
Highway	2%	39%	59%

Figure 2.21: First three major directions

As for microplastic emission into the air, the fraction of *PM10* is estimated to range from *1%* to *7%*, depending on the case. Based on a recent study (*Unice et al., 2018*), $RelR_{air}$ is estimated to be *2%.*

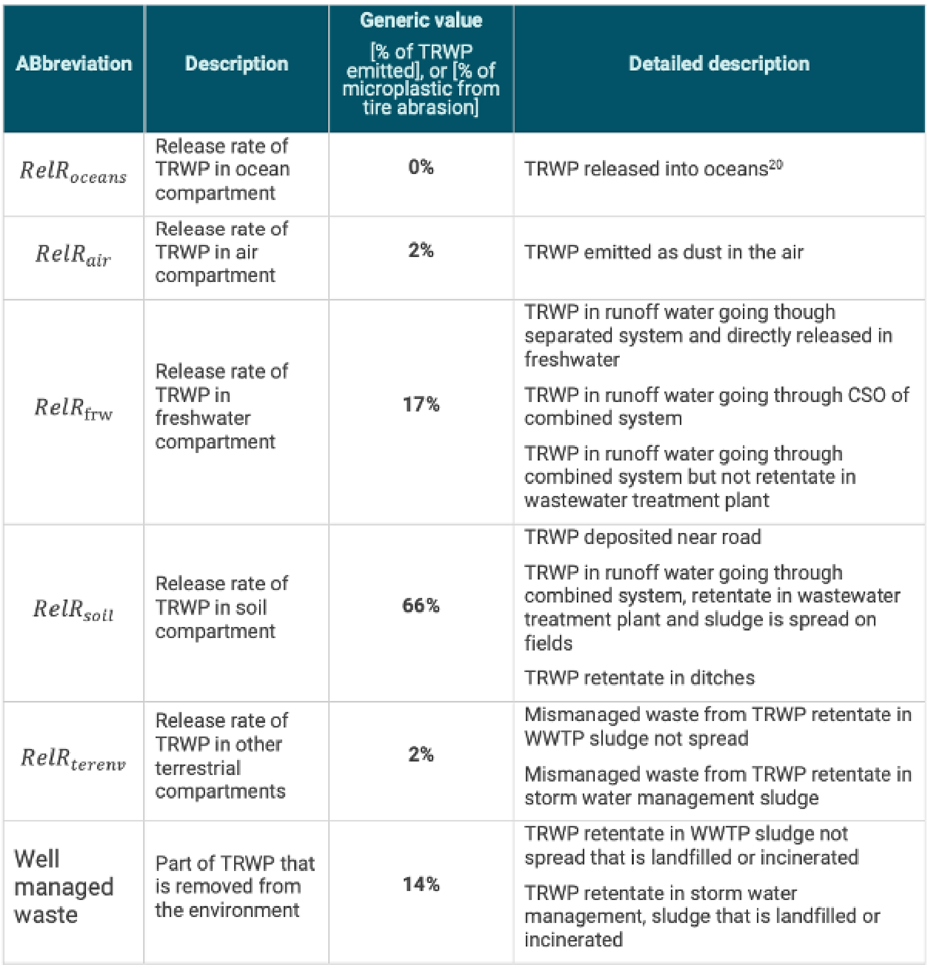
The deposition near the road and in the initial compartments concerns particles greater than 10 μ*m* and the soil is considered to be the first of these initial compartments, $RelR_{soil,1}$.



Type of road	Share separated sewage system[18] + no system (both flows go directly to freshwater) $(RelR_{frw1})$	Share combined sewage system	Retention in storm water management system	To ditches (goes directly to soil) $(RelR_{soil2})$
Rural	25%	0%		75%
Urban	25%	75%		
Highway	50%	0%	50%	

Figure 2.22: Default values of the release rates in the different zones

One of the main limitations of this guideline is the lack of data, particularly regarding road runoff that flows from the freshwater sources to the oceans. The missing data does not allow the precise evaluation of release and redistribution rate; it is assumed that 100% of surface water is freshwater, into which runoff is released.



ABbreviation	Description	Generic value [% of TRWP emitted], or [% of microplastic from tire abrasion]	Detailed description
$RelR_{oceans}$	Release rate of TRWP in ocean compartment	0%	TRWP released into oceans[20]
$RelR_{air}$	Release rate of TRWP in air compartment	2%	TRWP emitted as dust in the air
$RelR_{\mathrm{frw}}$	Release rate of TRWP in freshwater compartment	17%	TRWP in runoff water going though separated system and directly released in freshwater TRWP in runoff water going through CSO of combined system TRWP in runoff water going through combined system but not retentate in wastewater treatment plant
$RelR_{soil}$	Release rate of TRWP in soil compartment	66%	TRWP deposited near road TRWP in runoff water going through combined system, retentate in wastewater treatment plant and sludge is spread on fields TRWP retentate in ditches
$RelR_{terenv}$	Release rate of TRWP in other terrestrial compartments	2%	Mismanaged waste from TRWP retentate in WWTP sludge not spread Mismanaged waste from TRWP retentate in storm water management sludge
Well managed waste	Part of TRWP that is removed from the environment	14%	TRWP retentate in WWTP sludge not spread that is landfilled or incinerated TRWP retentate in storm water management, sludge that is landfilled or incinerated

Figure 2.23: Initial release rates

The microplastics loss, *Leak_micro*, is evaluated as the sum of the microplastic loss due to the tire abrasion (*TotTireLoss*), multiplied by the release rates (*RelR*) and the redistribution rates (*RedR*) in every specific terrestrial compartment.

$$RedR_{frw\_ocean} = 1 - R_{freshsed} = 1 - 0.9 = 0.1 = 10\% \tag{2.23}$$

The $R_{freshed}$ value, proposed by the *Unice et al. 2018* study, is equal to *90%* of *TRWP* released into freshwater.

$$\begin{aligned} Leak_{micro_{oceans}} &= \sum \left(TotTireLoss \cdot RelR_{frw} \cdot RedR_{frw_{ocean}} \right) = (2.068\, kg \cdot 0.17 \cdot 0.1) \\ &= 0.035\, kg \end{aligned} \tag{2.24}$$

And evaluating it for *one* sole:

$$Leak_{micro_{oceans}} = \sum\left(TotTireLoss \cdot RelR_{frw} \cdot RedR_{frw_{ocean}}\right) = (1.5 \cdot 10^{-5}\ kg\ \cdot 0.17 \cdot 0.1) = 2.55 \cdot 10^{-7} kg \tag{2.25}$$

The release of microplastics into freshwater is evaluated as:

$$Leak_{micro_{freshwater}} = \sum\left(TotTireLoss \cdot \left(RelR_{frw} \cdot RedR_{frw_{frw}} + RelR_{air} \cdot RedR_{air_{frw}}\right)\right) = \left(2.068 \cdot (0.17 \cdot 0.1 + 0.02 \cdot 0.03)\right) = 0.036\ kg \tag{2.26}$$

And evaluating it for *one* sole:

$$Leak_{micro_{freshwater}} = \sum\left(TotTireLoss \cdot \left(RelR_{frw} \cdot RedR_{frw_{frw}} + RelR_{air} \cdot RedR_{air_{frw}}\right)\right) = \left(1.5 \cdot 10^{-5} \cdot (0.17 \cdot 0.1 + 0.02 \cdot 0.03)\right) = 2.64 \cdot 10^{-7}\ kg \tag{2.27}$$

Where $RedR_{frw,frw} = RedR_{frw,ocean}$, with $RedR_{air,frw} = 3\%$.

For *one* sole in *a* year:

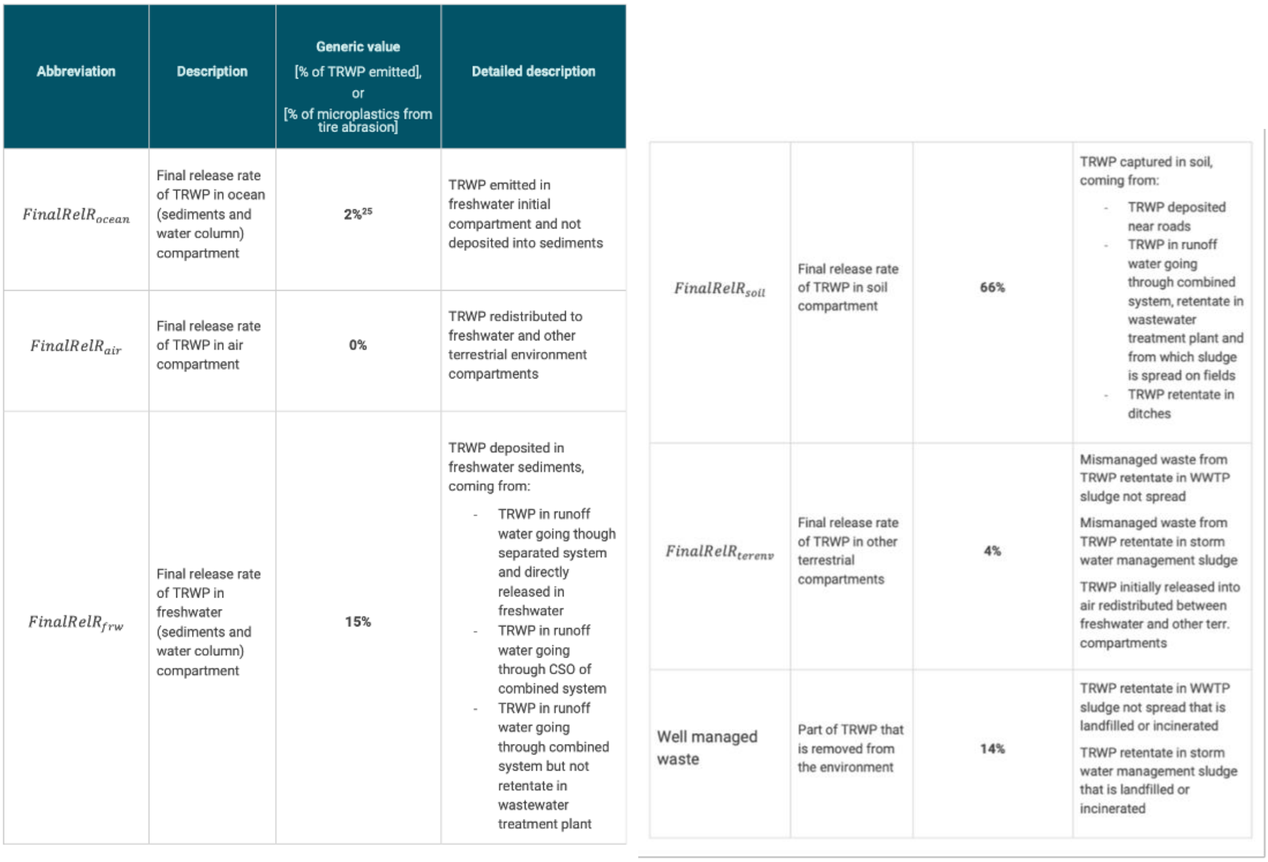
$$Leak_{micro_{soils}} = \sum\left(MiPL \cdot RelR_{soil} \cdot RedR_{soil_{soil}}\right) = 9.2\ mg \cdot 0.66 \cdot 1 = 6.07\ mg \tag{2.28}$$

where $RedR_{soil,soil} = 100\%$.

And, to conclude:

$$Leak_{micro_{terenv}} = \sum\left(MiPL \cdot RelR_{terenv} \cdot RedR_{terenv_{terenv}} + RelR_{air} \cdot RedR_{air_{terenv}}\right) = 9.2\ mg \cdot 0.02 \cdot 1 + 0.02 \cdot 0.97 = 0.20\ mg \tag{2.29}$$

where $RedR_{terenv,terenv} = 100\%$ and $RedR_{air,terenv} = 97\%$.



Abbreviation	Description	Generic value [% of TRWP emitted], or [% of microplastics from tire abrasion]	Detailed description
$FinalRelR_{ocean}$	Final release rate of TRWP in ocean (sediments and water column) compartment	2%[25]	TRWP emitted in freshwater initial compartment and not deposited into sediments
$FinalRelR_{air}$	Final release rate of TRWP in air compartment	0%	TRWP redistributed to freshwater and other terrestrial environment compartments
$FinalRelR_{frw}$	Final release rate of TRWP in freshwater (sediments and water column) compartment	15%	TRWP deposited in freshwater sediments, coming from: - TRWP in runoff water going though separated system and directly released in freshwater - TRWP in runoff water going through CSO of combined system - TRWP in runoff water going through combined system but not retentate in wastewater treatment plant
$FinalRelR_{soil}$	Final release rate of TRWP in soil compartment	66%	TRWP captured in soil, coming from: - TRWP deposited near roads - TRWP in runoff water going through combined system, retentate in wastewater treatment plant and from which sludge is spread on fields - TRWP retentate in ditches
$FinalRelR_{terenv}$	Final release rate of TRWP in other terrestrial compartments	4%	Mismanaged waste from TRWP retentate in WWTP sludge not spread Mismanaged waste from TRWP retentate in storm water management sludge TRWP initially released into air redistributed between freshwater and other terr. compartments
Well managed waste	Part of TRWP that is removed from the environment	14%	TRWP retentate in WWTP sludge not spread that is landfilled or incinerated TRWP retentate in storm water management sludge that is landfilled or incinerated

Figure 2.24: Final release rates

2.8.5 Microplastic loss during its production

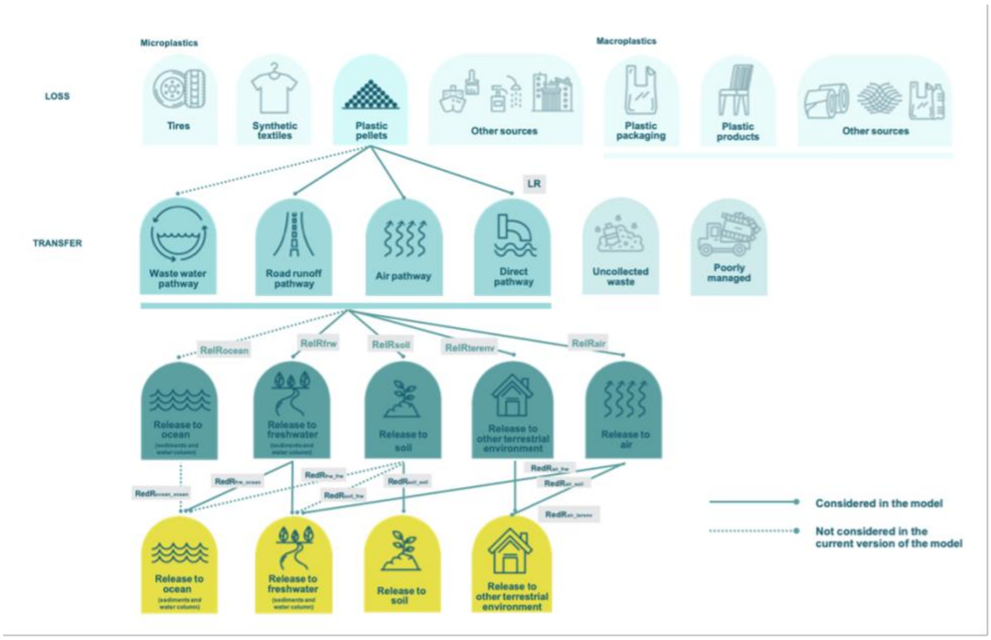


Figure 2.25: Losses, transfer pathways and plastic release compartments for pellets

In the guideline used, "*pellet loss*" refers to plastic pellets that escape during production and are not recovered, thus entering the environment. It does not include all pellets "lost" during the production process, such as those that are properly contained and disposed of as pellet waste.

