Review

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*Review*

# Risks Associated with the Presence of PVC in the Environment and Methods of Its Elimination

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**Abstract:** Plastics have recently become an indispensable part of everyone's daily life due to their versatility, durability, light weight and low production costs. The increasing production and use of plastics poses a great danger due to the very long period of degradation, but also the negative impact on living organisms. Decomposing plastics lead to the formation of microplastics, which accumulate in the environment and living organisms becoming part of the food chain. Polyvinyl chloride (PVC) contamination of soil and water seriously threatens ecosystems around the world. The durability and low weight make microplastic particles easily transported with water or air and end up in the soil. Thus, the problem of microplastic pollution affects the entire ecosystem. Since microplastics are commonly found in both drinking and bottled water, humans are also exposed to the harmful effects of microplastics. Because of the existing risks associated with PVC microplastic contamination of the ecosystem, intensive research is underway to develop methods to clean and eliminate it from the environment. Pollution of the environment with plastic, especially microplastic, results in the reduction of both water and soil resources used for agricultural and utility purposes. This review provides an overview of PVC's environmental impact and disposal options.

**Keywords:** polyvinyl chloride; pollution; aquatic environment; soil; degradation

## 1. Introduction

Plastics are an ubiquitous material used in a wide range of human activities due to their durability, low cost, and technological versatility [De-la-Torre, 2021].

In 2020, about 368 million tons of plastics were produced in a world [Europe, Plastics, 2021]. Moreover, almost 80% of plastic waste was discharged directly or indirectly into the environment [Europe, Plastics, 2021; Qi, 2021; Geyer, 2023]. Such uncontrolled disposal of materials can cause serious environmental damage, especially to the atmosphere, agricultural soils and groundwater [Bouaicha, 2022; Xu, 2023].

Environmental factors such as wind, sunlight and rain can affect degradation of polymers, leading to the formation of small and durable particles: microplastics (MPs) with a size of 1-1000 μm and nanoplastics (NPs) with a size of (1-1000 nm) [Bermúdez, ; 2021; Barili, 2023]. It is important to detect MPs in the environment as soon as possible to avoid the biological damage they cause. The amount and type of plastics in the environment is assessed, among other things, by means of Fourier transform infrared spectroscopy, time-of-flight secondary ion mass spectrometry, thermogravimetric analysis technique, differential scanning calorimetry, scanning electron microscope, atomic force microscopy, water contact angle, and ion chromatography [Xu, 2023].

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Of particular importance among microplastics is polyvinyl chloride (PVC), which is one of the six commonly used plastics (accounting for as much as 10% of global plastic production) [Europe, Plastics, 2021]. PVC is the popular plastic due to its durability and good mechanical, chemical, electrical and thermal properties. World production of PVC in 2009 amounted to approximately 34 million tons. At the global level, PVC production in 2015 exceeded 35 million tons, and annual growth was forecast at approximately 2%. At that time, European PVC consumption was approximately 7 million tons per year [1].

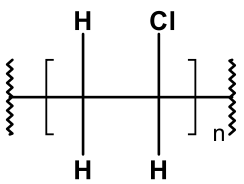
In 2022 the PVC capacity was 59.97 million tons. The market has been expected to achieve an annual growth of more than 3% during 2022-2027 [2].

This plastic is strong, durable, long-lasting, lightweight and versatile, so it is widely used in many industries, such as in construction, the automotive industry, for pipes and cables, and household goods. The service life of PVC in construction is more than 10 years [Miliute-Plepiene, 2021]. PVC can present a number of challenges at various stages of its life cycle, particularly at the waste stage. Sound waste management and disposal is essential, due to the potential emission of PVC additives (e.g., heavy metals) into the air (in the case of incineration) and soil (in the case of landfilling), but also to illegal dumping and incineration. Various PVC additives have also hazardous properties and therefore, when emitted, can pose a threat to the environment and human health [EU Commission, 2022].

PVC is considered as the most environmentally damaging plastic and one of the most toxic substances for inhabitants of our planet. From cradle to grave, the PVC Lifecycle (production, use and disposal) results in the release of toxic, chlorine based chemicals and one of the world's largest dioxin sources. These toxins build up in water, air and in the food chain. They cause severe health problems, including cancer, immune system damage and hormone disruption. Everyone has measureable levels of chlorinated toxins in their bodies [3-7].

## 2. PVC characteristics

According to the IUPAC a systematic name of PVC is poly(-1-chloroethylene) [Titow, 1990; Fisher, 2014; Gilbert, 2017]. It presents the linear, in majority atactic polymer, with the degree of polymerization ranging 500-1500; corresponding to a theoretical molecular weight range of about 31000-94000 Da. Polyvinyl chloride is white in color and relatively stiff plastic with high resistance to impact, chemicals, corrosion, water, and weather [Tu, 2016].




PVC

**Figure 1.** The general structure of Poly(Vinyl Chloride) (PVC).

PVC is synthesized by a free-radical polymerization occurring by the head-to-tail tri-stage mechanism depicted in Figure 2 [Endo, 2002].

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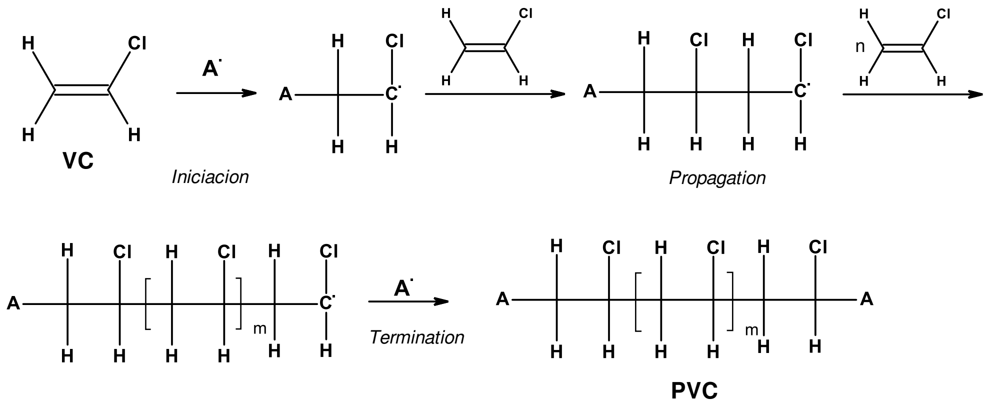



**Figure 2.** Free-radical polymerization of Vinyl chloride (VC) (m = n + 1).

In industrial practice, developed since 1930 [Braun, 2001, 2004], vinyl chloride (VC) is polymerized in suspension processes (approximately 80% of the market), in emulsion (~10-15%), in bulk (~10%), and in solution (~1%), respectively [Saeki, 2002; Gilbert, 2017].

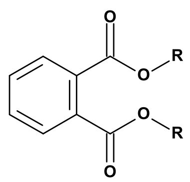
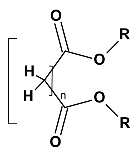
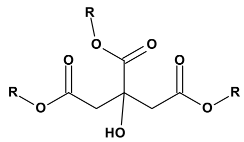
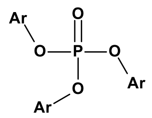
PVC presents for decades the one of the most widely used plastic, with a world consumption of almost 34 million tons in 2009 [1], and 60 million tons in 2022 [2]. The market is expected to achieve an AAGR (Average annual growth rate) of more than 3% during 2022-2027 [globaldata].

PVC is classified into two broad categories: rigid PVC (unplasticised PVC, uPVC, rPVC, RPVC) (used for automobile, health care, electronics, building and construction) and flexible PVC (fPVC) (used for cables, wires, fittings, films, profiles, tubes, pipes, sheets, and bottles [Howard, 2023]. Moreover, chlorinated PVC, molecularly oriented PVC, and modified PVC [Moulay, 2010; Skelly, 2022; Lieberzeit, 2022] are also produced ona smaller scale.

Pure PVC, due to mechanical properties, requires some additives for improvement of its processability and application needs. The most common additives used in PCV industry are in particular focused on the following additives: plasticizers, stabilizers, fillers, impact modifiers, and/or pigments [Babinsky, 2006].

The list of representative plasticizers used in PCV industry is given in Table 1.

**Table 1.** Representative PCV Plasticizers [Ambrogi, 2017; Elgharbawy, 2022].

|  |  | |  |  |
|---|---|---|---|---|
| Phthalates | Adipates | Sebacates | Citrates | Phosphates |
| DEHP (R = $iC_8$); DIDP ($R=iC_{10}$), DINP ($R=iC_9$) | (n = 4) DINA (R = $iC_9$); DIDA ($R-iC_{10}$)) | (n = 8) DBS (R = $C_4$); DOS (R = $iC_{10}$) | TEC (R = Et ) | TCP (Ar = Tol) |

*2.1. PVC physical properties*

PVC is classified as a self-extinguishing material. A limiting oxygen index (LOI) of rigid PVC is approximately 44–49% [Mark, 2007].

Solubility of PVC is the one of major factors facilitating PVC leaching. Thus, satisfactory resistance PVC in aqueous environment is caused by its legible solubility in water [PPI, 2023].

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Conversely, PVC is not resistant in majority of organic solvents, due to its substantial solubility, the most in tetrahydrofuran (THF), dimethylformamide (DMF), dimethylformamide (DMA), and/or pyridine [Grause, 2015].

### 2.2. PVC chemical properties

PVC as a facto polychloroalkanes exhibit typical alkyl chloride reactivity, namely, nucleophilic substitution of chloride anion *(1)* [Kameda, 2009; 2010], nucleophilic elimination of hydrogen chloride *(2)* [Bacaloglu, 1995], and a free radical chlorination *(3)* [Ge, 2016], illustrated in Figure 3. These reactions, due to negligibly solubility of polymer in water [PPI, 2023] seems to occur on the polymer surface, facilitating its leaching.

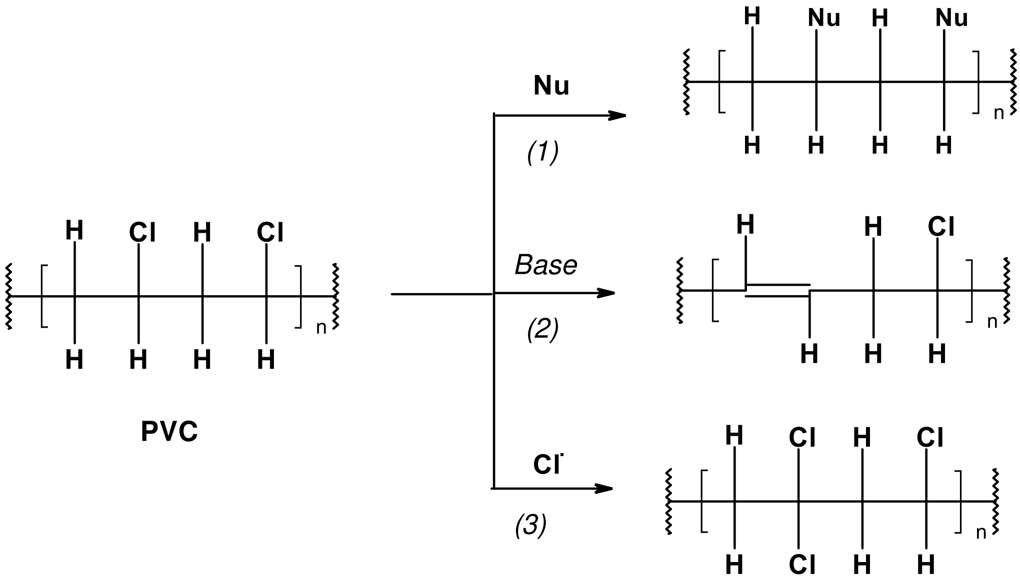


**Figure 3.** Reaction paths of PVC: nucleophilic substitution of chloride anion (1), nucleophilic elimination of hydrogen chloride (2) and free radical chlorination (3).

