Journal of Hazardous Materials 476 (2024) 135042

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Are eco-friendly “green” tires also chemically green? Comparing metals, rubbers and selected organic compounds in green and conventional tires

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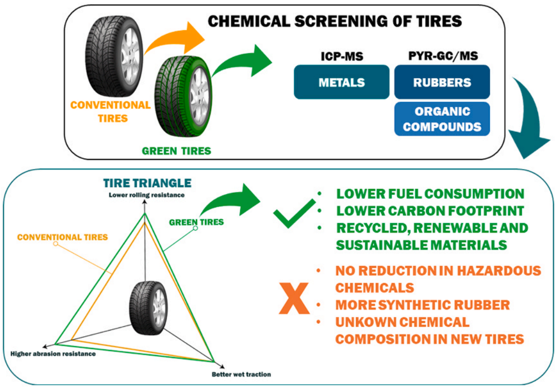
HIGHLIGHTS

- New “green, sustainable and eco-friendly” tires were compared to “conventional” tires.
- No significant difference in composition between “green” and “conventional” tires was observed.
- No significant difference in chemical composition between brands was observed.
- Significant difference was observed for tires classified by seasonal use.
- The rubber composition explained 19 % of the variation in metals and organic compounds.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Dr. C. Baiyang

Keywords:
Tires
Rubber particles
Metals
Organic tire compounds
Pyrolysis GC/MS
ICP-MS

ABSTRACT

Tires are a major source of synthetic and natural rubber particles, metals and organic compounds, in which several compounds are linked to negative environmental impact. Recent advances in material technology, coupled with focus on sustainability, have introduced a new range of tires, sold as “green, sustainable, and eco-friendly”. Although these “green” tires may have lower impact on the environment on a global scale, there is no current knowledge about the chemical composition of “green” tires, and whether they are more eco-friendly when considering the release of tire wear particles or tire-associated chemicals. Here we have investigated the chemical composition of nine “green” vehicle tires, one “green” bike tire and seven “conventional” vehicle tires. No significant difference was found between “green” and “conventional” tires tested in this study. For N-(1,3-dimethylbutyl)-N’-phenyl-p-phenylenediamine (6PPD), the average concentration in “green” tires were higher (16 ± 7.8 µg/mg) compared to “conventional” tires (8.7 ± 4.5 µg/mg). The relationship between metals, selected organic compounds and rubbers demonstrated large variation across brands, and lower variability between tires grouped according to their seasonal use. This study indicates that more work is needed to understand how the shift towards sustainable tires might change the chemical composition of tires.

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https://doi.org/10.1016/j.jhazmat.2024.135042
Received 23 January 2024; Received in revised form 20 June 2024; Accepted 25 June 2024

1. Introduction

Tire road wear particles (TRWP) are among the top sources of microplastics released from land [1–4]. Several studies have reported their presence in the road environment [5–12], air samples [13–15], in rivers [16–18], soil [19,20] and marine environments [21]. Recent studies have also demonstrated the presence of tire-associated compounds (TAC) in the environment [16,17,22–27] leaching from tires, tire particles and rubber granulates to the environment. This has so far been found to have severe negative impacts on selected aquatic [28–31] and terrestrial [32] species, especially linked to the antioxidant and antiozonant N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD), and its transformation product 6PPD-Quinone (6PPD-Q). In addition, tires are a major source of metal contamination, with negative effects reported especially in the aquatic environment [33–36], especially from zinc (Zn), lead (Pb), copper (Cu) and cadmium (Cd). However, there is still limited understanding of TRWP and TAC in the environment: the constant evolution of new and "improved" tires from different tire producers complicates the understanding of their composition and potential impact on the environment by the research community, environmental authorities, and stakeholders. Without a complete knowledge on the variability of these compounds in commercial tires, a thorough control over the risk posed by TRWP to the environment and human health will not be possible [37].

