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Chemical Analysis of Organic Compounds in Footwear

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Introductory remark

This Diploma work was carried out at the Swedish Environmental Research Institute (IVL) in collaboration with the Department of Materials and Environmental Chemistry at Stockholm University. The project is a part of the research programme ChEmiTecs, funded by Swedish EPA. The goal of the research programme is “to improve the understanding of emissions of organic substances from articles” by pinpointing problematic chemicals, articles and patterns of use as well as to quantify/estimate chemical emission from products. By relating the result with other emission sources e.g. industries and transport, the program aims to “clarify and determine the magnitude of chemical emission from articles” as well as to “support development of Swedish and European management programmes to minimise risks from harmful substances” (ChEmiTecs).

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Abstract
In view of that chemical emission from point sources such as industries has decreased over the years; chemical emission from articles has been pointed out to be of increasing concern. Hence, it is important to get a better understanding of the chemical content in different types of articles. The aim of this study was to provide information regarding the organic chemical content in footwear by chemical analysis of materials sampled from three shoes from well known brands (Ecco, Nike and Vagabond). Materials from the outsole, midsole, upper and the lining were extracted by methanol and analysed with GC-MS and HPLC-MS/MS. Overall, 31 compounds were identified at levels of parts per million in the sampled materials. Both plasticizers, antioxidants, solvents, vulcanization agents, surfactants, flame retardants, oxidants and biocides were found. Among the compounds identified, 11 high production volume chemicals and six compounds classified as either toxic to aquatic organisms, carcinogenic or toxic for reproduction were found. Three of these compounds (diisobutyl phthalate, dibutyl phthalate and bis(2-etyhylhexyl)phthalate) are included on the candidate list for authorization within REACH. However, the levels were approximately 100-1000 times lower than the limit stated in the European chemical regulation (REACH), for which requirements are put on manufacturers and importers. As an attempt to model weathering and leatching in the environment, outsole material from each shoe was subjected to soaking extraction using synthetic brackish water. The water samples obtained were found to contain only a few organic chemicals at levels of parts per million. The number of compounds was less compared to when outsole material was extracted using methanol. Hence, not all organic compounds identified in the three outsoles seem to have potential to be released under environmental conditions through leaching. The water samples were also used to evaluate the toxicity of footwear outsoles. The toxicity tests were carried out at the Department of Applied Environmental Science (ITM) by Ellen Kahn as a part of her diploma work. Both larval development test and growth inhibition tests were performed using *Nitocra spinipes* and *Ceramium tenuicorne*. The toxic effects observed by Ellen Kahn could not be explained by the levels of organic compounds identified in the water samples. Instead inorganic compounds (e.g zinc) were pointed out as the probable cause.

Even though the levels of organic chemicals identified in this study were found to be low, the great number of different chemicals identified in the sampled materials raises the question about the widespread use of chemicals in articles.

1. Introduction

Chemicals play an important role in today's production of articles and are found in a number of different materials. In the year 2000, the global production of chemicals was estimated to be 400 million tons with an increasing production in Asia and Latin America [1]. In articles, chemicals can be found as constituents in synthetic material, glues and dyes etc. or used as additives to give a material certain properties. Even though a chemical substance may provide important functionality in a material or article, once released into the environment the same substance may cause concern for the public health and the environment [2]. Chemical emission is dependent on the properties of the emitting material as well as the physico-chemical properties of the substance released. Weathering, UV-light, temperature and use are other factors known to affect the rate of chemical emission from articles [1].

Historically, much effort has been done to decrease chemical emission from manufacturing industries, focusing on release to air and water [2]. In view of that emission from industries in general has decreased over the years, along with manufacturing shifting towards countries outside the European Union. Chemical emission from articles through consumption, disposal, recycle and use, has been pointed out to be of increasing relevance [1]. With more products being produced and manufactured abroad, more articles containing chemicals are imported. The knowledge regarding the chemical use through out the manufacturing steps of an imported article is often lacking. Hence, the new European Chemical Regulation, REACH, aims to ensure better information regarding chemical content in articles by putting more requirements on manufacturers and importers [2]. Furthermore, the Swedish Environmental Code (chapter 2) and the Swedish product Safety Ordinance (2004:469) requires producers of articles to have sufficient knowledge of potential environmental and/or health impacts of their products [3].

Lately, chemicals in footwear have been pointed out as a group of articles being of concern [3-5]. Footwear is a heterogeneous group of goods and includes all types of shoes such as sport shoes, boots and sandals etc. In Sweden, the native manufacturing of shoes is quite small and the vast majority of all shoes sold are imported from abroad [5]. In 2008, 28125 tons of footwear and material used in footwear industry were imported to Sweden [6]. The majority of imported shoes come from Vietnam, China, Italy and Portugal according to data from 2000. In Sweden mostly shoes with special application areas are manufactured, such as winter boots, shoes used for protection and footwear for children. Due to their application area, shoes may consist of various types of materials such as leather, artificial leather, rubber, textile and plastic [5]. Chemicals are often added to these materials to give them certain properties e.g. softeners, dyes and flame retardants etc. Footwear materials may also contain contaminants and residues from chemicals used in the manufacturing steps e.g. formaldehyde and vinyl chloride monomers. In **Table 1,** critical substances potentially present in footwear and footwear materials is presented [7].

Table 1. Is based on information obtained from the report (TC 309 WI) prepared by the Technical Committee [7] and gives a survey of critical substances potentially present in footwear and footwear components and the materials in which they might be found.

Substance	Different types of materials
Acrylonitrile	rubber, adhesives
Aromatic amines	leather, coated leather, leather board, polyester, polyamide, chloride fibre, natural textile, print for textile
Chloroorganic carriers	polyester
Colophony	adhesives
Dimethylformamide	PU-TPU elasthan
Dimethylfumarate	leather, coated leather, leather board, rubber, polyester, polyamide, chloride fibre, polyacrylic, natural textile, wood, cork, print for textile
Disperses dyes and dye stuff	polyester, polyamide, chloride fibre, polyacrylic, natural textile
Flame retardants	leather, coated leather, leather board, PVC, EVA foam, rubber, PU-TPU elasthan, PE-T PP, polyester, polyamide, chloride fibre, polyacrylic, latex, natural textile, wood, cork, print for textile, cellulosic material
Formaldehyde	leather, coated leather, leather board, polyester, polyamide, chloride fibre, polyacrylic, natural textile, wood, cork, cellulosic material
Mercaptobenzothiazole	rubber
N-ethylphenylamine	rubber, latex
Nitrosamines	rubber
Nonylphenol	leather, coated leather, leather board, polyester, polyamide, chloride fibre, natural textile
Alkylphenolethoxylates	leather, coated leather, leather board, polyester, polyamide, chloride fibre, natural textile
Ortho-phenylphenol	leather, coated leather, leather board, rubber, latex
CFCs	polyester, polyamide, chloride fibre, polyacrylic, natural textile
pentachlorophenol	leather, coated leather, leather board
tetrachlorophenol	leather, coated leather, leather board
trichlorophenol	leather, coated leather, leather board
Pesticides	leather, coated leather, leather board, natural textile, cellulosic material
Perfluorooctane sulfonate	leather, coated leather, leather board, polyester, polyamide, chloride fibre, polyacrylic, natural textile
Perfluorooctanoic acid	leather, coated leather, leather board, polyester, polyamide, chloride fibre, polyacrylic, natural textile
Phtalates	coated leather, PVC, EVA foam, rubber, PU-TPU elasthan, PE-T PP, polyester, polyamide, chloride fibre, polyacrylic, natural textile, print for textile
Polychlorinated biphenyls (PCBs)	leather, coated leather, leather board, polyester, polyamide, chloride fibre, polyacrylic, natural textile
Polychloroprene	rubber, adhesives
Paraphenylene diamine	leather, coated leather, leather board, polyester, polyamide, polyacrylic, natural textile, print for textile, cellulosic material
Paratertiary butyl phenol formaldehyde	adhesives
Chlorinated paraffines	leather, coated leather, leather board, rubber, polyester, polyamide, chloride fibre, polyacrylic
TCMTB	leather, coated leather, leather board
Thiuram and Thiocarbamate	rubber
Vinyl chloride monomer	coated leather, PVC
Bezothiazoler and Benzendiaminer	rubber
Benzotriazoler	natural textile

leather	
coated leather	
leather board	
PVC	
EVA foam	
rubber	
PU-TPU elasthan	
PE-T PP	
polyester	
polyamide	
chloride fibre	
polyacrylic	
latex	
natural textile	
wood, cork	
adhesives	
print for textile	
cellulosic material	

The Swedish Society of Nature Conservation (SSNC) has recently published two reports [3, 4] presenting the content of some hazardous substances identified in sandals and leather shoes. In sandals, high levels of phthalates were reported when parts consisting of poly vinyl chloride (PVC) were analysed [4]. Phthalates are commonly used as softeners in plastic and rubber but are utilized as fixing agents and carriers in different textile materials as well [8]. According to the SSNC report, bis(ethylhexyl)phthalate (DEHP) was the most abundant phthalate identified, but dibutyl phthalate (DBP), di-*n*-octyl phthalate (DNOP), di-iso-nonyl phthalate (DINP) and di-iso-decyl phthalate (DIDP) were found as well. In addition to phthalates, dibutyl tin (DBT) and a number of heavy metals (e.g. As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb and Zn) were identified in the sandals as well [4].

In leather shoes, trivalent chromium was found to be the most common metal, but hexavalent chromium, cadmium, nickel, cupper, lead and zinc were identified according to the SSNC report [3]. Among the organic chemicals analysed; 2,4,6-tribromophenol and Formaldehyde were identified. 2,4,6-tribromophenol is a used as fungicide, bactericide and a flame retardant and is very toxic to many aquatic organisms [3]. Formaldehyde has several areas of use such as in adhesives, binders for plastic, textile and leather [3]. Formaldehyde is also used as a preservative and in the production of tanning resins leather. In addition, two aromatic amines; 4-aminodiphenyl and benzidine, regulated in REACH due to their carcinogenicity were identified as well [3].

1.1 Aims

This diploma work aimed to give further knowledge regarding organic chemicals found in footwear materials by providing chemical analysis of materials from three different shoes. The goal was to identify and quantify the extractable content of organic chemicals in the studied materials. Hence, this project was closely linked to a diploma work carried out by Ellen Kahn at the Department of Applied Environmental Science (ITM, Stockholm University) were toxicity of footwear outsoles were tested on aquatic species (*Ceramium tenuicorne* and *Nitocra spinipes*). As an attempt to model the situation in the environment, soaking extraction of outsole material using synthetic brackish water, was performed and the water leachates were used in the toxicology studies described above. The water leachates were subjected to chemical analysis with the aim to identify and quantify their content of organic chemicals, as a part of this diploma work.

2. Materials and methods

2.1 Samples

Three different shoes were used in this study and materials from four different parts of each shoe were sampled (the midsole, the outsole, the lining and the upper). In **Table 2.** information about the shoes are presented along with information about the materials sampled. All materials except the outsole were sampled using a scalpel and a pair of scissor, the outsole was sampled using a Bacho grater, article nr: 343-10-2 (SNA Europe, Enköping, Sweden). The tools were washed with water and methanol before they were used and the materials were collected on sheets of foil. The midsole material, the upper and the lining were cut into small pieces (~ 5×5 mm) before transferred into test tubes and subjected to chemical analysis.

Table 2. Presents information about the shoes used in the present study (the producer/agent, country of manufacture, shop of purchase and materials used in the upper, the lining, the midsole and the outsole)

			
Number	1	2	3
Name of the shoe or article number	ECCO Ultra Terrain 1.1 Alaska	Nike Air Pegasus +26	2833-040-20
Producer/agent	ECCO	Nike	Vagabond
Country of manufacture	China	China	Vietnam
Shop of purchase	ECCO	Stadium	Scorett
Material in the upper	Synthetic material and fibre including a GoreTex® lining	Polyester [b] and Polyamide (nylon) fibre [c]	Leather
Material in the lining	Synthetic fibre	Polyester fibre and Polyamide (nylon) fibre	Polyester fibre and cotton
Material in the midsole	Compression-moulded EVA[a]	Natural and synthetic rubber	SBR rubber [e]
Material in the outsole	EVA	Carbonrubber [d]	SBR rubber
References	Customer service Ecco [9]	Customer service Stadium [10]	Customer service Vagabond [11]

[a] polymer composed of polymerised ethyl vinyl acetate. [b] polymer with ester bonds in the main string. [c] linear polymer with amide bonds in the main string. [d] synthetic rubber with carbon added [e] polymer composed of styrene and 1,4-butadiene or 1,2-butadiene.

