20 case studies on how to prevent the use of toxic chemicals frequently found in the Mediterranean Region

Weber, Roland ; Fantke, Peter; Hamouda, Amel Ben; Mahjoub, Borhane

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HOW TO PREVENT THE USE OF TOXIC CHEMICALS

frequently found in the Mediterranean Region

United Nations Environment Programme

Mediterranean Action Plan
Barcelona Convention

Regional Activity Centre for Sustainable Consumption and Production

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Supervision and coordination: Magali Outters (SCP/RAC), Kimberley de Miguel (SCP/RAC)

Authors: Roland Weber (POPs Environmental Consulting, Germany), Peter Fantke (Technical University of Denmark), Amel Ben Hamouda and Borhane Mahjoub (Institution of Agricultural Research and Higher Education, University of Sousse, Tunisia)

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For further information, please contact:
www.switchmed.eu
moutters@scprac.org

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ACRONYMS AND ABBREVIATIONS

ABS	Acrylonitrile butadiene styrene
ACQ	Alkaline copper quaternary
AFFF	Aqueous Film-Forming Foam
AFFF-AR	Alcohol Resistant Aqueous Film-Forming Foam
APEOs	Alkylphenol ethoxylates
AR	Alcohol resistant
ATO	Antimony trioxide
ATSDR	Agency for Toxic Substances and Disease Registry
BADP	Bisphenol-A diphenyl phosphate
BAT	Best Available Techniques
BBP	Butyl benzyl phthalate
BEP	Best Environmental Practices
BFR	Brominated Flame Retardant
BiVa	Bismuth Vanadate
BOD	Biological Oxygen Demand
BPA	Bisphenol A
BPADP	Bisphenol A diphosphate
BPF	Bisphenol F
BPS MAE	Phenol,4-[[4-(2-propen-1-yloxy) phenyl] sulfonyl]
BW	Body weight
CAA	Clean Air Act
CAS	Chemical Abstracts Service
CCA	Copper Chromium Arsenate
CDC	Centers for Disease Control and Prevention
CEPA	Canadian Environmental Protection Act
CICP	Complex Inorganic Coloured Pigments
CMR	Carcinogenic, mutagenic, reprotoxic
CO_2	Carbon dioxide
COD	Chemical Oxygen Demand
CoRAP	Community Rolling Action Plan
CSTEE	Scientific Committee for Toxicity, Ecotoxicity and the Environment
DALYs	Disability Adjusted Life Years
DBP	Dibutyl phthalate
DCPS	4,4'-Dichlorodiphenyl sulphone
DecaBDE	Decabromodiphenyl ether
DecaBDPE	Decabromodiphenyl ethane
DEHP	Bis(2-ethylhexyl) benzene-1,2-dicarboxylate
DHPS	4,4'-Dihydroxydiphenyl sulphone
DIDP	Diisodecyl phthalate
DNOP	Di-n-octyl phthalate
DINP	Di-iso-nonyl phthalate
DINCH	1,2-Cyclohexanedicarboxylic acid, diisononylester
DPS	Diphenyl sulphone
EAF	Electric arc furnace
EALs	Environmentally adapted lubricants
EC	European Commission
ECHA	European Chemicals Agency
ECMO	Extracorporeal Membrane Oxygenation
EDC	Endocrine disrupting chemical
EFSA	European Food Safety Authority
EPA	Environmental Protection Agency
ESIS	European chemical Substances Information System
EU	European Union
EVA	Ethylene vinyl acetate
F3	Fluorine-free foams
FAO	Food and Agriculture Organization of the United Nations
FDA	Federal Drug Administration
FTAs	Fluorotelomer acrylates
FTOHs	Fluorotelomer alcohols
GHG	Greenhouse gas
GSPI	Green Science Policy Institute
HCB	Hexachlorobenzene
HCWH	Health Care Without Harm
HDPE	High density polyethylene
HFC	Hydrofluorocarbons
HHPs	Highly hazardous pesticides
HIPS	High Impact Polystyrene
IARC	International Agency for Research on Cancer
IFOAM	International Federation of Organic Agriculture Movements
IHME	Institute for Health Metrics and Evaluation
IPM	Integrated Pest Management
IV	Intravenous
LCO_2	Liquid carbon dioxide
LDPE	Low density polyethylene

LCCPs	Long-chain chlorinated paraffins
MBHA	Methyl bis(4-hydroxyphenyl) acetate
MCCPs	Medium-chain chlorinated paraffins
MENA	Middle East and North Africa
MSDS	Material Safety Data Sheet
MWF	Metal working fluid
NPEOs	Nonylphenol ethoxylates
NPs	Nonylphenols
NICU	Neonates in intensive care units
ODS	Ozone depleting substance
OFPA	Organic Foods Production Act of 1990 (US)
PA	Polyamide
PAA	Primary aromatic amines
PAH	Polycyclic aromatic hydrocarbons
PAN	Pesticide Action Network
PbB	Blood lead
PBAT	Polybutyrate adipate terephthalate
PBDD/Fs	Polybrominated dibenzo-p-dioxins and dibenzofurans
PBDE	Polybrominated diphenyl ether
PBDF	Polybrominated dibenzofurans
PBS	Poly(butylene succinate)
PBT	Persistent, bioaccumulative, and toxic
PC	Polycarbonate
PCBs	Polychlorinated biphenyls
PCE	Perchloroethylene (perc)
PCDD/Fs	Polychlorinated dibenzo-p-dioxins and dibenzofurans
PCL	Polycaprolactone
PE	Polyethylene
PERC	Perchloroethylene; tetrachloroethane
PES	Polyethersulfone
PET	Polyethylene terephthalate
PFAA	Perfluoroalkyl alkyl acid
PFASs	Per- and polyfluorinated alkylated substances
PFCs	Per- and polyfluorinated chemicals
PFHxA	Perfluorohexanoic acid
PFOS	Perfluorooctanesulfonic acid; Perfluorooctanesulfonate
PFR	Phosphorus Flame Retardant
PHA/PHB	Polyhydroxyalkanoates
PLA	Polylactide
POP	Persistent organic pollutant
PP	Polypropylene
Ppm	Parts per million
PPO	Poly(p-phenylene oxide)
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl chloride
RDP	Resorcinol-bis(diphenylphosphate
RDAs	Recommended Dietary Allowances
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
RoHS	Restriction of Hazardous Substances
SAICM	Strategic Approach to International Chemicals Management
SCCPs	Short-chain chlorinated paraffins
SDGs	Sustainable Development Goals
SF	Solvent-free
SVHC	Substance of Very High Concern
TCE	Trichloroethylene
TCP	Trichloropropane
TDI	Tolerable daily intake
TOTM	Tris(2-ethylhexyl) benzene-1,2,4- tricarboxylate
TPEs	Thermoplastic elastomers
TSCA	Toxic Substances Control Act
UC	Use classes
UNEA	United Nations Environment Assembly
UNEP	United Nations Environment Programme
US	United States
USD	United States dollars
UU	Urea Urethane
vPvB	Very persistent and very bioaccumulative
w/w	Wet weight
wt%	Percent weight
WHO	World Health Organization
ZRPs	Zinc-rich primers

Between 1930 and 2000 the global production of man-made chemicals increased from 1 million to 400 million tonnes each year.[1] In 2015 alone, nearly 22% of the world chemical exports came from the European Union, making it the largest chemicals exporting region in the world[2] . It is evident that the chemical industry is a manufacturing success story and a wealth-generating sector of the economy.

While chemicals bring significant benefits to society, there is also overwhelming available evidence of the widespread contamination chemicals have caused to our planet. We are surrounded by man-made chemicals, from ingredients in cosmetics and clothing to plastic additives and pesticides - our 21st century society depends on chemicals more than ever.

Each and every second, more than 300 kg of harmful chemicals are released into our air, land and water by industrial facilities around the world, which represents approximately 10 million tonnes every year[3]. Emitted chemicals are absorbed by wildlife and humans through the skin or ingested via food and water and although their long-term effects are often unknown, over 2 million tonnes are recognized carcinogens. Effects associated with exposure to chemicals may include allergies and hypersensitivity, damage to the nervous system, reproductive disorders and disruption of the immune system. The negative impacts of our chemicals have been found in households, industrial regions, marine systems, the tropics and even the Arctic.

Growing scientific research on chemical contamination has exposed a bitter truth, stressing the need to take urgent action to combat chemical emissions and exposure at a national and global level. This is the purpose of global conventions on the management of highly toxic chemicals, such as the Stockholm Convention on Persistent Organic Pollutants, as well as other legally binding international instruments. The implementation of such instruments is designed to gradually decrease the presence of chemicals that are proved to be highly toxic, very persistent and bioaccumulative in the environment.

The recent United Nations' Sustainable Development Goals (SDGs) also set some targets related to chemical pollution. The goal on responsible consumption and production aims at achieving the environmentally sound management of chemicals and all wastes throughout their life cycle and significantly reduce their release to air, water and soil in order to minimize their adverse impacts on human health and the environment by 2020.

Being aware of the risks that the release of toxic chemicals poses on the environment, in the Mediterranean region, the 22 Contracting Parties to the Barcelona Convention for the Protection of the Marine Environment and the Coastal Region have adopted a Regional Plan on Persistent Organic Pollutants (POPs) which are especially harmful chemical substances. The plan identifies a series of actions that the countries commit to implement to ensure the prevention, phase-out and sound management of those toxic chemicals. In that line, one of the strategic objectives of the Mediterranean Action Plan mid-term strategy 2016-2021 is to prevent, reduce and control selected pollutants inputs, oil discharges and spills.

Furthermore, the Regional Action Plan on Sustainable Consumption and Production in the Mediterranean, adopted by the Contracting Parties to the Barcelona Convention, indicates the need to promote, use and develop tools such as eco-design, Life Cycle Management, risk assessment of chemicals, substitution of hazardous chemicals and Cradle to Cradle design to facilitate the sustainable design and production of manufactured goods.

In that context, the Regional Activity Centre for Sustainable Consumption and Production (SCP/RAC) is highly involved in the implementation of policies and pilot actions to prevent the use of toxic chemicals in southern Mediterranean countries. SCP/RAC is a centre for international cooperation supporting the implementation of sustainable consumption and production and circular economy approaches, it develops its activities under both the Barcelona Convention for the Protection of the Marine Environment and the Coastal Region of the Mediterranean and the Stockholm Convention on Persistent Organic Pollutants.

In order to tackle that issue, SCP/RAC, with the support of the EU-Funded SwitchMed Programme (www.switchmed.eu), has identified 20 case studies on how to prevent and minimize the use of selected toxic chemicals that are widely used in the Southern Mediterranean region.
Safe and innovative alternatives are showcased here as a viable way to phase out and substitute toxic chemicals found in everyday products while encouraging responsible consumption and production among consumers, businesses, entrepreneurs and civil society organizations in the Mediterranean region. The solutions that are described are equally capable of generating revenues from all parts of the globe and have been prioritized through a multi-criteria analysis of their effectiveness and replicability in the Middle East and North Africa region.

Through this publication, SCP/RAC calls on green entrepreneurs, committed Civil Society Organizations, innovators and change-makers in the Mediterranean to develop and scale the most adaptable solutions and on policy makers to further implement global and regional agreements and action plans and develop the necessary national regulatory framework.

Gaetano Leone
Coordinator
UN Environment/Mediterranean
Action Plan Coordinating Unit
Barcelona Convention Secretariat

Enrique de Villamore Martín
Director
Regional Activity Centre for Sustainable
Consumption and Production (SCP/RAC)
UN Environment/Mediterranean Action Plan

Why is urgent action needed to tackle the issue of toxic chemicals in the Mediterranean region?

Acute exposure to harmful chemicals can lead to death or serious illness. Long-term exposure to these substances can increase the risk of developmental and reproductive disorders, immune system and endocrine disruption, impaired nervous-system function and development of certain cancers. Examples include additives used to enhance the performance of plastics, certain metals and solvents as well as pesticides and fertilizers, which can infiltrate water sources – ending up as marine litter, contaminating drinking water and animal species. Such contamination not only leads to a range of public health and environmental impacts but also poses large social and economic costs.   There are a variety of hazardous synthetic chemicals, which are of particular concern and **currently being used in our everyday products.** These include:

1. Very persistent and very bioaccumulative (vPvB) chemicals, which break down slowly or not at all and accumulate in the fatty tissue of living organisms and are found in higher concentrations at higher levels of the food chain;
2. Endocrine disrupting chemicals (EDCs), which interfere with the hormone systems of animals and/or humans;
3. Chemicals, which cause cancer, reproductive problems, or damage DNA, labelled CMR (carcinogenic, mutagenic or toxic for reproduction).

What further complicates the situation is the general **lack of clear safety information provided,** such as toxicity and exposure potentials of chemicals. The Globally Harmonized System of Classification and Labelling of Chemicals (GHS) is not thoroughly established in the region. Increasing the implementation of GHS labelling on products could improve the safety and contribute to reducing the exposure of the population to toxic chemicals.

It is often the case that hazardous chemicals, which have been restricted or banned in the European Union (EU) or other industrialized regions, are still used in the Southern Mediterranean region. Good management, use and disposal of chemicals is particularly important in developing countries, where economies may be heavily reliant on these industries and where awareness of risks from chemical exposures is very low; the magnitude of the problem is often unknown and policies to address sound chemicals management are limited or non-existent.

What are the key Global and European policy frameworks related to toxic chemicals relevant for the Mediterranean region?

It is widely recognised that **regulations are the main drivers for change** and this is specially the case for the issue of toxic chemicals. Those regulations are providing private and public institutions with the legal instruments to fight this battle. The implementation of policies at a national level to improve regulation and control of sale, distribution and use as well as the global conventions on the management of highly toxic chemicals is critical.

At the global level, the Stockholm Convention, bans the trade of POPs for which Parties have eliminated production and use, allowing the exportation only for environmentally sound disposal. The Convention is a legally binding instrument and it also allows Parties to register for specific exemptions on a country-by-country basis, which is often the case in the countries of the Southern Mediterranean region where countries may request exemptions for particular use. A reduction of emissions and exposure to harmful chemicals at the global level is also promoted through the global sustainability agenda via 17 SDGs with specific targets combating chemical pollution. Some examples include the achievement of the environmentally sound management of chemicals and all wastes throughout their life cycle by 2020[4] , the prevention and significant reduction of marine pollution of all kinds, in particular from land-based activities by 2025[5] and the reduction of the number of deaths and illnesses from hazardous chemicals and air, water and soil pollution and contamination by 2030[6].

Another important tool aiming to improve the protection of human health and the environment, that could inspire further regulatory actions in the Mediterranean, is the EU chemical legislative framework. It includes the CLP (Regulation on Classification, Labelling and Packaging) for better and earlier identification of the intrinsic properties of chemical substances and REACH (regulation for Registration, Evaluation, Authorisation and Restriction of Chemicals), which creates procedures for restricting the use of substances that do not meet specified safety standards, encouraging substitution of harmful chemicals by safer alternatives.

What are the most suitable approaches for the substitution of toxic chemicals in products?

The substitution of hazardous substances is horizontal to many policies dealing with workers' health and safety, products' safety and the environment and is thoroughly explained and promoted in the EU Study for the strategy for a non-toxic environment of the 7th EAP.[7]

Experts advise that there is a **need for a knowledge-based, preventive approach to chemicals risks management** throughout their life cycle in order to reduce the risks to human health and ecosystems.

However, there are several challenges and obstacles present in the current phasing out process of hazardous chemicals[8]: substitution by chemicals with similar properties have resulted in regrettable substitutions, phase-out agreements are often voluntary and do not cover all relevant manufacturers or have a wide range of exemptions. It is also problematic to find a suitable alternative achieving the same performances in the applications, without altering other functions, properties or processes.

Pressure from the supply chain and from within businesses have also contributed to substitution. A variety of voluntary and mandatory policy tools have also been used, such as education, procurement, lists of chemicals of concern, eco-labelling, research and development on safer substitutes and chemical phase-out requirements, to encourage companies using chemicals to develop safer substitutes. The chemical sector is strategic and if it moves toward sustainability it could have an essential contribution to sustainable development and the country's competitiveness, since its activity has repercussions in other sectors.

What is the objective of this SwitchMed Publication?

It is in support of the global (SDGs) and Mediterranean (Barcelona Convention) sustainability agenda that **the SwitchMed Programme** (www.switchmed.eu) is contributing to tackle the issue of toxic chemicals. This publication aims to raise awareness and provide an overview of safe alternatives for 20 selected hazardous substances used in the Mediterranean region in various product applications and to involve policy makers, businesses, retailers, academia, civil society and consumers in order to redesign the way in which goods and services are produced and consumed.

With that, the SwitchMed Programme aims to facilitate the regional and global transition towards sustainable consumption and production (SCP) in the southern Mediterranean region, namely in Morocco, Algeria, Tunisia, Libya, Egypt, Israel, Palestine, Jordan and Lebanon. This multidimensional regional initiative is funded by the European Union and implemented thanks to collaboration between the EU, UNIDO, UN Environment /Mediterranean Action Plan and its Regional Activity Centre for Sustainable Consumption and Production (SCP/RAC) and UN Environment, Economy Division.

How to use this publication

This publication has been conceived as a useful and practical tool for consumers, entrepreneurs, businesses and civil society organizations worldwide who are willing to contribute to combating hazardous chemicals as well as supporting socioeconomic development in the region. At the same time, in order to trigger concrete action, the SwitchMed Programme has made funds available so some of these initiatives are replicated and adapted in selected countries of the Middle East and North Africa region.

In order to make it as clear and understanding as possible, the 20 identified chemicals described in this report have been grouped in 7 different classes. Grouping strategies have been proposed by institutions and environmental organisations such as Greenpeace and the European Commission[9]. This is the case of the Green Science Policy Institute which has developed the Six Classes program (http://www.sixclasses.org/) that focuses on reducing the use of entire classes of chemicals of concern, rather than phasing out individual problematic chemicals one at a time.

A key element of the approach is to bring together scientists and decision-makers from business, government, academia and non-for-profit organizations to develop coordinated strategies for reducing the production and use of chemicals of concern. Tackling entire groups of chemicals can prove more effective, because there are a great number of chemicals in use, most of which have not been well studied and their impacts on human and environmental health are not sufficiently understood. Moreover, when a harmful chemical is phased out, often after years of research and advocacy, the replacement is likely to be a "chemical cousin" with similar structure and potential for harm. The Six Classes approach can help to prevent such "regrettable substitutions" and accelerate reductions in toxics use.

The summary table shows a brief description of each selected chemical with key information to guide the reader. This will allow the user of this publication to find the most relevant information according to two criteria:

- **The application:**
  Authors discuss case studies on a range of different uses and industries including automotive, agriculture and medical to industrial processes such as metal working, wood treatments and textiles. Other applications include consumer goods, such as plastic bags, personal care products and childcare. So for example you can search for toxic chemicals used in consumer articles like toys with rubber or plastic components that come into contact with the human skin or the oral cavity.

- **The 7 classes:**
  The grouping used in this work has included the 6 classes described by the GSPI (www.greensciencepolicy.org): Antimicrobials, bisphenols and phthalates, flame retardants, highly fluorinated substances, metals and solvents; plus an additional type which highlights one of the first kind of chemicals addressed by the Stockholm Convention and the Strategic Approach of International Chemical Management (SAICM): hazardous pesticides. The seven categories have been listed in alphabetical order and are defined as follows:

1. Antimicrobials and surfactants

are chemicals added to products to kill or inhibit the growth of microbes. They are also called antibacterials or biocides. Antimicrobials of concern include halogenated aromatic compounds such as triclosan and triclocarban, nanosilver and quaternary ammonium salts (quats) such as benzalkonium chloride.

2. Bisphenols and phthalates

are chemicals that have many uses, including making plastics stronger or more flexible. Bisphenols are present in some polycarbonate plastic products (including water bottles, food storage containers and packaging, sports equipment and compact discs), epoxy resin liners of aluminum cans and cash register receipts. Phthalates can be found in some polyvinyl chloride (PVC) plastic products (including vinyl flooring, shower curtains, toys, plastic wrap and food packaging and containers), glues, caulks, paints, personal care products and air fresheners.

3. Flame retardants and short chain chlorinated paraffins

are additives that are designed to slow ignition and prevent fires and they are used to meet flammability regulations. Flame retardants of concern include organohalogen and organophosphate chemicals such as polybrominated diphenyl ethers (PBDEs) and chlorinated tris (TDCPP). Short chain chlorinated paraffins are used in some applications as flame retardants but also for other industrial uses addressed in this section.

4. Highly Fluorinated

sometimes referred to as PFCs, are used in many consumer products and industrial applications because of their oil, stain and water-repellent properties. Examples of chemicals in this class include PFOA, PFOS and more than 4000 other PFASs.[10]

5. Certain metals (and their salts)

Mercury, arsenic, cadmium and lead are elements that occur naturally in the earth's crust. Mining and smelting, fossil fuel combustion, industrial processes and the use and disposal of products containing them have led to widespread environmental contamination and human exposure and health harm.

6. Pesticides

A pesticide is any substance used to control pests which may be target insects, vegetation, fungi, etc. Most pesticides control the pests by poisoning them. Unfortunately, pesticides can be poisonous to humans as well. Some are very poisonous, or toxic and may seriously injure or even kill humans.

7. Solvents

are a diverse class of chemicals that are used to dissolve or disperse other substances. Some solvents of concern include aromatic hydrocarbon solvents (e.g., toluene, xylene, benzene) and halogenated organic solvents (e.g., methylene chloride, perchloroethylene, trichloroethylene).

After the summary table, an in-depth description of each case study can be found, following the same structure. An introductory chapter describes the use of the substance with its standard labelling, classification and products where it can be found followed by its hazard profile and regulatory distribution in the Mediterranean.

The focus of each case study comprises the second half which includes the description of the proposed safe alternatives, the identification and availability in the Mediterranean Region. Finally, the selected substances are put into their technical, economical and risk profile, taking into account circularity aspects such as the life cycle considerations and environmental impacts.

Rationale for case study selection. Context and limitations

In order to identify a set of relevant substitution cases that can serve as a first list of case studies for boosting phase-out of hazardous chemicals in various product applications, we systematically screened several existing substitution lists. These were included in the screening are the substitution portal SUBSPORT, SwitchMed reports, REACH case studies, the Plastics Ban List from the Better Alternatives Now project, reports from the OSPAR Commission and the U.S., Swedish and Danish Environmental Protection Agencies. More than 1100 reported cases of substituting a hazardous substance in a specific product application have been screened.

Based on this overview, a sub-set of cases was selected for the present project, based on the following criteria:

- Economic, exposure and environmental relevance of the hazardous substance,
- Economic relevance of the product application where the hazardous substance is used,
- Applicability of the substitution case to the Mediterranean region,
- Restriction in international context or REACH,
- Easiness of implementation of the substitution.

The focus was on existing alternatives at the time of writing this work, however, newer and better solutions might become available in future. Further research into alternatives is to be encouraged and promoted, together with better regulation systems so that larger changes can be made within the current consumption and production system.

All sensitive information contained in this publication has been appropriately referenced and can be found in the annex.

This study is based on current available data of the substances and of the manufacturing processes; the proposed alternative substances had a less problematic toxicological profile at the time of writing this publication. However, it is recommended to check the most recent valid information on hazards, risks and life cycle considerations before replacing with the described alternatives.