Degradation of polyvinyl chloride (PVC) is mainly caused by the thermal dehydro-chlorination reaction (Figure 4) leading to a formation a conjugated double bonds or chlorine substitution (hydrolytic degradation) [Zakharyan, 2020.1, 2020.2; Lewandowski, 2022].

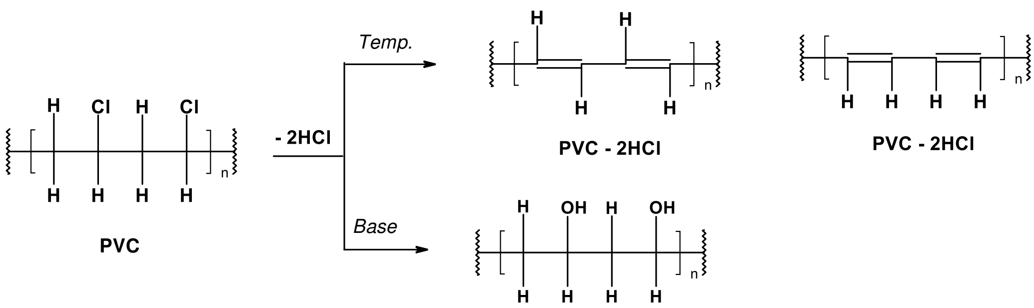


**Figure 4.** Degradation of PVC by dehydrochlorination.

PVC waste is resistant to decomposition in the environment due to its high molecular weight and highly stable covalent bonds and hydrophobic surface properties, making it a huge environmental problem during its production and disposal [Xu, 2023]. PVC waste is highly resistant to decomposition in the environment, but often releases harmful chlorinated compounds that

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negatively affect the health of organisms and the ecosystem [Barili, 2023]. PVC is classified as a substance with strong mutagenic and carcinogenic properties, and is more toxic than other plastics due to the presence of chlorine atoms [Colzi, 2022]].

Traditional methods of storage and incineration of PVC waste lead to the release of harmful chlorinated compounds (hydrogen chloride, chlorinated dioxins) (Figure 5) [Pospı̃šil, 1999; Carroll, 2001].

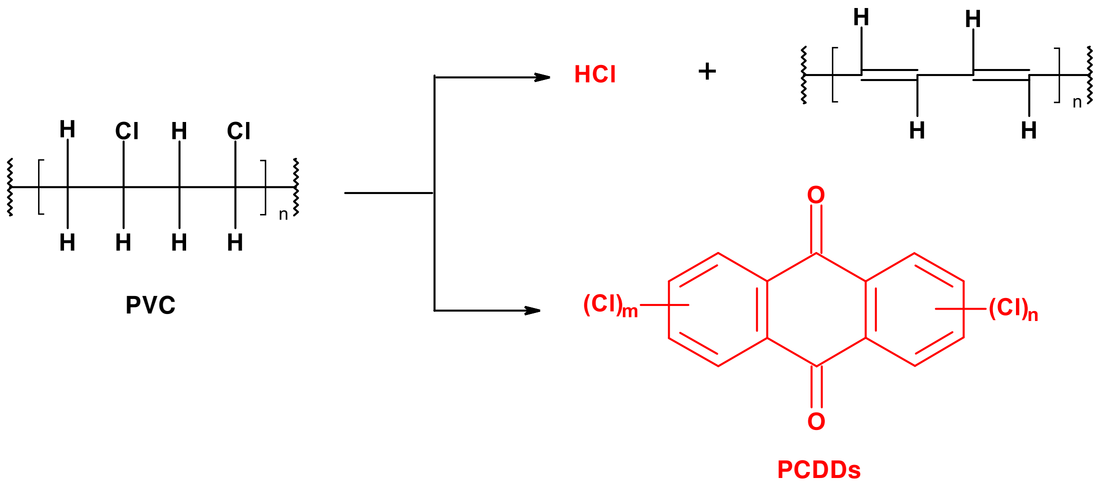


**Figure 5.** Formation from PCV harmful chlorinated compounds (PCDDs, where *m* and *n* can range from 0 to 4).

Pure PVC can only be used in the temperature range from -10 to + 60°C. Stabilized softened PVC can be used in the temperature range from -30 to + 100 °C. The greatest problems are encountered during the processing of PVC, because the thermal decomposition of PVC with the release of hydrogen chloride begins visibly at a temperature of 135 °C. In addition, the released hydrogen chloride in the presence of oxygen from the air accelerates the polymer decomposition process to such an extent that at a temperature of 200 °C the PVC decomposes almost completely [8].

In the thermal degradation of vinyl polymers, cleavage outside the main chain or statistical cleavage of the main chain may occur. Light ageing occurs as a result of absorbed light energy, as a result of which polymers undergo photolysis, oxidation and cross-linking reactions. PVC products used in atmospheric conditions are exposed to the destructive effects of atmospheric factors, such as: UV radiation, precipitation and temperature changes leading to physical and chemical ageing of the material. Under the influence of UV radiation, free radicals are formed, causing the bonds in the PVC main chain to be broken, hydrogen chloride to be split off, and new double bonds to be formed, causing the material to turn yellow. The next stage of degradation is the photo-oxidation process leading to whitening of the material and cross-linking due to the formation of oxygen bridges. The most characteristic changes caused by degradation are the appearance of newly formed C=C double bonds, C=O carbonyl groups and hydroxyl groups –OH in the chain, as well as the release of hydrogen chloride and carbon dioxide. Yellowing of the material is caused by high temperature and low humidity. The PVC degradation process is a complex phenomenon resulting primarily from the dechlorination process, the course of which depends on the stabilizers used. PVC is the largest contributor to environmental pollution with dioxins on
a global scale [8].

There are two types of degradation in PVC [8]:

- preliminary (occurring under the influence of temperature, so-called thermal) in anaerobic conditions at the molecular or ionic level,
- secondary as a result of increased temperatures and oxygen (thermo-oxidative degradation).

Because of the many concerns raised about PVC usage since the 1970s, PVC has become one of the most researched plastic materials from an environmental point of view. Despite all the technical and economic problems and the public discussions on the environmental dangers and hazards of chlorine chemistry, poly(vinyl chloride) (PVC) is the second most produced plastic (with a worldwide capacity of about 60 million tons in 2022 [2]), placing after polyolefins and before styrene polymers [9]. But PVC also plays an important role in many environmental discussions on polymers, e.g. chlorine chemistry, toxicity of vinyl chloride, or waste and recycling problems. Within the time frame of 70 years, some recent developments in controlled polymerization of vinyl chloride, stabilization, modification of bulk properties and chemical and material recycling of PVC are discussed.

### *2.3. Biological Activity of polyvinyl chloride*

Plastic products contain hundreds of potentially toxic chemical additives, which drive toxicity currently [Rodrigues, 2019; Chen, 2022]. Micro/nano-plastics may pose acute toxicity, (sub)chronic toxicity, carcinogenicity, genotoxicity, and developmental toxicity [Yuan, 2022]. This results from polymer matrix, additives, degradation products and adsorbed contaminants.

PVC, in contradiction to its carcinogenic monomer [Wagoner, 1983; Huang, 1997; Sass, 2005; Kapp, 2014] is biologically inert due to its low chemical reactivity [Chen, 2022]. For instance, its not digestible, even at surface, for common strains (*Lactobacillus acidophilus; L. plantarum* and *L. rhamnosus*) representing functional bacterial groups in the human gut microbiota. However, cytotoxicity investigations of PVC using the human cell lines Caco-2, HepG2 and HepaRG (possible impact on intestine and liver) [Mahadevan, 2021; Stock, 2021; Paul, 2022] and pulmonary cell cultures revealed the induction of cytotoxic effects [Xu, 2003]. Occupational exposures at a polyvinyl chloride production facility are associated with significant changes to the plasma metabolome [Guardiola, 2016]. PVC micro- and nano-particles can induce carcinogenesis to humans [Kumar, 2022].

It was reported that PVC particles produced a moderate *in vitro* toxicity for human pulmonary cells [Oleru, 1992; Xu, 2002] and cardiometabolic toxicity [Zelko, 2022]. PVC induces changes in the microenvironment and secondary structure of human serum albumin (HAS) (decrease in $\alpha$-helix) [Ju, 2020] and bovine serum albumin (BSA) [Ju, 2021] and liver injury and gut microbiota dysbiosis [Chen, 2022, STE; Chen, 2022, EES]. PVC dust exerts haemolytic effect on lung fibroblast cultures [Richards, 1975], liver angiosarcoma and lung cancer [Wagoner, 1983].

Toxicity of water after contact with PVC materials was found to be dependent on the type of PVC composition components and the temperature [Sharman, 1987; Sampson, 2011; Olkova, 2021; Zimmermann, 2021]. Aquatic toxicity of PVC microplastics towards marine organisms (microalgae, crustaceans and echinoderms) is due to leaching of chemical additives, and not to ingestion of microplastics (MPs) [Fishbein, 1984; Beiras, 2021]. The aging of MPs release additives that may cause severe genotoxicity [Yang, 2023].

PVC microplastics reduced sediment catalase, polyphenol oxidase (PO), and urease activities, and decreased physicochemical indicators, including total organic carbon (TOC), total nitrogen (TN), and pH value [Li, 2022].

Cytotoxicity studies on combustion gas of thermoplastic polyvinyl chloride shows its cytotoxicity [human fetal lung tissue cell (MRC-5), African green monkey kidney cell (Vero), Chinese hamster ovary cell (CHO)] with molecular chlorine as the major toxicant [Shue, 2009].

PVC composites for linoleum are equipped with antibacterial agents (1,3-dioxanes, wollastonite, quaternary ammonium biocides) therefore exhibit the functions of biostatics inhibiting the growth of microorganisms and of bactericides killing microorganisms [Sokolova, 2018; Gotlib, 2019].