The transport sector has changed rapidly in the past few years and is expected that sales volume will significantly expand in the next decades [38]. Environmental concerns, such as climate change and pollution, are influencing the innovation agenda of the transport industry. In Europe, the "EU Tyre Label" can be used to rank tires on the commercial market. Within this approach, three factors are considered: rolling resistance, abrasion resistance and wet grip. These three factors make up what is defined as the "tire triangle" (Fig. 1). All tires are given a rank (A to E) according to rolling resistance and wet grip, where low rolling resistance (A) will give lower fuel consumption, and high wet grip (A) will give better traffic safety. In addition, the EU Tyre Label also considers the noise level. It both gives the measured noise level in decibel (dB) and a ranking (A-C). Both rolling resistance and wet grip are important factors used to enhance tire performance according to specific needs and area of use.

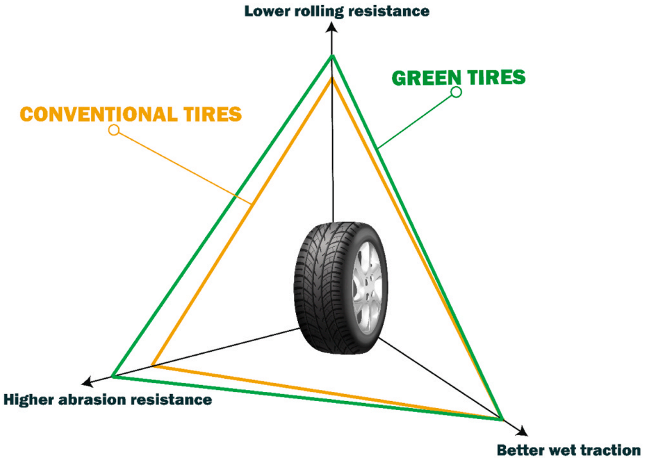

Fig. 1. The "tire triangle" illustrates the features of commercial tires, where optimal tires have low rolling resistance, high wet traction and high resistance against abrasion. The orange triangle illustrates the current focus of conventional tires, whereas the green triangle illustrates the focus of "green" tires.

As part of the new Euro7 package, a set of emission regulations set by the European Commission expected to be implemented in 2025, new regulations aimed at controlling the release of tire wear particles from vehicles will be likely introduced by the end of 2024 (EC, 2022). Although no standardized emission test is currently in place, the ongoing developments of both on-vehicle tests and laboratory-based drum-tests are suggesting that tire wear particle emissions from the use of commercial tires will be regulated to meet emission criteria by focusing on testing the abrasion resistance of new tires on the market. This is already sparking technological developments that focused on design, raw materials, and possibly chemical additives mixture to meet the demand of low TRWP releases, safety, noise reduction, and reduced fuel consumption.

Currently, all major tire manufacturers are developing new vehicle tires that are aimed at increasing sustainability and being more environmentally friendly [39,40] Tires marketed as "eco-friendly, "green" or "sustainable" are in fact already available in the market. The narratives provided by producers supporting these claims links to lower fuel consumptions and lower wear rates (according to the EU tire label [41] and reduced CO_2 emission during manufacturing, especially by replacing fossil-based materials with biobased or recycled materials, is frequently mentioned as a green approach: some examples of alternative materials are rice husk ash silica from the rice industry or recycled carbon black from scrap tires. These approaches have been tested for Pirelli's new P Zero E tire, where the tire producers also introduced a new logo for tires with >50 % sustainable materials to increase customer awareness [42]. These types of labelling of "sustainable" or "green" tires are important to ensure that customers can make conscious choices, however, there is currently no standardization of how to label tires according to "sustainability" or "green" criteria. Several tire companies, such as Bridgestone and Michelin, have announced long-term goals of having 100 % sustainable materials in their tires by 2050 [43,44]. In consideration of this, a standardized labelling system for tires would improve both transparency and customer awareness. In addition, several tire companies are working on changing their supply of natural rubber from the rubber tree (Hevea brasiliensis) produced in Asia to natural rubbers produced locally, aiming to both decrease local environmental impact due to rubber production and decrease CO2 emissions from the extensive transport of rubber from Asia. In Europe, Continental has already released a bike tire made with rubbers from the Russian Dandelion [45] and has announced that new car tires are following as soon as the industrialization of dandelion rubber is in place. In addition, both Bridgestone and Nokian are currently working on producing natural rubbers from the desert shrub guayule [46,47]. The use of synthetic rubbers is shifting towards recycled, renewable rubbers [48–50], and even materials mentioned as "environmentally friendly rubbers" such as bio-butadiene rubber produced from ethanol [51].