According to *Hann et al., 2018*, pellets typically arrive at sites in *three* different types of packaging containers: bulk product tankers, boxes on pallets, and *25 kg* bags.

- When pellets are transported to processing sites via tankers, a vacuum system is used to transfer the pellets from the tanker to a silo through a pipe. The most common point of spillage occurs when the pipes are connected or disconnected from the tanker or silo. Both the tanker and silo are generally located outdoors.
- Boxes and bags are handled with forklifts on pallets or moved individually, which in- creases the risk of spills and losses compared to deliveries via tanker.

Based on *Hann et al., 2018*, and *Cole and Sherrington, 2016*, data relating to pellet loss in processes — *0.04%* (according to *Sundt et al., 2014*) and *0.001% - 0.01%* (based on *Lassen et al., 2015*) — seem to be the most reliable. Unfortunately, these estimates also have their limitations, as they are based on a single process and not direct measurements.

Lassen et al., 2015, one of the key references for pellet loss during packaging production, represents estimations from various processes in *OCS* facilities[26], which are expected to have lower pellet emissions compared to *non – OCS* facilities. An average was calculated based on all references, including both *OCS* and *non – OCS* facilities[27].

It is assumed that the figures for pellet loss at processors are consistent across all stages of the value chain in *Hann et al., 2018*, excluding transportation.

	Description	Loss rate/leakage in the environment	References
Production	Producers create polymers and extrude resin pellets from powders or liquids. Spills occur during handling, loading and unloading, as well as	0.01% - 0.4%	Lassen et al., 2015 Sundt et al., 2014

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[26] OCS: Operation Clean Sweep, a voluntary international program aimed at preventing plastic pellet loss during handling

[27] *Sundt et al., 2014*, *Cole and Sherrington, 2016*

	leakage from containers and storage silos.		Cole and Sherrington, 2016
Suppliers	Logistics suppliers, providing intermediary services to all stakeholders in the value chain, i.e., including warehousing, redistribution, packaging, transport, etc. These intermediary points are important as they represent additional stages at which pellets are handled and can therefore be lost. Transport includes loading and unloading, accidental loss from railcars and trucks (due to unsuitable packaging, spills and so on) that transfer pellets from producers to processors. This estimate is based on an average transportation distance between the plastic pellets production plant and the plastic processing plant.	0.01% - 0.04%	Lassen et al., 2015 Sundt et al., 2014 Cole and Sherrington, 2016
Shipping (transportation by boat only)	Shipping includes loading and unloading, accidental loss from shipping containers	0.001% - 0.002%	Hann et al., 2018
Processing	Processors (or converters), which melt and remold plastic pellets (usually compounds) into final plastic products. Spills occur during handling, loading and unloading, as well as leakage from containers and storage silos.	0.01% - 0.04%	Lassen et al., 2015 Sundt et al., 2014 Cole and Sherrington, 2016
Waste management	Management of producers and processors' waste: pellet loss mostly occurs during storage for disposal	0.01% - 0.04%	Lassen et al., 2015 Sundt et al., 2014

	when pellets are either disposed of with mixed residual waste or blown away from bins stored outside.		Cole and Sherrington, 2016
Recycling	Recyclers, which sort, clean and process waste plastics (predominantly packaging) into recycled plastic pellets and compounds.	0.01% - 0.04%	Lassen et al., 2015 Sundt et al., 2014 Cole and Sherrington, 2016

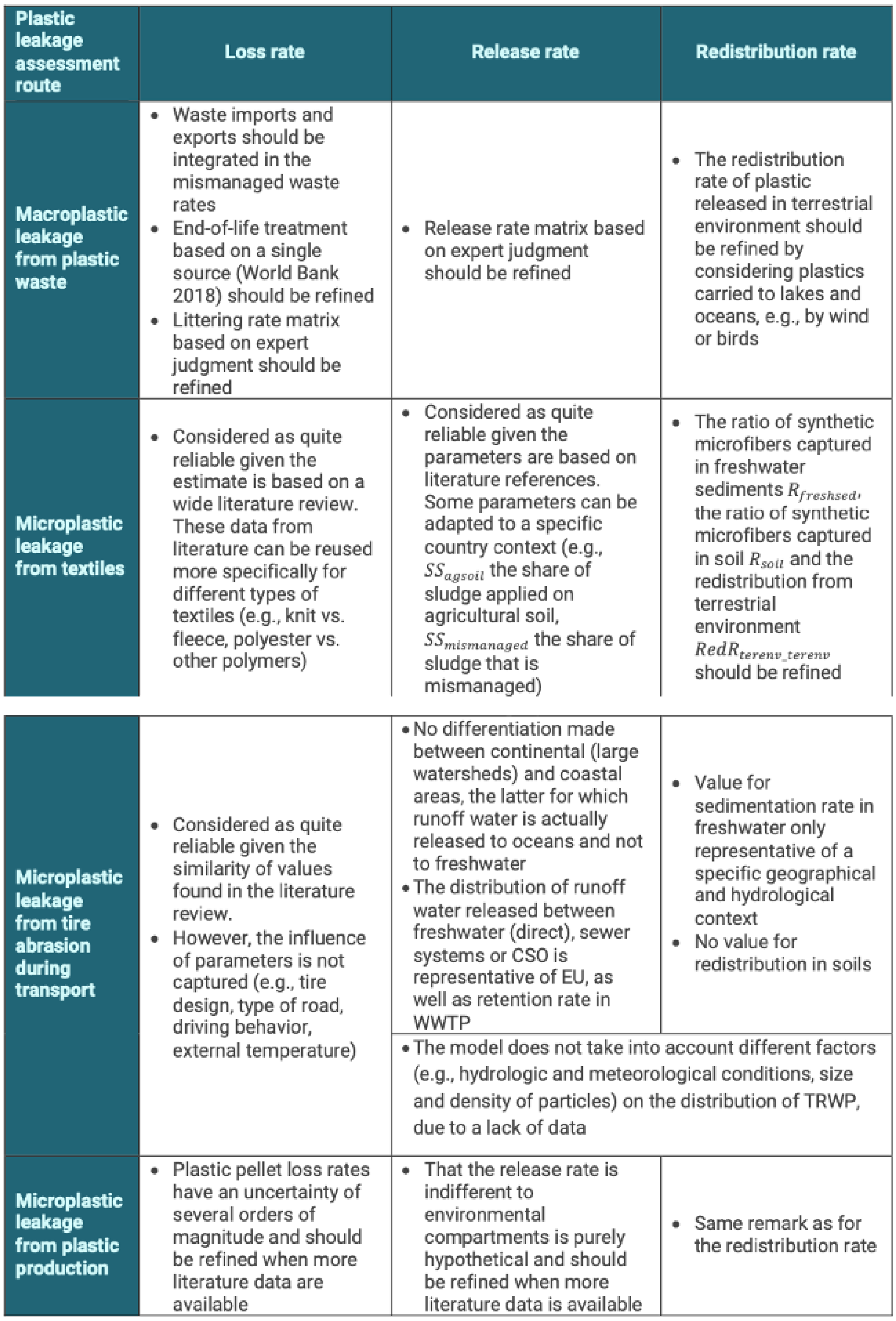
Table 2.2: estimates of the losses of pre-production plastics

By summing each stage reported in *Table 2.2*, values ranging from *0.0051%* to *0.2020%* were calculated. From this calculation, it was determined that the orders of magnitude for pellet loss rates range from *0.001%* to *0.1%*. Given the high level of uncertainty, it is suggested to use these orders of magnitude rather than the exact values. Due to this significant uncertainty and the considerable impact this value can have on the results, it is recommended to use a median order of magnitude value of *0.01%*.

2.8.6 Release and redistribution rates evaluation

It is assumed that the release and redistribution rates of pellet losses across different compartments follow similar pathways to those of microplastics from tire abrasion, except for the retention rate value in freshwater sediments, which is set at *30%* based on *Hurley et al., 2018*.

A retention rate of *30%* is assumed for river sediments, while a retention rate of *100%* is assumed for soil.



Plastic leakage assessment route	Loss rate	Release rate	Redistribution rate
Macroplastic leakage from plastic waste	• Waste imports and exports should be integrated in the mismanaged waste rates • End-of-life treatment based on a single source (World Bank 2018) should be refined • Littering rate matrix based on expert judgment should be refined	• Release rate matrix based on expert judgment should be refined	• The redistribution rate of plastic released in terrestrial environment should be refined by considering plastics carried to lakes and oceans, e.g., by wind or birds
Microplastic leakage from textiles	• Considered as quite reliable given the estimate is based on a wide literature review. These data from literature can be reused more specifically for different types of textiles (e.g., knit vs. fleece, polyester vs. other polymers)	• Considered as quite reliable given the parameters are based on literature references. Some parameters can be adapted to a specific country context (e.g., SS_{agsoil} the share of sludge applied on agricultural soil, $SS_{mismanaged}$ the share of sludge that is mismanaged)	• The ratio of synthetic microfibers captured in freshwater sediments $R_{freshsed}$, the ratio of synthetic microfibers captured in soil R_{soil} and the redistribution from terrestrial environment $RedR_{terenv\_terenv}$ should be refined
Microplastic leakage from tire abrasion during transport	• Considered as quite reliable given the similarity of values found in the literature review. • However, the influence of parameters is not captured (e.g., tire design, type of road, driving behavior, external temperature)	• No differentiation made between continental (large watersheds) and coastal areas, the latter for which runoff water is actually released to oceans and not to freshwater • The distribution of runoff water released between freshwater (direct), sewer systems or CSO is representative of EU, as well as retention rate in WWTP	• Value for sedimentation rate in freshwater only representative of a specific geographical and hydrological context • No value for redistribution in soils
		• The model does not take into account different factors (e.g., hydrologic and meteorological conditions, size and density of particles) on the distribution of TRWP, due to a lack of data	
Microplastic leakage from plastic production	• Plastic pellet loss rates have an uncertainty of several orders of magnitude and should be refined when more literature data are available	• That the release rate is indifferent to environmental compartments is purely hypothetical and should be refined when more literature data is available	• Same remark as for the redistribution rate

Figure 2.26: Key limitations for generic data supporting each plastic leakage

Results obtained from PLP analysis

In the following graphs, the results obtained from this guideline is summarized.

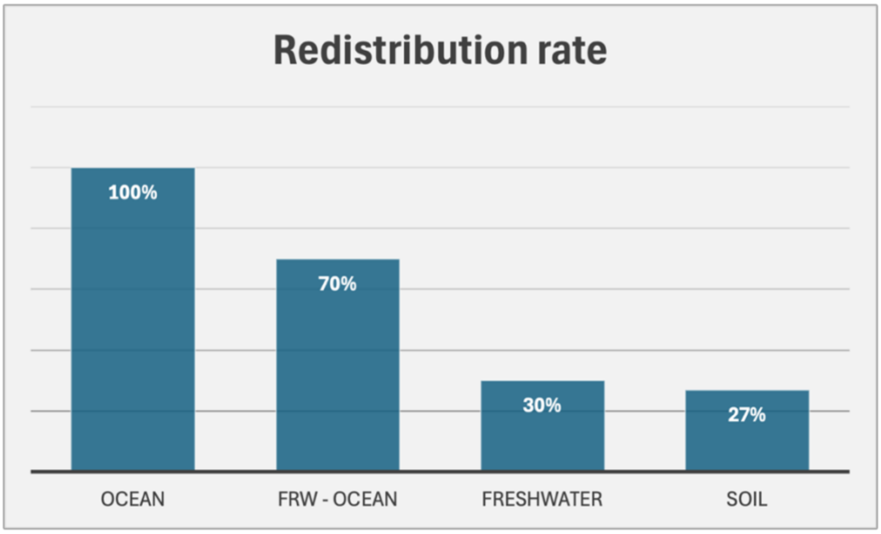


Figure 2.27: Redistribution rates

Figure 2.27 highlights the redistribution rates results. To better understand the meaning of these results, when the redistribution rate is *100%*, the microplastics remain in that compartment. In this case, the redistribution rate for ocean is *100%*, indicating that once microplastics reach the ocean, they remain there.