2.2 Chemicals

All solvents used, e.g methanol (MeOH), methyl-*tert*-butyl ether (MTBE) and *n*-hexane (Hx), were of analytical grade obtained from Rathburn chemicals (Walkerburn, Scotland). In the preparation of the samples, phosphoric acid, sodium sulfate, sodium acetate, acetic anhydride, ammonium acetate and potassium carbonate from Merck (Darmstadt, Germany) were used. The silica gel was purchased from Merck (Darmstadt, Germany) and heated at 400°C in 4 hours before used in any cleanup. In samples analysed using gas chromatography/mass spectrometry (GC/MS), biphenyl obtained from Accurate chemical (Westbury, United States) was used as internal standard. A phthalate mixture, containing bis(2-ethylhexyl)phthalate (CAS: 117-81-7), butyl benzyl phthalate (CAS: 85-68-7), dibutyl phthalate (CAS: 84-74-2), diethyl phthalate (CAS: 84-66-2), dimethyl phthalate (CAS: 131-11-3) and dioctyl phthalate (CAS: 117-84-0) purchased from Ultra Scientific (Boras, Sweden) was used as external standard along with 2,6-bis(1,1-dimethylethyl)-4-methyl-phenol) (CAS: 128-37-0) from Sigma-Aldrich (St Louis, United States). ^{13}C-labelled perfluorooctane sulfonate

(^{13}C-PFOS) and ^{13}C-labelled perfluorooctanoic acid (^{13}C-PFOA) purchased from Wellington (Guelph, Canada) was added as internal standards in the samples analysed using high performance liquid chromatography/mass spectrometry (HPLC/MS-MS)

2.3. Soaking extraction and sample work up

The extraction was carried by soaking the shoe material in MeOH. Each type of material, approximately 0.2 g, was extracted by adding 20 ml solvent to each sample. The samples were heated for 5 hours at 70 °C on a BT3 heating block (Gant instruments, Barrington, Cambridge, England) and kept at room temperature for 66 hours. The crude extracts were filtered off using GF/A 9.0 cm glass microfibre filters (Whatman, England) and collected.

The crude extract (5 ml) from each sample was reduced to 1 ml by evaporation using nitrogen. Each extract (0.5 ml) was spiked with ^{13}C-PFOS (59.5 ng) and ^{13}C-PFOA (34.5 ng) and analysed on a high performance liquid chromatograph/mass spectrometer (HPLC/MS-MS). Another 5 ml of the crude extract from each sample were reduced to 1 ml by evaporation using nitrogen. Acidic water (4 ml, pH 1) was added along with Hx (5ml). The samples were shaken for 10 minutes and centrifuged at 3000 rpm for 10 minutes using a Wifug centrifuge (Winkelcentrifug, Elmhult, Sweden). The organic phase was transferred and reduced to 0.5 ml by evaporation using nitrogen. The samples were cleaned up on silica gel columns which consisted of 0.5 g silica activated with Milli-Q water (5-weight %). The columns were eluted with Hx (2ml, fraction 1), Hx:MTBE (9:1, 5 ml, fraction 2) and MTBE (5 ml, fraction 3). Fraction two and three from each sample were reduced to 2 ml by evaporation using nitrogen. The samples (0.5 ml) were spiked with biphenyl as internal standard (25.2 ng) and analysed on a gas chromatograph/mass spectrometer (GC/MS).

Another 5 ml of the crude extract from each sample was reduced to 1 ml by evaporation using nitrogen. Acidic water (4 ml, pH 1) was then added, along with Hx (5 ml). The samples were shaken for 10 minutes and centrifuged at 1500 rpm for 5 minutes. The organic phase was transferred and dried with sodium sulfate. The dried extracts (2 ml) from each sample were transferred into new test-tubes and derivatized by adding sodium acetate (~100 mg) and acetic anhydride (125 µl) to each sample. The samples were heated for 30 min at 75 °C on a heating block before potassium carbonate (4 ml, 0.8 M) was added and the samples were shaken and centrifuged at 3000 rpm for 10 min. The organic phase was transferred and reduced to 0.5 ml. The samples were cleaned up on silica gel columns (0.5 g silica activated with Milli-Q water) and the columns were eluted with Hx (2 ml, fraction 1), Hx:MTBE (9:1, 5 ml, fraction 2) and MTBE (5 ml, fraction 3). Fraction two and three from each sample were reduced to 2 ml by evaporation using nitrogen and 0.5 ml was spiked with biphenyl
(25.2 ng) as internal standard and analysed by GC/MS.

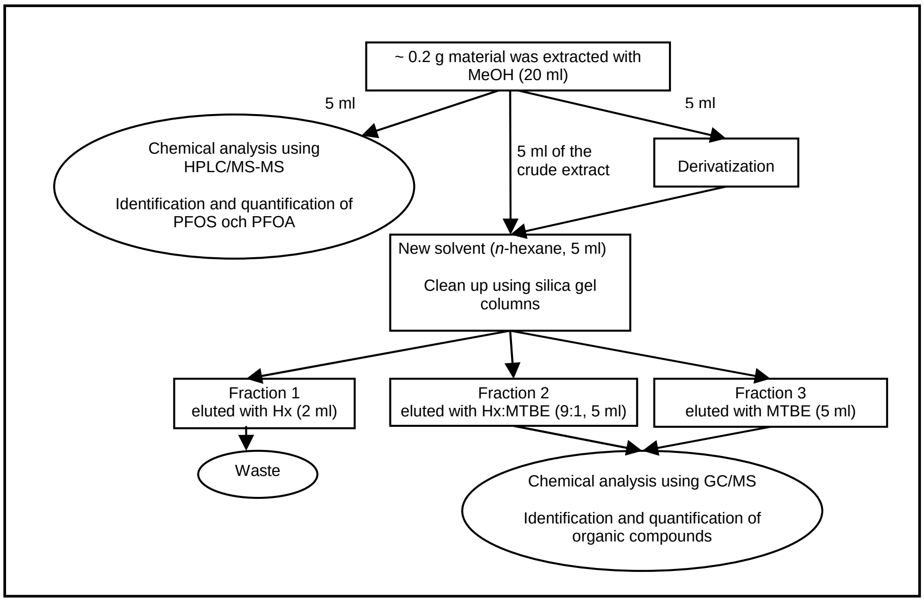


Figure 1. A schematic picture of the extraction and sample work up.

The grated outsole material from each shoe was subjected to water extraction. Approximately 1 g material was extracted using 1 litre of synthetic brackish water (7 ‰). The samples were placed on an orbital shaker SO1 (Stuart scientific, UK) at 54 rpm in room temperature for 29 days before the crude extract was filtered using qualitative folder filter paper, V5 (Muntell, Falun, Sweden) and collected. The water was transferred into dark bottles and acidified to pH 1-2 using phosphoric acid (6M). The bottles were stored in room temperature for two weeks before further work up and analysis was carried out.

Water from each sample (90 ml) was transferred to separation funnels after which Hx:MTBE (3:1, 20 ml) was added to each funnel. The funnels were shaken for 10 minutes and the organic phase was collected. The extraction was repeated once more with Hx:MTBE (3:1, 20 ml). The organic phases were combined and reduced to 5 ml by evaporation using nitrogen. The samples (0.5 ml) were spiked with biphenyl as internal standard (25.2 ng), respectively and analysed by GC/MS.

Since PFOA had been identified in the outsole material sampled from shoe number two, the water leachate from shoe number two was further analysed using HPLC/MS-MS. This was carried out by taking 100 ml of the acidified water extract and adding 200 µl ammonium acetate (1 M) to the sample. ^{13}C-PFOS (59.5 ng) and ^{13}C-PFOA (69.0 ng) were added as internal standards. An Oasis HLB cartridge (Waters Corporation, Milford, Massachusetts, USA) was rinsed with MeOH (20 ml) and conditioned using Milli-Q water (10 ml) before the sample was added (100 ml). The cartridge was rinsed again by adding MeOH:H_2O (40:60, 1 ml) to the column. The column was eluted with MeOH (8 ml) and the sample extract was evaporated to 1 ml before being analysed on HPLC/MS-MS.

2.4 Instrumental analysis

2.4.1 GC/MS analysis

Analysis and quantification were performed applying a gas chromatography/mass spectrometry instrument (6890N, 5973N, Agilent). The gas chromatograph was fitted with a VF-5MS factor four capillary column (30.0m × 0.25 mm i.d., 0.25 µm phase thickness, Varian) and helium was used as carrier gas. For analysis, 1.0 µl of the sample was injected using splitless mode at an injector temperature of 240 °C. The oven was programmed from 45 °C (1 min) with 15 °C/min to 200 °C, thereafter the temperature increased with 5 °C/min to 300 °C, this temperature was then held for 4 min. The instrument was operated in the electron ionization mode (EI) and the electron energy was 70eV. The samples were analysed in full scan mode, monitoring *m/z* 45 to *m/z* 450 by a mass selective detector.

2.4.2. HPLC/MS-MS analysis

Analysis and quantification PFOA and PFOS were carried out by using a high performance liquid chromatography/mass spectrometry (HPLC/MS-MS) employing an API 4000 triple quadropole mass spectrometer (Applied Biosystems) and a Prominence UFLC liquid chromatograph (Shimadzu) equipped with two pumps (LC 20AD), degasser (DGU-20A5), autosampler (SIL-20ACHT) and a column oven (CTO-20AC). Separation was achieved by using a Thermo HyPurity C8 column (50 mm * 3 mm, particle size 5 µm, Dalco Chromtech) at a column temperature of 40 °C. Two mobile phases were used, A and B. The mobile phase A was a solution of 2 mM ammoniumacetate in water. The mobile phase B consisted of 2 mM ammoniumacetate in methanol. The flow rate was set at 0.4 mL min^{-1} and a gradient elution were performed; 0-2 min 40% B, 2-8 min a linear increase of B to 95%, 8-10 min isocratic 95% of B, 10-11 min a linear decrease to 40% of B, 11-16 min isocratic of B. The samples were injected at a volume of 10.0 µl respectively and analysed using electrospray ionization (ESI) in negative mode.

2.5 Identification and quantification

For samples analysed using GC/MS only peaks with a signal to noise larger than 10 were considered for identification and quantification. Identification was performed using the mass spectrometry library (MSD ChemStation, Agilent technologies) by comparing the obtained mass spectrum of an unknown peak with the mass spectrum of a substance suggested by the reference library. This search procedure uses a probability-based matching (PBM) algorithm which identifies substances within the reference library database having similar spectra as the spectrum obtained from the unknown compound. How well the spectrum resembles the one suggested by the reference library is measured as a quantity (%), called match quality. For substances for which authentic reference standards were available (e.g. diethyl phthalate, dibutyl phthalate, bis(2-ethylhexyl)phthalate and 2,6-bis(1,1-dimethylethyl)-4-methyl-phenol), identification was performed using both the reference library and retention times. Quantification was performed using relative response factors for substances for which authentic reference standards were available (e.g. diethyl phthalate, dibutyl phthalate, bis(2-ethylhexyl)phthalate and 2,6-bis(1,1-dimethylethyl)-4-methyl-phenol), other substances were quantified as equivalents of the internal standard (Biphenyl). The limit of detection (LOD) and the limit of quantification (LOQ) were determined as three and five times the peak area of the blank at a given retention time, respectively. A compound was considered detected if the peak area (sample peak area – blank peak area) was larger than LOD.

Identification of PFOA (*m/z* 413.0/369.0) and PFOS (*m/z* 498.7/80.0 and *m/z* 498.7/99.0) was performed using multiple reaction monitoring (MRM). For quantification, calibration curves of PFOS and PFOA were created with four standard solutions ranging from 0 to 10 ng ml^{-1}. To each standard solution ^{13}C-PFOA (70 ng) and ^{13}C-PFOS (60 ng) were added as internal standards. For complete identification of PFOS, the peak area ratio between fragment ions *m/z 80.0* and *m/z* 99.0 in each sample had to correspond to the ratios obtained in the standard solutions. The limit of detection (LOD) and the limit of quantification (LOQ) of PFOA and PFOS were determined as three and five times the concentration obtained in the blank, respectively. PFOS was quantified using fragment ion *m/z* 99.0.

3. Results

In **Table 3**, a summary of the substances identified in the sampled materials from shoe number one, two and three after extraction using methanol is presented. Overall, 31 different compounds were identified in the sampled materials and their concentrations are reported as µg/g shoe material in **Table 3.** Please note that the concentrations have been calculated as equivalents of the internal standard (biphenyl) and that the reported levels only show the extractable content obtained. Since the efficiency of the extraction procedure applied has not been evaluated, the result presented in **Table 3** may not be the total chemical content in the sampled materials. Further information regarding the chemicals presented in **Table 3** is given in **Appendix 1.**

As presented in **Figure 2**, the greatest number of compounds was identified in the outsole material of shoe number two, were 13 different compounds were found. A number of compounds were also identified in the midsole material of shoe number three (11) and in the upper of shoe number one (10). In all three shoes, the smallest number of chemicals was identified in the material sampled from the lining.