20 TOXIC CHEMICALS: OVERVIEW

Page	Chemical	Application	Overview
ANTIMICROBIALS AND SURFACTANTS			
22	Triclosan	in personal care products	Used as an antimicrobial in more than 2,000 consumer products including soaps, toothpastes, detergents, clothing, toys, carpets, plastics and paints. No evidence has been found to prove that the use of triclosan improves consumer health.
24	Alkylphenol ethoxylates as surfactants	in textile industry	This case study focuses on nonylphenol ethoxylates (NPEOs) which biodegrade into nonylphenols in wastewater treatment plants and in the environment, causing long-term adverse effects in the aquatic environment and impairing human fecundity.
BISPHENOLS AND PHTHALATES			
28	Bisphenol A based polycarbonate	in baby bottles	Polycarbonate baby bottles are produced from bisphenol A monomer which remains as an impurity in the final product or depolymerize and migrates into baby food. It is a recognised endocrine disrupting chemical (EDC) causing estrogenic effects.
30	Bisphenol A as a developer	in thermal paper	Bisphenol A (BPA) is a commonly used colour developer in thermal paper, found in tickets, receipts, sales slips and other applications, it is an endocrine disrupting chemical (EDC) with its major exposure pathway being through skin contact.
33	Polyethylene	in plastic bags	The main plastics used in bags are high density polyethylene (HDPE) and low density polyethylene (LDPE), which is derived from non-renewable natural gas and petroleum. Globally, millions of single-use plastic shopping bags are discarded every day into mixed-waste streams.
36	DEHP in PVC	in medical appliances	DEHP is the most widely used plasticiser in single-use medical devices and is classified as toxic to reproduction. There are many non-PVC materials available which do not require phthalates or other softeners.
39	PVC	in toys and childcare products	PVC toys and childcare products can contain toxic additives including softeners such as phthalates and heavy metals that lead to children's exposure due to mouthing behaviour. Alternatives include other plastics, wood or books.
FLAME RETARDANTS AND SHORT CHAIN CHLORINATED PARAFFINS			
44	Commercial decabromodiphenyl ether (c-DecaBDE)	in textiles	A widespread flame retardant used in textiles, it leads to human exposure to polybrominated diphenyl ethers (PBDEs) and brominated dioxins indoors and in vehicles and can be substituted by using alterative fibres or alternative flame retardants.
48	Short chain chlorinated paraffins (SCCPs)	as metal working fluids	Metal working fluids are used to lubricate parts that experience extreme pressures, such as deep drawing, tube bending or cutting and grinding and as coolants in metal processing. More than 90% of SCCPs are released into the environment.
51	Commercial decabromodiphenyl ether (c-DecaBDE)	in flame retarded plastic	This was a widely used flame retardant in electronics including plastic housings such as heating home appliances, irons, fans and other plastic parts in vehicles and aircrafts. Alternative materials and re-designed electronics are available.
54	Short chain chlorinated paraffins (SCCPs)	for fat liquoring in leather	This is an open application with related exposure to workers and consumers and has been restricted in the EU since 1990s. Better alternatives are available including natural oils such as vegetable oil and fish oil.

Page	Chemical	Application	Overview
HIGHLY FLUORINATED			
58	Per- and polyfluorinated alkylated substances (PFASs)	in fire fighting foam	The use of fire fighting foam containing perfluorooctanesulfonic acid (PFOS) and other PFASs can result in the contamination of groundwater, drinking water and surface water, including the Mediterranean Sea.
61	Per- and polyfluorinated alkylated substances (PFASs)	in textile hydrophobing	Fluorinated polymers can be applied on textiles to create a durable water repellent coating. PFASs or their degradation products are highly persistent in the environment and several low-hazard alternatives are readily available.
CERTAIN METALS (AND THEIR SALTS)			
66	Lead chromate pigments	in decorative paints	Major lead pigments in decorative paints are highly toxic and are used in the Southern Mediterranean countries, particularly for colouring cooking pots. Alternatives are available and are widely used in industrial countries.
70	Lead oxide	in rustproof primer paints	Elevated levels of lead in blood have been reported in the region's inhabitants, including children. Elevated lead levels in children are causing decreased intelligence and increased behavioural issues.
74	Chromate Copper Arsenate (CCA)	in wood treatment	CCA is used in wood treatment contains carcinogenic arsenic and chromium (VI). Waste wood is sometimes used in Southern Mediterranean countries for baking bread and cooking indoor, resulting in associated exposures.
77	Chromium	in leather tanning	One of the main alternatives to chromium leather tanning is the use of vegetable tanning. This can prevent adverse environmental and human health impacts while promoting local employment and sustainable economic opportunities.
PESTICIDES			
82	Synthetic pesticides	in agriculture	Hundreds of synthetic chemical pesticide active ingredients are used in agricultural practices resulting in unwanted exposures that cannot be adequately assessed while polluting the environment due to wind drift, run-off and leaching.
SOLVENTS			
88	Perchloroethylene	in dry cleaning	Perc is used by professional cleaners and has resulted in widespread contamination of groundwater and soil at dry cleaning sites. Exposure to perc is associated with a variety of adverse human health effects. CO_2 technology can be used instead.
90	Perchloroethylene	in metal cleaning	Perc is used as a degreasing agent in vapour and liquid forms. Alternatives include aqueous cleaning technologies and dry ice blasting technologies which have proven performance with low health and environmental impacts.

ANTIMICROBIALS AND SURFACTANTS

1. Triclosan in Personal Care Products

Background, identity and use

Triclosan is used as an antimicrobial in more than 2,000 consumer products including soaps, toothpastes, detergents, clothing, toys, carpets, plastics and paints.[11] To date, no evidence has been found to prove that the use of triclosan improves consumer or patient health or prevents disease in personal care products such as hand soap, toothpaste, or cosmetics.[12, 13, 14] Hence, for certain products, the use of triclosan can simply be ended - as recently highlighted in a Science Statement.[14]

Hazard profile

Triclosan is very toxic to aquatic life and has long-lasting effects, causing serious eye irritation and skin irritation. It is an endocrine disruptor with anti-thyroid effects and androgenic and estrogenic activity.[15] It can contribute to antibiotic/antimicrobial resistance.[13] Additionally, Triclosan used in consumer products is released to the environment, with adverse effects to fish and biota.[13]

Status in the Mediterranean region and internationally

In Europe, triclosan has been banned for human hygiene purposes when applied on or in contact with human skin or scalp for the primary purpose of disinfecting the skin or scalp, including application such as soap, shampoo, deodorants, household detergents and toothpaste.[16]

The US Food and Drug Administration (FDA) banned triclosan, triclocarban and a range of other antimicrobials, in over-the-counter consumer antiseptic wash products based on insufficient evidence demonstrating their safety for long-term daily use and their ability to reduce the spread of illness and infection.[13] However, in the Southern Mediterranean region, triclosan is not restricted and is currently in use in personal care products.

CHEMICAL	CAS/EC Number
IUPAC: 5-Chloro-2-(2,4-dichlorophenoxy)phenol Mol. formula: $C_{12}H_7Cl_3O_2$	CAS No.: 3380-34-5 EC /List no.: 222-182-2

Table 1 Chemical identity of triclosan

Hazard profile

Selected alternatives

to triclosan in personal care products

Identification and availability

Traditional soap, shampoo, toothpaste and other personal care products without triclosan are available and can be used instead. One example is curd soap, which is sufficiently potent and has germicidal properties. In personal care products for example, triclosan can simply be removed without the need for substitution with other biocides. This is the case of some multinational companies that have removed triclosan from all their products,[17] and triclosan-free products can be found in the market. The US Centre for Disease Control and Prevention (CDC) recommends that when soap and water are not available, consumers should use an alcohol-based hand sanitizer containing at least 60% alcohol.[11]

Technical feasibility

Washing with plain soap and running water remains one of the most effective steps that consumers can take to avoid getting sick and to prevent spreading germs to others.[12]

Economic feasibility

Since triclosan in soap, shampoo, or toothpaste can simply be removed without substitution by other biocides, the manufacturing cost are usually reduced, making the products without the additive cheaper.

Furthermore, external costs like aquatic life impacts and related biodiversity loss are avoided, as are the adverse human health impacts, leading to savings in the health care sector.

Hazards, risks and life cycle considerations

Soap, shampoo, or toothpaste without triclosan and other biocides do not result in hazards or risks associated with this toxic substance. The alternative to triclosan, benzethonium chloride, has no reported endocrine disrupting effects although it is a human skin sensitizer and very toxic to aquatic life.[16] Ethanol in hand sanitizers has no specific health or environmental risk. However, personal care products may contain other hazardous additives that provide specific properties (e.g. siloxanes D4 or D5).

2. Alkylphenol Ethoxylates as Surfactants in Textile Industry

Background, identity and use

Alkylphenol ethoxylates (APEOs) comprise a large class of substances. In many cases, the alkyl chain has nine carbon atoms. Thus, this case study focuses on nonylphenol ethoxylates (NPEOs) which biodegrade into nonylphenols (NPs) in wastewater treatment plants and in the environment. NPs are very toxic to aquatic organisms, causing long-term adverse effects in the aquatic environment and may also impair human fecundity and harm the fetus.

In some countries like Germany, the substitution of APEOs/NPEOs in all relevant applications started 30 years ago. When, alternatives with good biodegradability and proven technical performance were available for almost all applications. Cost-effective biodegradable alternatives with equal or similar technical performance are readily available nowadays, such as the fatty acid alcohol ethoxylates. Nonylphenols and other alkylphenols are used in manufacturing antioxidants, lubricating oil additives, laundry and dish detergents, emulsifiers and solubilizers.[18] These compounds are precursors to the commercially non-ionic surfactants APEOs and NPEOs which are common in many chemical formulations used to produce apparel and footwear materials, such as industrial laundry detergents, scouring agents, wettings agents, spinning oils, dispersing agents for dyes and prints, impregnating agents, pigment and leather-finishing preparations. However, APEOs/NPEOs are used for many other purposes where they can also be substituted. Commonly used NPEOs are listed in Table 2.

Hazard profile and problems

NPs, the main NPEO metabolites, are very toxic to aquatic life and may cause long-term adverse effects in the aquatic environment. They are also associated with reproductive and developmental effects in rodents[19] and act as endocrine disruptors and xenoestrogens in humans. NPs have been detected in human breast milk, blood and urine and are known to impair human fecundity and harm the fetus.[19] NPEOs can also cause skin and eye irritation.

Status in the Mediterranean region and internationally

The production and use of NPs and NPEOs is prohibited in the European Union since 2003.[20] NPEOs have been listed under REACH Annex XVII. After February 2021, they must not be placed on the market in textile articles that can be expected to be washed in water during their normal lifecycle

INDIVIDUAL NPEOs	CAS Number
Poly(oxy-1,2-ethanediyl), alpha-(nonylphenyl)-omega-hydroxy-	9016-45-9
Poly(oxy-1,2-ethanediyl), alpha-(4-nonylphenyl)-omega-hydroxy-	26027-38-3
Poly(oxy-1,2-ethanediyl), alpha-(isononylphenyl)-omega-hydroxy-	37205-87-1
Poly(oxy-1,2-ethanediyl), alpha-(nonylphenyl)-omega-hydroxy-, banched	68412-54-4
Poly(oxy-1,2-ethanediyl), alpha-(4-nonylphenyl)-omega-hydroxy-, branched	127087-87-0

Table 2 Chemical identity of commonly used NPEOs

Hazard profile

GHS01 Explosive
GHS02 Flammable
GHS03 Oxidizing
GHS04 Compressed Gas
GHS05 Corrosive
GHS06 Toxic
GHS07 Harmful
GHS08 Health hazard
GHS09 nvironmental hazard
CMR Carcinogenic/ Mutagenic/ reprotoxic
EDC Endocrine disrupting chemicals
Persistent organic pollutant

at concentrations equal to or greater than 0.01%. This requirement does not apply to second-hand textile articles or to new textile articles produced exclusively from recycled textiles and without added NPEOs.

Many textile sector retailers and brands (e.g., Rewe, Lidl, Nike, Adidas, Levi Strauss, Puma, Tchibo) demand their suppliers to avoid and substitute APEOs/NPEOs.

In the North African countries, no related regulations have been identified. However, laboratories from Morocco and Tunisia participated[21] in a recent proficiency test for AP & APEO in textiles, indicating that industries or authorities are aware of the restrictions and are implementing monitoring activities.

> *About 30 years ago, four German industry associations (TEGEWA, FIR, IKW and IPP) issued a voluntary commitment to substitute APEOs in household and commercial applications encouraging substitution of APEOs in all household cleaning products and in various industrial sectors: oil, photographic, surface metal treatment and ferrous metal processing, leather and fur manufacturing, paper and industrial-scale cleaning operations.*

Selected alternatives

alkylphenol ethoxylates as surfactants in textile industry

Identification and availability

The following substances have been identified as examples of safer alternatives in the textile sector but they might be applicable to other sectors as well. Fatty acid alcohol ethoxylates (the first two compounds in Table 3) are the most important alternatives.

Economic feasibility

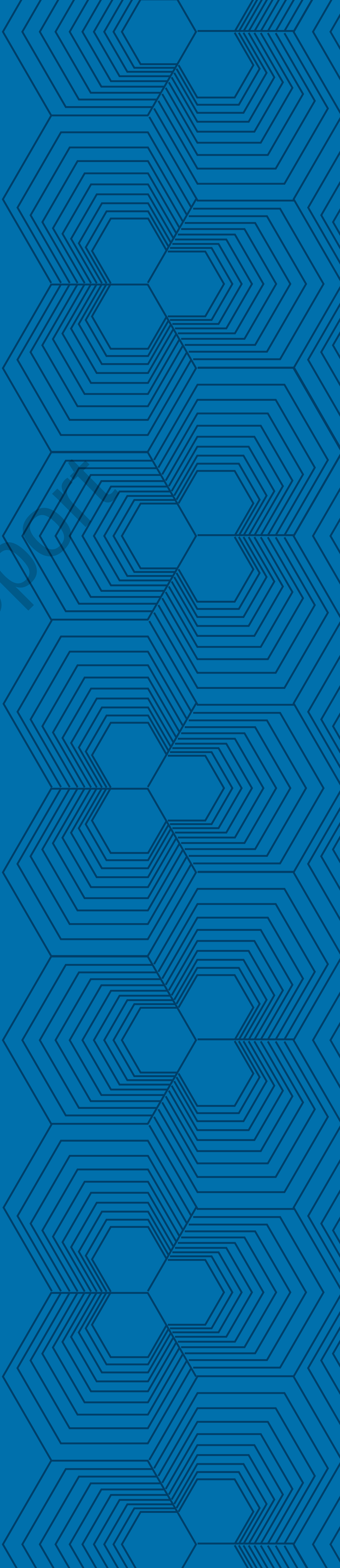
The available alternatives are cost-effective and have equal or similar technical performance. Their use avoids external costs such as adverse aquatic impacts, biodiversity loss and adverse human health impacts. Germany was able to demonstrate 30 years ago that the substitution of APEOs/NPEOs in household products and practically all relevant industrial sectors is economically viable.

Hazards, risks and life cycle considerations

The environmental releases from the application of APEO/NPEO alternatives do not result in specific hazards or risks. Fatty acid alcohol ethoxylates, are readily biodegradable and do not form toxic metabolites.

CAS No.	Chemical characterization
68439-46-3	$C_{9\text{-}11}$ alcohols, ethoxylated (6EO)
68131-39-5	$C_{12\text{-}15}$ alcohols, ethoxylated (9EO)
64366-70-7	Oxirane, methyl-, polymer with oxirane, mono(2-ethylhexyl ether): Ecosurf EH 9
68515-73-1	Glucopyranose, oligomeric, decyl octyl glycosides
68411-30-3	Benzenesulfonic acid, C10-13-alkyl deris., Na salt
151-21-3	Sodium lauryl sulfate
9004-82-4	Polyoxy(1,2-ethanediyl), alpha-sulfo-omegadodecyloxy-, Na salt
1338-41-6	Sorbitan monostearate

Table 3 Chemical identity of available safer alternatives for NPEOs[22]



BISPHENOLS AND PHTHALATES

3. Bisphenol A-based Polycarbonate in Baby Bottles

Background, identity and use

Polycarbonate (PC) baby bottles are produced from bisphenol A (BPA) monomer used as building block for the PC polymer. Some BPA monomer remains as an impurity in the final product and migrates into baby food. Further BPA is generated and released from depolymerization upon continuous or frequent washing with detergents, sterilization and usage. BPA is a recognised endocrine disrupting chemical (EDC) causing estrogenic effects in vivo (xenoestrogen). The release from PC bottles can exceed the Tolerable Daily Intake (TDI) of 0.01 mg/kg body weight.

Bisphenol A (BPA) is one of the world's best-selling chemicals, primarily used as monomer to make polycarbonate (PC) plastics.[23] PC is used to produce baby bottles but also for other food contact materials, toys and a wide range of other applications. PC is characterised by its good physical properties such as transparency, high mechanical strength, wear resistance and good thermal stability such that it can be sterilized in boiling water. Therefore, for decades PC was a major material used globally and is still widely used for baby bottles in the Southern Mediterranean region.[24]

Hazard profile and problems

BPA is a well-described endocrine disruptor, causing reproductive, neurobehavioural, brain development, immune and metabolic system effects.[25] Human exposure to BPA may elevate risk of obesity, diabetes and coronary heart diseases.[26] BPA was also found to affect kidney and liver weight in animals.[25,26] BPA enters the body through ingestion (e.g. diet, dust) or dermal contact (e.g., cosmetics, thermal paper).

As is the case with most polymers, the non-polymerised residual BPA monomer can migrate from the PC material over the lifetime of the article. The amount of BPA present depends on the quality of the PC. It is sensitive to hydrothermal effects which results in additional BPA release from the polymer. The release rate of BPA originating from hydrolytic degradation of the polymer is positively correlated with higher pH (alkaline conditions).[27] Therefore, the release of BPA from PC stems from two different mechanisms: (1) Diffusion-controlled release of residual BPA and (2) hydrolysis of the polymer at the material surface followed by an increase in BPA migration. The long-term release of BPA from PC is primarily due to degradation of the polymer rather than diffusion.[27]

Through these mechanisms, BPA can leach out of PC used in baby bottles and other food containers made of PC or other BPA-containing resins. The release from baby bottles can exceed the Tolerable Daily Intake (TDI) of 0.01 mg/kg of body weight.[27]

Status in the Mediterranean region and internationally

The European Union and Canada have banned BPA use in baby bottles. The US Food and Drug Administration (FDA) has ended its authorization for the use of BPA in baby bottles and infant formula packaging. With minor exceptions, legal or voluntary BPA restriction (including in PC baby bottles) is virtually absent in developing countries of Africa, SE

CHEMICAL	CAS/EC Number
4,4'-isopropylidenediphenol (BPA)	CAS No: 80-05-7 EC No: 201-245-8
Polycarbonate (PC)	CAS No.: 25037-45-0

Table 4 Chemical identity of BPA and PC

Hazard profile

Asia and South and Central America. Thus far only South Africa, Brazil and Colombia have passed some legislation on BPA use in food contact materials.[28] Currently, no regulations exist in the Southern Mediterranean countries to restrict BPA or the use of PC in baby bottles which means they are still widely used in Southern Mediterranean countries.[24]

Selected alternatives

to polycarbonate in baby bottles

Identification and availability

A range of materials are used as alternatives for polycarbonate baby bottles including other plastic, glass and stainless steel. The alternative plastic materials include polyamide (PA), polyethersulfone (PES), polypropylene (PP), polyethylene (PE) and copolyester.[29]

Technical feasibility

A range of plastics are available on the market and have been used for baby bottles for many years, particularly in countries where PC has been phased out. Glass bottles were used before plastic bottles and can be appropriately used. Stainless steel baby bottles are also available on the market. Both these options are heavier and small babies might have difficulties holding the bottle. However, the World Health Organization (WHO) recommends exclusive breast feeding for the first 6 months and these bottles can be handled appropriately after this period, as they have been for generations.

Economic feasibility

Most non-BPA containing plastic bottles are price competitive with PC bottles. Glass bottles and stainless steel bottles have somewhat higher prices than PC baby bottles, however they can be used for a long time, even over generations. Some glass and stainless steel bottles have lids that can be switched out and can become a sippy cup, straw cup, or water bottle. Therefore, the price difference might be compensated by longer life cycle/durability.

Hazards, risks and life cycle considerations

Glass bottles do not release pollutants and are easy to clean. Stainless steel bottles are also easy to clean and do not release pollutants. Plastic bottles are more difficult to clean, as they have a tendency to scratch and can harbour bacteria if not properly cleaned.

The EU JRC laboratory detected a wide range of chemicals released into the milk substitute in an assessment of 449 alternative plastic baby bottles in the European market.[29] BPA was detected and quantified in 20 out of 27 polyamide bottles, with concentrations ranging between 0.5 to 250 µg/kg in 19 bottles . One bottle released even more than 1000 µg/kg in the first migration.[29] This value is higher than those found in the same survey for PC bottles.[30] None of the 30 polyethersulphone (PES) bottles tested released any detectable amounts of 4,4'-dichlorodiphenyl sulphone (DCPS) or 4,4'-dihydroxydiphenyl sulphone (DHPS; bisphenol S) and only two bottles released a very low amount of diphenyl sulphone (DPS) (~1 µg/kg compared to a regulatory limit of 3000 µg/kg). The levels of contaminants found in polypropylene bottles were compliant with the limits set in the EU food contact legislation. No hazardous compound was detected in bottles made from copolyester.[29]

4. Bisphenol A as a Developer in Thermal Paper

Background, identity and use

Bisphenol A (BPA) is a well-known endocrine disrupting chemical (EDC) with its major exposure pathway being through skin contact. BPA is a commonly used colour developer in thermal paper, found in tickets, receipts, sales slips etc. Therefore, human, including children's, exposure to the chemical is widespread. The total human exposure to EDCs is of concern and unnecessary additional exposure needs to be avoided.

Alternatives are used in the European market and some of them have shown no EDC activity. By switching to these substances, EDC exposure can be reduced. The most suitable and most widely used alternative developer in thermal paper in the EU seems to be Pergafast 201, which has no estrogenic property and no documented other EDC activity. However, during the production, use and end of life treatment, the releases of Pergafast 201 to water bodies need to be controlled due the high aquatic toxicity of the chemical.

There is a recent innovative thermal paper namely Ökobon® that does not contain chemical developer. In this system the coating reacts to the heat of the thermal printhead. The paper is on the European market and used since the beginning of 2017.

BPA is used as a colour developer in printing thermal paper, at concentrations ranging from approximately 0.9 to 2.1%.[31] Thermal paper is widely used in daily life and includes receipts, sales slips, cash register receipts, ticket papers, bank papers, fax paper, etc.

Hazard profile and problems

BPA is a well-described endocrine disruptor, causing reproductive, neurobehavioral, brain development, immune and metabolic system effects.[32] Human exposure to BPA may elevate the risk of obesity, diabetes and coronary heart diseases.[33] BPA was also found to affect kidney and liver weight in animals.[32,33] BPA enters the body through ingestion (e.g., diet, dust) or dermal exposure (e.g., thermal paper, cosmetics). BPA applied to thermal paper is not bound, thus relatively large exposures may occur during normal handling.[34] Skin absorption of BPA while handling thermal papers is believed to be a significant route of exposure[34], particularly for cashiers who have higher estimated levels compared to the general population.[35] Due to the use of thermal paper in everyday life, most people are exposed to BPA, including children.

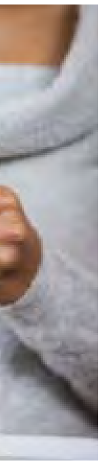
The European Food Safety Association (EFSA) estimate that the typical exposure to BPA is below its

CHEMICAL	CAS/EC Number
4,4'-isopropylidenediphenol (BPA)	CAS No: 80-05-7 EC No: 201-245-8

Table 5 Chemical identity of Bisphenol A (BPA)

Hazard profile

- GHS01 Explosive
- GHS02 Flammable
- GHS03 Oxidizing
- GHS04 Compressed Gas
- GHS05 Corrosive
- GHS06 Toxic
- GHS07 Harmful
- GHS08 Health hazard
- GHS09 Environmental hazard
- CMR Carcinogenic/ Mutagenic/ reprotoxic
- EDC Endocrine disrupting chemicals
- Persistent organic pollutant



temporary TDI of 4 µg/kg bw/day. However, the total human exposure to EDCs is of concern and unnecessary additional exposure needs to be avoided. Therefore, the substitution of BPA in thermal paper should be promoted considering that alternatives are widely used in European countries.[36]

Status in the Mediterranean region and internationally

BPA has been listed in the EU as a substance of very high concern under REACH. In December 2016, the European Commission decided to restrict BPA in thermal paper in the EU. This ban will take effect in 2020. Therefore, European retailers, banks and other institutions using thermal papers are substituting BPA-containing thermal paper.

There are no legal or voluntary activities to restrict BPA in Africa except for South Africa.[37] Therefore, currently no regulation or motivation exists in the Southern Mediterranean countries for restriction of BPA, including in thermal paper. Most thermal paper currently used in the Southern Mediterranean countries is likely to contain BPA as a developer. Exemptions are retailers or other institutions with a global policy of phasing out BPA use in the company (e.g., IKEA in Egypt or Morocco).

Selected alternatives
to bisphenol A in thermal paper production

Identification and availability

Alternative developers in thermal paper

The chemicals identified by the SUBSPORT database (http://www.subsport.eu/) as potential alternatives to BPA in thermal paper, can be seen in Table 6.