All steps taken to reduce the environmental footprint of tires, from production to on-vehicle use and as end-of-life tires are necessary and positive on a global scale. However, the local impact of tires is highly driven by the chemical composition of tires, as both TRWP and tire-related chemicals have been demonstrated to cause toxic effect on various organisms [52]. As such, changes made in the tire production to reduce CO_2 emissions or deforestation to create "green" tires would not necessarily reduce the local impact unless the changes also include changes in the chemical formulation of tires, and this topic remain currently overlooked by the research community and the tire industry [40].

A first step towards assessing the impact on a local scale is to understand the chemical composition of these new tire types, which is the purpose of our research work. This study aims at investigating two major hypotheses. Hypothesis 1 states that "Tires labelled as "green" by manufacturers contain lower levels of tire chemicals associated with negative environmental impact, such as metals, rubbers and selected organic compounds (6PPD, 6PPD-Q, DPG, HMMM, TMQ)". Hypothesis 2 states that "The selected chemical composition of tires can be used as a classifier to segregate tires labelled as "green" vs "conventional" tires". To investigate these two hypotheses, nine green and seven conventional car tires, as well as one green bike tire, were screened for metals, rubbers and selected organic compounds.

2. Experimental details

2.1. Sample collection and processing

Tread samples were collected from 17 unused tires (Table 1). Seven of these tires are classified as “conventional” car tires, nine of these tires are classified as “green” car tires and in addition, one “green” bike tire is included for comparison. The tires used in this study were selected to cover a range in brands, types and seasonality. Seven of the major global tire brands are represented, and the tires represent both summer and winter (studded and non-studded) tires. New and unused tires were used in the study to limit the potential variation in chemical composition due to age and environmental weathering in the tires in use. All tires were stored in a cool, dry basement with no daylight. From each tire, a thin top layer of tire tread (1–2 mm) was removed from the tire tread surface using knives with ceramic blades (Slice TM). Then a fresh new tire tread piece was cut from the tire tread area and placed in plastic containers (metal analysis) or brown glass containers (rubber and organic compound analysis). Blades were pre-cleaned (with ultrapure water) blades for each tire.

2.2. Elemental composition

The dissolution of tire samples was performed through microwave-assisted acid digestion. An ETHOS One (Milestone MLS) microwave digestion system equipped with 10 Polytetrafluoroethylene (PTFE) vessels was used for acid digestion. About 50 mg of sample (finely cut using a ceramic knife) was weighed and inserted into a PTFE vessel. 5 mL of ultrapure HNO_3 (produced by sub-boiling distillation, see [53], from commercial HNO_3 (Carlo Erba, 65 % pure), 0.2 mL of ultrapure H_2SO_4 (Analytika, 95 % pure) and 1 mL of H_2O_2 (Fisher Chemical, 30–32 % for trace analysis) were added into the PTFE vessel. The samples were then digested by applying a temperature ramp reaching 200 °C. This temperature was kept for 1 h. The digested solution was then left to cool at room temperature. After mineralization, samples were transferred to low density polyethylene (LDPE) bottles, diluted to 30 g with ultrapure water and filtered with a 0.22 µm PTFE filter prior to the analysis via inductively coupled plasma-mass spectrometry (ICP-MS). Diluted solutions were analyzed using a Thermo Scientific ICAP Q ICP-MS using a He-collision cell in kinetic energy discrimination (KED) mode, under the operating conditions summarized in Table 2. Trace element quantification was performed by external calibration and Rhodium and Rhenium were spiked to the solutions as internal standards to compensate eventual instrumental drifts (recoveries were in the ± 10 % interval).