## 3. Threat related to the production and use of PVC

High durability, corrosion resistance, low price and ease of installation made polyvinyl chloride (PVC) used not only in industry but also in everyday life [Tran, 2022]. The largest PVC sales markets include the production of window profiles (respectively 27% of the total PVC application in Europe) and pipes supplying e.g. drinking water (22% of the total PVC application in Europe). According to

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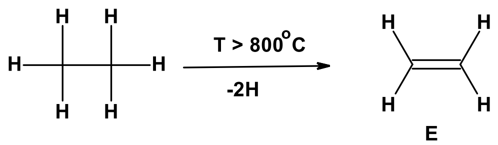
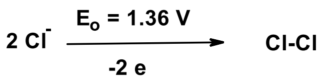
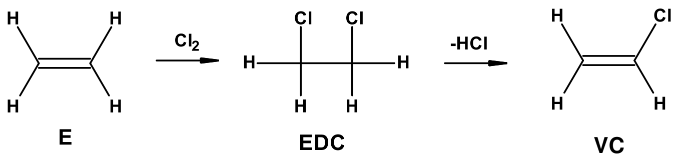
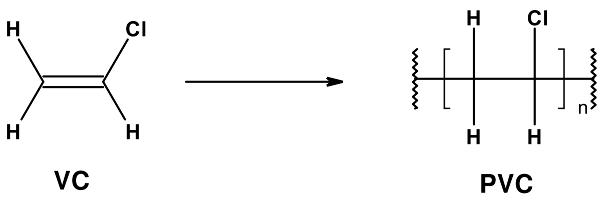
the inventory model of PVC production, a total of 2.4638 kg of wastewater is generated during the production of 1 kg of polyvinyl chloride from suspension polymerization (S-PVC) (Table 2).

The life cycle of PVC (from the extraction of raw materials to the end of production) is considered to be harmful to the environment. This is due to the fact that many pollutants are involved in the entire process [Bottausci, 2021]. In addition, it is believed that an important phase of the potential environmental impact of PVC pipes is also their installation [SSC, 2017].

It has been shown that the production of PVC has a significant share in e.g. human toxicity potential (HTP), photochemical ozone creation potential (POCP), acidification potential (AP) and global warming potential (GWP) (Table 3) [Shi, 2019; Comanita, 2015]. During the production of 1,2-dichloroethane from ethylene and chlorine, dioxins can be formed during the thermal cracking of vinyl chloride monomer (VCM). This is reflected in the HTP values. Higher values recorded for POCP are due to the processing of crude oil, which causes emissions of volatile organic compounds (VOCs).

**Table 2.** Summary of water consumption and wastewater generated during the production of 1 kg of S-PVC ([Bottausci, 2021], modified).

| St. | **PVC production process steps** | **WI** [kg][/a] | **WsWO** [kg][/a] |
|---|---|---|---|
| **1** | **Ethylene (E) and Chlorine ($Cl_2$) Production** | | |
| **1.1.** |  | 0 | 0 |
| **1.2** |  | 0 | 0 |
| **2** | **VCM production process** | 1.03 | 0.63 |
| |  | | |
| **3** | **PVC production process** | 2.24 | 1.83 |
| |  | | |
| 1-3 | **Total** | **2.24; 3.27** | **2.46** |

**E** – Ethylene; **EDC** – **E**thylene **D**i**C**hloride; **VC** - **V**inyl **C**hloride; **PVC** – **P**oly**V**inyl **C**hloride;

**WI** - Water input; **WsWO** - Wastewater output. In the Oxy-chlorination process ethylene reacted with the mixture of chlorine and oxygen.

[/a] Rounded to the second decimal place.

| |
|---|
| 1.2 According to Lakshmanan & Murugesan, 2014]. |

**Table 3.** The assessment of PVC pipes environmental impact ([Shi, 2019], modified).

| Impact category | Unit | Manufacturing | Use and waste disposal | Total impact |
|---|---|---|---|---|
| **Global warming** | g $CO_2$ eq | 272 308.0 | 223 031.1 | 495 339.1 |
| **Acidification** | H+ moles eq | 63 922.6 | 25 215.8 | 89 138.5 |
| **Human health-cancer** | g $C_6H_6$ eq | 44,720.6 | 428.5 | 45 149.1 |
| **Human health-noncancer** | g $C_7H_7$ eq | 56 880 581.6 | 627 435.7 | 57 508 017.3 |
| **Eutrophication** | g N eq | 94.2 | 47.4 | 141.7 |
| **Ecotoxicity** | g 2,4-D eq | 3 304.5 | 223.5 | 3 528.0 |
| **Smog** | g NOx eq | 858.7 | 214.2 | 1 072.9 |
| **Habitat alteration** | T&E count | $1.55 \cdot 10^{-13}$ | $4.65 \cdot 10^{-13}$ | $6.2 \cdot 10^{-13}$ |
| **Ozone depletion** | g CFC-11 eq | 0.0008 | 0.004 | 0.006 |

The biggest amounts of energy during the production of PVC is consumed during ethylene production processes. In addition, energy-intensive is chlorine production, which causes $CO_2$ and $SO_2$ emissions, that contributes to high GWP and AP values [Comaniță, 2015]. A simulation conducted by Ye et al. showed that chlorine, carbon dioxide and nitrogen oxides are the key compounds from PVC production contributing to the overall environmental burden [Ye, 2017]. For example, polyvinyl chloride in China is mainly produced using coal-based technologies with approximately three times higher $CO_2$ emissions than it is in case of oil-based technologies. Only in 2017, the Chinese PVC industry emitted an estimated 123.54 million tons of $CO_2$, three-quarters of which came from coal-based production [Ren, 2021].

It has also been shown that plasticizers such as phthalates or citrates added to PVC can migrate to the medium such solid, gas or liquid, which is in contact with this plastic. The course of the migration process may depend on e.g. the molecular weight of the polymer, the nature and amount of the plasticizer, and environmental conditions [Marcilla, 2004].

Analyzes conducted on the leaching of dibutyl phthalate (DnBP) from PVC microplastics in aqueous solutions corresponding to water and soil environments showed the relationship between the amount of released plasticizer and the size of polyvinyl chloride particles, concentration of added phthalate, as well as aging of the plastic. The release of phthalates was higher for smaller particles and particles with a higher content of plasticizer. While aging of plastics due to solar radiation can either increase the release of phthalates (by increasing plastic hydrophilicity) or decrease it (by reducing readily available fractions), solution pH and ionic strength have little effect on this [Yan, 2021]. The relationship between the size of PVC particles and the amount of additives released from it was also shown by Ye et al. [Ye, 2020].

Smaller PVC fragments released greater amounts of di-n-butyl phthalate than larger fragments. It has also been proven that temperature is a factor that affects the rate and size of migration much more than, for example, exposure to light or particle size, and with increasing temperature (from 4.25 to 45 °C) both speed and migration frequency increased [Ye, 2020]. Analyzes conducted by Skjevrak et al. [Skjevrak, 2003] showed that from PVC pipes volatile organic compounds (VOCs) are also released into water. Identified compounds included hexanal, octanal, nonanal and decanal. Only trace amounts of hexanal and octanal were found in the analyzed water, while nonanal and decanal were present in concentrations ranging from 170 ng/L to 280 ng/L. The volatile compounds - 2,3-

dichloro-1-propanol and dichloroacetic acid, have also been detected in bottled water. Moreover, the vinyl chloride monomer, benzene and the semi-volatile organic compounds such as di-n-octyl adipate and bis(2-ethylhexyl) phthalate were also identified in some samples [Fayad, 1997]. The use of intramolecular diffusion (IPD) and aqueous boundary layer diffusion (ABLD) models showed that the diffusion-determining process for continuous phthalate leaching is ABLD, and a high diffusion coefficient of PVC (~$8\times10^{-14}$ m$^2$/s) enhances IPD. Although the desorption half-lives of the tested PVC microplastics are longer than 500 years, under the influence of environmental factors they can undergo strong changes, and the microplastics themselves are a long-term source of phthalates in the environment [Henkel, 2022]. The combustion process also has a significant impact on the release of volatile compounds from PVC. The results of pollutant emission tests from burning pipes showed the presence of chlorinated compounds, i.e. hydrogen chloride, chlorine dioxide, methyl chloride, methylene chloride, allyl chloride, vinyl chloride, ethyl chloride, 1-chlorobutane, tetrachlorethylene or chlorobenzene. The analysis of leachate from PVC pipes showed the presence of 40-60 components, mainly belonging to long-chain hydrocarbons (e.g. tetradecane, hexadecane, octadecane, docosane) [Chong, 2019].

The long life and high durability of PVC compared to other plastics make it one of the most common plastic wastes in the environment. Estimated durability of PVC pipes is over 100 years [Susteinable Solution Corporation, 2017]. Nevertheless, a large amount of additives used in the production of PVC, susceptibility to weathering processes and the use of various advanced treatments, required for its isolation from environmental samples, lead to changes in the surface of PVC microplastics, which may result in large underestimations of its amount in environmental studies [Fernández-González, 2022].

## 4. Worldwide pollution of the aquatic environment by the polyvinyl chloride industry

Durability and low weight mean that plastic microparticles are easily transported along with air and water currents. Research on floating debris in the ocean clearly shows that plastics are the most common type of pollution found in surface waters. The numerous methods of measuring microplastics in aquatic environments have been published recently [Mai, 2018; Cutroneo, 2020; Lakshmi Kavya, 2020]. Thus, the Pan’s report on microplastics in the Northwestern Pacific indicate the ubiquity of MPs with an average abundance of $1.0\times10^4$ items km$^{-2}$. The Micro-Raman spectroscopic analysis of the MPs samples collected indicated that the dominant MPs are polyethylene (57.8%), polypropylene (36.0%), nylon (3.4%), polyvinyl chloride (1.1%), polystyrene (0.6%), rubber (0.9%), and polyethylene terephthalate (0.2%) [Pan, 2019].

Due to the fact, that PVC is one of the most commonly used synthetic polymers and is characterized by a high density, not only it occurs in surface waters, but also is particularly identified in sediments [Facchetti, 2020; Lakshmi Kavya, 2020; Suman, 2021]. Representative papers on environmental pollution by PVC are presented in Table 4.