CHEMICAL	CAS Number
methyl bis(4-hydroxyphenyl) acetate (MBHA)	5129-00-0
4,4'-(1-phenylethylidene) bisphenol (Bisphenol AP)	1571-75-1
4-hydroxyphenyl sulfone (Bisphenol S)	80-09-1
phenol,4-[[4-(2-propen-1-yloxy) phenyl] sulfonyl] (BPS MAE)	97042-18-7
4-[4'-[(1'-methylethyloxy) phenyl] sulfonyl] phenol (D-90)	191680-83-8
N-(p-Toluenesulfonyl)-N'-(3-p-toluenesulfonyloxyphenyl) urea (Pergafast 201)	232938-43-1
4-Hydroxyphenyl 4-isoprooxyphenylsulfone (D-8)	95235-30-6
Bis(4-hydroxyphenyl)methane (Bisphenol F; BPF)	620-92-8
Urea Urethane (UU)	321860-75-7

Table 6 Chemical alternatives to bisphenol A (US EPA 2014)[38]

Thermal paper without chemical developers

There is a recent innovative Oekobon® thermal paper (http://www.oekobon.com/), the first thermal paper that does not need a developer. Oekobon® was specially developed for this forward-looking type of thermal technology. In this system, the coating reacts to the heat of the thermal printhead. In contrast to existing thermal papers, it contains fine bubbles, which collapse due to selective heat transfer of the thermal printer. Through this purely physical reaction, the underlying black layer is made visible, thus creating the typeface on the receipt without a chemical developer. The paper is available on the market since 2017.

Technical and economic feasibility

- *Alternative developers in thermal paper*
  A range of developers (BPS, Pergafast 201, D-8, D-90, BPS-MAE) are already in use in several European countries (including Spain)[36] and therefore have proven technical and economic feasibility. The alternatives are somewhat more expensive (by approximately 70%) compared to BPA-containing thermal paper. However, since thermal paper is a minor expense for a shop, the additional cost is insignificant, as demonstrated by the shift to alternatives in the EU.

- *Thermal paper without chemical developers*
  Oekobon GmbH offer Oekobon® thermal paper without developer as an innovative alternative. The paper can be used with the same equipment in the same way as the other thermal papers with developers. The system is stable against UV light with a lifetime of more than 25 years.
  Currently the price for this paper is approx. twice the price of BPA-containing thermal paper and comparable to thermal papers with alternative developers. Since thermal paper is a minor expense for a shop, the cost increase is also minor. Considering the lack of restriction of BPA in the Southern Mediterranean region, there is a need for raising awareness regarding BPA exposure of customers.

Hazards, risks and life cycle considerations

Some of the alternatives to Bisphenol A with similar structure have been found to also exhibit EDC properties (for example Bisphenol S, Bisphenol F)[39] . Therefore, these cannot be considered suitable alternatives.
Pergafast 201, D-8, D-90, TGSA and BPS-MAE have shown no or minimal estrogenic activity.[36] However, TGSA and D-8 induced similar teratogenic effects as BPA in zebrafish embryos.[36]
Exposure and risk can also be reduced by minimizing the release of the compound from thermal paper. Of the above-mentioned alternatives, Pergafast 201 and Bisphenol AP have the lowest release potential. Also, in this respect Pergafast 201 seems a suitable alternative, though it has high aquatic toxicity[38] that needs to be considered for the life cycle management of Pergafast 201 treated thermal paper. The releases of Pergafast 201 to water bodies should be controlled during the production and end of life treatment.

5. Polyethylene Plastic Bags

Background, identity and use

Shopping bags have become an integral part of our everyday lives. Single-use polyethylene plastic bags are the most commonly used in many countries. Globally, millions of single-use plastic shopping bags are discarded every day into mixed-waste streams or are thrown into the environment as post-consumer plastic litter. The Mediterranean Sea coastline is littered every year with an estimated 25 million plastic bags per 1,000 kilometres of coastline. Plastic bags and packaging account for 56% of the total beached waste and 83% of floating litter[40]. Traditional reusable bags made from alfa, cotton or jute are readily available on the market, as are paper and biodegradable plastic bags.

Plastic shopping bags have been used by consumers worldwide since the 1960s. The main plastics used are high density polyethylene (HDPE) and low density polyethylene (LDPE). The production monomer ethylene is derived from non-renewable natural gas and petroleum. Globally, millions of single-use plastic shopping bags are discarded every day into mixed-waste streams.[41] We are therefore faced with the need of seeking an alternative to single-use plastic bags.

Approximately 100 billion plastic bags are produced yearly and are placed on the market in the European Union (EU) alone. Plastic bags are widely used in Southern Mediterranean countries. For instance, Tunisians consume roughly one billion plastic bags each year, equalling 30,000 tonnes of plastic waste.

Hazard profile and problems

Plastic bags cause negative environmental impacts by becoming a post-consumer plastic litter source and due to their non-renewable resource consumption and chemical use (such as inks and other additives).[42] Plastic bags are one of the most widespread waste types in oceans and seas, making up 75% of the plastic content of total marine litter. Plastic bags are harmful to the environment and to wildlife. They have been identified as the type of microplastic litter most harmful to marine biota, killing thousands of animals each year.[43, 44] Plastic might take hundreds of years to break down in the environment.

Plastic bags can clog pipes and thus contribute to flooding in cities. Their pollution of landscapes in the Mediterranean region has caused economic damage to the tourism sector. Plastic waste recycling rates in the Mediterranean region are low due to a lack of household collection and segregation, commodity value volatility and competition for virgin plastic.[45]

Status in the Mediterranean region and internationally

The United Nations Environment Assembly (UNEA) 3 has recently adopted a resolution on

*Polyetylene is not classified as environmental hazard under GHS. However, it is very hazardous to the marine environment and to wildlife

Hazard profile*

GHS01 Explosive
GHS02 Flammable
GHS03 Oxidizing
GHS04 Compressed Gas
GHS05 Corrosive
GHS06 Toxic
GHS07 Harmful
GHS08 Health hazard
GHS09 Environmental hazard*
CMR Carcinogenic/ Mutagenic/ reprotoxic
EDC Endocrine disrupting chemicals
Persistent organic pollutant

marine litter microplastics and urges countries and other stakeholders to use plastic responsibly, while endeavouring to reduce unnecessary use and promote research and application of environmentally-sound alternatives.[46]

In the EU, plastic waste needs to be collected separately. The Circular Economy Action Package adopted in December 2015 makes plastics a priority topic. This Package proposes rising the recycling target for plastic packaging to 55% and reducing landfilling to no more than 10% by 2030. In 2015, the EU issued Directive 2015/720 to reduce the consumption of lightweight plastic carrier bags.

Some Mediterranean countries (France and Morocco) are aiming for a total ban of plastic bags, apart from those that are biodegradable and compostable. Others such as Croatia, Malta, Israel and some municipalities or districts of Spain, Greece and Turkey, are introducing a tax on single use plastic bags. Tunisia has banned non-biodegradable plastic bags in large-chain supermarkets but still allows their use in small shops.

Selected alternatives

to polyethylene plastic bags

Identification, availability, and technical feasibility

Environmentally friendly alternatives to non-degradable plastic bags include reusable bags from natural materials and biodegradable plastic or paper bags.

A) Reusable bags

Reusable bags include bags made from cotton, jute or alfa. The Tunisian “Koffa” (Figure 1) are traditional bags made of palm leaves or alfa (*Stipa tenacissima*), a common grass of North Africa that covers approximately 3 million hectares in Algeria and more than 400 thousand hectares in Tunisia. Organic cotton bags can also be a more sustainable alternative to non-degradable plastic bags, especially if the organic agriculture contributes to new fertile soil generation as demonstrated by the SEKEM farm in Egypt, which also produces organic cotton.[47] Jute bags are another environmentally friendly alternative because the material derives from a plant fibre, consisting mostly of cellulose and is biodegradable after use.

Figure 1 Reusable alfa bags “Koffa”

B) Paper bags

Paper bags are made out of cardboard paper and are a commonly used alternative to plastic shopping bags for packaging fruits or bakery goods. Paper bags can also be produced from recycled paper; however, not all paper is suitable for being recycled into paper bags packaging food items due to possible problems with cross-contamination (i.e. chemical residues in the recycled paper that might lead to increased exposure of consumers).

Figure 2 Multiple-use carrier bag

C) Biodegradable plastic bags

Biodegradable plastic bags are another alternative to non-degradable plastic bags. They can be made from bio-based and biodegradable bioplastics such as polylactic acid (PLA), polyhydroxyalkanoates (PHA and PHB) and starch blends. Bags can also be made from fossil fuel-based biodegradable plastics such as polybutyrate adipate terephthalate (PBAT), polycaprolactone (PCL) and poly(butylene succinate) (PBS).[48,49] PLA is a biodegradable and bio-active thermoplastic aliphatic polyester derived from corn starch, cassava roots, chips, starch, or sugarcane and the plastic bags take a few months to fully degrade when buried in compost.[49]

However, biodegradable bioplastics and especially non-degradable bioplastics, such as bio-based polyethylene (PE), polyethylene terephthalate (PET) and Nylon (Polyamide; PA), do not have an advantage in respect to marine litter pollution, since biodegradation in this context is usually limited to industrial compositing conditions (e.g. with temperatures much higher than in the natural environment, such as marine water). Hence, biodegradable plastic bag is a suitable alternative to non-degradable plastic bags when composted after use in order to effectively reduce marine litter pollution or ensuring that the bio-plastic degrade also under marine condition.

Policy makers, industry, retailers, entrepreneurs and consumers must all contribute to the switch to sustainable alternatives.[50] Behavioural change toward the use of more sustainable shopping bags is of great importance. Consumers can reduce their plastic bags use through a variety of behaviours: bringing their own reusable bags (i.e., reduce and reuse), opting for a biodegradable bag (i.e., substitute), combining all their purchases into one biodegradable/reusable bag or adding to an existing bag received from another vendor (i.e., reduce). Municipalities can further help by enforcing that all biodegradable bags are composted to facilitate effective waste handling. Combining education on the impacts of shopping bags with general education on sustainable consumption can change consumer behaviour and considerably increase citizens' environmental awareness.

6. PVC with DEHP in Medical Appliances

Background, identity and use

Soft PVC with DEHP (Bis(2-ethylhexyl) benzene-1,2-dicarboxylate) as softeners is the most widely used plastic in single-use medical devices. DEHP is classified as toxic to reproduction (class 1B) which means it may damage fertility and may damage the unborn child. A range of alternatives polymers to PVC in medical appliances without softeners are available and safe product alternatives have already been compiled e.g. by Health Care Without Harm. Also alternative softeners to DEHP with lower toxicity and leachability are available and used in medical devices. Soft PVC with DEHP (Bis(2-ethylhexyl) benzene-1,2-dicarboxylate) as softeners is used in single-use medical devices such as intravenous tubing and bags, IV catheters, nasogastric tubes, dialysis bags and tubing, blood bags and transfusion tubing and air tubes. These medical devices are used for screening, diagnosis, treatment and care. Medical PVC accounts for about 40% of all plastics-based medical devices used in hospitals.[51]

Hazard profile and problems of soft PVC/DEHP in health care products

DEHP is classified as toxic to reproduction (class 1B) which means it may damage fertility and may damage the unborn child.[52] Based on the testicular toxicity of DEHP, the European Food Safety Authority (EFSA) Panel set a Tolerable Daily Intake (TDI) of 0.05 mg/kg body weight, based on a 'No Observed Adverse Effect Level' (NOAEL) of 5 mg/kg bw/day and an uncertainty factor of 100 used for the risk assessments.[53]

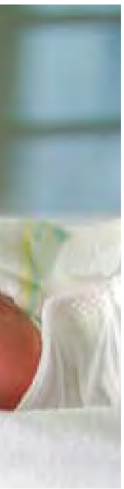
The EFSA TDI is significantly exceeded in patient groups due to exposure from DEHP containing PVC medical devices including adult patients undergoing haemodialysis and premature neonates in intensive care units. For adults, the highest acute-short term exposure may result from transfusions of blood components, reaching DEHP doses up to approximately 8,000-10,000 µg/kg body weight/day in trauma patients and in patients undergoing ECMO, whereas the highest chronic treatment is represented by haemodialysis, during which the maximum reported exposure is 2200 µg/kg/d.[52] Premature neonates in intensive care units (NICU), being dependent on multiple medical procedures, may receive even higher DEHP exposures (up to 6000 µg/kg bw/d).[52] Such exposures may occur for a period of weeks or even months with associated developmental risk.

CHEMICAL	CAS Number
DEHP; Bis(2-ethylhexyl) benzene-1,2-dicarboxylate Bis(2-ethylhexyl) phthalate	CAS No. 117-81-7 EC No. 204-211-0

Table 7 Chemical identity of DEHP (Bis(2-ethylhexyl) phthalate)

Hazard profile

GHS01 Explosive	GHS02 Flammable	GHS03 Oxidizing	GHS04 Compressed Gas	GHS05 Corrosive	GHS06 Toxic	GHS07 Harmful	**GHS08 Health hazard**	GHS09 Environmental hazard	**CMR** Carcinogenic/ Mutagenic/ reprotoxic	**EDC** Endocrine disrupting chemicals	Persistent organic pollutant



Therefore soft PVC containing DEHP should be phased out in exposure relevant articles such as health care devices.[54, 55, 56]

Furthermore PVC can be a driver for Dioxin (PCDD/F) and other unintentional POPs formation in non-BAT incinerators.[57] Hospital waste incinerators in Southern Mediterranean countries are normally small scale incinerators operated with daily start up or even as batch with bad combustion quality[58] where PCDD/F formation correlates with chlorine/PVC content. Such hospital waste incinerators can have large impact on the surrounding.[59] Furthermore hospital waste might be treated in cement kiln where chlorine content is a limiting factor for accepting and treating waste.[60, 61]

Status in the Mediterranean region and internationally

Several countries have already taken action[62] including the EU which recently updated the regulatory framework for medical devices including the phase out of use of devices with EDC like DEHP (and CMR chemicals) above 0.1%[63]. DEHP is listed as Substance of Very High Concern under REACH and it is listed as endocrine disrupting chemical. The EU recently updated the medical devises regulatory framework. Annex I.II.10.4.1, of the MDR includes a 0.1% concentration limit[64] for category 1A and 1B carcinogenic, mutagenic and reprotoxic (CMR) substances and EDCs in devices that are invasive and come into direct contact with the body.[65]

In Denmark under the Danish PVC Tax Act (Law no. 253, of 19 March 2007), goods that contain phthalates are taxed based on the weight of phthalates they contain.[62] This tax stimulated the use of alternatives. Between 1998 and 2011, the use of 17 different phthalates halved. At the request of the Danish Environmental Protection Agency (EPA), local and provincial authorities are giving priority to phthalate-free alternatives in all public procurements (Green Public Procurement).[56]

Over 100 healthcare institutions around the world are reducing or phasing out PVC and phthalates.

In the South Mediterranean countries no substitution activity of medical devices containing PVC/DEHP have been conducted up to now. Also no regulations have been developed for restricting DEHP in medical devices. However, Egypt has restricted DEHP in toys and childcare items.

Selected alternatives for PVC with DEHP in medical appliances

Identification and availability

1) Alternatives materials to PVC

There are many non-PVC materials available, suitable for a wide variety of medical applications, which do not require phthalates or other softeners. These materials include polypropylene (PP), polyethylene (PE), other polyolefins, ethylene vinyl acetate (EVA) or silicone among others.[66] Lists on non-PVC alternative have been compiled from Health Care Without Harm (HCWH) for the United States/Canada for general medical devices[67] and for Neonatal Intensive Care Unit (NICU)[68] or from Swedish authorities.[66] Furthermore HCWH Europe has developed "The Safer Medical Devices Database" (http://safermedicaldevices.org/about) with currently approx. 200 alternative products to PVC medical devices.

Some major alternatives and use areas are:

- Bags: PVC-free bags made of ethylene vinyl acetate (EVA), multilayer polyethylene or polypropylene are cost-effective and technically competitive with PVC bags.
- PVC-free intravenous and other bags are available for all applications.
- Tubing: PVC-free tubing from polyurethane or silicone is on the market for most medical applications.
- Gloves: Alternatives made from nitrile for disposable gloves are readily available.

2) PVC with alternative plasticisers

PVC products softened with plasticisers other than DEHP are available on the market. The alternative softeners used include e.g. Hexamol DINCH (1,2-Cyclohexanedicarboxylic acid, diisononylester), DINP (di-iso-nonyl phthalate), TOTM (Tris(2-ethylhexyl)benzene-1,2,4-tricarboxylate), Citrates, Adipates, Trimellitates.[52, 56]

Technical feasibility

There are clinics, which have entirely substituted PVC with alternatives in invasive applications demonstrating the technical feasibility.[69] Furthermore there are examples where clinics have gone nearly[70] PVC free already a decade ago demonstrating that the substitution of PVC (including PVC/DEHP) is technically feasibility for hospitals.[67] Medical device manufacturers in Europe generally offer both PVC and PVC-free versions of the same device. Also PVC with alternative softener (e.g. Hexamoll® DINCH® or DINP) are available since several years as alternatives in medical devices.[66] Technically, DINCH® can be processed on existing machinery, requiring only minor adjustments in formulation and process parameters.[71]

Economic feasibility

Alternative material to PVC are normally more expensive than the PVC. How large a price difference, if any, depends greatly on national markets and the individual contracts between hospitals and suppliers. Hospitals can lower per-unit costs by purchasing in large volumes: Here price differences can be negotiated down to a minimum. The case of Denmark with ecological/health tax on DEHP and PVC was a driver for alternative products[56] and could be assessed and considered for Mediterranean countries.

It needs to be stressed that there are often material benefits to alternatives. For example, PVC-free IV bags won't stiffen with use, as softeners are not removed from the plastic by the bag contents. And while nitrile gloves are more costly than PVC they are also more durable.

The benefits to health can outweigh higher costs, especially when considering the long-term benefits for society at large. The total external health cost of DEHP use/exposure due to the endocrine effect is estimated to 16.2 billion Euro per year in Europe.[72]

The price for alternative softeners are mostly higher compared to DEHP (price 800 to 1300 USD/tonne). Cost of DINCH® (07/2017) is 3000 to 3500 USD/t. compared to phthalates.

Hazards, risk and life cycle considerations

A) Non PVC alternatives

Alternative polymers do not leach DEHP or other softeners. Major alternative polymers used (e.g. polypropylene, polyethylene, other polyolefins, ethylene vinyl acetate) have low or no release potential since they do not use softeners or other additives in high amount. Whenever possible, material with low release potential should be used.[52] In the end of life these non-chlorinated polymers can be incinerated or thermally recovered without additional generation of dioxins.

B) Alternative softeners

For the alternative plasticizers, the critical endpoint for toxicity is generally different from reproductive effects. DINCH does not exert any reproductive toxicity, nor genotoxicity or carcinogenicity. The critical endpoint is the effects observed in kidney and are not considered as relevant for humans. The GreenScreen™ assessment concluded a DINCH benchmark classification of 2e (Moderate Toxic) due to moderate Endocrine Activity, Skin Irritation and Persistence.[73]

Overall the substitution of PVC by other plastic with better life cycle performance (Figure 3) and chemical footprint properties is preferred. At the end of life, all PVC increase the potential of PCDD/F and other UPOP release in the non-BAT hospital waste incinerators in South Mediterranean countries and the chlorine content result in problems with co-incineration in cement kilns.

7. PVC in Toys and Childcare Products

Background, identity and use

Soft PVC in toys and childcare products can contain toxic additives including softeners such as phthalates and heavy metals (lead and cadmium). PVC toys lead to children's exposure due to mouthing behaviour. The levels of hazardous chemicals ingested by the baby or child can exceed safe exposure margins. A range of alternatives to PVC toys are available, including other plastics or wood. Furthermore, a better alternative to plastic toys are books that encourage babies to interact with parents/caretakers and support language development at a young age, thus improving communication skills with long-lasting positive implications for overall academic success. Fewer toys and increased outdoor play time can reduce future consumption addiction.

Soft PVC toys are widely used including in teethers, pacifiers, doll parts, figurines and inflatable toys. Soft PVC contains up to 50% plasticizers by weight, usually phthalate esters such as bis (2-ethylhexyl) phthalate (DEHP), dibutyl phthalate (DBP), butyl benzyl phthalate (BBP), diisononyl phthalate (DINP), diisodecyl phthalate (DIDP) and di-n-octyl phthalate (DNOP) (Table 8).

CHEMICAL	CAS/EC Number
DEHP; Bis(2-ethylhexyl) benzene-1,2-dicarboxylate Bis(2-ethylhexyl) phthalate	CAS No. 117-81-7 EC No. 204-211-0
Dibutyl phthalate (DBP)	CAS No. 84-74-2 EC No. 201-557-4
BBP; Butyl benzyl phthalate	CAS No. 85-68-7 EC No. 201-622-7
DINP, diisononyl phthalate	CAS No. 28553-12-0; and 68515-48-0 EC No. 249-079-5
DIDP; diisodecyl phthalate	CAS No. 26761-40-0 EC No. 247-977-1
DNOP; di-n-octyl phthalate	CAS No. 117-84-0 EC No. 204-214-7

Table 8 Main phthalates used as plasticizers in soft PVC toys[74]

Hazard profile and problems

Soft PVC contains up to 50% plasticizers by weight, usually phthalate esters, which are not chemically bound to the plastic and therefore leach out. The phthalates most commonly used as softeners have hazardous properties (Table 9). Furthermore, lead, cadmium, barium/zinc, or organotin compounds are added to PVC as stabilizers. One study screened toys for heavy metals in Tunisia (2012) and found that numerous PVC toys contained high levels of lead and cadmium.[75]

Toys made of PVC put children at a risk of severe exposure, above safe levels, to softeners such as

Hazard profile

GHS01 Explosive
GHS02 Flammable
GHS03 Oxidizing
GHS04 Compressed Gas
GHS05 Corrosive
GHS06 Toxic
GHS07 Harmful
GHS08 Health hazard
GHS09 Environmental hazard
CMR Carcinogenic/ Mutagenic/ reprotoxic
EDC Endocrine disrupting chemicals
Persistent organic pollutant

phthalates.[76] Heavy metals like lead or cadmium can also leach from the PVC, leading to associated health risks. PVC is challenging to recycle.[77] While PVC recycling has somewhat improved in Europe, hazardous chemicals like DEHP or lead are recycled into new products requiring an exemption to REACH registration.[78]

Status in the Mediterranean region and internationally

In the EU, the restriction under the General Product Safety Directive banned the use of phthalates in toys after a series of risk assessments including the three classified phthalates: Bis (2-ethylhexyl)phthalate (DEHP), Dibutyl phthalate (DBP) and Butyl benzyl phthalate (BBP) and the three non-classified phthalates: Diisononyl phthalate (DINP), diisodecyl phthalate (DIDP) and di-n-octyl phthalate (DNOP). The ban is now included in Annex XVII of REACH covering toys and childcare articles.

Cheap PVC toys are heavily marketed and used in the Southern Mediterranean region without regulatory restriction in most countries. Only Egypt has restricted (2013) the use in toys and childcare items of the 6 phthalates listed under REACH (Table 8).

Phthalate	Critical Toxic Effect on	Tolerable daily intake (in mg per kg body weight per day)	EU ban
DEHP	Reproduction	0.05	Banned in all toys and childcare articles, and in cosmetics
BBP	Reproduction and development	0.5	
DBP		0.01	
DINP	Liver	0.15	Banned in toys and childcare products that children could put into their mouths
DIDP			
DNOP	Liver and thyroid	No TDI available	
DIBP	Reproduction and development		

Table 9 Phthalate plasticizers critical toxic effects and Tolerable Daily Intakes (TDI)

Selected alternatives

to PVC in toys and childcare products

Identification, availability and technical feasibility

Several natural materials, such as organic textiles or wood, have traditionally been used to make toys, teethers and pacifiers. These materials are well tried and tested over the years, are usually durable and repairable and are available on the market. These materials are preferable to any petrochemical-based plastics because of the global environmental impacts of non-renewable fossil fuels. A wide range of toys made from wood or other plastics are on the market.

