



M 2022

MICROPLASTICS ON THE TURF

ARE THEY A THREAT IN SYNTHETIC SPORTS FACILITIES?

TIAGO FILIPE LARANJO FERREIRA
MASTER'S THESIS PRESENTED TO THE
FACULTY OF ENGINEERING OF THE
UNIVERSITY OF PORTO IN BIOENGINEERING

Masters in Bioengineering

Microplastics on the turf - are they a threat in synthetic sports facilities?

Master's Thesis

of

Tiago Filipe Laranjo Ferreira

Developed within the discipline of Dissertation

Conducted at

Laboratory for Process Engineering, Environment, Biotechnology and Energy

Faculty of Engineering, University of Porto

FEUP Advisor: Dr. Nuno Ratola

FEUP Co-Advisor: Dr. Vera Homem



julho de 2022

Acknowledgements

First and foremost, I would like to send a huge thank you to the two people who gave me the opportunity to work in such a great project: my advisor, Dr. Nuno Ratola, and my co-advisor, Dr. Vera Homem. You made me feel comfortable from the very first meeting and were always tremendously helpful whenever I needed any sort of explanation/suggestion. It was a pleasure working with you.

A huge thank you also goes out, of course, to all the staff of laboratory E201, my workplace in the past five months. You definitely made all the hard work a lot easier. Thank you, Sofia, for all the tutorials and advice that you gave me, and especially for making me feel welcome from the very first moment that I stepped foot in the lab. I will never forget that. Thank you, Sara F. and Sandra, for all the fun moments and talks about food. Thank you, Ana Sofia, not only for this semester but also for the past four years. Thank you, Filipe, for correcting my stupid rookie mistakes. Also, a big thank you to Zizina, Maria Francisca, Niki, Teresa and Sara S. I will always cherish all the wonderful moments that we shared - the lunches, the picnics and (of course) the Rally Tascas. Thank you for, more than being my colleagues, being my friends.

Thank you to all the amazing people that I met in these five years. To the ones that have been with me from the very beginning, to my amazing housemates during my Erasmus stay in Gent (Francisco, João, Guilherme and Patrícia) and to all the good “Latino” friends that I made there (Leo, Quique, Irene, Mati and Lisa). Even though technically you have not been an active contributor to this thesis, I could never afford to leave you out of this message.

And last but not least, the biggest thank you definitely goes out to my family, particularly to my parents. I am sorry for all the weekends that I could not travel with you because I needed stay at home working. Let’s make up for that now.

I also acknowledge the Department of Chemical Engineering (Faculty of Engineering, University of Porto) and LEPABE (Laboratory for Process Engineering, Environment, Biotechnology and Energy) for granting the conditions and facilities to the development of this work. Financial support was provided by: (i) Base Funding - LA/P/0045/2020 (ALiCE), UIDB/00511/2020 and UIDP/00511/2020 (LEPABE), funded by national funds through FCT/MCTES (PIDDAC); (ii) Project SAFEGOAL (Ref. PTDC/EQU-EQU/28101/2017; POCI-01-0145-FEDER-028101), funded by FEDER funds through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) and by national funds (PIDDAC) through FCT/MCTES.

Resumo

Recentemente, tem-se vindo a verificar uma convergência no paradigma global para a sustentabilidade, que se reflete inclusivamente nos sistemas de gestão de pneus “em fim de vida” (ELTs). Um dos possíveis “destinos” da borracha derivada de pneus reciclados são os campos sintéticos de relvado artificial, onde este material é aplicado como enchimento sob a forma de pequenos grânulos - *crumb rubber* (CR) - recentemente incluídos na família dos microplásticos (< 5 mm). Apesar dos diversos benefícios desta medida de uma perspetiva de economia circular, têm surgido várias preocupações no âmbito da saúde pública relativamente ao contacto regular com CR durante o exercício físico, uma vez que múltiplos estudos demonstraram a presença de químicos potencialmente nocivos nesta matriz, incluindo hidrocarbonetos aromáticos policíclicos (PAHs), plastificantes e metais pesados, entre outros.

Uma classe de microcontaminantes emergentes nunca antes analisada em CR é a dos organosiloxanos. Estes compostos encontram-se referenciados devido às suas possíveis propriedades toxicológicas; contudo, são produzidos em grande escala em virtude da sua vasta gama de aplicações (e.g., produtos de cuidado pessoal e polímeros de silicone - que podem estar presentes em pneus). O ano passado viu entrar em vigor as primeiras restrições à utilização dos siloxanos D4 e D5 em alguns cosméticos, contudo a maioria das suas aplicações continua a não ser regulada - entre as quais a CR.

O principal objetivo deste trabalho consistiu em avaliar a presença de metilsiloxanos voláteis (VMSs), uma classe de siloxanos com baixo peso molecular, em CR. Analisou-se um total de 126 amostras - 120 amostras de campo (108 de CR e 12 de outros materiais) e 6 amostras de CR comercial. Visto que esta foi a primeira vez que siloxanos foram analisados em CR, a parte inicial deste trabalho foi dedicada à otimização e validação do método analítico. Sete VMSs - três lineares (L3, L4 e L5) e quatro cíclicos (D3, D4, D5 e D6) - foram analisados. O protocolo de extração consistiu numa extração por ultrassons (UAE), utilizando uma mistura 1:1 (v/v) de *n*-hexano e diclorometano, com uma metodologia QuEChERS de *clean-up*. A quantificação dos extratos foi efetuada por cromatografia gasosa com deteção por espetrometria de massa (GC-MS). Os limites de deteção do método (MDLs) situaram-se entre os 0.006 e os 4.46 ng.g⁻¹ (para D5 e D3, respetivamente).

Os VMSs foram detetados em todas as amostras, com concentrações totais compreendidas entre os 10.29 e os 5,089 ng.g⁻¹. O D3 e os compostos lineares não foram detetados nas amostras de campo - apenas na CR comercial. A concentração média das amostras de CR comercial (976.1 ± 2,016 ng.g⁻¹) foi 17.6 vezes superior à das amostras de campo (34.50 ± 16.09 ng.g⁻¹), enquanto a cortiça foi o único material com concentração média inferior à de CR (27.14 ± 31.22 ng.g⁻¹). A partir destes resultados, doses de exposição humana foram estimadas para utilizadores assíduos de campos sintéticos de futebol: jogadores jovens (6-11 anos de idade), jogadores adultos e trabalhadores de manutenção do relvado. As doses orais para o “*worst-case scenario*” situaram-se entre os 8.23 e os 21.3 ng.kg⁻¹.ano⁻¹ e as dérmicas entre os 0.598 e os 0.898 ng.kg⁻¹.ano⁻¹. Estes valores irão constituir uma base importante para um estudo de avaliação de risco que será realizado *a posteriori*.

Palavras-chave: pneus “em fim de vida”, *crumb rubber*, metilsiloxanos voláteis, QuEChERS, GC-MS, exposição humana.

Abstract

Recent years have seen a substantial shift in the global paradigm towards sustainability, with this trend also being reflected in the management of used rubber tyres - End-of-Life Tyres (ELTs). One of the possible “destinations” of recycled tyre rubber are synthetic turf sports’ facilities, where this material is commonly applied as infill, in the form of small granules - crumb rubber (CR) - now included in the family of microplastics (< 5 mm). In spite of the benefits that this approach carries from a circular economy perspective, several public health concerns have been raised regarding a recurrent contact with CR during physical exercise, with several studies having detected the presence of potentially hazardous chemicals in this matrix, including polycyclic aromatic hydrocarbons (PAHs), plasticizers and heavy metals, among others.

One class of emerging microcontaminants which has never been targeted in CR is organosiloxanes. These compounds are referenced by environmental entities due to their possible toxicological properties. However, they are produced at a large scale due to their wide range of applications (e.g., personal care products and silicone polymers - which may enter tyre manufacture). Last year saw the implementation of the first legal restrictions to the use of siloxanes D4 and D5, in some cosmetics, although most of their applications remain unregulated to this day - including CR.

The main goal of this work was to evaluate the presence of volatile methylsiloxanes (VMSs), a class of low molecular weight siloxanes, in CR. A total of 126 samples were analysed - 120 field samples (108 of CR and 12 of other infill materials) and 6 commercial CR samples. Since this was the first time that siloxanes were analysed in CR, the first part of this work was dedicated to the optimization and validation of the analytical method. Seven VMSs were analysed - three linear (L3, L4 and L5) and four cyclic (D3, D4, D5 and D6). The employed extraction protocol consisted of an ultrasound-assisted extraction (UAE), using a 1:1 (v/v) mixture of *n*-hexane and dichloromethane, with a QuEChERS (“Quick, Easy, Cheap, Effective, Rugged and Safe”) clean-up methodology. The quantification of the extracts was carried out by gas chromatography coupled with a mass spectrometry detector (GC-MS). The method detection limits (MDLs) ranged from 0.006 to 4.46 ng.g⁻¹ (for D5 and D3, respectively).

VMSs were detected in all samples, in total concentrations ranging from 10.29 to 5,089 ng.g⁻¹. D3 and the linear compounds were not detected in any of the field samples - only in commercial CR. The mean concentration of commercial samples ($976.1 \pm 2,016$ ng.g⁻¹) was 17.6 times larger than field CR (34.50 ± 16.09 ng.g⁻¹), while cork was the only infill material with a lower mean concentration than CR (27.14 ± 31.22 ng.g⁻¹). From these results, oral and dermal exposure doses were estimated for assiduous users of synthetic turf football fields: young players (6-11 years old), adult players and turf maintenance workers. “Worst-case scenario” oral doses ranged from 8.23 to 21.3 ng.kg⁻¹.year⁻¹ and dermal doses from 0.598 to 0.898 ng.kg⁻¹.year⁻¹. These values will provide an important basis for an extensive risk assessment study to be carried out *a posteriori*.

Keywords: end-of-life tyres, crumb rubber, volatile methylsiloxanes, QuEChERS, GC-MS, human exposure.

Declaração

Declara, sob compromisso de honra, que este trabalho é original e que todas as contribuições não originais foram devidamente referenciadas com identificação da fonte.



Handwritten signature of Tiago Ferreira, written in black ink, positioned above a horizontal line.

4 de julho de 2022

Table of Contents

1. Background and Presentation of the Project	1
2. Introduction	2
2.1. End-of-Life Tyres (ELTs).....	2
2.2. Crumb Rubber	3
2.2.1. Composition	3
2.2.2. Harmful Chemicals in Crumb Rubber	4
2.2.3. Current Legislation on Crumb Rubber	5
2.2.4. Human Exposure to Crumb Rubber	6
2.3. Siloxanes.....	7
2.3.1. Characterization and Physicochemical Properties	7
2.3.2. Consumption and Safety	9
2.3.3. Current Legislation on Siloxanes.....	9
2.3.4. Human Exposure to Siloxanes	10
2.4. Analysis of Organic Microcontaminants from Crumb Rubber	11
2.4.1. Ultrasound-Assisted Extraction	11
2.4.2. Soxhlet Extraction	11
2.4.3. Instrumental Analysis (GC-MS)	12
2.5. Analysis of Siloxanes from Solid Matrices	13
2.5.1. UAE with QuEChERS	13
2.5.2. Pressurized Liquid Extraction	15
3. State of the Art.....	16
3.1. Organic Microcontaminants in Crumb Rubber	16
3.2. VMSs in Solid Matrices.....	26
3.3. Human Exposure to Crumb Rubber	30
4. Materials and Methods	32
4.1. Chemicals and Materials	32
4.2. Standards Preparation	32

4.3.	QuEChERS Preparation	32
4.4.	Samples	32
4.5.	Optimization and Validation Strategy	33
4.6.	Sample Extraction and Clean-up	34
4.6.1.	SAFEGOAL (Original).....	34
4.6.2.	Dry Sludge	34
4.6.3.	SAFEGOAL (Modified).....	35
4.7.	Instrumental Analysis	35
4.8.	Quality Assurance/Quality Control.....	35
4.9.	Waste Management	36
4.10.	Model for Human Exposure Estimation	36
4.11.	Statistics	37
5.	Results and Discussion	38
5.1.	Method Optimization	38
5.2.	Method Validation.....	39
5.2.1.	Calibration and Linearity	39
5.2.2.	Limits of Detection and Quantification.....	40
5.2.3.	Accuracy	40
5.2.4.	Precision	41
5.3.	Concentration of Siloxanes in Crumb Rubber	43
5.3.1.	Indoor vs. Outdoor.....	44
5.3.2.	Country.....	45
5.3.3.	Granulometry.....	46
5.3.4.	Field Age	47
5.4.	Concentration of Siloxanes in Other Materials	47
5.4.1.	Crumb Rubber vs. Other Materials	49
5.5.	Human Exposure to Siloxanes from Crumb Rubber	49
5.5.1.	Oral Exposure	50
5.5.2.	Dermal Exposure	50

6. Conclusions	52
7. Evaluation of the Accomplished Work	53
7.1. Accomplished Objectives	53
7.2. Additional Work	53
7.3. Recommendations and Future Work	53
8. References	54
Appendix 1. List of Analysed Samples	69
Appendix 2. Extraction/Clean-up Protocols	73
Appendix 3. GC-MS Quantification Parameters	75
Appendix 4. Method Optimization.....	76
Appendix 5. Method Validation	77
5.1. Calibration Curves	77
5.2. Linearity	79
5.3. Accuracy and Precision	79
Appendix 6. Concentration of Siloxanes in Crumb Rubber	81
Appendix 7. Concentration of Siloxanes in Other Materials.....	85
Appendix 8. Statistical Analysis.....	86
8.1. Pairwise T Tests	86
8.2. Non-Parametric Tests	87
Appendix 9. Human Exposure Parameters.....	89

List of Figures

Figure 1. Schematic representation of the main parts of a GC-MS system (Emwas et al., 2015).....	12
Figure 2. Scheme of QuEChERS extraction (adapted from Paíga et al. (2015)).	14
Figure 3. Results from the recovery assays carried out for the selection of the extraction protocol - SAFEGOAL (SG) vs. Dry Sludge (DS).....	38
Figure 4. Calibration curve for the analysis of D5 in crumb rubber.	40
Figure 5. Accuracy for the analytical method to quantify VMS in crumb rubber (SG method at 100 ng.g ⁻¹ and 500 ng.g ⁻¹ spike levels).	41
Figure 6. Repeatability for the analytical method to quantify VMS in crumb rubber (SG method at 100 ng.g ⁻¹ and 500 ng.g ⁻¹ spike levels).	42
Figure 7. Intermediate precision for the analytical method to quantify VMS in crumb rubber (SG method at 100 ng.g ⁻¹ and 500 ng.g ⁻¹ spike levels).	42
Figure 8. Individual VMS profile in crumb rubber samples from synthetic football fields.	43
Figure 9. Individual VMS profile in commercial crumb rubber samples.	44
Figure 10. Mean total concentration (ng.g ⁻¹) of VMSs in CR from indoor and outdoor fields.	44
Figure 11. Mean total concentration (ng.g ⁻¹) of VMSs in crumb rubber from synthetic football fields (left) and commercial crumb rubber (right), by country.	45
Figure 12. Mean total concentration (ng.g ⁻¹) of VMSs in CR from synthetic football fields, by granulometry.	46
Figure 13. Mean total concentration (ng.g ⁻¹) of VMSs in CR from synthetic football fields, by field age.	47
Figure 14. Individual VMS profile in alternative infill materials.	48
Figure 15. Mean total concentration (ng.g ⁻¹) of VMSs in alternative synthetic turf infill materials, by type of material.	48
Figure 16. Mean total concentration (ng.g ⁻¹) of VMSs in CR and alternative infill materials, by type of material.	49
Figure A2.1. Diagram of the DS protocol for VMS extraction from crumb rubber.	73
Figure A2.2. Diagram of the modified SG protocol for VMS extraction from crumb rubber.	74
Figure A4.1. Results from the recovery assays carried out for the selection of the extraction solvent - n-hexane (Hex) vs. dichloromethane (DCM) vs. ethyl acetate (EtAc).	76
Figure A4.2. Results from the recovery assays carried out for the selection of the extraction solvent (cont.) - dichloromethane (DCM) vs. n-hexane/dichloromethane (Hex/DCM) 1:1 (v/v).	76

<i>Figure A4.3. Results from the recovery assays carried out for the filtration step - 0.20 μm vs. 0.45 μm vs. no filtration (NF).</i>	<i>76</i>
<i>Figure A5.1.1. Calibration curve for the analysis of D3 in crumb rubber.</i>	<i>77</i>
<i>Figure A5.1.2. Calibration curve for the analysis of L3 in crumb rubber.</i>	<i>77</i>
<i>Figure A5.1.3. Calibration curve for the analysis of D4 in crumb rubber.</i>	<i>77</i>
<i>Figure A5.1.4. Calibration curve for the analysis of L4 in crumb rubber.</i>	<i>78</i>
<i>Figure A5.1.5. Calibration curve for the analysis of L5 in crumb rubber.</i>	<i>78</i>
<i>Figure A5.1.6. Calibration curve for the analysis of D6 in crumb rubber.</i>	<i>78</i>
<i>Figure A8.2.1. Results of the Mann-Whitney U test for the country distribution (commercial crumb rubber).</i>	<i>87</i>
<i>Figure A8.2.2. Results of the Kruskal-Wallis test for the type of material distribution (alternative material).</i>	<i>87</i>
<i>Figure A8.2.3. Results of the Kruskal-Wallis test for the type of material distribution (crumb rubber from synthetic turf fields vs. commercial crumb rubber vs. alternative material).</i>	<i>.....</i>

List of Tables

<i>Table 1. Main constituents of new car tyres - adapted from (ECHA, 2017b).</i>	3
<i>Table 2. Nomenclature and structure of common lVMSs and cVMSs (adapted from Gaj (2020)).</i>	8
<i>Table 3. Overview of the scientific literature on the analysis and quantification of PAHs in CR.</i>	20
<i>Table 4. Overview of the scientific literature on the analysis and quantification of plasticizers in CR.</i>	22
<i>Table 5. Overview of the scientific literature on the analysis and quantification of other additives in CR.</i>	24
<i>Table 6. Overview of the scientific literature on the analysis and quantification of VMSs in solid matrices.</i>	28
<i>Table 7. Content of the samples included in the recovery assays.</i>	33
<i>Table 8. Exposure scenarios to CR in synthetic football fields (Peterson et al., 2018).</i>	36
<i>Table 9. Limits of detection and quantification for the analysis of VMS in crumb rubber.</i>	40
<i>Table 10. Estimated doses for oral exposure to CR ($\text{ng.kg}^{-1}.\text{year}^{-1}$) in outdoor synthetic turf football fields.</i>	50
<i>Table 11. Estimated doses for dermal exposure to CR ($\text{ng.kg}^{-1}.\text{year}^{-1}$) in outdoor synthetic turf football fields.</i>	51
<i>Table A1.1. List and details of the 108 synthetic turf crumb rubber samples analysed in this work.</i>	69
<i>Table A1.2. List and details of the 12 synthetic turf alternative infill material samples analysed in this work.</i>	72
<i>Table A1.3. List and details of the 6 commercial crumb rubber samples analysed in this work.</i>	72
<i>Table A3.1. Retention time and quantifier/qualifier ions of the VMSs analysed by GC-MS.</i>	75
<i>Table A5.2.1. Linearity validation parameters for VMS analysis in crumb rubber.</i>	79
<i>Table A5.3.1. Results of the accuracy tests for VMS analysis in crumb rubber (SG method at 100 ng.g^{-1} and 500 ng.g^{-1} spike levels).</i>	79
<i>Table A5.3.2. Results of the precision tests - repeatability and intermediate precision for VMS analysis in crumb rubber (SG method at 100 ng.g^{-1} and 500 ng.g^{-1} spike levels).</i>	80
<i>Table A6.1. Concentration of VMSs in crumb rubber (ng.g^{-1}).</i>	81
<i>Table A6.2. Mean total VMS concentrations in crumb rubber, by country.</i>	84
<i>Table A6.3. Mean total VMS concentrations in crumb rubber, by granulometry.</i>	84
<i>Table A6.4. Mean total VMS concentrations in crumb rubber, by field age.</i>	84

<i>Table A7.1. Concentration of VMSs in other materials (ng.g⁻¹).</i>	<i>85</i>
<i>Table A8.1.1. p-values of the pairwise T tests for the country distribution (crumb rubber from synthetic turf fields).</i>	<i>86</i>
<i>Table A8.1.2. p-values of the pairwise T tests for the granulometry distribution (crumb rubber from synthetic turf fields).</i>	<i>86</i>
<i>Table A8.1.3. p-values of the pairwise T tests for the field age distribution (crumb rubber from synthetic turf fields).</i>	<i>86</i>
<i>Table A9.1. Oral exposure dose calculation parameters for VMS exposure from crumb rubber.</i>	<i>89</i>
<i>Table A9.2. Dermal exposure dose calculation parameters for VMS exposure from crumb rubber.</i>	<i>89</i>

List of Acronyms

2-MBTZ	2-Mercaptobenzothiazole
A	Peak Area
a	Slope
ABS	Dermal Absorption Factor
Acet	Acetone
AF	Skin Adherence Factor
ANOVA	Analysis of Variance
APCI	Atmospheric Pressure Chemical Ionization
B	Relative Oral Bioaccessibility Factor
b	Y-intercept
BaA	Benzo[a]anthracene
BaP	Benzo[a]pyrene
BbFA	Benzo[b]fluoranthene
BBP	Benzyl Butyl Phthalate
BeP	Benzo[e]pyrene
BjFA	Benzo[j]fluoranthene
BkFA	Benzo[k]fluoranthene
BPA	Bisphenol A
BW	Body Weight
C	Concentration
C18	Octadecyl-silica
CAGR	Compound Annual Growth Rate
CAS	Chemical Abstracts Service
CCR	Coloured Crumb Rubber
CDC	Center for Disease Control and Prevention
CHR	Chrysene
CLM	Central Limit Theorem
CR	Crumb Rubber
C _{Risk}	Cancer Risk
cVMS	Cyclic Volatile Methylsiloxane
D3	Hexamethylcyclotrisiloxane
D4	Octamethylcyclotetrasiloxane
D5	Decamethylcyclopentasiloxane
D6	Dodecamethylcyclohexa-siloxane
DBaH	Dibenzo[a,h]anthracene
DBP	Dibutyl Phthalate
DCM	Dichloromethane
DED	Dermal Exposure Dose

DEHP	Diethylhexyl Terephthalate
DIBP	Di-isobutyl Phthalate
DINP	Diisononyl Phthalate
DS	Dry Sludge
EC	European Commission
ECHA	European Chemicals Agency
EF	Exposure Frequency
EFSA	European Food Safety Authority
ELT	End-of-Life Tyre
EPA	Environmental Protection Agency
ERASSTRI	European Risk Assessment Study on Synthetic Turf Rubber Infill
EtAc	Ethyl Acetate
ETRMA	European Tyre & Rubber Manufacturers' Association
EU	European Union
GC	Gas Chromatography
GI	Gastrointestinal
GSC	Global Silicones Council
HAC	Heterocyclic Aromatic Compound
HI	Hazard Index
HPLC	High Performance Liquid Chromatography
IDL	Instrumental Detection Limit
IQL	Instrumental Quantification Limit
IR	Ingestion Rate
IS	Internal Standard
IUPAC	International Union of Pure and Applied Chemistry
L2	Hexamethyldisiloxane
L3	Octamethyltrisiloxane
L4	Decamethyltetrasiloxane
L5	Dodecamethylpentasiloxane
LC	Liquid Chromatography
LOD	Limit of Detection
LOQ	Limit of Quantification
IVMS	Linear Volatile Methylsiloxane
M4Q	Tetrakis(trimethylsilyloxy)silane
MDL	Method Detection Limit
MEPS	Microextraction in Packed Sorbent
MIBK	Methyl Isobutyl Ketone
MP	Microplastic
MQL	Method Quantification Limit
MS	Mass Spectrometry

<i>n</i> -Hex	Hexane
NPCA	Norwegian Pollution Control Authority
OED	Oral Exposure Dose
PAE	Phthalate Esther
PAH	Polycyclic Aromatic Hydrocarbon
PBT	Persistent, Bioaccumulative and Toxic
PCB	Polychlorinated Biphenyl
PCP	Personal Care Product
PDMS	Polydimethylsiloxane
PEM	Polyethermethylsiloxane
PLE	Pressurized Liquid Extraction
POP	Persistent Organic Pollutant
PP	Polypropylene
PSA	Primary and Secondary Amine
PTFE	Polytetrafluoroethylene
PVA	Polyvinyl Acetate
PVC	Polyvinyl Chloride
PVDC	Polyvinylidene Chloride
QuEChERS	Quick, Easy, Cheap, Effective, Rugged and Safe
R	Correlation Coefficient
R ²	Determination Coefficient
RCF	Rubber/Coconut Fibre
RCR	Risk Characterization Ratio
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
Rec	Recovery
RF	Instrumental Response Factor
RSD	Relative Standard Deviation
S/N	Signal-to-Noise Ratio
SA	Exposed Skin Surface Area
SBR	Styrene Butadiene Rubber
SBSE	Stir Bar Sorptive Extraction
SE	Soxhlet Extraction
SVHC	Substance of Very High Concern
SVOC	Semi-Volatile Organic Hydrocarbon
UAE	Ultrasound-Assisted Extraction
VMS	Volatile Methylsiloxane
VOC	Volatile Organic Hydrocarbon
vPvB	Very Persistent and Very Bioaccumulative
WBCSD	World Business Council for Sustainable Development
WWTP	Wastewater Treatment Plant

1. Background and Presentation of the Project

According to the European Tyre & Rubber Manufacturers' Association (ETRMA), a tyre production of 4.24 kton was registered in the European Union (EU) during 2020, with this value resulting from a 16% decrease in comparison to pre-COVID-19 pandemic times - when the yearly tyre production surpassed the 5 kton mark (ETRMA, 2021). Once these tyres become worn out - End-of-Life Tyres (ELTs) - they must be adequately managed in order to avoid substantial environmental impact caused by conventionally employed methods (e.g., landfill disposal and incineration). As a result, multiple strategies were developed to combat this major issue, such as whole tyre reuse in civil engineering applications (Skoczyńska et al., 2021), pyrolysis for energy recovery (Czajczyńska et al., 2019), and recycling through tyre transformation to granular or powder form - crumb rubber (CR).

One of the many applications of CR is as infill in synthetic turf sports facilities and in children playgrounds (ECHA, 2021). Even so, despite its contribution to ELTs management, recent years have seen several safety concerns being raised. In 2017, the European Chemicals Agency (ECHA) published an official report stating that exposure to recycled rubber granules is safe and does not present any alarming health risks (ECHA, 2017a) - although this conclusion is not decisive as there are some uncertainties which must be addressed (e.g., the analysed samples may not be truly representative of synthetic fields in the EU and there are considerable knowledge gaps in terms of what substances are present in synthetic rubber granules). Nevertheless, this topic is subject to heavy scientific debate as numerous recent studies have demonstrated the presence of hazardous substances in CR (e.g., heavy metals and carcinogenic polycyclic aromatic hydrocarbons (PAHs)) (Armada et al., 2022; Celeiro et al., 2018).

There is, however, one class of emerging organic contaminants (Lu et al., 2011), which have not yet been analysed in CR but may very well be in its constitution - siloxanes. Although there is not currently any bibliographical data confirming the use of siloxanes in tyre manufacturing, this hypothesis will be assessed due to their numerous current applications, which include the automotive industry (Chavoshani et al., 2020). Moreover, even if siloxanes are not added during the tyre production stage, they are present in the environment due to their common use in consumer and industrial products (Gaj & Pakuluk, 2015), and can potentially adsorb to tyre rubber on account of their hydrophobic nature (Teuten et al., 2009).

This work presents the first known study performed on siloxane extraction and quantification from CR applied as artificial turf infill in synthetic football fields, resorting to an ultrasound-assisted extraction (UAE) technique with QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) clean-up, followed by gas chromatography-mass spectrometry (GC-MS) quantification. Also, the human exposure to VMSs in CR from synthetic turf football fields (through incidental ingestion and dermal absorption) was estimated based on models developed by other authors. This study will pave the way for a subsequent risk assessment study, which will evaluate whether human contact with these contaminants may result in serious health repercussions.

2. Introduction

2.1. End-of-Life Tyres (ELTs)

End-of-Life Tyres (ELTs) are defined as ‘used tyres that cannot be/are not reused for its originally intended purpose and are not retreaded’ (MWH, 2004). The World Business Council for Sustainable Development (WBCSD) estimates that approximately one billion ELTs are generated globally on a yearly basis (WBCSD, 2021). This number will likely continue to increase in the upcoming years, as the global tyre industry is expected to follow an average compound annual growth rate (CAGR) of 3.3% from 2019 to 2024 (Smithers, 2019).

ELTs require several decades for the natural degradation process to take place, due to the cross-linked structure of rubber and the presence of stabilizers and other additives (Ferrão et al., 2008). In the past, these tyres would be illegally disposed in stockpiles, prone to cause soil, air or water pollution (USTMA, 2020). This led to an effort being made by legal authorities in order to eliminate these stockpiles and instead dispose of ELTs in specifically assigned landfills or incinerators. However, this approach is still not ideal, as both options can carry a substantial environmental impact. Tyres in landfills, besides occupying a large space, can present a fire hazard, harbour disease vectors (e.g., mosquitoes and vermin) and leach toxic contaminants (e.g., metals and low molecular weight additives) (Adhikari et al., 2000; EPA, 2010). Incineration, on the other hand, leads to the emission of not only air macropollutants (carbon dioxide (CO₂), nitrogen and sulphur oxides (NO_x and SO_x, respectively)), and particulate matter (Ortiz-Rodríguez et al., 2017), but also of micropollutants such as polycyclic aromatic hydrocarbons (PAHs), benzene, styrene, phenols and butadiene (EPA, 2016b).

In 1999, the EU released the Directive on the Landfill of Waste (*Directive (EC) No 1999/31*, 1999), banning the disposal of used whole tyres by 16 July 2003 and shredded tyres by 16 July 2006. Moreover, emission limits regarding incineration of ELTs were updated in the Directive on Incineration of Waste (*Directive (EC) No 2000/76*, 2000) in December 2008. As a result of these legal measures, sustainable management of ELTs has rapidly become the prioritized approach: according to ETRMA, 91% of ELTs were collected and treated for recycling and energy recovery in 2018 (ETRMA, 2020).

In Portugal, since 2001, there is a non-profit society established by the national tyre producers - Valorpneu - responsible for the management system of used tyres. Its most recent annual activity report, from 2020, states that 43,500 out of the 67,095 used tyres collected that year by Valorpneu (65%) were recycled. From the remaining fraction, 25% were used for energy recovery and 4% were retreaded, with the rest being submitted to other material recovery methods. Remarkably, none of the collected tyres were disposed in landfills, which demonstrates a good performance of the current management system. A portion of recycled tyre granulate (34%) was applied as infill in synthetic turf fields (Valorpneu, 2021).

2.2. Crumb Rubber

One way of recycling ELTs is through the production of crumb rubber (CR), which can be applied in artificial turf sports facilities, playgrounds, general safety surfaces, trails and walkways (Simon, 2010). It is estimated that 100-120 tons of CR are used on a full-size artificial turf football field, which is equivalent to approximately 25,000 ELTs (Halsband et al., 2020).

2.2.1. Composition

In 2017, the European Chemicals Agency (ECHA) published a report containing, based on information provided by ETRMA, a detailed list of chemicals used in tyre manufacturing (ECHA, 2017b). The average composition of car tyres commercialized in the EU market, prior to vulcanisation (*i.e.*, a chemical process used to improve the mechanical properties of rubber through heating at 140-160 °C, resulting in cross-linking of long rubber molecules (Nair & Joseph, 2014)), along with the respective function of each constituent, is presented in Table 1. Some of the following components are lost during the tyres' lifetime, while others may be acquired from the contact with asphalt. However, the composition of ELTs generally does not differ significantly from the one of brand-new tyres (Gomes et al., 2021).

Table 1. Main constituents of new car tyres - adapted from (ECHA, 2017b).

Material	Function	w/w (%)
Rubber - generally styrene butadiene rubber (SBR)/Elastomers	Traction/Stability (Bridgestone, 2022)	43
Carbon black and silica	Fillers (Halsband et al., 2020)	28
Metals	Reinforcement (Horner, 1996)/Adhesion (Fulton, 2005)	13
Oils	Rubber processing/Improved road adherence (ETRMA, 2010)	7.0
Textile	Reinforcement (Continental, 2022)	5.0
Accelerators/antidegradants	Faster vulcanization (Nocil Ltd., 2022) and improved rubber resistance (Sharj-Sharifi et al., 2020), respectively	2.5
Zinc oxide	Vulcanisation activator (USTMA, 2022)	2.0
Sulphur	Vulcanisation agent (Nair & Joseph, 2014)	1.0
Stearic acid	Softener/Filler dispersing agent (Dschagarowa et al., 2014)	1.0

Styrene butadiene rubber (SBR), the main constituent of car tyres (43% w/w), refers to a group of synthetic rubbers obtained from the copolymerization of styrene and butadiene (Speight, 2020), in which the hardness increases with the styrene/butadiene ratio (Song, 2017). SBR does not possess a crystalline molecular structure, meaning that it is often coupled with reinforcing fillers (28% w/w) in order to improve its physical properties (*e.g.*, resistance to abrasion and heat) (Chandrasekaran, 2010). The most common fillers are carbon black and silica, which are usually added in hybrid blends (Rattanasom et al., 2007). Regarding metals, typically the third most used material (13% w/w), lead is present in steel fibres which are used for reinforcement purposes (Horner, 1996), while cobalt acts as an adhesion promoter

between these fibres and rubber (Fulton, 2005). Other metals such as zinc are also employed in the composition of rubber additives. Aromatic oils are added to facilitate the processing of rubber compounds and improve tyre performance by providing increased road adherence (ETRMA, 2010), and textile materials (e.g., rayon, nylon and polyester) are applied in the manufacturing process of tyre cords, which also serve as reinforcement (Continental, 2022). Minor tyre constituents may include dispersing agents (e.g., stearic acid) and rubber vulcanization additives (e.g., zinc oxide and sulphur), among others.

CR essentially consists of ground/size-reduced recycled rubber (EPA, 2016a), and it is expected that its composition reflects the previous tyre manufacture. It can be obtained from two separate grinding methods: mechanical and cryogenic (Zafar, 2021). Before grinding, whole used tyres are pre-treated by being passed through a shredder which breaks them into chips. In the mechanical process, the chips are inserted in a granulator which turns them into small granules. Rubber is then separated from metals and textile, with the former being removed with magnets and the latter by combining shaking screens and wind sifters. If smaller granules are required, further grinding takes place in a secondary granulator and/or in a high-speed rotary mill. Meanwhile, in the cryogenic process the chips are first cooled to about -80 to -120 °C in a freezing chamber, using liquid nitrogen or other refrigerant fluids. At this temperature, rubber becomes more fragile, and as a result can be easily ground in a hammer mill. Cryogenic grinding, although more expensive, produces smaller and more homogeneous CR than the mechanical option (Zafar, 2021). In Portugal, there are currently two industrial facilities which produce CR from recycled tyre rubber: Genan, S.A. (formally Biosafe) and Biogoma, Lda., both employing the mechanical grinding method. Another company (Recipneu) was using the cryogenic method, but the facilities were closed in 2019.