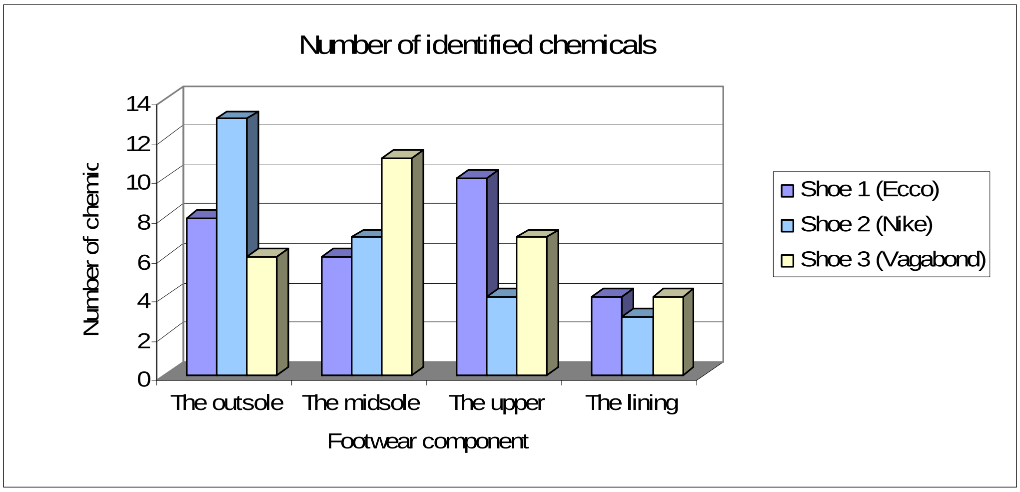
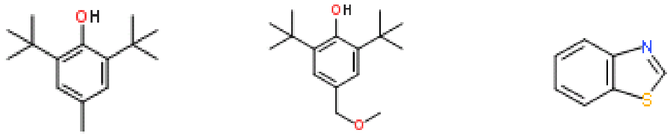


Figure 2. The figure is based on data from **Table 2** and presents the number of compounds identified in different footwear components.

Among the chemicals identified 2,6-bis(1,1-dimethylethyl)-4-methyl-phenol (CAS:128-37-0) was found to be the most abundant according to **Table 2**. This compound was found in all samples, except in the upper and the lining material of shoe number two and in the outsole of shoe number three. In addition, 2,6-bis(1,1-dimethylethyl)-4-(methoxymethyl)-phenol (CAS: 87-97-8) and benzothiazole (CAS: 95-16-9) were identified more or less in all samples as well.



CAS: 128-37-0 CAS: 87-97-8 CAS: 95-16-9

Figure 3. Chemical structures of the most abundant chemicals identified.

3.1. Chemicals identified in the outsoles

The greatest number of compounds was identified in shoe number two (13), closely followed by shoe number one (8) and three (6) as presented in **Figure 2**. The structures of all compounds identified are shown in **Appendix 1.** 2,6-bis(1,1-dimethylethyl)-4-(methoxymethyl)-phenol (CAS: 87-97-8), 2-(1-phenylethyl)-phenol (CAS: 4237-44-9) and benzothiazole (CAS: 95-16-9) were identified in all three shoes (**Table 3**). In shoe number one and two, the concentration of 2,6-bis(1,1-dimethylethyl)-4-methyl-phenol (CAS: 128-37-09) was 5.8×10^2 µg/g material and 1.2×10^4 µg/g material, respectively.

3.2. Chemicals identified in the midsoles

As given in **Table 3**, only 2,6-bis(1,1-dimethylethyl)-4-methyl-phenol (CAS:128-37-0) and 2,6-bis(1,1-dimethylethyl)-4-(methoxymethyl)-phenol (CAS: 87-97-8) were identified in the midsoles of all three shoes. The concentration of 2,6-bis(1,1-dimethylethyl)-4-methyl-phenol (CAS: 128-37-0) in shoe number two was much higher (6.6×10^3 µg/g material) than the levels obtained in shoe number one and three (77 and 65 µg/g, respectively). The highest concentration of 2,6-bis(1,1-dimethylethyl)-4-(methoxymethyl)-phenol (CAS: 87-97-8) was found in shoe number one (7.2 µg/g material), followed by shoe number two (1.4 µg/g material) and shoe number three (0.63 µg/g material). In addition, shoe number two was found to contain relatively high levels (90 µg/g material) of acetophenone (CAS: 98-86-2). This compound was also found in the midsole of shoe number one at a level of 10 µg/g material

3.3 Chemicals identified in uppers

The greatest number of compounds was identified in the upper material in shoe number one. In this material 10 different compounds was identified, whilst only seven and four compounds were identified in shoe number three and two, respectively (**Figure 2**). According to **Table 3.** 2,6-bis(1,1-dimethylethyl)-4-methyl-phenol (CAS:128-37-0) was found in highest concentration (1.4×10^3 µg/g material), followed by acetophenone (CAS:98-86-2) and diethyl phthalate (CAS: 84-66-2) at 14 and 11 µg/g material respectively, in shoe number one. In shoe number two, acetophenone (CAS:98-86-2), dimethyl adipate (CAS: 627-93-0), 1,4-dimethyl ester 1,4-benzenedicarboxylic acid (CAS: 120-61-6) and (4-chlorophenyl)phenyl-methanone (CAS: 134-85-0) were identified at low levels. However, in shoe number three

2,6-bis(1,1-dimethylethyl)-4-methyl-phenol (CAS:128-37-0), was found at 56 µg/g material followed by 2-(thiocyanomethylthio) benzothiazole (CAS: 21564-17-0) detected at a concentration of 17 µg/g material.

3.4. Chemicals identified in lining materials

As presented in **Figure 2**, four different compounds were identified in the lining material of shoe number one. 2,6-bis(1,1-dimethylethyl)-4-methyl-phenol (CAS:128-37-0) was found in highest concentration (2.3×10^2 µg/g material), followed by 2,6-bis(1,1-dimethylethyl)-4-(methoxymethyl)-phenol (CAS: 87-97-8) at 18 µg/g material (**Table 3**). In shoe number two, three compounds were identified and 1,4-dimethyl ester 1,4-benzenedicarboxylic acid (CAS: 120-61-6) was found in highest concentration (21 µg/g material). In shoe number three, four compounds were identified. 2,6-bis(1,1-dimethylethyl)-4-methyl-phenol (CAS:128-37-0) was found at 42 µg/g material, followed by bis(2-ethylhexyl) phthalate (CAS: 117-81-7) at 3.4 µg/g material, 2,2',5,5'-tetramethyl-1,1'-biphenyl (CAS: 3075-84-1) at 0.88 µg/g material and benzothiazole (CAS: 95-16-9) at 0.79 µg/g material according to **Table 3**.

3.5. Chemicals identified in the water leachates

In **Table 4**, a complete summary of the chemicals identified after soaking extraction of outsole material using synthetic brackish water are reported. The concentrations are presented as ng/ml and µg/g material. Please note that substances which were identified only in the water leachate and not in the outsole material after extraction using methanol are written in *italic*. Further information regarding the compounds presented in **Table 4** can be found in **Appendix 1.**

In the three water leachates eight different compounds were found. Benzothiazole (CAS: 95-16-9), 2,6-bis(1,1-dimethylethyl)-4-methyl-phenol (CAS:128-37-0) and diethyl phthalate (CAS: 84-66-2) were identified in all three samples. However, the concentration of diethyl phthalate (CAS: 84-66-2) from shoe number three was below the limit of quantification. Hence, diethyl phthalate was only identified (not quantified) in this sample. Benzothiazole (CAS: 95-16-9) and 2,6-bis(1,1-dimethylethyl)-4-methyl-phenol (CAS: 128-37-0) were found at highest concentration in the water leachate obtained from shoe number two (19 ng/ml and 16 ng/ml, respectively). In the samples from shoe number two and three, 2-(methylthio)benzothiazole (CAS: 615-22-5) were identified as well. In addition triallyl isocyanurate (CAS: 1025-15-6) and 1,6-dimethyl-4-(1-methylethyl)-naphthalene (CAS:483-78-3) were identified in the sample from shoe number one. In the water leachate from shoe number two, 1,6-dimethyl-4-(1-methylethyl)-naphthalene (CAS:483-78-3) was identified along with 2(3H)-benzothiazolethione (CAS:149-30-4) In the sample from shoe number three, 2-(1-phenylethyl)-phenol (CAS:4237-44-9) was identified.

Table 3. Presents a summary of chemicals identified in materials from three different shoes. The table is based on data given in **Appendix 2**. The materials were sampled from the outsole, the midsole, the upper and the lining of each shoe. Please note that the concentrations are reported as (µg/g material). Substances which were identified but at levels below the limit of quantification are denoted as < LOQ.

	Substance / Sample	Acetophenone	Dimethyl glutarate	Azulene	Dimethyl adipate	Benzothiazole	2,6-di-*tert*-butyl-*para*-benzoquinone	2,6-bis(1,1-dimethylethyl)-4-methyl-phenol	1,4-dimethyl ester 1,4-benzenedicarboxylic acid	Diethyl phthalate	2-(methylthio)-benzothiazole	Tributyl phosphate	Triallyl isocyanurate	Azobenzene	1,2,3,4-tetrahydro-9,10-dimethyl-anthracene	2,6-bis(1,1-dimethylethyl)-4-(methoxymethyl)-phenol	1,1'-(1-butenylidene)bis-benzene
		98-86-2	**1119-40-0**	**275-51-4**	**627-93-0**	**95-16-9**	**719-22-2**	**128-37-0**	**120-61-6**	**84-66-2**	**615-22-5**	**126-73-8**	**1025-15-6**	**103-33-3**	**94573-50-9**	**87-97-8**	**1726-14-3**
Shoe 1 	**The outsole**					6.9		5.8E2					2.6			26	
	The midsole	10						77					5.8			7.2	
	The upper	14				0.55	0.60	1.4E3		11					0.83	9.0	
	The lining							2.3E2		7.8						18	
Shoe 2 	**The outsole**	12			3.2	8.0		1.2E4								1.6	
	The midsole	90	1.4		0.56			6.6E3				1.7				1.4	
	The upper	6.2			7.5				2.5								
	The lining	6.2			6.5				21								
Shoe 3 	**The outsole**					22					0.56					1.3	
	The midsole			0.45		13		65			0.65					0.63	0.56
	The upper					3.6		56			0.38			0.66			
	The lining					0.79		42									

Table 3 continues. The table presents a summary of chemicals identified in materials from three different shoes. The table is based on data given in **Appendix 2**. The materials were sampled from the outsole, the midsole, the upper and the lining of each shoe. Please note that the concentrations are reported as (µg/g material). Substances which were identified but at levels below the limit of quantification are denoted as < LOQ.

		2,2',5,5'-tetramethyl-1,1'-biphenyl	1,2,3-trimethyl-4-(1E)-1-propen-1-yl-naphthalene	2-(1-phenylethyl)-phenol	3,5-bis(1,1-dimethylethyl)-4-hydroxy-benzealdehyde	(4-chlorophenyl)phenyl-methanone	1,1'-(3-methyl-1-propene-1,3-diyl)bis-benzene	Diisobutyl phthalate	Dibutyl phthalate	2-(thiocyanomethylthio) benzothiazole	1-methyl-7-(1-methylethyl)-phenanthrene	1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)-(1R-4aS,10aR)-1-phenanthrenecarboxaldehyde	1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)-, methyl ester, (1R,4aS,10aR)-1-phenanthrene	2,4-bis(1-phenylethyl)-phenol	bis(2-ethylhexyl) phthalate	Perfluorooctanoic acid (PFOA)
	Substance / **Sample**	**3075-84-1**	**26137-53-1**	**4237-44-9**	**1620-98-0**	**134-85-0**	**7614-93-9**	**84-69-5**	**84-74-2**	**21564-17-0**	**483-65-8**	**13601-88-2**	**1235-74-1**	**2769-94-0**	**117-81-7**	**335-67-1**
Shoe 1 	**The outsole**			77			4.1	17						62		
	The midsole				1.4			< LOQ								
	The upper	2.0											3.9			0.020
	The lining				0.88											
Shoe 2 	**The outsole**	1.1		16	3.5						2.4	4.1	7.3		5.5	0.014
	The midsole	1.6														
	The upper					1.8										
	The lining															
Shoe 3 	**The outsole**			1.3E2			9.0							10		
	The midsole			1.3E2			25		<LOQ				5.0	3.6E2		
	The upper		0.70		1.2					17						
	The lining	0.88													3.4	

Table 4. Presents a summary of chemicals identified after soaking extraction of outsole material from each shoe using synthetic brackish water. The table is based on data given in **Appendix 3**. The concentrations are reported as ng/ml and µg/g material, substances which were identified but at levels below the limit of quantification are denoted as <LOQ. Please note that substances which were identified only in the water leachate and not in the outsole material after extraction using methanol are written in *italic*.