The main plastics that can be used instead of soft PVC in toys are thermoplastic elastomers (TPEs), ethylene vinyl acetate (EVA) and polyolefins (polyethylene/polypropylene).[79] All three materials fulfill requirements for safety, ease of processing (if possible on the same equipment as PVC), aesthetic appeal and lessened environmental and health impacts.[79] Bio-based plastics are also used for some toys. The first biodegradable plastics have been introduced for beach toys.[80]

Another solution is the overall reduction of toys by altering society’s consumption patterns. This approach is practiced in toy-free kindergartens in Germany[81] and in the increasingly popular outdoor and forest kindergartens.[82]

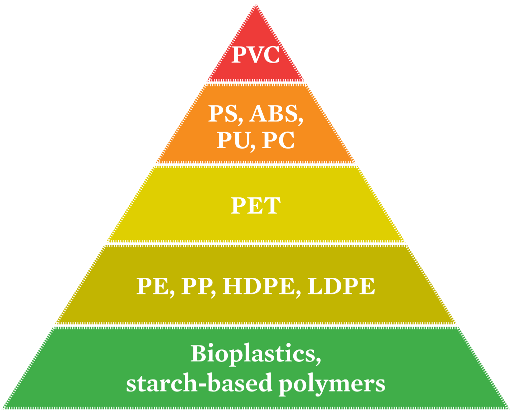


Figure 3 Ranking of plastic according to life cycle considerations (Greenpeace International)

Furthermore, books are preferred alternatives to toys since, unlike plastic and electronic toys, they encourage interaction with parents/caregivers[83] and support language development at a young age, thus improving communication skills with long-lasting positive implications for overall academic success.[84] The increasing switch to books can contribute to the "Arab Regional Agenda for Improving Education Quality," considering also early childhood development.

Economic feasibility

PVC is the cheapest plastic. Therefore, plastic toys made from alternative materials are somewhat more expensive. Considering the poor life cycle performance of PVC (Figure 3), the chemical footprint of PVC is high,[85] leading to external costs.

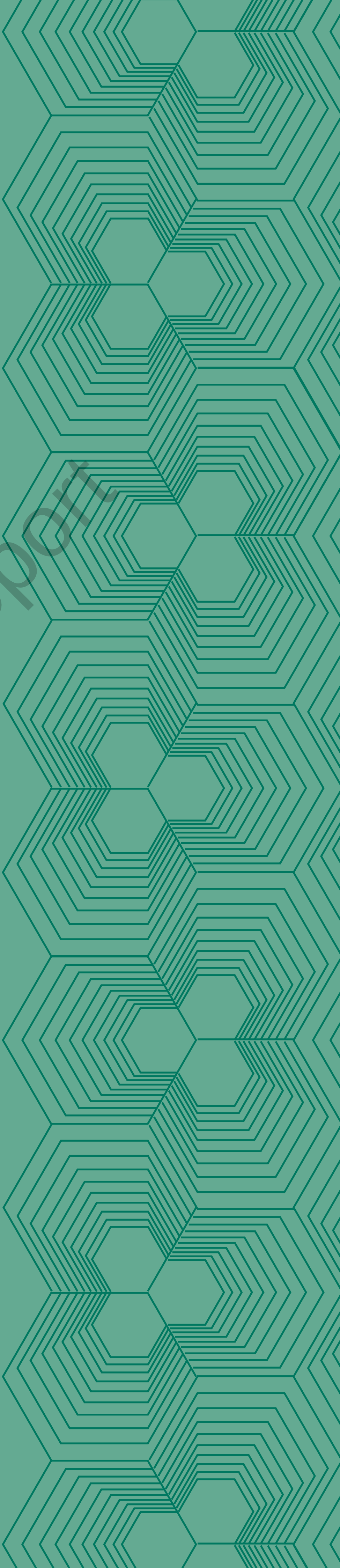
Books can be rented from libraries often for free.

Hazards, risks and life cycle considerations

Renewable materials such as organic textiles or wood are preferable to any petrochemical-based plastics because of the global environmental impacts of non-renewable fossil fuels.

Alternative plastics do not require phthalate plasticizers to become soft and flexible. All alternative plastics require smaller amounts of additives overall (0-2% of the polymer mixture) compared to soft PVC (up to 50%), resulting in much lower exposure potential. Furthermore, a ranking of plastics based on lifecycle considerations indicates that all other plastic types are better than PVC (Figure 3). Chemical footprint assessments for plastics lead to a similar conclusion.[85]

The paper used in books is made from renewable resources and is ideally produced from certified wood. Books can be rented from libraries, further minimizing their ecological footprint.



FLAME RETARDANTS
AND SHORT CHAIN CHLORINATED PARAFFINS

8. Commercial Decabromodiphenyl Ether in Textiles

Background, identity and use

Decabromodiphenyl ether (DecaBDE) was listed in 2017 as a persistent organic pollutant (POP) under the Stockholm Convention with exemptions. DecaBDE is still used in the Mediterranean region, further generating POPs stockpiles which are difficult and expensive to manage in Southern Mediterranean countries that lack POPs destruction capacity. The use of DecaBDE in textiles can lead to human exposure to polybrominated diphenyl ethers (PBDEs) and brominated dioxins indoors and in cars.

DecaBDE can be substituted in textiles by using alterative fibres or alternative flame retardants. Although some alternatives might be more expensive, the substitution is economically preferable when considering the high cost of end of life management of DecaBDE containing-waste.

Commercial decabromodiphenyl ether (c-DecaBDE) (see Table 10) was and possibly still is, a widespread flame retardant in textiles. The main textiles treated with c-DecaBDE appear to be used in commercial upholstered furniture, automotive and airplane upholstered furniture, curtains, drapery and mattress ticking, especially in hotels and other public buildings.[86] Other niche applications include tents, awnings and related fabric applications. DecaBDE is typically applied to the back of textile fabric in a coating with antimony trioxide (ATO) synergist in an acrylic or ethylene-vinyl acetate copolymer.[86] The DecaBDE back coatings can be used on a variety of fabrics including nylon, polypropylene, acrylics and other blends such as nylon–polyester.

Commercial DecaBDE (c-DecaBDE) consists predominantly of the congener BDE-209 (≥97%), with low levels of other polybrominated diphenyl ether (PBDE) congeners such as nonabromodiphenyl ether (0.3-3%) and octabromodiphenyl ether (0-0.04%).[87, 88] The sum of tri, tetra, penta, hexa and heptaBDEs present in the mixture is typically at levels below 0.0039% w/w.[88]

Hazard profile and problems

DecaBDE can be released from textiles as (micro) fibres or as particles from back coating and can accumulate in house dust. Indoor exposure is a major human exposure pathway for PBDEs.[89] Its exposure from textiles cannot be controlled or managed without product labelling, yet today DecaBDE-containing products are not labelled.

DecaBDE is used with the synergist ATO, which is suspected of causing cancer by inhalation. Polybrominated dibenzo-p-dioxins and polybrominated dibenzofurans (PBDD/Fs) are manufacturing impurities in c-DecaBDE.[90] PBDD/Fs are also formed from DecaBDE throughout the life cycle due to thermal stress or UV exposure. High levels of PBDFs are detected in house dust, likely formed from PBDEs released from textiles (and possibly electronics) into the indoor environment.[91, 92]

According to the Stockholm Convention, DecaBDE-containing materials are not allowed for recycling and might impact the recycling of textiles. South Mediterranean countries currently either lack the destruction capacity for POPs waste or have very limited capacity. This leads to high management costs for highly halogenated waste, approximately 250 to 2000 USD/tonne depending on the halogen content.

CHEMICAL	CAS/EC Number
Decabromodiphenyl ether (DecaBDE)	CAS No: 1163-19-5 EC No: 215-693-7

Table 10 Chemical identity of c-DecaBDE and its main constituent, BDE-209

Hazard profile

Source: Eurostat (2013)

Table 11 Eurostat data on EU27 DecaBDE imports (tonnes) for the years 2000-2012

YEAR	Belgium	Germany	UK	Ireland	Italy	Netherlands	Other	All EU Member States
2000	6,935	415.5	1968.5	1583.6	262	37.2	15.3	11,290
2004*	6,354	205.1	1799.6	1244.7	839.8	88.8	92.6	10,624
2008	5,145	271.6	983.1	21.7	2470.2	787.1	209.3	9,888
2012	2,352	183.7	86	5.4	732.1	634.2	139.1	4,133

*Eight central and eastern European countries – the Czech Republic, Estonia, Latvia, Lithuania, Hungary, Poland, Slovenia and Slovakia – joined the EU. Cyprus and Malta also became members.

"Other" include: Bulgaria, the Czech Republic, Denmark, Spain, Finland, France, Greece, Hungary, Poland, Romania, Sweden, Slovenia and the Slovak Republic.

Status in the Mediterranean region and internationally

Following the listing of DecaBDE in Annex A of the Stockholm Convention with a range of exemptions, Parties to the Convention have the obligation to take measures to manage the production and use of DecaBDE at national level. If requiring exemptions, the Parties must assess the most appropriate and feasible alternatives to DecaBDE. Countries from the Mediterranean region asked for exemptions for DecaBDE use as flame retardants at the Conference of the Parties 2017.

In February 2017, c-DecaBDE was included under REACH in Annex XVII to Regulation (EC) No 1907/2006. The US EPA believes that DecaBDE domestic manufacturers and importers have voluntarily phased out c-DecaBDE. In May 2017, DecaBDE was listed as a POP in the Stockholm Convention in Annex A, with a range of exemptions. In 2012, the EU still imported 4133 tonnes of DecaBDE. Turkey and Italy are among the countries using DecaBDE (see Table 11). Italy accounted for the majority of DecaBDE imports to the Mediterranean region (732 tonnes), with minor imports also in France, Spain and Greece.[93] 8.5 tonnes of DecaBDE were exported from the EU to Turkey in 2012. Former DecaBDE exports from the EU to Tunisia and Morocco were also reported. This indicates that DecaBDE is used in the Mediterranean region and textiles are likely a major use.

The African Mediterranean countries lack measurement and tracking capacity for DecaBDE. Therefore, there is no or very limited control for products in the market. Given the lack of control and destruction capacity, environmentally sound management is currently unfeasible in the region.

Selected alternatives to c-DecaBDE flame retardants in textiles

Identification and availability

Different flame retardants, fibres and barriers are available as DecaBDE alternatives for textile applications.[94] Different technologies should be selected depending on the application.

A) Alternative fibres

Inherently fire-resistant fibres, such as aramid fibres, can be used as alternatives to DecaBDE-treated synthetic fibres that require high durability. Some synthetic fibres are made inherently-fire resistant by applying non-halogenated additives during the melt spinning process, such as the use of phosphorus-based additives in polypropylene and polyester fibres.[94] Natural fibres can be fire-resistant without halogens, such as wool, with a high ignition temperature of 570 to 600°C and a high Limiting Oxygen Index of 25.[95]

For other applications, natural fibres alone might be sufficient to meet flammability standards. For instance, mattresses from Coco-mat (www.coco-mat.com) made only from natural fibres meet flammability standards of European hotels[96] and the stringent flammability standards in the US.[97] Also, Cottonsafe® mattresses made only from cotton and other natural materials meet the stringent UK standards.[98] Cotton might substitute some of the synthetic fibres or blends in some products and need less flame retardants or, for some application like mattresses or furniture, no added flame retardants at all.[98]

B) Alternative flame retardants

Several chemically-applied DecaBDE substitutes are commonly available on the market if natural cellulosic fibres such as cotton, wool, rayon and linen need additional treatment. The most common non-halogenated DecaBDE substitutes for cellulosic materials include dimethylphosphono (N-methylol) propionamide (phosphonic acid) and tetrakis (hydroxymethyl) phosphonium salt (or chloride) compound with urea.[94] For synthetic fabrics such as acrylic, acetate, nylon and polypropylene, another halogenated flame retardant may be used, such as DecaBDPE (CAS No 84852-53-9) in an acrylic polymer coating. For polyester, which accounts for 30% of world fibre production, the most common non-halogenated flame retardant is polyethylene terephthalate with built-in phosphorus on the polyester. This modified polyester is used in the majority of textile applications, is wash-resistant and is thought to be a good substitute for the DecaBDE/antimony flame retardants.

C) Fire barriers

Manufacturers use fire barrier technologies between the surface fabric and the interior foam core in furniture and mattress construction. Manufacturers also thermally or mechanically bind flame-retardant laminates to the back of fabrics to achieve compliance with fire standards.[94] However, while barriers can be regarded as alternatives to flame retarded textiles from the point of view of furniture manufacturers, they are not alternatives for the textile industry. Therefore, this technology is not evaluated in this assessment.

Technical feasibility

The individual technologies listed above were already in use in 2005 [94], proving the technical feasibility of alternative fibres and flame retardants. These technologies were or continue to be applied in countries with more stringent flammability standards such as the US. Therefore, they can be applied in the Mediterranean region, which typically has less stringent flammability standards, including in products intended for export to countries with more stringent flammability standards. However, more stringent flammability standards do not necessarily mean higher safety.[99] Sometimes these flammability standards lead to the use of more flame retardants without a significant safety gain but with higher exposure risk[100] and fire toxicity.[98]

Some of the DecaBDE chemical substitutes available on the market have limited durability due to their water solubility and tendency to wash out during laundry.[94] In these cases, dry cleaning may be required.

Economic feasibility

When estimating the cost of alternatives, the end of life treatment options and cost of DecaBDE-containing waste need to be considered. Currently, North African countries do not incinerate waste containing DecaBDE or other brominated flame retardants (BFR) due to their limited waste destruction capacity. Energy recovery in cement kiln is an option in these countries but needs further assessment with respect to bromine accumulation.[101] The POPs waste might need to be exported with associated high management cost for this highly halogen containing waste (approximately 250 to 2000 USD/tonne depending on the halogen content). Considering that one tonne DecaBDE impacts 10 to 20 tonnes of textiles, the environmentally-sound management of 1 tonne of DecaBDE in treated textiles can cost 5,000 to 40,000 USD.

A) Alternative fibres

Aramid fibres are patented (e.g. Keflar and Twaron) and in the higher price tier (8 to 40 USD/m²). Natural fibres such as wool are produced in the region and might be relatively cheap. The production of sheep wool in Europe exceeds demand and sometimes become waste. Recycling this waste wool might be a business opportunity and the material might meet the flammability requirements for a range of applications.

The production of organic cotton saves 3 tonnes of CO_2 per hectare, but these benefits are currently not included in cost calculations. Organic cotton is currently more expensive compared to conventional cotton or to cheap synthetic fibres like polyester but might become price-competitive under the regulatory framework proposed in the Action Plan for Sustainable Consumption and Production.[102]

B) Alternative flame retardants

Brominated flame retardant: Decabromodiphenyl ethane (DecaBDPE)

The price of DecaBDPE (4500 to 5500 USD/tonne) exceeds that of DecaBDE (1300 to 2500 USD/tonne). Due to their similar structure, DecaBDPE needs to be used in the same amount as DecaBDE to flame retard textile, thereby increasing the overall product cost. The halogen content of the impacted waste will also lead to high waste management costs that need to be considered.

Non-halogenated flame retardants

Non-halogenated flame retardants are somewhat more expensive compared to DecaBDE. However, the end of life management of non-halogenated waste has no additional cost. Therefore, the overall life cycle cost of these alternatives is likely lower compared to DecaBDE and other halogenated flame retardants.

Organic agriculture has resulted in the generation of fertile soil in Egypt, which is extremely important considering that fertile soil is a scarce in all Mediterranean countries (with the exception of France) to sustain the local food consumption. Furthermore, considering that North Africa and the Middle East might become partly inhabitable within the next 50 years due to climate change, greenhouse gas emission is a high priority and needs to be appropriately assessed when considering external costs in the region.

Hazards, risks and life cycle considerations

A) Alternative fibres

Natural fire-resistant fibres like wool usually do not pose unacceptable risks during product life cycle, including during end of life management. Industrial cotton production involves the use of high amounts of synthetic pesticides and can lead to worker and environmental exposure.[103] However, while in the production of organic cotton and other organic fibres the use of pesticides based on naturally occurring chemicals (e.g. nicotine) is common, associated exposures are usually lower as compared to synthetic pesticides. Organic agriculture can contribute to CO_2 sequestration in soil and to production of new fertile soil as demonstrated by the SEKEM farm in Egypt,[104] which also produces organic cotton.[105]

B) Alternative flame retardants

The hazards and risks of flame retardant substitutes vary. Fire toxicity can increase due to the use of flame retardants.[106, 98] DecaBDPE has a high bioaccumulation factor (1000 – 5000)[107] and high persistence.[107] While BFRs are effective flame retardants, in case of fires they can increase fire toxicity by forming CO, HBr and PBDD/Fs.[98, 106] DecaBDPE is also used with the synergist ATO suspected of causing cancer by inhalation. This needs to be considered for the plastic manufacturing.

Currently, BFR-containing plastic waste is separated and not recycled in the EU due to the RoHS restriction. Instead, it needs to be properly destroyed. Some chlorine-containing phosphorous flame retardants (PFRs) are considered carcinogenic,[108] and some have other negative human health effects similar to trichloropropane (TCP), which suggest that they would not be suitable alternatives for BFRs.

From an environmental perspective, resorcinol-bis(diphenylphosphate) (RDP), bisphenol-A diphenyl phosphate (BADP) and melamine polyphosphate could be good alternatives to BFRs.[108]

9. Short-Chain Chlorinated Paraffins as Metal Working Fluids

Background, identity and use

Short-chain chlorinated paraffin (SCCPs) have been listed under the Stockholm Convention in May 2017, with a range of exemptions including metal working fluids (MWFs).[109] MWFs are a major use of SCCPs to lubricate parts that experience extreme pressures and are used in deep drawing, tube bending, cold heading or cutting and grinding and as coolants in metal processing. More than 90% of SCCPs from MWF use are released into the environment.[110]

This use of SCCPs has already been restricted in the EU since the 1990s and was stopped in 2004. Alternatives have been used for over 20 years, including a range of environmentally adapted lubricants (EALs) with high biodegradability and low toxicity such as vegetable oil-based lubricants, sulfur-, nitrogen- and phosphor containing oils, mineral oils and their mixtures.

Short-chain chlorinated paraffins (SCCPs) are one of the most common metal working fluids (MWF), used as lubricants and coolants in metalworking fluids. Back in the 1990s when SCCPs were still allowed in Europe, MWFs were a major use. In general, lubricants are designed to lubricate parts that experience extreme pressures and are used in deep drawing, tube bending, cold heading and as cutting oils.[111] The application for metal processing has been listed as exemption to the Stockholm Convention and can therefore continue.

Hazard profile and problems

CCPs are persistent chemicals that bioaccumulate and have toxic properties and were therefore listed as persistent organic pollutants (POPs) in Annex A of the Stockholm Convention in May 2017.[109] SCCPs are classified as toxic to aquatic organisms and carcinogenic to rats and mice. SCCPs (average chain-length of C12, chlorination degree 60 wt%) were categorised in group 2B as possibly carcinogenic to humans by the International Agency for Research on Cancer (IARC).

The use of SCCPs as MWF leads to workers' exposure to the fluids by breathing aerosols generated in the machining process, or through skin contact when handling parts covered with the fluids. More than 90% of SCCPs from MWF are released into the environment.[110] SCCPs from MWF might also contaminate consumer products containing metal parts.[112] The widespread use of SCCPs in consumer products results in contamination of the indoor environment.[113] Recent studies also showed high SCCP levels in human milk and biota.

According to Stockholm Convention, SCCP-containing materials are not allowed to be recycling. SCCP oils might contaminate and hinder waste oil recycling.

Currently, South Mediterranean countries either lack the destruction capacity for POPs waste, or have only very limited capacity. Therefore, SCCP-containing waste might need to be exported. This

CHEMICAL	CAS Number*
IUPAC: Alkanes, C10-13, chloro Short-chain chlorinated paraffins (SCCPs)	CAS No. 85535-84-8; CAS No. 68920-70-7; CAS No. 71011-12-6; CAS No. 85536-22-7; CAS No. 85681-73-8; CAS No. 108171-26-2.

*These CAS numbers can contain short chain chlorinated paraffins

Table 12 Chemical identity of short-chain chlorinated paraffins (SCCPs)

Hazard profile

- GHS01 Explosive
- GHS02 Flammable
- GHS03 Oxidizing
- GHS04 Compressed Gas
- GHS05 Corrosive
- GHS06 Toxic
- GHS07 Harmful
- GHS08 Health hazard
- GHS09 Environmental hazard
- CMR Carcinogenic/ Mutagenic/ reprotoxic
- EDC Endocrine disrupting chemicals
- Persistent organic pollutant

leads to high management and destruction costs for highly halogenated waste, approximately 500 to 2000 USD/tonne depending on the halogen content.

Status in the Mediterranean region and internationally

Following the listing of SCCPs in Annex A of the Stockholm Convention with a range of exemptions, all Parties to the Convention have the obligation to take measures to manage the production and use of SCCPs at national level. This includes taking legislative and regulatory actions, inventorying and managing stocks and waste. If requiring exemptions, the Parties must assess the most appropriate and feasible alternatives to SCCPs.

SCCPs have been listed in the EU POP Regulation since 2004. This prohibits the production, placing on the market and use of SCCPs, of preparations containing SCCPs in concentrations greater than 1% by weight and of articles containing SCCPs in concentrations greater than 0.15% by weight. These restrictions place limit the presence of SCCPs in products (1.0%) and articles (0.15%). Since May 2017, SCCPs are listed as POPs under the Stockholm Convention (Annex A).

When SCCPs were listed in the Stockholm Convention, developing countries including countries from the Southern Mediterranean region requested a range of exemptions such as the use as MWF. This indicates that SCCPs are likely used in the Mediterranean region for this purpose.

Since the amendment enters into force only in 2018 and compliance is required only by 2020, SCCPs are still used as MWF without restriction.

South Mediterranean countries lack the capacity to measure SCCPs, therefore there is little to no control as to the chain length (short versus medium) of chlorinated paraffins on the market. Considering the lack of regulatory and monitoring control and destruction capacity, an environmental sound management is currently not feasible in the region.

Selected alternatives

for SCCPs as metal working fluids

Identification and availability

For the substitution of SCCPs in MWF, a range of environmentally adapted lubricants (EALs) have been developed and are already in use. EALs have been defined under the EU draft ecolabel as lubricants with high biodegradability, low toxicity and performance equal to or better than conventional alternatives.[114] Several EALs, including vegetable oil-based (oleochemical) ingredients can be used in traditional water-based and straight-oil formulations in place of SCCPs.[115]

Other alternatives to SCCPs include sulphur-based compounds (e.g., zinc dialkyl dithiophosphate, sulfonated fatty esters, overbased calcium sulphonates), phosphorus-based compounds (e.g., tributyl phosphate, alkyl phosphate esters, phosphate acid esters, hydrogen phosphites), nitrogen-based compounds, boundary acid esters and complex esters.[109,116, 117, 118] Medium-chain chlorinated paraffins (MCCPs) and long-chain chlorinated paraffins (LCCPs) are also used as alternatives to SCCPs.

Other alternative processes and emerging processes include dry machining, which requires no cutting fluid and cryogenic machining, which uses liquefied gases.[119]

Technical feasibility

Since alternatives have replaced SCCPs for more than 20 years in many countries, their use has already been optimized for these applications. The technical suitability of alternative chemicals and processes depends on the requirements of each specific process. Alternative MWFs may not be suitable for all applications or processes. Knowledge transfer is important and should be considered in the implementation of the Stockholm Convention.

Currently, most South Mediterranean countries lack the destruction capacity for halogenated POPs waste. Therefore, these countries cannot manage SCCPs at the end of life and their use eventually leads to environmental contamination at the site of use or waste disposal. The end of life management of alternatives MWF such as vegetable oils and mineral oils is technically feasible in these countries since these oils can be incinerated in boilers or cement kilns and vegetable oils degrade when released into the environment with consideration for BOD/COD limits.

Economic feasibility

There is limited information regarding pricing of individual alternatives.[116] Since SCCPs have been substituted for the past 20 years in many countries, the alternatives are commercially available and economically feasible in many regions, including the EU.

SCCPs are very cheap MWFs, so alternatives are normally more expensive. SCCPs might even be cheaper compared to mineral oil-based MWFs, since mineral oils are often subjected to tax. To fully understand the price competitiveness of alternatives, the external costs of SCCP use, including environmental costs, need to be added on using taxes or similar policies. An environmentally sound management of SCCP-containing waste must be required and implemented, including wastewater treatment and management/destruction of impacted sludge and other waste. Since such destruction capacity is currently lacking in most of these countries, this might require expensive export of SCCP waste. Furthermore, the cost of the negative impact on waste oil recycling must be considered and included in the pricing. Considering all these external cost factors, the alternatives should be cheaper or at least price competitive.