2.2.2. Harmful Chemicals in Crumb Rubber

Many chemicals which were found in CR composition are considered hazardous by ECHA and deserve a close attention - PAHs, heavy metals, phthalates, and volatile/semi-volatile organic hydrocarbons (VOCs and SVOCs, respectively), among others (ECHA, 2017a).

PAHs are formed during the incomplete combustion of fossil fuels (Gomes et al., 2021) and can occur in tyres as impurities both in carbon black and extender oils (ECHA, 2017b; Geiss et al., 2018). A number of PAHs have caused tumours, reproductive problems and other effects in animals submitted to laboratorial tests (EPA, 2008), with eight of them being included in the EU's Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) law due to their carcinogenic properties. Out of the hundreds of known existing PAHs, sixteen have been designated by the United States (US) Environmental Protection Agency (EPA) as High Priority Pollutants: 16 EPA PAHs category (EPA, 2014b).

About heavy metals, several of them have been detected in tyre tread: manganese (Mn), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), cadmium (Cd) and lead (Pb) (Fukuzaki et al., 1986). Zn appears as the prevalent element (Gomes et al., 2021), deriving from the zinc oxide (ZnO) used in the vulcanisation process - see Table 1. Lead and cobalt are also present in rubber tyre composition, as previously discussed. The remaining heavy metals are not part of a tyre's original composition, but instead are likely assimilated during contact with the road surface - these particles are emitted as part of brake dust, road paint, diesel exhaust particles, road construction materials, or car catalyst materials

(Adachi & Tainosho, 2004). Heavy metals may present a substantial problem in synthetic football fields, as leachates originated from rainwater and watering for maintenance purposes are transported to nearby sewage waters, groundwater and/or natural surface waters (Gomes et al., 2021).

Plasticizers are employed in rubber formulations to lower its viscosity and increase its flexibility at low temperatures (Zhao et al., 2018). Phthalate esters (PAEs) and bisphenol A (BPA) are commonly used as plasticizers and have many other applications besides the tyre industry: phthalates are commonly used in food packages and children's toys (Mu et al., 2018), while BPA is used in coatings and dental fillers (Staples et al., 1998). Both PAEs and BPA have been referenced by the Center for Disease Control and Prevention (CDC) as contaminants of ecosystems and humans (CDC, 2018).

The US EPA defines VOCs as compounds that have a high vapour pressure and low water solubility (EPA, 2022). The main sources of VOCs in CR are solvents used in tyre production for multiple purposes - binding different layers of rubber, extruding, sidewall, curing press spray and finishing paint (EPA, 2000; Okopol, 2009). SVOCs, on the other hand, are a subgroup of VOCs which possess higher molecular weight and lower vapour pressure. SVOCs are slowly emitted and partition among the gas phase, airborne particles and dust fractions (Ait Bamai, 2020). The main SVOCs present in CR are PAHs and phthalates (EPA, 2017), although other semi-volatile chemicals have been detected (e.g., polychlorinated biphenyls (PCBs)) - suggesting that they can also be included in tyre formulations (Gomes et al., 2021). There are studies indicating that the inhalation of VOCs and SVOCs could be hazardous (Simon, 2010), and therefore watering of artificial turf football fields should be performed regularly in order to prevent excessive surface temperatures which degrade the properties of the material and favour the granules-to-air partition of VOCs and SVOCs (Gomes et al., 2021). This can be particularly relevant in indoor fields (especially if they lack adequate ventilation), as the concentration of VOCs can be up to ten times higher indoors in comparison to outdoors (EPA, 2022).

Other potentially toxic compounds found in rubber tyre formulations are nitrosamines (formed during vulcanisation), benzothiazoles (vulcanisation accelerators) and secondary amines (rubber antioxidants) (van Rooij & Jongeneelen, 2009).

2.2.3. Current Legislation on Crumb Rubber

Several of these hazardous chemicals are currently restricted (or even banned) in some of its specific applications under international environmental legislation: eight PAHs, heavy metals (Zn, Pb, As, Cr and Cd), phthalates, PCBs and nonylphenols. However, except for the PAHs, none of the restrictions apply explicitly to CR.

Eight PAHs are included in EU's REACH law (*Regulation (EC) No 1907/2006*, 2006) as carcinogenic (REACH-8 PAHs): benzo[a]pyrene (BaP), benzo[e]pyrene (BeP), benzo[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbFA), benzo[j]fluoranthene (BjFA), benzo[k]fluoranthene (BkFA), and dibenzo[a,h]anthracene (DBAhA). The previous classification results from these PAHs' ability to release highly reactive intermediates capable of interacting with cellular macromolecules (WHO, 2000). On July 2021, the EU published an amendment (*Regulation (EU) No 1199/2021*, 2021), taking effect from August 2022, which expanded the scope of restricted REACH-8 PAHs applications to 'granules or mulches' used as 'infill material in synthetic turf pitches' and/or 'in loose form on playgrounds or in sport applications'

- restricting the total concentration of these PAHs to $\leq 20 \text{ mg.kg}^{-1}$ (or 0.002% weight). According to the same amendment, granules are defined as ‘mixtures that appear as 1-4 mm solid particles, which are made from rubber or other vulcanized or polymeric material of recycled or virgin origin, or obtained from a natural source’ and mulches as ‘mixtures that appear as 4-130 mm length by 10-15 mm width flake-shaped solid particles, which are made from rubber (...)’. This limit is, however, 20 times higher in comparison to the one established by REACH for rubber components in general consumer products which ‘come into direct as well as prolonged or short-term repetitive contact with the human skin or oral cavity, under normal or reasonably foreseeable conditions of use’ (e.g., clothing, accessories, household utensils and sport equipment) - 1 mg.kg^{-1} (*Regulation (EU) No 1199/2021*, 2021).

Four plasticizers are also included in REACH (REACH-4 plasticizers): di-isobutyl phthalate (DIBP), dibutyl phthalate (DBP), benzyl butyl phthalate (BBP) and diethylhexyl terephthalate (DEHP). Its concentration is limited to 1 g.kg^{-1} (or 0.1% weight) ‘in toys or childcare articles of plasticized material’, with this value applying both to individual and total concentration of these plasticizers. The stated ‘plasticized material’ includes ‘polyvinyl chloride (PVC), polyvinylidene chloride (PVDC), polyvinyl acetate (PVA), polyurethanes, any other polymer (including rubber material) except silicone rubber and natural latex coatings (...)’. Although this restriction does not explicitly apply to CR, it is still of relevance as this material consists of recycled rubber tyres and children can frequently come in contact with it in sports fields and in playgrounds, where there is a risk of exposure to harmful substances through dermal contact, incidental ingestion and inhalation (NIH, 2018).

Moreover, the Stockholm Convention on Persistent Organic Pollutants (POPs) explicitly prohibits the production and use of PCBs, as there are studies which report adverse effects from exposure to these chemicals (Warmuth & Ohno, 2013). The Convention’s parties are obliged to completely eliminate the use of PCBs by 2025 (*Stockholm Convention on Persistent Organic Pollutants*, 2001).

In spite of some studies performed over recent years on the detection of these hazardous chemicals in CR samples collected from synthetic turf football fields, to this day none have focused on siloxanes as a target class of compounds, meaning that this work will therefore become a pioneer on this subject.

2.2.4. Human Exposure to Crumb Rubber

Naturally, the detection of hazardous chemicals in CR, with some of them even being considered as carcinogenic, has caused concern among environmental entities regarding the safety of people who frequently come into contact with this material (e.g., athletes in synthetic sports fields and children in playgrounds). For instance, the aforementioned ECHA report from 2017 (ECHA, 2017a), although not stating a clear health hazard, underlined the scarcity of studies in this matter and urged for further assessments. And in fact, EPA is currently working on the second part of an official report named Federal Research Action Plan on Recycled Tire Crumb Used on Playing Fields and Playgrounds (FRAP), which will include results from a biomonitoring study aimed to investigate the risks associated with CR infill synthetic fields (EPA, 2019a). The results from this study will certainly provide a more detailed assessment of human exposure to CR. Nevertheless, there are already others which have been carried out on this subject - see State of the Art.

2.3. Siloxanes

Although there is a lack of bibliographical data indicating that siloxanes are deliberately added to the rubber tyre manufacturing process, the fact that numerous additives are included in tyres to improve its overall performance and resistance, along with the current widespread use of siloxanes, has led to the formulation of the hypothesis that they may be present in CR. Regarding the potential use of siloxanes as additives, a study conducted by Brinke (2002) suggested that silica (SiO_2) can be used as a reinforcement filler in rubber tyres together with silane coupling agents containing siloxane bonds. Nevertheless, there is no actual bibliographical confirmation of the presence of siloxanes in this process.

Moreover, CR has recently been included in the microplastics (MPs) group by ECHA (ECHA, 2021) - defined by the EU as fragments of plastic smaller than 5 mm (EU, 2022). Tyre particles are not considered plastics from a material perspective, nevertheless they are commonly included in the MPs group since they possess man-made, synthetic products of environmental concern (Lange et al., 2021), in light of the microplastic definition proposed by (Verschoor, 2015). In addition to the danger posed to ecosystems due to MPs ingestion by animals, which can lead to fatal outcomes as enzymes are not able to degrade them, MPs can also be harmful to the environment by acting as vectors of chemical pollutants (Arienzo et al., 2021). Some of the physicochemical properties of siloxanes lead to them being highly persistent and accumulative, and as such their potential accumulation in CR must be taken into consideration.

2.3.1. Characterization and Physicochemical Properties

The International Union of Pure and Applied Chemistry (IUPAC) defines siloxanes as ‘saturated silicon-oxygen hydrides with unbranched or branched chains of alternating silicon (Si) and oxygen (O) atoms’ (Gold, 2019). Various substituent groups, usually organic, (e.g., methyl, ethyl, propyl, phenyl, fluoroalkyl, aminoalkyl) - organosiloxanes - can be bound to each Si atom (Mojisiewicz-Pieńkowska et al., 2016), with methylsiloxanes being the predominant form. In fact, many of the distinct properties of siloxanes originate from the presence of methyl instead of larger organic substituents (Owen, 1980). Methylsiloxanes can be classified, in increasing order of molecular weight, as volatile methylsiloxanes (VMSs), polydimethylsiloxanes (PDMSs), or polyethermethylsiloxanes (PEMSs) (Fromme, 2019). This work will focus on the detection and quantification of VMSs.

VMSs are found in either linear or cyclic structures (LVMSs or cVMSs, respectively), depending on their polymerization degree and spatial configuration. Since the polymeric structure of these compounds can be somewhat complex, an abbreviated nomenclature system was implemented: linear siloxanes are represented by the capital letter L and cyclic siloxanes by D, followed by the number of Si atoms present in the molecule (Gaj, 2020). The name (full and abbreviated), Chemical Abstracts Service (CAS) registry number, molecular formula/structure, molar mass, boiling point and vapour pressure (at 25 °C) of some representative LVMSs and cVMSs are listed in Table 2.

Table 2. Nomenclature and structure of common LVMSs and cVMSs (adapted from Gaj (2020)).

VMS type	Full name Abbreviated name CAS No.	Formula	Structure	Molar mass (g.mol ⁻¹) ^[1]	Boiling point (°C) ^[1]	Vapour pressure at 25 °C (mmHg) ^[a]
LVMS	Hexamethyldisiloxane L2 107-46-0	Si ₂ -O- (CH ₃) ₆		162.4	99.0	42.10
	Octamethyltrisiloxane L3 107-51-7	Si ₃ -O ₂ - (CH ₃) ₈		236.5	153.0	3.34
	Decamethyltetrasiloxane L4 141-62-8	Si ₄ -O ₃ - (CH ₃) ₁₀		310.7	194.0	0.37
	Dodecamethylpentasiloxane L5 141-63-9	Si ₅ -O ₄ - (CH ₃) ₁₂		384.8	232.0	0.10
cVMS	Hexamethylcyclotrisiloxane D3 541-05-9	Si ₃ -O ₃ - (CH ₃) ₆		222.5	134.0	3.53
	Octamethylcyclotetrasiloxane D4 556-67-2	Si ₄ -O ₄ - (CH ₃) ₈		296.6	175.8	1.05
	Decamethylcyclopentasiloxane D5 541-02-6	Si ₅ -O ₅ - (CH ₃) ₁₀		370.8	210.0	0.20
	Dodecamethylcyclohexasiloxane D6 540-97-6	Si ₆ -O ₆ - (CH ₃) ₁₂		444.9	245.0	0.02

^[a] Data collected from PubChem - <https://pubchem.ncbi.nlm.nih.gov> (Accessed in March 2022).

VMSs are widely present in personal care products' (PCPs) formulations (e.g., creams, lotions, bath soaps, shampoo and hair care products) (Capela et al., 2016) due to their distinctive physicochemical properties (e.g., low surface tension, hydrophobic nature, transparency, lack of smell) (Gaj, 2020), with particular relevance to cVMSs, which are used in cosmetics as emollients and solvents (Johnson et al., 2011). Moreover, they are used as intermediates in the manufacturing process of many products of consumer and industrial applications (e.g., silicone polymers, elastomers and resins) (Horii & Kannan, 2020). However, despite all their virtues, VMSs also possess some physicochemical properties which make

them potential persistent environmental pollutants: lipophilicity (bioaccumulation risk in hydrophobic particles), high durability (can potentially undergo long-range transport), high volatility at ambient conditions (compromises air quality) and high organic carbon/water partition coefficient (K_{OC}). The latter promotes adsorption in sediment and sewage sludge and, as a consequence, siloxanes can enter anaerobic digestors at wastewater treatment plants (WWTPs) and volatilize into biogas (Gaj, 2020).

2.3.2. Consumption and Safety

The special physicochemical properties of siloxanes make them suitable to a wide spectrum of applications. It is estimated that this number exceeds 150,000 (Mojsiewicz-Pieńkowska et al., 2016), and as such it is required that these compounds are produced at a very large scale in order to meet the existing demand - predicted to have totalled more than 3 million tons in 2021 (ECHEMI, 2021). Siloxanes first emerged as a priority environmental pollutant in 2010, and as they started being measured in air, wastewater, river water and landfill gases, chronic exposure has become a high-priority public health concern (Tilley & Fry, 2015).

Naturally, the mass production of siloxanes, along with their status as environmental pollutants, have raised many questions regarding their safety. Several research tests have shown that PDMS polymers are neutral to warm-blooded organisms (although further investigation is required for corroboration). The same, however, cannot be said for VMs, since there are laboratorial studies conducted on animals which have concluded that some of them may be toxic for the human body. One of them reported that high inhalation doses of cVMS D4 exhibited reproductive effects in rats (Gaj, 2020), while a high chronic exposure to D5 was found to be carcinogenic; no conclusions were made regarding the toxicity of D6, however this siloxane is also of particular relevance due to its structural resemblance to D4 and D5 (Rücker & Kümmerer, 2015). Furthermore, *ex-vivo* studies performed on human skin have shown that D4, D5 and D6 are able to overcome the skin barrier and penetrate into its deeper layers (*i.e.*, epidermis and dermis), although a cytotoxicity analysis on HaCaT cells concluded that they are non-toxic to this particular cell line (Krenczkowska et al., 2019). Nevertheless, the fact that these compounds can accumulate in skin layers where blood and lymphatic vessels are located is very worrying, and therefore further cytotoxicity studies must be performed in other cells in order to obtain a more detailed overall assessment of the safety of siloxanes.

The ECHA identified D4, D5 and D6 as substances of very high concern (SVHC): persistency, bioaccumulation and toxicity criteria led to all three being classified as very persistent and very bioaccumulative (vPvB), with D4 being considered as persistent, bioaccumulative and toxic (PBT) (ECHA, 2018). This assessment, however, is disputed by the Global Silicones Council (GSC, 2020), who are convinced that, based on available scientific data, D4, D5 and D6 are safe for human health and the environment, and therefore should not be regarded as PBTs/vPvBs.

2.3.3. Current Legislation on Siloxanes

In the EU, there is only a single situation where the use of siloxanes is regulated. D4 and D5 are currently restricted under the REACH law, with these cVMSs having been added to Annex XVII on 10 January 2018. Entry M46 states that D4 and D5 'shall not be placed on the market in wash-off cosmetic products in a concentration equal to or greater than 0.1% by weight of either substance, after 31 January

2020'. Wash-off cosmetics are defined as 'cosmetic products that, under normal conditions of use, are washed off with water after application' (*Regulation (EC) No 1223/2009*, 2009).

The current legislation, however, merely imposes restrictions on a specific class of PCPs, while cosmetics which do not require wash-off, along with domestic and industrial use products, remain completely unrestricted as of today. Moreover, D6, which ECHA classified as vPvB, as mentioned previously, is not included in REACH's list of chemicals. These notable gaps in siloxane legislation led to ECHA releasing, on 14 April 2021, a formal recommendation (ECHA, 2021) stating that all applications of cVMSs D4, D5 and D6 should be tightly regulated, as they are hazardous, produced in high volumes and widely used. The European Commission (EC) has not made a final decision on this matter, and once again the GSC firmly advocated against ECHA's recommendation (GSC, 2021).

2.3.4. Human Exposure to Siloxanes

As aforementioned, VMSs are frequently applied in PCPs. However, they can also appear in a variety of domestic and industrial products as impurities released from the hydrolysis of PDMSs (Accettola et al., 2008). VMSs can occur in product formulations in concentrations ranging from a few nanograms per gram to several tens of weight percent (Tran et al., 2019).

A study performed on samples from 123 different PCPs commercialized in Portugal (Capela et al., 2016) concluded that VMSs were present in 96% of the analysed samples: lVMSs were found in 52% of the samples with a maximum concentration of $7.85 \mu\text{g.g}^{-1}$ (L5 in aftershave), while cVMSs were the most predominant compounds: detected on 94% of the samples with a maximum of $1,203 \mu\text{g.g}^{-1}$ (D3 in adult shampoo). Regarding other products besides PCPs, high concentrations of lVMSs and cVMSs - maximum of 8,280 and 72,700 $\mu\text{g.g}^{-1}$, respectively (Xu et al., 2015) - were measured in several industrial products and additives commercialized in China (e.g., spot remover, fabric softening agents, lubricants, polishes and paints). VMSs were also detected in products destined for children (e.g., pacifiers, tethers and toys), although at considerably lower levels - ranging from 0.005 to 22.2 $\mu\text{g.g}^{-1}$ (Xu et al., 2017).

Since VMSs are present in a large number of daily-use products and were found in numerous environmental matrices, it is important to study and estimate possible routes of human exposure. There are three main routes of human exposure to siloxanes: dermal absorption (e.g., through use of PCPs), inhalation and ingestion (e.g., through dust particles), with the two latter being especially relevant in indoor environments. Exposure doses can be estimated based on Equation 1 (Tran et al., 2019):

$$ED = \frac{C_{VMS} \times f}{BW} \quad (1)$$

where ED is the exposure dose, C_{VMS} the concentration of VMSs in PCPs, air, or dust (whether the exposure is being quantified through absorption, inhalation or ingestion, respectively), f the absorption/inhalation/ingestion rate and BW the average body weight of the analysed population. Several exposure studies (for L2-L16 and D3-D7) conducted in indoor environments from numerous countries located in Europe, America and Asia showed maximum human exposure doses of 3.19 and 0.011 $\mu\text{g.kg}_{BW}^{-1}.\text{d}^{-1}$ (for inhalation and ingestion, respectively) (Tran et al., 2019). On the other hand, Capela et al. (2016) estimated a dermal exposure dose (for L2-L5 and D3-D6) of 25.0 $\mu\text{g.kg}_{BW}^{-1}.\text{d}^{-1}$ for adults and 0.350 $\mu\text{g.kg}_{BW}^{-1}.\text{d}^{-1}$ for children regarding PCPs commercialized in Portugal, with the main "contributors"

being body moisturizer for adults and shampoo/shower gel for children. From these results, it can be concluded that dermal absorption is the main route of human exposure to VMSs in PCPs.

2.4. Analysis of Organic Microcontaminants from Crumb Rubber

Tyre rubber, as mentioned above, is a complex matrix comprised of several different chemicals and components which in most cases demand an adequate (and often complex) analytical procedure (including extraction, clean-up and quantification) to correctly determine their content in CR samples, with VMSs being no exception to this rule. As previously discussed, to this day there are still no published studies on siloxane analysis in CR, and therefore the methods here introduced were divided in two categories: those commonly used for the analysis of micropollutants in CR (in the present section), and the ones used for the analysis of VMSs in other solid matrices (in section 2.5).

2.4.1. Ultrasound-Assisted Extraction

Ultrasound-assisted extraction (UAE) is a highly versatile technique which can be applied to extract multiple organic contaminants from food and environmental samples (Albero et al., 2019), in order to improve solvent extraction efficiency and reduce the time of analysis (Moldoveanu & David, 2021).

Samples are exposed to ultrasonic waves, with this eventually leading to cavitation (*i.e.*, the generation of small vacuum bubbles in the liquid) (Weggler et al., 2020), which causes localized increases in temperature and pressure (Mussatto, 2015) and, consequently, the mass transfer of the analytes is improved (Herrero et al., 2012). UAE is a technique of simple application, has relatively low instrumental requirements (all it takes is an ultrasonic probe or bath), is fairly cheap in comparison to other methods (*e.g.*, Soxhlet extraction) (Mussatto, 2015) and reduces the amount of organic solvent used in the extractions, while still providing high recovery values and short extraction times (Pingret et al., 2012).

Recent studies have resorted to UAE for the extraction of PAHs, plasticizers (phthalates and phenols) and other additives (*e.g.*, PCBs) in CR (Armada et al., 2022; Celeiro et al., 2021; Halsband et al., 2020; Skoczyńska et al., 2021).

2.4.2. Soxhlet Extraction

Soxhlet extraction (SE) is one of the most popular methods for the extraction of analytes from solid materials (Zygler et al., 2012) and has also previously been applied (although not as often) in CR samples for the analysis of PAHs (Zhang et al., 2008). The samples are first placed in a disposable thimble which is gradually filled with condensed fresh solvent coming from a distillation flask. Once the thimble becomes practically filled, a siphon aspirates the liquid (containing the extracted analytes) back into the distillation flask, and this procedure is repeated several times to improve target analyte recovery (Luque de Castro & García Ayuso, 2000).

SE is commonly used mainly due to its simplicity and good extraction results (Mussatto, 2015), but it is time-consuming (de Boer, 2005) and not highly selective, and therefore generally requires further clean-up (Ridgway et al., 2012).

2.4.3. Instrumental Analysis (GC-MS)

GC-MS has long been considered the “gold standard” concerning the analysis of VOCs and SVOCs in complex mixtures (Stein, 1999), and it is by far the predominant method applied in the studies found in the literature targeting CR. GC-MS combines two techniques - gas chromatography (GC) and mass spectrometry (MS) - as illustrated in Figure 1.

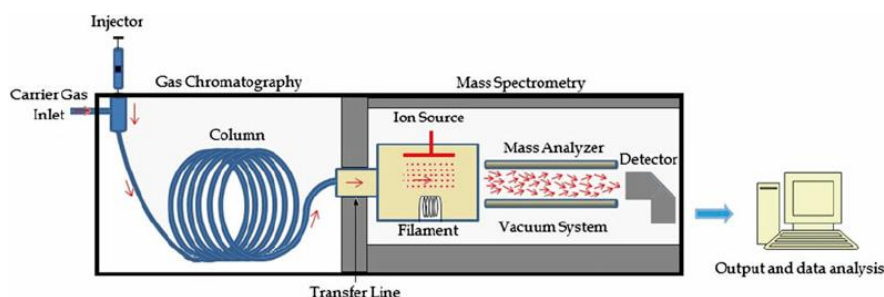


Figure 1. Schematic representation of the main parts of a GC-MS system (Emwas et al., 2015).

GC is an analytical technique which allows the separation of highly complex mixtures based primarily upon differences of boiling point/vapor pressure and polarity of its different constituents. Samples are inserted in the equipment via the injector, and the carrier gas (mobile phase) - an inert gas with low adsorption capacity (e.g., helium and nitrogen) (Forgács & Cserhádi, 2003) - drags the sample onto the column (stationary phase), where the different volatile compounds are separated (Stauffer et al., 2008). There are two main types of GC columns: packed (*i.e.*, short, thick columns made of glass or stainless-steel tubes) and capillary (*i.e.*, a thin, fused silica glass or metal tube). Packed columns can handle very large sample volumes, however capillary columns are generally preferred as they produce sharper peaks and provide better separation, especially in high-sensitivity analyses (Shimadzu, 2022). Injectors, in turn, can operate in either split or splitless mode: in the former, the split vent (used to purge excess sample flow) is permanently open, while in the latter the vent is closed during part of the injection process, leading to a larger portion of sample entering the column (Marriot & Carpenter, 1996).

After the chromatographic separation, the components enter a detector able to quantify their respective concentrations in the injected sample. The MS presents numerous advantages over other types of detectors (e.g., flame ionization, electron capture, flame photometric and infrared absorption detectors), since it can provide unique information that facilitates the identification of a samples' constituents and shows high sensitivity for volatile compounds (Abian, 1999). MS measures the mass-to-charge ratio (m/z) of charged particles of ionized molecules in the gas phase (Noberini et al., 2016).

There are three key constituents to a MS: ionizer, analyzer and detector (Sengupta et al., 2019). The ionizer transfers large analytes of interest into gas-phase ions, which are then stored in a mass analyzer that separates them based on their respective m/z ratios. A type of analyzer frequently used in GC-MS is the quadrupole analyzer, which determines m/z by applying radio frequency and direct current voltages to four precisely parallel rods. As the voltage increases, only ions with a high enough m/z will be able to pass through the quadrupole and reach the detector. 3D ion trap analyzers are also common. These instruments operate similarly to a quadrupole, but instead of the parallel rods, there are two

hyperbolic metal electrodes (facing each other) and a ring electrode placed between them (Clarke, 2017). Ions are confined in a circular flight path and released in increasing order of m/z (March, 2017).

An electric field is generated by each ion, whose amplitude will be scanned by the detector, allowing the emission of a mass spectrum (Rauniyar et al., 2007). The selectivity of MS can be further optimized by employing a multiple reaction monitoring (MRM) scan mode, consisting of monitoring multiple transitions for a particular precursor ion (Meng & Veenstra, 2013).

Generally, the major challenge in evaluating a mass spectrum is the vast number of generated peaks (Lederer & Brandt, 2021). This is the main reason why GC is performed before MS, since it will provide a high-resolution separation which will minimize this difficulty.

2.5. Analysis of Siloxanes from Solid Matrices

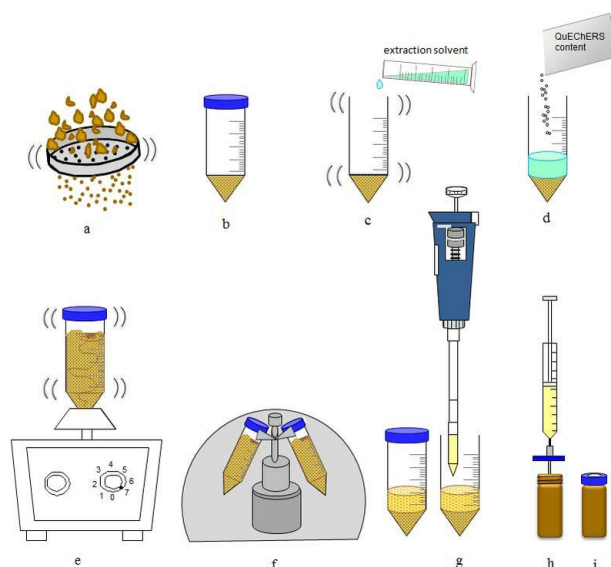
The instrumental analysis/quantification of VMSs in environmental matrices is also predominantly carried out by GC-MS (Ramos et al., 2016), but since this technique was addressed above, the present section will focus on extraction methods.

VMS extraction can prove to be a very challenging process, as the presence of siloxane-based materials everywhere poses a significant problem in terms of external contamination of samples: both from PCPs used by people handling the samples and from siloxanes which may be present in laboratorial equipment/consumables (e.g., PDMS-coated capillary columns, GC injector septa and solvents). Therefore, the employed extraction methods must be expedite and reliable (Ramos et al., 2016). The following methods employed for VMS extraction will be addressed: UAE with QuEChERS, pressurized liquid extraction (PLE) and Soxhlet extraction (SE).

2.5.1. UAE with QuEChERS

QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) was first introduced for the determination of pesticide residues in fruits and vegetables as a rapid, simple, inexpensive, effective, safe alternative to conventional methods. QuEChERS uses a low amount of solvents (environmental-friendly), does not require any special equipment, avoids the use of glassware (eliminating the need for time-consuming cleaning and large storage spaces), while still providing high quality results (Anastassiades et al., 2003). Over the years, this technique has seen its popularity increase due to its many virtues (e.g., simplicity and adaptability to multiple matrices (Perestrelo et al., 2019)) and its scope of target compounds has expanded to pharmaceuticals, PAHs and several persistent organic pollutants (POPs) (Kim et al., 2019).

A scheme of a QuEChERS extraction procedure (for solid matrices) is presented in Figure 2.



a: sieving; b: falcon tube with solid sample; c: addition of extraction solvent; d: addition of QuEChERS reagents; e: vortex; f: centrifugation; g: supernatant removal; h: syringe filtration; i: final extract.

Figure 2. Scheme of QuEChERS extraction (adapted from Paiga et al. (2015)).

QuEChERS extraction of solid samples is comprised of three main steps (in this order): comminution, extraction and clean-up. Comminution (*i.e.*, the reduction of solid particle size) (Yang, 2015) is a sample pre-treatment step which allows a maximized surface area and, consequently, a more efficient extraction (Kim et al., 2019). The selected extraction solvent, meanwhile, must have a high affinity with the target analyte. A non-polar solvent is, in theory, fit for VMSs (due to their low polarity), with hexane (*n*-Hex) having proved to be a good selection for VMSs in PCPs, since high recovery values were obtained (74-104%) (Capela et al., 2016). However, depending on the matrix, other solvents may prove to be better for extraction (*e.g.*, in VMSs extraction from pine needles, *n*-Hex was coupled with polar solvents dichloromethane (DCM) or acetone (Acet) in 1:1 (v/v) mixtures (Ramos et al., 2016)). Ideally, multiple solvent options should be tested to assess which one is more suited to the specific matrix in question. After adding the extraction solvent, the samples can be vortexed in order to increase the specific area for mass transfer and reduce the diffusion distance (Zimila et al., 2021). The main extraction step can include UAE, with the extraction likely facilitated by the presence of drying and ionic strength-promoting salts (*e.g.*, magnesium sulphate (MgSO_4) and sodium chloride (NaCl), respectively) (Kim et al., 2019).

For the dispersive-SPE clean-up process, sorbents are added to the analytical solution followed by agitation (*e.g.*, in a vortex), which promotes the contact between the sorbent and the analytes (Islas et al., 2017). Primary and secondary amine (PSA) bonded silica sorbent and octadecyl-silica (C18) are effective sorbents for VMS extraction from PCPs, as no significant matrix effects were experienced during its quantification. PSA and C18 are used to remove polar and non-polar interferences, respectively (Capela et al., 2016). Finally, the obtained extract can be further purified by carrying out a filtration with polytetrafluoroethylene (PTFE)-membrane syringe microfilters. This technique allows the removal of small impurities which can clog the GC syringe during sample injection.

Overall, extractions carried out with QuEChERS clean-up generally perform better in comparison to other methods (*e.g.*, microextraction in packed sorbent (MEPS) and stir bar sorptive extraction (SBSE)).

However, there are a few instances in which this trend was not confirmed (Perestrelo et al., 2019). As such, two alternatives have also been used for VMS extraction: SE (already discussed) and pressurized liquid extraction (PLE).

2.5.2. Pressurized Liquid Extraction

This technique has been used to extract VMSs from silicone products (silicone nipples and bakeware) (K. Zhang et al., 2012). Samples are first dispersed with an inert material (*e.g.*, sand) to prevent agglomeration (Zhang & Wong, 2011) and then placed in an extraction vessel/cell, which is inserted in an oven. The solvent is pumped from an external bottle into the extraction cell, and the extraction procedure is performed under pressure (500-3000 psi) and heat (50-200 °C) (Picó, 2012).

PLE is an automated, fast, and solvent-reducing (Lehotay & Schenck, 2000) method which provides excellent extraction efficiency, can be applied to a wide variety of samples (Zhang & Wong, 2011) and may include a clean-up step (*e.g.*, using diatomaceous earth as a sorbent in the extraction cell (Toledo-Neira et al., 2013)). However, it requires a significant initial investment and may not be able to withstand a highly effective extraction process in complex matrices (Basheer et al., 2012).

3. State of the Art

3.1. Organic Microcontaminants in Crumb Rubber

This is a pioneer work in the sense that although several studies have been conducted over recent years on the determination of hazardous chemicals in CR samples collected from synthetic football fields, none of which have included siloxanes (in particular VMSs) as a target analyte. Naturally, there is no previous evidence to serve as basis for comparison, but it is possible to present an overview of some relevant recent studies on related subjects, namely the methodologies carried out and their main results and conclusions. Many of the same principles will be transferred to VMSs analysis since the extraction matrix is essentially identical, even though there are several variables which can come into play - associated not only to the ELTs themselves (*e.g.*, tyre manufacturer, age and conditions of use during its lifespan) but also to the fields in which they are applied (CR granulometry, type of field - indoor or outdoor - and location).

The various methodologies used by EPA for the field sample collection and standard operational procedures (SOPs) (*i.e.*, research methods reviewed and approved internally by EPA to meet established data quality objectives) developed to examine CR used as infill in synthetic turf fields are compiled in the following document: EPA (2019b). Although these methods are specific and were not subjected to any validation procedures, EPA claims that they can easily be modified or adapted to other studies performed on similar matrices. The studies consisted of direct measurement of metals and SVOCs (PAHs, phthalates, thiazoles and other rubber-related compounds) in CR particles. Samples were collected from 40 fields (indoor and outdoor) located in the USA, with seven different sampling locations being identified for each field. The collected individual samples were then divided in equal portions, composited and submitted to laboratorial analysis. In terms of organic contaminants (the closest in terms of properties to VMSs, the focus of this work), SVOCs were extracted with 10 mL of Acet/*n*-Hex 1:1 (without ultrasound) and quantified through GC-MS with a 5% phenyl-methyl (VF-5ms) capillary column. It is important to state that although not official, the large majority of studies performed on CR rely on the methods described by EPA, although slight modifications are usually implemented in each case to optimize analytical performance.