	Benzothiazole	2,6-bis(1,1-dimethylethyl)-4-methyl-phenol	Diethyl phthalate	2-(methylthio)benzothiazole	Triallyl isocyanurate	2-(1-phenylethyl)-phenol	1,6-dimethyl-4-(1-methylethyl)-naphthalene	2(3H)-benzothiazolethione
Substance / **Sample**	**95-16-9**	**128-37-0**	**84-66-2**	**615-22-5**	**1025-15-6**	**4237-44-9**	**483-78-3**	**149-30-4**
The water leachate (shoe 1) 	1.6 ng/ml 1.5 µg/g material	7.3 ng/ml 6.9 µg/g material	*0.75 ng/ml* *0.70 µg/g material*		1.1 ng/ml 1.0 µg/g material		*5.3 ng/ml* *5.0 µg/g material*	
The water leachate (shoe 2) 	19 ng/ml 16 µg/g material	16 ng/ml 13 µg/g material	*0.49 ng/ml* *0.41 µg/gmaterial*	*1.1 ng/ml* *0.93 µg/g material*			*0.85 ng/ml* *0.72 µg/g material*	*0.68 ng/ml* *0.57 µg/g material*
The water leachate (shoe 3) 	11 ng/ml 8.9 µg/g material	*3.7 ng/ml* *3.1 µg/g material*	*<LOQ*	3.9 ng/ml 3.2 µg/g material		19 ng/ml 16 µg/g material		

4. Discussion

This study has shown how common articles such as footwear, can contain a great number of extractable organic chemicals. In this study 31 compounds were identified in footwear materials at levels of parts per million (ppm). The sampled materials were subjected to soaking extraction using methanol as solvent prior to analysis. The efficiency of this extraction procedure has not been evaluated and the levels reported should therefore be viewed cautiously. Nevertheless, since the same method has been applied on all samples, the results presented give a comparative view of the concentration of chemicals obtained in the sampled materials. Soaking extraction using dichloromethane was carried out as well but resulted in extensive extraction of polymers from the sampled materials, causing a great background noise which disabled identification. Hence, extraction using methanol was preferred. Derivatization (acetylation) did not result in any additional compounds being identified and therefore derivatization was not included in the final preparation and analysis of the samples. The majority of all compounds reported in this study were identified using solely the mass spectrometry library, only diethyl phthalate, dibutyl phthalate, bis(2-ethylhexyl)phthalate, 2,6-bis(1,1-dimethylethyl)-4-methyl-phenol) and PFOA were identified with help of authentic reference standards. Hence, the accuracy of the identification can be discussed. Although this study has its shortcomings, the results presented give an apprehension of the chemical content in common footwear.

4.1 Chemical content in shoes

In this study both plasticizers, antioxidants, solvents, vulcanization agents, surfactants, flame retardants, oxidants and biocides were identified in the sampled materials. Among the compounds identified, 11 substances listed on the 2007 OECD list of high production volume chemicals were found. Hence, these compounds are produced or imported at levels greater than 1,000 tonnes/year in at least one OECD member country [12]. As presented in **Figure 2**, the greatest number of chemicals (13) was identified in the outsole material of shoe number two, a material composed of carbonrubber [10]. In general, the greatest number of chemicals was identified in either the outsole or midsole material of each shoe. Hence, rubbers seem to contain a variety of chemicals. However, in shoe number one the greatest number of compounds was obtained in the upper, where 10 different compounds were identified. This material was composed of both synthetic materials and synthetic fibres including a GoreTex lining [9]. In addition, seven compounds were identified in the leather material of shoe number three as well. The number of chemicals identified in materials sampled from the lining in each shoe was considerably fewer.

Among the chemicals identified, 2,6-bis(1,1-dimethylethyl)-4-methyl-phenol was found to be the most abundant. This chemical, used as an antioxidant for synthetic rubbers, plastics and oils [13] and regarded as a high production volume chemical [12], was identified in almost all samples. The highest concentrations of 2,6-bis(1,1-dimethylethyl)-4-methyl-phenol was obtained in the outsole and midsole of shoe number two. Other chemicals found in more or less all samples, were 2,6-bis(1,1-dimethylethyl)-4-(methoxymethyl)-phenol and benzothiazole. 2,6-bis(1,1-dimethylethyl)-4-(methoxymethyl)-phenol is structurally similar to the antioxidant 2,6-bis(1,1-dimethylethyl)-4-methyl-phenol, but its area of use is unknown. The highest concentration of 2,6-bis(1,1-dimethylethyl)-4-(methoxymethyl)-phenol was found in the outsole of shoe number one, followed by the upper material in shoe number one. The highest concentration of benzothiazole was obtained in the outsole and midsole material in shoe number three. This result is in agreement with benzothiazole being commonly used as a vulcanization agent in the production of rubber [14]. Benzothiazole is a high production volume chemical, hence are produced or imported at levels greater than 1,000 tonnes/year in at least one OECD member country [12].

According to the results, 2,6-bis(1,1-dimethylethyl)-4-(methoxymethyl)-phenol, 2-(1-phenylethyl)-phenol and benzothiazole seems to be common constituents in footwear outsoles. All three compounds were identified in materials sampled from the outsole of each shoe. 2,6-bis(1,1-dimethylethyl)-4-(methoxymethyl)-phenol was also found in the midsole in all shoes along with the antioxidant 2,6-bis(1,1-dimethylethyl)-4-methyl-phenol. These materials consisted of different types of rubbers such as EVA (polymer composed of ethyl vinyl acetate), SBR (polymer composed of styrene and 1,4-butadiene or 1,2-butadiene), natural- and synthetic rubber and carbonrubber [9-11] and can be thought to represent materials commonly used in footwear outsoles.

As presented in **Figure 2**, a great number of different compounds were identified in the upper of shoe number one and three as well. The upper of shoe number one consisted of synthetic material and synthetic fibre including a GoreTex lining [9] whilst the upper of shoe number three was composed of leather [11] In shoe number one, 2,6-bis(1,1-dimethylethyl)-4-methyl-phenol was found in highest concentration followed by acetophenone and diethyl phthalate. Acetophenone is a high production volume chemical [12] and used as solvent in resins and plastics whilst diethyl phthalate is utilized as a plasticizer, wetting agent, dye carrier and as a solvent i resins [13]. In shoe number three, 2,6-bis(1,1-dimethylethyl)-4-methyl-phenol and 2-(thiocyanomethylthio)benzothiazole were found to be the most abundant chemicals in the upper. The later has been used globally as a biocide in the leather industry for more or less 20 years [14]. In the upper of shoe number two, consisting of polyester and polyamide fibre, only four different compounds were identified. In general, the smallest number of compounds was identified in the materials composed of textile in this study.

4.2 Potentially hazardous substances

Among the compounds identified in the sampled materials, some potentially harmful substances were found. For example were, tributyl phosphate and azobenzene, both classified as carcinogens identified at low levels (ppm).

Tributyl phosphate is used as a plasticizer, solvent, flame retardant and as defoamer in textile industries [13]. This compound was found in the midsole of shoe number two. Tributyl phosphate is classified as a carcinogen, category 3 with the risk phrase R40 (limited evidence of a carcinogenic effect). In the leather material sampled from shoe number three, azobenzene was identified. Azobenzene is classified as a carcinogen, category 2 and mutagen, category 3 with risk phrases R45 (may cause cancer) and R68 (Possible risk of irreversible effects). In addition, azobenzene is regarded as "very toxic to aquatic organisms" and "may cause long-term adverse effects in the aquatic environment" (risk phrase R50/53) as well [15] The substance is included in annex XVII in the European chemical regulation. Hence, the manufacture and use of azobenzene is restricted and the chemical should not be used in substances and preparations placed on the market for the general public [16]. Furthermore, was the biocide 2-(thiocyanomethylthio)benzothiazole identified in the upper of shoe number three. This compound is classified as "very toxic to aquatic organisms" and to "may cause long-term adverse effects in the environment" (risk phrase R50/53) [15].

In addition to the hazardous substance already mentioned, diisobutyl phthalate, dibutyl phthalate and bis(2-etyhylhexyl)phthalate were identified as well. These three substances are included on the candidate list of authorization [17] Hence, these chemicals are considered to be substances of very high concern (SVHCs) and by including them on the candidate list the use of these compounds are subjected to authorization under the REACH regulation [16].

Diisobutyl phthalate is a high production volume chemical [12] and was only recently (2010-01-13) included on the candidate list of authorization [17]. Diisobutyl phthalate is classified as toxic for reproduction, category 2 and 3; R61 (may cause harm to the unborn child) and R62 (possible risk of impaired fertility) [18]. Diisobutyl phthalate was identified in both the outsole and midsole of shoe number one. However, the concentration measured in the midsole was below the limit of quantification. Hence, diisobutyl was only identified (not quantified) in this material. Diisobutyl phthalate, dibutyl phthalate and di(2-ethylhexyl)phthalate are used as a plasticizers, additives used to increase the flexibility or plasticity in plastics [13]. Dibutyl phthalate is classified as toxic for reproduction, category 2 and 3; R61 (may cause harm to the unborn child), R62 (possible risk of impaired fertility) and R50 (very toxic to aquatic organisms) whilst bis(2-ethylhexyl) phthalate is classified as toxic for reproduction, category 2; R60 (may impair fertility) and R61 (may cause harm to the unborn child [15]. Dibutyl phthalate was only found in the midsole material of shoe number three. However, the concentration of dibutyl phthalate was below the limit of quantification. Hence, this compound was only identified in this material. Bis(2-ethylhexyl) phthalate on the other hand, was identified in both the outsole material of shoe number two and the lining material of shoe number three. Bis(2-ethylhexyl)phthalate is a high production volume chemical, hence is produced or imported at levels greater than 1,000 tonnes/year in at least one OECD member country [12].

According to article 7 in the European chemical regulation (REACH), manufacturers and importers of articles are required to notify the European Chemical Agency if an article contains a substance of very high concern (SVHCs) included on the candidate list. This requirement applies when the substance is in concentrations greater than 0.1% (w/w) and if the substance is used at more than one tonne per year per manufacturer and importer. Furthermore is the producer of such an article, required to pass information regarding the chemical content of SVHCs on to recipient of the article according to article 33 in REACH [16]. However, the level of diisobutyl phthalate was 17 ppm (w/w) in the outsole of shoe number one and the levels of bis(2-etyhylhexyl)phthalate in the outsole of shoe number two and in the lining material from shoe number three was 5.5 ppm (w/w) and 3.4 ppm (w/w), respectively. Hence, the levels reported in this study were approximately 100-1000 times lower than the limit stated for which requirements are put on manufacturers and importers according to the European chemical regulation.

4.3 Chemicals identified in the water leachates

When soaking extraction of outsole material using synthetic brackish water was performed, as an attempt to model weathering and leaching in the environment, eight different compounds were identified in the three water samples at levels of parts per million. In **Table 4**, the compounds identified in the three water samples are presented. Substances which were not identified in outsole materials after extraction using methanol are written in *italic*. Further information regarding the chemicals identified is given in **Appendix 1**.

In general, the number of compounds obtained in the water leachates was lower than the number of compounds identified the outsole material from each shoe, respectively. Hence the result shows that not all organic compounds seem able to be released under environmental conditions throughout leaching. However, as noticed some compounds identified in the water leachates were not found in the outsole materials after extraction using methanol or identified at higher concentrations in the water samples. Since soaking extraction with methanol is expected to be a harsher extraction procedure compared to water leaching, this result is diverging. Although it is hard to compare the two extraction procedures used, the deviating result might be explained by the limit of detection being in general much lower in the water leachates compared to the samples obtained after extraction using methanol. Hence, the background noise might have disabled identification of some substances present only at low concentrations in the methanol samples.

As mentioned in the introduction, the water leachates were used to evaluate the toxicity of footwear outsoles. The toxicity tests were carried out at the Department of Applied Environmental Science (ITM) by Ellen Kahn as a part of her diploma work. Both larval development test and growth inhibition tests were performed using *Nitocra spinipes* and *Ceramium tenuicorne*. According to the results reported a significant decrease in larval development could be observed in all three water samples. In the water leachates obtained from shoe number two and three, a decreased larval development was observed at the lowest concentrations tested, which corresponded to 148 mg shoe material and 151 mg shoe material per litre water, respectively. Whilst in shoe number one, a significant result was observed only at the highest concentration, which corresponded to 1.07 g shoe material/litre. In shoe number two and three, a significant increase in mortality of *Nitocra spinipes* was observed as well [19]. Since the levels of organic compounds identified in the water leachates were low (levels of parts per million), organic compounds are probably not causing the toxic effects observed. For comparison, aquatic toxicity data for a few of the compounds identified in the water samples is given in **Table 5.** Please note that toxicity data for triallyl isocyanurate, 2-(1-phenylethyl)-phenol, 1,6-dimethyl-4-(1-methylethyl)-naphthalene and 2(3H)-benzothiazolethione which were also identified in the water, is lacking. As noticed the effect concentrations given are approximately 1000 times greater than the levels identified in the water samples. Hence, the levels of organic compounds in the water leachates are not expected to be toxic based on this information.