Hazards, risk and life cycle considerations

A) Environmentally adapted lubricants (EALs); bio-based oils

Bio-based formulations have the potential to reduce waste treatment costs of MWF effluents. Bio-based oils have the smallest occupational health risks compared to other MWFs if bacteria are controlled. Compared to petroleum-derived cutting oils-containing CP additives, vegetable-based alternatives such as non-chlorinated canola, sunflower and soybean oils provide better heat dissipation and produce less smoke during machining.[120]

B) Mineral oil-based alternatives

Mineral oil-based MWFs can also lead to environmental contamination if not properly managed.

C) Sulfur-, nitrogen- and phosphorus-containing oils

Sulphur-, phosphorus- and nitrogen-based compounds have specific applications as MWFs. They form diverse lubricant groups with specific uses and have substituted SCCPs in most applications.

D) MCCPs and LCCPs

MCCPs and LCCPs are also persistent and might accumulate in the environment. MCCPs are accumulating in biota including human milk. Waste containing MCCPs or LCCPs is also difficult to manage in Southern Mediterranean countries. Therefore, these alternatives are not recommended.

10. Commercial Decabromodiphenyl Ether in Plastic Electronics and Transportation

Background, identity and use

Decabromodiphenyl ether (DecaBDE) was listed in 2017 as a persistent organic pollutant (POP) under the Stockholm Convention, with exemptions including plastic housings in certain electronics, such as plastic parts used for heating home appliances, irons, fans, immersion heaters and other plastic parts in vehicles and aircrafts.

Better alternatives are available, including flame retardants, materials and re-designed electronics. Suitable alternative flame retardants must not be toxic or increase fire toxicity in case of a fire event.

Commercial decabromodiphenyl ether (c-DecaBDE) (see Table 13) has been a widely used flame retardant in electronics. c-DecaBDE consists predominantly of the congener BDE-209 (≥97%), with low levels of other PBDE congeners such as nonabromodiphenyl ether (0.3-3%) and octabromodiphenyl ether (0-0.04%).[121, 122] In plastic it is normally used with Antimony(III) oxide (ATO) as synergist.

Hazard profile and problems

DecaBDE can be released from electronics or building materials and accumulate in house dust. Indoor exposure is a major human exposure pathway for PBDEs.[123] Polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs) are manufacturing impurities in c-DecaBDE.[124] PBDD/Fs are also formed from DecaBDE throughout its life cycle due to thermal stress, non-BAT (best available techniques) incineration, or UV exposure. High levels of PBDFs are detected in house dust, likely formed from PBDEs released from electronics, building materials and textiles into the indoor environment.[125, 126] DecaBDE is used with the synergist antimony trioxide (ATO), which is suspected of causing cancer by inhalation.

The use of DecaBDE in plastic is difficult to control or manage in products that are normally not labelled. DecaBDE has been found in recycled food contact materials such as kitchen tools or coffee cup lids. According to the Stockholm Convention, DecaBDE-containing materials must not be recycled and hinder the recycling of plastics from electronics.

Southern Mediterranean countries currently either lack the destruction capacity for POPs waste, or have

CHEMICAL	CAS/EC Number
Decabromodiphenyl ether (DecaBDE)	CAS No: 1163-19-5 EC No: 215-693-7
Antimony trioxide (ATO); Antimony(III) oxide; Sb_2O_3	CAS No: 1309-64-4 EC No: 215-474-6

Table 13 Chemical identity of c-DecaBDE and its Antimony(III) oxide (ATO) synergis

Hazard profile

very limited capacity. Therefore, POPs-containing waste might need to be exported, leading to high management costs for highly halogenated waste, approximately 250 to 2000 USD/tonne depending on the halogen content.

Status in the Mediterranean region and internationally

Following the listing of DecaBDE in Annex A of the Stockholm Convention, all Parties have the obligation to take measures to manage its production and use at national level. This includes taking legislative and regulatory actions, carrying out inventories and managing stocks and waste. If requiring exemptions, the Parties must assess the most appropriate and feasible alternatives to DecaBDE.

Countries from the Mediterranean region asked for exemptions for DecaBDE use as flame retardants at the Conference of the Parties 2017. EU import and export data indicate its use in the Mediterranean region (see chapter 8 and Table 11).[127]

The EU stopped the use of DecaBDE in new electronics in 2008 through the Restriction of Hazardous Substances (RoHS) Directive. C-DecaBDE has been included under REACH in Annex XVII to Regulation (EC) No 1907/2006 in February 2017.[128] The US EPA believe that domestic manufacturers and importers have voluntarily phased out c-DecaBDE.[129]

Selected alternatives

to DecaBDE in plastic electronics and transportation

Identification, availability and technical feasibility

Alternatives to DecaBDE in plastic housings are available and have been used for more than 10 years, ever since DecaBDE was banned in electronics in the EU. Some producers stopped the use of c-DecaBDE in the early 2000s, even before the regulations where established. Therefore, alternatives are available and have proven their technical feasibility for more than a decade.

Substitution can occur at three levels: product redesign, material substitution and substitution of the flame retardant only (Figure 4).[130, 131]

RESIN SYSTEM	Flame retardant
Blends of high impact polystyrene and polyphenylene oxide (HIPS/PPO)	Resorcinol bis diphenyl phosphate (RDP)
Blends of polycarbonate and acrylonitrile-butadiene-styrene (PC/ABS)	Bisphenol A diphosphate (BPADP)
Polycarbonate (PC)	Phosphate esters
Polylactide (PLA)	Metal hydroxide

Table 14 Alternative resin systems with non-halogenated flame retardants[130]

A) Flame retardant substitution

DecaBDPE (CAS No 84852-53-9) is a major substitute for DecaBDE as a flame retardant in all plastic applications, including the cheap and frequently-used high impact polystyrene (HIPS). A range of other brominated flame retardants are also used.[132]

B) Material (and flame retardant) substitution

The most cost-effective non-halogenated substitutes involve changing the resin system and using phosphorous-based flame retardants. Of these three replacement systems, only HIPS/Poly(p-phenylene oxide) (PPO) is 100% halogen-free. The polycarbonate (PC) / acrylonitrile butadiene styrene (ABS) and PC systems typically contain a very small amount of fluoropolymer (roughly 0.3%) for drip resistance. Other alternatives such as metal or wood are possible but not widely employed due to cost and performance issues.

C) Product redesign

Electronics could be redesigned to separate the voltage supply or the heat supply from ignitable plastics. Shielding the power supplies with metal components lowers flame retardancy requirements, making flame

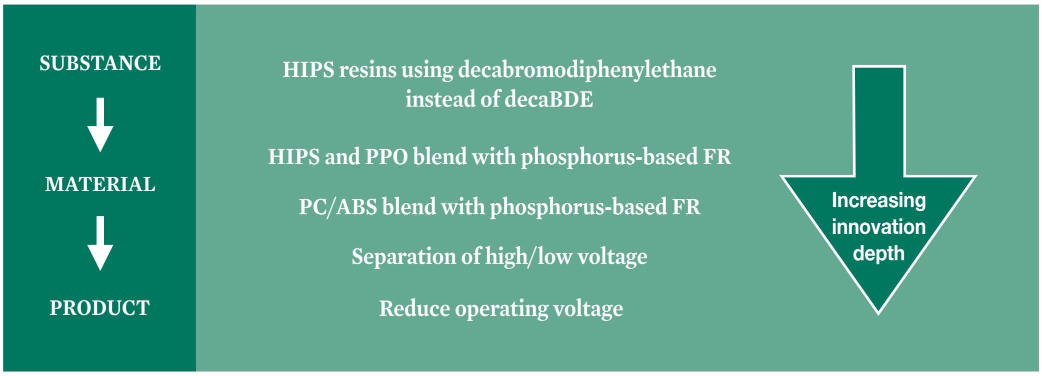


Figure 4 Approaches of flame retardant substitution[130]

retardant-free HIPS a viable alternative.[130] With such eco-design approaches, polymer parts do not need flame retardants or can be subject to a lower fire safety standard.

Economic feasibility

- *DecaBDPE*

  The price for DecaBDPE (4500 to 5500 USD/tonne) exceeds that of DecaBDE (1300 to 2500 USD/tonne). DecaBDPE needs to be used in the same amount as DecaBDE, thereby increasing the overall product costs. When calculating the cost over the entire life cycle, the price of managing halogen-containing waste needs to be considered, as well as the difficulty of treating such waste in the Southern Mediterranean countries.

- *Polymers with non-halogenated flame retardants*

  The price of the polymer alternatives with non-halogenated flame retardants is 40 to 100% higher compared to the cheap DecaBDE-containing HIPS polymer, resulting in 1.5 to 2.5% higher product cost.[130] However, the life cycle cost of the alternatives is lower considering their recyclability versus the high cost of environmentally sound management of DecaBDE-containing waste. Waste management cost savings, make up for the slightly higher price of the alternatives.

Hazards, risks and life cycle considerations

- *DecaBDPE*

  DecaBDPE has a high bioaccumulation factor (1000 – 5000) and very high persistence.[132]
  DecaBDPE is also used with the synergist ATO, which is suspected of causing cancer.
  Currently, BFR-containing plastic is separated and disposed of but not recycled due to the RoHS restriction and Stockholm Convention listing of PBDEs. While BFRs are effective flame retardants, they can increase fire toxicity in the case of fires (CO, HBr, PBDD/Fs).[133]

- *Polymers with non-halogenated flame retardants*

  These polymers (Table 14) have superior end of life performance. The ability to separate phosphorus flame retardants (PFR)-containing plastic for recycling has been demonstrated at full scale for PC/ABS.[134]
  The flame-retarded polylactic acid composite bioplastic contains >75% plant-derived polylactic acid. It has appropriate durability, chemical resistance, light resistance and surface hardness.[135]

11. Short Chain Chlorinated Paraffins in Fatliquoring in Leather

Background, identity and use

The short chain chlorinated paraffins (SCCP) have been listed in Annex A of the Stockholm Convention with specific exemptions. One of the specific exemptions is for the production and use of SCCP in leather industry, in particular fatliquoring in leather.[136] This is an open application with related exposure to workers and consumers and has been restricted in the EU since the 1990s. Better alternatives are available including natural oils such as vegetable oil and fish oil. From life cycle assessment the use of vegetable oils is preferred.

SCCPs are chlorinated paraffin mixtures (Table 15) that are viscous, colourless or yellowish dense oils.[137] SCCPs were and continue to be, used primarily as metalworking fluids and additive in PVC plastics or rubber.[138] The application for fatliquoring of leather has been listed as an exemption in the Stockholm Convention[136] and therefore its use is likely to continue in the future unless more environmental friendly alternatives are promoted.

Hazard profile and problems

SCCPs are persistent chemicals which bio-accumulate and have toxic properties and were therefore listed in Annex A of the Stockholm Convention as POPs in May 2017.[136] In mammals, SCCPs affect the liver, the thyroid hormone system and the kidneys.[138] SCCPs are particularly toxic to aquatic invertebrates and are endocrine disrupting substances.[138]

They are also proved to be and carcinogenic to rats and mice. SCCPs (average chain-length of C_{12}, chlorination degree 60 wt%) were categorised in group 2B as possibly carcinogenic to humans from the International Agency for Research on Cancer (IARC). They are also present in human breast milk both in temperate and Arctic populations.[138] Environmental releases occur during production, use, service-life and disposal of SCCPs and SCCPs containing products. Their wide industrial applications have provided a major source of environmental contamination.[138]

Their use in leather fatliquoring leads to exposure of workers to the fluids through skin contact when they handle the fluids and the leather. Also consumers can be exposed to SCCP from treated leather.[110] The wide use of SCCP in consumer products results in contamination of indoor environment.[139]

According to the Stockholm Convention SCCP containing materials are not allowed for recycling as they might contaminate and hamper leather recycling in future.

Currently the destruction capacity for POPs waste in Southern Mediterranean countries does not exist or exists only to a very limited extent. Therefore POPs waste containing SCCP might need to be exported with associated high management and destruction costs for highly halogenated waste (approx. 500 to 2000 USD/tonne depending on the halogen content).

Status in the Mediterranean region and internationally

As with all Stockholm Convention listed items, the obligations remain the same as regards to taking the appropriate measures to tackle the issue.

The use of SCCPs have been restricted by Canada, EU, Norway and the United States for more than a decade.[140]

They were initially regulated at the EU level in 2002 in Directive 2002/45/EC amending Council Directive 76/769/EEC, restricting their use in concentrations

Hazard profile

>1% for applications in metalworking and fat liquoring of leather. SCCPs have been restricted by the POP Regulation since their listing in Annex 1 of the regulation in 2012 (Commission Regulation (EU) No 519/2012) which generally allows low concentrations in substances and preparations (1%). Furthermore, the Regulation provides for a general exemption from control measures if a substance occurs as an unintentional trace contaminant. This exemption would apply to SCCPs present as unintentional contaminants in MCCPs.[141]

CHEMICAL	CAS Number*
IUPAC: Alkanes, C10-13, chloro Short chain chlorinated paraffins (SCCP)	CAS No. 85535-84-8; CAS No. 68920-70-7; CAS No. 71011-12-6; CAS No. 85536-22-7; CAS No. 85681-73-8; CAS No. 108171-26-2.

*These CAS numbers can contain short chain chlorinated paraffins

Table 15 Chemical identity of short-chain chlorinated paraffins (SCCPs)

Selected alternatives

to short chain chlorinated paraffins in fatliquoring in leather

Identification, availability and technical feasibility

Potential alternative substances available are:[142]

A) Animal and/or vegetable oils

Animal and vegetable oils are technically feasible and commercially available and have been used as leather fat for long time in fatliquoring leather even before the use of SCCPs. In particular refined fish oils have been used in the past.

B) Mineral oils

Mineral oils are available as highly refined oils or lower grade oils.

C) Long-Chain Chlorinated Paraffins (C18+) (LCCPs)

This potential alternative is technically feasible and commercially available.

Economic feasibility

All alternatives are economic feasible. It is likely that the alternatives are approx. 15% more expensive than SCCPs but this higher cost is considered to be negligible.

Hazards, risks and life cycle considerations

- *Animal and vegetable oils:*

Animal and vegetable oils are non-toxic and do not bioaccumulate. Considering life cycle assessment vegetable oils are more sustainable compared to fish oils.[143]

- *Mineral oils:*

Highly refined mineral base oils have low acute toxicity by ingestion and skin contact. They can cause slight skin and eyes irritation. Less refined oils might contain polycyclic aromatic hydrocarbons (PAH); some are known carcinogens. Mineral oil is harmful to aquatic life. Mineral oil has the potential to bioaccumulate.[144]

- *Long-Chain Chlorinated Paraffins (C18+) (LCCPs):*

Canadian assessment concluded that LCCP (C_{18-20}) are highly persistent and bioaccumulative and toxic to aquatic species at low concentrations. LCCPs with more than 20 carbons were found to be persistent but not bioaccumulative.[145] US EPA states that C_{18-20} (40-55 wt% Cl) are persistent to very persistent; higher chlorination can contribute to greater persistence under most environmental conditions and are potentially bioaccumulative. They also may cause long-term adverse effects in the aquatic environment.[146]

HIGHLY FLUORINATED

12. Per- and Polyfluorinated Alkylated Substances in Firefighting Foam

Background, identity and use

The use of firefighting foam containing perfluoro-otanesulfonic acid (PFOS) and other per- and polyfluorinated alkylated substances (PFASs) can result in the contamination of groundwater, drinking water and surface water, including the Mediterranean Sea. PFASs or their degradation products are highly persistent. Longer chain PFASs are bio-accumulative. Shorter chain PFASs accumulate in plants, including vegetables and fruits. There is no known degradation for perfluorinated substances in ground water or soil and therefore the contamination is long-term. PFASs are an issue of concern under the Strategic Approach International Chemical Management (SAICM).

For most firefighting foam applications, fluorine free foams (F3) are available today. They degrade in the environment and are not a long-term concern for ground and drinking water. A few of these foams are even solvent free.

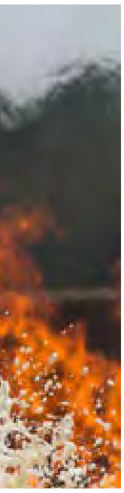
PFOS and other shorter chain PFASs are used in firefighting foams, mainly in aqueous film-forming foams (AFFF) and alcohol resistant aqueous film-forming foams (AFFF-AR). PFOS was first produced by a US-based company 3M. All PFAS-containing foams are mainly designed for large scale fires of burning liquids, especially hydrocarbon tank fires with crude-oil, jet fuel, petrol and others (so called class B fires). One of the advantages of PFOS-based foams is their ability to cover spills of leaked fuels and supress the vapour. The film-forming property gives them a high level of resistance to burnback. Still today, PFOS-based foams show the highest performance in this regard. The main advantage of these products is their ability to form a heat-resistant film and spread a vapour-proof seal on flammable liquids to stop the vapour and therefore extinguish the fire.

PFOS-containing foams quickly became the standard for multipurpose firefighting in all major industries due to their high performance on class B fires. They held this leading role until 2002 when 3M finally announced their decision to stop the production of all PFOS-based products within that same year. The decision was made after the indubitable worldwide evidence of the PBT-potential of PFOS.

In the same year, telomere surfactants (C6+2) have been introduced as drop-in replacements as a more environmentally friendly PFOS alternative for the market. Since then, alternatives have gradually developed due to rising market demand for environmentally friendly high-performance products suitable for fighting all kinds of fires.

*The GHS symbols and Stockholm Convention listing has been established for PFOS and PFOA. For most other PFAS the toxicoligical assessment is insufficient and PFAS has been listed as issue of concern under SAICM.

Hazard profile*



C6+2 products have now been replaced by pure C6 fluorosurfactants.

Hazard profile and problems

The use of PFOS and other PFASs can result in the long-term contamination of groundwater, surface water and related drinking water.[147] While the shorter chain PFASs have lower bioaccumulation potential, they remain highly mobile in the environment and accumulate in plants. There is a lack of toxicological data for most shorter chain PFASs. Due to the extreme persistence of PFASs and the uncertain toxicity profile of many PFASs, precautionary principles must be applied.

Status in the Mediterranean region and internationally

In the Mediterranean region AFFF, AFFF-AR and some fluorinated protein foams still remain almost exclusively PFAS-based.

The Stockholm Convention has listed a specific exemption for PFOS use as firefighting foams. In a range of countries that have requested exemptions, PFOS is still partly used and remains in stockpiles.

In European countries, PFOS was banned in 2009 by the EU POP regulation,[148] but fluorinated AFFF is still used by most fire brigades for hydrocarbon fires. However, as the new non-fluorinated replacements become available and are certified by accepted standards, the focus is shifting towards substitution with the available alternatives. As most firefighters have been used to AFFF for decades, it takes time for non-fluorinated replacements to gain acceptance. One approach gaining popularity for instance in western European refineries is the use of non-fluorinated F3 for the initial fire attack and the use of AFFF-stockpile only when the F3 stock has been depleted or when perceived performance differences remain, due to lack of training and use of the product.

Australia, starting with the state of Queensland, issued the strongest and most extensive restrictions for PFASs in 2015, effectively banning the use of PFAS-containing foam in all areas of firefighting, when retention of these chemicals away from soil and water cannot be guaranteed.[149] This restriction becomes effective on 31.12.2018.

Southern Mediterranean countries currently have no specific restriction of PFOS- or PFAS-containing foams. The lower price of these foams is driving the market demand without considerations for environmental pollution. Furthermore, the market might not be mature enough to change to newer technologies.

Selected alternatives to PFASs in firefighting foam

Identification and availability

A range of producers are offering fluorine free F3, including Solberg, Orchidee and 3FFF. F3 work differently than film-forming foams as they provide a very effective mechanism to shut off oxygen from the fuel surface. The F3 mechanism is to provide a very dense foam-structure to prevent oxygen from reaching the surface of liquid fuels, including in 2-dimensional fires.

F3 are available on the global market, including the North African region. Often the same suppliers and sellers have PFASs-based and fluorine-free foams, therefore availability is guaranteed.

Currently, there is only one solvent-free F3, provided by the 3FFF company,[150] which is in cooperation with a company in the MENA region.[150]

Technical feasibility

For all kinds of polar liquids and solvents, F3 performance is equal to that of AFFF, if not better. There is sufficient technical data to prove that F3 products already represent a real alternative to AFFF /AFFF-AR for most scenarios, when used appropiately.

Tests from big waste disposal companies in Germany have shown much better results with F3 in a one- to-one test against fluorinated AFFF, for example on compressed plastics and other materials, where the water-film is not responsible for extinguishing the fires. F3 are effective due to their better foam quality, foam density and penetration of solid fuels. Therefore, they have a better cooling effect paired with oxygen cut-off, which is more important for those kinds of materials.

The lack of fluorinated molecules in F3 results in minor fuel pickup upon initial contact with the hydrocarbon fuel. As of today, AFFF still have a slightly better performance on 2-dimensional fires such as tank fires with crude oil or other hydrocarbons. The poorer performance of F3 in this case can be overcome with a higher application rate.

Within the German Fire Brigade Association there is a working group for foams that already recommends the use of fluorinated foams only as a last resort for big tank storages and refineries, due to their risk of large 2-dimensional fires. For all other uses, such as at airport in sprinklers, in other foam-based systems, in fire-extinguishers and for all other kinds of fire brigades and users, the recommendation is to restrict the use of AFFF in the foreseeable future, as the existing alternatives already have proven high performance levels for most situations.

At low application rates (approximately 4 $l/min/m^2$), a “gentle” F3 application is recommended due the known “fuel pickup” effect. Firemen are already trained in the gentle application method for all kinds of alcohol-resistant (AR) foams, therefore no additional training is needed. At high application rates (> 4.5 $l/min/m^2$), this effect becomes irrelevant.

Economic feasibility

Generally, the price of F3 doesn’t differ significantly compared to other foams like AFFF used in Western Europe. However, Mediterranean countries generally buy very cheap and thus old technology-based foams, such as protein foams not considered best available techniques (BAT).

This history of price sensitivity makes it very difficult to introduce more rigorously produced and tested foams in these markets or to argue for environmental protection. Currently, South Mediterranean countries are unaware of the costs of removing PFASs from drinking water or remediation of contaminated groundwater.

Considering the price competitiveness of BAT for fluorinated and non-fluorinate foams, F3 have the economic benefit of avoiding the high cost of groundwater and drinking water clean up and other external costs related to negative human health, environmental and ecological impacts.

Hazards, risk and life cycle considerations

The chemicals in F3 readily degrade in the environment and do not contaminate the groundwater and drinking water. In a BAT F3 product, no PBT substances should be found.

Depending on the formulation, F3 application might result in a higher biological oxygen demand (BOD) and chemical oxygen demand (COD). However, the most advanced F3 from 3FFF use solvent free (SF) technology in its most advanced F3, which reduces COD and BOD to a minimum.

The foams can be used safely without changing or compromising the operators’ protection protocols, including heat radiation and distance protocols for fighting fires.

13. Per- and Polyfluorinated Alkylated Substances in Textile Hydrophobing

Background, identity and use

Per- and polyfluoroalkyl substances (PFASs), sometimes referred to as per- and polyfluorinated chemicals (PFCs), are a group of over 4000 man-made substances used in numerous applications, including textile hydrophobing. PFASs or their degradation products are highly persistent in the environment. Some PFASs bioaccumulate and some have known toxic effects. PFASs are of concern under the Strategic Approach International Chemical Management (SAICM). Several low-hazard alternatives are readily available for the use of PFASs in textile hydrophobing. Two PFAS subclasses are widely used in hydrophobic textiles:

1. Side-chain fluorinated polymers can be applied on textiles to create a durable water repellent coating. They consist of a urethane, acrylate or methacrylate polymer with hydrocarbon side chains and contain on average ~0.5% unreacted residuals and impurities such as fluorotelomer alcohols (FTOHs) and perfluoroalkyl acids (PFAAs).[151] They are not true polymers, because the fluorinated side chain can cleave off the backbone, degrading to PFAAs.
2. Fluoropolymers, such as polytetrafluoroethylene (PTFE), form membranes used as a laminate layer in protective weather outdoor apparel. Historically, PTFE was manufactured using perfluorooctanoic acid (PFOA), a PFAA with eight carbons in its molecule. After the phase-out of PFOA in most countries, PTFE is now manufactured using either shorter chain PFASs, such as perfluorohexanoic acid (PFHxA) (PFOA's six carbon equivalent), or perfluorinated ethers such as GenX, which have less toxicological information available but are highly persistent, mobile in the environment and found in increasing concentrations in surface waters.