The first study (from the ones found in the literature search - see Table 4) to report the content of organic hazardous substances in CR applied in synthetic football fields was carried out in Norway (Plesser & Lund, 2004). Rubber granulates were analysed for the presence of PCBs, 16-EPA-PAHs (*i.e.*, PAHs which were considered High Priority Pollutants by EPA in 1976 (Andersson & Achten, 2015)), phthalates and phenols. No detailed information could be found on the employed analytical procedures. Three samples of recycled CR were considered: samples 1 and 3 consisted of coarse-grained material, while sample 2 was fine-grained (coarse-grained particles are larger in comparison to fine-grained). Samples 2 and 3 were supplied by the same manufacturer. The concentration of PAHs (67 mg.kg⁻¹) largely exceeded the Norwegian Pollution Control Authority's (NPCA) normative value of 2.0 mg.kg⁻¹ in all samples, with the concentration of PCBs in sample 3 (0.20 mg.kg⁻¹) also exceeding NPCA's limits (0.01 mg.kg⁻¹). Despite

coming from the same manufacturer, samples 2 and 3 showed considerable variation (e.g., PCBs were detected in sample 3 but not in sample 2), which can possibly be related to the granulometry. However, this does not seem to be the case, as samples 1 and 2 showed similar results (despite also differing in terms of granulometry). Phthalates and phenols were present in all samples.

Zhang et al. (2008) determined the content of the 16-EPA-PAHs in samples of CR collected from synthetic turf parks located in the USA (with distinct field ages: from 2 months to 7 years after application). PAHs were extracted by means of a SE with DCM and quantified through High Performance Liquid Chromatography (HPLC). This study included samples from the same location but collected at different stages (the same field was sampled 2, 3 and 22 months after the synthetic turf's application), which allowed a pioneer assessment on the evolution of the concentrations of these chemicals as the field ages. PAH levels appeared to significantly decrease over time (38.2 to 35.4 mg.kg⁻¹ in a field age span of 2-3 months, and to just 4.4 mg.kg⁻¹ for a 22-month old field). It is important to state that this dynamic assessment is only valid in the event that CR is not added/replaced during the considered period.

The study carried out by De Groot et al. (2017) in the Netherlands started by analysing a group of samples collected from 100 fields located throughout the country. The CR samples were analysed for 45 different compounds: REACH-8 PAHs, phthalates, VOCs, benzothiazoles, phenols and PCBs. All of the target compounds were extracted using an organic solvent: petroleum ether and *n*-Hex for PAHs and phthalates (both solvents were tested separately), methanol for VOCs, and acetonitrile for PCBs and phenols. In all cases, instrumental analysis was performed by GC-MS. The measured concentrations of PAHs, phthalates, benzothiazoles and phenols showed to be consistent with the ones reported in other studies. Moreover, the concentration of PAHs was higher in more recent fields (as was reported by Zhang et al. (2008)), which indicates that these compounds can either be leached away with rain/irrigation water, evaporate (as they consist of SVOCs) or suffer chemical degradation. None of the analysed samples surpassed the 20 mg.kg⁻¹ (median of 5.8 mg.kg⁻¹ and maximum of 19.8 mg.kg⁻¹) limit for REACH-8 PAHs stated in the REACH legislation (*Regulation (EU) No 1199/2021*, 2021). The compliance with this limit could not be assessed in the previous studies since one of the eight carcinogenic PAHs was not analysed (BeP), likely due to the fact that the analyses took place several years before this restriction was first announced (in 2021).

The European Risk Assessment Study on Synthetic Turf Rubber Infill (ERASSTRI) (Schneider et al., 2020), carried out on behalf of European CR suppliers, began by quantifying the hazardous substance of infill CR material: the target organic analytes included PAHs, phthalates and 2-mercaptobenzothiazole (2-MBTZ), a vulcanisation agent referenced by EPA as a highly toxic substance (EPA, 1994). A total of 86 samples were collected - 29 from CR suppliers and 57 from synthetic turf sports fields - and divided in two groups: uncoated and coated (some recycling companies coat CR with coloured polyurethane, a binding agent (Garrett & Du, 2006)). PAHs were extracted by SE with *n*-Hex/toluene, while phthalates and 2-MBTZ were submitted to a simple organic solvent extraction - methyl *tert*-butyl ether (MTBE) for the former and methanol for the latter. 2-MBTZ was quantified via HPLC and the remaining substances via GC-MS. The REACH-8 PAHs concentrations (median of 4.71 mg.kg⁻¹) were similar to the ones reported by De Groot et al. (2017), with higher PAH concentrations being observed in uncoated material. However, a thorough explanation cannot be provided for these results as the number of coated samples is

significantly lower. This tendency was verified in practically all of the analysed contaminants. Only two phthalates (DEHP and diisononyl phthalate (DINP)) were found in the analysed samples and at low concentrations and 2-MBTZ was present at substantially lower concentrations than the other benzothiazoles.

Halsband et al. (2020) analysed three different groups of CR samples: one sent directly from a commercial supplier, and the remaining two destined for application as infill in football fields of Norway - one was already under usage for an unknown period and the other was yet to be applied (*i.e.*, used and unused, respectively). The commercial CR had a size range of 1.0-2.8 mm, and some of the granules were cryo-milled and sieved into three distinct size fractions: 250, 1000 and 1500 μm , respectively. The analysed chemicals consisted of metals, 16-EPA-PAHs, phenols, phthalates and specific organic additives (benzothiazole, *n*-cyclohexylformamide, acetophenone and phthalide). The organic compounds were analysed by GC-MS (after organic solvent extraction). 16-EPA-PAH concentrations were very similar to those reported by Plessner & Lund (2004) - mean of $52 \pm 8 \text{ mg.kg}^{-1}$ among the three sample groups. This time, PAH levels were higher in the “older” CR - this goes against the results of previous studies, which saw a time-decay of PAHs. However, it must be noted that in this case the samples were taken from two different fields, whereas previously they belonged to the same field. The commercial CR showed the highest PAH concentration: $58 \pm 7 \text{ mg.kg}^{-1}$. The most noticeable result to be reported was perhaps the substantial difference in additive concentration among the used and unused field samples: 39.6 and 737 mg.kg^{-1} , respectively. Nevertheless, there is a notable lack of information regarding the football fields where the sampling process occurred (namely the field age and the origin of the infill CR granules).

Celeiro et al. (2021) developed and validated an analytical method, consisting of UAE followed by GC-MS, for the analysis of numerous hazardous compounds in forty CR samples - PAHs, plasticizers (phthalates and adipates), antioxidants and vulcanisation agents. These samples were collected from synthetic football fields, outdoor and indoor playgrounds, urban pavements (tree protectors), commercial CR tiles (used for instance in gym floors), and scrap tires in the Galicia region (northwest Spain). This study also introduced the analysis of a possible alternative material to CR as infill for football fields: cork. BaP, considered the most carcinogenic out of the REACH-8 PAHs, was detected in all football field samples (in a maximum concentration of 3.6 mg.kg^{-1}). The median concentration of REACH-8 PAHs was identical to the one reported by De Groot et al. (2017): 6.0 mg.kg^{-1} . However, there were samples which exceeded the 20 mg.kg^{-1} limit for REACH-8 PAHs. 2-MBTZ was found in three of the samples (in a maximum concentration of 62 mg.kg^{-1}). In cork, only a few hazardous compounds were detected, and all of them at low concentrations: one PAH (phenanthrene (PHEN)), two plasticizers (diethyl phthalate (DEP) and BPA), and an antioxidant (butylated hydroxytoluene (BHT)). This indicates that cork granulate could potentially be a safer future alternative material to CR as infill for synthetic football fields.

Skoczńska et al. (2021) introduced an analytical method capable of extracting and quantifying a wide variety of aromatic compounds in CR: not only PAHs, but also heterocyclic aromatic compounds (HACs), including aromatic amines (*e.g.*, diphenylamine and *N*-phenyl-2-naphthylamine), which had not yet been previously targeted. This method consisted of UAE followed by SPE cartridge clean-up, and was based on procedures developed and implemented by other authors (Jonas & Covaci, 2013; Menichini et al., 2011). SPE was applied in order to minimize coelution of interfering analytes which were

compromising the GC-MS carried out *a posteriori* for sample analysis. Ten CR samples were collected from football fields in Amsterdam. 2-MBTZ was detected in two of the samples using GC-MS, however a quick screening carried out by liquid chromatography-atmospheric pressure chemical ionization-mass spectrometry (LC-APCI-MS) showed the presence of 2-MBTZ in all ten samples, meaning that GC-MS is not suitable for this compound due to its high LOD. The median concentration of REACH-8 PAHs was higher than the ones reported by De Groot et al. (2017) and Celeiro et al. (2021): 9.4 mg.kg⁻¹. None of the samples surpassed the 20 mg.kg⁻¹ limit for carcinogenic PAHs. Two HACs suspected to be potential carcinogens (acridine and carbazole) were identified in some of the samples.

The most recent study on the analysis of hazardous chemicals in CR samples from football fields was conducted by Armada et al. (2022). In terms of global sample representativity, this is the most complete study to date, as it does not restrict to CR samples from a single country (as the previous studies): 91 samples (including CR and alternative materials: cork and thermoplastic elastomers) were collected from 17 countries, located in 4 different continents. PAHs, plasticizers, antioxidants and vulcanisation additives were extracted by UAE and quantified by GC-MS. Overall, PAHs concentrations were consistent with the ones reported in the previously addressed studies. The country distribution of the total PAH concentrations showed that a sample from Chile had the highest reported concentration (230 mg.kg⁻¹) by a large margin, followed by a sample from Sweden (135 mg.kg⁻¹). This was likely due to the field being very recent and not extensively used. One Swedish sample and two Chilean samples exceeded the 20 mg.kg⁻¹ limit for REACH-8 PAHs, however the latter is not covered by this legislation (as it only applies to EU Member States). The REACH-4 plasticizers were detected in most of the samples, three of which exceeding the 1 g.kg⁻¹ limit (one EU and two non-EU samples). 2-MBTZ was detected in eight samples (with a maximum concentration of 146 mg.kg⁻¹). Finally, regarding the tested alternative materials, thermoplastic elastomers, despite showing low concentrations of PAHs, did show high concentrations of plasticizers (as expected). Moreover, they are non-degradable and, likewise to CR, pose an additional threat related to microplastic pollution. Cork granulate, on the other hand, showed significantly lower concentrations of hazardous chemicals across the board in comparison to CR, as reported by (Celeiro et al., 2021), which once again reinforces the status of this natural and biodegradable material as a highly viable, safer alternative to CR.

A detailed overview on these studies, consisting of sample characterization, target analytes, extraction/quantification methods and main results of the CR content analysis for PAHs, plasticizers (e.g., phthalates and phenols) and other additives (e.g., antioxidants, vulcanisation agents, and PCBs), is displayed in Tables 3-5, respectively.

It is important to reinforce that the present State of the Art focuses solely on the direct measurement of organic hazardous chemicals in CR, as this will be the type of analysis performed in this work for VMSs. However, this approach does not provide the full picture on CR's potential environmental impact, as many of these chemicals can migrate from CR to the nearby air and water (through volatilization and leaching, respectively). In the case of VMSs, volatilization becomes a more prevalent subject (due to the high vapour pressure of these compounds), and hence a follow-up study on air located close to the surface of synthetic football fields should be performed in the future to complement the results obtained from GC-MS analysis of CR samples.

Table 3. Overview of the scientific literature on the analysis and quantification of PAHs in CR.

No. Samples	Origin	Characteristics (granulometry, field age, indoor/outdoor)	Analyte(s)	Extraction	Analysis	% REC	LOD ^(a) ($\mu\text{g}\cdot\text{kg}^{-1}$)	LOQ ^(a) ($\mu\text{g}\cdot\text{kg}^{-1}$)	C ^(b) ($\text{mg}\cdot\text{kg}^{-1}$)	Reference
3	Norway (commercial CR prior to application in football fields)	2 samples of cross- grained material; 1 sample of fine- grained material	16-EPA- PAHs	n.a.	GC-MS	n.a.	10	Acenaphthene: 200; DBaHA: 400 (sample 1) and 200 (sample 2); remaining LOQs are n.a.	R: 51-76 Avg: 67	(Plesser & Lund, 2004)
7	USA (CR collected from parks)	Samples from outdoor parks with Field age: 2 months-7 years	16-EPA- PAHs	SE with DCM at 60 °C for 16 h	HPLC	n.a.	R: 0.009- 1.174	n.a.	R: 4.4-38.2 Avg: 24.3	(Zhang et al., 2008)
546 (from 91 fields)	Netherlands	Samples from outdoor football fields Field age: 1-15 years	REACH-8 PAHs	Extraction with petroleum ether and <i>n</i> -Hex	GC-MS	n.a.	500	n.a.	Max: 19.8 Med: 5.8	(De Groot et al., 2017)
86	15 European countries: Portugal, Spain, France, UK, Belgium, Netherlands, Denmark, Sweden, Germany, Switzerland, Poland, Austria, Italy, Romania, Greece	29 samples (25 uncoated and 5 coated) from CR recyclers/suppliers and 57 samples (47 uncoated and 10 coated) from synthetic turf sports fields	REACH-8 PAHs 16-EPA- PAHs	SE with <i>n</i> - Hex/toluene	GC-MS	n.a.	n.a.	100	<u>Uncoated</u> R: 3.2-11.7 Avg: 7.1 <u>Coated</u> R: 2.2-6.3 Avg: 4.2 <u>Uncoated</u> R: 36.4-78.7 Avg: 49.9 <u>Coated</u> R: 20.4-41.9 Avg: 33.9	(Schneider et al., 2020)

Table 3. Overview of the scientific literature on the analysis and quantification of PAHs in CR (cont.).

No. Samples	Origin	Characteristics (granulometry, field age, indoor/outdoor)	Analyte(s)	Extraction	Analysis	% REC	LOD ^(a) ($\mu\text{g.kg}^{-1}$)	LOQ ^(a) ($\mu\text{g.kg}^{-1}$)	C ^(b) (mg.kg^{-1})	Reference
3	Norway (2 field and 1 commercial CR samples)	Field samples (outdoor): 1 used and 1 unused; Size: 1.0-2.8 mm (commercial); n.a. for field samples	16-EPA-PAHs	UAE with DCM	GC-MS and LC-MS	n.a.	n.a.	n.a.	R: 47-58 Avg: 52	(Halsband et al., 2020)
13	Galicia, Spain	Outdoor football fields	REACH-8 PAHs 16-EPA-PAHs	UAE with EtAc; supernatant was filtered with 0.22 μm /25 mm PTFE filters (pore size/filter diameter)	GC-MS	72-116%	n.a.	R: 3-9	R: 3-30 Avg: 10 Med: 6 R: 8-91 Avg: 32 Med: 16	(Celeiro et al., 2021)
10	Amsterdam, Netherlands	Outdoor football fields	REACH-8 PAHs 16-EPA-PAHs	UAE with DCM and EtAc; SPE clean-up	GC-MS	90-110%	R: 0.5-20	n.a.	Max: 13 Med: 9.4 Max: 52 Med: 31	(Skoczyńska et al., 2021)
78	17 countries: Albania, Chile, Croatia, Finland, France, Germany, Greece, Italy, Netherlands, Poland, Portugal Spain, Sweden, Thailand, Turkey, UK and USA; from the 78 CR samples	From the 78 CR samples, 71 came from outdoor fields and 7 from indoor fields Size: 0.68-4.31 mm Field age: new-12/20 years	REACH-8 PAHs 16-EPA-PAHs	UAE with EtAc; supernatant was filtered with 0.22 μm /25 mm PTFE filters (pore size/filter diameter)	GC-MS	72-116% (method had been previously validated by (Celeiro et al., 2021))	R: 0.01-0.23	0.03-0.78	R: 0.25-107 Avg: 6.8 Med: 4.4 R: 0.63-212 Avg: 22 Med: 15	(Armada et al., 2022)

^(a) LODs and LOQs refer to individual PAHs; ^(b) C values refer to total PAHs.

n.a.: not available; % REC: recovery percentage; C: concentration; R: range; Avg: average; EtAc: ethyl acetate; PTFE: polytetrafluoroethylene; Max: maximum; Med: median.

Table 4. Overview of the scientific literature on the analysis and quantification of plasticizers in CR.

No. Samples	Origin	Characteristics (granulometry, field age, indoor/outdoor)	Analyte(s)	Extraction	Analysis	% REC	LOD ^(a) (µg.kg ⁻¹)	LOQ ^(a) (µg.kg ⁻¹)	C ^(b) (mg.kg ⁻¹)	Reference
3	Norway (commercial CR prior to application in football fields)	2 samples of cross- grained material; 1 sample of fine- grained material	Phthalates Phenols	n.a.	GC-MS	n.a.	R: 100-1000 R: 5-50	1,000 5,000	R: 34.8-104 Avg: 74.0 R: 28.7-54.9 Avg: 44.3	(Plesser & Lund, 2004)
546 (from 91 fields)	Netherlands	Samples from outdoor football fields Field age: 1-15 years	Phthalates Phenols	Extraction with petroleum ether and <i>n</i> - Hex Extraction with acetonitrile	GC-MS	n.a.	R: 500-10,000 R: 20-500	n.a.	Max: 92.7 Med: 43.5 Max: 24.9 Med: 5.3	(De Groot et al., 2017)
86	15 European countries: Portugal, Spain, France, UK, Belgium, Netherlands, Denmark, Sweden, Germany, Switzerland, Poland, Austria, Italy, Romania, Greece	29 samples (25 uncoated and 5 coated) from CR recyclers/suppliers and 57 samples (47 uncoated and 10 coated) from synthetic turf sports fields	Phthalates	Extraction with MTBE	GC-MS	n.a.	n.a.	5,000	<u>Uncoated</u> R: < LOD -23.8 Avg: 10.6 <u>Coated</u> R: < LOD-34.8 Avg: 19.1	(Schneider et al., 2020)
1	Norway	Field samples (outdoor): 1 used and 1 unused	Phthalates	UAE with DCM	GC-MS and LC- MS	n.a.	n.a.	n.a.	36.3	(Halsband et al., 2020)
2			Phenols	UAE with DCM/ <i>n</i> -Hex 1:1	HPLC				R: 2.3-6.3 Avg: 4.3	

Table 4. Overview of the scientific literature on the analysis and quantification of plasticizers in CR (cont.).

No. Samples	Origin	Characteristics (granulometry, field age, indoor/outdoor)	Analyte(s)	Extraction	Analysis	% REC	LOD ^(a) ($\mu\text{g.kg}^{-1}$)	LOQ ^(a) ($\mu\text{g.kg}^{-1}$)	C ^(b) (mg.kg^{-1})	Reference
13	Galicia, Spain	Outdoor football fields	REACH-4 plasticizers	UAE with EtAc; supernatant was filtered with 0.22 μm /25 mm PTFE filters (pore size/filter diameter)	GC-MS	72-116%	n.a.	R: 6-50	R: 1.5-37 Avg: 13 Med: 10	(Celeiro et al., 2021)
78	17 countries: Albania, Chile, Croatia, Finland, France, Germany, Greece, Italy, Netherlands, Poland, Portugal, Spain, Sweden, Thailand, Turkey, UK and USA; from the 78 CR samples	From the 78 CR samples, 71 came from outdoor fields and 7 from indoor fields Size: 0.68-4.31 mm Field age: new-12/20 years	REACH-4 plasticizers	UAE with EtAc; supernatant was filtered with 0.22 μm /25 mm PTFE filters (pore size/filter diameter)	GC-MS	72-116% (method had been previously validated by (Celeiro et al., 2021))	R: 0.1-1.3	0.33-4.1	R: 1.1-9,527 Avg: 262 Med: 36	(Armada et al., 2022)

^(a) LODs and LOQs refer to individual plasticizers; ^(b) C values refer to total plasticizers.

Table 5. Overview of the scientific literature on the analysis and quantification of other additives in CR.

No. Samples	Origin	Characteristics (granulometry, field age, indoor/outdoor)	Analyte(s)	Extraction	Analysis	% REC	LOD ($\mu\text{g.kg}^{-1}$)	LOQ ($\mu\text{g.kg}^{-1}$)	C (mg.kg^{-1})	Reference
3	Norway (commercial CR prior to application in football fields)	2 samples of cross- grained material; 1 sample of fine- grained material	PCBs 1-7, 28, 52, 101, 118, 138, 153, and 180	n.a.	GC-MS	n.a.	20 ^(a)	R: 50-175 ^(a)	R: < LOQ-0.4 Avg: 0.4	(Plesser & Lund, 2004)
7 (mixed samples from 7 fields)	Netherlands	Samples from outdoor football fields	PCBs 28, 101, 138, 153, and 180 2-MBTZ	Extraction with acetonitrile Extraction with methanol	GC-MS	n.a.	35 ^(b) n.a.	n.a.	Max: 0.074 Med: < LOQ Max: 7.6 Med: 2.6	(De Groot et al., 2017)
86	15 European countries: Portugal, Spain, France, UK, Belgium, Netherlands, Denmark, Sweden, Germany, Switzerland, Poland, Austria, Italy, Romania, Greece	29 samples (25 uncoated and 5 coated) from CR recyclers/suppliers and 57 samples (47 uncoated and 10 coated) from synthetic turf sports fields	2-MBTZ	Extraction with methanol	HPLC	n.a.	n.a.	5,000	<u>Uncoated</u> R: < LOD-7.0 Avg: 3.1 <u>Coated</u> R: < LOD-18.8 Avg: 9.3	(Schneider et al., 2020)
13	Galicia, Spain	Outdoor football fields	2-MBTZ BHT	UAE with EtAc; supernatant was filtered with 0.22 μm /25 mm PTFE filters (pore size/filter diameter)	GC-MS	72-116%	n.a.	15,000 9	R: ND-62 Avg: 43 Med: 39 R: 0.06-3.70 Avg: 1.1 Med: 1.0	(Celeiro et al., 2021)

Table 5. Overview of the scientific literature on the analysis and quantification of other additives in CR (cont.).

No. Samples	Origin	Characteristics (granulometry, field age, indoor/outdoor)	Analyte(s)	Extraction	Analysis	% REC	LOD ($\mu\text{g.kg}^{-1}$)	LOQ ($\mu\text{g.kg}^{-1}$)	C (mg.kg^{-1})	Reference
78	17 countries: Albania, Chile, Croatia, Finland, France, Germany, Greece, Italy, Netherlands, Poland, Portugal Spain, Sweden, Thailand, Turkey, UK and USA; from the 78 CR samples	From the 78 CR samples, 71 came from outdoor fields and 7 from indoor fields Size: 0.68-4.31 mm Field age: new- 12/20 years	2-MBTZ	UAE with EtAc; supernatant was filtered with 0.22 μm /25 mm PTFE filters (pore size/filter diameter)	GC-MS	72-116% (method had been previously validated by (Celeiro et al., 2021))	88	290	R: < LOD-146 Avg: 86 Med: 82	(Armada et al., 2022)
			BHT				0.02	0.06	R: < LOD-85 Avg: 3.7 Med: 0.82	

^(a) Referred to individual PCBs; ^(b) Referred to total PCBs.

3.2. VMSs in Solid Matrices

As mentioned previously, this is the first assessment of the presence of VMSs in CR. Therefore, it is important to mention some of the studies already performed in other environmental solid samples, as they are the closest to CR and the analytical methods employed may be an important basis for this work.

The first example developed and validated an analytical method - UAE with *n*-Hex and GC-MS instrumental analysis - later applied for the determination of VMSs (D4-D6 and L4-L14) in soil samples (Sánchez-Brunete et al., 2010). These were collected from various areas in Spain and consisted of agricultural soil, soil amended with sewage sludge and industrial soil. Multiple extraction solvents were tested - EtAc, EtAc/*n*-Hex 1:1, EtAc/*n*-Hex 1:4, *n*-Hex and methanol - with *n*-Hex being selected since it showed the best results in recovery assays (minimum recovery of 92%). Concerning cVMSs, D4 was only detected in one of the 15 samples (industrial soil); D5 and D6, on the other hand, were found in all samples. On average, agricultural soil showed the lowest cVMS concentrations (31.86 ng.g_{DW}⁻¹), followed by sludge-amended soil (61.40 ng.g_{DW}⁻¹). The industrial soil, meanwhile, clearly stood out from its counterparts - with a mean concentration of 266.9 ng.g_{DW}⁻¹ and maximum of 610.6 ng.g_{DW}⁻¹. lVMSs were found in all sludge-amended soil, and all but one industrial soil samples, although they were only detected in 25% of all agricultural soil samples. Total lVMS concentration values exceeded the ones for cVMS, with the samples following a similar trend in terms of average concentration - 215.4 ng.g_{DW}⁻¹ for agricultural soil, 354.0 ng.g_{DW}⁻¹ for sludge-amended soil and 3,321 ng.g_{DW}⁻¹ for industrial soil (with a maximum of 8,532 ng.g_{DW}⁻¹).

Bletsou et al. (2013) assessed the presence of VMSs (D3-D7 and L3-L14) in sludge from a WWTP in Athens, Greece. Sludge samples were mechanically dewatered, therefore being treated as a solid product. The employed extraction protocol consisted of three sequential liquid-liquid extractions - *n*-Hex, *n*-Hex/DCM (1:1) and *n*-Hex/EtAc (1:1) (in this order) - and was included in the optimization assays performed in the initial stages of this work (to assess if it could be also applicable to CR). The instrumental analysis was carried out by GC-MS. All the analysed VMSs were detected in each of the 7 dry sludge samples. The mean total VMS concentration was 75.0 µg.g_{DW}⁻¹, with this value exceeding all those reported in the studies included in this State of the Art. D5 was the predominant VMS (mean of 15.1 µg.g_{DW}⁻¹), although lVMSs prevailed over cVMSs: 72% of the 75.0 µg.g_{DW}⁻¹ (i.e., 53.9 µg.g_{DW}⁻¹) consisted of linear compounds, but this study included longer-chain VMSs (L6 to L14). Sample collection took place during 7 consecutive days to estimate the daily accumulation of siloxanes in sludge and the results showed that, on average, the mass loading of VMSs in sludge was of 8.2 kg.day⁻¹ (with 110,000 kg of dry sludge being produced in the WWTP on a daily basis).

Sanchís et al. (2015) analysed the VMS content (D3-D6 and L3-L6) of samples from terrestrial (soil and vegetation) and aquatic (phytoplankton and krill) ecosystems in the Antarctic Peninsula. This location was not selected randomly, but instead with the purpose of demonstrating the migration of these contaminants from its source - developed countries which heavily rely on the use of siloxane-containing products - to one of the most remote places on Earth. VMSs can enter aquatic ecosystems through phytoplankton, due to their high hydrophobicity, and are subsequently transferred to krill as

these organisms feed directly from phytoplankton. In terrestrial ecosystems, VMSs can be released from melting snow and deposit in soils and vegetation. VMS extraction was performed via UAE (with *n*-Hex) and quantification by GC-MS. IVMSs were only detected in soil and phytoplankton; cVMSs, on the other hand, were detected in almost all samples, with concentrations 2-3 orders of magnitude higher than the ones measured for IVMSs. Using the median as the reference statistical variable, D6 was the predominant VMS in soil ($20.3 \text{ ng.g}_{\text{DW}}^{-1}$) - higher than the one measured by Sánchez-Brunete et al. (2010) for some agricultural soil samples in Spain - and vegetation ($27.9 \text{ ng.g}_{\text{DW}}^{-1}$), D3 in phytoplankton ($3.00 \text{ ng.g}_{\text{DW}}^{-1}$) and D4 in krill ($41.1 \text{ ng.g}_{\text{DW}}^{-1}$). The maximum total concentration of cVMSs was found in krill ($357 \text{ ng.g}_{\text{DW}}^{-1}$) and of IVMSs in soil ($1,030 \text{ pg.g}_{\text{DW}}^{-1}$).

Another solid matrix where siloxanes have been found is coastal sediment. Lee et al. (2019) analysed VMSs D4-D9 and L3-L15 in sediment collected from bays located next to large-scale industrial areas in South Korea. Extraction was carried out using *n*-Hex/EtAc (1:1) (shaken for 30 min) and quantification by GC-MS. D5 and D6 were the predominant cVMSs - median of $20.7 \text{ ng.g}_{\text{DW}}^{-1}$ and $35.9 \text{ ng.g}_{\text{DW}}^{-1}$, respectively - and L10 and L11 the predominant IVMSs - $8.24 \text{ ng.g}_{\text{DW}}^{-1}$ and $7.79 \text{ ng.g}_{\text{DW}}^{-1}$, respectively. The total concentration results showed that cVMSs (median of $88.1 \text{ ng.g}_{\text{DW}}^{-1}$) were present in over twice the amount of IVMSs ($41.6 \text{ ng.g}_{\text{DW}}^{-1}$). The concentration of VMSs generally decreased as sampling sites moved away from the industrial areas, once again highlighting the significant contribution of industrial activity to siloxane contamination.

Finally, Capela et al. (2019) conducted a study on VMS analysis (D3-D6 and L3-L5) in beach sand from the Oporto region, in Portugal. The extraction method - UAE with QuEChERS (using *n*-Hex as the extraction solvent) - was adapted from the work of Homem et al. (2017), initially developed for the extraction of musks, also from beach sand. As in previous studies, the quantification was performed by GC-MS. Samples were collected at two different seasons - end of summer (September 2013) and end of winter (March 2014) - in order to assess the seasonal effect on VMS levels in beach sand. cVMSs were present in larger concentrations than IVMSs - mean concentration of $0.92 \text{ ng.g}_{\text{DW}}^{-1}$ for D5 and $3.28 \text{ ng.g}_{\text{DW}}^{-1}$ for D6), while all three individual IVMSs remained close to the $0.10 \text{ ng.g}_{\text{DW}}^{-1}$ mark. The highest total VMS concentrations, with the maximum being $21 \text{ ng.g}_{\text{DW}}^{-1}$, were registered in beaches with a larger attendance during the bathing season, which were also located next to large urban areas. In terms of the seasonal comparison, post-summer and winter VMS levels were slightly higher after the summer - $133 \text{ ng.g}_{\text{DW}}^{-1}$ post-summer and $115 \text{ ng.g}_{\text{DW}}^{-1}$ post-winter (total VMS concentration of the 23 beaches).

A detailed overview on the previous studies, following a similar structure to the one presented for the analysis of organic microcontaminants from CR, is displayed in Table 6.

Table 6. Overview of the scientific literature on the analysis and quantification of VMSs in solid matrices.

No. Samples	Origin	Characterization	Analysed VMSs	Extraction	Analysis	% REC	LOD ^(a) (ng.g _{dw} ⁻¹)	LOQ ^(a) (ng.g _{dw} ⁻¹)	C ^(b) (ng.g _{dw} ⁻¹)	Reference
15	Spain	8 samples of agricultural soil; 2 samples of sludge-amended soil; 5 samples of industrial soil	D4-D6; L4-L14	UAE with <i>n</i> -Hex	GC-MS	<u>cVMSs</u> 87.7%-108.0% <u>LVMSs</u> 84.9%-107.6% (at 10, 20 and 50 ng.g ⁻¹ spike levels)	0.4-1.1	1.5-4.0	<u>cVMSs</u> AG: 15.0-84.0 SA: 60.0-62.8 IND: 56.0-610.6 <u>LVMSs</u> AG: < LOD-292.4 SA: 170.8-537.3 IND: 431.4-8,532	(Sánchez-Brunete et al., 2010)
7	Greece	7 samples of mechanically dewatered WWTP sludge	D3-D7; L4-L14	Sequential extractions: <i>n</i> -Hex, <i>n</i> -Hex/DCM (1:1) and <i>n</i> -Hex/EtAc (1:1) (in this order)	GC-MS	<u>cVMSs</u> 71%-102% <u>LVMSs</u> 53.9%-93.0% (at six different spike levels)	0.002-3.3	0.006-9.9	<u>cVMSs</u> 18,967-24,052 <u>LVMSs</u> 50,250-59,673	(Bletsou et al., 2013)
50	Antarctica Peninsula	11 soil samples; 17 vegetation samples; 11 phytoplankton samples; 11 krill samples	D3-D6; L3-L6	UAE with <i>n</i> -Hex	GC-MS	Soil <u>cVMSs</u> 60.6%-104% <u>LVMSs</u> 71.1%-100% (at 16.7, 33.3 and 66.7 ng.g ⁻¹ spike levels)	Soil 0.018-0.096	Soil 0.06-4.7	Soil <u>cVMSs</u> 0.46-175 <u>LVMSs</u> 153-1,890	(Sanchis et al., 2015)

Table 6. Overview of the scientific literature on the analysis and quantification of VMSs in solid matrices (cont.).

No. Samples	Origin	Characterization	Analysed VMSs	Extraction	Analysis	% REC	LOD ^(a) (ng.g _{DW} ⁻¹)	LOQ ^(a) (ng.g _{DW} ⁻¹)	C ^(b) (ng.g _{DW} ⁻¹)	Reference
50	Antarctica Peninsula	11 soil samples; 17 vegetation samples; 11 phytoplankton samples; 11 krill samples	D3-D6; L3-L6	UAE with <i>n</i> -Hex	GC-MS	Biota (vegetation, phytoplankton and krill) <u>cVMSs</u> 71%-91% <u>lVMSs</u> 74%-92% (at 16.7, 33.3 and 66.7 ng.g ⁻¹ spike levels)	Biota 0.046-0.39	Biota 0.16-1.3	Biota <u>cVMSs</u> VG: 0.86-150 PK: 1.40-39.0 KR: 78.4-357 <u>lVMSs</u> VG: < LOD PK: 6.10-140 KR: < LOD - 81.6	(Sanchís et al., 2015)
69	South Korea	Coastal sediments from 4 bays located near industrial areas	D4-D9; L3-L15	Extraction with <i>n</i> -Hex/EtAc 1:1	GC-MS	n.a.	0.06-0.90	0.21-3.02	<u>cVMSs</u> 9.79-2,716 <u>lVMSs</u> 1.69-1,162	(Lee et al., 2019)
46	Portugal	Sand from 23 beaches collected at two different timepoints: post-summer (September 2013) and post-winter (March 2014)	D3-D6; L3-L5	UAE with QuEChERS (using <i>n</i> -Hex as the extraction solvent)	GC-MS	56% (L3)-111% (L4) (at 0.5, 1.0 and 5.0 ng.g ⁻¹ spike levels)	(0.002-1.01)×10 ⁻³	n.a.	<u>Total</u> 0.33-21	(Capela et al., 2019)

^(a) LODs and LOQs refer to individual VMSs; ^(b) C values refer to total VMSs.

DW: dry weight; AG: agricultural; SA: sludge-amended; IND: industrial; VG: vegetation; PK: phytoplankton; KR: krill.