Table 5. Toxicity data for some of the chemicals identified in the water leachates.

Substance	CAS	Toxicity data	References
Benzothiazole	95-16-9	EC50: 24.6 mg/l/48 hr EC50: 54.9 mg/l/7 days (*Ceriodaphnia dubia)*	[14]
2,6-bis(1,1-dimethylethyl)- 4-methyl-phenol	128-37-0	EC50: 1.44 mg/l/48 hr (*Daphnia pulex*)	[20]
Diethyl phthalate	84-66-2	LC50: 74.0 mg/l/96 hr (64.0-86.0 mg/l) *Nitocra spinipes*	[21]
2-(methylthio)benzothiazole	615-22-5	EC50: 4.19 mg/l/48 hr (3.52-5.09 mg/l) (*Ceriodaphnia dubia)*	[14]

In the report presented by Ellen Kahn it was concluded that the toxicity of the water leachates probably is due to inorganic compounds (e.g. Zinc). After analysing the water samples with regard of inorganic compounds they found that both the samples from shoe number one, two and three contained high concentrations of zinc (118, 1780 and 2520 µg/l, respectively) [19]. Zinc oxide is used as an activating agent in the vulcanisation of styrene-butadiene rubber

(SBR), natural rubber and butadiene rubber [8]. Zinc oxide is classified as “very toxic to aquatic organisms” and to “may cause long-term adverse effects in the aquatic environment” (risk phrase R50/53) [15]. According to Ellen Kahn the levels of zinc were so high that they may explain the toxic effects observed [19].

5. Conclusions

This study has shown how a common article such as footwear can contain a large number of different compounds. Among the chemicals identified, plasticizers, antioxidants, solvents, vulcanization agents, surfactants, fire retardants, oxidants and biocides were found at ppm levels. Eleven compounds were found to be high production volume chemicals. Hence, they are produced or imported at levels greater than 1,000 tonnes/year in at least one OECD member country [12]. In general, the greatest number of chemicals were obtained in either the outsole or the midsole of each shoe (except in shoe number one were the greatest number of compounds were found in the upper).The most abundant chemical identified in the sampled materials was 2,6-bis(1,1-dimethylethyl)-4-methyl-phenol followed by 2,6-bis(1,1-dimethylethyl)-4-(methoxymethyl)-phenol and benzothiazole. In addition, six compounds classified as either toxic to aquatic organisms, carcinogenic or toxic for reproduction were found. Among these were diisobutyl phthalate, dibutyl phthalate and bis(2-etyhylhexyl)phthalate found to be included on the candidate list for authorization [17]. The levels obtained in this study were found to be approximately 100-1000 times lower than the limit stated in the European chemical regulation [16], for which requirements are put on manufacturers and importers. Not all organic compounds identified in this study seem able to be released under environmental conditions. When soaking extraction using synthetic brackish water was performed, as an attempt to model leaching in the environment only eight different compounds were identified in the water samples. The number of compounds was less than the number obtained in the outsole material after extraction using methanol. Since the concentration of organic chemicals obtained in the water leachates were low (levels of ppm), their potential contribution to the toxic effects observed by Ellen Kahn is expected to be minor. Instead inorganic compounds (e.g zinc) were pointed out as the probable cause [19].

Hopefully, this study has provided some further information regarding the organic chemical content in footwear. As mentioned earlier, chemical emission from articles through consumption, disposal, recycle and use, has been pointed out to be of increasing relevance [1]. Even though the levels of organic chemicals identified in this study were found to be low, the great number of different chemicals identified in the sampled materials raises the question about the widespread use of chemicals in articles.

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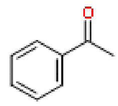
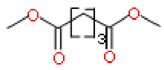
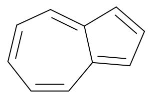
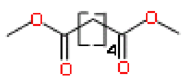
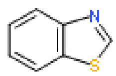
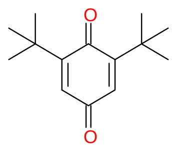
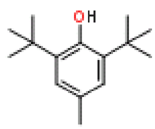
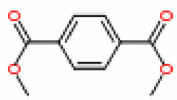
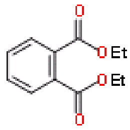
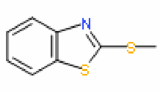
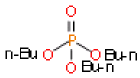
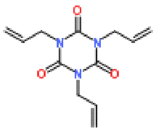
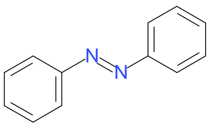
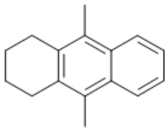
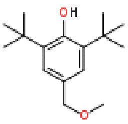
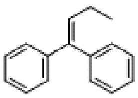
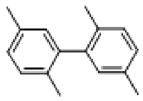
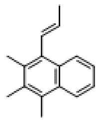
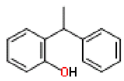
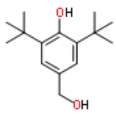
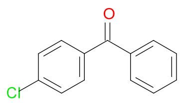
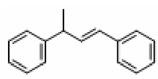
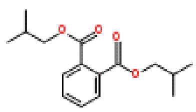
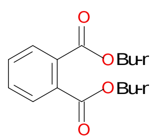
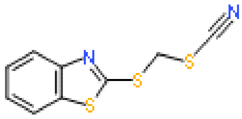
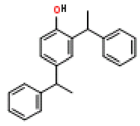
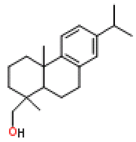
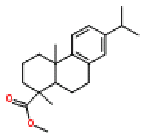
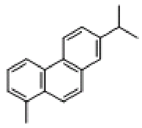
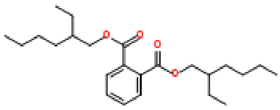
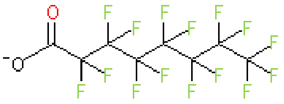
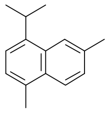
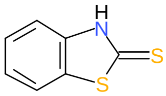
Appendix 1

Substance	CAS	Structure	Information
Acetophenone IUPAC name: 1-phenyl- ethanone	98-86-2		Acetophenone is used as a solvent in resins and plastics [13] and is included on the 2007 OECD list of high production volume chemicals. Hence, acetophenone is produced or imported at levels greater than 1000 tonnes/year in at least one OECD member country [12].
Dimethyl glutarate IUPAC name: 1,5-dimethyl ester pentanedioic acid	1119-40-0		Dimethyl glutarate is used as chemical intermediate for polyamide resins and polyester resins used in coatings [13] and is included on the 2007 OECD list of high production volume chemicals [12]
IUPAC name: Azulene	275-51-4		
Dimethyl adipate IUPAC name: 1,6-dimethyl ester, hexanedioic acid	627-93-0		Dimethyl adipate is used as a plasticizer for cellulose type of resins and as solvent in finish removers [13]. The substance is included on the OECD list of high production volume chemicals. Hence Dimethyl adipate is used or imported at levels greater than 1000 tonnes/year in at least one OECD member country [12].
IUPAC name: Benzothiazole	95-16-9		Benzothiazole is commonly used as a vulcanization agent in rubber manufacturing industries [14] but the substance can also be found as component in cyanine dyes or used as an antimicrobial agent [13]. Benzothiazole is regarded as a high production volume chemical [12].
2,6-di-*tert*-butyl-*para*- benzoquinone IUPAC name: 2,6-bis(1,1-dimethylethyl)- 2,5-cyclohexadiene-1,4-dione	719-22-2		2,6-di-*tert*-butyl-*para*-benzoquinone is used as an oxidant and polymerization catalyst. The environmental source of this compound may also result from degradation of 2,6-di-*tert*-butyl-phenol, an antioxidant with widespread use [13].
IUPAC name: 2,6-bis(1,1-dimethylethyl)-4-methyl-phenol	128-37-0		2,6-bis(1,1-dimethylethyl)-4-methyl-Phenol is used as an antioxidant for synthetic rubbers, plastics, oils etc. The substance is also used as a antiskinning agent in paints and inks [13]. The subtance is included on the 2007 OECD list of high production volume chemicals. Hence, is produced or imported at levels greater than 1000 tonnes/year in at least one OECD member country [12].
IUPAC name: 1,4-dimethyl ester 1,4-benzenedicarboxylic acid	120-61-6		1,4-dimethyl ester 1,4-benzenedicarboxylic acid is a industrial intermediate in production of polyethylene terephthalate (PET) and other types of polyester resins [13]. The substance is included on the 2007 OECD list of high production volume chemicals [12].

Diethyl phthalate IUPAC name: 1,2-diethyl ester 1,2-benzenedicarboxylic acid	84-66-2		Diethyl phthalate is used as a plasticizer, weeting agent, dye carrier and as solvent in resins. Former use of diethyl phthalate as an insect repellant has caused direct release of this compound to the environment [13]. Diethyl phthlate is included on the 2007 OECD list of high production volume chemicals. Hence, diethyl phthalate is produced or imported at levels greater than 1000 tonnes/year in at least one OECD member country [12].
IUPAC name: 2-(methylthio)benzothiazole	615-22-5		2-(methylthio)benzothiazole is a degradation product of the biocide 2-(thiocyanomethylthio) benzothiazole and the rubber additive 2-mercaptobenzothiazole [14].
Tributyl phosphate IUPAC name: Phosphoric acid tributyl ester	126-73-8		Tributyl phosphate is used as a plasticizer in plastics, vinyl resins and cellulose esters etc. It is also used as solvent, fire retardant and as defoamer in textile and paper industries[13]. Hence, tributyl phosphate is a high production volume chemical [12]. Tributyl phosphate is classified as: carcinogen, category 3 Risk phrase: R40 (Limited evidence of a carcinogenic effect) [15].
Triallyl isocyanurate IUPAC name: 1,3,5-tri-2-propenyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione	1025-15-6		
Azobenzene IUPAC name: 1,2-diphenyl-diazene	103-33-3		Azobenzene is classified as: carcinogen, category 2 and mutagen, category 3 and dangerous for the environment: Risk phrases: R45 (may cause cancer) R68 (Possible risk of irreversible effects), R50/53 (very toxic to aquatic organisms, may cause long term effects in the aquatic environment) [15].
IUPAC name: 1,2,3,4-tetrahydro-9,10-dimethyl-anthracene	94573-50-9		
IUPAC name: 2,6-bis(1,1-dimethylethyl)-4-(methoxymethyl)-phenol	87-97-8		
IUPAC name: 1,1'-(1-butenylidene) bis-benzene	1726-14-3		

IUPAC name: 2,2',5,5'-tetramethyl-1,1'-biphenyl	3075-84-1		
IUPAC name: 1,2,3-trimethyl-4-(1E)-1-propen-1-yl-naphthalene	26137-53-1		
IUPAC name: 2-(1-phenylethyl)-phenol	4237-44-9		
IUPAC name: 3,5-bis(1,1-dimethylethyl)-4-hydroxy-benzaldehyde	1620-98-0		
IUPAC name: (4-chlorophenyl)phenyl- methanone	134-85-0		
IUPAC name: 1,1'-(3-methyl-1-propene-1,3-diyl)bis-benzene	7614-93-9		
Diisobutyl phthalate IUPAC name: 1,2-bis(2-methylpropyl) ester 1,2-benzenedicarboxylic acid	84-69-5		The major use of diisobutyl phthalate is as a plasticizer, an additive used to increase the flexability or plasticity in plastics [13]. Diisobutyl is regarded as a high production volume chemical. Hence is produced or imported at levels greater than 1000 tonnes/year in at least one OECD member country [12]. The compound is classified as toxic for reproduction, category 2 and 3. With the risk phrases; R61 (may cause harm to the unborn child) and R62 (possible risk of impaired fertility) [18]. Hence this compound is classified as a substance of very high concern and is included on the candidate list for authorisation, REACH [17].
Dibutyl phthalate IUPAC name: 1,2-dibutyl ester 1,2-benzenedicarboxylic acid	84-74-2		Dibutyl phthalate is used as a plasticizer in plastics (PVC) and rubber [8]. The compound is classified as toxic for reproduction category 2 and 3, with risk phrases; R61 (may cause harm to the unborn child), R62 (possible risk of impaired fertility. The substance is also considered harmful to the environment, risk phrase R50 (very toxic to aquatic organisms) [15]. Hence this compound is considered

			to be a substanc e of very high concern and is included on the candidate list for authorization [17]. Dibutyl phthalate is also found on the 2007 OECD list of high production volume chemicals. Hence Dibutyl phthalate is produced or imported at levels greater than 1000 tonnes/year in at least on OECD member country. [12].
2-(thiocyanomethylthio) benzothiazole IUPAC name: (2-benzothiazolylthio) methyl ester thiocyanic acid	21564-17-0		2-(thiocyanomethylthio) benzothiazole has been used more or less in 20 years as a biocide in leather, pulp and paper industries [14]. The substance is classified very toxic to aquatic organisms (risk phrase R50) and to may cause long-term adverse effects in the aquatic environment (risk phrase R53)[15].
IUPAC name: 1-methyl-7-(1-methylethyl)-phenanthrene	483-65-8		
IUPAC name: 1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7- (1-methylethyl)-, (1R,4aS,10aR)-1-phenanthrenecarboxaldehyde	13601-88-2		
IUPAC name: 1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)-, methyl ester, (1R,4aS,10aR)-1-phenanthrene carboxylicacid	1235-74-1		
IUPAC name: 2,4-bis(1-phenylethyl)-phenol	2769-94-0		
bis(2-ethylhexyl) phthalate IUPAC name:1,2-bis(2-ethylhexyl) ester 1,2-Benzene dicarboxylic acid	117-81-7		Bis(2-ethylhexyl) phthalate is as a plasticizer mainly used in poly vinyl chloride resins but is used in other types of resins and synthetic rubbers as well [13]. The compound can also be found in textile materials as a fixing agent [8]. Prior use of bis(2-ethylhexyl) phthlate as an insecticide has resulted in direct release of the substance into the environment [13]. The compound is found on the 2007 OECD list of high production volume chemicals. Hence, Bis(2-ethylhexyl) phthalate is produced or imported at levels greater than 1000 tonnes/year in at least one OECD member country [12]. Bis(2-ethylhexyl) phthalate is classified as toxic for reproduction, category 2 with risk phrases; R60 (may cause impaired fertility) and R61 (may cause harm to the unborn child) [15]. Hence, this substance is regarded as a substance of very high concern and is included on the candidate list for authorization [17].