Southern Mediterranean countries have textile and carpet industries that use PFASs or other hydrophobing chemicals depending on the individual product requirements. Hydrophobic textiles sampled in Europe were found to contain PFASs, including PFOA, PFOS and PFHxS,[152] as well as FTOHs and fluorotelomer acrylates (FTAs), which further degrade into PFAAs.[153,154]

Hazard profile and problems

PFASs are highly persistent or form highly persistent degradation products in the environment. Many PFAAs bioaccumulate and biomagnify. PFAAs and some of their precursors like FTOHs and FTAs show a range of adverse health effects to humans and biota. People can be exposed to volatile FTOHs contained in the PFAS treatment as manufacturing impurities

*The GHS symbols and Stockholm Convention listing has been established for PFOS and PFOA. For most other PFAS the toxicoligical assessment is insufficient and PFAS has been listed as issue of concern under SAICM.

Hazard profile*

or intermediate degradation products. This can be of particular concern for workers in clothing stores and manufacturing plants.[155] Also, during laundering, PFAAs are released into wastewater, but wastewater treatment plants cannot effectively remove them. At the end of life, hydrophobic textiles are discarded in landfills. Landfill gases and leachate have been documented as major long-term sources of PFAAs, mainly from discarded textiles, to the environment, potentially contaminating human drinking water and food.[156]

Status in the Mediterranean region and internationally

The German Sporting Goods Industry, the Outdoor Industry Association and the European Outdoor Group are supporting research on alternatives to PFAS-based durable water repellents.[157] In September 2015, the European Outdoor Group formed a project group to help build knowledge about PFASs within the industry and support brands' decision-making processes.[158]

A Danish survey of children's clothing identified four companies that had previously used PFASs for achieving hydrophobicity but have now switched to PFAS-free dendrimer technology. They estimated that only 10-30% of rain covers or winter/ski clothing were treated with PFAS-based impregnating agents and an even smaller percentage of rainwear and jackets.[159]

Southern Mediterranean countries are currently developing a first regulatory framework on addressing PFOS and related substances within the framework of the Stockholm Convention. However, the larger group of PFASs have not yet been addressed.

Selected alternatives

to PFASs in textiles hydrophobing

Identification and availability

Available alternatives for textile hydrophobing can be grouped into four main categories: hydrocarbons, silicones, dendrimers and nanotechnology.

Hydrocarbon repellents mimic the natural low energy surfaces of plant leaves.[160] The oldest such formulations were based on paraffin compounds and waxes with metal (typically aluminium, zinc, or zirconium) salts of fatty acids (usually stearic acid) that attach to the textile fiber.[157, 161] Stearic acid-melamine repellents, formed by reacting stearic acid and formaldehyde with melamine, are a newer and more durable type of hydrocarbon repellents.[157] The newest forms of hydrocarbon repellents are acrylic and polyurethane-based emulsions.[160]

Examples of commercially available hydrocarbon repellents include:

ecorepel® from Schoeller, Texfin® HTF from TexChem®, zeroF from CHT/Bezema, Itoguard NFC from LJ Specialities, Arkophob FFR liq from Archroma Management GmbH, the Phobotex product range (APK, JVA, RCO and ZAN) from Huntsman and Purtex® from the Freudenberg Group.[157, 161]

The following PFAS-free alternatives are certified bio-based products: HeiQ Eco Dry (formaldehyde-free),[162] miDori® evoPel (partially based on plant seed oils),[163] Chemours' Zelan™ R3 finish (with 60 percent renewable sourced raw materials).[164]

There are two main types of **silicone waterproofing compounds**:[157] (1) elastomeric polydimethylsiloxanes (PDMS), which are polymers adhering to the textiles like a flexible protective membrane and (2) reactive silanes and siloxane resins with crosslinkable side chains, which are smaller molecules that chemically bind to the textiles, typically consisting of a silanol, a silane and a catalyst such as tin octane. Commercially available silicone-based water repellents include: Texfin®-HTF and Texfin®-SWR-A from TexChem, Phobotex series (Catalyst BC, SSR and WS Cone) from Huntsman, RHODORSIL TCS 7001 from Bluestar Silicones,[161] as well as products from Dow Corning®, Shin-Etsu and Wacker.[157, 165]

Dendrimers, highly branched monomers that create tree-like structures on the fabric surface, are another alternative. The term dendrimer refers to the structure. Chemically, they can contain fatty acids, hydrocarbons, polyurethanes, polyalkylsiloxanes, or PFASs (not all dendrimers are PFAS-free).[157,160] Examples include Rudolf Group's BIONIC-FINISH® ECO and RUCO-DRY ECO®.[157]

Nanotechnology can also provide textile hydrophobicity. For instance, Schoeller Technology has developed NanoSphere®, a self-cleaning surface finish.[165]

Technical feasibility

PFAS-free repellents can provide a similar level of hydrophobicity and some can resist aqueous-based stains but don't provide oil repellency[166] which is assumed to be needed to keep treated fabrics cleaner longer and prolong water repellency between washes. However, these features are not essential and PFAS-free technologies are sufficient for all but potentially the harshest environments.[157] A consumer survey conducted in 2016 in the EU revealed that oil repellency of outdoor garments exceeds user requirements, thus the use of PFAS finishes is over-engineering.[166]

Paraffin-based repellents typically need higher concentrations to be effective, while silicone repellents are highly effective at low doses, but excess application can reduce performance.[161] Some PFAS-free repellents may also be less durable when laundered, especially the physically bound waxes. Stearic acid-melamine repellents have good durability to laundering but can negatively affect some of the physical properties of the fabric, such as tear strength and abrasion resistance.[157] One test found that polyurethane repellents[157] were least resistant to prolonged exposure to water, compared to silicone, wax and PFAS-based repellents. Tumble drying heat for 30 minutes is effective at improving repellency performance after prolonged exposure to water.[157]

Economic feasibility

The raw materials and application of PFAS-free alternatives are generally more economical compared to PFASs.[166] Hydrocarbon repellents are generally less expensive, though some require higher dosage due to lower efficiency, making them in the end comparable in price to PFAS-based products.[161] Silicone and dendrimer-based repellents can be more or less expensive than PFAS-based ones.[161]

Hazards, risks and life cycle considerations

A recent hazard assessment concluded that hydrocarbon repellents generally have the lowest hazard, followed by silicone-based repellents and lastly by PFAS-based repellents. The study could not assess the hazards of dendrimer-based repellents and nanorepellents due to insufficient data.[160]

Hydrocarbon repellents can biodegrade completely in the environment over time. Pure paraffin wax is generally a low hazard substance, harmless to human health, readily biodegradable and not bioaccumulative.[160] However, some hydrocarbon-based formulations may contain other potentially hazardous ingredients such as isocyanates, dipropylene glycol and other unspecified compounds.[161] Stearic acid-melamine repellents tend to release formaldehyde which is toxic to human health.[157]

Some silicone repellents contain siloxanes as manufacturing impurities, including compounds with high human health hazard and ecotoxicity such as octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5).[160] Siloxanes can bioaccumulate in aquatic food webs. The waste water resulting from the finishing application process of silicon water repellents is toxic to fish, but overall, the risks associated with environmental releases of silicone-based repellents are lower than for PFAS-based repellents due to their lower environmental persistence.[161]

There is a lack of hazard assessment information for dendrimers. Some may contain residues of hazardous isocyanates, siloxanes or powerful irritating organic acids.[161]

While nanotechnology offers some advantages, including decreased water and solvent use, the small particle size may pose health risks by being readily transported in blood and other cells.[157]

CERTAIN METALS
(AND THEIR SALTS)

14. Lead Chromate Pigments in Paints

Background, identity and use

Major lead pigments in decorative paints were selected due to their high toxicity,[167] environmental pollution potential and widespread use in the Southern Mediterranean countries, including for colouring cooking pots. High blood lead levels have been detected e.g., in Morocco, Egypt and Lebanon. While at least 67 countries have certain restriction for lead paints, currently only Algeria has restricted lead paints out of all Southern Mediterranean countries. Therefore, the use of lead in paint would continue in the region leading to environmental and human contamination if alternatives are not promoted. Alternatives for lead in paints are available and widely used in Europe and other industrial countries.

Lead pigments are one of the main sources of lead in solvent-based one pack decorative paints.[168] The main lead pigments used (see Table 16) and addressed here are the yellow lead chromate pigments family, composed of:

- pure lead chromates,
- mixed phase pigment of lead chromate and lead sulphate (lead sulfochromate pigment) and
- mixed phase pigment of lead chromate, lead sulphate and lead molybdate (lead chromate molybdate sulphate pigment).

The words "lead chromate" or "chrome yellow" are usually used in literature to describe this whole family and can thus be mistaken for the right substance identification, since there are three different substances according to the European chemical Substances Information System (ESIS) classification.

Hazard profile and problems

Lead is a toxic heavy metal. The World Health Organization (WHO) lists lead exposure as one of the top ten environmental health threats globally.[169] The Institute for Health Metrics and Evaluation (IHME) has estimated that in 2013 lead exposure accounted for 853 000 deaths due to long-term effects on health, with the highest burden in low and middle income

CHEMICAL/PIGMENT	CAS/EC Number
Lead sulfochromate yellow; Chrome Yellow (C.I. Pigment Yellow 34)	CAS No: 1344-37-2 EC No: 215-693-7
Lead sulfo molybdato chromate; Lead chromate molybdate sulfate red (C.I. Pigment Red 104)	CAS No: 12656-85-81 EC No: 235-759-9
Lead chromate	CAS No: 7758-97-6 EC No: 231-846-0
Red lead, Minium, Mennige, Lead plumbate, Trilead tetroxide	CAS No: 1314-41-6 EC No: 215-235-6

Table 16 Chemical identity of lead chromate pigments used in paints

Hazard profile

GHS01 Explosive	GHS02 Flammable	GHS03 Oxidizing	GHS04 Compressed Gas	GHS05 Corrosive	GHS06 Toxic	GHS07 Harmful	GHS08 Health hazard	GHS09 Environmental hazard	Carcinogenic/ Mutagenic/ reprotoxic	Endocrine disrupting chemicals	Persistent organic pollutant
									CMR	EDC	

countries.[169] Children are especially vulnerable to negative health effects from lead, including decreased intelligence and increased behavioural issues.[169] Childhood lead poisoning, also during pregnancy, can have lifelong health impacts including: learning disabilities, anaemia and disorders in coordination, visual, spatial and language skills. No safe level of exposure to lead has been identified.[170]

Lead in paints is a rather dispersive use of lead. The use of lead pigments in paints for houses, kindergarten, schools and toys results in exposure of populations, including children.

Lead chromate molybdate sulfate red, lead sulfochromate yellow and lead chromate were identified as Substances of Very High Concern (SVHC) according to Article 57(a) and (c); they are classified according to Annex VI, part 3, Table 3.2 of CLP/GHS Regulation (EC) No 1272/2008 as carcinogens category 2, R45 (may cause cancer) and as toxic to reproduction category 1, R61 (may cause harm to the unborn child) and are therefore included in the candidate list for authorisation.

Due to the use of abrasive blasting for renewing paints in large metal constructions, the lead gets dispersed into the environment leading to environmental contamination even if containment measures are applied. Also, at the end of life of steel and other metal construction, the lead ends up in the fly ash and becomes hazardous waste. Therefore, the use of lead in paints results in environmental contamination and hazardous waste formation.

The relatively high blood lead (PbB) levels in Egypt, Lebanon and Morocco (including children) indicate important lead sources in the Southern Mediterranean region.[171, 172, 173] The Egyptian children studied had a mean PbB level of 13 µg/l. 55.8% of these children had PbB levels above the intervention level of 10 µg/dL adopted in the United States.[172] The mean PbB level in Lebanese children (age 1-3) was 66.0 µg/l, with 39 (14%) children having PbB ≥ 100 µg/l. The PbB levels in children (aged 6-12) in Morocco were also high, with a mean of 55.5 µg/l.[171]

Status in the Mediterranean region and internationally

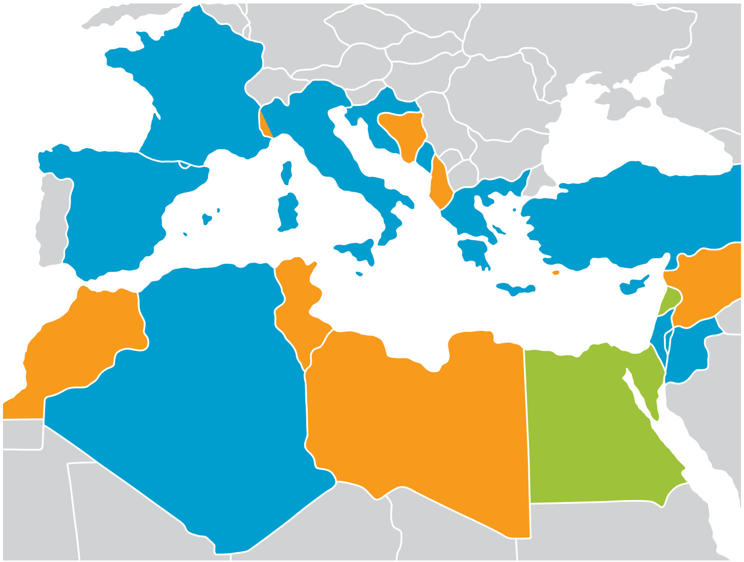
Lead use in paints is restricted in at least 67 countries.[174] In the EU, lead in paints is restricted under REACH[175,176] and lead paints have been phased out. From the South Mediterranean countries, only Algeria has restricted lead in paints. In other South Mediterranean countries lead and related pigments are currently not known to be restricted.[174, 177]

Lead in paints is a dispersive use of lead. Lead is partly leached from the materials, or paint flakes are released as the paints age. In the end of life, when paints on objects are renewed, abrasive blasting often releases lead paints into the environment via fine paint particles. Due to the lack of waste management in Southern Mediterranean countries, lead painted wood objects might be burned in the open. Also, ashes from other end of life treatment in metal plant or incinerators might lead to environmental contamination via air emissions. Environmentally sound management of ashes is currently lacking.

Figure 5

Map of Lead Paint Limits (Binding limits vs. Voluntary limits vs. No Limits Found)

Binding		Voluntary	No Limit Found
Algeria	Malta	Egypt	Albania*
Bulgaria	Monaco	Lebanon	Bosnia and Herzegovina*
Croatia	Montenegro		Libya
Cyprus	Spain		Morocco
France	Turkey		San Marino
Greece			Syrian Arab Republic*
Israel			Tunisia
Italy			
Jordan			



* in process of passing binding limit

United Nations Environment Programme,
Global Report on the Status of Legal Limits on Lead in Paint

Selected alternatives

to lead chromate pigments in paints

Identification, availability and technical feasibility

For over 30 years, pigment manufacturers have been offering lead free alternatives to the coatings industry[178] and have substituted lead pigments in paints. The aim is to develop paints and coatings with the same colour and required performance. Available alternatives include:[178]

1) Organic pigments with different colours (yellow, orange, red)

2) Inorganic pigments:

- Bismuth Vanadium Oxide (Bismuth Vanadate; BiVa),
- Complex Inorganic Coloured Pigments (CICP),
- Iron Oxides

3) Bismuth Vanadate + organic pigments

4) Hybrid pigments[179]

The most suitable alternatives which are used in the coatings industry are listed in Table 17. These pigments are well known and used in the entire European paint and coatings industry. The decorative paint and OEM automotive branch switched to lead free formulations more than 15 years ago. For lead chromate alternatives, sufficient production capacities exist worldwide and the components are broadly available.

Technical feasibility

There is no one-to-one plug-in substitute but the available organic and inorganic pigments can be mixed or blended to formulate lead free paints and coatings with the desired properties.[178] The technical solution is to combine various inorganic pigments that provide opacity (e.g., Bismuth Vanadate, CICP's and Iron Oxides) with organic pigments that offer clean and high chroma shades until the required shade is achieved.[178]

1. For clean shades: [178]

Organic pigments in different colours (yellow / orange / red) are used.

2. For opacity: [178]

inorganic pigments are used (BiVa, CICP and Iron Oxides and mixtures). Inorganic pigments meet the demands of dispersion, weatherfastness and opacity, but are low in chroma and tint strength.

3. For opacity + clean shades: [178]

Bismuth Vanadium Oxide + organic pigments or hybrid pigments can be used. They achieve the colour spaces of bright orange, yellow and red, offering the best-priced alternative for many heavy metal-free formulations.

Great knowledge and experience has been established in the substitution PY34 and PY104 by organic and inorganic pigments in Europe and other countries which can be used in the Southern Mediterranean countries. The use of colour matching tools such as software and equipment, is a technical standard within the entire paint and coatings industry.

The available alternative pigments can:[178]

- Cover the entire colour space (from yellow, via orange to red);
- Supply clean colour shades;
- Fulfil high opacity requirements by combining organic and inorganic pigments;
- Cover different performance levels for interior and exterior use, very high light and weather resistance;
- Provide heat resistance >200°c;
- Have no bleeding issues;
- Fulfil technical requirements regarding coating manufacturing equipment.

There is no practical need for a single lead-free pigment alternative that covers all of these technical properties in one. Many alternatives are available in the relevant shade areas (yellow, orange and red), but have different performance levels. Paint manufacturers must select the alternatives according to their end user demands and specifications.

NO.	CAS-Reg.-No.	Chemical Group / Trade / Industry Name(s)
1.	8007-18-9	Antimony Nickel Titanium Oxide (Rutile Yellow)
2.	68186-90-3	Chrome Antimony Titanium Oxide (Rutile Brown)
3.	14059-33-7	Bismuth Vanadate
4.	30125-47-4	Quinophthalone
5.	36888-99-0	Isoindoline (Azo)
6.	6358-31-2	Arylide Yellow GY (Azo)
7.	31837-42-0	Benzimidazolone Yellow H4G (Azo)
8.	84632-65-5	Diketopyrrolopyrrole
9.	6535-46-2	Naphtol AS (Azo)
10.	51274-00-1	Iron Hydroxide Oxide Yellow
11.	1309-37-1	Diiron Trioxide; Hematite
12.	5567-15-7	Diarylide Yellow HR (Disazo)
13.	15793-73-4	Pyrazolone Diarylide Orange (Disazo)
14.	74336-59-7	Pyrazoloquinazolone (Azo)
15.	84632-59-7	Diketopyrrolopyrrole
16.	5280-66-0	BON Red 2B; Permanent Red 2B, manganese-laked (Azo)
17.	923954-49-8	Tin Titanium Zinc Oxide
18.	85536-73-8	Tin Zinc Rutile
19.	3520-72-7	Disazopyrazolone
20.	79953-85-8	Disazo condensation; Disazo Yellow GG
21.	13463-67-7	Titanium dioxide Titanium White
22.	82199-12-0	Benzimidazolone (Azo)
23.	12236-62-3	Benzimidazolone (Azo)
24.	2786-76-7	Naphtol AS (Azo); Naphthol Red F5RK
25.	6528-34-3	Benzimidazolone (Azo)
26.	120500-90-5	Diketopyrrolopyrrole
27.	5590-18-1	Isoindolinone
28.	6528-34-3	Arylide Yellow RN; Acetoacetarylide (Azo)
29.	980-26-7	Quinacridone

Table 17 Substances used as alternatives for the lead chromate pigment family[178]

Economic feasibility

The use of alternatives is feasible from an economic perspective. In one submission to ECHA,[178] lead free formulation were compared, based on actual market prices, to lead containing formulations for selected colour areas (RAL shades) and different performance levels (as described above). At the highest performance level, the cost for lead chromate free formulations are 2-3 times higher; at the mid-performance level the costs are already comparable and in the lower performance area they are already cheaper.[178]

Bismuth Vanadate has a higher price compared to the lead pigments. The final price of the paint is however determined by the mixture of pigments.

Hazards, risks and life cycle considerations

Based on current knowledge of the substances and manufacturing processes, alternative colorants have a lower problematic toxicological profile.[178] None of the pigments listed above are in the candidate list for Annex XIV of REACH Regulation 1907/2006/EC.[178]

All organic and inorganic pigments are primarily supplied in powder or granule dust free form. Safe handling of the products is described in the respective MSDS (Material Safety Data Sheet)[178] which can help manage the associated risks. In Europe, all manufacturing processes for synthesizing these products must be approved by the relevant authorities.[178] Detailed toxicological summaries based on REACH registration dossiers can be found in a submission to ECHA.[178]

Please note: Some organochlorine pigments can contain unintentional POPs like polychlorinated biphenyls (PCBs) and hexachlorobenzene (HCB). These unintentional POPs can be minimized by best available techniques (BAT) / best environmental practices (BEP) production.

15. Lead Oxide in Rustproof Primer Paints

Background, identity and use

Trilead tetroxide (Minium, Red Lead; Pb_3O_4) in rustproofing primer paints was selected for this study due to its high toxicity,[180] the potential for human and environmental exposures and its widespread use in the North African and Middle East countries. Furthermore, elevated levels of lead in blood have been reported in the region's inhabitants, including children. Elevated lead levels in children are causing decreased intelligence and increased behavioural issues. While at least 67 countries have certain restrictions for lead paints, currently only Algeria has restricted lead paints out of all Southern Mediterranean countries. Therefore, the use of lead in paint would continue in the region leading to environmental contamination if alternatives are not promoted and appropriate regulations are not set.

The main alternatives to lead anticorrosive primer paints are zinc compounds, widely available and in use since decades in Europe and other industrial regions. Zinc paints and anticorrosive coatings are the general state-of-the-art corrosion protection for metal constructions used in countries that regulate lead in paints.

Lead is used in rustproofing primer paints (Table 18) for corrosion protection of metal constructions. Lead paints, which are highly effective for corrosion protection, have been globally used in the past and are still widely used in developing countries.

Lead anticorrosive primer paints have an excellent performance in corrosion protection of metal constructions. The paint has high flexibility, making it suitable even for sharp edges of metal constructions.

Hazard profile and problems of lead oxide in rust proof primer paints

Lead oxide is an important industrially used lead compound. The problem of lead toxicity has been known from the 19th century when intoxication by lead acetate was observed in London after consumption as surrogate "sweets." The World Health Organization (WHO) lists lead exposure as one of the top ten environmental health threats globally.[181] The Institute for Health Metrics and Evaluation (IHME) has estimated that in 2013 lead exposure accounted for 853 000 deaths due to long-term effects on health, with the highest burden in low and middle income countries.[181] Children are especially vulnerable to negative health effects from

PIGMENT DESIGNATION	CAS/EC Number
Red lead, Minium, Mennige, Lead plumbate, Trilead tetroxide; Lead (II, IV) oxide; Pb_3O_4	CAS No: 1314-41-6 EC No: 215-235-6

Table 18 Chemical identity of lead oxide used in rustproof primer paints

Hazard profile

GHS01 Explosive
GHS02 Flammable
GHS03 Oxidizing
GHS04 Compressed Gas
GHS05 Corrosive
GHS06 Toxic
GHS07 Harmful
GHS08 Health hazard
GHS09 Environmental hazard
CMR Carcinogenic/ Mutagenic/ reprotoxic
EDC Endocrine disrupting chemicals
Persistent organic pollutant

lead, including decreased intelligence and increased behavioural issues.[181] Childhood lead poisoning, including during pregnancy, can have lifelong health impacts such as learning disabilities, anaemia and disorders in coordination, visual, spatial and language skills. No safe level of exposure to lead has been identified.[182]

When inhaled, lead (II, IV) oxide irritates lungs. High doses result in chest and abdominal pain. When ingested, it is dissolved in the gastric acid and absorbed, leading to lead poisoning. High concentrations can also be absorbed through the skin. Long-term contact with lead (II, IV) oxide may lead to accumulation of lead compounds in organisms and to symptoms of acute lead poisoning. Chronic poisoning displays as agitation, irritability, vision disorders, hypertension and a greyish facial hue. Lead (II, IV) oxide was shown to be carcinogenic for laboratory animals.[181]

Lead in paints is a dispersive use of lead in houses and construction. Chalking, leaching, flaking, weathering, scraping and sandblasting of leaded paint result in lead deposits in the soil near houses or other constructions. Due to the use of abrasive blasting of paints during renovation of metal constructions, the lead gets dispersed into the environment leading to environmental contamination.[183] Also, at the end of life of painted iron constructions, the lead ends up in smelters, is partly released in air and ashes and becomes hazardous waste. Therefore, lead in paints result in environmental contamination and in hazardous waste.