3.3. Human Exposure to Crumb Rubber

In terms of the issue of human exposure to crumb rubber, there are a few studies already published, but concerning contaminants other than siloxanes. One conducted by the Ministry of Health, Welfare and Sport of the Netherlands (De Groot et al., 2017) quantified the release of hazardous substances - PAHs, metals (Pb, Cd and Co), BPA and benzothiazoles - from synthetic turf CR into artificial sweat and gastrointestinal (GI) fluids, and also their volatilization in hot air conditions (60 °C): in order to simulate dermal, ingestion and inhalation exposures, respectively. Exposure risks were calculated based on the maximum measured concentrations of each substance. EPA defines cancer risk (C_{Risk}) as ‘the incremental probability of an individual developing cancer over a lifetime as a result of exposure to a carcinogen’ (EPA, 1989). For PAHs, the estimated C_{Risk} due to contact with CR was of 0.8-1.2 per million exposed people for someone who is a lifelong outfield player; the risk was slightly higher for goalkeepers, as increased dermal and ingestion exposures were considered in the baseline scenario (2.2-3.0 per million). Benchmark limit values for negligible and maximum permissible risks, established by EPA (EPA, 1991), are of one per million (10^{-6}) and one per ten thousand (10^{-4}), respectively, meaning that the calculated risks were virtually negligible. Moreover, the estimated exposure to PAHs in CR (37-98 ng.d⁻¹) was much lower than the one estimated for adults via food intake (1,800-4,900 ng.d⁻¹) (EFSA, 2008). Cd, Co, phthalates and benzothiazoles showed no associated C_{Risk} , while for Pb the exposure through CR was lower than the safety limit for this metal. In short, no major evidence of CR potentially posing significant health repercussions to synthetic field users was found.

In June 2016, following a formal request from the European Commission, ECHA released a human exposure risk assessment report on CR (ECHA, 2017a), based on hazardous substance concentration values reported in existing studies. Inhalation, dermal and oral exposure routes were considered. Unlike most studies, which focus solely on the active users of the sports facilities (the players), this report also included field workers (for turf installation and maintenance). The hazardous substances evaluated for the risk characterization study were the REACH-8 PAHs, phthalates, methyl isobutyl ketone (MIBK) - which can cause serious eye and respiratory irritation (ECHA, 2017a) - benzothiazole, 2-MBTZ, formaldehyde and benzene. Cancer risk reference doses were estimated according to the European Food Safety Authority’s (EFSA) methodology (EFSA, 2016), which relies on the application of statistical tests to the results of laboratorial experiments carried out with animals. The BMDL10 was used as a reference parameter - the lower bound of the 95% confidence interval for an exposure dose that causes cancer in 10% of the tested animals. The calculated excess lifetime cancer risk values were below 1.0 per million in all scenarios - these results indicate that ‘there is a very low level of concern from exposure to substances found in the granules’ (ECHA, 2017a). However, ECHA also states that there were numerous uncertainties in its evaluation (e.g., representativity of the available studies, knowledge gaps regarding the substances known to be present in CR, and unknown composition of imported rubber granules) and that further studies were needed to enhance the (scarce) current knowledge.

Another relevant study on this matter was based on a literature search of available North American data on the chemical composition of recycled rubber and air sampling on synthetic turf fields (Peterson et al., 2018). Exposure pathways (once again through dermal contact, ingestion and inhalation) were

evaluated according to EPA risk assessment guidelines under multiple exposure scenarios - youth football players (6-18 years old), adult spectators and child spectators. The obtained results were consistent with those of the previous study, as for all considered scenarios the calculated CRs had a degree of magnitude of either 10^{-7} or 10^{-6} , similar to the ones estimated in the Netherlands and well below the EPA maximum permissible limit of 10^{-4} . In addition, C_{Risk} levels for synthetic CR-infilled fields were comparable to those of natural soil fields. A further variable analysed during the course of this study was the non-cancer hazard index (HI). The HI limit established by EPA is 1.0 (EPA, 1989): for values above this threshold, there is a potential risk of adverse, non-carcinogenic effects to occur during a lifetime as a result of chemical exposure, while for values below 1.0 the risk is negligible. All calculated HI values were below EPA's maximum limit.

The final part of the ERASSTRI project consisted of a risk assessment study on human exposure to CR (Schneider et al., 2020a). For this study, unlike the previous two - in which the variable chosen to quantify the exposure risk was C_{Risk} (calculated following EPA guidelines) - risk was measured by means of route-specific risk characterization ratios (RCRs), which were added up to calculate the total risk - $\text{RCR}_{\text{total}}$. In this approach, estimated exposure levels were normalized by reference values collected from toxicological databases - therefore, the threshold acceptance value for $\text{RCR}_{\text{total}}$ was set at 1 (*i.e.*, when the calculated risk equals the reference value). Multiple exposure groups were considered in this study, based on age - small children (below 4 years old), children, teenagers, adults or veterans - and type of action - spectators, outfield players or goalkeepers. For each group, the following parameters were assumed/estimated: exposed skin contact area, amount of CR in contact with skin/ingested per occurrence (for dermal and ingestion exposures, respectively), body weight and exposure duration. With the exception of three exposure groups - teenager outfield players, adult outfield players and adult goalkeepers (1.22, 3.89 and 1.22, respectively) - all calculated $\text{RCR}_{\text{total}}$ values were lower than 1. The authors justified these outliers by stating that the used reference values 'were mainly based on conservative assumptions' and concluded that, overall, there were no relevant health risks resulting from exposure to CR in the considered scenarios.

The three presented studies concluded that the application of CR as infill in synthetic fields does not pose an alarming danger for its users. However, the followed methodology presents some limitations (*e.g.*, the results are highly dependable of the assumptions made for each scenario and only a limited number of them were considered). Therefore, stating that exposure to CR is safe would be a premature assessment as more scientific data is required to corroborate it and fill the existing gaps. Moreover, a recent study conducted by Tarafdar et al. (2020) determined a C_{Risk} of 1.3×10^{-5} for children in playgrounds containing CR: a value over ten times higher in comparison to playgrounds which do not possess CR in its pavement. This result is slightly worrying, as the C_{Risk} cannot be considered negligible (well above the 10^{-6} EPA limit) and edges closer to the EPA maximum permissible limit of 10^{-4} .

Naturally, siloxanes were not included in these assessments since their presence in CR has never been evaluated/reported. The results obtained in this work will, therefore, be used (in a future work) to conduct a preliminary risk assessment study on human exposure to VMSs in CR, this way contributing to fill the existing knowledge gaps on this subject.

4. Materials and Methods

The analytical method employed for the extraction and quantification of VMSs in CR samples was selected based on the results obtained from validation tests (mainly focusing on recovery assays) performed with two previously developed methods, in which slight modifications were introduced to the original protocols for preliminary optimization purposes. The first method to be tested was implemented in the framework of the SAFEGOAL (SG) project for the analysis of PAHs from CR and the second was designed for VMS analysis from dry sludge (DS).

4.1. Chemicals and Materials

The analytes targeted in this work were lVMSs octamethyltrisiloxane, decamethyltetrasiloxane and dodecamethylpentasiloxane (L3, L4 and L5, respectively), and cVMSs hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane and dodecamethylcyclohexa-siloxane (D3, D4, D5 and D6, respectively). Individual standards of these siloxanes, the internal standard (IS) used - tetrakis(trimethylsilyloxy)silane (M4Q) - and the QuEChERS reagents C18 and PSA were supplied by Sigma-Aldrich (St. Louis, MO, USA); the organic extraction solvents *n*-Hex, DCM and EtAc (with minimum purities of 95.0%, 99.8%, and 99.7%, respectively) by VWR (Fontenay-sous-Bois, France); anhydrous MgSO₄ (also used in QuEChERS preparation) by ITW (Barcelona, Spain); and N₂ and He (the first used for solvent evaporation and the second as a carrier gas in the GC-MS) by Air Liquide (Maia, Portugal).

4.2. Standards Preparation

Individual stock solutions of each VMS were prepared in *n*-Hex at 1.0 g.L⁻¹. Subsequently, the solutions were combined and diluted in the same solvent in order to obtain a VMS mix spike solution at 5 mg.L⁻¹. In parallel, a 5 mg.L⁻¹ solution of M4Q was prepared by diluting in *n*-Hex an initial stock solution of 1.0 g.L⁻¹. These solutions were stored in amber glass vials and preserved in a freezer at -20 °C.

4.3. QuEChERS Preparation

Both the SG and DS methods included a QuEChERS clean-up step after extraction. The QuEChERS were prepared in 15 or 50 mL (depending on the case) polypropylene (PP) Falcon-type tubes from Corning (New York, USA) and consisted of a mixture of C18, PSA and anhydrous MgSO₄. The latter was baked overnight at 450 °C prior to its use in order to eliminate volatile interferences. The weighed amount of PSA and MgSO₄ was the same for the two methods (300 mg), with the only difference being the amount of C18: 200 mg for SG and 50 mg for DS.

4.4. Samples

In this work, a total of 126 samples were analysed: 120 samples collected in outdoor and indoor synthetic turf fields from 12 countries (11 European - Albania, Croatia, Finland, France, Germany, Greece, Italy, Poland, Portugal, Spain and Sweden - and Chile) - 108 CR samples and 12 alternative

material samples (cork, coloured CR and rubber/coconut fibre) - and 6 samples sent directly from CR manufacturers. The detailed characterization of all samples analysed during this work - sample ID, country, type of pitch, pitch age, collection date, material and granulometry - can be consulted in Appendix 1 (Tables A1.1 - A1.3).

4.5. Optimization and Validation Strategy

The initial stage of this work consisted of developing a reliable and robust method for VMS extraction and quantification from CR. Prior to its implementation, multiple recovery assays were carried out, first for the method's optimization (testing a series of potential improvements to existing protocols) and then for its validation.

The optimization process started from the base SG and DS protocols. In the first set of recovery assays, both protocols were implemented in order to select the one that led to better results. Within the DS protocol, which described a three-step sequential extraction (with *n*-Hex, *n*-Hex/DCM 1:1 and *n*-Hex/EtAc 1:1, in this order), three separate recovery assays were carried out: the first with only *n*-Hex (DS1), the second with *n*-Hex and *n*-Hex/DCM 1:1 (DS2), and the latter with *n*-Hex, *n*-Hex/DCM 1:1 and *n*-Hex/EtAc 1:1 (DS3). The selected protocol ended up being SG. The next step consisted of selecting the extraction solvent - *n*-Hex, DCM or EtAc. A 1:1 mixture of *n*-Hex/DCM was selected. Thereafter, different solvent volumes were tested - 5 mL and 10 mL (the first was selected). The last detail to be assessed was related to the filtration clean-up step, in which three alternatives were tested: 0.20 µm PTFE filters, 0.45 µm PTFE filters and no filtration at all. The 0.20 µm filter prevailed. The rationale behind these decisions is explained in detail in the Results and Discussion section.

Once the final protocol was established, the necessary parameters for the method's validation were determined - linearity, limits of detection and quantification, accuracy and precision. For the optimization assays, the spike concentration was kept at 500 ng.g⁻¹. The validation recovery assays, meanwhile were performed with VMS-spiked CR samples at two different spike levels: 100 ng.g⁻¹ and 500 ng.g⁻¹. Non-spiked CR samples and procedural/laboratorial blanks (*i.e.*, samples that did not contain the matrix but were submitted to the same protocol) were also analysed with every extraction batch. The content of these samples is detailed in Table 7.

Table 7. Content of the samples included in the recovery assays.

Sample	Content
Protocol/Laboratorial blank	Solvent; QuEChERS reagents; M4Q
Non-spiked sample	Solvent; QuEChERS reagents; M4Q; CR
Spiked sample	Solvent; QuEChERS reagents; M4Q; CR; VMS spike

4.6. Sample Extraction and Clean-up

4.6.1. SAFEGOAL (Original)

First, 200 mg of CR sample were weighed into 15 mL polypropylene (PP) tubes, to which 5 mL of EtAc, 500 ng of M4Q and 100 ng or 500 ng of VMS spike solution (depending on the spike level) were added. The samples were then vortexed for 1 min, sonicated for 20 min in a J.P. Selecta ultrasonic bath (Barcelona, Spain), and centrifuged for 5 min at 4000 rpm (2670 G) in a Rotofix 32A centrifuge from Hettich (Kirchlengern, Germany). The supernatant was removed using Pasteur pipettes and transferred to new 15 mL PP tubes. The pre-weighed QuEChERS were added to the supernatant, which was then vortexed for 1 min and centrifuged for 5 min at 4000 rpm. The supernatant was transferred to 12 mL amber vials and its volume was reduced (until approximately 1.5 mL) under a gentle stream of N₂. The extract was then filtered into GC vials through 0.2 µm/25 mm (pore size/filter diameter) PTFE syringe membranes - supplied by VWR North America (Radnor, PA, USA) - which were first slightly wetted with the extraction solvent in order to improve the filtration efficiency. Finally, the volume was adjusted to 1 mL in each vial by means of a second N₂ evaporation prior to injection in the GC-MS equipment.

4.6.2. Dry Sludge

As mentioned previously, the DS protocol described a three-step extraction with different solvents: *n*-Hex, *n*-Hex/DCM 1:1, and *n*-Hex/EtAc 1:1 (in this order), with three separate variations being tested in the optimization recovery assays - DS1, DS2 and DS3.

The initial part of the protocol was the same for DS1, DS2 and DS3. First, 200 mg of CR sample were weighed inside 15 mL PP tubes, to which were added 5 mL of *n*-Hex, 500 ng of M4Q and 100 ng or 500 ng of VMS spike solution. The samples were then vortexed for 1 min, sonicated for 10 min, and centrifuged for 5 min at 4000 rpm (2670 g).

In DS1, the supernatant was removed using Pasteur pipettes and transferred to new 15 mL PP tubes. In DS2 and DS3, on the other hand, the supernatant was transferred to new 50 mL PP tubes (since the volume of extract was higher on account of the combined supernatant of the consecutive extractions). 5 mL of *n*-Hex/DCM 1:1 (v/v) were added to the centrifugation pellet and a second extraction was carried out - 1 min vortex, 10 min ultrasound bath and 5 min/4000 rpm centrifugation. In DS2, the supernatant was transferred to the 50 mL tubes containing the supernatant of the previous extraction. Finally, in DS3 5 mL of *n*-Hex/EtAc 1:1 (v/v) were added to the centrifugation pellet and a third extraction was carried out - once again, 1 min vortex, 10 min ultrasound bath and 5 min/4000 rpm centrifugation. The supernatant was then combined with the ones of the first two extractions.

The pre-weighed QuEChERS were added to the DS1, DS2 and DS3 extracts, which were then vortexed for 1 min and centrifuged for 5 min at 4000 rpm. The resulting supernatant was transferred to amber vials (12 mL vials for DS1 and DS2; 15 mL vials for DS3) and its volume was reduced (to approximately 1.5 mL) under a gentle stream of N₂. As for the SG protocol, the extract was then filtered into GC vials through 0.2 µm/25 mm (pre-wetted) PTFE syringe membranes. The volume was adjusted to 1 mL by N₂ evaporation prior to injection in the GC-MS equipment. A schematic representation of the followed experimental procedure, according to this protocol, is presented in Appendix 2 (Figure A2.1).

4.6.3. SAFEGOAL (Modified)

The first series of recovery assays were dedicated to the selection/optimization of the analytical method for VMS extraction from CR. The obtained results showed that the SG protocol was better suited for this purpose - see Results and Discussion - and during the different tests a few modifications ended up being made to the original protocol for its optimization.

In summary, the following modifications were undertaken: 1.0 g of sample was weighed (instead of 0.2 g), as the SG protocol was designed for PAH extraction, which are likely present in CR in a higher amount than VMSs; a 30 minute interval was established before adding the extraction solvent, so that the standards could be better adsorbed by the sample; and a 5 mL mixture of *n*-Hex/DCM 1:1 was used for the extractions (instead of 5 mL of *n*-Hex) - DCM by itself had slightly better VMS extraction results in comparison to *n*-Hex/DCM - see Results and Discussion - but it originated a significantly “dirtier” extract (meaning that more interferences were present in the chromatographic resolution). In fact, the use of DCM in GC-MS has shown to cause a gradual deterioration of chromatographic signals (Brocks & Hope, 2014). A schematic representation of the followed experimental procedure, according to this protocol, is presented in Appendix 2 (Figure A2.2).

4.7. Instrumental Analysis

The extracts were quantified using a Varian 4000 Ion Trap GC-MS system (Palo Alto, CA, USA), with the MS operating in the electron ionization (EI) mode at 70 eV. A low-bleed Agilent (Santa Clara, CA, USA) J&W DB-5 MS (30 m × 0.25 mm, 0.25 µm film thickness) ultra-inert capillary column was used for separating the analytes, with He as a carrier gas at a constant flow of 1.0 mL.min⁻¹. The oven was programmed with the following temperature sequence: 35 °C held for 5 minutes, then a 10 °C.min⁻¹ increase to 95 °C, a 5 °C.min⁻¹ rise to 140 °C, and finally a 35 °C.min⁻¹ increase to 300 °C (held for 5 minutes) - resulting in a total analysis time of 30 minutes. Injection (1 µL) was carried out in splitless mode in the first minute, then a split ratio of 100 from 1 to 5 min and then with a split ratio of 5. Manifold, injector, ion trap and transfer line temperatures were maintained at 50, 200, 250 and 250 °C, respectively. The filament emission current measured at 50 µA. Selected ion storage (SIS) mode was applied for the quantification of the target analytes. The retention time and m/z ratio of the quantifier/qualifier ions of each analyte are presented in Appendix 3 (Table A3.1).

4.8. Quality Assurance/Quality Control

Since the compounds targeted in this work are siloxanes, their extensive use and possible presence in the laboratory environment requires that special precautions are ensured to minimize external sample contamination. All non-volumetric glass material and anhydrous MgSO₄ were baked overnight at 450 °C covered in aluminium foil. Syringes used for IS/siloxane mix spike solution volume measurements and needles used for N₂ evaporation were washed prior to and after its use - the former were rinsed multiple times with Acet and *n*-Hex, and the latter were covered in Acet and placed in a 10 minute ultrasound bath. Silicon-free PP tubes were used for the extractions and disposed of upon its conclusion. All non-essential PCPs were avoided by the lab analysts (e.g., fragrances, hair gel, creams and lotions). Duplicate

procedural blanks were performed with every extraction batch and their GC-MS data subtracted for all reported results. Chromatographic blanks were also performed in order to assess the presence of memory effects - none were observed. In the GC-MS, the injector was adapted with a Merlin Microseal (in alternative to conventional silicone rubber septa) and an ultra-inert column was used to minimize the bleeding of the siloxanes which comprise its stationary phase.

4.9. Waste Management

Liquid (organic solutions containing trace amounts of siloxanes) and solid (QuEChERS reagents and CR granules) extraction residues were collected in specifically assigned containers, correctly labelled, stored in a location protected from light and ignition sources, and later sent to the Environmental Management System of FEUP - EcoFEUP - for further specialized treatment.

4.10. Model for Human Exposure Estimation

There are several approaches to determine the human exposure to contaminants, but in this work the strategy to estimate the human exposure to VMSs found in CR relied on the adaptation of the methodology described by Peterson et al. (2018), which follows the guidelines of EPA (EPA, 1989). This study was selected since it refers specifically to hazardous compounds present in synthetic turf CR: PAHs, metals, PCBs, phthalates and phenols. Three exposure pathways (respiratory, oral and dermal) and five exposure scenarios were considered (Table 8).

Table 8. Exposure scenarios to CR in synthetic football fields (Peterson et al., 2018).

Scenario	Description
1	Youth outdoor football player (6-18 years old)
2	Youth indoor football player (6-18 years old)
3	Youth composite football player (6-18 years old) ^(a)
4	Adult spectator (> 18 years old)
5	Child spectator (< 6 years old)

^(a) Plays both outdoor and indoor football.

For this work, some modifications were made on the scenarios and parameters to reflect the reality of European football practice and the properties/data available for VMSs. Thus, only the oral and dermal exposure doses will be included, since the calculation of the exposure through inhalation would require the measurement/estimation of the VMS concentration in air - not done in this work, but a possibility for future research in the subject. Human intake levels by incidental CR ingestion and by dermal contact can be calculated by Equations 2 and 3, respectively (adapted from Peterson et al. (2018)).

$$OED = \frac{C_{CR} \times B \times IR \times EF \times 10^{-6}}{BW} \quad (2)$$

where OED represents the oral exposure dose (mg.kg⁻¹.year⁻¹), C_{CR} the concentration of the target chemical in CR (mg.kg⁻¹), B the relative oral bioaccessibility factor (unitless), IR the CR ingestion rate (mg.day⁻¹), EF the exposure frequency (day.year⁻¹), and BW the average body weight (kg) of a specific target group.

$$DED = \frac{C_{CR} \times ABS \times AF \times SA \times EF \times 10^{-6}}{BW} \quad (3)$$

where DED represents the dermal exposure dose ($\text{mg} \cdot \text{kg}^{-1} \cdot \text{year}^{-1}$), ABS the dermal absorption factor (unitless), AF the CR-to-skin adherence factor ($\text{mg} \cdot \text{cm}^{-2}$) and SA the total exposed skin surface area ($\text{cm}^2 \cdot \text{day}^{-1}$).

This estimation can serve as the foundation of future risk assessment studies.

4.11. Statistics

The statistical tests applied to the synthetic turf CR results - single-factor Analysis of Variance (ANOVA) and 2-sample T-test (performed on Microsoft® Excel) - were based on the assumption that the experimental data follows a normal distribution. This approximation is valid, according to the Central Limit Theorem (CLM), since the sample size ($N=108$) is well above the established limit of 30 (Ross, 2017). The same, however, does not apply to the commercial CR ($N=6$) and alternative material ($N=12$) samples, due to its low sample size, and therefore non-parametric tests - Mann-Whitney U test and Kruskal-Wallis test (performed on IBM® SPSS) - had to be used in these cases.

5. Results and Discussion

5.1. Method Optimization

As mentioned previously, multiple recovery assays were carried out to optimize the extraction method for VMSs in CR. The first step consisted of selecting the base protocol for the extractions: SG or DS (with either one, two or three extractions - DS1, DS2 and DS3, respectively). VMS recovery (Rec) is given by Equation 4 - a higher Rec value translates a more effective extraction of the VMSs (added through the spike solution) from the CR matrix.

$$Rec (\%) = \frac{A_S/A_{IS} - A_{NS}/A_{IS}}{A_{std}/A_{IS}} \times 100 \quad (4)$$

where A_S , A_{NS} , A_{std} and A_{IS} represent the chromatographic peak areas of the spiked samples, non-spiked samples, control standard (with the same concentration as the spike) and M4Q, respectively. The results are presented in Figure 3.

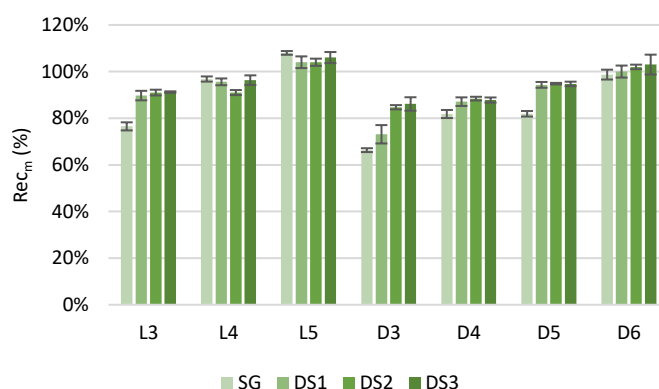


Figure 3. Results from the recovery assays carried out for the selection of the extraction protocol - SAFEGOAL (SG) vs. Dry Sludge (DS).

The mean recoveries (Rec_m) ranged between 66.3% (D3 in SG) and 108% (L5 in SG). All protocols provided good Rec values. From this primary assessment, DS2 and DS3 ended up being excluded - since no significant improvement was observed that would justify having a more solvent and time-consuming procedure (as a longer procedure increases the probability of contamination).

The subsequent optimization approach included the SG and DS1 protocols and consisted of selecting one of the two plus the extraction solvent. The original SG protocol used *n*-Hex, a common solvent for VMSs, nevertheless the two other solvents used in the DS protocol were also tested - EtAc and DCM. The results are presented in Appendix 4 (Figure A4.1). The mean recoveries ranged from 64.9% (D3 in DS1 with EtAc) to 105% (L5 in SG with EtAc). Again, good Rec values were obtained in all experiments. Regarding the protocol, since Rec values were very similar in both cases, SG ended up being selected since it was originally validated for CR (even if for PAH extraction). Overall, DCM was the solvent showing an apparent higher extraction. However, as discussed previously - see Materials and Methods - DCM originates a “dirtier” extract and may cause the deterioration of the GC column. Therefore, testing a

mixture of DCM and *n*-Hex (1:1) would be a more cautious approach, so the next set of recovery assays aimed to assess if this dilution led to an improvement. *n*-Hex was chosen as the co-solvent, since it is the most frequently employed for VMS extraction in several matrices.

For this purpose, two separate assays were carried out: the first with DCM and the second with a 1:1 *n*-Hex/DCM mixture. All mean Rec values stayed within the 90%-110% range: 91.2% (D6 with *n*-Hex/DCM)-107% (D3 with both solvents) and were practically identical in both cases (results are presented in Appendix 4 (Figure A4.2)). Considering the aforementioned concerns regarding DCM, the final decision was to use the 1:1 *n*-Hex/DCM mixture as the extraction solvent.

The final set of recovery assays concluded the analytical method optimization process and aimed at defining two parameters: the volume of solvent (5 mL were used in the previous assays, but since the sample amount was increased from 0.2 g to 1.0 g in relation to the original protocol, 10 mL were tested instead) and the type of filter used after extraction (the 0.20 µm PTFE filters used previously; higher pore size of 0.45 µm to check if the smaller filter retained part of the extracted VMSs; and no filtration at all). As seen in Appendix 4 (Figure A4.3), the mean recoveries ranged between 91.0% (D5 for 5 mL solvent and no filtration) and 112% (L5 for 10 mL solvent and no filtration). The 10 mL assays showed, in general, a higher variation between recoveries, so the solvent volume was set at 5 mL (faster procedure and lower solvent consumption). Filtration did not seem to have a negative effect on VMS extraction - therefore, the filtration step was kept, as during the experiments there were visible solid particles present in the extract. The smaller 0.20 µm filter did not seem to show an important VMS retention, and therefore were kept onwards.

5.2. Method Validation

5.2.1. Calibration and Linearity

Individual VMS calibration curves were constructed by the direct injection of 8 standards (prepared in *n*-Hex) at different concentrations: 5, 25, 50, 100, 250, 500, 750 and 1000 µg.L⁻¹ (all containing M4Q at 500 µg.L⁻¹). The instrumental response factors (RF) (*i.e.*, the ratio between VMS and IS peak areas) were correlated with the VMS concentrations (C_{VMS}) by applying a linear regression to the experimental data - Equation 5.

$$RF = a \times C_{VMS} + b \quad (5)$$

where *a* represents the slope and *b* the y-intercept. In this work, since the analysed compounds are often present at very low concentrations and the *b* values are very close to 0, the calibration curves were forced to pass through the origin (*i.e.*, *b* = 0) so that the concentration will be null when there is no signal. As an example, the calibration curve for D5, including the linear regression and its coefficient of determination (R^2), is presented in Figure 4, while those for the remaining VMSs can be consulted in Appendix 5 (Figures A5.1.1 - A5.1.6).

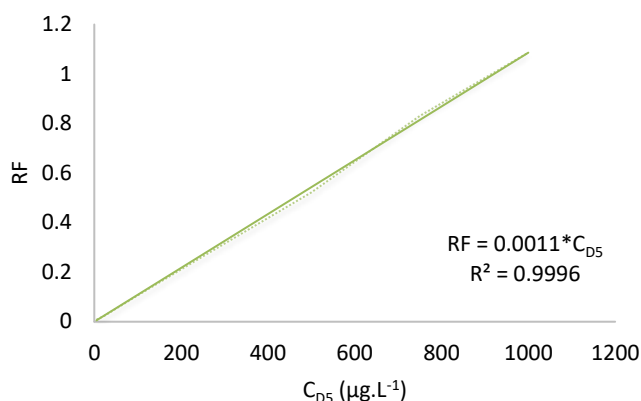


Figure 4. Calibration curve for the analysis of D5 in crumb rubber.

The following validation parameters were selected for linearity: the correlation coefficient (R) should be higher than 0.995, the number of calibration standards (N) equal or higher than 5, the ratio between the most and least concentrated standards (C_1/C_2) higher than 10, and the relative standard deviation of the slope (s_a/a) lower than 5%. The values of these parameters presented in Appendix 5.2 (Table A5.2.1) show that all calibration curves complied with the requirements.

5.2.2. Limits of Detection and Quantification

Limits of detection and quantification were calculated based on a signal-to-noise ratio (S/N) equal to 3 and 10, respectively. These limits were determined for both the quantification instrument (the GC-MS) and the analytical method - Table 9.

Table 9. Limits of detection and quantification for the analysis of VMS in crumb rubber.

Compound	IDL (pg)	IQL (pg)	MDL (ng.g ⁻¹)	MQL (ng.g ⁻¹)
L3	2.50	8.33	0.014	0.045
L4	1.50	5.00	1.74	5.80
L5	1.88	6.25	1.83	6.11
D3	3.00	10.0	4.46	14.9
D4	1.00	3.33	1.58	5.27
D5	0.001	0.005	0.006	0.018
D6	0.600	2.00	1.93	6.44

IDL: instrumental detection limit; IQL: instrumental quantification limit; MDL: method detection limit; MQL: method quantification limit.

MDL values ranged between 0.006 and 4.46 ng.g⁻¹, and MQL values between 0.018 and 14.9 ng.g⁻¹. The highest values were obtained for D3 and the lowest for D5.

5.2.3. Accuracy

The accuracy of an analytical method is defined by 'the degree of agreement of test results generated by the method to the true value' (Rao, 2018). This validation parameter is determined by spiking samples with a known concentration of the analytes and comparing this value with the one returned by the instrumental analysis. Accuracy can be measured by carrying out recovery assays and

calculating the analytes' recovery (see Equation 4 in Materials and Methods). In this work, the assays were performed using a VMS mix spike solution at two concentration levels: 100 ng.g⁻¹ and 500 ng.g⁻¹. The latter is the intermediate standard of the calibration curve, while the first level was included to assess the method's performance on a lower range of the calibration curve. The Rec_m from five replicates at each level is presented in Figure 5. The complete results of the precision tests can be consulted in Appendix 5 (Table A5.3.1).

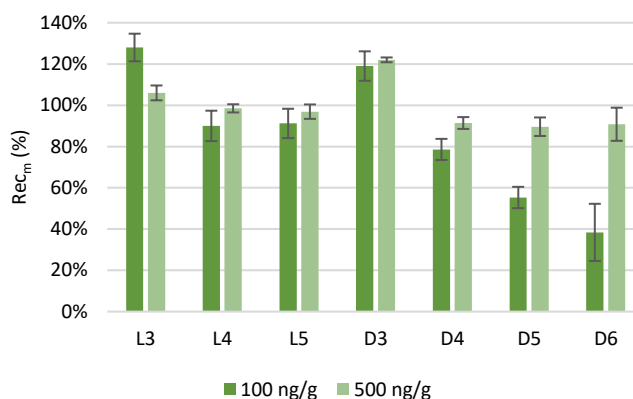


Figure 5. Accuracy for the analytical method to quantify VMS in crumb rubber (SG method at 100 ng.g⁻¹ and 500 ng.g⁻¹ spike levels).

The mean recovery obtained (taking into account all VMSs) was 85.8% for the 100 ng.g⁻¹ spike and 99.4% for the 500 ng.g⁻¹ spike. Low Rec values were registered for D5 and D6 (55.3% and 38.4%, respectively) with the more diluted spike. This may be explained by the sample containing VMSs at a significantly higher concentration than the one present in the spike (100 ng.g⁻¹), which would cause the results to be more susceptible to variations.

5.2.4. Precision

Precision consists of 'the degree of agreement among individual test results when the procedure is applied repeatedly to multiple samplings' (Rao, 2018). Precision tests were performed by analysing a set of CR sample replicates in the same day (repeatability/intra-day precision tests) and in two different days (intermediate precision/inter-day precision tests) for the same spike levels of the recovery assays. The parameter used for quantifying precision was the relative standard deviation (RSD), given by Equation 6.

$$RSD (\%) = \frac{stddev(Rec)}{Rec_m} \times 100 \quad (6)$$

The International Union of Pure and Applied Chemistry (IUPAC) sets the precision acceptance limit for analytical methods at 10% RSD (Thompson et al., 2002). The complete results of the precision tests can be seen in Appendix 5 (Table A5.3.2).

5.2.4.1. Repeatability (intra-day precision)

The obtained RSD values for the repeatability tests, performed with five replicates at 100 ng.g⁻¹ and 500 ng.g⁻¹ spike levels, are presented in Figure 6.

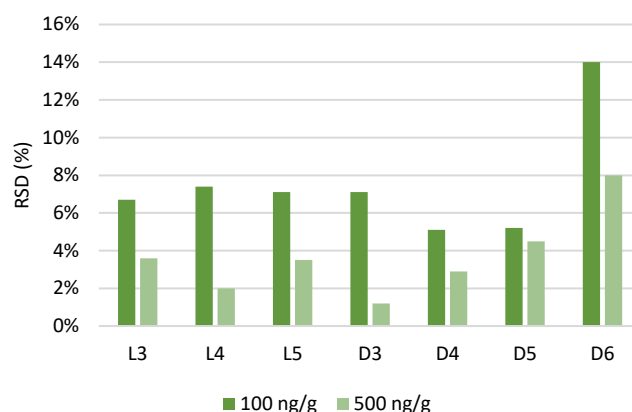


Figure 6. Repeatability for the analytical method to quantify VMS in crumb rubber (SG method at 100 ng.g⁻¹ and 500 ng.g⁻¹ spike levels).

In all cases, RSD values were higher for the less concentrated spike, which is to be expected. In general, the results complied with the 10% IUPAC limit, and therefore repeatability is considered to be very good, the exception being D6 with the 100 ng.g⁻¹ spike (14 %).

5.2.4.2. Intermediate precision (inter-day precision)

The obtained RSD values for the intermediate precision tests, performed with three replicates at the 100 ng.g⁻¹ and 500 ng.g⁻¹ spike levels in three different days each are presented in Figure 7.

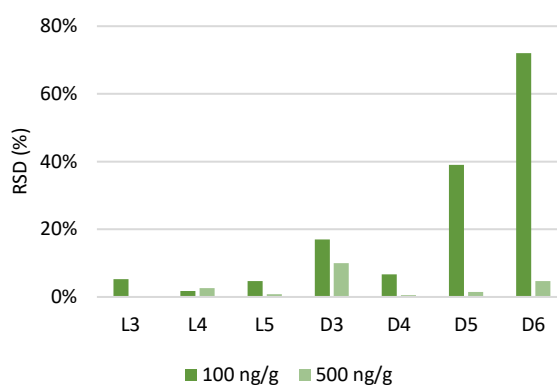


Figure 7. Intermediate precision for the analytical method to quantify VMS in crumb rubber (SG method at 100 ng.g⁻¹ and 500 ng.g⁻¹ spike levels).