**Table 4.** Representative occurrence of PVC in environmental waters, sediments and organisms of marine animals.

| | | |
|---|---|---|
| | Waters & Sediments | |
| Water supply | Changsha (Hunan), China | Yin, 2019; Shen, 2021 |
| | NW Germany | Mintenig, 2019 |
| Surface fresh water | Wei River, Yellow River's tributary, China | Ding, 2019 |
| | Pearl River catchment, China | Fan, 2019; Yan, 2019 |
| | Honghu Lake, China | Xiong, 2021 |

| | | | |
|---|---|---|---|
| Sediments & surface fresh water | | West Lakes, China | Jiang, 2018; Wang, 2019 |
| Surface and sub-surface seawater | | Korean coastal regions | Chae, 2015; Song, 2015 |
| | | Marmara Sea | Tunçer, 2018 |
| | | Kuantan of Malaysia | Khalik, 2018 |
| | | Greenland | Morgana, 2019 |
| | | Arctic Ocean | Lusher, 2015 |
| | | NW Pacific | Pan, 2019 |
| Water column | | NW Mediterranean Sea | Lefebvre, 2019 |
| | | Bohai Sea-Yellow Sea | Dai, 2018 |
| Floating and bottom sediment microplastics | | Adriatic Sea | Zeri, 2018; Palatinus, 2019 |
| | | W. Mediterranean Sea | de Haan, 2019 |
| | | Cilacap, Java (Indonesia) | Syakti, 2017 |
| Surface seawater and sediment | | Melbourne coastal metropolis | Su, 2020 |
| | | Suva coastal area of Fiji | Ferreira, 2020 |
| Bottom sediments | | Arctic Ocean | Kanhai, 2019 |
| | | Norwegian fjords | Gomiero, 2019 |
| | | Venetian islands | Vianello, 2013 |
| | | Singapore coastline mangrove ecosystems | Nor, 2014 |
| Sand seashore | | Atlantic seashore, Cape Town, South Africa | Vilakati, 2020 |
| | | Atlantic seashore, Punta del Este, Uruguay | Lozoya, 2016 |
| Marine Animals and Organisms | | | |
| Fishes | *Siganus fuscescens* | Coastal sediments, Negros, Philippine | Bucol, 2020 |
| | *Nephrops norvegicus* | Coasts of Ireland. | Hara, 2020 |
| | Sardines | NW Mediterranean Sea | Lefebvre, 2019 |
| | *Triglops nybelini*, *Boreogadus saida* | Arctic Ocean | Lusher, 2015 |
| | Various species | Australian markets | Wootton, 2021 |
| | | Suva coastal area, Fiji | Ferreira, 2020 |

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| | | | |
|---|---|---|---|
| | | Markets in Fujian, China | Fang, 2019 |
| Shellfishes | *Mytilus edulis* | Mussel and oyster farming zone, Pen-Bé, France | Phuong, 2018 |
| | *Meretrix meretrix* | Markets in Fujian & Xiamen, China | Fang, 2019 |
| | Various species | Sal Estuary River, Goa, India | Saha, 2021 |

**5. Toxicity of polyvinyl chloride to surface water trophic networks and humans**

It is estimated that rivers are responsible for the transport of 70-80% of the total amount of plastic that ends up in the oceans. There they interact with see animals. The data from 778 publications based on field and experimental studies (LITTERBASE) are presented schematically on Figure 6.

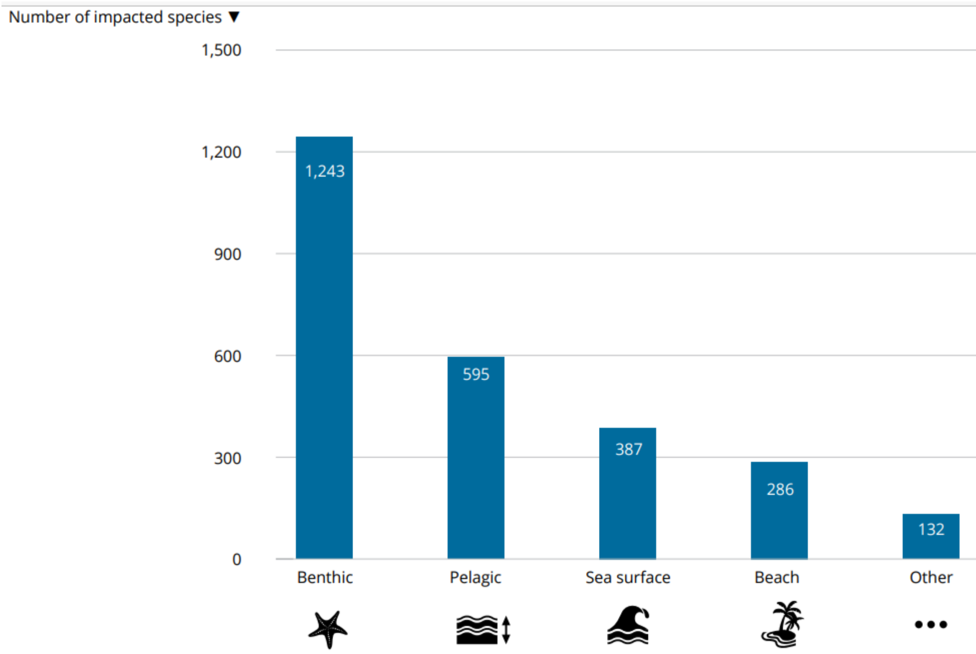


**Figure 6.** Number of species affected by pollution on the sphere that they inhabit. The figure reproduced from the book of Tekman, M. B., Walther, B. A., Peter, C., Gutow, L. and Bergmann, M. (2022): Impacts of plastic pollution in the oceans on marine species, biodiversity and ecosystems, 1–221, WWF Germany, Berlin. DOI: 10.5281/zenodo.5898684 with permission of the editors (WWF Germany).

Most of it comes from manufacturing processes, agriculture and wastewater treatment plants discharging wastewater into water systems [Waring, 2018]. Microplastics such as PVC, once released into the environment, pose a serious threat to ecosystems. Due to their small size (<5 mm), microplastics are easily absorbed by biota, causing negative effects on its development, reproduction and survival [Zhang, 2020; Wright, 2013; Halden, 2010].

It has been shown, among others, that PVC MPs accumulate and negatively affect such aquatic organisms as invertebrates [Facchetti, 2020], zooplankton [Zimmermann, 2020] or fish [Vijayaraghavan, 20200; Ding, 2019] (Table 4).

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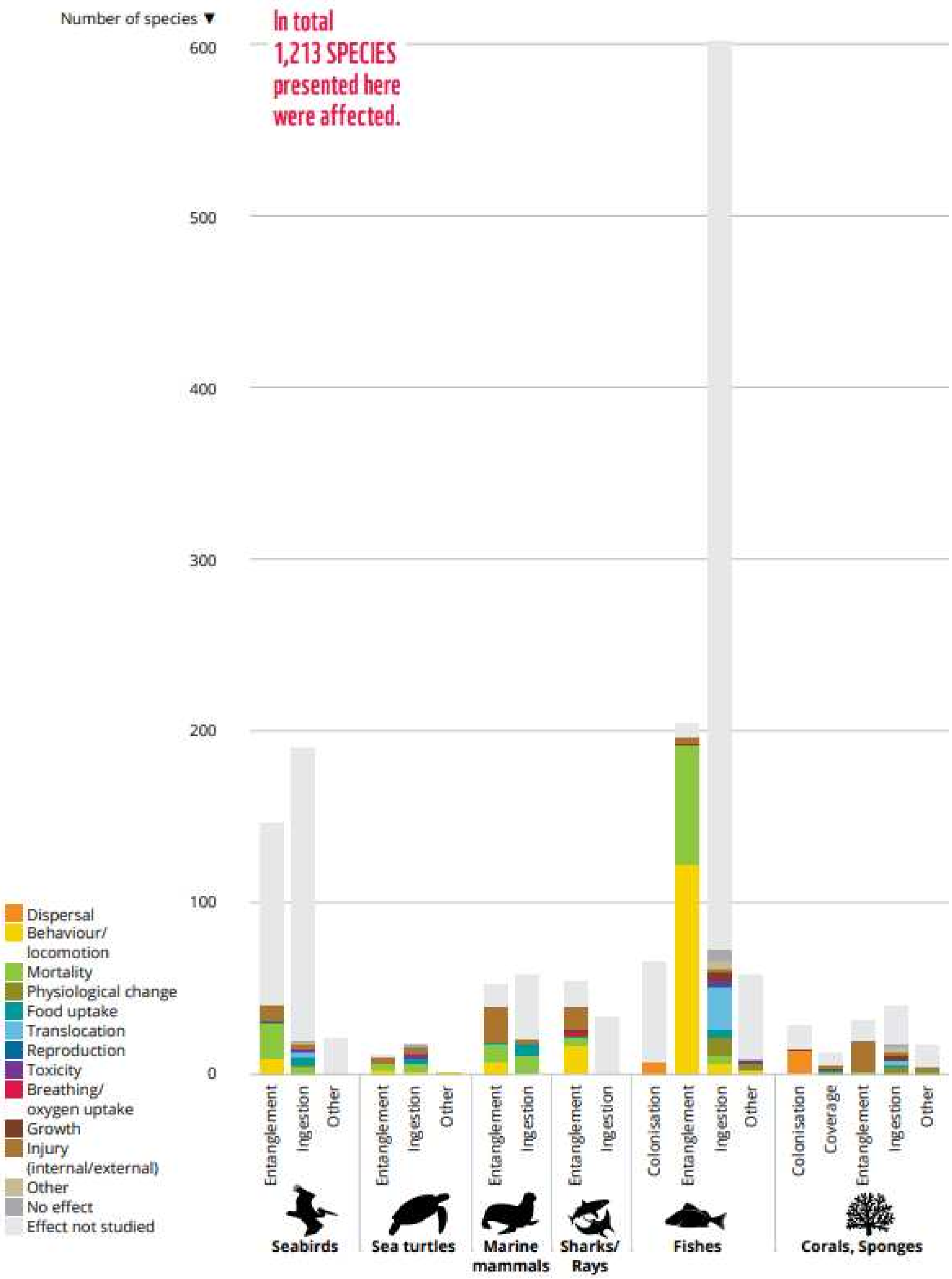


**Figure 7.** The effects of interactions with plastic on various see animals. The height of the bars refers to the number of species. The figure reproduced from the book of Tekman, M. B., Walther, B. A., Peter, C., Gutow, L. and Bergmann, M. (2022): Impacts of plastic pollution in the oceans on marine species, biodiversity and ecosystems, 1–221, WWF Germany, Berlin. DOI: 10.5281/zenodo.5898684. with permission of the editors (WWF Germany).

The harmful effects that microplastics can cause on aquatic species include: neurotoxicity, behavioral changes, histopathological damage, biochemical and hematological changes, and embryotoxicity. In addition, due to their size similar to plankton, microplastics are easily absorbed by aquatic organisms from various trophic levels and, accumulating at their higher levels, they enter the food chain, thus posing a threat not only to animals but also to humans [Waring, 2018; Elizalde-Velázquez, 2021]. Moreover, plastic waste can cause injury and abrasion of coral tissues, thus facilitating the invasion of pathogens such as *Rhodobacterales*, which dominate the biofilm that forms on polyvinyl chloride (PVC) in the marine environment [Lamb, 2018].

Plastic not only threatens the survival of more than 800 species of animals, including large marine mammals (e.g., whales and dolphins) and various birds, but also through the transfer and

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release of toxic chemicals such as harmful additives, persistent organic pollutants and heavy metals (e.g. lead ), result in chemical pollution of the environment, invasion of exotic species and degradation of local tourism and fishing industries [Yuan, 2022; Boyle, 2020; Chen, 2019].