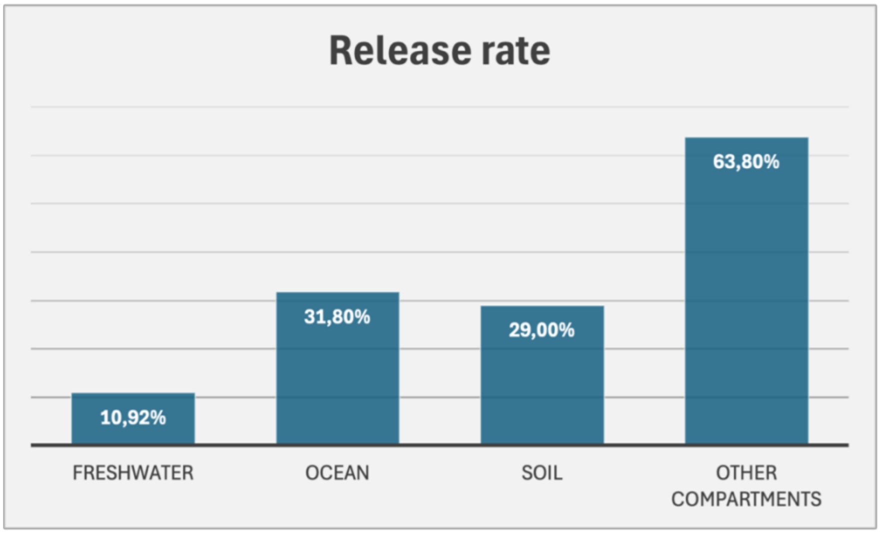


Figure 2.28: Release rates

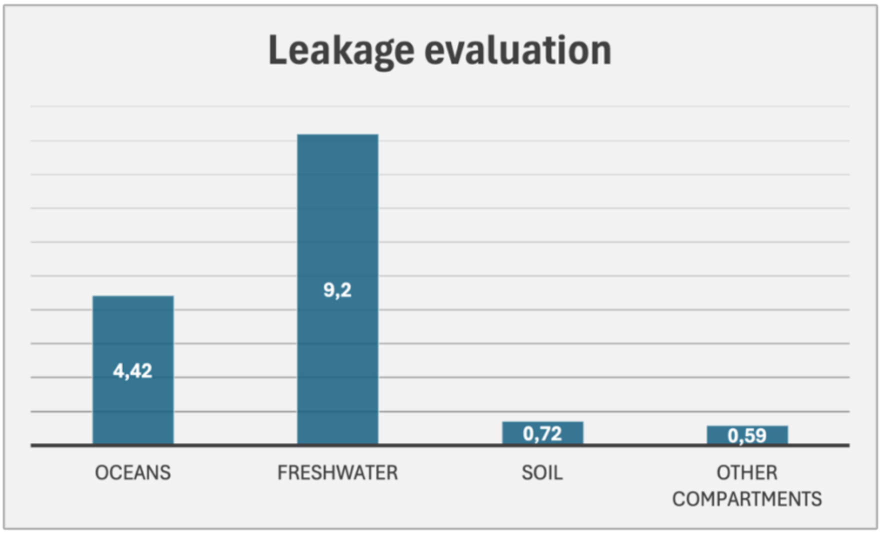


Figure 2.29: Leakage evaluation

Figure 2.29 puts in highlight the total amount of plastic leakage during a year. All the values are expressed in *milligrams per year*, evaluating a total amount of *14,92 mg/year*.

Chapter 3

Dispersion model

3.1 Introduction

Microplastics have been found in all environments: soil, water, air, polar regions, and within organisms. It is expected that concentrations will continue to increase across all compartments, but our understanding of how microplastics disperse in nature remains limited.

Microplastic emissions from shoe sole wear are primarily generated by the friction between the sole and the ground, leading to their release into the environment.
Several studies have shown that the particle size of microplastics from shoe wear, similar to tire wear on roads, varies in the micrometer range, meaning they can disperse through various pathways and media.

Microplastic particles can generally appear in many different shapes, ranging from round to fragmented, and their shape significantly affects how they are transported through different media.

Microplastics particles generated from the contact between the sole and the ground can either disperse into the atmosphere or remain in the soil (with only a small portion released into the air).

Runoff from roads often enters stormwater systems, where rain and meltwater from hard sur- faces like buildings and roads are channeled directly into streams, lakes, oceans, or stormwater collection facilities. Some stormwater is directed to wastewater treatment plants, where a significant portion of microplastics remains in the sludge. When sludge is used as fertilizer, it can contribute to microplastic contamination in agricultural soils.

Snow piles stored on land or dumped into water can also contain microplastics, which may then disperse to other areas. Microplastics that enter waterways can be transported to the ocean, although they are expected to settle primarily along the way.
Additionally, microplastics can be absorbed by plants, animals, and potentially by humans.

Atmospheric dispersion modeling involves the mathematical representation of how contaminants are transported and spread through the atmosphere.

In this context, dispersion refers to the combined effects of *diffusion*, caused by turbulent eddy motion, and *advection*, driven by the wind, that take place in the air near the Earth's surface. The distribution of a contaminant released into the atmosphere can thus be modeled using the *advection – diffusion equation*, a second – order parabolic partial differential equation (*PDE*).

3.2 Different air quality models

A *model* is a tool used to represent reality, enabling the prediction and description of the *evolution of real – world phenomena*.

It will be possible to talk about *mathematical model* whenever a mathematical relationship will be used and, in particular, it can be subdivided into other *two* categories: *deterministic models* and *stochastic models*.

Deterministic models are based on cause – and – effect relationships, and it is possible to predict the concentration trends of the pollutants over time. In contrast, *stochastic models* are used when real – time pollutant measurements are available, typically in urban and industrial settings where continuous monitoring is required.

Deterministic models are the most commonly used, with input variables being fixed values which do not take into account uncertainty factors, as stochastic models do[28].

Deterministic models

Deterministic models allow the prediction of the concentration trend of pollutants over time and can be further categorized into *two* different categories: *eulerian models* and *lagrangian models*.

The eulerian models are referred to a cartesian plan and they are based on *diffusion differential equation*. Depending on how the equation is solved, it is possible to have *analytical models* (puff and gaussian models), *box models* or *grid models*.

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[28] It is possible to do that if Monte Carlo method is used

- *Analytical gaussian models* are able to describe the concentration trend due to continuous point source, described with a gaussian law. Easy to use, they adopt steady state conditions and homogeneity for meteorological conditions; no chemical reactions are considered.
- *Puff models* represent an expansion of the gaussian models, and they allow to reconstruct the concentration trend under non – homogeneous and non - steady state conditions; every puff follows the gaussian law.
- *Box models* divide the domain in one or more cells where the pollutants are perfectly mixed. This simplifies a lot the equation to be solved to obtain the concentration value.
- *Grid models* also divide the domain in one or more three – dimensional cells in which it is possible to distinguish different nodes, and the solution of the equation is obtained through finite difference technique on every node.

Lagrangian models, instead, refer to mobile coordinate system and it is possible to distinguish other *two* categories: *trajectory models* and *particle models*.

Criteria for models' applicability

There are different characteristics which are able to describe the problem:

- *Spatial scale*: models are able to reproduce the trend of the different pollutants in different spatial scales and they can be divided into *microscale* (*100 m – 1 km*), *local scale* (*1 km – 100 km*), *mesoscale* (*100 km – 1000 km*), *regional scale* (*1000 km – 5000 km*) and *global scale* (all over the terrestrial surface).
- *Time scale*: application of *short – term* (for critical episodes) or *long – term* (for cumulative exposure).
- *Domain*[29]: it is possible to distinguish the different types of soil considering *flat lands* (completely flat domains) and *complex terrains*, which can be divided into *urban* and *rural lands*.
- *Pollutant*: it is divided into *gas*, *particle* or *aerosol* and it can be *inert* or *reactive*.
- *Meteorology*: a set of meteorological variables influences the atmospheric dispersion of pollutants. The velocity and direction of the winds, the atmospheric turbulence and eventual thermal inversion significantly affect the dispersion of materials; humidity and temperature have less effect. Meteorological conditions are typically aggregated in classes of stability:

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[29] Domain: it corresponds to the area interested by the simulation

according to *Pasquill – Gifford*[30], the classes are *seven*, ranging from *A*[31] (very unstable) and *G*[32] (extremely stable).

P – G class	Definition	Definition
A	Very unstable	Unstable conditions, promoted dispersion
B	Moderately unstable	Unstable conditions, promoted dispersion
C	Slightly unstable	Unstable conditions, promoted dispersion
D	Neutral	Neutral conditions, no significant effects
E	Slightly stable	Stable conditions, not promoted dispersion
F	Moderately stable	Stable conditions, not promoted dispersion
G	Extremely stable	Stable conditions, not promoted dispersion

Table 3.1: Classes of stability

The wind is significantly influenced by the topographical features of the area (urban heat islands, mountain valley winds, ...). The wind has an entrainment effect that leads to the dispersion of pollutants and information on the wind is provided by a wind rose[33]. Its velocity changes with the height above the ground in the atmospheric boundary layer, according to the following relation:

$$u_s(z) = u_{s,ref} \cdot \left(\frac{z}{z_{ref}}\right)^P \tag{3.1}$$

where $u_s(z)$ is the wind speed at height z [$m\ s^{-1}$], $u_{s,ref}$ is the wind speed at height z_{ref} [$m\ s^{-1}$], z is the height [m], P is the parameter depending on stability class and type of context [-]; below the table for parameter *P* is reported.

Stability class	Rural area	Urban area
A	0.07	0.15
B	0.07	0.15
C	0.10	0.20
D	0.15	0.25

---

[30] Pasquill-Gifford stability model, 1976

[31] Class A: tend to develop vertical updrafts, increasing turbulence.

[32] Class G: tend to suppress vertical updrafts, reducing turbulence.

[33] Frequency of the winds according to their direction and velocity.

E	0.35	0.30
F	0.55	0.30

Table 3.2: Table for parameter P

Concentration in the atmosphere is *inversely proportional* to wind speed, meaning that lower wind velocity results in less dilution and, consequently, higher concentrations. For this reason, turbulence enhances dispersion. There are *two* types of turbulence: *mechanical turbulence*, which occurs when wind moves towards obstacles, creating a "sharp" interaction between adjacent air layers, and *bouyant turbulence*, which happens when surface air is heated or cooled.

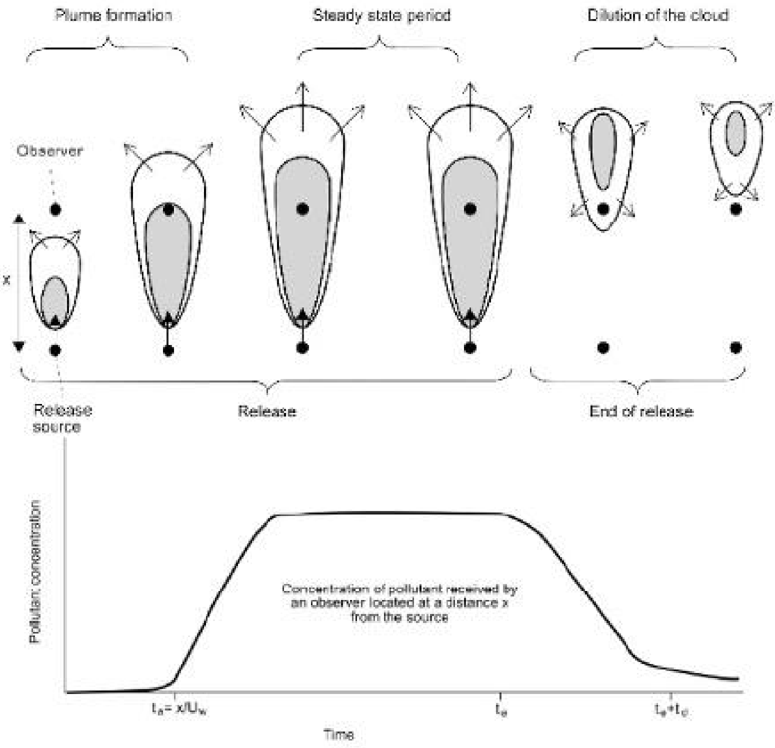

Figure 3.1: Differentiation between plume and puff

The release can also be either *instantaneous* or *continuous*. An instantaneous release (puff) occurs when the time required for the particles to diffuse to a specific site is greater than the duration of the release, typically lasting less than *1* minute.

In contrast, a continuous release (plume) happens when the release duration exceeds the time required for the particles to reach a specific site, typically lasting more than *1* minute, as described by the following expression:

$$\frac{u \cdot t_r}{x} \geq 2.5 \tag{3.2}$$

where:

u: velocity at distance x, *m/s*

t_r: release rate, *s*

x: downwind distance, *m*

- *Emission sources*: they are typically divided into point source or source with finite size (area, volume) and they can be on the ground, with H = 0, or at a height $H \neq 0$.

Within *EPA*[34], the reliability about dispersion models is based on *AERMOD*, *AERMOD PRIME*, *CALPUFF* and many others.

AERMOD and *CALPUFF* are *two* eulerian models: the first one is an analytical plume model, and the second one is an analytical puff model. These *two* are advised by *EPA* for a local usage (up to *50 km - 100 km*), the first one (AERMOD) for a stationary condition, while the second one (CALPUFF) for a non - stationary condition.

3.3 The algorithm of the model

The equation obtained through the mass balance, evaluated for an infinitesimal volume (*dxdydz*) in a defined time interval *dt*:

$$\frac{\partial C}{\partial t} = -\nabla(\nu C) + \nabla \cdot (K \cdot \nabla C) + \nabla \cdot (D \cdot C) - R + S \tag{3.3}$$

Where:

C: pollutant concentration at the receptor, g/m^3

ν: velocity vector of wind at the referred height, *m/s*

D: diffusivity coefficient, m^2/s

K: turbulent diffusivity tensor, m^2/s

R: removal term, $g/(m^3 \cdot s)$

S: source term, $g/(m^3 \cdot s)$

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[34] EPA: Environmental Protection Agency

In practice, to simplify *Equation 3.3*, different assumptions are made:

- Molecular diffusion negligible respect to the turbulence.
- Vertical component of the wind velocity negligible. This hypothesis cannot be taken into account in the case of complex terrain or sea breeze.
- Horizontal turbulent diffusivity coefficients K_{xx} and K_{yy} are independent by x and y, while K_{zz} depends on the vertical coordinate z. In some applications K_{xx} and K_{yy} are neglected.
- Removal term related to atmospheric chemistry, negligible if the pollutant is inert or slightly reactive.
- The wind transports the cloud.