RSD values were, once again, higher for the less concentrated spike - except for L4. Focusing on the 500 ng.g⁻¹ spike, all of the previous complied with the 10% IUPAC limit, although D3 showed a considerably higher RSD in comparison to the other congeners, set at the threshold value. For the 100 ng.g⁻¹ spike, on the other hand, the situation was different, as three of the VMSs registered RSD values which exceeded the IUPAC limit: D3 (17%), D5 (39%) and D6 (72%).

Overall, the validation parameters can be considered perfectly acceptable for the chosen protocol to be used in the assessment of VMS in CR.

5.3. Concentration of Siloxanes in Crumb Rubber

VMSs were detected in all 114 CR samples analysed in this work (108 samples collected from synthetic football fields and 6 sent from manufacturers), with total concentrations ranging from 10.29 ng.g⁻¹ (CR114) to 72.49 ng.g⁻¹ (CR124) in the field samples and from 90.17 ng.g⁻¹ (C4) to 5,089 ng.g⁻¹ (C2) in the commercial ones. cVMSs (as a whole) were detected in all samples and at higher concentrations (maximum of 3,912 ng.g⁻¹ for D6 in C2) than lVMSs, which were only detected in the commercial samples (maximum of 6.30 ng.g⁻¹ for L5 in C2). D3 was also only detected in commercial CR. D5 was the predominant compound - the only to be detected in the totality of the samples. All concentrations are reported in Appendix 6 (Table A6.1).

In general, VMS concentrations were lower than those of other hazardous substances analysed in CR (PAHs, plasticizers and other additives) - see State of the Art. These reported concentrations ranged from 400 ng.g⁻¹ in PCBs (Plesser & Lund, 2004) to 262,000 ng.g⁻¹ in plasticizers (Armada et al., 2022). Only one out of the 114 CR analysed samples reached this interval: commercial sample C2, at 5,089 ng.g⁻¹. This sample was, however, an outlier in relation to the remaining, with the second highest total concentration being 279.1 ng.g⁻¹ (commercial sample C1). The concentrations found in artificial turf samples were considerably lower, with the highest being 72.49 ng.g⁻¹ (CR124). The weathering of the material, from the meteorological conditions it was exposed to, and the activity of the players may be responsible for some depletion of the VMSs, which are volatile and prone to release to the atmosphere.

On the other hand, the concentrations obtained in this work were very similar to those of VMSs in soil, vegetation, and coastal sediment samples (10⁻¹-10³ degree of magnitude). Moreover, they were globally superior to VMS concentrations in sand (Capela et al., 2019), with only 26 CR samples below the maximum value measured in sand samples (21 ng.g⁻¹), but considerably lower than the reported levels in dewatered sludge (from 69,217 to 83,725 ng.g⁻¹). This is expected since the organic content of CR is likely between that of sand (lower) and sludge (higher), and VMSs are organic hydrophobic chemicals.

The individual VMS distribution percentage (*i.e.*, the ratio of individual VMS concentrations by the total concentration) in field and commercial CR is presented in Figures 8 and 9, respectively.

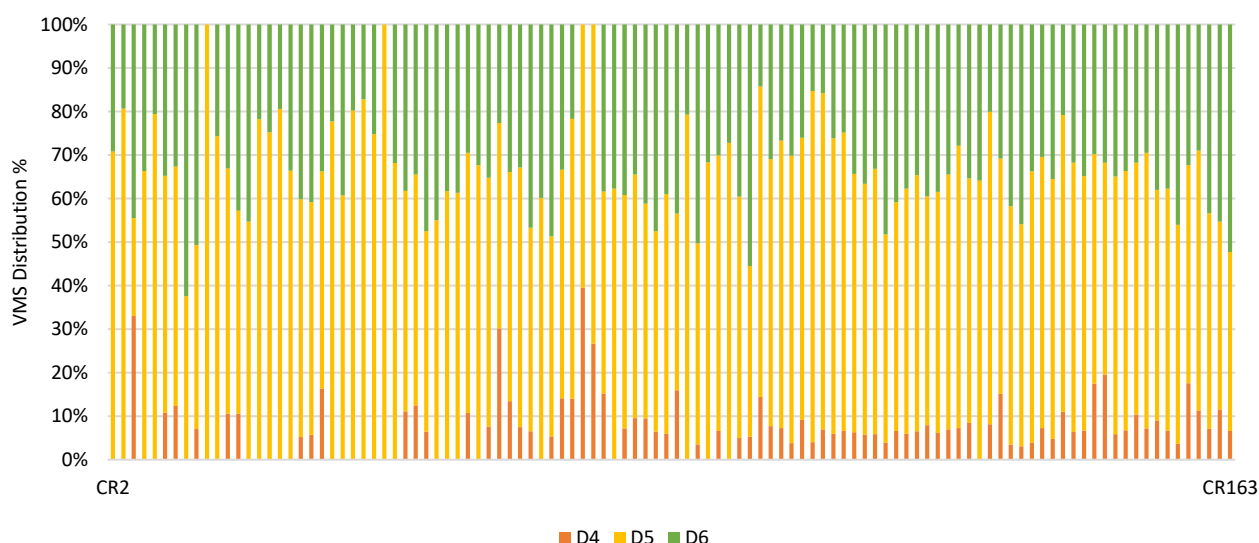


Figure 8. Individual VMS profile in crumb rubber samples from synthetic football fields.

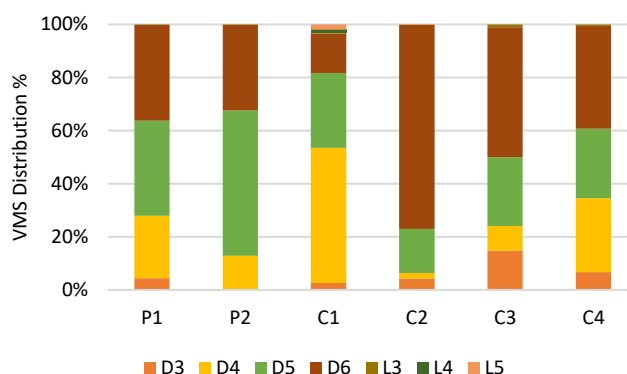


Figure 9. Individual VMS profile in commercial crumb rubber samples.

Within the field CR group, it can be observed that the profiles are predominantly similar, suggesting similar types of VMS sources, likely related to the manufacture of the tyres. The main variability factor is the presence/absence of D4 - detected in 73.2% of the field samples. Overall, there is a predominance of D5, which is expected since it is the most commonly used congener in numerous product formulations (ECHA, 2019). For the commercial samples, the profiles are more heterogeneous. In sample C2 (from China), already referenced due to the abnormally high concentration of VMSs, there is a visible difference in cVMS distribution, with D6 being the clear stand-out (76.9% of the total VMS concentration). This sample likely incorporated a considerable amount of this VMS in the manufacture process.

Since this work contained a large number of samples, a statistical analysis was conducted to infer the potential influence of some independent variables in the obtained results: for the field samples, the pitch placement (*i.e.*, indoor or outdoor), the origin (country), CR granulometry and field age; and for the commercial samples only the country where the CR was manufactured. The complete results of the statistical tests are presented in Appendix 8.

5.3.1. Indoor vs. Outdoor

CR samples were collected from outdoor and indoor fields, although the former are much more frequent than the latter - 101 outdoor and 7 indoor samples. The mean total VMS concentrations were of $59 \pm 18 \text{ ng.g}^{-1}$ for indoor samples and $45 \pm 15 \text{ ng.g}^{-1}$ for outdoor samples - Figure 10.

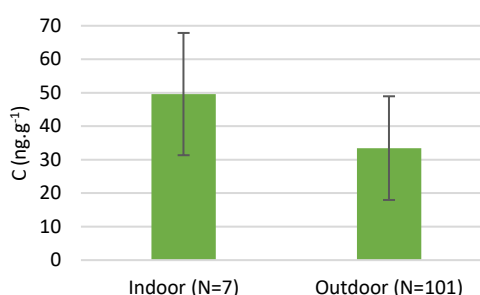


Figure 10. Mean total concentration (ng.g^{-1}) of VMSs in CR from indoor and outdoor fields.

As mentioned previously for VOCs and SVOCs, their concentration is expected to be higher in indoor fields (EPA, 2022). This is essentially due to a couple of factors: first, as indoor fields are not directly exposed to sunlight, the temperature of the pitch will be lower (and so will the volatilization rate of

VMSs), and second, the eventual lack of adequate ventilation will also hinder the release of VMSs from the granules, mainly to the surrounding air. The results seem to confirm it, with the mean VMS concentration being 1.48 times higher for indoor fields. Statistical analysis, by means of a 2-sample T test (with a 95% confidence interval) confirmed that there are, indeed, significant differences in the two types of fields, with the test returning a p -value of 0.48% ($< 5\%$). However, more indoor samples are required for further corroboration.

Other studies have also highlighted this distinction between indoor and outdoor fields for PAHs (Ginsberg et al., 2011) and VOCs (Simcox et al., 2011), measured in air samples. For heavy metals, meanwhile, Graça et al. (2022) concluded that, for most elements - 19 out of the 28 analysed - there were not statistical differences between both types of fields. This is expected since most metals are non-volatile (Sievers & Sadlowski, 1978).

For the remaining independent variables (country, granulometry and field age) only the outdoor samples were considered, due to the low indoor sample size and the statistical differences verified between the two groups.

5.3.2. Country

In terms of geographical representativity, CR samples came from 12 countries (Albania, Croatia, Finland, France, Germany, Greece, Italy, Poland, Portugal, Spain, Sweden and Chile) and the mean total VMS concentration in field CR samples by country (with the respective standard deviations) is presented in Figure 11. The mean total concentrations ranged from 13 ng.g^{-1} (Albania) to $45 \pm 21 \text{ ng.g}^{-1}$ (Sweden). For commercial CR samples the results also presented in Figure 11 show mean concentrations of $143 \pm 16 \text{ ng.g}^{-1}$ for the Portuguese samples and $1,392 \pm 2,466 \text{ ng.g}^{-1}$ for the Chinese samples (the high variability is caused by sample C2). The remaining values can be consulted in Appendix 6 (Table A6.2).

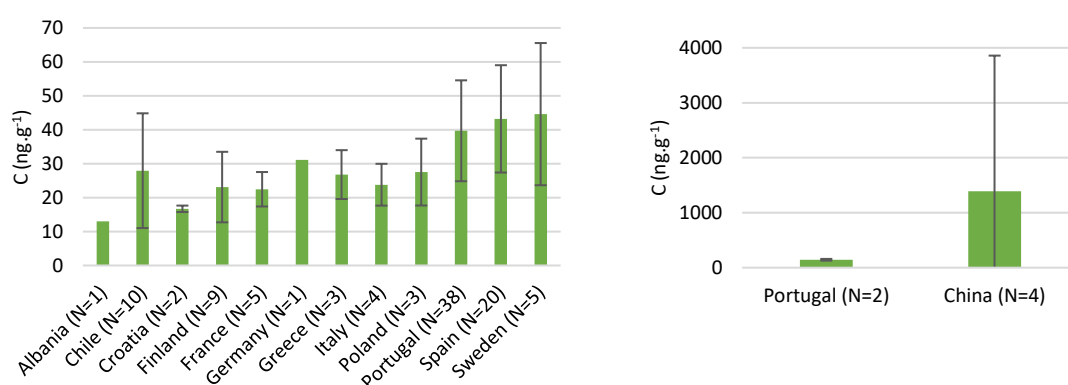


Figure 11. Mean total concentration (ng.g^{-1}) of VMSs in crumb rubber from synthetic football fields (left) and commercial crumb rubber (right), by country.

A single-factor ANOVA test was employed for field samples and a Mann-Whitney U test for commercial samples - both with a 95% confidence interval. A p -value of 0.09% was obtained in ANOVA and a significance (sig.) of 100% in the U test. This means that the country should be regarded as a variance factor in VMS concentration for field CR, but not for commercial CR (this result seems to be affected by the low number of samples, as there appears to be a noticeable difference between the Portuguese and Chinese commercial samples).

2-sample T tests were performed for all possible combinations of countries to address the source of variability - the results did not show a clear outlier in the population, but may suggest that Portugal, Spain and Sweden belong to a different population (as the p -values of the T tests carried out for these 3 countries are substantially higher than the remaining). However, this subject is quite complex and requires further investigation, as the amount of collected samples substantially varies from country to country (e.g., there are 38 samples from Portugal and only a single sample from Albania and Germany) and, on the other hand, the rubber applied in a certain field may not have necessarily been manufactured in the same country where the field is located. In fact, on most occasions probably not, as the owners often search for the least expensive material. Moreover, the fact that CR is produced from recycled tyres makes it very hard to trace its origin.

5.3.3. Granulometry

CR granulometry (mean of measurements performed on 20 randomly selected granules) ranged from 0.7 ± 0.2 mm (CR145) to 4 ± 1 mm (CR39), and therefore these particles can be classified as microplastics, as they are smaller than 5 mm. The collected data was separated in 4 subgroups according to the granulometry: < 1 mm, 1-2 mm, 2-3 mm and > 3 mm. The results are presented in Figure 12 and the mean total concentrations ranged from 31 ± 15 ng.g⁻¹ (1-2 mm) to 44 ± 14 ng.g⁻¹ (2-3 mm). The remaining values can be consulted in Appendix 6 (Table A6.3).

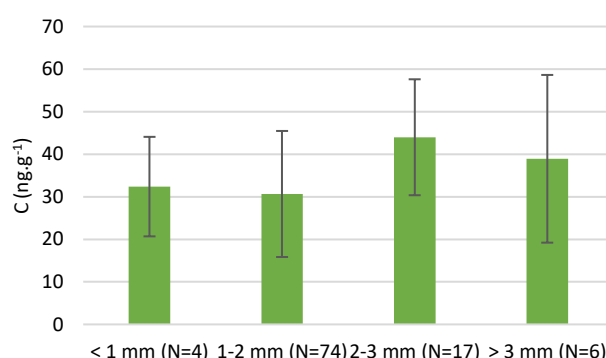


Figure 12. Mean total concentration (ng.g⁻¹) of VMSs in CR from synthetic football fields, by granulometry.

A single-factor ANOVA test with a 95% confidence interval returned a p -value of 2.77%. This indicates that the granulometry has a significant statistical effect on VMS concentration. 2-sample T tests were performed for all possible subgroup combinations, and the results indicated that the < 1 mm and 1-2 mm subgroups seem to belong to the same population, as do the 2-3 mm and > 3 mm subgroups. As such, rubber granules smaller than 2 mm appear to have lower VMS concentrations, possibly due to the more extensive wearing that also may change the size and shape of the granules.

Plessner & Lund (2004) and Graça et al. (2022) have also evaluated the potential effect of CR granulometry in PAH and metal levels, respectively, but concluded that particle size did not seem an influential factor.

5.3.4. Field Age

The final independent variable to be evaluated was the field age, with 5 subgroups being considered: < 1 year, 1-5 years, 5-10 years, > 10 years and unknown (age not possible to obtain). The results are presented in Figure 13 and the mean total concentrations ranged from $26 \pm 14 \text{ ng.g}^{-1}$ (unknown) to $46 \pm 14 \text{ ng.g}^{-1}$ (< 1 year). The remaining values can be seen in Appendix 6 (Table A6.4).

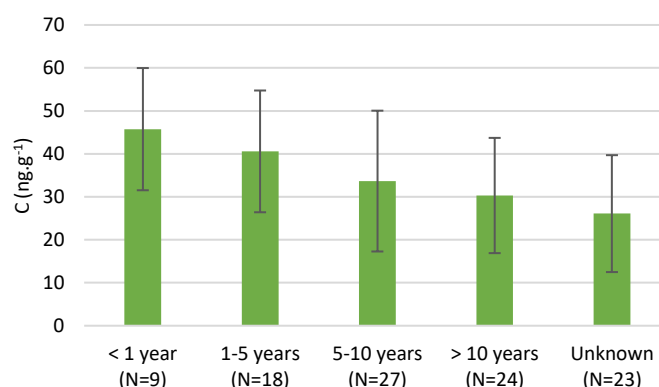


Figure 13. Mean total concentration (ng.g^{-1}) of VMSs in CR from synthetic football fields, by field age.

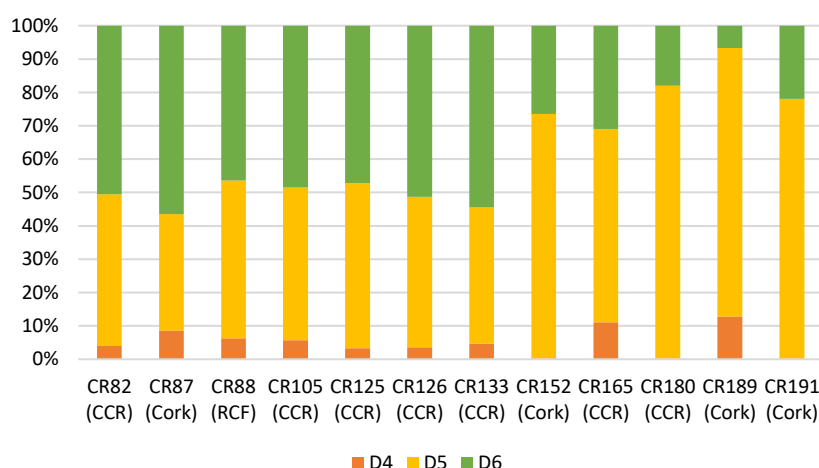
Due to their volatile nature and the constant wearing of the material, it is expected that VMS concentration in CR decreases over time, although this decrease can be somewhat balanced by the potential adsorption of “new” siloxane molecules, which may be present in the environment and/or the PCPs used by the players. It can be observed that total VMS concentration tends to decrease over time (this can be seen with particular relevance in the transition between the 1-5 years and 5-10 years period). The ANOVA test returned a p -value of 3.22%, which indicates (for this confidence interval) that field age may have a significant impact on VMS concentration. 2-sample T-tests were performed for all possible subgroup combinations, and the results indicate that the < 1 year and 1-5 years subgroups seem to belong to the same population, as do the 5-10 years and > 10 years subgroups. The “unknown” subgroup is statistically different from all subgroups except for the > 10 years. It appears, therefore, that VMSs gradually disappear from the rubber particles. There is, however, a very important consideration to be made regarding field age: since in many fields the CR is replaced occasionally, the field age may not correspond to the actual time that the CR spent on the field. Therefore, the robustness of these types of tests depends on the field owners/workers registering the dates when the CR is replaced, which is not a common practice in most countries.

5.4. Concentration of Siloxanes in Other Materials

In this work, 12 samples from 3 other materials (which can also be applied as synthetic turf infill) were analysed: coloured CR, cork, and a rubber/coconut fibre. It is worth mentioning that coloured CR may contain other additives other than colouring agents, as in some samples was observed the formation of a film in the extract’s surface which offered great resistance to filtration. In fact, one of the extracted samples had to be excluded as the filtration could not be properly carried out (even when using a larger $0.45 \mu\text{m}$ filter instead of a $0.20 \mu\text{m}$ one). The extracts of this sample were injected in the GC-MS but clogged the syringe, hence their exclusion.

VMSs were detected in all 12 samples, in total concentrations ranging from 7.79 ng.g⁻¹ (CR152, cork) to 99.2 ng.g⁻¹ (CR126, coloured CR). Unlike for other hazardous substances - see State of the Art - in which reported concentrations were considerably lower in alternative materials than in CR (Armada et al., 2022; Celeiro et al., 2021), for siloxanes they were very similar to the ones of field CR - 10.9-72.5 ng.g⁻¹. As was the case for the field samples, D3, L3, L4 and L5 were not detected. These results are detailed in Appendix 7 (Table A7.1).

The siloxane distribution percentage in the alternative infill materials is presented in Figure 14.



CCR - coloured crumb rubber; RCF - rubber/coconut fibre.

Figure 14. Individual VMS profile in alternative infill materials.

It can be observed that the profiles of samples CR82, 87, 88, 105, 125, 126 and 133 are very similar, showing a small amount of D4 (< 10%) and then approximately equal fractions of D5 and D6. CR165 and 189, on the other hand, had larger fractions of D4 and D5 and the remaining two samples (CR180 and 191) did not contain D4, with D5 clearly being the major component. In general, these profiles resemble the ones of synthetic turf CR.

As for CR, a statistical analysis was used to assess the influence of independent variables - this time, only the type of material. The mean total VMS concentration of the analysed samples distributed by type of material is presented in Figure 15. The values were of 55 ± 33 ng.g⁻¹ for coloured CR, 27 ± 31 ng.g⁻¹ for cork and 74 ng.g⁻¹ for the rubber/coconut fibre.

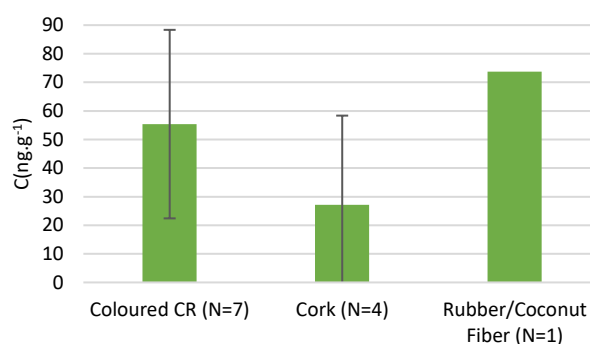


Figure 15. Mean total concentration (ng.g⁻¹) of VMSs in alternative synthetic turf infill materials, by type of material.

From the three materials, cork was the one which showed the lowest siloxane content, following the same trend as all the other classes of microcontaminants analysed in CR (Armada et al., 2022; Celeiro et al., 2021). This further reinforces the argument that this material is a safer alternative to CR in synthetic fields. Although there are CR samples with lower VMS content than the cork samples and their means are similar - $34 \pm 16 \text{ ng.g}^{-1}$ for field CR, as just mentioned other studies have shown lower levels of hazardous substances in cork. However, its higher cost compared to CR (about four times) is likely preventing it from being an extended alternative yet. A Kruskal-Wallis test (with a 95% confidence interval) returned a sig. of 24.3%, indicating that there are no significant statistical differences between the subgroups. However, it must be said that the robustness of the test is not very high, due to the low number of analysed samples and that the tendency for lower VMS presence in cork is perceived.

5.4.1. Crumb Rubber vs. Other Materials

The final results to be presented - Figure 16 - consist of a comparison of CR (field and commercial) with the three alternative materials. Sample C2, the clear outlier in the commercial CR population (abnormally high concentration), was excluded from this analysis.

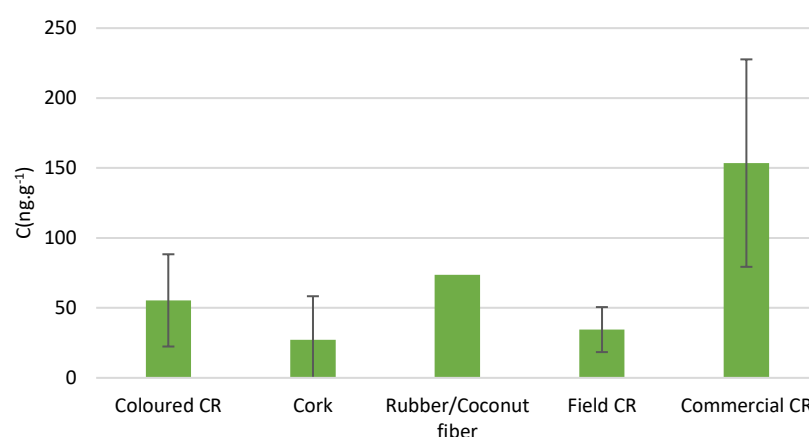


Figure 16. Mean total concentration (ng.g^{-1}) of VMSs in CR and alternative infill materials, by type of material.

A Kruskal-Wallis test (with a 95% confidence interval) clearly indicated that there is significant variation between subgroups - sig. < 0.01%. Pairwise comparisons between the different subgroups showed that commercial CR substantially differs from field CR and cork (sig. < 0.01%). These results corroborate the ones obtained in the field age analysis, indicating that the VMS composition of CR is affected by its application in sports fields.

5.5. Human Exposure to Siloxanes from Crumb Rubber

From all the results gathered in CR from synthetic football pitches, it was possible to estimate human exposure doses to siloxanes in CR by incidental ingestion and dermal absorption, using Equations 2 and 3 (see Materials and Methods) for three exposure scenarios/targets: young players (6-11 years old), adult players (> 18 years old) and turf maintenance workers. Two exposure doses were calculated for each scenario: the average expected exposure (from the mean VMS concentration of the 101 outdoor field CR samples) and the “worst-case scenario” (from commercial sample C2, the one with the highest

concentration reported in this work). The total exposure dose consists of the sum of the doses for D4, D5 and D6. D3, L3 and L5 were also detected in sample C2, however they were not considered for this exposure study due to the lack of available toxicological information on these substances. The values considered for the different toxicological and exposure parameters are presented in Appendix 9.

5.5.1. Oral Exposure

B values for D4, D5 and D6 were obtained from ECHA's database for toxicological properties (ECHA, 2022). Peterson et al. (2018) reported an IR of 50 mg.day⁻¹ for incidental CR ingestion - half of the rate stated in an official EPA Directive for outdoor soil and dust ingestion (EPA, 2014a), which was also adopted in this work. For EF, it was assumed that adult players use the fields 4 days a week in 3 h sessions during 11 months of the year (approximately 24.0 days.year⁻¹), young players 3 days a week in 3 h sessions during 10 months of the year (approximately 16.5 days.year⁻¹) and maintenance workers once a week in 8 h shifts during 11 months of the year (approximately 16.0 days.year⁻¹). Finally, the mean BW values for 6-11 year olds and adults (31.8 and 80.0 kg, respectively) were taken from EPA guidelines (2011).

The estimated oral exposure doses (OEDs) - average exposure and "worst-case scenario" exposure - for young players, adult players and turf maintenance workers are presented in Table 10.

Table 10. Estimated doses for oral exposure to CR (ng.kg⁻¹.year⁻¹) in outdoor synthetic turf football fields.

Scenario	Average Exposure				"Worst-Case Scenario"			
	D4	D5	D6	Total	D4	D5	D6	Total
Adult Player	0.01	0.05	0.03	0.09	0.45	2.19	8.80	11.44
Young Player	0.02	0.09	0.05	0.16	0.77	3.79	15.22	19.78
Worker	0.01	0.03	0.02	0.06	0.30	1.46	5.87	7.62

The highest total OED was the one of young football players - 19.78 ng.kg⁻¹.year⁻¹.

5.5.2. Dermal Exposure

As was the case for the oral bioaccessibility, ABS values for D4, D5 and D6 were obtained from ECHA's database for toxicological properties (ECHA, 2022). The AF of 0.40 mg.cm⁻² was the mean value reported by EPA for football players (EPA, 1989). The exposed SA values were calculated based on guidance from EPA's Exposure Factors Handbook (EPA, 2011). This document contains, for different age groups, the mean total body surface area as well as the mean percent surface area of each body part. It was considered that the body parts exposed during physical exercise were the head, forearms, hands, lower legs and feet. According to the same reference, the forearms were assumed to represent 45% of the arms and the lower legs 40% of the legs.

The estimated dermal exposure doses (DEDs) - average exposure and "worst-case scenario" exposure - for young players, adult players and turf maintenance workers are presented in Table 11.

Table 11. Estimated doses for dermal exposure to CR ($\text{ng.kg}^{-1}.\text{year}^{-1}$) in outdoor synthetic turf football fields.

Scenario	Average Exposure				“Worst-Case Scenario”			
	D4	D5	D6	Total	D4	D5	D6	Total
Adult Player	1.40×10^{-3}	1.73×10^{-2}	3.11×10^{-5}	0.02	0.05	0.75	0.01	0.80
Young Player	1.27×10^{-3}	1.56×10^{-2}	2.81×10^{-5}	0.02	0.04	0.67	0.01	0.72
Worker	9.35×10^{-4}	1.16×10^{-2}	2.07×10^{-5}	0.01	0.03	0.50	0.01	0.54

In this case, the highest total DED was the one of adult players: $0.898 \text{ ng.kg}^{-1}.\text{year}^{-1}$. Oral exposures were, in all cases, larger (up to 27 times) than dermal exposures, which indicates that the oral pathway (through incidental ingestion of CR) is more significant in terms of VMS exposure.

The estimated siloxane exposure doses by themselves are insufficient to evaluate the potential hazards of continuous activity in CR-infilled synthetic football fields, as they do not provide information regarding cancer and non-cancer risks. Nonetheless, they consist of an important starting point for a possible future work on this subject.

6. Conclusions

This work was pioneer in the analysis of volatile methylsiloxanes (L3 to L5 and D3 to D6) in crumb rubber (CR), a material derived from recycled tyres which is frequently applied as infill in synthetic turf sports' facilities. These compounds were extracted using an ultrasound-assisted extraction (UAE) technique with QuEChERS clean-up, while instrumental analysis was carried out by GC-MS. A total of 126 samples were analysed - 120 samples collected from football fields (108 crumb rubber samples and 12 of other infill materials - cork, coloured CR and a rubber/coconut fibre) and 6 samples obtained from crumb rubber manufacturers.

Volatile methylsiloxanes (VMSs) were detected in all samples, reaching a maximum total concentration of 72.49 ng.g⁻¹ in the CR field samples, 5,089 ng.g⁻¹ in the commercial CR samples and 99.16 ng.g⁻¹ in the alternative materials (coloured CR). The highest concentration of a single compound was measured in sample C2, from China - 3,912 ng.g⁻¹ for D6. Linear siloxanes were only detected in commercial CR, and at considerably lower levels than cyclic siloxanes - maximum of 6.30 ng.g⁻¹ for L5. From the cyclic siloxanes, D5 was the predominant one in terms of detection frequency - 100% (vs. 97.6% for D6, 78.6% for D4 and 3.97% for D3).

A statistical analysis procedure was carried out to assess the influence of five independent variables - field placement (indoor vs. outdoor), country of collection/manufacturing (for field and commercial samples, respectively), particle granulometry, field age and type of material - on the reported concentrations of VMSs. It was observed that the mean total VMS concentration was 1.48 times higher in indoor fields and that there was an increase with particle size. Moreover, it seems that field application leads to a gradual decrease in VMS levels. The other parameters do not seem to have a significant impact in the distribution of VMSs. In terms of alternative materials, cork may be a safer option in the future for artificial turf infill, given the generally lower levels of found VMSs.

The final part of this work consisted of a preliminary study on human exposure to VMSs in synthetic turf football fields. Oral and dermal exposure doses were estimated for three different exposure scenarios (young players (6-11 years old), adult players (> 18 years old) and turf maintenance workers) and the highest obtained oral and dermal exposure doses ("worst-case scenarios") were of 19.8 ng.g⁻¹ (for young players) and 0.803 ng.g⁻¹ (for adult players), respectively.

CR is now considered part of the family of microplastics, and this is enough to raise even more the awareness to this material and its potential health and environmental impacts.

The results of this thesis will be used to write a scientific paper which will include the development and validation stages of the analytical method, the obtained concentrations of volatile methylsiloxanes in crumb rubber, and also the continuation of the human exposure study - which will aim to translate the estimated exposure doses into perceptible cancer and non-cancer risks for synthetic field users.

7. Evaluation of the Accomplished Work

7.1. Accomplished Objectives

The main objectives initially set for this work were the following: development of a reliable, robust method for the analysis of volatile methylsiloxanes (VMSs) in crumb rubber; application of this method to a set of crumb rubber (CR) samples to evaluate the presence of VMSs in this material; and finally, an estimation of human exposure doses to VMSs in synthetic turf football fields. The first two objectives were completely fulfilled. The latter, on the other hand, was only partially completed due to the fact that one of the possible exposure pathways - inhalation - could not be calculated. In order to do so, the migration of VMSs from CR to the surrounding air would have to be estimated to quantify its concentration in this gaseous matrix, but this was impossible to do within the timeframe available.

7.2. Additional Work

The additional work which was not stated in the main objectives consisted of the analysis of three other materials that can be used as infill in synthetic turf - cork, coloured CR and a rubber/coconut fibre - with the goal of evaluating whether they are viable, safer alternatives to CR - and also the possibility of including commercial CR samples in the study.

7.3. Recommendations and Future Work

The main recommendations to improve the quality of the present work are the following: test the method's performance (in terms of accuracy and precision) for other spike levels besides 100 ng.g⁻¹ and 500 ng.g⁻¹; increase the representativity of the samples (*e.g.*, collect samples from other countries), aim to balance the sample size of the different statistical subgroups to improve the robustness of the tests (*e.g.*, there were 101 samples from outdoor fields but only 7 from indoor fields, and some countries only had a single sample); and expand the range of analysed siloxanes to include the higher molecular weight compounds, since despite its low volatility they can still be relevant in terms of oral and dermal exposure.

For future work, as mentioned previously the human exposure doses results will be the starting point for an elaborate risk assessment study, which will aim to quantify the cancer and non-cancer risk of exposure to siloxanes in synthetic turf football fields. For this study, it will be necessary to measure/estimate the concentration of VMSs in the air the field users breathe, since the inhalation exposure doses are yet to be quantified. Moreover, it would also be interesting to conduct an analysis of siloxanes in the leachates coming from the watering of the fields.