Perfluorooctanoic acid	335-67-1		Perfluorooctanoic acid is used as a surfactant but can be found in fire fighting applications, greases, polishes, lubricants, paints and adhesives etc [13].
IUPAC: 1,6-dimethyl-4-(1-methylethyl)-naphthalene	483-78-3		
IUPAC: 2(3H)-benzothiazolethione	149-30-4		2(3H)-benzothiazolethione is a high production volume chemical (OECD). The substance is classified as very toxic to aquatic organism, may cause long term adverse effects in the aquatic environment (risk phrase R50-53) [15]. The substance is included on the 2007 OECD list of high production volume chemicals. Hence, the substance is produced or imported at levels greater than 1000 tonnes/year in at least on OECD member country [12].

Appendix 2

Table 1. This table presents a summary of compounds identified in the outsole material sampled from shoe number one. The table presents name, CAS registry number, match quality (%), retention time (min), and concentration (ng/ml) for each substance identified in fraction one and two, respectively. Please note that only compounds with a signal to noise.>10 and a match quality ≥ 85% are presented. Only 0.193 g material was subjected to extraction.

The outsole (shoe 1)			Fraction 2				Fraction 3					
Substance	CAS	Match Quality (%)	Retention time (min)	Concentration (ng/ml)	LOD (ng/ml)	LOQ (ng/ml)	Retention time (min)	Concentration (ng/ml)	LOD (ng/ml)	LOQ (ng/ml)	Concentration total (ng/ml) (contribution from both fractions)	Concentration in the material (µg/g material)
Benzothiazole	95-16-9	94	9.324	66	1.8	2.9	---	---	---	---	66	6.9
2,6-bis(1,1-dimethylethyl)-4-methyl-phenol	128-37-0	94	11.603	5.6E3	2.6	4.3	---	---	---	---	5.6E3	5.8E2
Diethyl phthalate	84-66-2	97	12.348	< LOD	49		---	---	---	---	---	---
Triallyl isocyanurate	1025-15-6	96	12.958	25	0.28	0.47	---	---	---	---	25	2.6
2,6-bis(1,1-dimethylethyl)-4-(methoxymethyl)-phenol	87-97-8	94	13.179	2.5E2	0.16	0.26	---	---	---	---	2.5E2	26
2-(1-phenylethyl)-phenol	4237-44-9	93	13.726	7.5E2	0.92	1.5	---	---	---	---	7.5E2	77
1,1'-(3-methyl-1-propene-1,3-diyl)bis-benzene	7614-93-9	97	14.333	40	1.8	3.1	---	---	---	---	40	4.1
Diisobutyl phthalate	84-69-5	86	15.071	1.7E2	30	50	---	---	---	---	1.7E2	17
Dibutyl phthalate	84-74-2	94	16.226	< LOD	1.8E2	2.9E2	---	---	---	---	---	---
2,4-bis(1-phenylethyl)-phenol	2769-94-0	94	23.665	6.0E2	1.7	2.8	---	---	---	---	6.0E2	62

Table 2. This table presents a summary of compounds identified in the upper material sampled from shoe number one. The table presents name, CAS registry number, match quality (%), retention time (min), and concentration (ng/ml) for each substance identified in fraction one and two, respectively. Please note that only compounds with a signal to noise >10 and a match quality ≥ 85% are presented. Only 0.222 g material was subjected to extraction.

The upper (shoe 1)			**Fraction 2**				**Fraction 3**					
Substance	**CAS**	**Match Quality (%)**	**Retention time (min)**	**Concentration (ng/ml)**	**LOD (ng/ml)**	**LOQ (ng/ml)**	**Retention time (min)**	**Concentration (ng/ml)**	**LOD (ng/ml)**	**LOQ (ng/ml)**	**Concentration total (ng/ml) (contribution from both fractions)**	**Concentration in the material (µg/g material)**
Acetophenone	98-86-2	91	7.572	1.6E2	1.5	2.5	---	---	---	---	1.6E2	14
Benzothiazole	95-16-9	87	9.332	6.1	1.8	2.9	---	---	---	---	6.1	0.55
2,6-di-*tert*-butyl-*para*-benzoquinone	719-22-2	95	11.304	6.7	1.7	2.9	---	---	---	---	6.7	0.60
2,6-bis(1,1-dimethylethyl)-4-methyl-phenol	128-37-0	94	11.604	1.6E4	2.6	4.4	---	---	---	---	1.6E4	1.4E3
Diethyl phthalate	84-66-2	95	12.349	1.3E2	49	82	---	---	---	---	1.3E2	11
1,2,3,4-tetrahydro-9,10-dimethyl-anthracene	94573-50-9	87	13.057	9.2	3.1	5.2	---	---	---	---	9.2	0.83
2,6-bis(1,1-dimethylethyl)-4-(methoxymethyl)-phenol	87-97-8	94	13.182	1.0E2	0.16	0.26	---	---	---	---	1.0E2	9.0
2,2',5,5'-tetramethyl-1,1'-biphenyl	3075-84-1	93	13.279	22	2.1	3.5	---	---	---	---	22	2.0
Dibutyl phthalate	84-74-2	94	16.226	< LOD	1.8E2	2.9E2	---	---	---	---	---	---
1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)-, (1R, 4aS, 10aR)-1-phenanthrenecarboxaldehyde	1235-74-1	93	21.681	44	7.3E-2	0.12	---	---	---	---	44	3.9

Table 3. This table presents a summary of compounds identified in the lining material sampled from shoe number one. The table presents name, CAS registry number, match quality (%), retention time (min), and concentration (ng/ml) for each substance identified in fraction one and two, respectively. Please note that only compounds with a signal to noise >10 and a match quality ≥ 85% are presented. Only 0.184 g material was subjected to extraction.

The lining (shoe 1)			**Fraction 2**				**Fraction 3**					
Substance	**CAS**	**Match Quality (%)**	**Retention time (min)**	**Concentration (ng/ml)**	**LOD (ng/ml)**	**LOQ (ng/ml)**	**Retention time (min)**	**Concentration (ng/ml)**	**LOD (ng/ml)**	**LOQ (ng/ml)**	**Concentration total (ng/ml) (contribution from both fractions)**	**Concentration in the material (µg/g material)**
2,6-bis(1,1-dimethylethyl)-4-methyl-phenol	128-37-0	93	11.603	2.1E3	2.0	3.4	---	---	---	---	2.1E3	2.3E2
Diethyl phthalate	84-66-2	96/98	12.347	< LOQ	38	63	12.351	72	8.0	13	72	7.8
2,6-bis(1,1-dimethylethyl)-4-(methoxymethyl)-phenol	87-97-8	94	13.180	1.6E2	0.12	0.20	---	---	---	---	1.6E2	18
3,5-bis(1,1-dimethylethyl)-4-hydroxy-benzaldehyde	1620-98-0	94	14.070	8.1	0.35	0.59	---	---	---	---	8.1	0.88
Dibutyl phthalate	84-74-2	94/83[a]	16.227	< LOD	1.4E2	2.3E2	16.229	< LOD	1.2E2	2.0E2	---	---

[a] Dibutyl phthalate was identified using an authentic reference standard.

Table 4. This table presents a summary of compounds identified in the midsole material sampled from shoe number one. The table presents the name, CAS registry number, match quality (%), retention time (min), and concentration (ng/ml) for each substance identified in fraction one and two, respectively. Please note that only compounds with peak signal to noise >10 and a match quality ≥ 85% are presented. Only 0.198 g material was subjected to extraction.

The midsole (shoe 1)			Fraction 2				Fraction 3					
Substance	CAS	Match Quality (%)	Retention time (min)	Concentration (ng/ml)	LOD (ng/ml)	LOQ (ng/ml)	Retention time (min)	Concentration (ng/ml)	LOD (ng/ml)	LOQ (ng/ml)	Concentration total extract (ng/ml) (contribution from both fractions)	Concentration in the material (µg/g material)
Acetophenone	98-86-2	90	7.571	1.0E2	1.2	2.0	---	---	---	---	1.0E2	10
2,6-bis(1,1-dimethylethyl)-4-methyl-phenol	128-37-0	95	11.604	7.6E2	2.1	3.5	---	---	---	---	7.6E2	77
Diethyl phthalate	84-66-2	95/59[a]	12.350	< LOD	39	65	12.352	< LOD	8.2	14	---	---
Triallyl isocyanurate	1025-15-6	94/93	12.961	52	0.16	0.26	12.962	5.6	0.23	0.38	58	5.8
2,6-bis(1,1-dimethylethyl)-4-(methoxymethyl)-phenol	87-97-8	94	13.181	71	0.12	0.21	---	---	---	---	71	7.2
3,5-bis(1,1-dimethylethyl)-4-hydroxy-benzaldehyde	1620-98-0	93	14.073	14	0.36	0.60	---	---	---	---	14	1.4
Diisobutyl phthalate	84-69-5	90	15.073	< LOQ	24	40	---	---	---	---	< LOQ	< LOQ
Dibutyl phthalate	84-74-2	94/78[a]	16.229	< LOD	1.4E2	2.3E2	16.228	< LOD	1.2E2	2.1E2	---	---

[a] Diethyl phthalate and Dibutyl phthalate were identified using authentic reference standards.

Table 5. This table presents a summary of compounds identified in the midsole material sampled from shoe number two. The table presents name, CAS registry number, match quality (%), retention time (min), and concentration (ng/ml) for each substance identified in fraction one and two, respectively. Please note that only compounds with peak signal to noise >10 and a match quality ≥ 85% are presented. Only 0.181 g material was subjected to extraction.