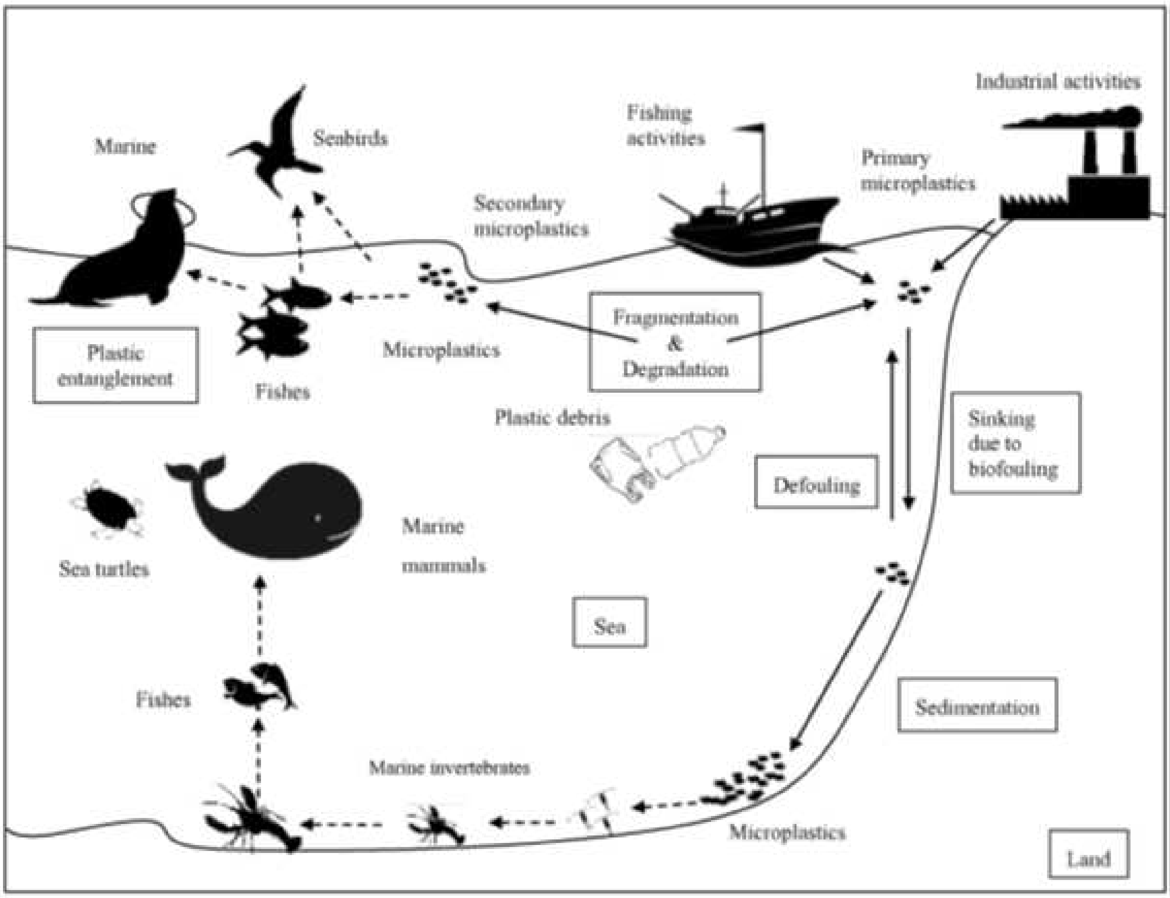


**Figure 8.** Pathways of plastic debris and microplastics transportation and its biological interactions ([Meem, 2021] – permission according to Creative Commons Attribution 4.0 License (MCMS.MS.ID.000591).

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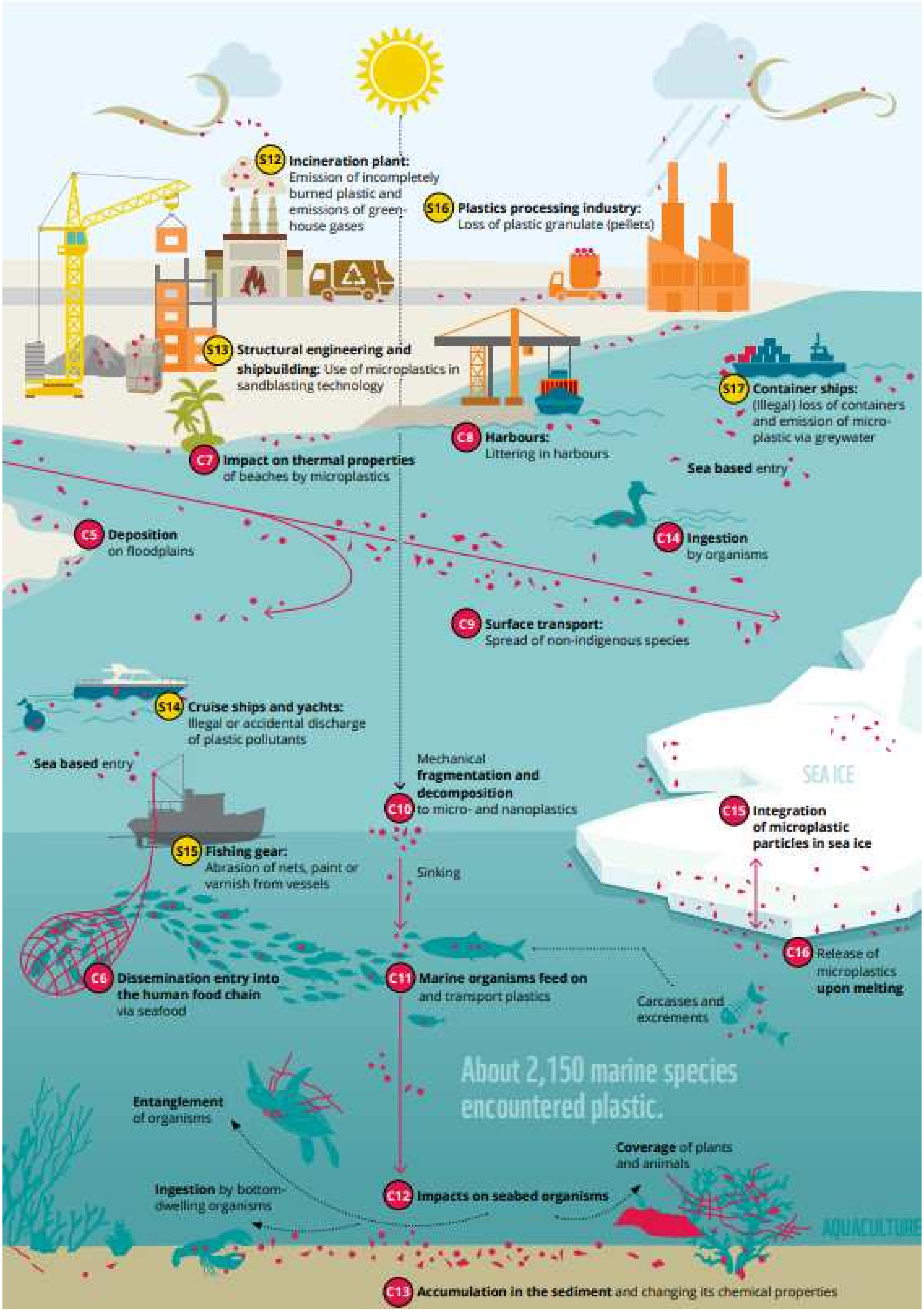


**Figure 9.** The pathways of plastic in the environment. The figure was reproduced from the book of Tekman, M. B., Walther, B. A., Peter, C., Gutow, L. and Bergmann, M. (2022): Impacts of plastic pollution in the oceans on marine species, biodiversity and ecosystems, 1–221, WWF Germany, Berlin. DOI: 10.5281/zenodo.5898684. with permission of the editors (WWF Germany).

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Most of the additives are not covalently bound to the plastic, therefore they can easily migrate on the surface of the material and be released into the environment [Capolupo, 2020]. Among the additives exhibiting toxic properties towards organisms, there can be distinguished e.g. bisphenols [Canesi, 2015] and phthalates [Sree, 2023]], which are indicated as potential endocrine-disrupting chemicals (EDCs) in both animals and humans [UNE Program, 2017]. The monomer used in the production of PVC – vinyl chloride (VCM) is also highly toxic [Akovali, 2012].

On the example of *Daphnia magna*, it has been proven that PVC has a negative effect on, among others, the reproductive processes of zooplankton. PVC microplastics at concentrations of 10-500 mg/L led to a decrease in reproduction efficiency, and at a concentration of 500 mg/L it delayed it. The toxic nature of PVC was due to the substances added to it, as it was the chemicals extracted from it that were harmful to the model organism [Zimmermann, 2020]. The delay of the hatching period combined with the occurrence of oxidative stress and changes in the expression of genes related to reproduction and detoxification in *D. magna* exposed to PVC microplastics (PVC-MPs) at sizes of 2 and 50 µm were also demonstrated by Liu et al. [Liu, 2022]. Chronic exposure to tested microplastic, e.g. extended the days to the first brood, increased the total number of broods per female, reduced the number of her offspring, disturbed the activity of superoxide dismutase (SOD) and catalase (CAT), and increased the level of i.e. glutathione (GSH) . Studies conducted on *Phaeodactylum tricornutum*, *Chaetoceros gracilis* and *Thalassiosira sp.* also showed the toxic properties of PVC MPs towards representatives of diatoms. The high concentration of PVC (200 mg/L) reduced the content of chlorophyll in their cells and negatively affected the processes of photosynthesis. In addition, PVC MPs caused physical damage to the diatom cell structure [Wang, 2020].

**Table 5.** Impact of PVC microplastics (PVC-MPs) on aquatic organisms.

| Organism | Genus/Species | PVC-MPs conc. [unit] | Effect of PVC-MPs on the organism | Ref's |
|---|---|---|---|---|
| Algae | *Chlamydomonas reinhardtii* | 10 – 200 [mg/L] | Growth inhibition; reduction of chlorophyll-A level. | Wang, 2020 |
| | *Skeletonema costatum* | 1-50 [mg/L] | Inhibition of growth; inhibition of photosynthesis efficiency via decrease of chlorophyll content; adsorption and aggregation in algal cells | Zhang, 2016 |
| Corals | *Zoanthus sociatus* | 10 mg/L | Increase of adhesion to coral epidermis; OS induction; changes in photosynthethic efficiency | Rocha, 2020 |
| Plants | *Utricularia aurea* | 50 [mg/L] | Growth, length and biomass inhibition; negative effects on physiological parameters (chlorophyll content) | Zhou, 2020 |
| Mussels | *Perna viridis* | 21.6-2160 [mg/L] | Decrease of clearance, respiration rates and byssus production; decrease of | Rist, 2016 |