8. References

- Abian, J. (1999). The coupling of gas and liquid chromatography with mass spectrometry. *Journal of Mass Spectrometry*, 34(3), 157-168. [https://doi.org/10.1002/\(SICI\)1096-9888\(199903\)34:3<157::AID-JMS804>3.0.CO;2-4](https://doi.org/10.1002/(SICI)1096-9888(199903)34:3<157::AID-JMS804>3.0.CO;2-4)
- Accettola, F., Guebitz, G. M., & Schoeftner, R. (2008). Siloxane removal from biogas by biofiltration: Biodegradation studies. *Clean Technologies and Environmental Policy*, 10(2), 211-218. <https://doi.org/10.1007/s10098-007-0141-4>
- Adachi, K., & Tainosho, Y. (2004). Characterization of heavy metal particles embedded in tire dust. *Environment International*, 30(8), 1009-1017. <https://doi.org/10.1016/j.envint.2004.04.004>
- Adhikari, B., De, D., & Maiti, S. (2000). Reclamation and recycling of waste rubber. *Progress in Polymer Science*, 25(7), 909-948. [https://doi.org/10.1016/S0079-6700\(00\)00020-4](https://doi.org/10.1016/S0079-6700(00)00020-4)
- Ait Bamai, Y. (2020). Semi-Volatile Organic Compounds (SVOCs): Phthalates and Phosphorous Frame Retardants and Health Risks. In R. Kishi, D. Norbäck, & A. Araki (Eds.), *Indoor Environmental Quality and Health Risk toward Healthier Environment for All* (pp. 159-178). Springer. https://doi.org/10.1007/978-981-32-9182-9_8
- Albero, B., Tadeo, J. L., & Pérez, R. A. (2019). Ultrasound-assisted extraction of organic contaminants. *TrAC Trends in Analytical Chemistry*, 118, 739-750. <https://doi.org/10.1016/j.trac.2019.07.007>
- Anastassiades, M., Lehotay, S. J., Štajnbaher, D., & Schenck, F. J. (2003). Fast and Easy Multiresidue Method Employing Acetonitrile Extraction/Partitioning and “Dispersive Solid-Phase Extraction” for the Determination of Pesticide Residues in Produce. *Journal of AOAC INTERNATIONAL*, 86(2), 412-431. <https://doi.org/10.1093/jaoac/86.2.412>
- Andersson, J. T., & Achten, C. (2015). Time to Say Goodbye to the 16 EPA PAHs? Toward an Up-to-Date Use of PACs for Environmental Purposes. *Polycyclic Aromatic Compounds*, 35(2-4), 330-354. <https://doi.org/10.1080/10406638.2014.991042>
- Arienzo, M., Ferrara, L., & Trifuoggi, M. (2021). The Dual Role of Microplastics in Marine Environment: Sink and Vectors of Pollutants. *Journal of Marine Science and Engineering*, 9(6), 642. <https://doi.org/10.3390/jmse9060642>
- Armada, D., Llompart, M., Celeiro, M., Garcia-Castro, P., Ratola, N., Dagnac, T., & de Boer, J. (2022). Global evaluation of the chemical hazard of recycled tire crumb rubber employed on worldwide synthetic turf football pitches. *Science of The Total Environment*, 812, 152542. <https://doi.org/10.1016/j.scitotenv.2021.152542>
- Basheer, C., Alhooshani, K., Nuhu, A. A., Kanimozhi, S., & Lee, H. K. (2012). 3.34—Sample Preparation of Complex Biological Samples in the Analysis of Trace-Level Contaminants. In J. Pawliszyn (Ed.), *Comprehensive Sampling and Sample Preparation* (pp. 681-700). Academic Press. <https://doi.org/10.1016/B978-0-12-381373-2.00109-5>

- Bletsou, A. A., Asimakopoulos, A. G., Stasinakis, A. S., Thomaidis, N. S., & Kannan, K. (2013). Mass Loading and Fate of Linear and Cyclic Siloxanes in a Wastewater Treatment Plant in Greece. *Environmental Science & Technology*, 47(4), 1824-1832. <https://doi.org/10.1021/es304369b>
- Bridgestone. (2022). *Tire construction*. <https://www.bridgestoneamericas.com/en/corporate-social-responsibility/safety/tires-101/tire-construction>. (Last accessed in March 2022)
- Brinke, A. (2002). *Silica reinforced tyre rubbers - PhD Thesis*, University of Twente, 143 p.; Twente University Press, The Netherlands. <https://ris.utwente.nl/ws/portalfiles/portal/6073378/t000003d.pdf>
- Brocks, J. J., & Hope, J. M. (2014). Tailing of chromatographic peaks in GC-MS caused by interaction of halogenated solvents with the ion source. *Journal of Chromatographic Science*, 52(6), 471-475. <https://doi.org/10.1093/chromsci/bmt068>
- Capela, D., Alves, A., Homem, V., & Santos, L. (2016). From the shop to the drain—Volatile methylsiloxanes in cosmetics and personal care products. *Environment International*, 92-93, 50-62. <https://doi.org/10.1016/j.envint.2016.03.016>
- Capela, D., Homem, V., Alves, A., & Santos, L. (2016). Volatile methylsiloxanes in personal care products: Using QuEChERS as a “green” analytical approach. *Talanta*, 155, 94-100. <https://doi.org/10.1016/j.talanta.2016.04.029>
- Capela, D., Vila, M., Llompart, M., Dagnac, T., García-Jares, C., Alves, A., & Homem, V. (2019). Footprints in the sand - Assessing the seasonal trends of volatile methylsiloxanes and UV-filters. *Marine Pollution Bulletin*, 140, 9-16. <https://doi.org/10.1016/j.marpolbul.2019.01.021>
- CDC. (2018). *Fourth National Report on Human Exposure to Environmental Chemicals*. https://www.cdc.gov/exposurereport/pdf/FourthReport_UpdatedTables_Volume1_Mar2018.pdf
- Celeiro, M., Armada, D., Dagnac, T., de Boer, J., & Llompart, M. (2021). Hazardous compounds in recreational and urban recycled surfaces made from crumb rubber. Compliance with current regulation and future perspectives. *Science of The Total Environment*, 755, 142566. <https://doi.org/10.1016/j.scitotenv.2020.142566>
- Celeiro, M., Dagnac, T., & Llompart, M. (2018). Determination of priority and other hazardous substances in football fields of synthetic turf by gas chromatography-mass spectrometry: A health and environmental concern. *Chemosphere*, 195, 201-211. <https://doi.org/10.1016/j.chemosphere.2017.12.063>
- Chandrasekaran, V. C. (2010). CHAPTER 6—Rubbers, Chemicals and Compounding for ‘O’ Rings and Seals. In V. C. Chandrasekaran (Ed.), *Rubber Seals for Fluid and Hydraulic Systems* (pp. 57-69). William Andrew Publishing. <https://doi.org/10.1016/B978-0-8155-2075-7.10006-1>
- Chavoshani, A., Hashemi, M., Mehdi Amin, M., & C. Ameta, S. (2020). Chapter 3—Personal care products as an endocrine disrupting compound in the aquatic environment. In A. Chavoshani, M. Hashemi, M. Mehdi Amin, & S. C. Ameta (Eds.), *Micropollutants and Challenges* (pp. 91-144). Elsevier. <https://doi.org/10.1016/B978-0-12-818612-1.00003-9>

- Clarke, W. (2017). Chapter 1 - Mass spectrometry in the clinical laboratory: Determining the need and avoiding pitfalls. In H. Nair & W. Clarke (Eds.), *Mass Spectrometry for the Clinical Laboratory* (pp. 1-15). Academic Press. <https://doi.org/10.1016/B978-0-12-800871-3.00001-8>
- Continental. (2022). *Tyre production*. <https://www.continental-tyres.co.uk/car/all-about-tyres/tyre-essentials/tyre-production>
- Czajczyńska, D., Czajka, K. M., Krzyżyńska, R., & Jouhara, H. (2019). Experimental analysis of waste tyres as a sustainable source of energy. *E3S Web of Conferences*, 100, 00012. <https://doi.org/10.1051/e3sconf/201910000012>
- De Groot, G. M., Oomen, A. G., & Mennen, M. G. (2017). *Evaluation of health risks of playing sports on synthetic turf pitches with rubber granulate: Scientific background document* [Report]. Rijksinstituut voor Volksgezondheid en Milieu RIVM. <https://rivm.openrepository.com/handle/10029/620805>
- Dschagarowa, E., Zheleva, D., & Tipova, N. (2014). *Stearic acid in rubber chemistry and technology* (pp. 25-58).
- Directive (EC) No 1999/31, (1999). *Council Directive 1999/31/EC of 26 April 1999 on the landfill of waste*. <https://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:31999L0031:EN:HTML>
- Directive (EC) No 2000/76, (2000). *Directive 2000/76/EC of the European Parliament and of the Council of 4 December 2000 on the incineration of waste*. <https://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CONSLEG:2000L0076:20081211:EN:PDF>
- Regulation (EC) No 1907/2006, (2006). *Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC*. <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:02006R1907-20210101>
- Regulation (EC) No 1223/2009, (2009). *Regulation (EC) No 1223/2009 of the European Parliament and of the Council of 30 November 2009 on cosmetic products*. <https://eur-lex.europa.eu/legal-content/PT/ALL/?uri=CELEX%3A32009R1223>
- Regulation (EU) No 1199/2021, (2021). *Commission Regulation (EU) 2021/1199 of 20 July 2021 amending Annex XVII to Regulation (EC) No 1907/2006 of the European Parliament and of the Council as regards polycyclic-aromatic hydrocarbons (PAHs) in granules or mulches used as infill material in synthetic turf pitches or in loose form on playgrounds or in sport applications*. <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A32021R1199>
- ECHA. (2017a). *An evaluation of the possible health risks of recycled rubber granules used as infill in synthetic turf sports fields*. https://echa.europa.eu/documents/10162/13563/annex-xv_report_rubber_granules_en.pdf/dbcb4ee6-1c65-af35-7a18-f6ac1ac29fe4

- ECHA. (2017b). *An evaluation of the possible health risks of recycled rubber granules used as infill in synthetic turf sports fields*. https://echa.europa.eu/documents/10162/13563/annex-xv_report_rubber_granules_en.pdf/dbcb4ee6-1c65-af35-7a18-f6ac1ac29fe4
- ECHA. (2017c). *Annex XV Report - Rubber granules evaluation (Ver 1.01)*, 120 p. https://echa.europa.eu/documents/10162/17220/annexes_to_axv_report_rubber+granules_en.pdf/f3cc9f58-8ab3-8e4a-0258-51466817f0fd. (Last accessed in March 2022).
- ECHA. (2018). *Draft Minutes of the 60th Meeting of the Member State Committee (MSC-60) 12-14 June 2018*. https://echa.europa.eu/documents/10162/2200413/msc-60_minutes_en.pdf/f407b9e7-78a4-966d-cc51-9d36b8c7ee3e?t=1551257817661
- ECHA. (2019). *Annex XV Restriction Report - proposal for a restriction*, 91 p. https://echa.europa.eu/documents/10162/13641/rest_d4d5d6_axvreport_en.pdf/c4463b07-79a3-7abe-b7a7-5c816e45bb98
- ECHA. (2021). *Granules and mulches on sports pitches and playgrounds*. <https://echa.europa.eu/en/hot-topics/granules-mulches-on-pitches-playgrounds>. (Last accessed in March 2022)
- ECHA. (2022). *Decamethylcyclopentasiloxane—Toxicological Information*. <https://echa.europa.eu/pt/brief-profile/-/briefprofile/100.007.969>. (Last accessed in June 2022)
- ECHEMI. (2021). *Global silicone demand*. <https://www.echemi.com/cms/141795.html>. (Last accessed in March 2022)
- EFSA. (2016). *Use of the benchmark dose approach in risk assessment*. European Food Safety Authority, 51 p. <https://www.efsa.europa.eu/sites/default/files/consultation/160714.pdf>
- EFSA, E. F. S. (2008). Polycyclic Aromatic Hydrocarbons in Food—Scientific Opinion of the Panel on Contaminants in the Food Chain. *EFSA Journal*, 6(8), 724. <https://doi.org/10.2903/j.efsa.2008.724>
- Emwas, A.-H., Al-Talla, Z., Yang, Y., & Kharbatia, N. (2015). Gas Chromatography-Mass Spectrometry of Biofluids and Extracts. *Methods in Molecular Biology (Clifton, N.J.)*, 1277, 91-112. https://doi.org/10.1007/978-1-4939-2377-9_8
- EPA. (1989). *Risk Assessment Guidance for Superfund Volume I Human Health Evaluation Manual (Part A)*. Office of Emergency and Remedial Response, EPA/540/1-89/002, Washington, D.C., 291 p. https://www.epa.gov/sites/default/files/2015-09/documents/rags_a.pdf
- EPA. (1991). *Role of the Baseline Risk Assessment in Superfund Remedy Selection Decisions*. Office of Solid Waste and Emergency Response, Directive 9355.0-30, Washington, D.C., 11 p. <https://nepis.epa.gov/Exe/ZyNET.exe/910165CR.TXT?ZyActionD=ZyDocument&Client=EPA&Index=1991+Thru+1994&Docs=&Query=&Time=&EndTime=&SearchMethod=1&TocRestrict=n&Toc=&TocEntry=&QField=&QFieldYear=&QFieldMonth=&QFieldDay=&IntQFieldOp=0&ExtQFieldOp=0&XmlQuery=&File=D%3A%5Czyfiles%5CIndex%20Data%5C91thru94%5CTxt%5C00000028%5C910165CR.txt&User=ANONYMOUS&Password=anonymous&SortMethod=h%7C-&MaximumDocuments=1&FuzzyDegree=0&ImageQuality=r75g8/r75g8/x150y150g16/i425&Display=hpfr&>

DefSeekPage=x&SearchBack=ZyActionL&Back=ZyActionS&BackDesc=Results%20page&MaximumPages=1&ZyEntry=1&SeekPage=x&ZyPURL

- EPA. (1994). *Prevention, Pesticides and Toxic Substances (7508W): Sodium and zinc salts of 2-mercaptobenzothiazole*. https://www3.epa.gov/pesticides/chem_search/reg_actions/reregistration/fs_PC-051701_1-Sep-94.pdf
- EPA. (2000). *National Emission Standards for Hazardous Air Pollutants: Rubber Tire Manufacturing*. <https://www.govinfo.gov/content/pkg/FR-2000-10-18/pdf/00-26224.pdf>
- EPA. (2008). *Polycyclic Aromatic Hydrocarbons (PAHs)*. Office of Solid Waste and Emergency Response, Washington, D.C., 4 p. <https://archive.epa.gov/epawaste/hazard/wastemin/web/pdf/pahs.pdf>
- EPA. (2010). *Guideline: Waste tyres*. https://www.epa.sa.gov.au/files/4771416_guide_tyres.pdf. (Last accessed in March 2022)
- EPA. (2011). *Exposure Factors Handbook: 2011 Edition*. Office of Research and Development, Washington, D.C., 1436 p. <https://cfpub.epa.gov/ncea/risk/recorddisplay.cfm?deid=236252>
- EPA. (2014a). *OSWER Directive 9200.1-120*. https://www.epa.gov/sites/default/files/2015-11/documents/oswer_directive_9200.1-120_exposurefactors_corrected2.pdf
- EPA. (2014b). *Priority pollutant list*. <https://www.epa.gov/sites/default/files/2015-09/documents/priority-pollutant-list-epa.pdf>
- EPA. (2016a). *Ground Rubber Applications - asphalt rubber* (last updated on 22 February 2016). <https://archive.epa.gov/epawaste/conservation/materials/tires/web/html/ground.html>. (Last accessed in April 2022)
- EPA. (2016b). *Tire Fires* (last updated on 22 February 2016). <https://archive.epa.gov/epawaste/conservation/materials/tires/web/html/fires.html>. (Last accessed in April 2022)
- EPA. (2017). *Characterization of Semi-Volatile Organic Chemicals from Tire Crumb Rubber*. https://cfpub.epa.gov/si/si_public_record_report.cfm?Lab=NERL&dirEntryId=337843
- EPA. (2019a). *Federal Research on Recycled Tire Crumb Used on Playing Fields*. <https://www.epa.gov/chemical-research/federal-research-recycled-tire-crumb-used-playing-fields>
- EPA. (2019b). *Tire Crumb Characterization Study: Field Collection and Laboratory Standard Operating Procedures (SOPs)*, Office of Research and Development, Washington, D.C., 508 p. https://www.epa.gov/sites/default/files/2019-07/documents/tire_crumb_characterization_study_field_collection_and_laboratory_standard_operating_procedures_sops.pdf
- EPA. (2022). *Indoor Air Quality (IAQ)* (last updated on 4 January, 2022). <https://www.epa.gov/indoor-air-quality-iaq/what-are-volatile-organic-compounds-vocs>. (Last accessed in March 2022)

- ETRMA. (2010). *Replacement of highly aromatic oils in tyres*. European Tyre & Rubber Manufacturers Association, Brussels, Belgium, 6 p. <https://www.etrma.org/wp-content/uploads/2019/09/20100712-etrma-qanda-replacement-of-ha-oils-in-tyres.pdf>
- ETRMA. (2020). *Europe - 91% of all End of Life Tyres collected and treated in 2018*. <https://www.etrma.org/library/europe-91-of-all-end-of-life-tyres-collected-and-treated-in-2018>. (Last accessed in April 2022)
- ETRMA. (2021). *European tyre & rubber industry – 2021 statistics report*. <https://www.etrma.org/wp-content/uploads/2021/12/20211215-Statistics-booklet-2021VF.pdf>
- Stockholm Convention on Persistent Organic Pollutants*, (2001). Official Journal of the European Union, <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex%3A22006A0731%2801%29>
- EU. (2022). *Microplastics*. https://ec.europa.eu/environment/topics/plastics/microplastics_pt. (Last accessed in March 2022)
- Ferrão, P., Ribeiro, P., & Silva, P. (2008). A management system for end-of-life tyres: A Portuguese case study. *Waste Management*, 28(3), 604-614. <https://doi.org/10.1016/j.wasman.2007.02.033>
- Forgács, E., & Cserhádi, T. (2003). 9–Gas chromatography. In M. Lees (Ed.), *Food Authenticity and Traceability* (pp. 197-217). Woodhead Publishing. <https://doi.org/10.1533/9781855737181.1.197>
- Fromme, H. (2019). Cyclic Volatile Methylsiloxanes: Occurrence and Exposure. In J. Nriagu (Ed.), *Encyclopedia of Environmental Health (Second Edition)* (pp. 805-812). Elsevier. <https://doi.org/10.1016/B978-0-12-409548-9.11241-2>
- Fukuzaki, N., Yanaka, T., & Urushiyama, Y. (1986). Effects of studded tires on roadside airborne dust pollution in Niigata, Japan. *Atmospheric Environment* (1967), 20(2), 377-386. [https://doi.org/10.1016/0004-6981\(86\)90041-7](https://doi.org/10.1016/0004-6981(86)90041-7)
- Fulton, W. (2005). Steel Tire Cord-Rubber Adhesion, Including the Contribution of Cobalt. *Rubber Chemistry and Technology*, 78, 426-457. <https://doi.org/10.5254/1.3547891>
- Gaj, K. (2020). Properties, Potential Toxicity, and Transformations of VMSs in the Environment. In V. Homem & N. Ratola (Eds.), *Volatile Methylsiloxanes in the Environment* (pp. 1-31). Springer International Publishing. https://doi.org/10.1007/698_2018_360
- Gaj, K., & Pakuluk, A. (2015). Volatile Methyl Siloxanes as Potential Hazardous Air Pollutants. *Polish Journal of Environmental Studies*, 24(3), 937-943. <https://doi.org/10.15244/pjoes/34668>
- Garrett, T. M. C., & Du, X. X. P. (2006). *Adhesive polyurethane composition used as, e.g. Binders for rubber crumb, has first isocyanate isomer having faster reaction rate than second isocyanate isomer and reacting with proton donor to increase concentration of the second isomer* (Germany Patent No. DE102006003103A1). <https://patents.google.com/patent/DE102006003103A1/en>
- Geiss, O., Senaldi, C., Bianchi, I., Lucena, A., Tirendi, S., & Barrero-Moreno, J. (2018). A fast and selective method for the determination of 8 carcinogenic polycyclic aromatic hydrocarbons in rubber and plastic materials. *Journal of Chromatography A*, 1566, 13-22. <https://doi.org/10.1016/j.chroma.2018.06.047>

- Ginsberg, G., Toal, B., Simcox, N., Bracker, A., Golembiewski, B., Kurland, T., & Hedman, C. (2011). Human Health Risk Assessment of Synthetic Turf Fields Based Upon Investigation of Five Fields in Connecticut. *Journal of Toxicology and Environmental Health, Part A*, 74(17), 1150-1174. <https://doi.org/10.1080/15287394.2011.586942>
- Gold, V. (Ed.). (2019). *The IUPAC Compendium of Chemical Terminology: The Gold Book* (4th ed.). International Union of Pure and Applied Chemistry (IUPAC). <https://doi.org/10.1351/goldbook>
- Gomes, F. O., Rocha, M. R., Alves, A., & Ratola, N. (2021). A review of potentially harmful chemicals in crumb rubber used in synthetic football pitches. *Journal of Hazardous Materials*, 409, 124998. <https://doi.org/10.1016/j.jhazmat.2020.124998>
- Graça, C. A. L., Rocha, F., Gomes, F. O., Rocha, M. R., Homem, V., Alves, A., & Ratola, N. (2022). Presence of metals and metalloids in crumb rubber used as infill of worldwide synthetic turf pitches: Exposure and risk assessment. *Chemosphere*, 299, 134379. <https://doi.org/10.1016/j.chemosphere.2022.134379>
- GSC. (2020). *Frequently Asked Questions—D4, D5 & D6* (last updated in January 2020). <https://globalsilicones.org/wp-content/uploads/2020/11/FAQ-D4-D5-D6.pdf>
- GSC. (2021). *Industry position on latest regulatory updates*. <https://www.silicones.eu/regulatory/>. (Last accessed in March 2022)
- Halsband, C., Sørensen, L., Booth, A. M., & Herzke, D. (2020). Car Tire Crumb Rubber: Does Leaching Produce a Toxic Chemical Cocktail in Coastal Marine Systems? *Frontiers in Environmental Science*, 8. <https://www.frontiersin.org/article/10.3389/fenvs.2020.00125>
- Herrero, M., Plaza, M., Cifuentes, A., & Ibáñez, E. (2012). 4.08—Extraction Techniques for the Determination of Phenolic Compounds in Food. In J. Pawliszyn (Ed.), *Comprehensive Sampling and Sample Preparation* (pp. 159-180). Academic Press. <https://doi.org/10.1016/B978-0-12-381373-2.00132>
- Homem, V., Magalhães, I., Alves, A., & Santos, L. (2017). Assessing seasonal variation of synthetic musks in beach sands from Oporto coastal area: A case study. *Environmental Pollution (Barking, Essex: 1987)*, 226, 190-197. <https://doi.org/10.1016/j.envpol.2017.04.022>
- Horii, Y., & Kannan, K. (2020). Main Uses and Environmental Emissions of Volatile Methylsiloxanes. In V. Homem & N. Ratola (Eds.), *Volatile Methylsiloxanes in the Environment* (pp. 33-70). Springer International Publishing. https://doi.org/10.1007/698_2019_375
- Horner, J. M. (1996). Environmental Health Implications of Heavy Metal Pollution from Car Tires. *Reviews on Environmental Health*, 11(4), 175-178. <https://doi.org/10.1515/REVEH.1996.11.4.175>
- Ionas, A. C., & Covaci, A. (2013). Simplifying multi-residue analysis of flame retardants in indoor dust. *International Journal of Environmental Analytical Chemistry*, 93(10), 1074-1083. <https://doi.org/10.1080/03067319.2013.763248>
- Islas, G., Ibarra, I. S., Hernandez, P., Miranda, J. M., & Cepeda, A. (2017). Dispersive Solid Phase Extraction for the Analysis of Veterinary Drugs Applied to Food Samples: A Review. *International Journal of Analytical Chemistry*, 2017, 8215271. <https://doi.org/10.1155/2017/8215271>

- Johnson, W., Bergfeld, W. F., Belsito, D. V., Hill, R. A., Klaassen, C. D., Liebler, D. C., Marks, J. G., Shank, R. C., Slaga, T. J., Snyder, P. W., & Andersen, F. A. (2011). Safety Assessment of Cyclomethicone, Cyclotetrasiloxane, Cyclopentasiloxane, Cyclohexasiloxane, and Cycloheptasiloxane. *International Journal of Toxicology*, 30(6_suppl), 149S-227S. <https://doi.org/10.1177/1091581811428184>
- Kim, L., Lee, D., Cho, H.-K., & Choi, S.-D. (2019). Review of the QuEChERS method for the analysis of organic pollutants: Persistent organic pollutants, polycyclic aromatic hydrocarbons, and pharmaceuticals. *Trends in Environmental Analytical Chemistry*, 22, e00063. <https://doi.org/10.1016/j.teac.2019.e00063>
- Krenczkowska, D., Mojsiewicz-Pieńkowska, K., Wielgomas, B., Cal, K., Bartoszewski, R., Bartoszezowska, S., & Jankowski, Z. (2019). The consequences of overcoming the human skin barrier by siloxanes (silicones) Part 1. Penetration and permeation depth study of cyclic methyl siloxanes. *Chemosphere*, 231, 607-623. <https://doi.org/10.1016/j.chemosphere.2018.09.154>
- Lange, K., Magnusson, K., Viklander, M., & Blecken, G.-T. (2021). Removal of rubber, bitumen and other microplastic particles from stormwater by a gross pollutant trap—Bioretention treatment train. *Water Research*, 202, 117457. <https://doi.org/10.1016/j.watres.2021.117457>
- Lederer, A., & Brandt, J. (2021). Chapter 2—Multidetector size exclusion chromatography of polymers. In M. I. Malik, J. Mays, & M. R. Shah (Eds.), *Molecular Characterization of Polymers* (pp. 61-96). Elsevier. <https://doi.org/10.1016/B978-0-12-819768-4.00012-9>
- Lee, D., Park, M.-K., Lee, I.-S., & Choi, S.-D. (2019). Contamination characteristics of siloxanes in coastal sediment collected from industrialized bays in South Korea. *Ecotoxicology and Environmental Safety*, 182, 109457. <https://doi.org/10.1016/j.ecoenv.2019.109457>
- Lehotay, S. J., & Schenck, F. J. (2000). MULTIRESIDUE METHODS: EXTRACTION. In I. D. Wilson (Ed.), *Encyclopedia of Separation Science* (pp. 3409-3415). Academic Press. <https://doi.org/10.1016/B0-12-226770-2/05621-0>
- Lu, Y., Yuan, T., Wang, W., & Kannan, K. (2011). Concentrations and assessment of exposure to siloxanes and synthetic musks in personal care products from China. *Environmental Pollution (Barking, Essex: 1987)*, 159(12), 3522-3528. <https://doi.org/10.1016/j.envpol.2011.08.015>
- Luque de Castro, M. D., & García Ayuso, L. E. (2000). ENVIRONMENTAL APPLICATIONS | Soxhlet Extraction. In I. D. Wilson (Ed.), *Encyclopedia of Separation Science* (pp. 2701-2709). Academic Press. <https://doi.org/10.1016/B0-12-226770-2/06681-3>
- March, R. E. (2017). Ion Trap Mass Spectrometers☆. In J. C. Lindon, G. E. Tranter, & D. W. Koppenaal (Eds.), *Encyclopedia of Spectroscopy and Spectrometry (Third Edition)* (pp. 330-337). Academic Press. <https://doi.org/10.1016/B978-0-12-409547-2.12675-7>
- Marriot, P. J., & Carpenter, P. D. (1996). Capillary Gas Chromatography Injection: An Exercise for Students of Instrumental Analysis. *Journal of Chemical Education*, 73(1), 96. <https://doi.org/10.1021/ed073p96>
- Meng, Z., & Veenstra, T. D. (2013). Chapter 26—Mass Spectrometry-Based Approach for Protein Biomarker Verification. In H. J. Issaq & T. D. Veenstra (Eds.), *Proteomic and Metabolomic Approaches to Biomarker Discovery* (pp. 407-424). Academic Press. <https://doi.org/10.1016/B978-0-12-394446-7.00026-1>

- Menichini, E., Abate, V., Attias, L., De Luca, S., di Domenico, A., Fochi, I., Forte, G., Iacovella, N., Iamiceli, A. L., Izzo, P., Merli, F., & Bocca, B. (2011). Artificial-turf playing fields: Contents of metals, PAHs, PCBs, PCDDs and PCDFs, inhalation exposure to PAHs and related preliminary risk assessment. *Science of The Total Environment*, 409(23), 4950-4957. <https://doi.org/10.1016/j.scitotenv.2011.07.042>
- Mojsiewicz-Pieńkowska, K., Jamróiewicz, M., Szymkowska, K., & Krenczkowska, D. (2016). Direct Human Contact with Siloxanes (Silicones) - Safety or Risk Part 1. Characteristics of Siloxanes (Silicones). *Frontiers in Pharmacology*, 7. <https://www.frontiersin.org/article/10.3389/fphar.2016.00132>
- Moldoveanu, S., & David, V. (2021). Chapter 6—Solvent extraction. In S. Moldoveanu & V. David (Eds.), *Modern Sample Preparation for Chromatography (Second Edition)* (pp. 191-279). Elsevier. <https://doi.org/10.1016/B978-0-12-821405-3.00015-0>
- Mu, X., Huang, Y., Li, J., Yang, K., Yang, W., Shen, G., Li, X., Lei, Y., Pang, S., Wang, C., Li, X., & Li, Y. (2018). New insights into the mechanism of phthalate-induced developmental effects. *Environmental Pollution*, 241, 674-683. <https://doi.org/10.1016/j.envpol.2018.05.095>
- Mussatto, S. I. (2015). Chapter 11—Generating Biomedical Polyphenolic Compounds from Spent Coffee or Silverskin. In V. R. Preedy (Ed.), *Coffee in Health and Disease Prevention* (pp. 93-106). Academic Press. <https://doi.org/10.1016/B978-0-12-409517-5.00011-5>
- MWH. (2004). *End-of-Life Tyre Management—Final Report for the Ministry of the Environment*, MWH New Zealand, 36 p. <https://environment.govt.nz/assets/Publications/Files/end-of-life-tyre-management.pdf>
- Nair, A. B., & Joseph, R. (2014). 9—Eco-friendly bio-composites using natural rubber (NR) matrices and natural fiber reinforcements. In S. Kohjiya & Y. Ikeda (Eds.), *Chemistry, Manufacture and Applications of Natural Rubber* (pp. 249-283). Woodhead Publishing. <https://doi.org/10.1533/9780857096913.2.249>
- NIH. (2018). *Crumb Rubber in Playgrounds and Children's Health* (last reviewed on 12 December 2018). https://www.niehs.nih.gov/research/supported/translational/peph/podcasts/2018/mar20_crumb-rubber/index.cfm. (Last accessed in March 2022)
- Noberini, R., Cuomo, A., & Bonaldi, T. (2016). Chapter 10—Mass Spectrometry for the Identification of Posttranslational Modifications in Histones and Its Application in Clinical Epigenetics. In J. L. García-Giménez (Ed.), *Epigenetic Biomarkers and Diagnostics* (pp. 195-214). Academic Press. <https://doi.org/10.1016/B978-0-12-801899-6.00010-3>
- Nocil Ltd. (2022). *Vulcanisation & accelerators*. 35 p <https://www.nocil.com/Downloadfile/DTechnicalNote-Vulcanization-Dec10.pdf>
- Okopol. (2009). *Guidance on VOC Substitution and Reduction for Activities Covered by the VOC Solvents Emissions Directive (Directive 1999/13/EC)*. https://www.varam.gov.lv/sites/varam/files/content/files/voc_guidance_210509.pdf
- Ortíz-Rodríguez, O. O., Ocampo-Duque, W., & Duque-Salazar, L. I. (2017). Environmental Impact of End-of-Life Tires: Life Cycle Assessment Comparison of Three Scenarios from a Case Study in Valle Del Cauca, Colombia. *Energies*, 10(12), 2117. <https://doi.org/10.3390/en1012117>

- Owen, M. J. (1980). The Surface Activity of Silicones: A Short Review. *Industrial & Engineering Chemistry Product Research and Development*, 19(1), 97-103. <https://doi.org/10.1021/i360073a023>
- Paíga, P., Domingues, V. F., Wanderley, K. A., Júnior, S. A., & Delerue-Matos, C. M. (2015). QuEChERS: A sample preparation for extraction of carbaryl from rat feces. *Toxicological & Environmental Chemistry*, 97(6), 687-699. <https://doi.org/10.1080/02772248.2015.1059974>
- Perestrelo, R., Silva, P., Porto-Figueira, P., Pereira, J. A. M., Silva, C., Medina, S., & Câmara, J. S. (2019). QuEChERS - Fundamentals, relevant improvements, applications and future trends. *Analytica Chimica Acta*, 1070, 1-28. <https://doi.org/10.1016/j.aca.2019.02.036>
- Peterson, M. K., Lemay, J. C., Pacheco Shubin, S., & Prueitt, R. L. (2018). Comprehensive multipathway risk assessment of chemicals associated with recycled ('crumb') rubber in synthetic turf fields. *Environmental Research*, 160, 256-268. <https://doi.org/10.1016/j.envres.2017.09.019>
- Picó, Y. (2012). 3.28—Recent Advances in Sample Preparation for Pesticide Analysis. In J. Pawliszyn (Ed.), *Comprehensive Sampling and Sample Preparation* (pp. 569-590). Academic Press. <https://doi.org/10.1016/B978-0-12-381373-2.00101-0>
- Pingret, D., Fabiano-Tixier, A. S., & Chemat, F. (2012). 4.19—Accelerated Methods for Sample Preparation in Food. In J. Pawliszyn (Ed.), *Comprehensive Sampling and Sample Preparation* (pp. 441-455). Academic Press. <https://doi.org/10.1016/B978-0-12-381373-2.00143-5>
- Plessner, T. S. W., & Lund, O. J. (2004). Potential health and environmental effects linked to artificial turf systems-final report. *Norwegian Building Research Institute (Report to the Norwegian Football Association)*.
- Ramos, S., Silva, J., Homem, V., Cincinelli, A., Santos, L. S., Alves, M. A., & Ratola, N. (2016). Solvent-saving approaches for the extraction of siloxanes from pine needles, soils and passive air samplers. <https://doi.org/10.1039/c6ay00506c>
- Rao, T. N. (2018). Validation of Analytical Methods. In *Calibration and Validation of Analytical Methods—A Sampling of Current Approaches*. IntechOpen. <https://doi.org/10.5772/intechopen.72087>
- Rattanasom, N., Saowapark, T., & Deeprasertkul, C. (2007). Reinforcement of natural rubber with silica/carbon black hybrid filler. *Polymer Testing*, 26(3), 369-377. <https://doi.org/10.1016/j.polymertesting.2006.12.003>
- Rauniyar, N., Stevens, J., Stanley, & Prokai, L. (2007). Fourier transform ion cyclotron resonance mass spectrometry of covalent adducts of proteins and 4-hydroxy-2-nonenal, a reactive end-product of lipid peroxidation. *Analytical and Bioanalytical Chemistry*, 389, 1421-1428. <https://doi.org/10.1007/s00216-007-1534-2>
- Ross, S. M. (2017). Chapter 7—Distributions of Sampling Statistics. In S. M. Ross (Ed.), *Introductory Statistics (Fourth Edition)* (pp. 297-328). Academic Press. <https://doi.org/10.1016/B978-0-12-804317-2.00007-2>
- Rücker, C., & Kümmerer, K. (2015). Environmental Chemistry of Organosiloxanes. *Chemical Reviews*, 115(1), 466-524. <https://doi.org/10.1021/cr500319v>