The relatively high blood lead (PbB) levels in Egypt. Lebanon and Morocco (including children) indicate significant lead sources in the Southern Mediterranean region.[184, 185, 186] The Egyptian children studied had a mean PbB level of 13 μg/l. 55.8% of these children had PbB levels above the intervention level of 10 μg/dL adopted in the United States.[185] The mean PbB level in Lebanese children (age 1-3) was 66.0 μg/l, with 39 (14%) children having PbB ≥ 100 μg/l. The PbB levels in children (aged 6-12) in Morocco were also high, with mean PbB level of 55.5 μg/l.[184]

Status in the Mediterranean region and internationally

UN Environment and other stakeholders have initiated the Global Alliance to eliminate lead in paints. Lead in paints is already restricted in at least 67 countries.[187] In the EU, lead in paints is restricted under REACH.[188,189] Out of the South Mediterranean countries, only Algeria has restricted lead in paints. In other South Mediterranean countries lead in paint is not currently known to be restricted.[187, 190]

A major use of lead in paints in the Mediterranean countries is for corrosion protection of metal constructions (normally iron or steel), e.g., pylons, bridges, pipelines. Lead paints are also used on private infrastructure for corrosion protection of buildings and other constructions.

Selected alternatives

to lead oxide in rustproof primer paints

Identification, availability

For over 30 years, pigment manufacturers have been offering lead free alternatives to the coatings industry[191] and have substituted lead pigments in paints.

Activated zinc primers

Zinc-rich coatings and primers (ZRPs) have the unique ability to provide galvanic protection to the steel surfaces to which they are applied. These coatings contain a large amount of metallic zinc combined with the binder. ZRP's binder is usually an organic resin such as epoxy, alkyd or urethane. After the proper application of a zinc-rich coating to a steel substrate, the binder holds the zinc particles in contact with one another and the steel surface. These zinc primers can be applied as paint or by powder coating.

- *Zinc phosphate primer*

  Zinc phosphate primer is used for corrosion protection of steel, iron or aluminium construction. Zinc phosphate primer paints are offered by many suppliers and widely used. Zinc phosphate primer can also be applied as powder coating in industrial applications.

- *Industrial zinc coating system – Hot-dip galvanization*

  Hot-dip galvanization is the process of coating iron and steel with zinc. In this process the zinc alloy is coating the surface of the base metal when immersing the metal in a bath of molten zinc at a temperature of approximately 450 °C.

- *Electrogalvanization/zinc plating*

  Electrogalvanizing is a process in which a layer of zinc is bonded to steel in order to protect against corrosion. The process involves electroplating, running a current of electricity through a saline/zinc solution with a zinc anode and steel conductor. Compared to hot dip galvanizing, electroplated zinc offers the following advantages:
  - Lower thickness deposits needed to achieve comparable performance;
  - Broader conversion coating available for increased performance and more colour options
  - Brighter, more aesthetically appealing, deposits

Technical feasibility

All the above-mentioned technologies are technically feasible and have been used for decades in practice. Zinc primer paints are readily available in the market and widely used by private parties and professionals. If the iron or steel is professionally painted/covered, zinc also provides extremely good corrosion protection. Hot-dip galvanization is widely used for industrial galvanized steel when corrosion resistance is needed without the cost of stainless steel. Zinc is more electropositive compared to steel, which means that when a galvanized coating is damaged and the steel exposed to the atmosphere, zinc can continue to protect steel through galvanic corrosion, making it superior to lead corrosion paints. Hot-dip galvanization is already available in Egypt (e.g., Egyptian Manufacturing & Advanced Systems), Morocco (e.g., Maghreb Steel) and Tunisia (e.g., Maklada). The galvanizing process is in accordance with: German Standard DIN 50976, British Standard BS 729 and American Standard ASTM.

Zinc electroplating is also widely used, thus technically feasible. According to the International Zinc Association, more than 5 million tonnes are used yearly for both Hot-Dip Galvanizing and Electroplating.

The preparations for zinc primer paint application are more demanding than for lead paint. Corrosion protection of sharp edges and thick layers with zinc need the right technique.

Economic feasibility

Zinc primer paints cost more compared to lead paints. However, since zinc is a relatively cheap metal, the prices are still reasonable.

The more demanding preparations for zinc primer paint application somewhat increase the overall cost of using zinc-containing paints compared to lead paints.

The widespread use of zinc galvanization and electroplating, including in the Southern Mediterranean region, shows that both processes are economically feasible.

The safe removal of lead paints/coating is expensive and in some countries only licensed remediation experts are allowed to perform it. Furthermore, the health effects including developmental toxicity caused by lead exposure are associated with high external costs. Therefore, considering the life cycle of lead- and zinc-based corrosion protection, the zinc alternative is more economical and its use in the region demonstrates that the switch is feasible.

Hazards, risks and life cycle considerations

Zinc is one of the most abundant elements in the Earth's crust. Zinc is found in air, soil, water and in all foods.[192] Zinc is an essential element often used as an additive in human food, animal feed and plant fertilizer. Zinc has a considerably lower toxicity compared to lead. Also, zinc phosphate is non-toxic and zinc aluminium phosphate is used as dental cement.

Ingesting too much zinc through food, water, or dietary supplements can also affect health. The levels of zinc that produce adverse health effects are much higher than the Recommended Dietary Allowances (RDAs) for zinc of 11 mg/day for men and 8 mg/day for women. Women who nurse their babies need 12–13 mg/day. If large doses of zinc (10–15 times higher than the RDA) are ingested, stomach cramps, nausea and vomiting may occur.[192]

Inhaling large amounts of zinc (as zinc dust or fumes from smelting or welding) can cause a short-term disease called metal fume fever, which is generally reversible once exposure to zinc ceases.[181]

Safe handling of zinc-containing paint products is described in their MSDS (Material Safety Data Sheet).[191] Following these recommendations, hazards can be managed and risks can be avoided.

Soil contamination with zinc can also be problematic, so there are limits for zinc in soil. Therefore, abrasive blasting of painted objects is not recommended and requires appropriate housing or other measures to prevent the removed paint from distributing into the environment.

At the end of life of painted iron/steel constructions, the iron is normally recovered in an electric arc furnace (EAF). The zinc is largely transferred into the EAF fly ash. The collected EAF fly ash is normally transferred to a zinc recovery plant (e.g., Waelz kiln/process)[193] and zinc recovered for reuse by thermal reduction. Therefore, the recovery potential of zinc from coated iron is high and the life cycle is (nearly) closed.

16. Copper Chromium Arsenate in Wood Treatment

Background, identity and use

Copper chromium arsenate (CAA) used in wood treatment contains carcinogenic arsenic and chromium(VI). Waste wood is sometimes used in Southern Mediterranean countries for baking bread and cooking indoor, resulting in associated exposures. CCA has been banned in a range of countries and is restricted for use in the EU. Several lower toxicity alternatives are available such as copper salts and linseed envelope. Another alternative is thermally treated wood without additives which can be suitable depending on wood use class requirements and preservation needs. For most outdoor uses in the Mediterranean region, environmentally friendly solutions like thermally modified wood could be used. For more demanding applications such as that used in contact with salt water, creosote treatment can be used.

Copper chromium arsenate (CCA) consists of a mixture of chromic acid, arsenic acid and cupric oxide in a ratio of 5:3:2, respectively (POP RC, 2014). CCA was the world's most widely used wood preservative and has been used for timber treatment since the mid-1930s. Chromium acts as a chemical fixing agent and helps the other chemicals bind to the timber. Copper acts primarily to protect the wood against decay, fungi and bacteria, while the arsenic is the main insecticidal component of CCA, providing protection from wood-attacking insects, including termites and marine borers.

Hazard profile and problems

The European Commission Enterprise Directorate General identified a number of unacceptable risks from CCA-treated timber, including: risks to children (from CCA-treated outdoorplay equipment); other human health risks; environmental risks from combustion and disposal (including leaching in landfill); and risks to aquatic organisms.[194] The European Communities' Scientific Committee for Toxicity, Ecotoxicity and the Environment (CSTEE) evaluated this risk assessment and determined that no threshold exists for the carcinogenic effects of arsenic (which is also known to be genotoxic). The CSTEE could not establish the arsenic-related risks from landfill disposal of CCA-treated timber, which was classified as a hazardous waste by the Commission in 2000 and thus concluded that it is appropriate to apply the precautionary principle and reduce the production of CCA-treated timber as much as possible, because it is likely to cause serious harm.[195] Furthermore, work place exposures above recommended occupational exposure levels have been measured at indoor work sites and occasionally at outdoor work sites.[196]

Status in the Mediterranean region and internationally

CCA-treated wood has been banned altogether in several countries including Denmark, Switzerland,

CHEMICAL	CAS/EC Number
Arsenic(V) oxide Arsenic oxide Arsenic anhydride	CAS No. 1303-28-2 EC No. 215-116-9
Copper(II) oxide Cupric oxide	CAS No. 1317-38-0 EC No. 215-269-1
Chromium(VI)	CAS No. 1333-82-0 EC No. 215-607-8

Table 19 Chemical identity of copper chromium arsenate

Hazard profile

Vietnam and Indonesia. The use of CCA-treated timber has been restricted in the EU and arsenic compounds may not be used *'in the preservation of wood. Furthermore, wood so treated may not be placed on the market.'* The only exceptions are for wood to be used in industrial installations where *'the structural integrity of the wood is required for human or livestock safety and skin contact by the general public during its service life is unlikely.'*[197] The following uses are specifically prohibited:

- in residential or domestic constructions, whatever the purpose;
- in any application where there is a risk of repeated skin contact;
- in marine waters;
- for agricultural purposes other than for livestock fence posts and structural uses;
- in any application where treated wood may come into contact with intermediate or finished products intended for human and/or animal consumption.

The EU amendment therefore restricts the marketing and use of both CCA and CCA-treated timber. In the US, wood intended to be used in residential settings, such as playground equipment, decks, picnic tables, landscaping timbers, residential fencing, patios, walkways and boardwalks, cannot be treated with CCA.[198]

CCA is not restricted in the Southern Mediterranean Countries and is still used in wood treatment or in imported wood products.

Selected alternatives

to copper chromium arsenate in wood treatment

Identification and availability

One class of alternatives to CCA combines copper and organic preservatives. Alkaline copper quaternary (ACQ) is a preservative made of copper, a fungicide and a quaternary ammonium compound such as didecyl dimethyl ammonium chloride, an insecticide that also increases the fungicidal treatment. Copper salt are also augmented by an azole co-biocide, for instance organic triazoles such as tebuconazole or propiconazole "Copper azoles". Copper naphthenate is an oil-borne wood preservative consisting of a mixture of copper salts and naphthenic acid.[199]

Creosote is a tar-based preservative, one of the oldest wood treatments and an alternative commonly used for demanding applications that come in direct contact with saltwater, groundwater, or fresh water.[200]

Linseed oil has been incorporated in preservative formulations as a solvent and water repellent to "envelope treat" timber. This involves treating only the outer 5 mm of the cross-section of timber with a preservative such as permethrin.

Thermally modified wood is that altered by a controlled pyrolysis process involving heating (> 180 °C) in the absence of oxygen. This result in some chemical changes to the wood cell wall components (lignin, cellulose and hemicellulose) in order to increase durability. Different producers use different technologies including nitrogen gas, steam and hot oil.[201] For example, in Turkey, thermally modified wood is commercially produced and research has already started in the Magreb region.[202, 203]

Technical feasibility

ACQ can be used for all use classes (UC)[204] except for marine use (UC5). Copper salt with triazole biocide or copper naphtenate can cover most application types including decking and posts.[205] Both have been extensively tested and generally perform as well as CCA. Copper salts are corrosive to metals, particularly aluminium.

For marine use (UC5) and other highly demanding outdoor use with continuous wetting (UC4), creosote is the preferred wood preservative.[200] Thermally modified wood can be used for aboveground non-structural uses such as siding, decking, flooring, garden furniture, playground furniture, window and door frames and indoor furniture. "Envelope" treated wood with linseed oil and permethrin can also be used for such applications.

Economic feasibility

The "envelope" treatment with linseed oil and permethrin is cheaper, as it uses far less preservative. The cost of creosote treatment is similar to the CCA treatment, while other copper-based wood treatments have somewhat higher costs. After the phase-out of CCA treated wood in the EU, the industry has flourished and benefited from the changes, as treated wood continues to be the material of choice.[206] Therefore, the switch to alternatives did not have a negative impact on the market. Thermally modified wood is more expensive to purchase but cheaper to maintain. After the first or second maintenance of chemically-treated wood, the cost can equal that of thermally modified wood. Long term, the cost of thermally modified wood is likely to be lower compared to chemically-treated wood. At the end of life, thermally modified wood can be recycled or thermally recovered together with natural wood, while chemically-treated wood must be disposed in waste incinerators or landfills.

Hazards, risks and life cycle considerations

Thermally modified wood does not contain chemical additives and therefore does not have specific environmental or health concerns. The wood can be thermally recovered at the end of life like virgin wood, or recycled into other wood products. The ashes recovered from thermally modified wood can be used for soil amendment. Therefore, thermally modified wood is a preferred option for suitable uses. Linseed "envelope" treatment with permethrin also has low risk.

The alternative copper and organic preservatives are more environmentally friendly compared to CCA, as they do not contain chromium or arsenic. Similar to CCA treated wood, chemically-treated wood with copper salts and pesticides must be disposed of as hazardous waste in incinerators and the ashes cannot be used for soil amendments due to the heavy metal or polychlorinated dibenzo-p-dioxin and dibenzofurans (PCDD/Fs) content.[207]

Creosote has a harmonised classification in accordance with Regulation (EC) No 1272/2008 as carcinogen in category IB and contains constituents considered persistent, bioaccumulative and toxic in accordance with the criteria set out in Annex XIII to Regulation (EC) No 1907/2006. It should only be used in applications where no other alternatives are available. Creosote treated wood can be thermally recovered in biomass plants and does not lead to heavy metal transfer into ashes or increased formation of PCDD/Fs.

In Southern Mediterranean countries with weak or non-existing regulations for waste wood management, chemically treated wood bears the risk of being used in private heating or even cooking and bread baking, leading to increased risk of heavy metal and PCDD/F contamination.[207]

17. Chromium in Leather Tanning

Background, identity and use

Tanning is the process of treating animal skins and hides to produce leather, which is more durable and less susceptible to decomposition. The main chromium compound used for leather tanning is chromium (III) hydroxide sulphate, $Cr(OH)SO_4$.

The main alternative to chromium leather tanning is the use of vegetable tanning. This method can prevent adverse environmental and human health impacts while promoting local employment and sustainable economic opportunities.

With the novel vegetable tanning process using olive residues, it became possible to produce leathers showing good shape retention but also exceptional softness, lightness and durability. Olive leaves are a by-product from olive production used as sustainable resource for the tanning extract.

Hazard profile and problems

Chromium(III) salts used in chromium tanning have a relative low toxicity. However, chromium(III) is partly oxidised to carcinogenic chromium(VI)[208] and therefore a considerable proportion of leather contains chromium(VI). In a German survey of 850 mostly imported leather products, 50% exceeded the current regulatory limit for chromium(VI) of 3 mg/kg and approximately 17% contained chromium(VI) above 10 mg/kg.

Chromium together with nickel and cobalt constitute the most frequent causes of contact allergy in the general population.[209] While chromium(VI) is the major allergen, chromium(III) also contributes to the allergic reaction.[210] Chromium allergies from leather have significantly increased in Denmark between 1995 and 2005.[211] Workers in the Southern Mediterranean region are exposed to chromium in leather tanning, exhibiting adverse health effects including rhinitis, cough, expectoration, wheezes, dyspnea, chest pain, chronic bronchitis, asthma and skin diseases.[212]

Releases from tanneries result in environmental contamination of water, air and wastes. Chromium is an important pollutant generating contaminated wastes including chromium shavings, chromium split, chromium leather trimmings and chromium-containing sludge from wastewater treatment.

The protein-rich chromium-containing solid waste from tanning is used in developing countries as chicken and fish feed, resulting in widespread contamination of chicken and eggs with chromium(VI).[208,213, 214]

Status in the Mediterranean region and internationally

In the EU REACH Regulation, the use of chromium (VI) in leather products is regulated and, since 2015, leather products that come into contact with skin are not allowed on the EU market if chromium(VI) content is equal to or exceeds 3.0 mg/kg dry weight of the leather.

A first restriction for chromium(VI) to a maximum of 3 mg/kg [215] in leather exists in Egypt (the same limit as in the EU).

CHEMICAL	CAS/EC Number
Chromium (III) hydroxide sulphate, $Cr(OH)SO_4$	CAS No. 12336-95-7; EC No. 235-595-8.
Chromium(VI)*	CAS No. 1333-82-0 EC No. 215-607-8
*Chromium(VI) is formed as a by-product of Chromium(III) oxidation and is not directly applied to the product	

Table 20 Chemical identity of chromium species used or formed in chromium tanning

Hazard profile

Selected alternatives

to chromium in leather tanning

Identification and availability

Alternatives to chromium tanning are organic tanning products, including vegetable tannins, glutaraldehyde, oxazolidine, phosphonium salts, melamine and methacrylic resins which show different properties and collagen reaction capacity.[216]

Natural vegetable tanning is the preferred alternative as it uses tannins that occur naturally in the bark, wood, fruits and leaves of many plants. Tannins bind to the collagen protein in the hide and coat them, causing them to become less water-soluble, more resistant to bacterial attack and also a bit more flexible.

In the Mediterranean region, residues from olive production, particularly the leaves, are an abundant source for the production of a new type of natural vegetable tanning agent. The patented tanning process from olive leaves has been developed by wet-green® GmbH[217] and some tanneries in Europe have started to use this technology and produce healthy olive leaf tanned leather. Considering the quantity of olive leaves generated as a residue from olive production in the Mediterranean region, theoretically up to 40% of the world's leather production – i.e., up to approximately 700 million m² – could be made using the wet-green® tanning technology.[217]

Technical feasibility

Due to the careful tanning process and the natural tannins, vegetable-tanned leather usually develops a rich and beautiful patina which improves with time and use. It doesn't crack or dry out and thus has a long lifespan potentially superior to chromium-tanned leather.

The leathers obtained can reach shrinkage temperatures of up to 80 – 85 °C, which gives them a thermal stability adequate for the manufacture of products such as leather goods and some footwear. The shrinkage temperature of chromium leather is higher (approximately 100 °C), but in most cases this is not required for further processing.

Based on the classical vegetable tanning characteristics, a very limited leather spectrum can be achieved with conventional vegetable tanning. In particular, the limited dyeability and lower softness are significant. Vegetable tanning is a more complex tanning process which leads to higher tanning material costs, water consumption and processing times.

However, the olive leaf extract combines the advantages of organic synthetic reactive tanning agents (like glutaraldehyde) that result in stable chemical bonds (covalent bonds) with those of organic sourcing like the other vegetable tanning. This is done by the present vegetable polyphenols, which additionally generates a better separation of fibres, a filling effect and a pleasant round feel. Using the vegetable tanning process with olive residues, it became possible to produce leathers showing good shape retention but also exceptional softness, lightness and durability. The leather tanned with olive leaf extract is suitable for applications in all kinds of areas like furniture for the residential, commercial and automotive sectors, as well as shoes, watch straps, clothing and other leather goods.

Compared to conventional system, tanning with olive leaf extract significantly reduces water consumption and processing time, similar to chromium tanning.

Overall, the vegetable tanning method including the olive tanning requires more skilled craftsmen.

Economic feasibility

Vegetable tanning agents are required in higher amounts and thus have higher associated costs. Conventional vegetable tanning is slower and therefore costlier than chromium-based tanning, which takes less than a

day. Due to the more complex process, labour costs of vegetable tanning are higher. This also means that vegetable tanning can provide reliable work, especially useful in areas with high youth unemployment. Olive tanning has similar processing time to chromium tanning and no additional cost in this respect.

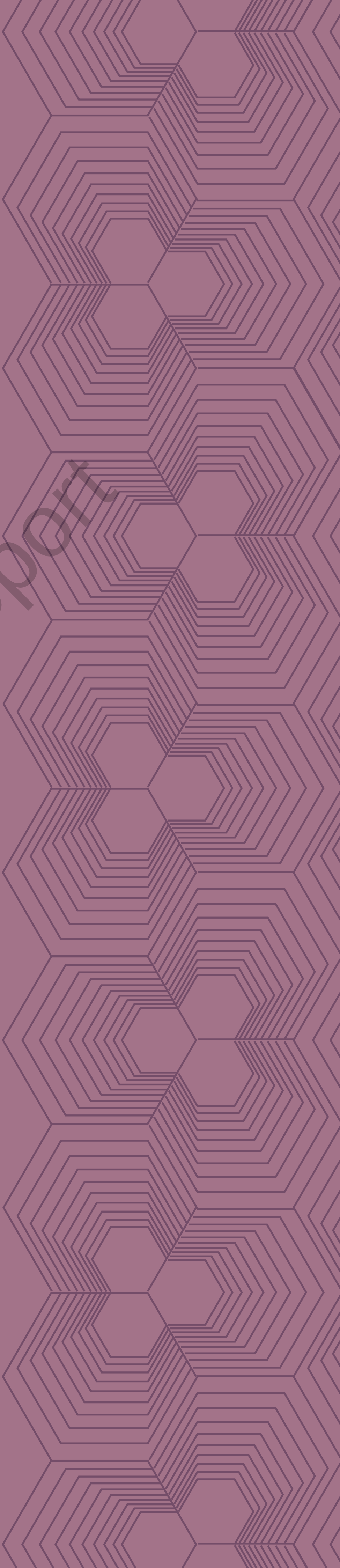
The waste management costs of vegetable tanning are lower if the waste disposal cost are appropriately set. Also the wastewater is less polluted, resulting in discharge-related cost savings.

Vegetable tanned leather, using only natural tannins, has no negative health and environmental impact if biological oxygen demand (BOD) and chemical oxygen demand (COD) are controlled. The leather can be better recycled or composted. Therefore, health and environmental costs are lower.

Hazards, risks and life cycle considerations

Vegetable-based tanning is not associated with any health risks and can make the leather skin-friendly. In the case of wet-green®, the tanning active substances are also present in extra virgin olive oil. The tanning agent wet-green® OBE showed a very good performance in a dermatological test (Dermatest®). Moreover, it has been awarded the Cradle to Cradle® GOLD certificate and the PLATINUM Material Health Certificate (Cradle to Cradle Products Innovation Institute, San Francisco, CA/USA).

Actually, huge amounts of olive leaves become residues of the olive harvest and, especially, of the subsequent olive tree trimming (pruning), i.e., they are a side-stream without any added value in the countries of origin. Most of these leaves are disposed or burned leading to negative environmental impacts. Therefore, the olive leaf tanning agent has a sustainable sourcing. For the production of wet-green® olive leaf tanning agent, an efficient aqueous extraction process has been developed completely free of organic solvents. The product is not subject to regulation under EU Directives or the German Ordinance on Hazardous Materials (German GefStoffV). The solid leaf residues from extraction are used by local farmers as soil amendments.



PESTICIDES

18. Synthetic Pesticides used in Agriculture

Background, identity and use

Hundreds of synthetic chemical pesticide active ingredients (pesticides) are used currently in agricultural practices resulting in unwanted exposure to pesticide mixtures that cannot be adequately assessed. Pesticide exposure poses health risks to workers and consumers alike, while polluting the environment after emissions due to wind drift, run-off and leaching. From a precautionary principle perspective, there is a need to reduce pesticide exposure. A wide range of alternative approaches for pest control are available and can be implemented within integrated pest management and organic farming, as well as substituting certain harmful pesticides with less harmful chemicals, all of which support a more sustainable use of pesticides in line with EU Directive 2009/128/EC[218].

The term pesticide covers a wide range of substances including insecticides, fungicides, herbicides, rodenticides, molluscicides, nematicides, plant growth regulators and others. Among these, several organochlorine insecticides, used successfully in controlling a number of vector-borne diseases until today, were banned or restricted for agricultural use after the 1960s in most technologically advanced countries. The introduction of other synthetic pesticides including organophosphate insecticides in the 1960s, carbamates in the 1970s, pyrethroids in the 1980s and diverse groups of herbicides and fungicides in the 1970s-1980s has contributed to improving pest control and increasing agricultural outputs.