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| | | | | |
|---|---|---|---|---|
| | | | median survival times with increasing pollution by PVC | |
| | *Mytilus galloprovincialis* | - | Accumulation in the organism | Gomiero, 2019b |
| Arthro-pods | *Daphnia magna* | 50 [mg/L] | Induction of mortality; increase of the immobilization | Renzi, 2019 |
| Fish | *Clarias gariepinus* | 0.50;1.50; 3.0 [% of diet] | Reduction of mean cell volume/ cell haemoglobin values; decrease of neutrophil counts; GPx alternation (brain, gill); SOD inhibition (brain, gill); CAD reduction (brain); increase of lipid peroxidation levels (brain); AChE inhibition (brain, gill); OS induction. | Iheanacho & Odo, 2020 |
| | *Cyprinus carpio* | 10- 30 [% of diet] | Growth inhibition; alternation of the antioxidant activities - inverse relationship between SOD, CAT after exposition on PVC; increase of the GPx activities; reduction of MDA levels; alternation of antioxidant-related gene expression in the livers of larvae; changes of the transcription; vacuolation of cytoplasmic in the liver under exposure over 20% additives of PVC to diet | Xia, 2020 |
| | *Dicentrarchus labrax* | 100; 500 [mg/kg diet] | Increase of the phagocytic and respiratory burst activities of head kidney leucocytes; decrease of immunity and OS induction. | Espinosa, 2019 |
| | *Dicentrarchus labrax* | 0.1 [% of diet] | Histopathological changes of the ingestine | Peda, 2016 |
| | *Etroplus suratensis* | 1.0 - 10.8 [mg/L] | Influence on SOD activity (increase at 1.03-1.8 mg/L; decrease at 3.0- 10.8 mg/L); behavioral changes (fin | Vijayaraghavan, 2022 |

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| | | | | |
|---|---|---|---|---|
| | | | flickering, burst swimming, and jerking movement); decrease of red and white blood cells; changes in antioxidant enzymes | |
| | *Sparus aurata* | 100; 500 [mg/kg diet] | Gene expression changes: *PRDX5* (decrease); *PRDX1, PRDX3* (increase); UCP1 (up-regulation). | Espinosa, 2017 |

AChE – acetylcholinesterase; CAT – catalase; GPx - glutathione peroxidase; MDA - malondialdehyde; **OS** - oxidative stress; SOD - superoxide dismutase

Since microplastics such as PVC are commonly found in drinking water [Kirstein, 2021; Pivokonsky, 2020; Pivokonsky, 2018] and even bottled water [Ibeto, 2021; Zhou, 2021], the human body is also exposed to their harmful properties [Stapleton, 2021; Wright, 2017].

It is estimated that people who consume the recommended daily amount of water only from bottled sources may consume up to 90,000 microplastics per year, compared to 4,000 microplastics consumed by people drinking only tap water [Cox, 2019]. In addition to exposure to microplastics along with water contaminated with them, the ways of human exposure to microplastics include the consumption of seafood, the global per capita consumption of which is over 20 kg per year (Figure 10) [Smith, 2018].

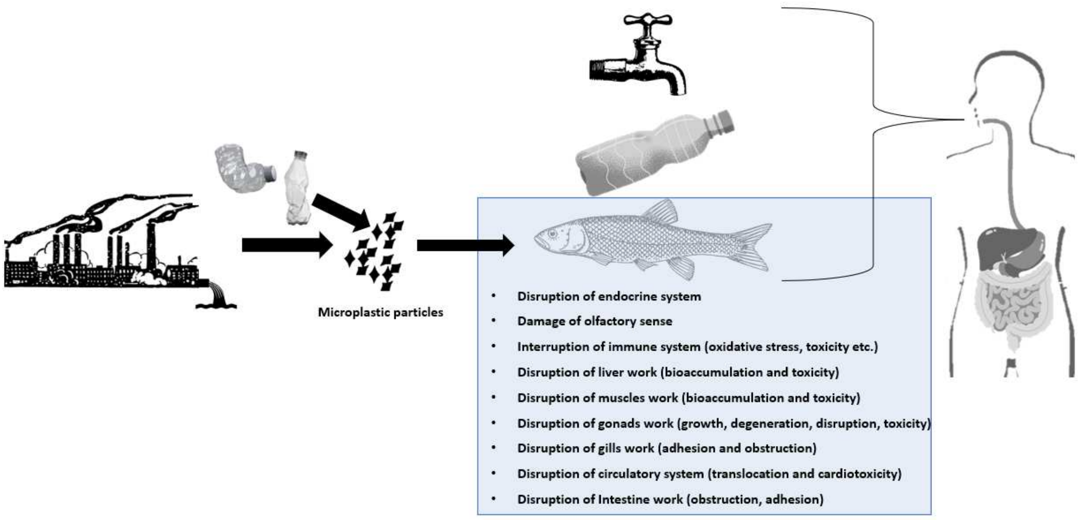


**Figure 10.** Sources of human exposure to microplastics and their impact on aquatic organisms [Gola, 2021]. This Figure was modified by Authors.

For example, research results indicate that the exposure of an average Irishman to microplastics accumulated in seafood intended for consumption, ranges from 15 to 4,471 particles per year [Hara, 2020]. Other estimates indicate that the maximum amount of microplastic particles absorbed by humans from seafood is 53,864 particles per year. These data are based on global consumption estimates of 15.21 kg of fish per year/person, 2.65 kg of molluscs per year/person and 2.06 kg of shellfish per year/person [Wendee, 2023].

Microplastics are also common in commercially available sea salt from the Atlantic Ocean and Mediterranean Sea, and the most frequently identified molecules in the Fischer et al. [Fischer, 2019] study were polypropylene and poly(ethylene terephthalate) (in 16 out of 17 samples), polyethylene (15/17), polystyrene (13/17) and poly(vinyl chloride) (7/17) [Fischer, 2019]. Potential human exposure to microplastic particles found in sea salt is estimated to be 0–1.674 particles/year [Danopoulos, 2020].

## 6. Contamination of soil with PVC

Plastic accumulation in soils is much higher than accumulation in aquatic habitats, and there is especially a lot of plastic in agricultural soils. It is estimated that the amount of plastic in soils worldwide is equal to about 0.6 mgkg$^{-1}$dry soil [Xu, 2023]]. Sources of plastic contamination of soils may include illegal dumping, irrigation with contaminated water, and atmospheric deposition [Xi, 2020; Barili, 2023].

Agricultural soil is deeply affected by pollution from microplastics and synthetic polymers. Contaminants come from beads fragments, plastic mulches, films, fibers or biodegradable plastics [Rillig, 2019]. Plastics are used in agriculture to improve production and ensure food safety for human health. Microplastics are subject to accumulation, which can be reduced by using biodegradable materials [Rajagopalan, 2022]. Polyethylene (PE), polyamide (PA), polystyrene (PS), polypropylene (PP), polyethylene terephthalate (PET) and polyvinyl chloride (PVC) are commonly found in soils [Fan, 2022]. Plastics can release toxic chemicals into soils, which then seep into ground water [136] [Alabi, 2019]. Plastics in soil reduce water percolation and limit soil aeration. Additionally, they contribute to climate change by releasing large amounts of $CO_2$ into the atmosphere during their production and degradation [Barili, 2023].

The effect of plastics on the physicochemical properties of the soil depends on the type, amount, shape and size of the polymer [Barili, 2023]. Since the polymer surface is sometimes charged, plastics can interact with charged ions found in the soil [Xu, 2018]. The large amount of microplastics present in the soil negatively affects the biophysical and chemical properties of the soil, including structure, porosity, texture, pH, surface area, and nutrient content [Tang, 2020]. Polymer particles can affect soil aggregation, which leads to a loss of soil strength. Due to the lack of oxygen below the soil surface, polymer aggregation is characterized by a slow rate of biodegradation. Importantly, the biodegradation process under anaerobic conditions produces methane and carbon dioxide [Tian, 2019]. MPs adsorb or release heavy metals during ageing. Any changes in soil pH and heavy metal availability due to microplastic particle contamination may be indirectly related to soil microbial activity [Meng, 2023]. The addition of PVC significantly increases the rate of soil nitrification and nitrate reductase activity, which may further promote soil denitrification [Huang, 2023]. Studies indicate that PVC increases $NH_4^+$-N content and decreases $NO_3$-N content [Shen, 2023]. The relative abundance of ammonium-oxidizing and denitrifying bacterial groups changes significantly after the addition of MPs. Moreover, the addition of PVC significantly increases the richness of denitrifying bacteria in the soil [Huang, 2023]. Microplastics react with natural fertilizers such as cow manure, causing a greater impact on natural greenhouse gas emissions such as nitrous oxide, ammonia, carbon dioxide, and methane [Sun, 2020].

Due to limited photo-oxidation and limited oxygen conditions necessary for degradation, microplastics can persist in the soil for more than 100 years [Barili, 2023]. MPs are also toxic when ingested by living organisms. A major danger is their accumulation in the biological chain [Yang, 2023]. Studies indicate that MPs smaller than 130 μm accumulate in human tissues and release toxic substances, affecting the function of organs such as the liver and lungs [Wright, 2017].

Different types of microplastics can exhibit different behaviors, causing different impacts on soil ecosystems [Zhu, 2022]. Microplastic particles with a size of 50 nm taken up by plants can penetrate the roots, where spherical plastic particles with a size of about 2 μm and a low degree of mechanical flexibility have been identified [Rajagopalan, 2022].

The study of Dainelli et al. [Dainelli, 2023] indicates that PVC causes a significant reduction in the shoot fresh weight and a decrease in the number of fruits of the plant *Solanum lycopersicum L.* Moreover, this plastic affects a marked increase in Ni and Cd, as well as a decrease in nutritionally valuable lycopene [Dainelli, 2023]. Studies were also conducted on the effects of various microplastic particles on the nutritional properties of the *Capsicum annuum* plant. PVC was more dangerous than other MPs and reduced the maximum protein content, strongly affected vitamin A and vitamin B6 in the fruit. Moreover, PVC reduced the content of oleic and linoleic acid, and seriously degraded the total content of flavonoids and phenols. The effect of this plastic on the macro and micronutrients of *C. annuum* fruit, especially Ca, K, Mg and Zn, is also not insignificant [Alharbi, 2023].

The presence of plastics in the soil can affect the community structure of soil bacteria and fungi, which are important components of the soil microbiota [Barili, 2023; Zhang, 2021]. This is because they play a fundamental role in regulating soil ecosystem functions. Soil bacteria and fungi have different sensitivities to environmental disturbances [Barili, 2023]. PVC reduces the diversity of microflora in the soil rhizosphere [Zhu, 2022].]. Microplastic particles affect a wide range of organisms, such as protists, flagellates, ciliates, nematodes, ameba, and isopods [Rillig, 2018]. Microplastic particles can restrict their movement by attaching to their external body surface, and ingestion can cause gastrointestinal damage, reduced responses and poor metabolism [Rajagopalan, 2022]. Earthworms are a key factor in maintaining a healthy soil ecosystem. These invertebrates modify the hydraulic properties of the soil and lead to microplastic transport through the formation of burrows, as has been demonstrated for the earthworm *Lumbricus terrestris* [Rillig, 2017]. Microplastic particles cause reduced fitness, reduced growth and increased fatality in earthworms. Exposure to as little as 1% and 2% (wt./wt.) has been shown to have lethal effects [Rajagopalan, 2022]. Nematodes are also used to study the effects of microplastics on soil organisms. Contact with microplastic particles on *Caenorhabditis elegans* causes inhibition of body length and reproduction rate. They have been observed to cause permanent intestinal damage due to reduced calcium levels and oxidative stress in the gut, which results from the accumulation of the enzyme glutathione S-transferase [Lei, 2018]. Even a one-day exposure of nematodes to higher concentrations of microplastic significantly affects the number of offspring [Rajagopalan, 2022]. As indicated by studies, microplastic exposure in soil is responsible for the reduction of body weight and reproductive capacity of collembolans and the modulation of Isopods' immune processes [Rajagopalan, 2022; Kokalj, 2018].