Assuming these hypotheses, *Equation 3.3* is simplified as follows:

$$\frac{\partial c}{\partial t} + \bar{u}\frac{\partial c}{\partial x} + \bar{v}\frac{\partial c}{\partial t} = K_{xx}\frac{\partial^2 c}{\partial x^2} + K_{yy}\frac{\partial^2 c}{\partial y^2} + \left(\frac{\partial}{\partial z}\left(K_{zz}\frac{\partial c}{\partial z}\right)\right) + s(x,y,z,t) \qquad (3.4)$$

The gaussian model takes into account the following facts:

- The concentrations at a given point are directly proportional to the emission rate.
- Parallel to the x – axis, the concentrations are inversely proportional to wind speed.
- Parallel to the y – axis, the concentrations are inversely proportional to the plume cross- wind spreading.
- Parallel to the z – axis, the concentrations are inversely to the vertical plume spreading.

Getting the following relation:

$$\bar{c}(x,y,z) = \frac{\dot{m}}{\left(\sqrt{2\pi}\right)^2 u\sigma_y\sigma_z}\exp\left(-\frac{y^2}{2\sigma_y^2}\right)\left\{\exp\left[-\frac{(z-H)^2}{2\sigma_z^2}\right] + \exp\left[-\frac{(z+H)^2}{2\sigma_z^2}\right]\right\} \qquad (3.5)$$

Where:

c: concentration at the point (x, y, z), *kg/m*^{3}

(x, y, z): spatial coordinates with respect to the source of emission, *m*

$\dot{m}$: mass flow rate of the emission, *kg/s*

σ_y, σ_z: plume spreading (dispersion coefficients), *m*, which are function of the distance downwind and atmospheric conditions

H: effective height above the ground, *m*

The equation for the calculation of the dispersion coefficients σy and σz for a continuous emission:

Stability class	$\boldsymbol{\sigma_y\ (m)}$	$\boldsymbol{\sigma_z\ (m)}$
Rural conditions		
A	$0.22x(1+0.0001x)^{-0.5}$	$0.20x$
B	$0.16x(1+0.0001x)^{-0.5}$	$0.12x$
C	$0.11x(1+0.0001x)^{-0.5}$	$0.08x(1+0.0002)^{-0.5}$
D	$0.08x(1+0.0001)^{-0.5}$	$0.06x(1+0.0015)^{-0.5}$
E	$0.06x(1+0.0001)^{-0.5}$	$0.03x(1+0.0003)^{-1}$
F	$0.04x(1+0.0001x)^{-0.5}$	$0.016x(1+0.0003)^{-1}$
Urban conditions		
A – B	$0.32x(1+0.0004x)^{-0.5}$	$0.24x(1+0.0001x)^{+0.5}$
C	$0.22x(1+0.0004x)^{-0.5}$	$0.20x$
D	$0.16x(1+0.0004x)^{-0.5}$	$0.14x(1+0.0003)^{-0.5}$
E – F	$0.11x(1+0.0004)^{-0.5}$	$0.08x(1+0.0015x)^{-0.5}$

Table 3.3: Dispersion coefficients (the distance x is in meters)

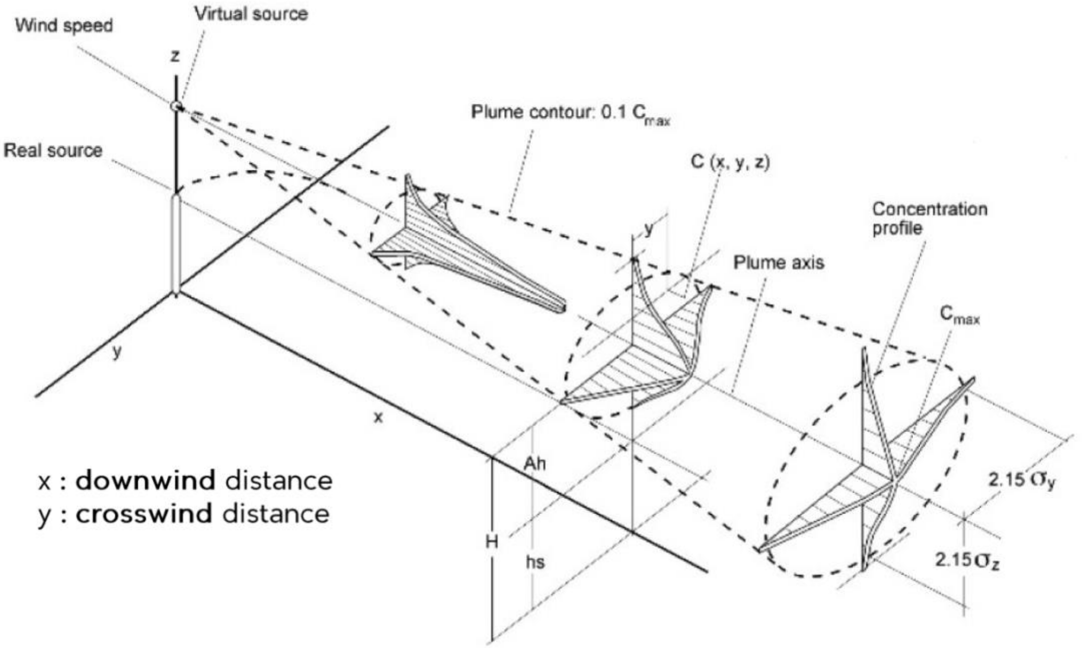

Figure 3.2: Gaussian model: dispersion model

According to the basic concept of *Gaussian model*, the cloud is transported by the wind, and the time – averaged concentration profiles in the crosswind direction (perpendicular to the transport direction) can be represented by a *Gaussian or normal distribution*.

3.4 Puff models

Puff models allow the simulation of pollutant behavior under *non - homogeneous* and *non - stationary* conditions. The emission is discretized into a series of individual puffs. Each of these units is transported within the computational domain for a certain time interval by the wind field present at the puff's centroid at a given moment. Turbulent diffusion is simulated by assuming that the pollutant is distributed within each individual unit according to a Gaussian distribution (a distribution that varies in space and time). The dispersion coefficients in the three directions are functions, as in the Gaussian case, of the distances and the dispersive characteristics of the atmosphere. The concentration at a given time t is the sum of the contributions of each individual puff.

With this model, it is also possible to simulate *calm of wind*, which is set by the user during the simulation, and complex terrain.

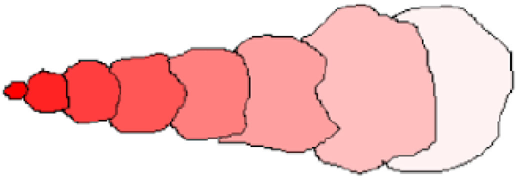

Figure 3.3: Decomposition from plume to puff

3.5 CALPUFF system

CALPUFF model is a *non – stationary*, *multilayer* and *multi – species model*. The pollutants diffusion is simulated considering a series of puffs, in which the pollutant distribution is the one of the *gaussian* model; it can be applied for short and long distances (up to *hundreds* of kilometers).

It is composed of *three* main components which constitute a pre – processor for meteorological data, a processor for the real calculus and a post – processor. The *three* main processors mentioned are *Calmet* (3D weather model), *Calpuff* (dispersion model) and *Calpost* (post – processing system which analyses the results obtained).

3.5.1 Calmet

The *Calmet* component is a meteorological model capable of generating wind fields that vary both temporally and spatially, and it is the starting point for the actual simulation model. This meteorological preprocessor considers factors like terrain elevation, land use, and meteorological conditions to create realistic simulations of how wind patterns influence pollutant dispersion.
The required data as input are meteorological data at the ground (wind, temperature, pressure, ...) and data on the water surfaces, when these are present.

The diagnostic model for calculating wind fields uses a *two – phase* algorithm. In the *first phase*, an initial estimate of the wind field is modified based on the kinematic effects of the terrain. After, in the *second phase*, the data observed by the weather stations are introduced into the field produced by phase *1*, thus obtaining the final wind field. However, there is the possibility of using wind fields produced by prognostic meteorological models as input.

One advantage of Calmet is its flexibility, allowing for the integration of both diagnostic and prognostic wind fields. This enhances the accuracy of the dispersion model, particularly in the alpine environment, where terrain influences wind patterns significantly.

3.5.2 Calpuff

The *Calpuff* model itself is the actual dispersion model and it is one of the most known and used puff models. It simulates the transport and dispersion of pollutants.
The model can use as input data the *three – dimensional meteorological fields* produced by *Calmet* or, alternatively, data coming from single monitoring stations of atmospheric parameters in a format compatible with other stationary *Gaussian models*.

It is capable to:

- treat point sources, as well as linear, areal, volumetric ones with variable characteristics over time
- treat complex meteorological conditions
- simulate a variable domain, in terms of extent

Since it is especially well - suited for complex terrain and non - stationary meteorological conditions, it is ideal for alpine environment. Unlike simpler models that assume constant conditions, Calpuff is capable of handling changing weather patterns and different types of pollutant sources.

3.5.3 Calpost

Calpost processes the primary output of the model, *i.e.*, the file with the hourly values of the pollutant concentration at the receptors, to obtain summary tables with the parameters of interest for the various case studies.

The function of this post processor is to analyze the *CALPUFF* output in order to extract the desired results and schematize them in a format which is suitable for good visualization.

3.6 Case study: PUR dispersion starting from Passo Giau

The simulation with *Calpuff* was applied to a real case, specifically in the *alpine environment* of *Passo Giau*.

Passo Giau is an alpine pass in the Dolomites, located at *2236 meters* in the province of *Belluno*, between the *Boite Valley* and the *Cordevole Valley*. It connects the municipalities of *Colle Santa Lucia* and *Selva di Cadore* with *Cortina d'Ampezzo*, and serves as the starting point for several hikes, including one to the *Mondeval Archaeological Site* and *Lago delle Baste*, making it one of the most popular destinations.

Figure 3.4: Passo Giau location in the map

Several assumptions were made to configure the software.

According to *ARPAV* guidelines, conducting a modeling study requires following certain rules. One of these is to apply precautionary assumptions in order to assess the maximum impact of the project under review. It is essential to report all the data and information necessary for the regulatory body to evaluate and, if needed, replicate the simulations using the same dispersion model or an alternative one (*e.g.*, data characterizing the emission sources input to the simulation model, the settings of the modeling chain, etc.). It is recommended to present the modeling inputs used in the simulation in a summarized format as well.

It is also important to always specify the physical state of the pollutant considered in the analysis (gas or particulate).

Regarding georeferencing, all significant elements of the impact study (sources, receptors, calculation grid, buildings, etc.) must be georeferenced within the same coordinate system. The use of a *Cartesian plane coordinate system* (*x, y*), specifically the *WGS84/UTM* Zone 32/33N reference system, is recommended.
Alternatively, geographic coordinates (latitude, longitude) based on the *WGS84* reference system can be used.

3.6.1 Model settings

Domain

Let's begin by analyzing and setting the domain: since the site of interest is located in the *Northern Italy*, the *WGS84/UTM* Zone is *33N.* To perform an optimal and precise evaluation, the domain is discretized into a *150*x*150* grid, with cell size of *100 meters*[35]. The origin is set starting from the South - West at *X(m): 269277; Y(m): 5149144*.

Four receptors have also been placed at different positions, and all set at the same altitude (*2236 m*):

- *Rec. 1*: X(m): *273708*; Y(m): *5152100*
- *Rec. 2*: X(m): *274000*; Y(m): *5152100*
- *Rec. 3*: X(m): *276000*; Y(m): *5150000*

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[35] Nesting factor: 1; Indices along x and y of the sampling grid from 1 to 150

- *Rec. 4*: X(m): *276727*; Y(m): *5156594*

Each receptor is positioned at ground level, at *0 meter*.

Regarding the source of the pollutant emission, an *aerial source* is considered, with the following points defined (listed *clockwise*, without crossing):

P1:	*271958,5*;	*5153854,5* (m)
P2:	*275831,5*;	*5153854,5* (m)
P3:	*275831,5*;	*5149981,5* (m)
P4:	*271958,5*;	*5149981,5* (m)

The surface area considered is equal to 15 *km*^{2}.

General settings for calculus

For the orography management mode, a *partial plume penetration correction* is applied. If a plume penetrates a high – level inversion, the pollutant concentration is significantly reduced, as the inversion aloft strongly inhibits diffusion toward the ground. In the opposite case, if the plume becomes trapped beneath the inversion, pollutant concentrations at ground level increase significantly.

In general, *Gaussian models* do not evaluate a plume's ability to penetrate a high – level inversion; instead, inversions typically act as upper boundaries, reflecting the plume back toward the ground.

The coefficients used in the partial plume penetration correction are the following:

- A: *0.5*
- B: *0.5*
- C: *0.5*
- D: *0.5*
- E: *0.35*
- F: *0.35*

For the evaluation of the dispersion coefficients, the *Pasquill Gifford* classification for rural areas is used (*Table 3.3*). The wind limit for calm conditions is set at *0.5 m/s*.

Emission evaluation

All emissions are assumed to be *continuous*, following an *hourly cycle* with *24* emission factors. It is assumed that tourists begin their excursions at *8:00 AM* and finish at *4:00 PM*, with an emission rate of $5.83 \cdot 10^{-8}\ g/s$ per *100* people.

This value has been calculated considering that *one* person, from the soles of their shoes, emits *9.2 mg* of *PUR* per year, equivalent to $5.04 \cdot 10^{-4}\ g/day$ per person for *two* soles.

For this specific case, an average of 4.5 *hours* of walking per person[36] has been considered, with an estimated *100* tourists per day during the winter period, as there is no precise count available (*e.g.*, from ticket offices or similar sources).

For *100* people, the emission rate is calculated as: $\dot{m} = 2.1 \cdot 10^{-4} \frac{\frac{g}{h}}{100\, people} = 5.83 \cdot 10^{-8} \frac{g/s}{100\, people}$.

3.6.2 Results

The results obtained are the ones reported below.

Figure 3.5 and *Figure 3.6* show the trend of the concentration, specifically the maximum trend reached in one hour (during the peak hour, 12:00 AM - 01:00 PM).