Hazard profile and problems

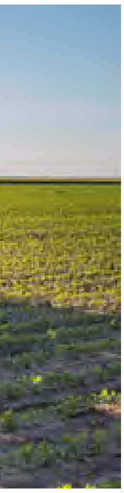
Pesticides pose serious threats to environmental quality and human health and have been linked to a range of illnesses including cancer, Alzheimer's and Parkinson's disease, hormone disruption, developmental disorders and sterility.[219] They can also cause numerous neurological health effects such as memory loss, loss of coordination, reduced visual ability and reduced motor skills. Other possible effects include asthma, allergies and hypersensitivity.[219]

The World Health Organization (WHO) estimated that nearly 3 million agricultural workers suffer from acute pesticide poisoning. Preventable pesticide ingestion was estimated to amount to 186,000 deaths and 4,420,000 Disability Adjusted Life Years (DALYs) in 2002; however, these are mainly due to intentional self-poisoning.[220] The cost of adverse endocrine health effects due to pesticide exposure in Europe is estimated at 120 billion euro per year.[221]

Due to the use of hundreds of pesticides in agriculture, humans are exposed to pesticide residues in food crops.[222] Furthermore, pesticides reach the environment and expose non-target organisms including pollinating insects and aquatic

Hazard profile*

* The labellings consider the classification of certain Highly Hazardous Pesticides.



ecosystems during and after application to field crops. Therefore, considering the precautionary approach, problematic synthetic pesticides should be substituted where possible with less toxic and more sustainable alternatives, starting with phasing out highly hazardous pesticides (HHPs)[223, 224] based on considering for instance the WHO pesticide classification by hazard.[225]

The use of synthetic pesticides has greatly increased in the Mediterranean region over the last twenty years, threatening the quality of groundwater and surface waters.[226] Agricultural run-off via rivers is the most important point-source of pesticide contamination in the Mediterranean. By 2025, countries on the southern and eastern rims of the basin are expected to show a five-fold increase in their agro-food activities making countries the most vulnerable to increased pollution and environmental pressure from such development.[227] Pesticides are one of the most frequently detected classes of micro-pollutants in water, especially in Mediterranean countries such as Spain and Italy, due to their widespread use in extensive areas of agricultural use.[226]

Status in the Mediterranean region and internationally

Directive 2009/128/EC aims to achieve a sustainable use of pesticides in the EU and reduce the risks and impacts of synthetic pesticide use on human health and the environment by promoting Integrated Pest Management (IPM) and alternative approaches, such as mechanical pest control alternatives. However, pesticide use has not decreased in the EU since 2009.[228] In 2013, approximately 300,000 tonnes of pesticide active ingredients were used in Europe[229] and approximately 500 active substances were authorised by the EU for application on various crops.[230]

EU-wide regulations do not only focus on synthetic pesticides, but also cover the organic farming supply chain – from production, to control and labelling. The EU has developed an Action Plan for the future of Organic Production in the European Union.[231]

The Southern Mediterranean region has weak restrictions on hazardous synthetic pesticides. For instance, 29 highly toxic active substances were identified in a short survey in Tunisia as currently in agricultural use. 16 of these are banned in Europe and 23 are included on the Pesticide Action Network (PAN)'s HHP list[224], revealing the need for better assessment and substitution.

The Regional Action Plan on Sustainable Consumption and Production in the Mediterranean includes IPM and organic farming and highlights that incentives should be provided for these good environmental practices.[232]

Selected alternatives to synthetic pesticides used in agriculture

Identification, availability

A) Integrated Pest Management (IPM)[233] is an ecosystem-based strategy that focuses on long-term prevention of pests through a combination of techniques such as biological control, habitat manipulation, modification of crop rotation practices and use of resistant varieties. Pesticides are used only after monitoring indicates that they are needed according to established guidelines and treatments are made with the goal of removing only the target organisms. Pest control tools are selected and applied in a manner that minimizes risks to human health, to beneficial and non-target organisms and to the environment.[233] The Food and Agriculture Organization of the United Nations (FAO) has compiled typical steps for IPM[234] and additional information is provided in the Sustainable Use of Pesticides strategy of the EU.[235]

B) Organic farming embodies an ecological approach to farming that does not rely on or allow toxic pesticides, chemical fertilizers, genetically modified organisms, or antibiotics.[236, 237] FAO has published sustainable development opportunities for organic farming in Africa.[238]

C) Biological approaches A wide range of biological alternatives are available for use instead of chemical pesticide and support IPM and organic farming. Biopesticides are made from naturally occurring substances that control pests by softer mechanisms developed by evolution in an eco-friendly manner. Alternatives that can be explored in the Mediterranean region include natural enemies, phytochemicals, microbes, natural pheromones, entomopathogenic fungi, biochemical agents, viruses (for a selection see Table 21). PAN has compiled information for non-chemical pest management in the tropics on an online information platform (http://www.oisat.org/controlmap.htm).

A first assessment of the availability of biopesticides in Tunisia found that only 5 insecticides, 8 fungicides, 2 nematicides and 3 pheromones or food attractants are on the market, compared to approximately 240 synthetic pesticides.

Technical and economic feasibility

Despite their low toxicity and environmental impact levels, biopesticides face a major obstacle in the form of higher costs and the need for more frequent reapplication, due to their lower persistence. Different biopesticides might need to be used for different pests because of their specificity.

A systematic overview of more than 100 studies comparing organic and conventional farming found that the crop yields of organic agriculture are higher than previously thought. The study, conducted by UC Berkeley researchers also found that certain practices could further shrink the productivity gap between organic crops and conventional farming.

The price for organic products are higher compared to conventional products and can overcompensate for the somewhat higher production cost. Considering the health implications and the high external cost of pesticide use,[221,239, 240] IPM and organic farming have usually lower life cycle costs, whereas technical feasibility challenges exist in the transition phase when changing from conventional to IPM practices, as changes and adaptations to the entire farming practice would have to be introduced.

Hazards, risks and life cycle considerations

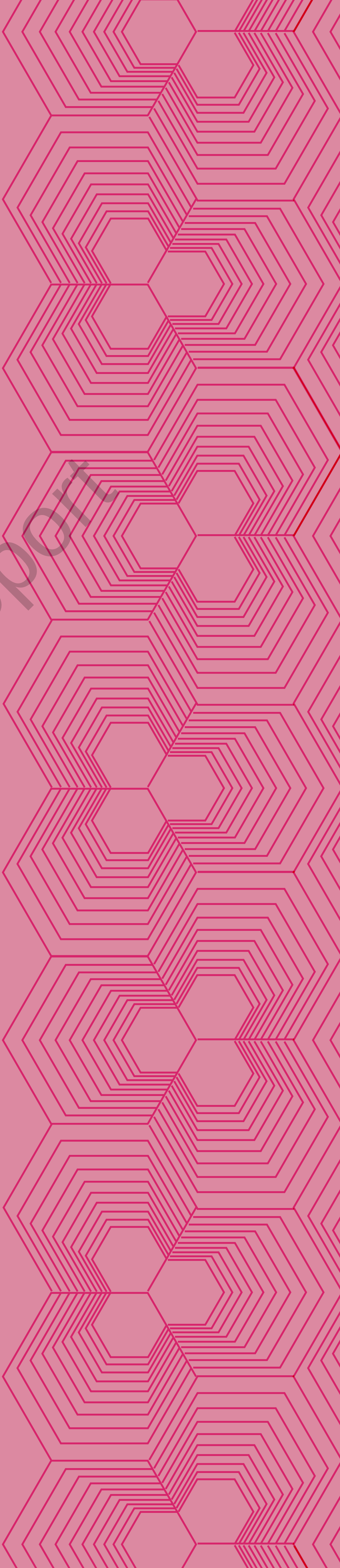
The toxicological risks and hazards are usually lowered or minimized by IPM and organic farming as compared to using synthetic pesticides. State of the art IPM and organic farming can contribute to achieving food self-sufficiency and food security and to reducing poverty[219] thus contributing to Sustainable Development Goals (SDGs). Furthermore, organic farming improves soil health[236, 241] by avoiding contamination of groundwater and drinking water with pesticides.

However, organic farming practices might use pesticides based on toxic metals (copper) and naturally occurring toxic chemicals (for example using naturally derived nicotine instead of synthetic, but structurally very similar neonicotinoids). In this context, it is important to seek lowest toxicity in selecting natural or biopesticides. Organic farming and IPM are usually still more sustainable options than using synthetic pesticides, mainly because reduced use of pesticides and using naturally occurring chemicals largely reduces manufacturing and synthesis-related impacts of chemically complex synthetic pesticides and avoids toxic end-of-life stockpiles including packaging.[242, 243]

Table 21 Some biological substitutes for synthetic pesticides

Alternative to synthetic pesticides	Type	Activity
Insecticides		
Nettle extract	Phytochemical	Fertilizer, repellent
Essential oil (Cinnamaldehyde)	Phytochemical	Repellent, fungicide, insecticide
Paecilomyces fumosoroseus	Microbe	Entomopathogenic fungus against mites and whiteflies
(Z,Z,E)-7,11,13-Hexadecatrienal	Pheromone	Pheromone of leaf minner
Essential oil (Limonene)	Phytochemical	Repellent, fungicide, insecticide
Beauveria bassiana	Entomopathogenic fungus	Repellent against many insects
Chrysoperla carnea	Natural enemy	Larvae are active predators of aphids and other small insects

Dacnusa	Natural enemy	Parasitic wasp used in the controlling of leaf miners
Diglyphus	Natural enemy	Parasitic wasp used in the controlling of leaf miners
Hypoaspis	Natural enemy	Mite predator of thrips
S-Kinoprene	Biochemical agent	Insect juvenile hormone analog
Garlic extract	Phytochemical	Repellent
Oleoresin capsicum	Phytochemical	Metabolic disruption, membrane damage, nervous system dysfunction and repellent
Essential oils (Mentha, Rosemary, Thymus, Clove)	Phytochemical	Repellent and toxic
Tagetes erecta oil	Phytochemical	Repellent
Neozygites floridana	Natural enemy	Mite against Tetranychus urticae
Sorbitol Octanoate	Biochemical	Mites and soft-bodied insects (dessication via loss of body fluids)
Sucrose octanoate esters	Biochemical	Mites and soft-bodied insects (dessication via loss of body fluids)
Phytoseiulus	Natural enemy	A predatory mite of two-spotted spider mites
Lecanicillium longisporum	Natural enemy	Entomopathogenic fungus of aphids
Neozygites fresenii	Natural enemy	Entomopathogenic fungus of Aphis gossypii
Aphidius	Natural enemy	Parasitic wasp of aphids
Aphidoletes	Natural enemy	Predator of aphids
Codling Moth Granulosis Virus	Virus	Codling moth
Metarhizium anisopliae	Natural enemy	Entomopathogenic fungus of many insects (thrips)
Rodolia cardinalis	Natural enemy	Ladybird beetle predator of Icerya purchase
Encarsia formosa	Natural enemy	Wasp parasitoid of whiteflies
Amblyseius	Natural enemy	Mite predator of thrips
Macrolophus pygmaeus	Natural enemy	Predatory bug of whiteflies
Saponins of *Chenopodium ambrosioides*	Phytochemical	Insecticidal
Spodoptera littoralis nucleopolyhedrovirus	Virus	Spodoptera littoralis
Heterorhabditis	Natural enemy	Nematode entomopathogenic
Nosema locustae	Natural enemy	Microsporidium fungi
Aluminum phosphide	Biochemical	Fumigant
Fungicides		
Essential oil component: Cinnamaldehyde	Phytochemical	Induce systemic acquired resistance in plants
Nettle extract	Phytochemical	Fertilizer, repellent
Bacillus strain	Natural enemy	Antagonistic fungi
Mandestrobin	Biochemical	(Amide, Strobin) inhibiting mitochondrial respiration in fungi
Herbicides		
Xanthomonas campestris pv. Poannua	Microbial	Against Poa annua
Essential oil: D-Limonene (from citrus peel)	Phytochemical	“Knock-down” herbicide
Pseudomonas fluorescens	Microbial	Inhibit growth and germination of a number of weeds
Nematicides		
Amurca (olive oil lees)	Phytochemical	Fertilizer
Extract of Tagetes erecta	Phytochemical	Repellent
Essential oil (Cinnamaldehyde)	Phytochemical	Fumigant nematicide
Extract of garlic	Phytochemical	Nematicidal
Compost and compost tea	Phytochemical	Nematicidal
Rodenticides		
Castor oil	Phytochemical	Natural dehydrant
Cellulose from Powdered Corn Cob	Phytochemical	Causing acute and ultimately lethal dehydration
Red squill glycoside	Phytochemical	Botanical containing a cardiac glycoside causing intoxication and pulmonary edema
Plant growth regulators		
Bacillus strains	Microbial	Plant growth promoting
Cytokinin	Phytochemical	Plant growth promoting
Cis-Zeatin	Phytochemical	Phytohormonal regulator



SOLVENTS

19. Perchloroethylene in Dry Cleaning

Background, identity and use

Tetrachloroethylene – better known as perchloroethylene, perc, or PCE – is a solvent used for dry cleaning garments and has been the solvent of choice for professional cleaners. Improper use, storage and disposal of perc has resulted in widespread contamination of groundwater and soil at dry cleaning sites. Exposure to perc is associated with a variety of adverse human health effects, especially in employees in this industry.

Alternative dry cleaning systems currently used include liquid carbon dioxide (LCO_2), wet cleaning and hydrocarbon solvent-based systems. Textile cleaning with LCO_2 is the most efficient in terms of utility and waste disposal and has comparable costs to those of perc.[244, 245, 256]

Perchloroethylene (perc, PCE, or tetrachloroethylene) is a chlorocarbon and colourless liquid widely used for dry cleaning and has a sweet odour detectable by most people at a concentration of 1 part per million (1 ppm). It has been used since the 1930s, becoming the standard solvent because of its effectiveness, ease of use and relatively low cost. It is thermally stable and recyclable and performs better for oil-based stains than for the more common water-soluble stains (coffee, wine, blood, etc.).[246] It can cause colour loss, especially at higher temperatures and may damage special trims, buttons and beads.[244]

Hazard profile and problems

Effects of chronic exposure to perc include dizziness, impaired judgement and perception, damage to liver and kidneys, respiratory disease[247] and immune and hematologic system effects.[248] A study also found an association between perc exposure and hypertensive end-stage renal disease[249] and some cancers.[247, 250] Other risks include neurotoxicity and reproductive and developmental toxicity.[248] Some studies suggest that frequent over-exposure to perc over time may cause lasting and possible permanent central nervous system effects. Fatigue, lack of muscle coordination, loss of concentration, short term memory loss, personality changes, anxiety and irritability are some of the potential permanent long-term effects.[251]

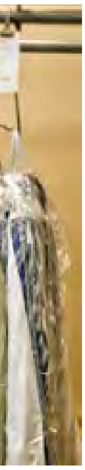
The most prevalent route of exposure to perc is by inhalation, also occurring orally through ingestion of contaminated water or food.[247] Perc inhaled by pregnant women can reach the developing foetus and has been found in the breastmilk.[247] The public is exposed to perc due to environmental and food contamination and potentially through the presence of residual perc in dry cleaned garments.[244] Perc released from dry cleaning operations has contaminated thousands of sites and its degradation in groundwater can take decades to centuries. Perc can also cause vapour

CHEMICAL	CAS/EC Number
Tetrachloroethene, Tetrachloroethylene, Perchloroethene, PCE, Perc., Per, 1,1,2,2-tetrachloroethylene, Ethylenetetrachloride	CAS No: 127-18-4 EC No: 204-825-9

Table 22 Chemical identity of perchloroethylene (perc)

Hazard profile

GHS01 Explosive
GHS02 Flammable
GHS03 Oxidizing
GHS04 Compressed Gas
GHS05 Corrosive
GHS06 Toxic
GHS07 Harmful
GHS08 Health hazard
GHS09 Environmental hazard
CMR Carcinogenic/ Mutagenic/ reprotoxic
EDC Endocrine disrupting chemicals
Persistent organic pollutant



intrusion in buildings.[247, 252] As a result, perc can be readily found in water, soil, air and sediments.[253]

Status in the Mediterranean region and internationally

Perc use in dry-cleaning is regulated by the European Solvents Emissions Directive and by the EU REACH and the majority of EU countries have implemented stringent regulatory requirements for the safe use of perc in dry cleaning. The measures implemented in Denmark are often considered a perc ban.[254] Stringent national regulations in Europe enforce the use of perc in closed facilities with modern equipment and well educated staff, to achieve low emission limits.[254]

In the US, according to the US EPA, dry-cleaning machines located in residential areas will be phased out by 2020. In Europe, this ban affects a smaller number of dry cleaning shops.[254] In Egypt high perc levels in air above 100 ppm was found in dry cleaning indicating low control.[255]

Selected alternatives

to perc in dry cleaning

Identification, availability and technical feasibility

Alternative dry cleaning systems currently on the market include carbon dioxide, hydrocarbon solvent-based systems and wet cleaning. Wet cleaning processes rely on water, detergent, conditioners or degreasers to clean the garment. The processes sometimes use specialized equipment designed to minimize temperature and agitation or to create a fine mist to deliver the water-based detergents to the materials in need of cleaning. Professional Wet Cleaning is a water-based process that uses computer-controlled washers and dryers along with biodegradable detergents and specialized finishing equipment to process delicate garments that would otherwise be dry cleaned. While this alternative is not new, technology has evolved in the past 5-10 years, resulting in significantly improved performance.[244] Carbon dioxide as a liquid (LCO_2) or a supercritical fluid can be used with specialized equipment to clean garments.[244, 256] It combines liquid carbon dioxide with specially formulated cleaning agents in a traditional basket-style machine under high pressure (4825 kPa).[244] Hydrocarbon solvent-based systems are widely used alternatives to perc.

Economic feasibility

A cost analysis concluded the following: [256] (1) Textile cleaning with LCO_2 is most efficient in terms of utility and waste disposal; (2) The costs of LCO_2 and detergents are comparable to those of perc; (3) The labour costs of LCO_2 textile cleaning are comparable to those of perc dry cleaning; (4) Investment-related costs of LCO_2 textile cleaning per annum are higher, but equal per kg cleaned garments due to the higher annual capacity of the LCO_2 textile cleaning machine (2 cycles per hour) compared to perc dry cleaning (2 cycles in 1,5 hour). The overall costs of LCO_2 textile cleaning were 20% lower than those of perc dry cleaning due to its shorter turn-around time. LCO_2 textile cleaning is best combined with wet cleaning to cover the entire spectrum of soiled consumer garments and other textiles. The cost of the LCO_2 machine is up to 90,000 USD more than that of a perc machine. The higher investment cost of this alternative has limited its adoption.[244, 245]

Hazards, risks and life cycle considerations

The various alternatives differ primarily with respect to their environmental and human health and safety characteristics. Overall the alternative solvents assessed exhibit lower persistence, human health impact, bio-accumulation potential, and aquatic toxicity compared to perc.[244, 245] The alternatives exhibit preferable human health characteristics compared to perc. A major concern for many of the alternatives is their flammability. The hydrocarbon solvents are Class IIIA or IIIB combustible liquids, thus requiring specialized equipment to protect against fire or explosion.[244, 245] Wet cleaning and carbon dioxide have no flammability concerns.

20.
Perchloroethylene in Metal Cleaning

Background, identity and use

Perchloroethylene, also known as perc, PCE, or tetrachloroethylene, is used in metal cleaning and vapour degreasing.[257, 258] Exposure to perc at workplace is associated with a variety of adverse human health effects. Improper use, storage and disposal of perc have resulted in widespread contamination of groundwater and soil.

Alternatives are aqueous cleaning technologies and dry ice blasting technologies having proven performance with low health and environmental impacts.

Perchloroethylene (perc) is used as a degreasing agent in vapour and liquid forms. It dissolves many organic compounds (including pitches and waxes) and inorganic compounds and can be used to clean metal parts. Perc along with trichloroethylene can be used in the vapour, boiling liquid, or ultrasonic cleaning of metalwork in the engineering industry. Because of its high boiling point, perc is effective in removing persistent deposits.

Hazard profile and problems

Effects of chronic exposure to perc include dizziness, impaired judgement and perception, damage to liver and kidneys, respiratory disease, and immune and hematologic system effects.[259] A study of dry cleaning workers also showed an association between perc exposure and hypertensive end-stage renal disease[260] and some cancer.[259, 260, 261, 262] Other risks include neurotoxicity and reproductive and developmental toxicity.[260] The most prevalent route of exposure to perc is by inhalation, though exposure can also occur orally through ingestion of contaminated water or food.[259] Perc inhaled by pregnant women can reach the developing foetus and has been found in the breastmilk of mothers exposed to the chemical.[259] The release of perc to groundwater has resulted in thousands of contaminated sites. Perc degradation in groundwater takes decades to centuries including formation of vinyl chloride. Perc can also cause vapour intrusion in buildings. [259, 260, 261, 262, 263]

Some studies suggest that frequent over-exposure to perc and over months or years may cause lasting and possibly permanent central nervous system effects. Fatigue, lack of muscle coordination, loss of concentration, short term memory loss, personality changes, anxiety and irritability are some of the potential permanent long-term effects.[263]

The average exposure level among workers degreasing metal and plastics in the US during 1944–2001 was 95 ppm.[264] In these industries, exposure levels have decreased by two orders of magnitude over a 60-year period in the US.[257, 265]

Status in the Mediterranean region and internationally

Perc use in metal cleaning is regulated by the European Solvents Emission Directive and by EU REACH. In the EU, perc was evaluated under the 2013 Community Rolling Action Plan (CoRAP), which concluded that no additional regulatory action was required.[265,266]

Perc is on the Canadian List of Toxic Substances

CHEMICAL	CAS/EC Number
Tetrachloroethene, Tetrachloroethylene, Perchloroethene, PCE, Perc., Per, 1,1,2,2-tetrachloroethylene, Ethylenetetrachloride	CAS No: 127-18-4 EC No: 204-825-9

Table 23 Chemical identity of perchloroethylene (perc)

Hazard profile

(CEPA 1999 Schedule 1)[267, 268] and is also regulated for use and sale as solvent degreaser under the Solvent Degreasing Regulations (SOR/2003-283) (Canada Gazette, Part II on August 13, 2003). The purpose of the regulation is to reduce perc releases to the environment from solvent degreasing facilities using more than 1,000 kilograms of perc per year. The regulation includes a market intervention establishing tradable allowances in solvent degreasing operations exceeding the 1,000 kilograms threshold per year.

In the US, at federal level, perc is listed under the Toxics Substances Control Act (TSCA) and the Clean Air Act (CAA).[269]

In the Southern Mediterranean region, no specific regulations for perc have been found. In Egypt, high perc levels (above 100 ppm) in air were found in workplaces, indicating low control.[270]

Selected alternatives

to perc in metal cleaning

Identification, availability and technical feasibility

A recent ECHA case study has compiled chemical and non-chemical alternatives to perc.[271] Alternative degreasing solvents include methylchloride, trichloroethylene (TCE), n-propylbromide, hydrofluorocarbons (HFC) and hydrofluoroethers.

As "non-chemical" alternatives technologies aqueous cleaning technologies, dry ice blasting and plasma technology were considered. From a technical perspective, aqueous cleaning technologies and dry ice blasting technologies have been proven. For degreasing using plasma cleaning technologies, less reliable information is available.[271]

Hazards, risks and life cycle considerations

All alternative solvent solutions were either carcinogenic, mutagenic, reprotoxic (CMR) or potential ozone depleting substances (ODS) or greenhouse gases (GHG) (Table 24).[271] Therefore, these alternatives constitute a rather incremental (if at all any) improvement and might introduce to shifting the burden from one problem to another, which should be avoided to select alternatives that are truly more sustainable and viable.

Although fresh aqueous cleaning solutions are usually classified as non-hazardous, they may accumulate enough contaminants during the cleaning process, such as metal powder or oil and grease, to be classified as hazardous waste when disposed. Spent solutions are typically treated in an on-site wastewater treatment system or shipped off site for disposal.[271]

Dry ice blasting uses and emits CO_2, which is a GHG that needs to be considered in life cycle costing.

CHEMICAL	CAS/EC Number
Trichloroethylene	CAS No. 79-01-6
Methylene chloride	CAS No. 75-09-2
n-propylbromide	CAS No. 106-94-5
Hydrofluorocarbons (HFC)	Various
Hydrofluoroether	Various

Table 24 Alternatives to perchloroethylene (perc) in metal cleaning [271]

Economic feasibility

The installation costs of the non-chemical alternatives are approximately:[271]

- 80,000 Eur for aqueous cleaning technologies;
- 85,000 Eur for dry ice blasting technologies;
- 150,000 Eur for plasma cleaning technologies.

The ECHA study, after considering cost and performance, selected the aqueous technology as the preferred alternative.[271]

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Sant Pau Art Nouveau Site – Nostra Senyora de la Mercè Pavillion
Carrer de Sant Antoni Maria Claret, 167.
08025 Barcelona, Catalunya (Spain)
Tel. +34 93 553 87 90

www.scprac.org