- Sánchez-Brunete, C., Miguel, E., Albero, B., & Tadeo, J. L. (2010). Determination of cyclic and linear siloxanes in soil samples by ultrasonic-assisted extraction and gas chromatography-mass spectrometry. *Journal of Chromatography A*, 1217(45), 7024-7030. <https://doi.org/10.1016/j.chroma.2010.09.031>
- Sanchís, J., Cabrerizo, A., Galbán-Malagón, C., Barceló, D., Farré, M., & Dachs, J. (2015). Unexpected Occurrence of Volatile Dimethylsiloxanes in Antarctic Soils, Vegetation, Phytoplankton, and Krill. *Environmental Science & Technology*, 49(7), 4415-4424. <https://doi.org/10.1021/es503697t>
- Schneider, K., Bierwisch, A., & Kaiser, E. (2020). ERASSTRI - European risk assessment study on synthetic turf rubber infill - Part 3: Exposure and risk characterisation. *Science of The Total Environment*, 718, 137721. <https://doi.org/10.1016/j.scitotenv.2020.137721>
- Schneider, K., de Hoogd, M., Madsen, M. P., Haxaire, P., Bierwisch, A., & Kaiser, E. (2020). ERASSTRI - European Risk Assessment Study on Synthetic Turf Rubber Infill - Part 1: Analysis of infill samples. *Science of The Total Environment*, 718, 137174. <https://doi.org/10.1016/j.scitotenv.2020.137174>
- Sengupta, P., Khanra, K., Chowdhury, A. R., & Datta, P. (2019). 4—Lab-on-a-chip sensing devices for biomedical applications. In K. Pal, H.-B. Kraatz, A. Khasnobish, S. Bag, I. Banerjee, & U. Kuruganti (Eds.), *Bioelectronics and Medical Devices* (pp. 47-95). Woodhead Publishing. <https://doi.org/10.1016/B978-0-08-102420-1.00004-2>
- Sharj-Sharifi, M., Taghvaei-Ganjali, S., & Motiee, F. (2020). The effect of protecting waxes on staining antidegradant performance in tyre sidewall formulation. *Journal of Rubber Research*, 23(2), 111-124. <https://doi.org/10.1007/s42464-020-00042-y>
- Shimadzu. (2022). *Gas Chromatography Columns*. <https://www.shimadzu.com/an/service-support/technical-support/analysis-basics/fundamentals/columns.html>
- Sievers, R. E., & Sadlowski, J. E. (1978). Volatile Metal Complexes. *Science*, 201(4352), 217-223.
- Simcox, N. J., Bracker, A., Ginsberg, G., Toal, B., Golembiewski, B., Kurland, T., & Hedman, C. (2011). Synthetic Turf Field Investigation in Connecticut. *Journal of Toxicology and Environmental Health, Part A*, 74(17), 1133-1149. <https://doi.org/10.1080/15287394.2011.586941>
- Simon, R. (2010). *Review of the Impacts of Crumb Rubber in Artificial Turf Applications*. <https://escholarship.org/uc/item/9zp430wp>
- Skoczyńska, E., Leonards, P. E. G., Llompart, M., & de Boer, J. (2021). Analysis of recycled rubber: Development of an analytical method and determination of polycyclic aromatic hydrocarbons and heterocyclic aromatic compounds in rubber matrices. *Chemosphere*, 276, 130076. <https://doi.org/10.1016/j.chemosphere.2021.130076>
- Smithers. (2019). *The Future of Tire Manufacturing to 2024*. Smithers, Akron, OH. <https://www.smithers.com/services/market-reports/transportation/the-future-of-tire-manufacturing-to-2024>. (Last accessed in February 2022).
- Song, K. (2017). 2—Micro- and nano-fillers used in the rubber industry. In S. Thomas & H. J. Maria (Eds.), *Progress in Rubber Nanocomposites* (pp. 41-80). Woodhead Publishing. <https://doi.org/10.1016/B978-0-08-100409-8.00002-4>

- Speight, J. G. (2020). Chapter 14—Monomers, polymers, and plastics. In J. G. Speight (Ed.), *Handbook of Industrial Hydrocarbon Processes (Second Edition)* (pp. 597-649). Gulf Professional Publishing. <https://doi.org/10.1016/B978-0-12-809923-0.00014-X>
- Staples, C. A., Dome, P. B., Klecka, G. M., Oblock, S. T., & Harris, L. R. (1998). A review of the environmental fate, effects, and exposures of bisphenol A. *Chemosphere*, 36(10), 2149-2173. [https://doi.org/10.1016/S0045-6535\(97\)10133-3](https://doi.org/10.1016/S0045-6535(97)10133-3)
- Stauffer, E., Dolan, J. A., & Newman, R. (2008). CHAPTER 8—Gas Chromatography and Gas Chromatography—Mass Spectrometry. In E. Stauffer, J. A. Dolan, & R. Newman (Eds.), *Fire Debris Analysis* (pp. 235-293). Academic Press. <https://doi.org/10.1016/B978-012663971-1.50012-9>
- Stein, S. E. (1999). An Integrated Method for Spectrum Extraction and Compound Identification from GC/MS Data. *Journal of the American Society for Mass Spectrometry*, 10(8), 770-781. [https://doi.org/10.1016/S1044-0305\(99\)00047-1](https://doi.org/10.1016/S1044-0305(99)00047-1)
- Tarafdar, A., Oh, M.-J., Nguyen-Phuong, Q., & Kwon, J.-H. (2020). Profiling and potential cancer risk assessment on children exposed to PAHs in playground dust/soil: A comparative study on poured rubber surfaced and classical soil playgrounds in Seoul. *Environmental Geochemistry and Health*, 42(6), 1691-1704. <https://doi.org/10.1007/s10653-019-00334-2>
- Teuten, E. L., Saquing, J. M., Knappe, D. R. U., Barlaz, M. A., Jonsson, S., Björn, A., Rowland, S. J., Thompson, R. C., Galloway, T. S., Yamashita, R., Ochi, D., Watanuki, Y., Moore, C., Viet, P. H., Tana, T. S., Prudente, M., Boonyatumanond, R., Zakaria, M. P., Akkhavong, K., ... Takada, H. (2009). Transport and release of chemicals from plastics to the environment and to wildlife. *Philosophical Transactions of the Royal Society of London. Series B, Biological Sciences*, 364(1526), 2027-2045. <https://doi.org/10.1098/rstb.2008.0284>
- Thompson, M., Ellison, S. L. R., & Wood, R. (2002). Harmonized guidelines for single-laboratory validation of methods of analysis (IUPAC Technical Report). *Pure and Applied Chemistry*, 74(5), 835-855. <https://doi.org/10.1351/pac200274050835>
- Tilley, S. K., & Fry, R. C. (2015). Chapter 6 - Priority Environmental Contaminants: Understanding Their Sources of Exposure, Biological Mechanisms, and Impacts on Health. In R. C. Fry (Ed.), *Systems Biology in Toxicology and Environmental Health* (pp. 117-169). Academic Press. <https://doi.org/10.1016/B978-0-12-801564-3.00006-7>
- Toledo-Neira, C., Enríquez, P., & Richter, P. (2013). Integrated pressurized solvent extraction-cleanup for the rapid determination of polychlorinated biphenyls in meat samples. *Journal of the Brazilian Chemical Society*, 24, 743-748. <https://doi.org/10.5935/0103-5053.20130095>
- Tran, T. M., Hoang, A. Q., Le, S. T., Minh, T. B., & Kannan, K. (2019). A review of contamination status, emission sources, and human exposure to volatile methyl siloxanes (VMSs) in indoor environments. *Science of The Total Environment*, 691, 584-594. <https://doi.org/10.1016/j.scitotenv.2019.07.168>
- USTMA. (2020). *Stockpile Cleanup*. US Tyre Manufacturers Association, Washington, D.C. <https://www.ustires.org/stockpile-cleanup>. (Last accessed in March 2022)

- USTMA. (2022). *Zinc and tyres*. US Tyre Manufacturers Association, Washington, D.C. <https://www.ustires.org/zinc-and-tires>. (Last accessed in March 2022)
- Valorpneu. (2021). *Relatório Anual de Atividades: 2020*. <https://www.valorpneu.pt/sobre-a-valorpneu/quem-somos/>. (Last accessed in April 2022)
- van Rooij, J. G. M., & Jongeneelen, F. J. (2009). Hydroxypyrene in urine of football players after playing on artificial sports field with tire crumb infill. *International Archives of Occupational and Environmental Health*, 83(1), 105. <https://doi.org/10.1007/s00420-009-0465-y>
- Verschoor, A. J. (2015). *Towards a definition of microplastics. Considerations for the specification of physico-chemical properties*. RIVM Letter report 2015-0116, National Institute for Public Health and the Environment, Bithoven, The Netherlands, 38 p.
- Warmuth, A., & Ohno, K. (2013). *The Stockholm Convention on Persistent Organic Pollutants and PCBs*. <http://chm.pops.int/Default.aspx?tabid=3016>
- WBCSD. (2021). *ELT Management Toolkit*. World Business Council for Sustainable Development, 23 p. <https://www.wbcsd.org/download/file/13232>
- Weggler, B. A., Gruber, B., Teehan, P., Jaramillo, R., & Dorman, F. L. (2020). Chapter 5—Inlets and sampling. In N. H. Snow (Ed.), *Separation Science and Technology* (Vol. 12, pp. 141-203). Academic Press. <https://doi.org/10.1016/B978-0-12-813745-1.00005-2>
- WHO. (2000). *Polycyclic aromatic hydrocarbons (PAHs)*. Air Quality Guidelines. World Health Organization Regional Office for Europe, Copenhagen, Denmark, 24 p. https://www.euro.who.int/__data/assets/pdf_file/0015/123063/AQG2ndEd_5_9PAH.pdf
- Xu, L., Shi, Y., Liu, N., & Cai, Y. (2015). Methyl siloxanes in environmental matrices and human plasma/fat from both general industries and residential areas in China. *The Science of the Total Environment*, 505, 454-463. <https://doi.org/10.1016/j.scitotenv.2014.10.039>
- Xu, L., Zhi, L., & Cai, Y. (2017). Methylsiloxanes in children silicone-containing products from China: Profiles, leaching, and children exposure. *Environment International*, 101, 165-172. <https://doi.org/10.1016/j.envint.2017.01.022>
- Yang, L. (2015). 1—Fundamentals of nanotechnology and orthopedic materials. In L. Yang (Ed.), *Nanotechnology-Enhanced Orthopedic Materials* (pp. 1-25). Woodhead Publishing. <https://doi.org/10.1016/B978-0-85709-844-3.00001-X>
- Zafar, S. (2021). *How is crumb rubber produced and what are its uses?* <https://www.ecomena.org/crumb-rubber-production-and-uses/>
- Zhang, J. (jim), Han, I.-K., Zhang, L., & Crain, W. (2008). Hazardous chemicals in synthetic turf materials and their bioaccessibility in digestive fluids. *Journal of Exposure Science & Environmental Epidemiology*, 18(6), 600-607. <https://doi.org/10.1038/jes.2008.55>

- Zhang, K., & Wong, J. W. (2011). 4.12—Solvent-Based Extraction Techniques for the Determination of Pesticides in Food. In J. Pawliszyn (Ed.), *Comprehensive Sampling and Sample Preparation* (pp. 245-261). Academic Press. <https://doi.org/10.1016/B978-0-12-381373-2.00136-8>
- Zhang, K., Wong, J. W., Begley, T. H., Hayward, D. G., & Limm, W. (2012). Determination of siloxanes in silicone products and potential migration to milk, formula and liquid simulants. *Food Additives & Contaminants: Part A*, 29(8), 1311-1321. <https://doi.org/10.1080/19440049.2012.684891>
- Zhao, S., Shao, X., Liu, X., Jiang, L., Zhao, Z., Xie, S., Li, L., & Xin, Z. (2018). Lubrication and plasticization behavior of large-size micro-spherical structured SiO₂ for natural rubber. *RSC Advances*, 8(55), 31783-31792. <https://doi.org/10.1039/C8RA05875J>
- Zimila, H. E., Mandlate, J. S., Artur, E. M., Muiambo, H. F., & Uamusse, A. A. (2021). Vortex-assisted Solid-Liquid Extraction for Rapid Screening of Oil Content in Jatropha Seed: An Alternative to the Modified Soxhlet Method. *South African Journal of Chemistry*, 75, 1-5. <https://doi.org/10.17159/0379-4350/2021/v75a1>
- Zygler, A., Słomińska, M., & Namieśnik, J. (2012). 2.04—Soxhlet Extraction and New Developments Such as Soxtec. In J. Pawliszyn (Ed.), *Comprehensive Sampling and Sample Preparation* (pp. 65-82). Academic Press. <https://doi.org/10.1016/B978-0-12-381373-2.00037-5>

Appendix 1. List of Analysed Samples

Table A1.1. List and details of the 108 synthetic turf crumb rubber samples analysed in this work.

Sample ID	Country	Type of pitch	Pitch age	Collection date	Material	Granulometry (mm) ^(a)
CR2	Portugal	Outdoor	Unknown	18/01/2017	Crumb rubber	1.36 ± 0.20
CR5	Portugal	Outdoor	Unknown	21/01/2017	Crumb rubber	1.78 ± 0.40
CR7	Spain	Outdoor	Unknown	22/01/2017	Crumb rubber	1.83 ± 0.54
CR15	Portugal	Outdoor	unknown	07/02/2017	Crumb rubber	1.71 ± 0.40
CR21	Portugal	Outdoor	4 years	12/02/2017	Crumb rubber	1.63 ± 0.40
CR23	Portugal	Outdoor	4 years	14/02/2017	Crumb rubber	1.69 ± 0.40
CR25	Portugal	Indoor	Unknown	15/02/2017	Crumb rubber	1.71 ± 0.36
CR31	Portugal	Outdoor	Unknown	20/02/2017	Crumb rubber	1.96 ± 0.43
CR32	Portugal	Outdoor	Unknown	20/02/2017	Crumb rubber	2.97 ± 0.81
CR34	Portugal	Outdoor	Unknown	24/02/2017	Crumb rubber	1.00 ± 0.20
CR37	Spain	Outdoor	Unknown	06/03/2017	Crumb rubber	1.49 ± 0.30
CR39	Spain	Outdoor	Unknown	09/03/2017	Crumb rubber	3.96 ± 1.18
CR41	Portugal	Outdoor	Unknown	28/03/2017	Crumb rubber	2.09 ± 0.41
CR52	Portugal	Outdoor	Unknown	26/07/2017	Crumb rubber	3.44 ± 0.76
CR53	Portugal	Outdoor	7 years	13/11/2017	Crumb Rubber	1.42 ± 0.29
CR55	Portugal	Outdoor	8 years	17/11/2017	Crumb Rubber	1.22 ± 0.29
CR56	Portugal	Outdoor	8 years	18/11/2017	Crumb Rubber	1.63 ± 0.37
CR59	Portugal	Outdoor	Unknown	17/12/2017	Crumb Rubber	1.50 ± 0.34
CR61	Portugal	Indoor	13 years	23/12/2017	Crumb Rubber	1.64 ± 0.25
CR62	Portugal	Outdoor	1 year	25/12/2017	Crumb Rubber	1.56 ± 0.38
CR63	Portugal	Outdoor	Unknown	25/12/2017	Crumb Rubber	1.14 ± 0.27
CR64	Spain	Outdoor	Unknown	28/12/2017	Crumb Rubber	1.27 ± 0.27
CR65	Spain	Outdoor	4 years	28/12/2017	Crumb Rubber	1.76 ± 0.30
CR67	Portugal	Outdoor	14 years	29/12/2017	Crumb Rubber	1.63 ± 0.40
CR69	Portugal	Outdoor	10 years	29/12/2017	Crumb Rubber	1.46 ± 0.29
CR70	Portugal	Outdoor	1 year	19/01/2018	Crumb Rubber	2.04 ± 0.23
CR71	Portugal	Outdoor	8 years	19/01/2018	Crumb Rubber	1.25 ± 0.30
CR72	Chile	Outdoor	5 years	11/04/2018	Crumb Rubber	1.48 ± 0.39
CR73	Chile	Outdoor	Unknown	12/04/2018	Crumb Rubber	1.60 ± 0.23
CR74	Chile	Outdoor	Unknown	12/04/2018	Crumb Rubber	1.96 ± 0.36
CR75	Chile	Outdoor	Unknown	12/04/2018	Crumb Rubber	2.00 ± 0.39
CR76	Chile	Outdoor	Unknown	12/04/2018	Crumb Rubber	1.92 ± 0.31
CR77	Chile	Outdoor	7 years	16/04/2018	Crumb Rubber	0.97 ± 0.24
CR79	Poland	Outdoor	Unknown	30/08/2018	Crumb Rubber	1.99 ± 0.29
CR80	Italy	Outdoor	7 years	12/09/2018	Crumb Rubber	1.48 ± 0.31
CR81	Italy	Outdoor	6/7 years	17/09/2018	Crumb Rubber	1.78 ± 0.29
CR83	Italy	Outdoor	10 years	18/09/2018	Crumb Rubber	1.53 ± 0.37
CR84	Italy	Outdoor	6/7 years	18/09/2018	Crumb Rubber	1.90 ± 0.30
CR85	France	Outdoor	2-3 months	29/09/2018	Crumb Rubber	2.19 ± 0.45
CR86	France	Outdoor	5 years	30/09/2018	Crumb Rubber	1.88 ± 0.37

Table A1.1. List and details of the 108 synthetic turf crumb rubber samples analysed in this work (cont.).

Sample ID	Country	Type of pitch	Pitch age	Collection date	Material	Granulometry (mm) ^(a)
CR90	Portugal	Outdoor	20 years	28/10/2018	Crumb Rubber	1.70 ± 0.28
CR92	Portugal	Outdoor	10 years	02/11/2018	Crumb Rubber	1.75 ± 0.35
CR94	Portugal	Outdoor	Installed but unused	02/11/2018	Crumb Rubber	1.62 ± 0.41
CR97	Portugal	Outdoor	10 years	03/11/2018	Crumb Rubber	1.68 ± 0.42
CR100	Portugal	Outdoor	2 years	03/11/2018	Crumb Rubber	1.59 ± 0.34
CR101	Spain	Outdoor	14 years	20/11/2018	Crumb Rubber	1.05 ± 0.35
CR102	Spain	Outdoor	< 1 year	20/11/2018	Crumb Rubber	1.14 ± 0.33
CR103	Spain	Outdoor	5 years	20/11/2018	Crumb Rubber	1.18 ± 0.29
CR104	Spain	Outdoor	4 years	20/11/2018	Crumb Rubber	1.68 ± 0.42
CR106	Spain	Outdoor	1 year	23/11/2018	Crumb Rubber	1.42 ± 0.34
CR107	Spain	Outdoor	12-20 years	23/11/2018	Crumb Rubber	1.51 ± 0.36
CR108	Portugal	Outdoor	6 years	30/11/2018	Crumb Rubber	1.71 ± 0.25
CR110	Portugal	Outdoor	6 years	09/12/2018	Crumb Rubber	1.54 ± 0.40
CR112	Portugal	Outdoor	11 years	09/12/2018	Crumb Rubber	1.82 ± 0.35
CR114	Portugal	Outdoor	Unknown	30/12/2018	Crumb Rubber	1.74 ± 0.40
CR116	Croatia	Outdoor	9 years	12/02/2019	Crumb Rubber	0.93 ± 0.27
CR117	Croatia	Outdoor	2 years	15/02/2019	Crumb Rubber	1.44 ± 0.40
CR120	Portugal	Outdoor	2 years	02/03/2019	Crumb Rubber	1.62 ± 0.27
CR121	Portugal	Outdoor	6 months	02/03/2019	Crumb Rubber	1.59 ± 0.35
CR122	Portugal	Outdoor	10 years	02/03/2019	Crumb Rubber	1.11 ± 0.39
CR123	Portugal	Outdoor	4/5 years	02/03/2019	Crumb Rubber	1.67 ± 0.26
CR124	Portugal	Indoor	2 years	02/03/2019	Crumb Rubber	1.59 ± 0.31
CR127	Spain	Outdoor	10 years	26/04/2019	Crumb Rubber	1.81 ± 0.40
CR128	Spain	Outdoor	12 years	27/04/2019	Crumb Rubber	1.81 ± 0.37
CR130	Spain	Outdoor	Installed but unused	03/05/2019	Crumb Rubber	1.61 ± 0.32
CR131	Spain	Outdoor	10 years	03/05/2019	Crumb Rubber	1.68 ± 0.42
CR132	France	Outdoor	8 years	12/05/2019	Crumb Rubber	1.09 ± 0.22
CR134	France	Outdoor	10 years	17/05/2019	Crumb Rubber	1.63 ± 0.36
CR135	France	Outdoor	5 years	17/05/2019	Crumb Rubber	2.37 ± 0.54
CR136	Finland	Outdoor	3 years	27/05/2019	Crumb Rubber	2.16 ± 0.91
CR137	Finland	Outdoor	10 years	28/05/2019	Crumb Rubber	2.08 ± 1.28
CR138	Finland	Outdoor	Unknown	28/05/2019	Crumb Rubber	1.74 ± 0.41
CR139	Finland	Outdoor	5 years	28/05/2019	Crumb Rubber	2.85 ± 0.60
CR140	Finland	Indoor	5 years	28/05/2019	Crumb Rubber	2.27 ± 0.82
CR141	Finland	Outdoor	5 years	28/05/2019	Crumb Rubber	3.01 ± 0.96
CR142	Finland	Outdoor	5 years	29/05/2019	Crumb Rubber	2.02 ± 0.59
CR144	Finland	Outdoor	2 years	29/05/2019	Crumb Rubber	3.40 ± 0.86
CR145	Finland	Outdoor	10 years	29/05/2019	Crumb Rubber	0.68 ± 0.18
CR146	Finland	Outdoor	1 year	29/05/2019	Crumb Rubber	3.18 ± 0.54
CR148	Spain	Outdoor	9 years	11/06/2019	Crumb Rubber	1.55 ± 0.30
CR154	Greece	Outdoor	10 years	18/06/2019	Crumb Rubber	3.28 ± 0.60
CR155	Greece	Outdoor	10 years	18/06/2019	Crumb Rubber	2.95 ± 0.74

Table A1.1. List and details of the 108 synthetic turf crumb rubber samples analysed in this work (cont.).

Sample ID	Country	Type of pitch	Pitch age	Collection date	Material	Granulometry (mm) ^(a)
CR156	Greece	Outdoor	10 years	18/06/2019	Crumb Rubber	2.69 ± 0.84
CR159	Portugal	Outdoor	Unknown	26/06/2019	Crumb Rubber	1.36 ± 0.30
CR162	Portugal	Outdoor	15 years	04/07/2019	Crumb Rubber	1.64 ± 0.31
CR164	Spain	Outdoor	20 years	05/08/2019	Crumb Rubber	1.41 ± 0.32
CR166	Spain	Outdoor	5 years	06/08/2019	Crumb Rubber	1.80 ± 0.42
CR167	Spain	Outdoor	Installed but unused	06/08/2019	Crumb Rubber	1.26 ± 0.24
CR168	Portugal	Outdoor	Installed but unused	31/08/2019	Crumb Rubber	1.40 ± 0.27
CR171	Sweden	Outdoor	Unknown	08/09/2019	Crumb Rubber	2.41 ± 1.13
CR172	Sweden	Outdoor	2 years	11/09/2019	Crumb Rubber	1.77 ± 0.71
CR173	Sweden	Outdoor	5/6 years	11/09/2019	Crumb Rubber	2.11 ± 0.97
CR174	Sweden	Outdoor	1 year	11/09/2019	Crumb Rubber	2.40 ± 0.97
CR175	Sweden	Outdoor	14/15 years	11/09/2019	Crumb Rubber	0.94 ± 0.29
CR177	Portugal	Outdoor	19 years	22/10/2019	Crumb Rubber	1.07 ± 0.27
CR179	Spain	Outdoor	7 years	23/10/2019	Crumb Rubber	1.55 ± 0.30
CR182	Poland	Outdoor	6 years	05/12/2019	Crumb Rubber	1.93 ± 0.54
CR183	Poland	Outdoor	6 months	05/12/2019	Crumb Rubber	1.71 ± 0.27
CR184	Albania	Outdoor	5 years	03/01/2020	Crumb Rubber	2.18 ± 0.56
CR186_1	Chile	Outdoor	1 year	04/03/2020	Crumb Rubber	1.82 ± 0.52
CR186_2	Chile	Outdoor	5 years	04/03/2020	Crumb Rubber	1.63 ± 0.44
CR187	Chile	Indoor	6 years	05/03/2020	Crumb Rubber	1.45 ± 0.18
CR188	Chile	Outdoor	2 years	11/03/2020	Crumb Rubber	2.14 ± 0.33
CR190	Chile	Outdoor	6 years	05/03/2020	Crumb Rubber	1.22 ± 0.24
CR192	Germany	Outdoor	12 years	08/05/2020	Crumb Rubber	1.43 ± 0.36
CR194	Portugal	Indoor	12 years	21/07/2020	Crumb Rubber	1.46 ± 0.32
CR195	Portugal	Indoor	Unknown	21/07/2020	Crumb Rubber	0.83 ± 0.18
CR163	Portugal	Outdoor	Unused Infill	04/07/2019	Crumb Rubber	1.53 ± 0.35

^{a)} Data from measurements performed on 20 randomly selected granules.

Table A1.2. List and details of the 12 synthetic turf alternative infill material samples analysed in this work.

Sample ID	Country	Type of pitch	Pitch age	Collection date	Material	Granulometry (mm)
CR82	Italy	Outdoor	1 year	18/09/2018	Coloured CR	1.18 ± 0.45
CR87	France	Outdoor	Installed but unused	04/10/2018	Cork	1.12 ± 0.32
CR88	Spain	Outdoor	3 years	17/10/2018	Rubber/Coconut fibre	1.98 ± 0.41
CR105	Spain	Outdoor	18 years	22/11/2018	Coloured CR	1.40 ± 0.32
CR125	Portugal	Outdoor	20 years	03/03/2019	Coloured CR	1.45 ± 0.50
CR126	Spain	Outdoor	< 1 year	26/04/2019	Coloured CR	1.62 ± 0.28
CR133	France	Outdoor	2 years	12/05/2019	Coloured CR	1.51 ± 0.32
CR152	Spain	Outdoor	1 year	13/06/2019	Cork	1.54 ± 0.26
CR165	Spain	Outdoor	10 years	06/08/2019	Coloured CR	1.85 ± 0.28
CR180	Spain	Outdoor	10 years	23/10/2019	Coloured CR	1.97 ± 0.43
CR189	Chile	Outdoor	1 month	05/03/2020	Cork	1.36 ± 0.28
CR191	Chile	Outdoor	Unused Infill	05/03/2020	Cork	1.51 ± 0.32

Table A1.3. List and details of the 6 commercial crumb rubber samples analysed in this work.

Sample ID	Country	Type of pitch	Pitch age	Collection date	Material	Granulometry (mm)
P1	Portugal	Commercial samples - criteria not applicable		2019	Crumb rubber	2.02 ± 0.72
P2	Portugal			09/2018	Crumb rubber	1.78 ± 0.71
C1	China			02/2017	Crumb rubber	5.94 ± 1.36
C2	China			11/2021	Crumb rubber	2.11 ± 0.70
C3	China			12/2021	Crumb rubber	1.15 ± 0.32
C4	China			12/2021	Crumb rubber	2.10 ± 0.60

Appendix 2. Extraction/Clean-up Protocols

In Figures A2.1 and A2.2 are represented the diagrams of the experimental procedures followed according to the Dry Sludge (DS) and modified SAFEGOAL (SG) volatile methylsiloxane (VMS) extraction protocols from crumb rubber.

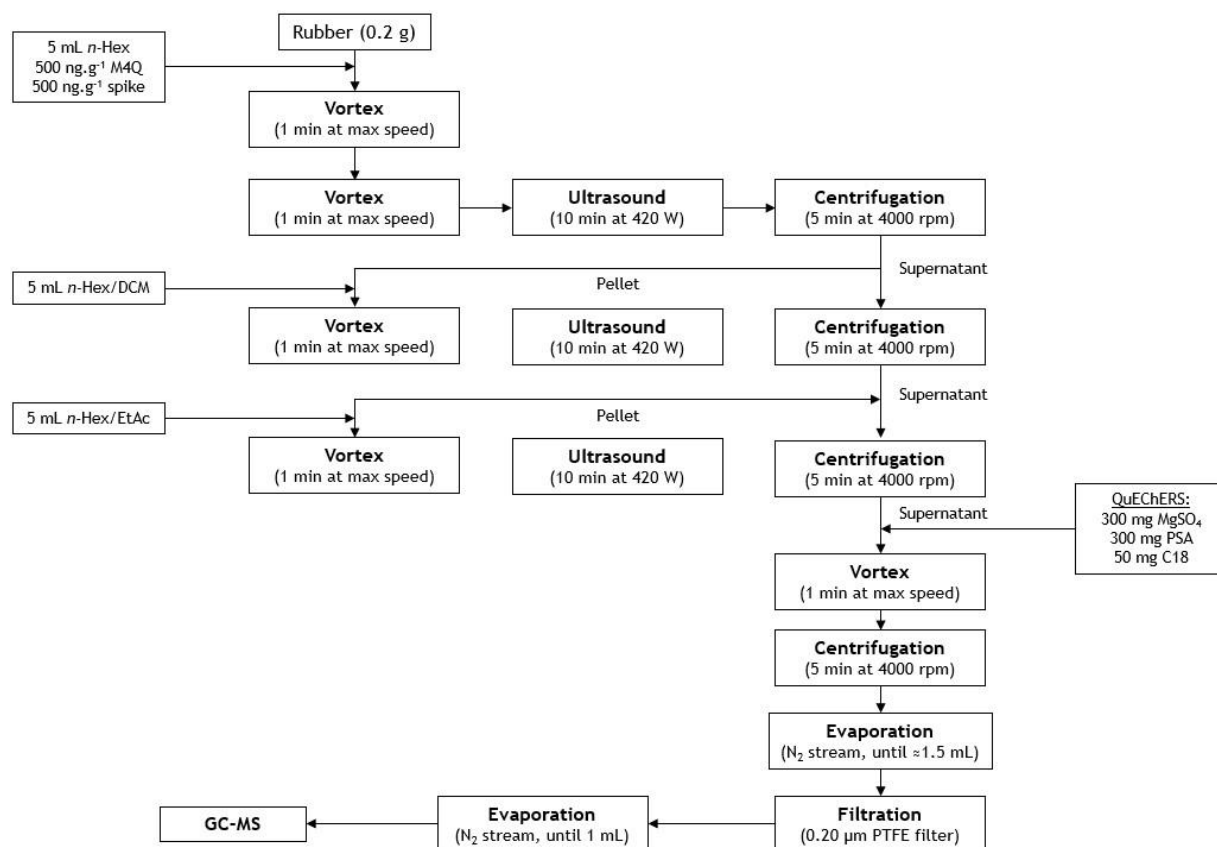


Figure A2.1. Diagram of the DS protocol for VMS extraction from crumb rubber.

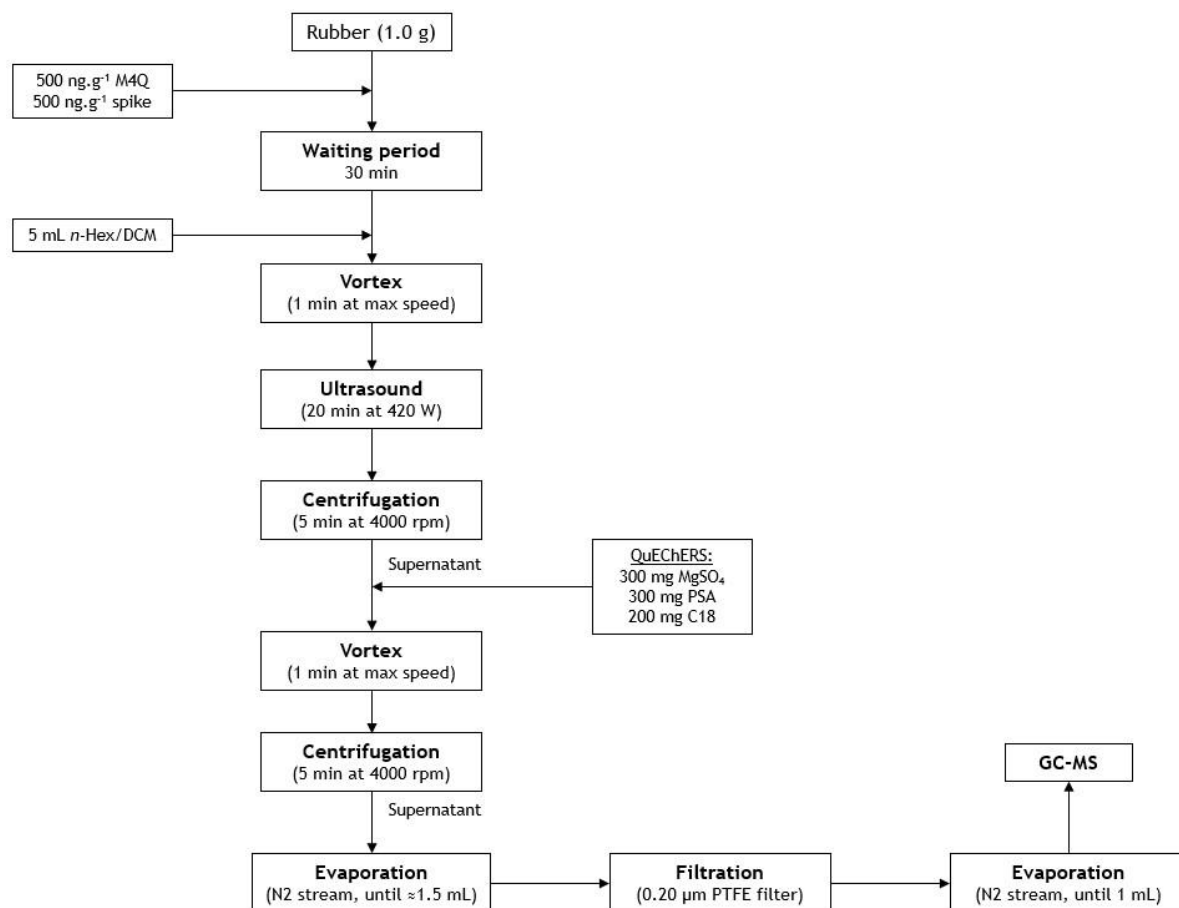


Figure A2.2. Diagram of the modified SG protocol for VMS extraction from crumb rubber.

Appendix 3. GC-MS Quantification Parameters

Table A3.1. Retention time and quantifier/qualifier ions of the VMSs analysed by GC-MS.