LDPE bottles underwent a three-step decontamination procedure: first, they were cleaned with ultrapure water and submerged in a 0.4 % w/w detergent solution (Nalgene L900) for one week; second, they were rinsed with ultrapure water and soaked in a 2 % w/w HNO_3 solution for another week; third, they were rinsed again with ultrapure water and soaked in a second 2 % w/w HNO_3 solution for one week [54]. All sample manipulation processes were conducted under a laminar flow hood to avoid the occurrence of contamination.

All digestions and analyses were performed in triplicate to assess precision of measurements. A total of 61 metals were investigated. Any metals with $>$ 50 % of samples below LOD were removed from the dataset. For samples <LOD, a replacement was made by dividing the LOD for that metal by 10. LOD were obtained after the analysis of 5 procedural blank samples (i.e., acid solutions underwent digestion and dilution without the addition of tires), and were calculated as 3 times the standard deviation of the blanks [55].

2.3. Organic composition

Tires were cut according to the description in 2.1 and cut on the same day as the analysis. The tire piece was taken out with tweezers and placed on clean aluminum foil. From this piece of tire tread, one tire particle was cut using a ceramic scalpel. The particles were cut in an elongated shape and similar size. Each particle was inserted into pyrolysis cups and weighed on a microbalance. Selected organic compounds were semi-quantified using cryo-trap thermal desorption gas chromatography mass spectrometry following the methods by Frontier Laboratories [56], with modification to the end temperature (350 °C) (Table 3) and the use of internal standards (ISTD). ISTDs were added short before the analysis of the samples, spike sample as well as calibration samples to compensate for matrix introduced variations during analysis of the different tires for and normalization of the analytes to the respective ISTD during quantification. Samples were analyzed with a Multi-Shot Pyrolyzer (EGA/PY-3030D) equipped with an Auto-Shot

Table 2
ICP-MS working parameters.

Parameter	Value
RF Power	1550 W
Nebulizer gas flow	1.06 L/min
Auxiliary gas flow	0.80 L/min
Cooling gas flow	13.99 L/min
Dwell time (ms)	300 ms
He flow rate (collision cell)	4.34 mL/min

Table 1
Summary of the 17 different tires used for this study: 7 “conventional” car tires (CT1–7), 9 “green” car tires (CT8–16) and 1 “green” bike tire (BT1). Among the car tires, 7 tires were winter tires and 9 were summer tires. The table summarizes the information related to fuel consumption save, reduced wear rate, the use of sustainable material or improved rubbers available on each tire through the commercial suppliers.

Type	Tire	Brand	Season	Fuel	Wear	Sustainability	Rubber
Conventional	CT1	Brand1	Winter NS	None	None	None	None
Conventional	CT2	Brand1	Winter S	None	None	None	None
Conventional	CT3	Brand2	Winter S	None	None	None	None
Conventional	CT4	Brand2	Summer	Fuel saver	None	None	None
Conventional	CT5	Brand3	Winter NS	Fuel saver	Lower wear	None	None
Conventional	CT6	Brand4	Winter S	None	None	None	None
Conventional	CT7	Brand5	Summer	Fuel saver	Lower wear	None	None
Green	CT8	Brand6	Summer	Fuel saver	Lower wear	None	None
Green	CT9	Brand6	Summer	Fuel saver	None	None	None
Green	CT10	Brand7	Winter NS	Fuel saver	Lower wear	None	New-rubber-mix
Green	CT11	Brand3	Summer	Fuel saver	None	None	Triple polymer
Green	CT12	Brand5	Winter S	Fuel saver	None	None	New-rubber-mix
Green	CT13	Brand5	Summer	Fuel saver	None	Bio-based	Durable rubber
Green	CT14	Brand1	Summer	Fuel saver	None	None	None
Green	CT15	Brand1	Summer	Fuel saver	None	None	None
Green	CT16	Brand2	Summer	Fuel saver	Lower wear	Rec-PET	Reduced rubber loss
Green	BT1	Brand2	BIKE TIRE	None	None	None	Dandelion NR