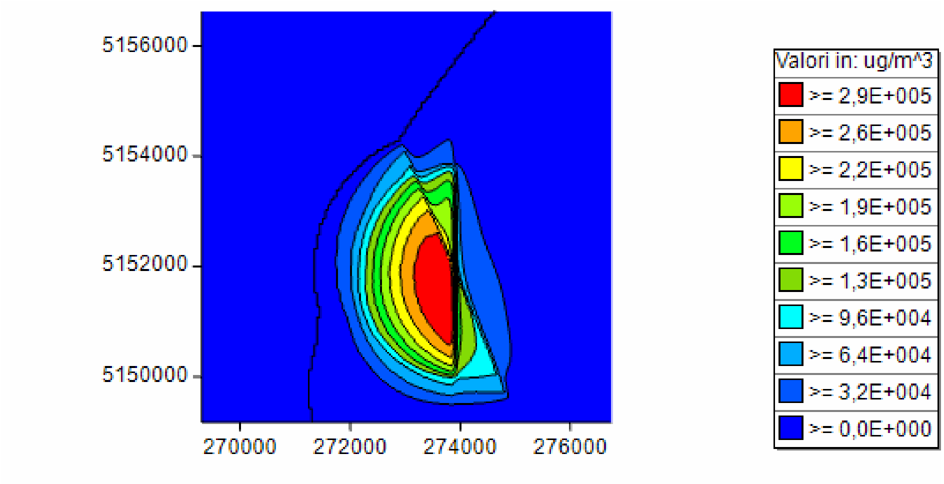

Figure 3.5: Maximum concentration reached in 1 hour, 12:00 AM - 01:00 PM

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[36] Value estimated from Belluno Dolomites website

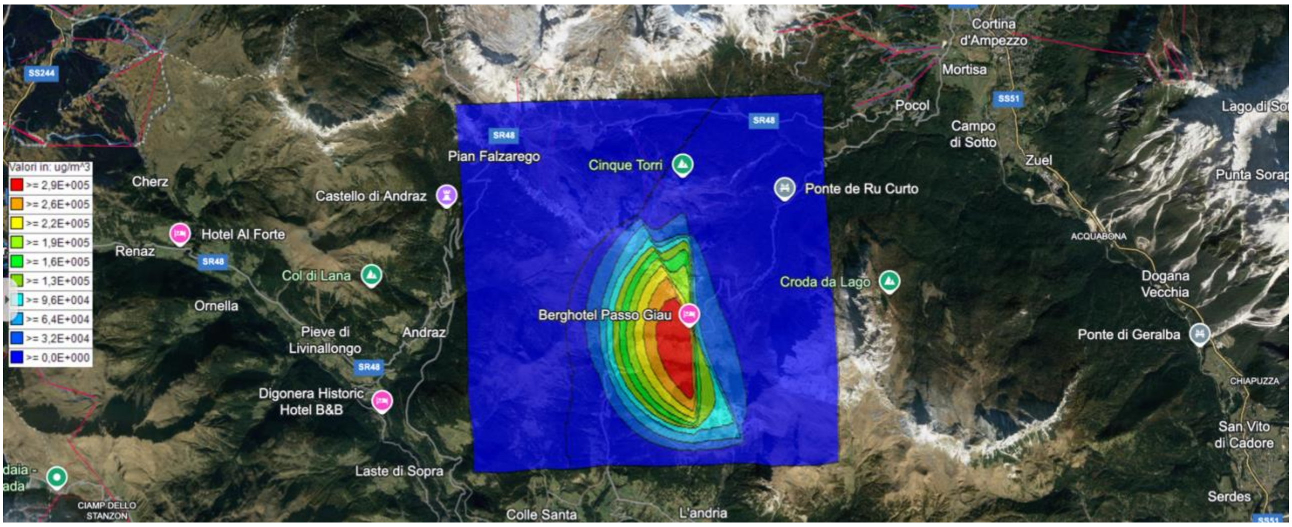

Figure 3.6: Maximum concentration reached in 1 hour, 12:00 AM - 01:00 PM, map from Google Earth

The modeling shows that the maximum concentration of *PUR* particles occurs during peak hours, particularly between *12:00 AM* and *1:00 PM*, when tourist activity is at its highest. The calculated concentration for this *one - hour* window illustrates how local conditions, such as increased human movement, directly contribute to heightened levels of particle release. This is particularly significant in areas like *Passo Giau*, where popular trekking routes lead to concentrated microplastic emissions in localized hotspots.

Figure 3.7 and *Figure 3.8* show the trend of the concentration, specifically the maximum concentration reached by the PUR in a day.

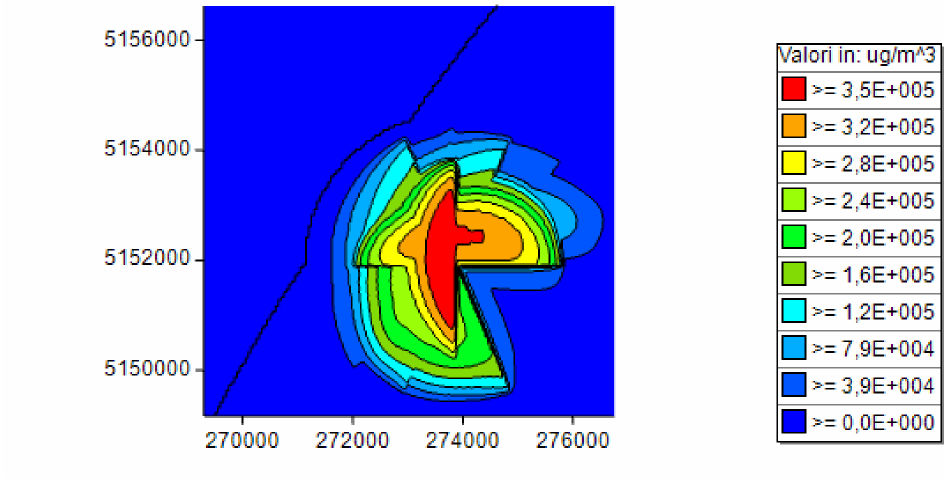

Figure 3.7: Maximum concentration reached in a day

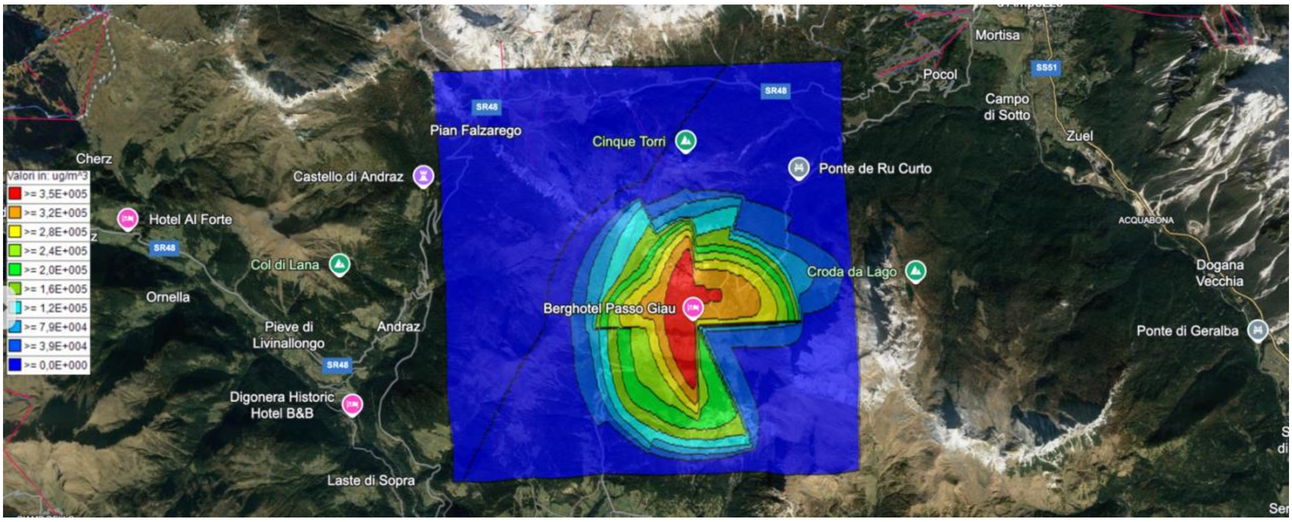

Figure 3.8: Maximum concentration reached in a day, map from Google Earth

The second part of the analysis evaluates the maximum concentration over a *full day*, highlighting the persistence of *PUR particles* in the environment long after peak activity periods have ended. While emissions peak during midday, the data shows that microplastic concentration levels remain elevated throughout the day.

The map overlays of these concentration trends illustrate how microplastic particles disperse across broader areas, influenced by terrain features and wind patterns.

Figure 3.9 and *Figure 3.10*, instead, show the trend of the average concentration reached by the *PUR* in *10 days*.

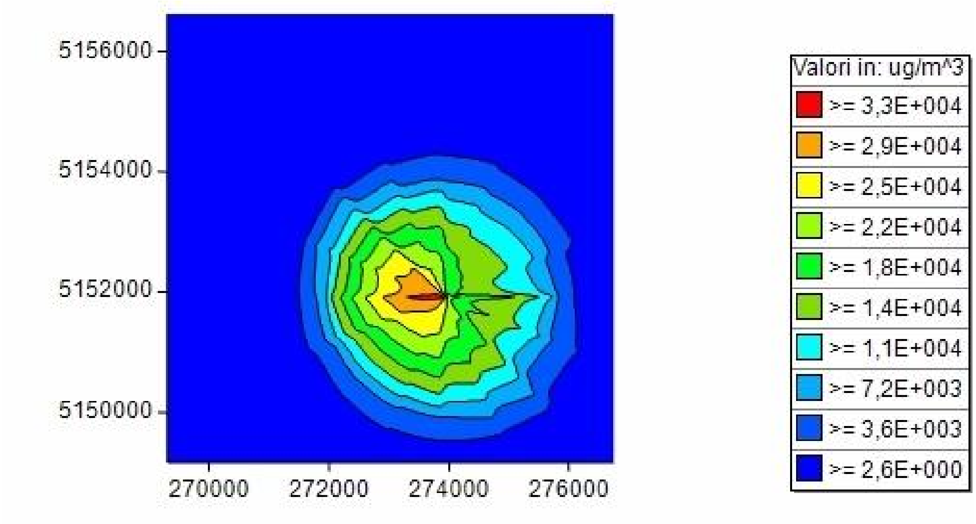

Figure 3.9: Average concentration reached in 10 days

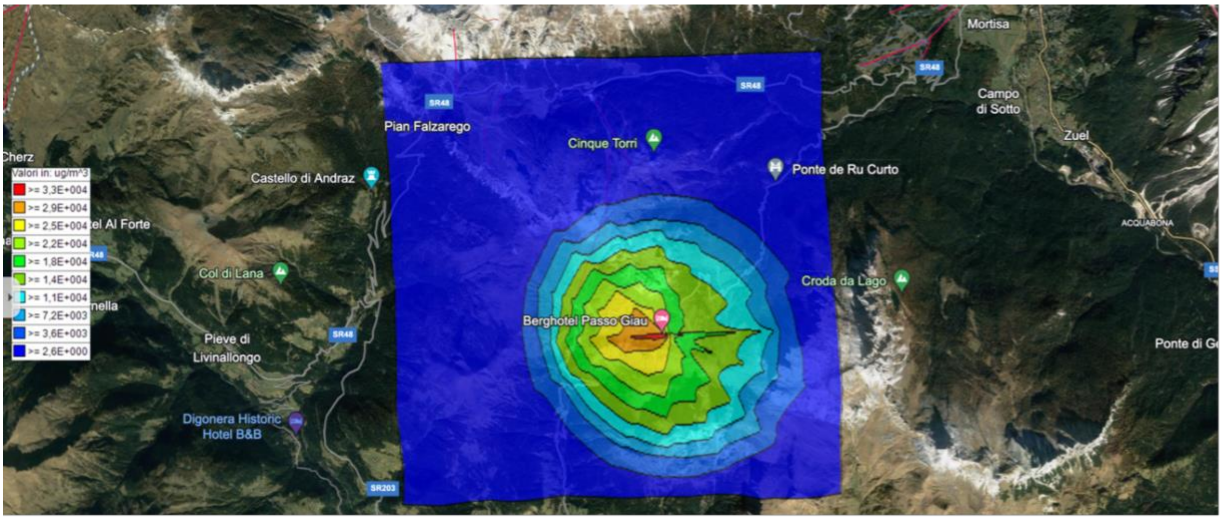

Figure 3.10: Average concentration reached in 10 days, map from Google Earth

The evaluation of average concentrations over a *10 – day* period offers deeper insights into the cumulative impact of *PUR* dispersion in the environment. Unlike the short – term peak emissions seen in hourly and daily data, the *10 – day* average shows the settling behavior of microplastics in alpine terrains, with a more even distribution across various environmental compartments such as soil and freshwater systems.

This prolonged period of analysis reinforces the concern about microplastic persistence. The fact that microplastics continue to accumulate and remain detectable in the environment even after several days suggests that these particles can become embedded in the ecosystem, leading to long – term contamination.

The total deposition has also been evaluated.

Figure 3.11 and *Figure 3.12* show the trend of the total deposition reached in *one hour*, considering the same period as before.