### 7. Methods of eliminating polyvinyl chloride from the environment

In the face of increasing levels of environmental pollution from plastics, the development of highly efficient and environmentally friendly methods for their degradation is urgently needed. In 2000, the European Commission published a Green Paper for PVC waste [EC 2000], which assessed various environmental and health aspects and the possibility of reducing the impact. It paid particular attention to measures leading to solutions to PVC waste management problems.

For example, the Vinyl2010 Voluntary Commitment detailed measures to reduce organochlorine emissions through the sustainable use of additives and various controlled-cycle management strategies. Its successor, VinylPlus, set an annual recycling target of 900,000 tons by 2025 and at least 1,000,000 tons by 2030 [VinylPlus, 2018; Miliute-Plepiene, 2021].

**Table 6.** Examples of methods for PVC and plastic neutralization and elimination from the environment.

| Method | Type | Mechanism | Ref's |
|---|---|---|---|
| chemical dechlorination | chemical neutralization | modification consisting in replacing some chlorine atoms with various nucleophilic reagents | Lu, 2019 |
| hydrothermal dechlorination | physico-chemical neutralization | conducting modifications in supercritical or subcritical water which works as a solvent | Li, 2017 |

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| | | | |
|---|---|---|---|
| | | and reagent for reactions of organic compounds | |
| photodegradation | physical degradation | breaking down the chemical bonds in a polymer by ultraviolet (UV) radiation | Yousif, 2015 |
| mechanical recycling | mechanical modification | recycling technique consisting in extruding and mixing the material with primary polymers | Sadat-Shojai & Bakhshandeh, 2011 |
| pyrolysis | physico-chemical degradation | polymers decomposition under high temperature | Yu, 2016 |
| biodegradation | biological degradation | polymers decomposition by the microorganisms such as bacteria and filamentous fungi, and organisms such as insects | Vivi et al., 2019 Giacomucci, 2019 Tsochatzis, 2021 |
| biofragmentation | biological modification | the breakdown of polymers into monomers, dimers or oligomers during a lytic process, involving decrease of reducing the molecular weight of the polymer and oxidation of the lower weight molecules using specific enzymes (oxidoreductases and hydrolases), as well as free radicals | Restrepo-Flórez, 2014 |

It seems promising to carry out complete dechlorination processes before degradation. Thanks to full dechlorination, PVC can be treated in the same way as common halogen-free plastics [Takeshita, 2004 ]. Such methods include chemical modifications, the near-critical methanol process for PVC dechlorination and recovery of additives, and the near-critical process using an aqueous ammonia solution. Among these techniques, a well-known method is chemical modification consisting in replacing some chlorine atoms with various nucleophilic reagents [Lu, 2019]. Another technique used to convert waste into energy with simple, fast reactions is hydrothermal treatment. In this technique, super- or sub-critical water is used as a solvent and reagent for the reaction of organic compounds. Various additives and solvents such as NaOH or dimethylsulfoxide are used to improve the dechlorination efficiency, however, when large amounts are used, their recycling causes a problem [Li, 2017]. Moreover, despite the frequent use of certain chemicals in hydrothermal dechlorination of waste, their role in this process has not been fully understood. Analyzes by Zhao et al. [Zhao, 2018] conducted with the use of $Na_2CO_3$, KOH, NaOH, $NH_3{\cdot}H_2O$, CaO and $NaHCO_3$ in water containing $Ni^{2+}$ showed that the alkalinity of additives has a significant impact on the effectiveness of dechlorination. The most effective additive in these studies was $Na_2CO_3$

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(concentration 0.025 M) with a maximum efficiency of 65.12% [Zhao, 2018]. The processes carried out using subcritical water-NaOH (CW-NaOH) and subcritical water-$C_2H_5OH$ (CW- $C_2H_5OH$) proved that the main mechanism in the case of dechlorination in CW-NaOH is nucleophilic substitution of hydroxyl, while in CW-$C_2H_5OH$ nucleophilic substitution and direct dehydrochlorination were equally significant processes [Xiu, 2020]. The key element in the dechlorination process is temperature. As the efficiency of this process also decreases with the decrease in temperature, the above-mentioned additives have been used to improve the efficiency. Unfortunately, the incorporation of additives not only increased the costs of dechlorination, but also generated secondary pollution [Xiu, 2021]. Temperature has also been shown to be important in the removal of chlorine (Cl) from PVC in gas-liquid fluidized bed reactor studies where hot $N_2$ was used as the fluidizing gas to fluidize the polymer melt [Yuan, 2014].

Although polyvinyl chloride is a commercially important polymer, it is also one of the most sensitive to UV radiation. A study by Yang et al. [Yang, 2023] showed that the rate of photo-ageing of plastics is faster than other ageing processes therefore it is one of the most common methods of PVC degradation. UVA radiation in deionized water, sea sand and air was used to photodegrade plastics. The results showed that PVC effectively absorbs UVA radiation in air, and this is where the ageing efficiency was greatest. The ageing process included photoinitiation, chemical bond breaking and oxygen oxidation [Yang, H., 2023, Yang, R., 2023].

Under the influence of UV radiation (in the wavelength range of 253-310 nm) and in the presence of oxygen and moisture, PVC underwent very rapid processes of dehydro-chlorination and peroxidation to form polyenes. The irradiated material crumbles, lost its stretch, elasticity and impact resistance, and the surface of the degraded polymer was significantly modified, i.e. loss of abrasion resistance, gloss and interfacial free energy were observed [Yousif, 2015; Decker, 1984].

The use of photodegradation process makes it easier to eliminate plastics from the environment. In order to accelerate the photodegradation of plastics, semiconductor photocatalysts such as $TiO_2$, ZnO, $Fe_2O_3$, CdS, ZnS were also used. For example, it was observed that the addition of ZnO to PVC increased the decomposition of the composite by 4.13% in the case of irradiation with artificial UV radiation, and by 9.7% in the case of solar radiation, respectively [Sil, 2010]. A photogradable composite film was prepared by doping polyvinyl chloride plastic with nano-graphite (Nano-G) and $TiO_2$ photocatalyst. After exposure to UV radiation (for 30h) the weight loss rates of Nano-G/PVC, $TiO_2$/PVC and Nano-G/$TiO_2$/PVC films were 7.68%, 8.94% and 17.24%, respectively, while PVC decreased its weight by only 2.12 % [Zhang, 2020].

PVC is less biodegradable than other plastics [Ali, 2009; Bahl, 2021]. Therefore, there are many studies on the thermal decomposition and photodegradation of PVC, but there are few literature reports on the biodegradation of polyvinyl chloride compared to them [Alshehrei, 2017], and microorganisms capable of decomposing it are sought both in the aquatic environment [Giacomucci, 2020] and soil [Sakhalkar, 2013].

### *7.1. Recycling and utilization of PVC*

PVC can be recycled using various material and energy recovery methods [ ] [Čolnik, 2022].

Recycling techniques include:

- mechanical methods – consisting in extruding and mixing the material with primary polymers,
- chemical methods – changing the polymer structure of the material using chemical and thermal agents [Yin, 2021].

The mechanical recycling is the most-recommended way to recycle PVC [Lewandowski, 2022]. Conventional mechanical recycling processes are based on separation, shredding and application of shredded material with unchanged chemical composition to processing equipment. In this technique, plastics are collected and sorted by hand and/or machine at recycling plants, then flaked in a high-speed mill and cleaned with detergent and water. Finally, the dry flakes are melted and cast into pellets from which new products can be made [Sadat-Shojai, 2011]. The limitation of mechanical or secondary recycling is that it can be used in the case of unmodified PVC waste of known composition and origin [ Čolnik, 2022].

For economic and environmental reasons the is feedstock recycling of PVC is used, including waste that cannot be mechanically recycled. This relatively simple method of PVC recycling allows energy recovery, which consists of gasification of fuels or direct combustion in specialised thermal utilisation plants. In the case of energy recovery, a fraction of PVC is mixed with other types of waste. The thermal process consists of two steps: dechlorination and and the use of remaining hydrocarbons. Through the thermal recycling of PVC waste hydrogen chloride is recovered and the chemicals obtained can find various applications, especially in the chlorine industry [Lewandowski, 2022].

Some new mechanical recycling technologies are based on selective dissolution, for recycling PVC in an economically feasible way. However, currently only a small amount of PVC post-consumer waste is being recycled. Incineration, in conjunction with municipal waste disposal, is a simple option that allows for the partial recovery of energy and chemical substances, if state-of-the-art technology is applied [Baitz et al., 2004].

One of the common chemical recycling techniques is pyrolysis, divided into hydrocracking, thermal cracking and catalytic cracking [Yu, 2016]. Although pyrolysis is an effective method of converting PVC waste into energy, it produces products containing significant amounts of chlorine [Ali, 2005]. Release of harmful substances such as polychlorinated dibenzo-p-dioxins (dioxins) and polychlorinated dibenzofurans (furans) also occurs in processes such as incineration [Yin, 2021]. During the thermal degradation of PVC, HCl is eliminated leading to the formation of conjugated double bonds, and in turn attacks other compounds with double bonds, leading to the production of organochlorine compounds [Lu, 2002]. Even if PVC is landfilled instead of incinerated, during the process it may release, among others, phthalates and heavy metals such as lead, cadmium and tin [Takeshita, 2004]. Therefore, these processes, including storage, pose a significant risk of releasing chlorinated organic compounds, microplastics and pollutants into soils and waters [Ma, 2021]. Due to the low efficiency of recycling and the tendency to secondary pollution, the traditional methods of disposal of plastic waste - incineration and landfilling - have been banned [Yin, 2021]. Therefore, it has become important to develop techniques to reduce Cl migration.

### *7.2. Biological utilization of PVC waste*

Biodegradation of plastics found in soil is a complex process. The efficiency of this process was influenced by the availability of substrate assimilable by microbial consortia, molecular weight, surface and morphology characteristics, as well as the structure of the polymers [Ammala, 2011]. Biodegradation included the formation of microbial biofilms on plastic surfaces, followed by the enzymatic degradation of the polymer structure, which led to the release of oligomers and monomers [Barili, 2023]. Biochemical transformation of resistant polymers by microorganisms usually involves the transformation of complex compounds into simpler forms, leading to a reduction in molecular weight, loss of mechanical strength and surface properties of plastics. The biochemical degradation processes of PVC proceeded in ~~to~~ five stages: colonization, biodeterioration, biofragmentation, assimilation, and mineralization. The first stage of the biodegradation mechanism was the colonization of microorganisms on the plastic surface. It involved the adhesion of living microorganisms (bacteria and fungi) to the surface of plastics and used them for microbial growth and reproduction. During colonization, microorganisms formed biofilms, which caused damage to the polymer surface [Amobonye, 2023]. The physical and chemical action of microorganisms led to biodeterioration and superficial degradation of many kinds of polymers, including PVC. It caused a change of their physical, mechanical and chemical properties [Ganesh, 2020].