Compound	Retention time (min)	Quantifier ions (m/z)	Qualifier ions (m/z)
D3	7.67	207	133, 191
L3	8.89	221	73, 133
D4	11.19	281	193, 265
L4	12.66	207	73, 191, 295
D5	14.45	267	73, 355
M4Q	15.19	281	73, 147, 369
L5	16.57	281	73, 148, 369
D6	18.49	341	73, 325, 429

Appendix 4. Method Optimization

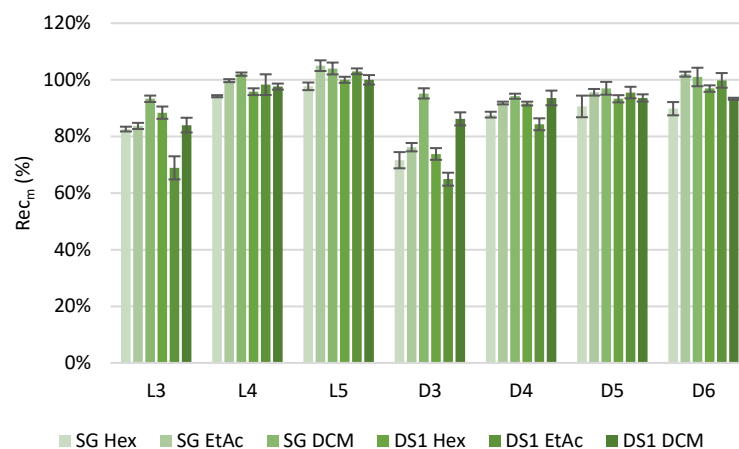


Figure A4.1. Results from the recovery assays carried out for the selection of the extraction solvent - *n*-hexane (Hex) vs. dichloromethane (DCM) vs. ethyl acetate (EtAc).

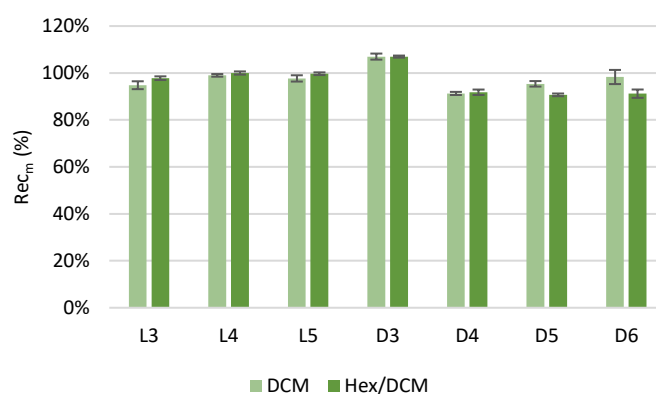


Figure A4.2. Results from the recovery assays carried out for the selection of the extraction solvent (cont.) - dichloromethane (DCM) vs. *n*-hexane/dichloromethane (Hex/DCM) 1:1 (v/v).

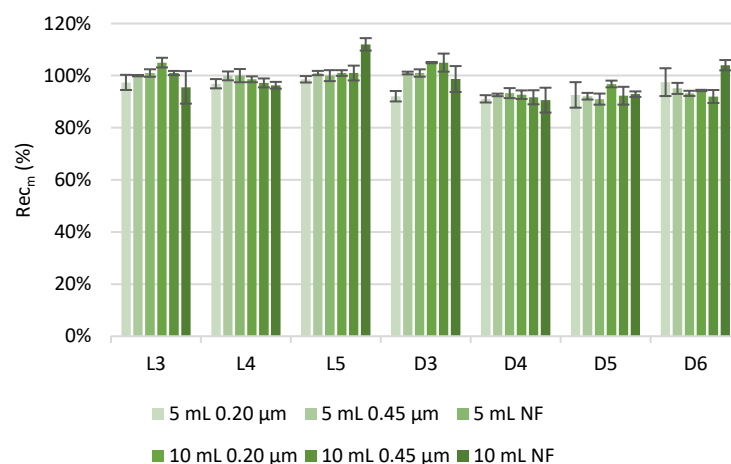


Figure A4.3. Results from the recovery assays carried out for the filtration step - 0.20 μ m vs. 0.45 μ m vs. no filtration (NF).

Appendix 5. Method Validation

5.1. Calibration Curves

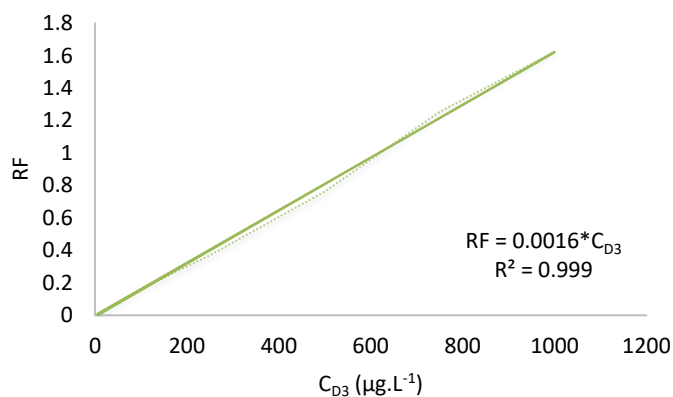


Figure A5.1.1. Calibration curve for the analysis of D3 in crumb rubber.

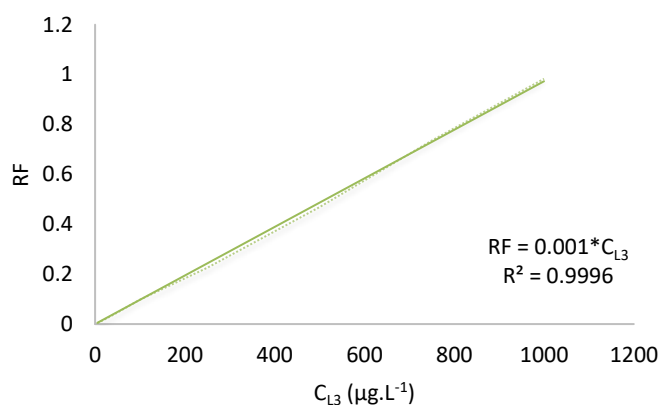


Figure A5.1.2. Calibration curve for the analysis of L3 in crumb rubber.

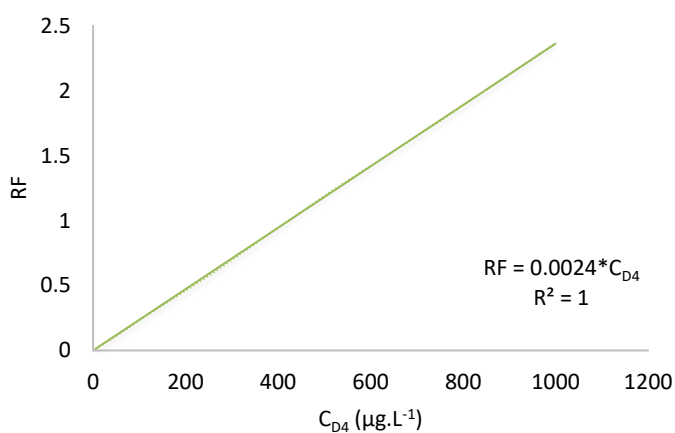


Figure A5.1.3. Calibration curve for the analysis of D4 in crumb rubber.

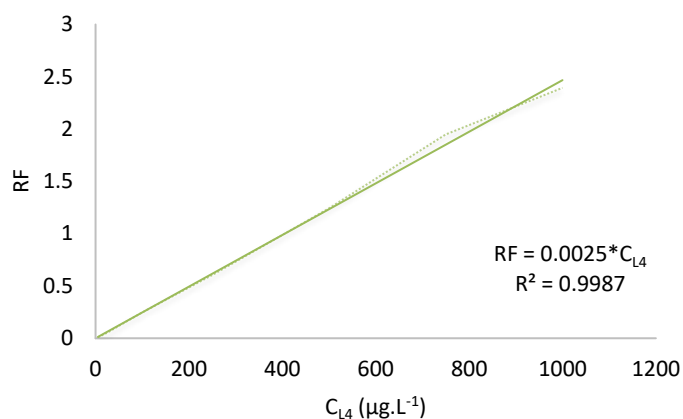


Figure A5.1.4. Calibration curve for the analysis of L4 in crumb rubber.

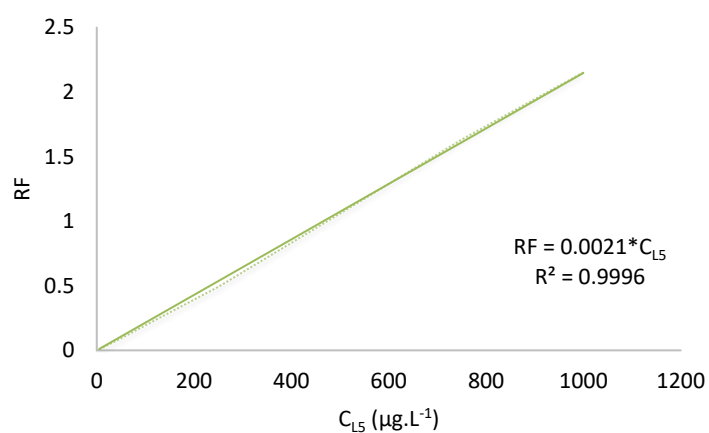


Figure A5.1.5. Calibration curve for the analysis of L5 in crumb rubber.

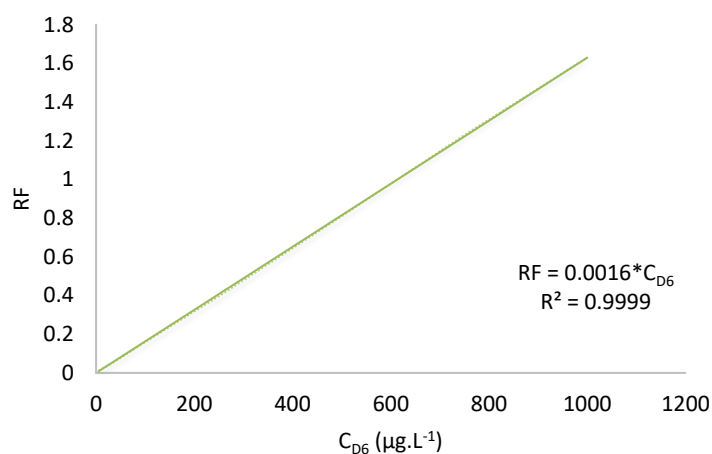


Figure A5.1.6. Calibration curve for the analysis of D6 in crumb rubber.

5.2. Linearity

Table A5.2.1. Linearity validation parameters for VMS analysis in crumb rubber.

Compound	R	N	C ₁ /C ₂	S _a /a
L3	1.000	8	$\frac{1000}{5} = 200$	1.02%
L4	0.999			2.06%
L5	1.000			0.83%
D3	0.999			1.70%
D4	1.000			0.34%
D5	1.000			1.04%
D6	1.000			0.39%

5.3. Accuracy and Precision

Table A5.3.1. Results of the accuracy tests for VMS analysis in crumb rubber (SG method at 100 ng.g⁻¹ and 500 ng.g⁻¹ spike levels).

Compound	Spike level (ng.g ⁻¹)	Rec _m (%)
L3	100	128 ± 7
	500	106 ± 4
L4	100	90.0 ± 7.4
	500	98.5 ± 2.0
L5	100	91.2 ± 7.1
	500	96.9 ± 3.5
D3	100	119 ± 7
	500	122 ± 1
D4	100	78.6 ± 5.1
	500	91.4 ± 2.9
D5	100	55.3 ± 5.2
	500	89.6 ± 4.5
D6	100	38.4 ± 13.8
	500	90.8 ± 8.0

Table A5.3.2. Results of the precision tests - repeatability and intermediate precision for VMS analysis in crumb rubber (SG method at 100 ng.g⁻¹ and 500 ng.g⁻¹ spike levels).

Compound	Spike level (ng.g ⁻¹)	RSD - repeatability (%)	RSD - intermediate precision (%)
L3	100	6.7	5.3
	500	3.6	0.27
L4	100	7.4	1.8
	500	2.0	2.6
L5	100	7.1	4.7
	500	3.5	0.80
D3	100	7.1	17
	500	1.2	10
D4	100	5.1	6.7
	500	2.9	0.54
D5	100	5.2	39
	500	4.5	1.5
D6	100	14	72
	500	8.0	4.7

Appendix 6. Concentration of Siloxanes in Crumb Rubber

Table A6.1. Concentration of VMSs in crumb rubber (ng.g⁻¹).

Sample ID	D3	D4	D5	D6	ΣD3-D6	L3	L4	L5	ΣL3-L5	Total
CR2	n.d.	n.d.	9.23	3.81	13.0	n.d.	n.d.	n.d.	n.d.	13.0
CR5	n.d.	n.d.	11.5	2.75	14.2	n.d.	n.d.	n.d.	n.d.	14.2
CR7	n.d.	3.25	2.22	4.39	11.3	n.d.	n.d.	n.d.	n.d.	11.3
CR15	n.d.	< LOD	19.1	9.69	28.8	n.d.	n.d.	n.d.	n.d.	28.8
CR21	n.d.	n.d.	15.6	4.04	19.6	n.d.	n.d.	n.d.	n.d.	19.6
CR23	n.d.	3.19	16.0	10.2	29.7	n.d.	n.d.	n.d.	n.d.	29.7
CR25	n.d.	6.67	29.8	17.7	54.4	n.d.	n.d.	n.d.	n.d.	54.4
CR31	n.d.	< LOD	7.06	11.7	18.8	n.d.	n.d.	n.d.	n.d.	18.8
CR32	n.d.	4.02	24.1	28.8	57.1	n.d.	n.d.	n.d.	n.d.	57.1
CR34	n.d.	< LOD	11.2	n.d.	11.2	n.d.	n.d.	n.d.	n.d.	11.2
CR37	n.d.	n.d.	9.97	3.44	13.4	n.d.	n.d.	n.d.	n.d.	13.4
CR39	n.d.	1.91	10.2	5.97	18.2	n.d.	n.d.	n.d.	n.d.	18.2
CR41	n.d.	1.81	8.00	7.34	17.4	n.d.	n.d.	n.d.	n.d.	17.4
CR52	n.d.	n.d.	8.77	7.26	16.0	n.d.	n.d.	n.d.	n.d.	16.0
CR53	n.d.	< LOD	12.2	3.38	15.6	n.d.	n.d.	n.d.	n.d.	15.6
CR55	n.d.	< LOD	13.3	4.40	17.7	n.d.	n.d.	n.d.	n.d.	17.7
CR56	n.d.	< LOD	12.0	2.89	14.9	n.d.	n.d.	n.d.	n.d.	14.9
CR59	n.d.	< LOD	15.4	7.78	23.2	n.d.	n.d.	n.d.	n.d.	23.2
CR61	n.d.	1.73	18.3	13.4	33.5	n.d.	n.d.	n.d.	n.d.	33.5
CR62	n.d.	2.07	19.4	14.8	36.4	n.d.	n.d.	n.d.	n.d.	36.4
CR63	n.d.	6.99	21.4	14.5	43.2	n.d.	n.d.	n.d.	n.d.	43.2
CR64	n.d.	< LOD	17.5	5.00	22.5	n.d.	n.d.	n.d.	n.d.	22.5
CR65	n.d.	< LOD	13.8	8.97	22.8	n.d.	n.d.	n.d.	n.d.	22.8
CR67	n.d.	< LOD	9.43	2.32	11.8	n.d.	n.d.	n.d.	n.d.	11.8
CR69	n.d.	< LOD	15.4	3.19	18.6	n.d.	n.d.	n.d.	n.d.	18.6
CR70	n.d.	< LOD	18.4	6.20	24.6	n.d.	n.d.	n.d.	n.d.	24.6
CR71	n.d.	< LOD	17.1	< LOD	17.1	n.d.	n.d.	n.d.	n.d.	17.1
CR72	n.d.	< LOD	15.2	7.09	22.3	n.d.	n.d.	n.d.	n.d.	22.3
CR73	n.d.	3.28	15.0	11.3	29.8	n.d.	n.d.	n.d.	n.d.	29.8
CR74	n.d.	3.86	16.4	10.6	31.1	n.d.	n.d.	n.d.	n.d.	31.1
CR75	n.d.	2.25	16.1	16.6	35.1	n.d.	n.d.	n.d.	n.d.	35.1
CR76	n.d.	< LOD	12.6	10.3	22.9	n.d.	n.d.	n.d.	n.d.	22.9
CR77	n.d.	< LOD	13.8	8.56	22.4	n.d.	n.d.	n.d.	n.d.	22.4
CR79	n.d.	< LOD	19.0	12.0	31.0	n.d.	n.d.	n.d.	n.d.	31.0
CR80	n.d.	2.11	11.8	5.80	19.8	n.d.	n.d.	n.d.	n.d.	19.8
CR81	n.d.	< LOD	11.9	5.72	17.7	n.d.	n.d.	n.d.	n.d.	17.7
CR83	n.d.	2.03	15.2	9.35	26.7	n.d.	n.d.	n.d.	n.d.	26.7
CR84	n.d.	6.16	9.7	4.62	21.1	n.d.	n.d.	n.d.	n.d.	21.1
CR85	n.d.	5.20	20.3	13.1	38.9	n.d.	n.d.	n.d.	n.d.	38.9
CR86	n.d.	1.68	13.4	7.40	22.6	n.d.	n.d.	n.d.	n.d.	22.6

Table A6.1. Concentration of VMSs in crumb rubber (ng.g⁻¹) (cont.).

Sample ID	D3	D4	D5	D6	ΣD3-D6	L3	L4	L5	ΣL3-L5	Total
CR90	n.d.	1.61	11.5	11.4	24.7	n.d.	n.d.	n.d.	n.d.	24.7
CR92	n.d.	< LOD	9.00	5.97	15.0	n.d.	n.d.	n.d.	n.d.	15.0
CR94	n.d.	2.79	23.9	25.3	52.1	n.d.	n.d.	n.d.	n.d.	52.1
CR97	n.d.	4.56	16.9	10.8	32.5	n.d.	n.d.	n.d.	n.d.	32.5
CR100	n.d.	5.62	25.7	8.68	40.2	n.d.	n.d.	n.d.	n.d.	40.2
CR101	n.d.	4.00	6.14	< LOD	10.8	n.d.	n.d.	n.d.	n.d.	10.8
CR102	n.d.	5.76	15.8	< LOD	21.9	n.d.	n.d.	n.d.	n.d.	21.9
CR103	n.d.	3.70	11.3	9.34	24.7	n.d.	n.d.	n.d.	n.d.	24.7
CR104	n.d.	< LOD	14.9	9.03	23.9	n.d.	n.d.	n.d.	n.d.	23.9
CR106	n.d.	3.02	22.5	16.4	42.1	n.d.	n.d.	n.d.	n.d.	42.1
CR107	n.d.	1.89	11.1	6.83	20.0	n.d.	n.d.	n.d.	n.d.	20.0
CR108	n.d.	4.00	20.9	17.4	42.5	n.d.	n.d.	n.d.	n.d.	42.5
CR110	n.d.	2.08	14.8	15.3	32.4	n.d.	n.d.	n.d.	n.d.	32.4
CR112	n.d.	2.26	20.6	14.6	37.6	n.d.	n.d.	n.d.	n.d.	37.6
CR114	n.d.	1.58	4.01	4.30	10.3	n.d.	n.d.	n.d.	n.d.	10.3
CR116	n.d.	< LOD	18.1	4.75	22.9	n.d.	n.d.	n.d.	n.d.	22.9
CR117	n.d.	1.98	26.0	28.3	56.3	n.d.	n.d.	n.d.	n.d.	56.3
CR120	n.d.	< LOD	22.0	10.2	32.2	n.d.	n.d.	n.d.	n.d.	32.2
CR121	n.d.	1.99	19.2	9.09	30.4	n.d.	n.d.	n.d.	n.d.	30.4
CR122	n.d.	< LOD	17.7	6.60	24.3	n.d.	n.d.	n.d.	n.d.	24.3
CR123	n.d.	2.05	22.7	16.2	41.0	n.d.	n.d.	n.d.	n.d.	41.0
CR124	n.d.	3.84	28.4	40.2	72.5	n.d.	n.d.	n.d.	n.d.	72.5
CR127	n.d.	2.45	12.1	2.43	17.2	n.d.	n.d.	n.d.	n.d.	17.2
CR128	n.d.	3.23	25.8	13.0	42.2	n.d.	n.d.	n.d.	n.d.	42.2
CR130	n.d.	4.08	37.3	15.1	56.6	n.d.	n.d.	n.d.	n.d.	56.6
CR131	n.d.	1.61	28.0	12.8	42.5	n.d.	n.d.	n.d.	n.d.	42.5
CR132	n.d.	3.49	24.8	9.92	38.3	n.d.	n.d.	n.d.	n.d.	38.3
CR134	n.d.	2.67	53.4	10.1	66.2	n.d.	n.d.	n.d.	n.d.	66.2
CR135	n.d.	3.65	40.3	8.25	52.2	n.d.	n.d.	n.d.	n.d.	52.2
CR136	n.d.	2.86	32.8	12.6	48.4	n.d.	n.d.	n.d.	n.d.	48.4
CR137	n.d.	3.14	32.7	11.8	47.8	n.d.	n.d.	n.d.	n.d.	47.8
CR138	n.d.	3.41	32.1	18.6	54.2	n.d.	n.d.	n.d.	n.d.	54.2
CR139	n.d.	2.70	27.0	17.2	47.0	n.d.	n.d.	n.d.	n.d.	47.0
CR140	n.d.	3.09	32.0	17.5	52.7	n.d.	n.d.	n.d.	n.d.	52.7
CR141	n.d.	2.71	33.0	33.3	69.1	n.d.	n.d.	n.d.	n.d.	69.1
CR142	n.d.	3.59	28.8	22.3	54.8	n.d.	n.d.	n.d.	n.d.	54.8
CR144	n.d.	2.78	26.4	17.6	46.9	n.d.	n.d.	n.d.	n.d.	46.9
CR145	n.d.	2.48	22.5	13.2	38.3	n.d.	n.d.	n.d.	n.d.	38.3
CR146	n.d.	3.29	21.9	16.5	41.8	n.d.	n.d.	n.d.	n.d.	41.8
CR148	n.d.	2.54	22.9	15.9	41.4	n.d.	n.d.	n.d.	n.d.	41.4
CR154	n.d.	2.86	24.2	14.2	41.4	n.d.	n.d.	n.d.	n.d.	41.4
CR155	n.d.	2.48	22.3	9.58	34.5	n.d.	n.d.	n.d.	n.d.	34.5
CR156	n.d.	2.41	16.1	10.1	28.8	n.d.	n.d.	n.d.	n.d.	28.8

Table A6.1. Concentration of VMSs in crumb rubber (ng.g⁻¹) (cont.).

Sample ID	D3	D4	D5	D6	ΣD3-D6	L3	L4	L5	ΣL3-L5	Total
CR159	n.d.	< LOD	21.0	11.7	32.7	n.d.	n.d.	n.d.	n.d.	32.7
CR162	n.d.	1.71	15.0	4.20	21.0	n.d.	n.d.	n.d.	n.d.	21.0
CR164	n.d.	2.76	9.87	5.62	18.5	n.d.	n.d.	n.d.	n.d.	18.5
CR166	n.d.	1.79	28.5	21.7	52.1	n.d.	n.d.	n.d.	n.d.	52.1
CR167	n.d.	1.80	29.5	26.5	57.9	n.d.	n.d.	n.d.	n.d.	57.9
CR168	n.d.	2.13	33.6	18.2	53.0	n.d.	n.d.	n.d.	n.d.	53.0
CR171	n.d.	3.24	27.8	13.5	44.6	n.d.	n.d.	n.d.	n.d.	44.6
CR172	n.d.	2.64	32.3	19.2	54.3	n.d.	n.d.	n.d.	n.d.	54.3
CR173	n.d.	4.36	27.0	8.22	39.7	n.d.	n.d.	n.d.	n.d.	39.7
CR174	n.d.	3.94	38.3	19.6	62.0	n.d.	n.d.	n.d.	n.d.	62.0
CR175	n.d.	3.05	26.8	16.0	46.0	n.d.	n.d.	n.d.	n.d.	46.0
CR177	n.d.	4.37	13.2	7.43	25.3	n.d.	n.d.	n.d.	n.d.	25.3
CR179	n.d.	3.03	7.56	4.94	15.9	n.d.	n.d.	n.d.	n.d.	15.9
CR182	n.d.	2.70	27.2	16.0	46.0	n.d.	n.d.	n.d.	n.d.	46.0
CR183	n.d.	4.28	37.6	21.3	63.4	n.d.	n.d.	n.d.	n.d.	63.4
CR184	n.d.	4.54	25.4	13.9	44.1	n.d.	n.d.	n.d.	n.d.	44.1
CR186_1	n.d.	2.67	23.6	11.0	37.3	n.d.	n.d.	n.d.	n.d.	37.3
CR186_2	n.d.	2.37	13.9	9.97	26.4	n.d.	n.d.	n.d.	n.d.	26.4
CR187	n.d.	3.45	28.9	19.6	52.1	n.d.	n.d.	n.d.	n.d.	52.1
CR188	n.d.	2.60	35.6	32.5	70.8	n.d.	n.d.	n.d.	n.d.	70.8
CR190	n.d.	11.9	34.0	22.0	68.3	n.d.	n.d.	n.d.	n.d.	68.3
CR192	n.d.	4.05	21.3	10.4	35.9	n.d.	n.d.	n.d.	n.d.	35.9
CR194	n.d.	4.53	31.5	27.6	63.7	n.d.	n.d.	n.d.	n.d.	63.7
CR195	n.d.	2.08	7.80	8.18	18.3	n.d.	n.d.	n.d.	n.d.	18.3
CR163	n.d.	2.42	15.0	19.1	36.7	n.d.	n.d.	n.d.	n.d.	36.7
P1	6.84	36.4	55.4	55.7	154	0.34	< LOD	n.d.	0.34	155
P2	< LOD	17.0	72.3	42.8	132	0.18	< LOD	n.d.	0.18	132
C1	7.34	142	78.8	41.3	269	0.78	3.51	5.43	9.72	279
C2	216	106	848	3,912	5,082	0.33	n.d.	6.30	6.63	5,089
C3	16.4	10.4	28.9	54.6	110	1.11	n.d.	n.d.	1.11	111
C4	6.04	25.1	23.6	35.0	89.7	0.47	n.d.	n.d.	0.47	90.2

n.d.: non-detected (no signal emitted by the GC-MS); < LOD: concentration below the limit of detection (from the method - MDL).

Table A6.2. Mean total VMS concentrations in crumb rubber, by country.

Country	Number of samples	Total VMS concentration (ng.g ⁻¹)
Albania	1	13
Chile	10	28 ± 17
Croatia	2	17 ± 1
Finland	9	23 ± 10
France	5	23 ± 5
Germany	1	31
Greece	3	27 ± 7
Italy	4	24 ± 6
Poland	3	28 ± 10
Portugal	38	40 ± 15
Spain	20	43 ± 16
Sweden	5	45 ± 21

Table A6.3. Mean total VMS concentrations in crumb rubber, by granulometry.

Granulometry	Number of samples	Total VMS concentration (ng.g ⁻¹)
< 1 mm	4	32 ± 12
1-2 mm	74	31 ± 15
2-3 mm	17	44 ± 14
> 3 mm	6	39 ± 20

Table A6.4. Mean total VMS concentrations in crumb rubber, by field age.

Field age	Number of samples	Total VMS concentration (ng.g ⁻¹)
< 1 year	9	46 ± 14
1-5 years	18	41 ± 14
5-10 years	27	34 ± 16
> 10 years	24	30 ± 13
Unknown	23	26 ± 14

Appendix 7. Concentration of Siloxanes in Other Materials

Table A7.1. Concentration of VMSs in other materials (ng.g⁻¹).

Sample ID	Material	D3	D4	D5	D6	ΣD3-D6	L3	L4	L5	ΣL3-L5	Total
CR82	Coloured CR	n.d.	2.54	28.8	32.0	63.4	n.d.	n.d.	n.d.	n.d.	63.4
CR105	Coloured CR	n.d.	3.73	30.1	31.8	65.6	n.d.	n.d.	n.d.	n.d.	65.6
CR125	Coloured CR	n.d.	2.78	41.6	39.6	83.9	n.d.	n.d.	n.d.	n.d.	83.9
CR126	Coloured CR	n.d.	3.59	44.7	50.9	99.2	n.d.	n.d.	n.d.	n.d.	99.2
CR133	Coloured CR	n.d.	2.29	20.2	26.9	49.4	n.d.	n.d.	n.d.	n.d.	49.4
CR165	Coloured CR	n.d.	1.70	8.89	4.75	15.3	n.d.	n.d.	n.d.	n.d.	15.3
CR180	Coloured CR	n.d.	< LOD	8.88	1.95	10.8	n.d.	n.d.	n.d.	n.d.	10.8
CR87	Cork	n.d.	6.28	25.7	41.6	73.5	n.d.	n.d.	n.d.	n.d.	73.5
CR152	Cork	n.d.	< LOD	5.74	2.06	7.79	n.d.	n.d.	n.d.	n.d.	7.79
CR189	Cork	n.d.	2.26	14.2	1.17	17.7	n.d.	n.d.	n.d.	n.d.	17.7
CR191	Cork	n.d.	< LOD	7.47	2.10	9.57	n.d.	n.d.	n.d.	n.d.	9.57
CR88	Rubber/coconut fibre	n.d.	4.61	34.9	34.2	73.7	n.d.	n.d.	n.d.	n.d.	73.7

Appendix 8. Statistical Analysis

8.1. Pairwise T Tests

Table A8.1.1. p-values of the pairwise T tests for the country distribution (crumb rubber from synthetic turf fields).

	Albania	Chile	Croatia	Finland	France	Germany	Greece	Italy	Poland	Portugal	Spain	Sweden
Albania		22.16%	1.63%	9.07%	0.50%	n.a. ^(a)	3.75%	3.25%	8.65%	1.03%	2.60%	10.63%
Chile			29.94%	13.43%	17.82%	21.81%	14.60%	21.73%	15.20%	0.01%	0.19%	2.91%
Croatia				10.00%	0.34%	0.57%	1.62%	2.51%	5.34%	0.57%	1.67%	7.25%
Finland					47.55%	34.00%	35.43%	46.32%	36.02%	1.21%	3.44%	10.09%
France						10.78%	17.26%	46.80%	24.50%	3.30%	5.92%	10.90%
Germany							35.76%	20.30%	41.08%	36.53%	38.57%	40.56%
Greece								22.51%	49.85%	16.53%	20.47%	25.46%
Italy									27.77%	4.60%	7.69%	13.69%
Poland										16.66%	20.73%	26.16%
Portugal											49.22%	44.08%
Spain												44.81%
Sweden												

^(a) The test did not return a p-value for Albania vs. Germany since there was only 1 sample from each country.

Table A8.1.2. p-values of the pairwise T tests for the granulometry distribution (crumb rubber from synthetic turf fields).

	< 1 mm	1-2 mm	2-3 mm	> 3 mm
< 1 mm		33.95%	0.72%	26.52%
1-2 mm			0.22%	31.79%
2-3 mm				9.56%
> 3 mm				

Table A8.1.3. p-values of the pairwise T tests for the field age distribution (crumb rubber from synthetic turf fields).

	< 1 year	1-5 years	5-10 years	> 10 years	Unknown
< 1 year		40.71%	4.15%	0.72%	0.21%
1-5 years			2.98%	0.46%	0.05%
5-10 years				24.74%	2.88%
> 10 years					8.32%
Unknown					

8.2. Non-Parametric Tests

Nonparametric Tests

Hypothesis Test Summary				
	Null Hypothesis	Test	Sig. ^{a,b}	Decision
1	The distribution of Concentration is the same across categories of Country.	Independent-Samples Mann-Whitney U Test	1,000 ^c	Retain the null hypothesis.
a. The significance level is ,050. b. Asymptotic significance is displayed. c. Exact significance is displayed for this test.				

Independent-Samples Mann-Whitney U Test

Figure A8.2.1. Results of the Mann-Whitney U test for the country distribution (commercial crumb rubber).

Nonparametric Tests

Hypothesis Test Summary				
	Null Hypothesis	Test	Sig. ^{a,b}	Decision
1	The distribution of Concentration1 is the same across categories of TypeMaterial.	Independent-Samples Kruskal-Wallis Test	,243	Retain the null hypothesis.
a. The significance level is ,050. b. Asymptotic significance is displayed.				

Figure A8.2.2. Results of the Kruskal-Wallis test for the type of material distribution (alternative material).

Nonparametric Tests

Hypothesis Test Summary				
	Null Hypothesis	Test	Sig. ^{a,b}	Decision
1	The distribution of Concentration1 is the same across categories of TypeMaterial.	Independent-Samples Kruskal-Wallis Test	<,001	Reject the null hypothesis.
a. The significance level is ,050. b. Asymptotic significance is displayed.				

Figure A8.2.3. Results of the Kruskal-Wallis test for the type of material distribution (crumb rubber from synthetic turf fields vs. commercial crumb rubber vs. alternative material).

Pairwise Comparisons of TypeMaterial

Sample 1-Sample 2	Test Statistic	Std. Error	Std. Test Statistic	Sig.	Adj. Sig. ^a
Cork-FieldCR	-24,046	18,594	-1,293	,196	1,000
Cork-Coloured	45,929	22,888	2,007	,045	,448
Cork-Fiber	-82,500	40,827	-2,021	,043	,433
Cork-ComerCR	87,833	23,572	3,726	<.001	,002
FieldCR-Coloured	21,882	14,242	1,536	,124	1,000
FieldCR-Fiber	58,454	36,686	1,593	,111	1,000
FieldCR-ComerCR	63,787	15,317	4,165	<.001	,000
Coloured-Fiber	-36,571	39,038	-,937	,349	1,000
Coloured-ComerCR	-41,905	20,316	-2,063	,039	,391
Fiber-ComerCR	5,333	39,443	,135	,892	1,000

Each row tests the null hypothesis that the Sample 1 and Sample 2 distributions are the same.

Asymptotic significances (2-sided tests) are displayed. The significance level is ,050.

a. Significance values have been adjusted by the Bonferroni correction for multiple tests.

Figure A8.2.4. Results of the Kruskal-Wallis test for the type of material distribution (crumb rubber from synthetic turf fields vs. commercial crumb rubber vs. alternative material) (cont.).

Appendix 9. Human Exposure Parameters

Table A9.1. Oral exposure dose calculation parameters for VMS exposure from crumb rubber.

Parameter		Value	Unit
Relative oral bioaccessibility factor (B)	D4	0.280	Unitless
	D5	0.172	
	D6	0.150	
Ingestion rate (IR)		50.0	mg.day ⁻¹
Exposure frequency (EF)	Young player	16.5	days.year ⁻¹
	Adult player	24.0	
	Worker	16.0	
Body weight (BW)	Young player	31.8	kg
	Adult player	80.0	
	Worker	80.0	

Table A9.2. Dermal exposure dose calculation parameters for VMS exposure from crumb rubber.

Parameter		Value	Unit
Relative dermal bioaccessibility factor (ABS)	D4	5.00×10^{-3}	Unitless
	D5	1.00×10^{-2}	
	D6	3.00×10^{-5}	
Adherence factor (AF)		4.00×10^{-2}	mg.cm ⁻²
Exposed surface area (SA)	Young player	3,824	cm ²
	Adult player	7,325	
	Worker	7,325	