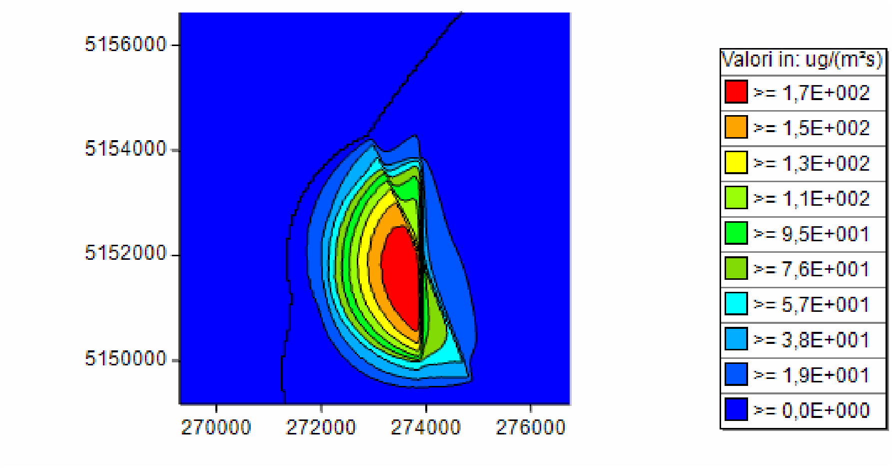

Figure 3.11: Deposition trend in one hour, 12:00 AM – 01:00 PM

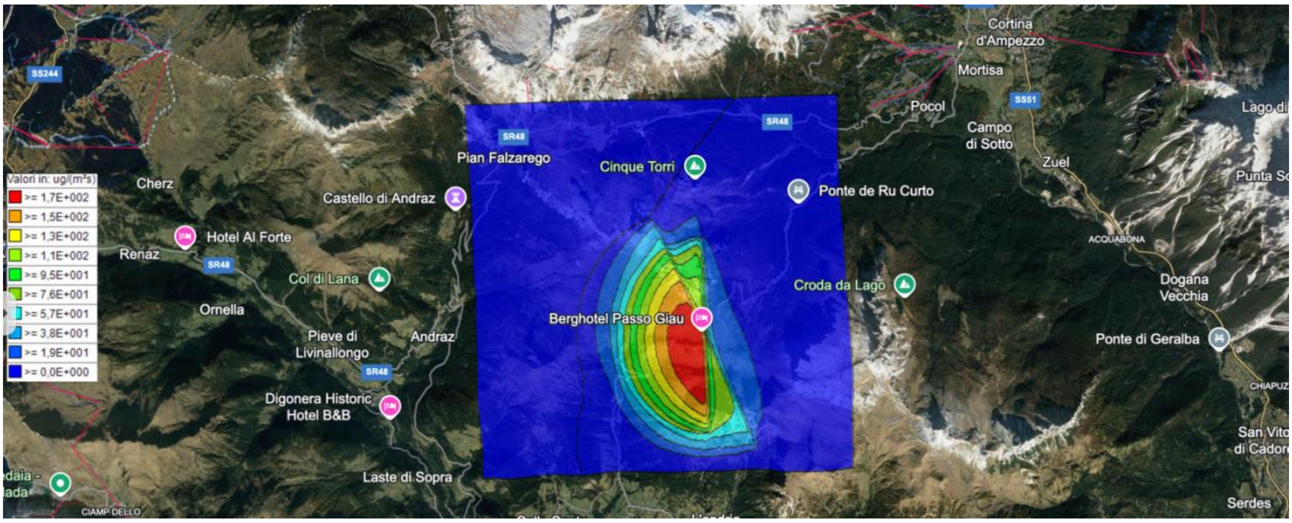

Figure 3.12: Deposition trend in one hour, 12:00 AM – 01:00 PM

Figure 3.13 and *Figure 3.14* show the trend of the maximum total deposition reached in *one* day by *PUR*.

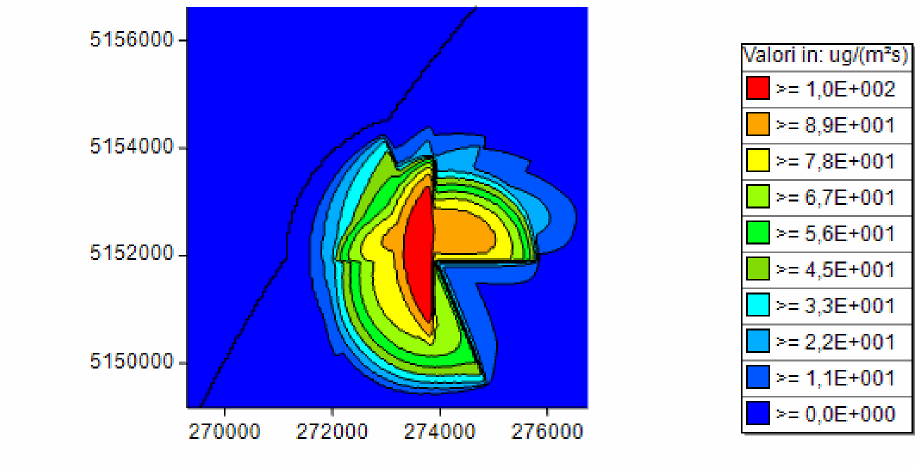

Figure 3.13: Maximum deposition reached in a day

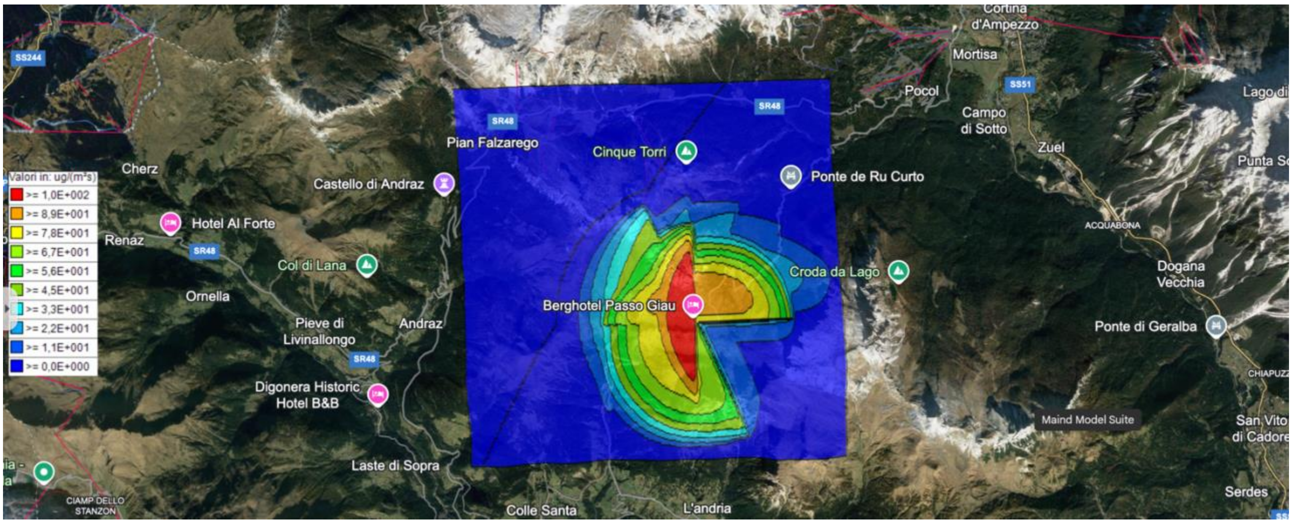

Figure 3.14: Maximum deposition reached in a day, map from Google Earth

Figure 3.15 and *Figure 3.16* show the average total deposition reached in *one day* by *PUR*.

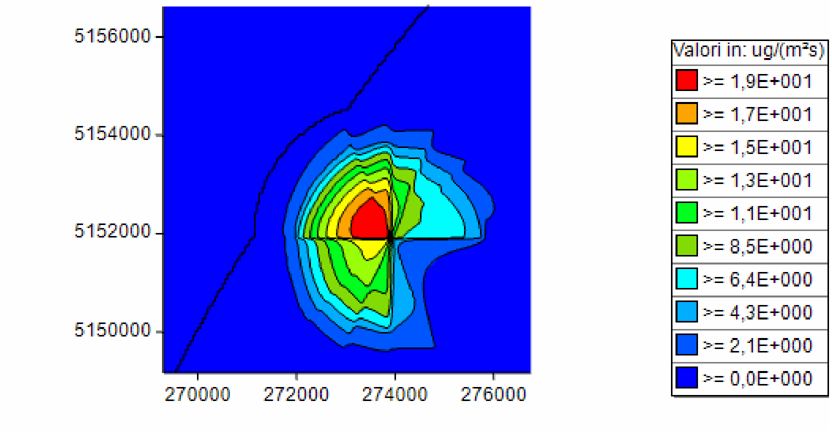

Figure 3.15: Average deposition reached in a day

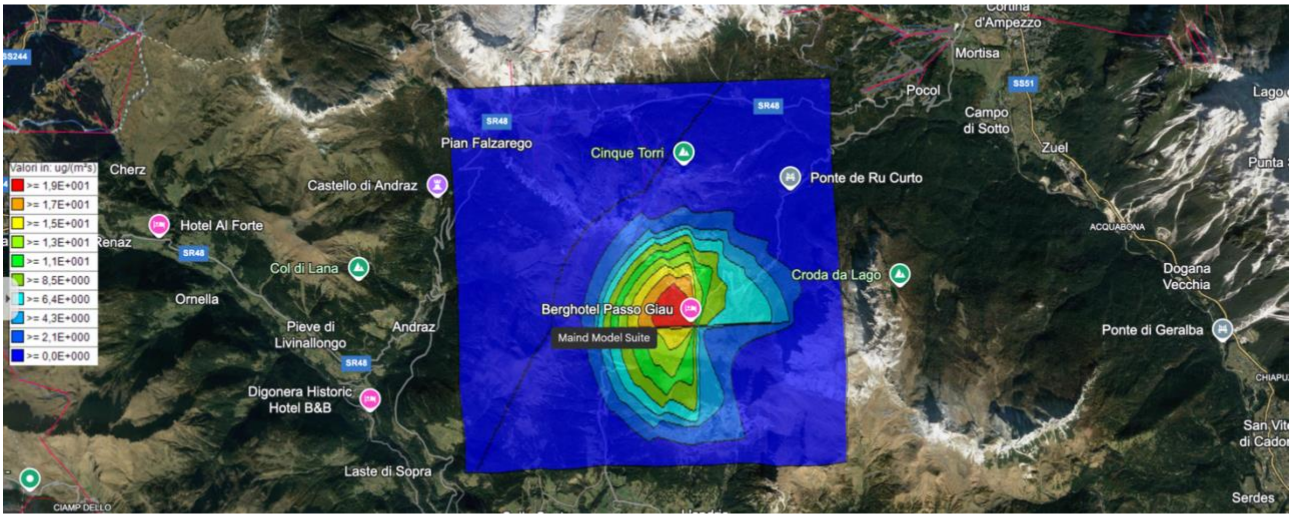

Figure 3.16: Average deposition reached in a day, map from Google Earth

Figure 3.17 and *Figure 3.18* show the average total deposition reached in *10* days.

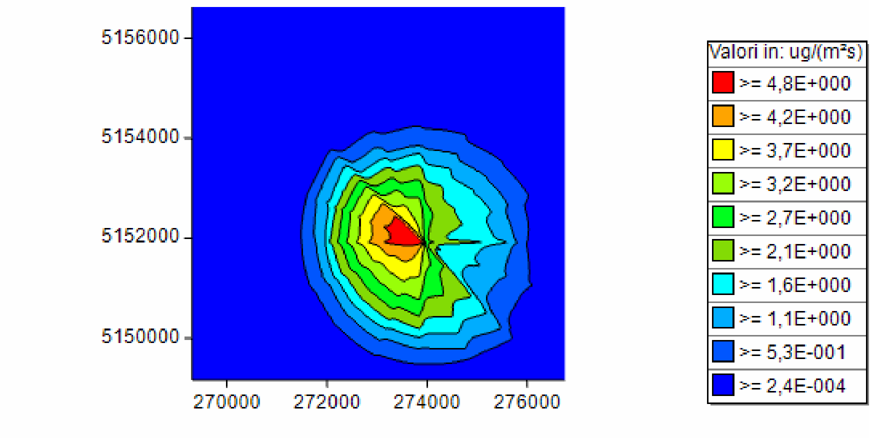

Figure 3.17: Average total deposition reached in 10 days

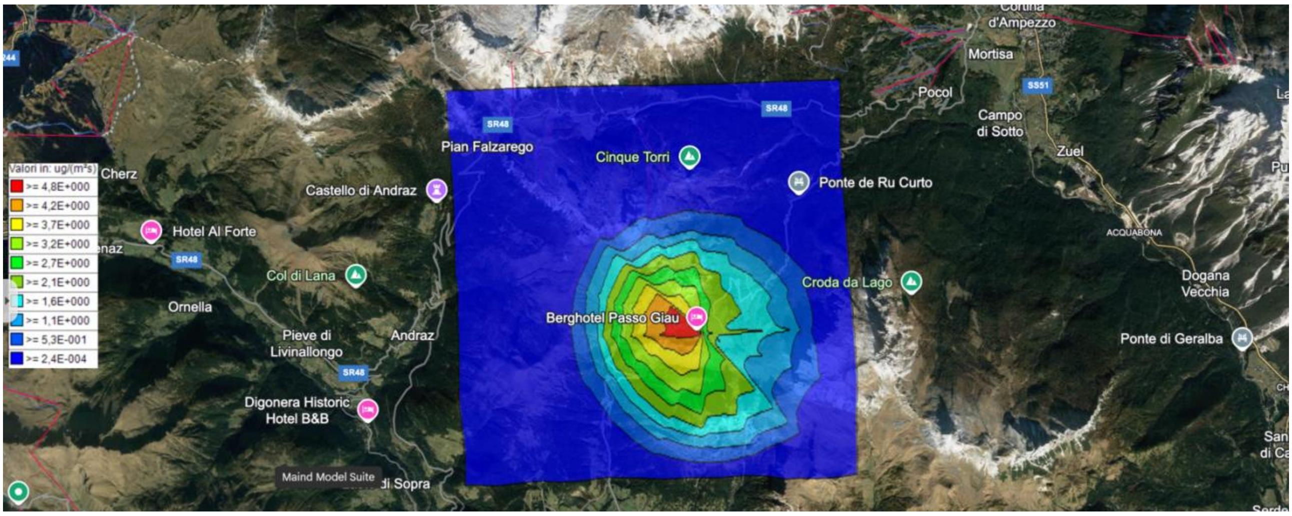

Figure 3.18: Average total deposition reached in 10 days, map from Google Earth

To conclude, *Figure 3.19* and *Figure 3.20* show the maximum total deposition reached in *10 days* by *PUR*.