Prolonged exposure to light, high temperatures and chemicals in the atmosphere facilitated the biodeterioration process. Microorganisms penetrated the polymers and increased pores and cracks. On the other hand, some microbial species with chemolithotrophic potential promote oxidation and reduction reactions and chemical biodeterioration [Amobonye, 2023]. Biofragmentation is a lytic process that allowed the breakdown of polymers into monomers, dimers or oligomers. The process involved decrease of ~~reducing~~ the molecular weight of the polymer and oxidation of the lower weight molecules using specific enzymes (oxidoreductases and hydrolases), as well as free radicals [Restrepo-Flórez, 2014] Enzymatic depolymerization of plastics released monomers that were transported into cells, where they underwent a series of enzymatic reactions leading to complete degradation. $CH_4$, $CO_2$, $H_2O$ and $N_2$ were formed [Ho, 2018]. The mineralization stage can be aerobic or anaerobic and was catalyzed by several enzymes: cutinase, laccase, esterase, peroxidase and lipase [Amobonye, 2023].

Enzyme specificity and temperature are of great importance in the degradation of plastics. Moreover, the use of several microbial consortia and several enzyme complexes allows for an increase in biodegradation efficiency compared to a single enzyme or single microorganisms [Barili, 2023]. It is known, however, that the biodegradation of PVC involves three main reactions, including chain depolymerization, oxidation processes and mineralization of the resulting intermediates [Temporiti, 2022]. An effective approach to bioremediation of the environment from plastics is their initial thermal treatment. After thermo-oxidative modifications of PVC, it was noticed that *Achromobacter denitrificans* bacteria isolated from compost were able to eliminate 12.3% of the plastic, which may be evidenced by its weight reduction [Rad, 2022]

Of all higher organisms, only some insects are capable of degrading various plastics and converting them to monomeric compounds. In particular, insects in their larval stages show the ability to degrade plastics [Tsochatzis, 2021]. Insects that metabolize plastic include yellow mealworms (*Tenebrio molitor*), giant mealworms (*Zophobas atratus*), and superworms (*Z. atratus*). It is thought that this unique "plastic-eating" phenomenon may be related to the ability of some of these insects to degrade lignin [Wertz & Béchade, 2020]. Insects have also been shown to ingest polymers, with the actual ingestion being led by microorganisms inhabiting their guts [Xu, 2023; Amobonye, 2023; Bożek, 2017; Wertz, 2023].

Some bacteria, e.g. *Pseudomonas citronellolis* were capable to degrade the PVC films. The 45-day incubation resulted in fragmentation of the material and a decrease in its average molecular weight by 10%. The maximum weight loss during the further stages of the experiment was 19% [Giacomucci, 2019]. Almost 12% weight loss of PVC was also observed in an experiment conducted in anaerobic microcosms using enriched anaerobic consortia from marine samples (waste and water). In addition, the material after 7 months of incubation showed lower thermal stability [Giacomucci, 2020]].

Changes in the mechanical properties of the material were also observed in the analyzes carried out using isolates of marine bacteria of the genus *Vibrio, Altermonas* and *Cobetia*. The most effective microorganisms in the elimination of PVC turned out to be *Altermonas* BP-4.3 strain, in case of which, after 60 days of incubation, a 1.76% loss in the weight of the polyvinyl chloride film was observed [Khandare, 2021]. *Micrococcus luteus* from areas heavily polluted with plastics were able to mineralize 8.87% of PVC. This level was achieved in cultures maintained for 70 days with mineral substrate [Patil, 2012].

The importance of microorganisms in processes such as PVC depolymerization was also demonstrated on the example of microorganisms living in the intestines of *Tenebrio molitor* larvae. After 5 weeks of experiments involving the introduction of polyvinyl chloride larvae into the diet, their survival rate with PVC as the only component of the diet was maintained at the level of up to 80% [Peng, 2020]. The ability of *T. molitor* to eliminate PVC was also confirmed by Bożek et al. After 21 days of exposure of mealworm to polyvinyl chloride in the diet, a 3% loss in mass of the material was observed [Bożek, 2017]. Two bacterial strains isolated from oil-contaminated soil (*Pseudomonas aeruginosa* and *Achromobacter sp*.) showed the ability to degrade PVC containing epoxidized vegetable oil (75% by weight), resulting in a change in the material's surface topography and a decrease in its tensile strength during an incubation period of 180 days [Das, 2012]. Some microorganisms are capable of degrading PVC. However, the PVC materials used in the study are largely plastics containing plasticizers. It was found that some bacterial strains acted mainly on PVC additives and there was a low ability to degrade PVC without additives [Giacomucci, 2019].

Apart from bacteria, microscopic filamentous fungi are also considered as organisms potentially capable of degrading PVC. Analyzes carried out using *Chaetomium globosum* (ATCC 16021) have

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shown, for example, that this fungus is able to adhere to the surface of PVC, which is the first stage of the degradation process [Vivi, 2019]]. Exposure of PVC fragments containing plasticizers - dioctyl phthalate and dioctyl adipate to the atmosphere for a period of 2 years showed that between the 25th and 40th week, the surface of the plastic was dominated by *Aureobasidium pullulans.* After 80 weeks, the next microorganisms identified were e.g. *Rhodotorula aurantiaca* and *Kluyveromyces* spp. All tested strains of *A. pullulans* grew in the presence of PVC, using it as a carbon source, degrading plasticizers, and producing extracellular esterase and reducing substrate weight during growth [Webb, 2019].

The biodegradation potential, through adhesion to polyvinyl chloride by *Lentinus tigrinus* PV2, *Aspergillus niger* PV3 and *Aspergillus sydowii* PV4 was also confirmed [Ali, 2014]. For fungi of the genus *Aspergillus* (*A. Niger* Sf1 and *A. glaucus* Sf2), it was observed, among others, 10% and 32% weight loss of PVC over 4 weeks of the experiment, respectively, while *Bacillus licheniformis* Sb1 and *Achromobacter xylosoxidans* Sb2, with the same observation time, were 15% and 17% [Saeed, 2022]. *Phanerochaete chrysosporium* PV1 strain showed the potential for PVC film degradation, for which Fourier transform infrared spectroscopy and nuclear magnetic resonance analysis showed significant structural changes in the material. This was confirmed by peaks corresponding to alkenes appearing, decreases in peak intensity appearing in the case of C–H stretching, and a decrease in the weight of the analyzed PVC itself [Ali, 2014[]. The decrease in PVC weight was also demonstrated during an experiment conducted for 12 weeks with strains isolated from the soil. Loss of 0.064 g/m² for *Mucor hiemalis*, 0.300 g/m² for *Aspergillus versicolor*, 0.341 g/m² for *Aspergillus niger*, 0.619 g/m² for *Aspergillus flavus*, 0.082 g/m² for *Penicillium* sp., 0.240 g/ m² for *Chaetomium globosum*, 0.330 g/m² for *Fusarium oxysporum*, 0.240 g/m² for *Fusarium solani*, 0.364 g/m² for *Phoma* sp., and 0.145 g/m² for *Chrysonilia sitophila* was observed respectively. The ability of *Mucor sp*. fungi to grow in the presence of polyvinyl chloride as the only source of carbon and energy was also demonstrated [Pardo-Rodríguez, 2021].

With regard to the fact that additives added to the polymer may increase physical and chemical degradation, it has also been shown that the addition of a small amount of cellulose to PVC may cause changes in its properties and facilitate its microbiological degradation [Abdel-Naby, 2014; Ali, 2009; Kaczmarek, 2007].

Under aerobic conditions vinyl chloride (VC) can serve as as the sole source of carbon and energy for *Pseudomonas putida* strain AJ and *Ochrobactrum* strain TD, which were isolated from hazardous waste sites. Analyzes conducted on the biodegradation of vinyl chloride, used as a substrate for PVC production, showed that it is alkene monooxygenase that is responsible for its metabolism in AJ strains of *Pseudomonas putida* and AD *Ochrobactrum bacteria* [Danko, 2004]. The degradation of acetate-modified PVC (PVA) involves, among others, enzymes such as oxidases [Othman, 2021]. PVA oxidase activity is correlated with PVA dehydrogenase. The β-diketone group was introduced into the PVA polymer molecule through the product of the reaction carried out by the dehydrogenase. This product, through the active site of serine hydrolase, initiated the oxidation reaction by PVA oxidase. This is followed by hydrolysis to form a monomer [Shimao, 2000]. While there is a lot of data on the enzymes involved in the degradation of modified polyvinyl chloride, scientific reports on the mechanisms and enzymes involved in the degradation of PVC are virtually nonexistent [Othman, 2021]. This is due to the high chemical stability and hydrophobicity of the C-C skeleton of PVC [Yang, 2023]. Among the few data, there is a mention that in the case of genus *Cochliobolus*, in the degradation of low molecular weight PVC, laccase was involved [Sumathi, 2016].

## 8. Conclusions

The widespread occurrence of microplastics in terrestrial systems has been confirmed by many studies, and their presence has the potential to alter soil chemical and physical properties and processes.

Around the world, plastics have become an important daily commodity. Demand for them is very high in all industrial sectors. Polymers and plastics are insoluble in water and pose a serious threat to the environment. They deplete natural resources by limiting their use. Water and soil contaminated with PVC and other plastics pose a threat to living organisms. Microplastics find their way into groundwater and even into drinking or bottled water, they also find their way into soils –

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contamination of agricultural soils is particularly dangerous. Microplastic accumulates in living organisms thus becoming part of the food chain.

The problem of microplastic pollution of agricultural soils is becoming a problem of continuous irrigation with wastewater, the use of sewage sludge and the use of plastic film mulching. Due to the slow rate of degradation, plastics can survive in the environment for centuries or even millennia. It follows that microplastic pollution is a long-term problem.

## 9. Future Directions

The widespread pollution of the environment, both water, air and soil, indirectly affects the reduction of natural resources such as water and soil. Polluted water and soil pose a threat to the life and health of all living organisms, from microorganisms and plants to animals and humans. One of the most common plastics in the environment is PVC, which massively contaminates resources. There is no information on the consumption of plastics, including PVC, by livestock. Microplastics can cause adverse effects on animal health and accumulate in their bodies thus becoming part of the food chain. Special attention should be paid to the aspect of the effects of microplastic pollution on the lives of higher organisms.

The accumulation of plastics from soils is expected to increase due to the continued growth in the production and use of plastics and the lack of effective plastic waste management strategies. A solution could be the use of biodegradable plastics, the production and use of which continues to grow. Biodegradable plastics breaking down can also produce microplastic particles. Given the scale of the plastics market and their degradation period, microplastic pollution is still a long-term problem.

Extensive long-term research is needed to determine the exact impact of microplastics on the environment and the health of living organisms. Only then are we in a position to know precise impact data and determine actions leading to improvements.

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