The outsole (shoe 2)			**Fraction 2**				**Fraction 3**					
Substance	**CAS**	**Match Quality (%)**	**Retention time (min)**	**Concentration (ng/ml)**	**LOD (ng/ml)**	**LOQ (ng/ml)**	**Retention time (min)**	**Concentration (ng/ml)**	**LOD (ng/ml)**	**LOQ (ng/ml)**	**Concentration total (ng/ml) (contribution from both fractions)**	**Concentration in the material (µg/g material)**
Acetophenone	98-86-2	94	7.572	1.1E2	1.1	1.8	---	---	---	---	1.1E2	12
Dimethyl adipate	627-93-0	91	---	---	---	---	9.190	29	0.75	1.2	29	3.2
Benzothiazole	95-16-9	94	9.322	73	1.3	2.1	---	---	---	---	73	8.0
2,6-bis(1,1-dimethylethyl)-4-methyl-phenol	128-37-0	95	11.608	1.1E5	4.0	6.6	---	---	---	---	1.1E5	1.2E4
Diethyl phthalate	84-66-2	78[a]	---	---	---	---	12.349	< LOD	37	61	---	---
2,6-bis(1,1-dimethylethyl)-4-(methoxymethyl)-phenol	87-97-8	92	---	---	---	---	13.179	14	1.2	2.0	14	1.6
2,2',5,5'-tetramethyl-1,1'-biphenyl	3075-84-1	91	13.280	10	0.85	1.4	---	---	---	---	10	1.1
2-(1-phenylethyl)-phenol	4237-44-9	91	13.726	1.5E2	0.59	0.99	---	---	---	---	1.5E2	16
3,5-bis(1,1-dimethylethyl) -4-hydroxy-benzaldehyde	1620-98-0	93	14.071	32	0.61	1.0	---	---	---	---	32	3.5
Dibutyl phthalate	84-74-2	94/72[a]	16.225	< LOD	3.4E2	5.7E2	16.225	< LOD	51	85	---	---
1-methyl-7-(-methylethyl)-phenanthrene	483-65-8	96	20.123	22	0.31	0.51		---		---	22	2.4
1,2,3,4,4a,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)-, (1R, 4aS, 10aR)-1-phenthrenecarboxaldehyde	13601-88-2	97	20.803	37	0.96	1.6		---		---	37	4.1
1,2,3,4,4a,9,10,10a-octahydro-1,4-dimethyl-7-(1-methylethyl), -methyl ester, (1R,4aS, 10aR)-1-phenanthrenecarboxylicacid	1235-74-1	95	21.682	66	0.56	0.93		---		---	66	7.3
bis(2-ethylhexyl)phtalate	117-81-7	49[a]	24.195	50	1.9	3.1		---		---	50	5.5

[a] Diethyl phthalate, dibutyl phthalate and bis(2-ethylhexyl)phthalate were identified using authentic reference standards

Table 6. This table presents a summary of compounds identified in the upper material sampled from shoe number two . The table presents name, CAS registry number, match quality (%), retention time (min), and concentration (ng/ml) for each substance in fraction one and two, respectively. Please note that only compounds with peak signal to noise >10 and a match quality ≥ 85% are presented. Only 0.252 g material was subjected to extraction.

The upper (shoe 2)			Fraction 2				Fraction 3					
Substance	CAS	Match Quality (%)	Retention time (min)	Concentration (ng/ml)	LOD (ng/ml)	LOQ (ng/ml)	Retention time (min)	Concentration (ng/ml)	LOD (ng/ml)	LOQ (ng/ml)	Concentration total (ng/ml) (contribution from both fractions)	Concentration in the material (µg/g material)
Acetophenone	98-86-2	91	7.570	78	1.2	1.9	---	---	---	---	78	6.2
Dimethyl adipate	627-93-0	91/ 91	9.191	38	0.47	0.79	9.189	57	0.68	1.1	95	7.5
1,4-dimethyl ester-1,4-Benzenedicarboxylic acid	120-61-6	94	11.619	31	0.31	0.52	---	---	---	---	31	2.5
Diethyl phthalate	84-66-2	96	12.353	< LOD	95	1.6E2	---	---	---	---	---	---
(4-chlorophenyl)phenyl-methanone	134-85-0	94	14.805	22	0.77	1.3	---	---	---	---	22	1.8
Dibutyl phthalate	84-74-2	94/50[a]	16.230	< LOD	3.7E2	6.2E2	16.229	< LOD	47	78	---	---

[a] Dibutyl phthalate was identified using an authentic reference standard

Table 7. This table presents a summary of compounds identified in the lining material sampled from shoe number two. The table presents name, CAS registry number, match quality (%), retention time (min), and concentration (ng/ml) for each substance identified in fraction one and two, respectively. Please note that only compounds with peak signal to noise >10 and a match quality ≥ 85% are presented. Only 0.246 g material was subjected to extraction.

The lining (shoe 2)			Fraction 2				Fraction 3					
Substance	CAS	Match Quality (%)	Retention time (min)	Concentration (ng/ml	LOD (ng/ml)	LOQ (ng/ml)	Retention time (min)	Concentration (ng/ml)	LOD (ng/ml)	LOQ (ng/ml)	Concentration total (ng/ml) (contribution from both fractions)	Concentration in the material (µg/g material)
Acetophenone	98-86-2	94	7.571	77	1.3	2.1	---	---	---	---	77	6.2
Dimethyl adipate	627-93-0	91/90	9.192	18	0.52	0.87	9.190	63	0.70	1.2	81	6.5
1,4-dimethyl ester-1,4-Benzenedicarboxylic acid	120-61-6	97	11.615	2.6E2	0.35	0.58	---	---	---	---	2.6E2	21
Diethyl phthalate	84-66-2	86	12.353	< LOD	1.1E2	1.8E2	---	---	---	---	---	---
Dibutyl phthalate	84-74-2	91/78[a]	16.228	< LOD	4.1E2	6.8E2	16.232	< LOD	48	80	---	---

[a] Dibutyl phthalate was identified using an authentic reference standard

Table 8. This table presents a summary of compounds identified in the midsole material sampled from shoe number two. The table presents name, CAS registry number, match quality (%), retention time (min), and concentration (ng/ml) for each substance identified in fraction one and two, respectively. Please note that only compounds with peak signal to noise >10 and a match quality ≥ 85% are presented. Only 0.219 g material was subjected to extraction.

The midsole (shoe 2)			Fraction 2				Fraction 3					
Substance	**CAS**	**Match Quality (%)**	**Retention time (min)**	**Concentration (ng/ml)**	**LOD (ng/ml)**	**LOQ (ng/ml)**	**Retention time (min)**	**Concentration (ng/ml)**	**LOD (ng/ml)**	**LOQ (ng/ml)**	**Concentration total extract (ng/ml) (contribution from both fractions)**	**Concentration in the material (µg/g material)**
Acetophenone	98-86-2	94	7.571	9.8E2	1.0	1.7	---	---	---	---	9.8E2	90
Dimethyl glutarate	1119-40-0	78					8.145	16	1.0	1.7	16	1.4
Dimethyl adipate	627-93-0	86	9.192	6.1	0.41	0.68	---	---	---	---	6.1	0.56
2,6-bis(1,1-dimethylethyl)-4-methyl-phenol	128-37-0	95 / 80[a]	11.606	7.2E4	3.7	6.2	11.605	59	8.1	14	7.2E4	6.6E3
Diethyl phthalate	84-66-2	96	12.348	< LOD	82	1.4E2	---	---	---	---	---	---
Tributyl phosphate	126-73-8	90					12.714	18	0.70	1.2	18	1.7
2,6-bis(1,1-dimethylethyl)-4-(methoxymethyl)-phenol	87-97-8	91	13.180	15	0.37	0.62	---	---	---	---	15	1.4
2,2',5,5'-tetramethyl-1,1'-biphenyl	3075-84-1	93	13.279	17	0.80	1.3	---	---	---	---	17	1.6
Diisobutyl phthalate	84-69-5	86	15.071	< LOD	60	1.0E2	---	---	---	---	---	---
Dibutyl phthalate	84-74-2	94/78[a]	16.226	< LOD	3.2E2	5.4E2	16.224	< LOD	56	94	---	---

[a] 2,6-bis(1,1-dimethylethyl)-4-methyl-phenol and dibutyl phthalate were identified using authentic reference standards

Table 9. This table presents a summary of compounds identified in the outsole material sampled from shoe number three. The table presents name, CAS registry number, match quality (%), retention time (min), and concentration (ng/ml) for each substance identified in fraction one and two, respectively. Please note that only compounds with peak signal to noise >10 and a match quality ≥ 85% are presented. Only 0.221 g material was subjected to extraction.

The outsole (shoe 3)			Fraction 2				Fraction 3					
Substance	**CAS**	**Match Quality (%)**	**Retemtion time (min)**	**Concentration (ng/ml)**	**LOD (ng/ml)**	**LOQ (ng/ml)**	**Retention time (min)**	**Concentration (ng/ml)**	**LOD (ng/ml)**	**LOQ (ng/ml)**	**Concentration total (ng/ml) (contribution from both fractions)**	**Concentration in the material (µg/g material)**
Benzothiazole	95-16-9	91	9.321	2.5E2	0.62	1.0	---	---	---	---	2.5E2	22
Diethyl phthalate	84-66-2	93	12.349	< LOD	2.0E2	3.3E2	---	---	---	---	---	---
2-(methylthio)-benzothiazole	615-22-5	87	12.783	6.1	0.55	0.89	---	---	---	---	6.1	0.56
2,6-bis(1,1-dimethylethyl)-4-(methoxymethyl)-phenol	87-97-8	80	13.180	14	0.39	0.64	---	---	---	---	14	1.3
2-(1-phenylethyl)-phenol	4237-44-9	93	13.726	1.4E3	0.71	1.2	---	---		---	1.4E3	1.3E2
1,1'-(3-methyl-1-propene-1,3-diyl)bis-benzene	7614-93-9	94	14.336	1.0E2	0.31	0.51	---	---	---	---	1.0E2	9.0
Dibutyl phthalate	84-74-2	91/59[a]	16.227	< LOD	9.3E2	1.5E3	16.222	< LOD	59	98	---	---
2,4-bis(1-phenylethyl)-phenol	2769-94-0	94	23.678	1.1E2	1.5	2.5	---	---	---	---	1.1E2	10

[a] Dibutyl phthalate was identified using an authentic reference standard.

Table 10. This table presents a summary of compounds identified in the upper material sampled from shoe number three. The table presents name, CAS registry number, match quality (%), retention time (min), and concentration (ng/ml) for each substance identified in fraction one and two, respectively. Please note that only compounds with peak signal to noise >10 and a match quality ≥ 85% are presented. Only 0.203 g material was subjected to extraction.

The upper (shoe 3)			Fraction 2				Fraction 3					
Substance	CAS	Match Quality (%)	Retention time (min)	Concentration (ng/ml)	LOD (ng/ml)	LOQ (ng/ml)	Retention time (min)	Concentration (ng/ml)	LOD (ng/ml)	LOQ (ng/ml)	Concentration total (ng/ml) (contribution from both fractions)	Concentration in the material (µg/g material)
Benzothiazole	95-16-9	91	9.322	37	0.28	0.47		---	---	---	37	3.6
2,6-bis(1,1-dimethylethyl)-4-methyl-phenol	128-37-0	94	11.602	5.7E2	5.4	9.0		---	---	---	5.7E2	56
Diethyl phthalate	84-66-2	96/90	12.347	< LOD	92	1.5E2	12.350	< LOD	17	29	----	---
2-(methylthio)-benzothiazole	615-22-5	94	12.776	3.8	0.11	0.19		---	---	---	3.8	0.38
Azobenzene	103-33-3	86	12.900	6.7	0.17	0.29		---	---	---	6.7	0.66
1,2,3-trimethyl-4-(1E)-1-propen-1-yl-naphthalene	26137-53-1	87	13.279	7.1	0.69	1.2		---	---	---	7.1	0.70
3,5-di-tert-butyl-4-hydroxybenzaldehyde	1620-98-0	96	14.072	12	1.2E-2	2.1E-2		---	---	---	12	1.2
Dibutyl phthalate	84-74-2	87/72[a]	16.222	< LOD	4.2E2	7.1E2	16.223	< LOD	24	40	----	---
2-(Thiocyanomethylthio) Benzothiazole	21564-17-0	98	19.218	1.7E2	1.4E-2	2.3E-2		---	---	---	1.7E2	17

[a] Dibutyl phthalate was identified using an authentic reference standard

Table 11. This table presents a summary of compounds identified in the lining material sampled from shoe number three. The table presents name, CAS registry number, match quality (%), retention time (min), and concentration (ng/ml) for each substance identified in fraction one and two, respectively. Please note that only compounds with peak signal to noise >10 and a match quality ≥ 85% are presented. Only 0.206 g material was subjected to extraction.

The lining (shoe 3)			Fraction 2				Fraction 3					
Substance	CAS	Match Quality (%)	Retention time (min)	Concentration (ng/ml	LOD (ng/ml)	LOQ (ng/ml)	Retention time (min)	Concentration (ng/ml)	LOD (ng/ml)	LOQ (ng/ml)	Concentration total (ng/ml) (contribution from both fractions)	Concentration in the material (µg/g material)
Benzothiazole	95-16-9	91	9.326	8.2	1.5	2.5	---	---	---	---	8.2	0.79
2,6-bis(1,1-dimethylethyl)-4-methyl-phenol	128-37-0	94	11.604	4.3E2	4.8	8.0	---	---	---	---	4.3E2	42
Diethyl phthalate	84-66-2	93	12.350	< LOD	1.1E2	1.8E2	---	---	---	---	---	---
2,2',5,5'-tetramethyl-1,1'-biphenyl	3075-84-1	95	13.279	9.1	1.0	1.7	---	---	---	---	9.1	0.88
Dibutyl phthalate	84-74-2	94/56[a]	16.225	< LOD	4.1E2	6.8E2	16.222	< LOD	47	78	---	---
bis(2-ethylhexyl) phthalate	117-81-7	47[a]	24.193	35	2.2	3.7	---	---	---	---	35	3.4

[a] Dibutyl phthalate and bis(2-ethylhexyl)phthalate were identified using authentic reference standards

Table 12. This table presents a summary of compounds identified in the midsole material sampled from shoe number three (0.202 g). The table presents name, CAS registry number, match quality (%), retention time (min), and concentration (ng/ml) for each substance identified in fraction one and two, respectively. Please note that only compounds with peak signal to noise >10 and a match quality ≥ 85% are presented. Only 0.202 g material was subjected to extraction.