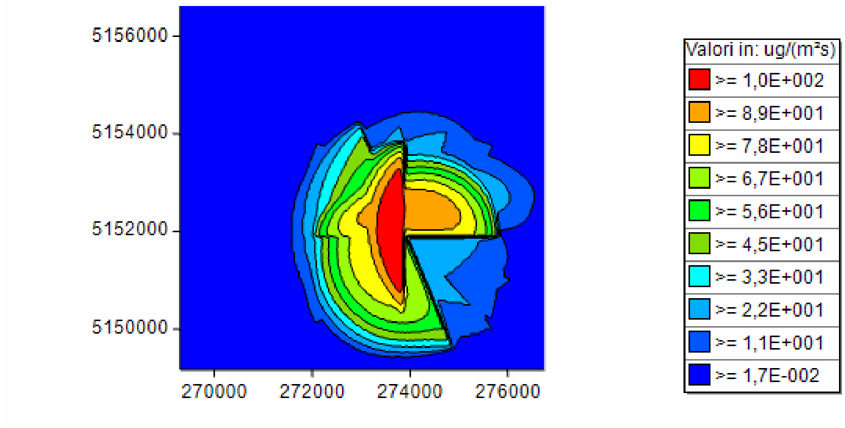

Figure 3.19: Maximum total deposition reached in 10 days

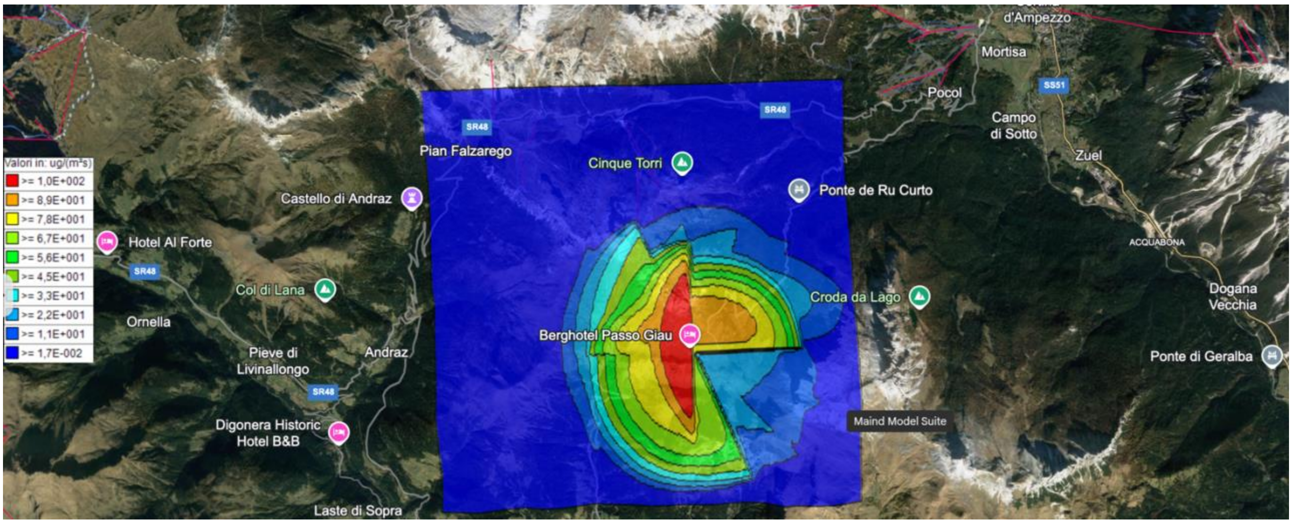

Figure 3.20: Maximum total deposition reached in 10 days

The final part of the analysis focuses on deposition trends — how much *PUR* is actually settling into the ground or water surfaces. The deposition results reveal that most *PUR* particles released during walking activities tend to settle close to their source. The total deposition evaluated over *one hour*, *a full day*, and over *10 days* suggests that areas with high foot traffic, such as tourist trails and popular hiking routes, are at a higher risk of accumulating plastic pollution over time.

3.6.3 PUR concentration evaluation at the sea

Considering the *Gaussian model equation* related to the evaluation of concentration (*Equation 3.5*), it is possible to estimate the concentration of *PUR* particles that reach at the nearest sea.
In this case study, the nearest sea to Passo Giau is *Jesolo Lido*, located *117.6 km* away. Assuming an average constant wind velocity of *1.1 m/s*, using a *MATLAB* code (see *Appendix A*), it was calculated that *PUR* particles would reach the sea after *29.7 hours*, with a concentration of $1.21 \cdot 10^{-16}\ kg/m^3$.

3.6.4 Soil dispersion modeling

It is assumed that the soil is divided into *three* different types: mountain soil, hilly soil and flat land. It is also important to highlight that the following calculations are based on several assumptions.

Water retention in alpine environment is very low; for this reason, it is assumed that *gravel* is the main component of Dolomitic soil, with a hydraulic conductivity of $k = 10^{-4}\ m/s$, typical of the gravel.

The hydrolic gradient is assumed to be $i = 0.02$, typical of moderate mountain slopes.

The effective porosity, instead, is considered to be $n_e = 0.25$, which is also typical for mountainous regions.

Using these data, the following result can be obtained:

$$v_e = \frac{k \cdot i}{n_e} = 8 \cdot 10^{-6}\, m/s \tag{3.6}$$

This means that *0.69 meters* are travelled each day by the aquifer, and thus by the particles. In this case study, the aquifer travels approximately *44.19 km* through mountain soil, specifically:

$$t = \frac{d}{v_e} = \frac{44190\, m}{8 \cdot 10^{-6}\, m/s} = 5.52 \cdot 10^{9}\, s \rightarrow 175\, years \tag{3.7}$$

Considering that 1 $year = 3.156\ \cdot 10^{7}\, s$.

For Venetian hills, soil varies from clayey, sandy and limy, so:

- $k = 5 \cdot 10^{-5}\, m/s,$ typical for sand or light gravel
- $i = 0.005$, moderate value for hills
- $n_e = 0.35$, typical for sand or gravel
- $d = 12.71\, km = 12710\, m$

Getting:

$$v_e = \frac{k \cdot i}{n_e} = 4.29 \cdot 10^{-6}\, m/s \tag{3.8}$$

This means that the aquifer travels *0.37 m/day*. And so:

$$t = \frac{d}{v_e} = \frac{12710\, m}{4.29 \cdot 10^{-6}\, m/s} = 2.96 \cdot 10^{9}\, s \rightarrow 93.8\, years \tag{3.9}$$

For Venetian flat land, the typical soil is sandy, clayey and also silt is present.

The following parameters are used:

- $k = 10^{-4}\, m/s,$ typical for well-assorted sand
- $i = 0.005$, typical for Venetian flat, with very low slope
- $n_e = 0.35$, typical for sand
- $d = 60.7\, km = 60700\, m$

And the following result is obtained:

$$v_e = \frac{k \cdot i}{n_e} = 1.67 \cdot 10^{-6}\ m/s \tag{3.10}$$

This means that the aquifer travels *0.14 m/day*, and getting at the end:

$$t = \frac{d}{v_e} = \frac{12710\ m}{4.29 \cdot 10^{-6}\ m/s} = 2.96 \cdot 10^{9}\ s \rightarrow 93.8\ years \tag{3.11}$$

At the end, the aquifer needs *1421.36* years to reach the nearest sea.

The total amount released during this period, specifically 4.481 · 1010 s, can be calculated in this way:

$$M_{tot} = Q \cdot t = 5.83 \cdot 10^{-8}\, {}^{g}/_{s} \cdot 4.481 \cdot 10^{10} s = 2612.57\ g = 2.6\ kg_{PUR} \tag{3.12}$$

Generally, *polyurethane* is not soluble in water and, since it is a polymer, *precursors* are usually taken into account for calculating the octanol – water partition coefficient; among these, *polyol* and *isocyanate*.
This is due to the fact that the octanol – water partition coefficient is available in literature just for simple components and not for polymer, so complex compounds.

The *n-octanol – water partition coefficient* (K_{ow}) is a measure of how a substance distributes itself between *two* immiscible phases: n-octanol and water. Commonly represented by the symbol *P* in *English literature*, K_{ow} is also known as the *n-octanol – water partition ratio*.

K_{ow} quantifies the balance between a substance's lipophilicity (its affinity for fat – like solvents such as n-octanol) and hydrophilicity (its affinity for water). A K_{ow} value greater than 1 indicates that a substance is more soluble in n-octanol, while a value less than 1 suggests higher solubility in water.

In cases where a substance exists in multiple chemical forms within the octanol – water system due to processes like association or dissociation, each form is assigned its own specific K_{ow}.

Its values are commonly used to evaluate the environmental behavior of persistent organic pollutants. Substances with high K_{ow} values tend to accumulate in the fatty tissues of organisms, a process known as bioaccumulation. According to *EPA*, chemicals with a $logK_{ow}$ higher than *3.5* are considered to be potentially dangerous for the environment, as a substance with an affinity for the organic phase, it binds stably to organic material and is difficult to desorb.

K_{ow} values also help estimate how a substance distributes within cells, particularly between the lipophilic bio membranes and the aqueous cytosol.

Isocyanates and *polyols* have very high K_{ow} partition coefficients, highlighting their *insolubility*. As a result, *PUR*, the polymer formed from these *two* substances, is also insoluble in water. To confirm this, the partition coefficient is calculated.

Typically, for calculating the partition coefficient, its *main precursor* is used, namely *MDI*[37], which has a high partition coefficient value. This indicates poor water solubility and a greater tendency to form bonds with fats. This type of precursor, when reacting with *polyols*, is capable of forming *polyurethane*.

In the literature, according to the safety data sheet, the *octanol – water partition coefficient* (K_{ow}) is:

$$\log K_{ow} = 4.51 \tag{3.13}$$

According to the *EPA*, as mentioned previously, compounds with $\log K_{ow} > 3.5$ should be considered potentially hazardous to the environment.

Their tendency to accumulate in fatty tissues can be significant. Based on the regression by *Karickhoff et al., 1979*, for contaminants that are primarily aromatic compounds, it is possible to evaluate the organic carbon - water partition coefficient K_{oc} thanks to the following correlation:

$$\log K_{oc} = a \log K_{ow} + b = \log K_{ow} - 0.21 = 4.3 \tag{3.14}$$

This correlation allows to evaluate partition coefficient of organic carbon, which is equal to $K_{oc} = 10^{4.3} = 19952.62\ l/kg$.

The organic carbon water partition coefficient K_{oc} is a dimensionless number defined as the ratio of a chemical's concentration absorbed per unit mass of soil, to its concentration in the aqueous phase. It represents the distribution coefficient normalized to total organic carbon content.

The following table (*Table 3.4*) summarizes the equations that can be used for evaluating the partition coefficient of organic carbon based on different compounds.

---

[37] MDI: methylene diphenyl diisocyanate

Authors	$\log K_{oc} = a \log K_{ow} + b$	r^2	Pollutants
Kenaga & Goring, 1978	$\log K_{oc} = -0.55 \log S_1 + 3.64$	0.71	106 contaminants of different nature
	$\log K_{oc} = 0.55 \log K_{ow} + 1.37$	0.74	45 contaminants of different nature
Karickhoff et al., 1979	$\log K_{oc} = -0.54 \log S_2 + 0.44$	0.94	10 contaminants, mainly aromatic compounds and polycyclic aromatics
	$\log K_{oc} = \log K_{ow} - 0.21$	1.00	10 contaminants, mainly aromatic compounds and polycyclic aromatics
Chiou et al., 1979	$\log K_{oc} = -0.557 \log S_3 + 4.277$	0.99	15 contaminants, chlorinated hydrocarbons

Table 3.4: Correlation equations of Koc as a function of other chemical - physical parameters (Clarke et al., 1990)

Considering only the mountainous area, the organic carbon fraction (f_{oc}), with data retrieved from *ARPAV*, is *5%*.

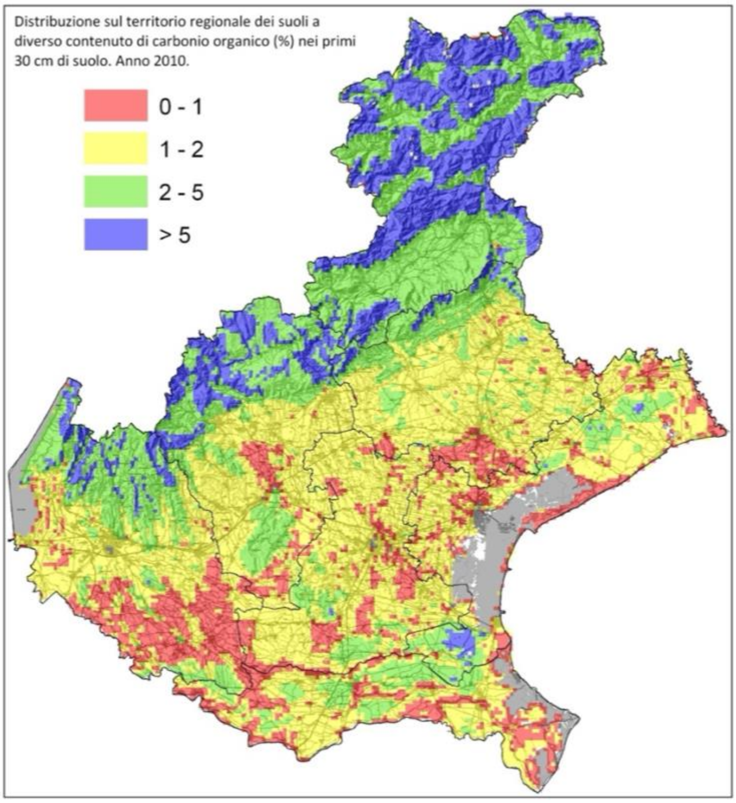

Figure 3.21: Organic carbon distribution, ARPAV

Therefore, it is possible to evaluate the soil-water partition coefficient:

$$K_d = f_{oc} \times K_{oc} = 0.05 \cdot 19952.62 \frac{l}{kg} = 997.63\, ml/g \tag{3.15}$$

Since the soil is about *2.5* times denser than water, *2 liters* of aquifer should contain *1 liter* of water and *2.5 kg* of soil. Therefore, *997.63 ml/g* of the contaminant would go into the water, and *2494.1 mg* would be absorbed by the soil.

The high value of the partition coefficient K_d confirms that *PUR* is a contaminant with low water solubility, as previously predicted.

For the calculation over a distance of 117.6 km, a weighted average is assumed for the amount of organic carbon fraction in the soil, as in the Belluno area f_{oc} = 5%, while in the remaining Veneto region $f_{oc} \approx$ 1%:

$$\overline{f_{oc}} = 0.67 \cdot 0.01 + 0.33 \cdot 0.05 = 0.0232 \tag{3.16}$$

Obtaining a partition coefficient value of $K_d = 0.0232 \cdot 9952.62 \approx 462.9\, ml/g$.