The midsole (shoe 3)			**Fraction 2**				**Fraction 3**					
Substance	**CAS**	**Match Quality (%)**	**Retention time (min)**	**Concentration (ng/ml)**	**LOD (ng/ml)**	**LOQ (ng/ml)**	**Retention time (min)**	**Concentration (ng/ml)**	**LOD (ng/ml)**	**LOQ (ng/ml)**	**Concentration total (ng/ml) (contribution from both fractions)**	**Concentration in the material (µg/g material)**
Azulene	275-51-4	86	8.921	4.5	0.38	0.64	---	---	---	---	4.5	0.45
Benzothiazole	95-16-9	95	9.321	1.3E2	0.37	0.61					1.3E2	13
2,6-bis(1,1-dimethylethyl)-4-methyl-phenol	128-37-0	97	11.604	6.6E2	7.0	12	---	---	---	---	6.6E2	65
Diethyl phthalate	84-66-2	96/72[a]	12.349	< LOD	1.2E2	2.0E2	12.351	< LOD	26	43	< LOD	---
2-(methylthio)-benzothiazole	615-22-5	96	12.782	6.6	0.32	0.53	---	---	---	---	6.6	0.65
2,6-bis(1,1-dimethylethyl)-4-(methoxymethyl)-phenol	87-97-8	90	13.180	6.3	0.23	0.38	---	---	---	---	6.3	0.63
1,1’-(1-butenylidene)bis-benzene	1726-14-3	87	13.246	5.7	0.74	1.2	---	---	---	---	5.7	0.56
2-(1-phenylethyl)-phenol	4237-44-9	87	13.725	1.3E3	0.42	0.70	---	---	---	---	1.3E3	1.3E2
1,1’-(3-methyl-1-propene-1,3-diyl)bis-benzene	7614-93-9	93	14.334	2.5E2	0.18	0.31	---	---	---	---	2.5E2	25
Dibutyl phthalate	84-74-2	93/50[a]	16.225	< LOD	5.5E2	9.1E2	16.222	< LOQ	36	60	< LOD	< LOQ
1,2,3,4,4a,9,10,10a-octahydro-1,4-dimethyl-7-(1-methylethyl), -methyl ester, (1R,4aS, 10aR)-1-phenanthrenecarboxylicacid	1235-74-1	97	21.684	51	0.71	1.2	---	---	---	---	51	5.0
2,4-bis-(1phenylethyl)-phenol	2769-94-0	90	22.886	3.6E3	0.86	1.4	---	---	---	---	3.6E3	3.6E2

[a] Diethyl phthalate and Dibutyl phthalate were identified using authentic reference standards

Table 13. This table presents the results obtained after analysis of Perfluorooctanoic acid (PFOA) in the sampled materials. The samples were spiked with ^{13}C-labelled PFOA (34.5 ng) as internal standard prior to analysis.

	Retention time (min)						
Sample name	Perfluorooctanoic acid *m/z* 369.0	^{13}C-labelled Perfluorooctanoic acid *m/z* 372.0	Concentration (ng/ml) Perfluorooctanoic acid	LOD (ng/ml)	LOQ (ng/ml)	Total amount (ng)	Concentration (µg/g material)
Blank 1	6.58	6.58	0.13	---	---	---	---
The outsole (shoe 1)	6.58	6.59	0.11	0.39	0.65	< LOD	---
The upper (shoe 1)	6.60	6.60	1.3	0.39	0.65	4.5	0.020
The lining (shoe 1)	6.58	6.59	0.28	0.39	0.65	< LOD	---
The midsole (shoe 1)	6.59	6.58	9.4E-2	0.39	0.65	< LOD	---
Blank 2	6.60	6.61	7.8E-2	---	---	---	---
The outsole (shoe 2)	6.55	6.57	0.70	0.23	0.39	2.5	0.014
The upper (shoe 2)	6.57	6.58	9.3E-2	0.23	0.39	< LOD	---
The lining (shoe 2)	6.62	6.61	9.1E-2	0.23	0.39	< LOD	---
The midsole (shoe 2)	6.59	6.58	9.3E-2	0.23	0.39	< LOD	---
Blank 3	6.61	6.60	0.12	---	---	---	---
The outsole (shoe 3)	6.52	6.56	0.22	0.36	0.60	< LOD	---
The upper (shoe 3)	6.58	6.56	0.10	0.36	0.60	< LOD	---
The lining (shoe 3)	6.58	6.63	8.7E-2	0.36	0.60	< LOD	---
The midsole (shoe 3)	6.58	6.57	0.12	0.36	0.60	< LOD	---

Table 14. This table presents the results obtained after analysis of Perfluorooctane sulfonate in the sampled materials. The samples were spiked with ^{13}C-labelled Perfluorooctane sulfonate (59.5 ng) as internal standard prior to analysis. Please note that quantification was performed using *m/z* 99.0

	Retention time (min)			Peak area ratio	Concentration (ng/ml)		
Sample name	Perfluorooctane sulfonate *m/z* 80.0	Perfluorooctane sulfonate *m/z* 99.0	^{13}C-labelled Perfluorooctane sulfonate *m/z* 99.0	Perfluorooctane sulfonate *m/z* 80.0 / *m/z* 99.0	Perfluorooctane sulfonate *m/z* 99.0	LOD (ng/ml) *m/z* 99.0	LOQ (ng/ml) *m/z* 99.0
Blank 1	7.16	7.18	7.16	4.78	0.18	---	---
The outsole (shoe 1)	7.16	7.16	7.16	3.78[a]	0.12	0.54	0.90
The upper (shoe 1)	7.15	7.16	7.15	8.25[a]	8.3E-2	0.54	0.90
The lining (shoe 1)	7.14	7.14	7.15	8.66[a]	7.0E-2	0.54	0.90
The midsole (shoe 1)	7.13	7.13	7.13	5.53[a]	0.15	0.54	0.90
Blank 2	7.12	7.11	7.13	5.60[a]	0.12	---	---
The outsole (shoe 2)	7.13	7.13	7.12	6.10[a]	0.12	0.36	0.60
The upper (shoe 2)	7.15	7.18	7.15	12.6[a]	5.1E-2	0.36	0.60
The lining (shoe 2)	7.14	7.12	7.16	11.2[a]	0.10	0.36	0.60
The midsole (shoe 2)	7.19	7.13	7.15	12.0[a]	9.8E-2	0.36	0.60
Blank 3	7.14	7.19	7.14	6.71[a]	0.15	---	---
The outsole (shoe 3)	7.10	7.12	7.13	5.43[a]	0.13	0.45	0.75
The upper (shoe 3)	7.12	7.10	7.13	12.3[a]	7.2E-2	0.45	0.75
The lining (shoe 3)	7.11	7.18	7.15	6.44[a]	0.11	0.45	0.75
The midsole (shoe 3)	7.12	7.10	7.13	12.4[a]	5.4E-2	0.45	0.75

[a] Perfluorooctane sulfonate was not considered identified since the ratio between fragment *m/z* 80 and *m/z* 99.0 did not correspond to the ratio (4.33) obtained in the four standard solutions.

Appendix 3

Table 1. This table presents a summary of the chemicals identified in the water leachate after soaking extraction of outsole material sampled from shoe number one (1.070 g material). Name, CAS registry number, match quality (%), retention time (min), and concentration (ng/ml) are given for each substance identified. Please note that only compounds with peak signal to noise >10 and a match quality ≥ 85% are presented.

Shoe 1							
Substance	**CAS**	**Match Quality (%)**	**Retention time (min)**	**Concentration (ng/ml)**	**LOD (ng/ml)**	**LOQ (ng/ml)**	**Concentration in the material (µg/g material)**
Benzothiazole	95-16-9	94	9.325	1.6	0.12	0.20	1.5
2,6-bis(1,1-dimethylethyl)-4-methyl-phenol	128-37-0	95	11.606	7.3	0.56	0.93	6.9
Diethyl phthalate	84-66-2	94	12.352	0.75	6.8E-2	0.11	0.70
Triallyl isocyanurate	1025-15-6	95	12.961	1.1	3.1E-2	5.1E-2	1.0
1,6-dimethyl-4-(1-methylethyl)-naphthalene	483-78-3	91	13.732	5.3	2.1E-2	3.6E-2	5.0
Dibutyl phthalate	84-74-2	78	16.230	< LOD	4.8	8.0	---

Table 2. This table presents a summary of the chemicals identified in the water leachate after soaking extraction of outsole material sampled from shoe number two (1.185 g material). Name, CAS registry number, match quality (%), retention time (min), and concentration (ng/ml) are given for each substance identified. Please note that only compounds with peak signal to noise >10 and a match quality ≥ 85% are presented.

Shoe 2							
Substance	**CAS**	**Match Quality (%)**	**Retention time (min)**	**Concentration (ng/ml)**	**LOD (ng/ml)**	**LOQ (ng/ml)**	**Concentration in the material (µg/g material)**
Benzothiazole	95-16-9	95	9.320	19	1.9E-2	3.2E-2	16
2,6-bis(1,1-dimethylethyl)-4-methyl-phenol	128-37-0	91	11.593	16	7.7E-2	0.13	13
Diethyl phthalate	84-66-2	86	12.349	0.49	3.9E-2	6.4E-2	0.41
2-(methylthio) benzothiazole	615-22-5	95	12.789	1.1	1.0E-2	1.7E-2	0.93
1,6-dimethyl-4-(1-methylethyl)-naphthalene	483-78-3	90	13.725	0.85	4.3E-2	7.2E-2	0.72
Dibutyl phthalate	84-74-2	78	16.216	< LOD	0.82	1.4	---
2(3H)-Benzothiazolethione	149-30-4	91	16.731	0.68	1.4E-2	2.3E-2	0.57

Table 3. This table presents a summary of the chemicals identified in the water leachate after soaking extraction of outsole material sampled from shoe number three (1.208 g material). Name, CAS registry number, match quality (%), retention time (min), and concentration (ng/ml) are given for each substance identified. Please note that only compounds with peak signal to noise >10 and a match quality ≥ 85% are presented.

Shoe 3							
Substance	**CAS**	**Match Quality (%)**	**Retention time (min)**	**Concentration (ng/ml)**	**LOD (ng/ml)**	**LOQ (ng/ml)**	**Concentration in the material (µg/g material)**
Benzothiazole	95-16-9	94	9.322	11	4.7E-2	7.9E-2	8.9
2,6-bis(1,1-dimethylethyl)-4-methyl-phenol	128-37-0	50	11.605	3.7	0.20	0.33	3.1
Diethyl phthalate	84-66-2	97	12.352	< LOQ	0.44	0.73	< LOQ
2-(methylthio) benzothiazole	615-22-5	99	12.781	3.9	1.2E-2	1.9E-2	3.2
2-(1-phenylethyl)-phenol	4237-44-9	91	13.731	19	5.8E-2	9.7E-2	16
Dibutyl phthalate	84-74-2	78	16.234	< LOD	4.4	7.3	---

Table 4. Presents the results obtained after analysis of Perfluorooctane sulfonate (PFOS) and Perfluorooctanoic acid (PFOA) in the water leachate obtained from shoe number two. The sample was spiked with ^{13}C-labelled Pefluorooctane sulfonate (59.5 ng) and ^{13}C-labelled Pefluorooctanoic acid (69.0 ng) and as internal standards prior to analysis. Please note that quantification of PFOS was performed using *m/z* 99.0

	Retention time (min)						**Concentration (ng/ml)**				
Sample Name	**PFOS** *m/z* **80.0**	**PFOS** *m/z* **99.0**	**PFOA** *m/z* **369.0**	**^{13}C-PFOA** *m/z* **372.0**	**^{13}C-PFOS** *m/z* **99.0**	**Peak area ratio PFOS** *m/z* **80.0 /** *m/z* **99.0**	**PFOA** *m/z* **369.0**	**PFOS** *m/z* **80.0**	**PFOS** *m/z* **99.0**	**LOD (PFOS) (ng/ml)** *m/z* **99.0**	**LOQ (PFOS) (ng/ml)** *m/z* **99.0**
Blank	7.08	7.07	6.48	6.48	7.06	6.1	< 0	3.0E-2	2.5E-3	---	---
The water lechate (shoe 2)	7.09	7.13	6.50	6.50	7.10	8.9[a]	< 0	0.15	4.3E-2	7.5E-3	1.3E-2

[a] Perfluorooctane sulfonate was not considered identified since the ratio between fragment *m/z* 80 and *m/z* 99.0 did not correspond to the ratio (4.5) obtained in the standard solutions.