Assuming the following data:

- $K_d = 462.9\, ml/g = 462.9\, l/kg$
- volume of water each unit: *1 l*
- mass of soil each unit: *2.5 kg*
- travel time: *1421.36 years*
- distance: *117.6 km*

It is possible to evaluate the total mass released of PUR:

$$M_{total} = C_w \cdot V_w + C_s \cdot M_{soil} \tag{3.17}$$

Where $C_s = K_d \cdot C_w$, so substituting C_s in *Equation 3.17* and collecting C_w:

$$M_{totale} = C_w \cdot V_w + K_d \cdot C_w \cdot M_{suolo} = C_w (V_w + K_d \cdot M_{suolo}) \tag{3.18}$$

From *Equation 3.18*, it is possible to obtain C_w:

$$C_w = \frac{M_{tot}}{V_w + K_d \cdot M_{suolo}} \tag{3.19}$$

The amount of the absorbed mass is evaluated as follows:

$$M_{ass} = C_s \cdot M_{suolo} = K_d \cdot C_w \cdot M_{suolo} \tag{3.20}$$

Substituting in *Equation 3.20* the value of C_w found in *Equation 3.19*, the following correlation is obtained:

$$M_{ass} = K_d \cdot \left(\frac{M_{tot}}{V_w + K_d \cdot M_{suolo}}\right) \cdot M_{suolo} = \frac{462.9 \cdot M_{tot} \cdot 2.5}{1 + 462.9 \cdot 2.5} = 0.9991 \cdot M_{tot} \tag{3.21}$$

This means that, over a long travel time, the contaminant has had sufficient time to reach equilibrium between the aqueous phase and the solid phase. This ensures that absorption by the soil is complete.

Given the high K_d value, almost all the *PUR* is absorbed by the soil (as confirmed by the very low concentration that reaches the sea, $8.92 \cdot 10^{-14}\ g/m^3$, a value calculated by the *Gaussian model*). Therefore, if *2612.57 grams* of *PUR* are released over *1421 years*, *2610.21 grams* will be absorbed into the soil, while the remaining *2.35 grams* will be released into the sea.
This estimate assumes that the release of *PUR* is constant over time and distance, and that the absorption process is complete, with no chemical reactions or degradation occurring.

In the following table, it is summarized different scenarios developed in *1, 5, 10, 20* and *50 years*.

Scenario	**Total mass released**	**Mass absorbed**
1 year	*1.838 g*	*1.836 g*
5 years	*9.193 g*	*9.184 g*
10 years	*18.385 g*	*18.368 g*
20 years	*36.771 g*	*36.737 g*
50 years	*91.927 g*	*91.844 g*

Table 3.5: Different scenarios during years

3.6.5 Analysis of results

The soil dispersion modeling previously outlined provides a comprehensive view of the *long – term* environmental implications of polyurethane (*PUR*) foam microplastic dispersion in alpine environments. By modeling the behavior of *PUR particles* over a range of soil types and timeframes, the study sheds light on several important factors affecting the fate and transport of these particles in various terrains.

Transport dynamics in different soil types

One of the critical insights from the model is the considerable variation in *PUR* microplastic transport depending on the type of soil. In mountainous areas, characterized by soils with high gravel content and significant hydraulic conductivity, *PUR* particles travel more rapidly, reaching *44.19 km* over a *175 – year period*. In contrast, soils in flat or low – lying areas, which typically have a higher clay or sandy content, exhibit *much slower transport rates*, with particles traveling only *60.7 km* over a span of *1152 years*.

This contrast is significant, as it highlights how topography and soil composition critically affect the rate at which microplastics are distributed. Areas with higher conductivity facilitate faster particle movement, which could result in quicker dispersion into broader ecosystems, including freshwater bodies. On the other hand, in soils with slower percolation rates, microplastics remain trapped for much longer, creating localized contamination "hotspots".

Temporal scenarios: slow but persistent accumulation

The different time horizons explored in this chapter (*1, 5, 10, 20*, and *50 years*) reveal the slow yet persistent nature of *PUR microplastic* accumulation in the environment. For example, after *1 year*, *1.838 grams* of *PUR* is released into the soil, with nearly *100%* absorption (*1.836 grams*). After *50 years*, this value climbs to *91.927 grams* released, with *91.844 grams* absorbed into the soil. These findings point to a high degree of retention in soil systems, with very little microplastic being transported away.

This slow accumulation raises concerns about the long – term persistence of microplastics in sensitive environments. Even though the initial release rates may seem small, over decades, the steady buildup of particles in the soil will have cumulative environmental impacts. Furthermore, the persistence of these materials in the soil implies potential risks for plant and microbial life, as well as for nearby aquatic ecosystems due to eventual runoff or transport.

Long – term environmental consequences

The results of this dispersion model clearly show that microplastics from *PUR foams* have the potential to remain in soil systems for *hundreds to thousands of years*, depending on the soil type and environmental conditions. In mountainous terrains, where transport is relatively faster, microplastics may eventually reach downstream ecosystems more rapidly, contributing to the wider problem of plastic pollution in freshwater and marine environments. However, in flat terrains with slower transport, the *long – term* retention of microplastics in soils could result in localized contamination, which may affect agriculture, water quality, and biodiversity.

Moreover, the *long – term* biodegradation of *PUR* foams remains uncertain. While these particles may eventually degrade, the timescales involved — *spanning centuries* — suggest that without intervention, these plastics will continue to accumulate in soils, contributing to chronic environmental pollution.

Mitigation and material innovation

Given the slow migration and high persistence of microplastics in soil, the study underscores the need for material innovation and better management strategies to minimize plastic leakage. While the model demonstrates that recycled polyol formulations can help reduce the environ- mental impact of *PUR foam*, the overall release of microplastics during use and transportation still presents a significant issue. These results call for further research into more sustainable material alternatives that can reduce the formation of microplastics or degrade more rapidly in the environment.

Model reliability and uncertainties

Although the model provides valuable insights into the behavior of *PUR microplastics*, it is important to note certain limitations. The model relies on *simplified assumptions about particle behavior*, such as uniform transport rates and environmental conditions over extended periods. Real – world factors like *changes in land use*, *extreme weather events*, and *variations in soil moisture content* could influence the actual dispersion patterns.
Additionally, the model does not account for the potential interactions between microplastics and other environmental contaminants, which could alter their transport and deposition dynamics.

3.6.6 Final comments

One third of the plastic produced globally ends up in the soil, and it is estimated that the amount of plastic in terrestrial ecosystems is *4* to *32* times greater than that present in the oceans. High concentrations of plastic in the soil also inhibit plant growth. The accumulation of plastic residues affects soil hydration, nutrient transport, microbial activity, and salinization, contributing to the retention of contaminants such as pesticides. Microplastics become part of the soil structure by binding to organic particles, particularly colloids. Through erosion caused by water and wind, these particles can even be transported to far away locations, reaching water bodies and oceans. Microplastics are then ingested by *micro-* and *mesofauna*, such as worms and parasites, thus accumulating in the food chain, with potential bio – amplification when birds feed on these small animals.

According to *WWF*, at least *8 million tons* of plastic end up in the sea every year, adding to the so – called "*plastic soup*", a danger to both humans and the environment. Over time, these floating plastic wastes break down into smaller parts, becoming microplastics and nano – plastics. However, microplastics also pollute groundwater and soil.

Depending on the type of microplastic and the soil it comes into contact with, these particles can undergo various stages of transformation and aging, including *photo-* and *thermo – oxidative degradation*, interaction with soil colloids, and biodegradation by soil organisms.

According to the study "*Microplastics in the soil-groundwater environment: Aging, migration, and co-transport of contaminants – A critical review*" (*Zhefan et al., 2021*), it has been demonstrated that differences in microplastic characteristics, including size, shape, density, sur- face charge and chemistry, as well as other environmental factors, influence the transport and distribution of microplastic particles in soils. It was found that smaller plastic particles move further downward because they can pass through soil pores and reach deeper soil layers[38]. *pH* also plays a crucial role in transport: the movement of microplastics increases as soil *pH* rises.

Previous studies have revealed that downward movement of microparticles can occur through soil pores and cracks when the size of the microplastic is smaller than the size of the soil pores.

Zhou et al., 2021, conducted a field study at *29* sites in riparian soils[39] and demonstrated that subsoils (*10 – 15 cm*) contained higher levels of microplastics compared to surface soils (*0 – 5 cm*), with small microplastics (< 200 μ*m*) accounting for approximately *70%.* The authors also confirmed that microplastic contamination was strongly correlated with rainfall, indicating that microplastics were transported downward through soil pores via leaching. So far, microplastic contamination in

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[38] Rilling et al., 2017

[39] Riparian soil: open areas leading to rivers or generic watercourses

groundwater has been overlooked, but it was detected at a level of *12 particles* L^{-1}, suggesting that microplastic transport from soil to groundwater has occurred[40].

According to the article "*Microplastic pollution in groundwater: a systematic review*" (*Lee et al., 2024*), a bibliometric analysis identified *201* research articles from the *Web of Science* database. While only *two* papers were published in *2017*, the number of studies has steadily increased over time. Despite rising public concern and interest in environmental microplastic contamination, there are still relatively few studies focusing on *MPs* in groundwater. This low research volume can be attributed to the fact that groundwater is not visible, making *MP* pollution harder for the public to recognize, even though plastic waste is widespread on the ground's surface. As a result, governments and environmental agencies tend to prioritize investigations and research funding for marine and surface water bodies over groundwater.

Moreover, the lack of standardized methods, such as *ISO guidelines* for sample collection, on-site pretreatment, and analytical procedures for *MPs* in groundwater, further limits research efforts. This gap has contributed to fewer studies and analyses conducted by the scientific community.

In *24* field – based studies worldwide are highlighted that various types of polymers are present, including polypropylene (*PP*), polyethylene (*PE*), polyethylene terephthalate (*PET*), polystyrene (*PS*), polyamide (*PA*), polyurethane (*PU*), *PVC*, and polyether sulfone (*PES*).

Beyond the research on the presence of *MPs* in groundwater, there is a noticeable gap in studies exploring the routes through which *MPs* enter aquifers, along with their fate and behavior within these systems. Comprehensive studies are urgently needed to better understand the pathways *MPs* take to reach groundwater. It is generally assumed that *MPs* deposited from the atmosphere or introduced directly into the soil can migrate vertically, eventually reaching aquifers, which is considered the primary route of entry. However, there is a scarcity of empirical research on how long this process takes, the potential chemical or biological changes *MPs* might undergo during migration, and the inflow rates (mass flux) at the soil-groundwater interface.

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[40] Panno et al., 2019

Conclusion

This thesis presents a detailed study of the dispersion and environmental impacts of polyurethane (*PUR*) foams in alpine environments, with a specific focus on their use in the soles of trekking shoes. Through the development and application of a dispersion model integrated with a comprehensive Life Cycle Assessment (*LCA*), several key insights were gained into the environ- mental behavior and consequences of *PUR foams* in sensitive mountain ecosystems.

A significant portion of this research involved the creation of a novel dispersion model tailored to alpine environments. The model was designed to simulate the pathways and environmental fate of polyurethane foam particles, especially microplastics, released from trekking soles due to wear and tear. The dispersion model incorporates key environmental factors unique to mountainous regions, such as altitude, temperature fluctuations, and varying wind patterns, all of which influence how and where these microplastics spread.

The model combines *advection* (movement due to wind) and *turbulent diffusion* (caused by eddy motion) to calculate the transport of microplastics once released into the atmosphere. It also simulates deposition patterns, predicting how these particles settle in different environmental compartments, including soil, water bodies, and snow. The case study of *PUR* dispersion starting from *Passo Giau* provided crucial real – world data to validate the model. The results revealed that most of the microplastics are deposited relatively close to their source, predominantly in soils and freshwater bodies, though some fraction could be transported to distant ecosystems via wind or water runoff.

The model also evaluated the redistribution of microplastics in various terrains, such as valleys and plateaus, and demonstrated that microplastics tend to accumulate in low – lying areas, which could pose risks to both the local ecosystem and downstream environments. In particular, the model projected that a fraction of the microplastics would eventually be transported to marine environments via river systems, contributing to the global issue of plastic pollution.

The integration of the dispersion model with the *LCA* allowed for a deeper understanding of the broader environmental impacts of *PUR foams*, not just in terms of their direct use, but also their long – term effects as pollutants. It was found that the use of recycled polyol formulations can reduce the environmental burden, especially when combined with lower isocyanate/polyol ratios. However, even with improvements in material formulation, the dispersion model indicates that microplastic release during the use phase remains a significant concern.

In conclusion, the novel dispersion model developed in this thesis provides a valuable tool for understanding the environmental fate of microplastics in alpine regions. The findings highlight the need for improved materials and waste management strategies to minimize the release of microplastics and mitigate their environmental impact. By accounting for both local and long – range transport of microplastics, this model can be adapted to assess similar issues in other sensitive ecosystems, guiding stakeholders toward more sustainable material choices and better environmental practices.

Appendix A

MATLAB code

The following *MATLAB code* is the one used for calculating the concentration of *PUR* particles that reach the sea.

```
%Parameters definition for Guassian equation
wind_spedd = 1.1;             % [m/s], annual average velocity
                              assumed constant
x = 117600;                   % 117.6 km in meters (distance from
                              Passo Giau to Jesolo Lido)
m = 5.83e-11;                 % emission rate [kg/s]

% Evaluation of the dispersion coefficients based on stability class
chosen for this case study, F, considering a continuous emission
sigma_y = 0.04*x*(1+0.0001*x)^(-0.5); %[m]
sigma_z = 0.016*x*(1+0.0003*x)^(-1); %[m]

% Actual height from the source (at ground level)
H = 0;

% Evaluation of the concentration at the sea
y = 0;                        % calculation along the wind axis
z = 10;                       % Concentration at 10 m from the ground
C = (m / (2 * pi * wind_speed * sigma_y * sigma_z)) *
... exp(-y^2/ (2 * sigma_y^2)) *
... exp(-(z - H)^2 / (2 * sigma_z^2));

% Evaluation of the time needed to reach the destination
time = x / wind_speed;        % time in seconds

% Conversion in hours
time_hour = time / 3600;
```

```
% Visualization of the results
fprintf('The particle concentration that reaches the sea is equal
to %.2e kg/m^3.', C);
fprintf('The time needed for the particle to reach the sea from Passo
Giau is about %.2f hours.', time_hour);
```

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