Sampler (AS-1020E), micro jet cryo-trap (MJT-2030E) and a multi-functional splitless sampler (MFS-2015E) (Frontier lab Ltd., Fukushima, Japan) and coupled to gas chromatography mass spectrometer (GC/MS) (5977B MSD with 8860 GC, Agilent Technologies Inc., CA, USA). The selected organic compounds were 1,3-diphenylguanidine (DPG), 6PPD, 6PPD-Q, 2,4,6-tris[bis(methoxymethyl)amino]− 1,3,5-triazine (HMMM), poly-(1,2-dihydro-2,2,4-trimethylquinoline) (TMQ), 2-aminobenzothiazole (ABT), 2-hydroxybenzothiazole (OHBT) (Table 4). All standards were obtained from TCI (Shang Hai, China), Accustandard (New Haven, CT), and Sigma-Aldrich (St. Louis, MO). Single-point calibration curves were used for the quantification of HMMM, DPG, 6PPD, 6PPD-Q, TMQ-A, TMQ-B and TMQ-C, using 20 µg of each compound (2 µg for 6PPD-Q). Two replicates of the calibration sample were analyzed, one analyzed in the beginning and one at the end of the batch to compensate for potential losses of volatile compounds. To minimize potential losses of volatile compounds, the samples were analyzed in three batches of maximum ten tire samples and not as one large batch. Internal standards (ISTD) were applied for all samples, including calibration samples and the spike sample. For compounds 6PPD and DPG, d10-pyrene was used as ISTD. For TMQ-A, TMQ-C and 6PPD-Q, d12-benzo(a)anthracene was used as ISTD. For TMQ-B, d12-perylene was used as ISTD. Signals for analytes were normalized by the respective ISTD. In addition, clean pyro cups were analyzed every 3–5 samples to detect analyte carry-over. ISTD samples without analyte were analyzed to validate the trueness of the calibration curves, forced through the origin. The calibration curves can be found in SI-1, Figs. S1-S7. Details about retention time, ions used for quantification can be found in Table 4. The recovery of the spike sample was between 78–101 %, except 6PPD-Q which had a recovery of 227 % (SI Table S4). Since 6PPD-Q was only detected in one sample, the reasons for too high recoveries were not further investigated. LOD for the organic compounds can be found in the Supplementary information (Table S3).

Table 4

Description of name, CAS number, mass (*m/z*) for quantifier (quan) and qualifier (qual) ion and retention time (RT) for the selected organic components (target) and the internal standards (ISTD) applied.

Analyte	Short name	Full name	CAS	*m/z* (quan/ qual)	RT
Target	DPG	1,3-diphenylguanidine	102-06-7	211/ 93	16.0
Target	6PPD	N-(1,3-dimethylbutyl)-N′-phenyl-p-phenylenediamine	793-24-8	268/ 211	16.8
Target	6PPD-Q	N-(1,3-dimethylbutyl)-N′-phenyl-p-phenylenediamine-quinone	2754428-18-5	298/ 255	19.1
Target	HMMM	2,4,6-tris[bis(methoxymethyl)amino]− 1,3,5-triazine	3089-11-0	375/ 343	17.2
Target	TMQ-A	poly-(1,2-dihydro-2,2,4-trimethylquinoline)	26780-96-1	158/ 346	18.6
Target	TMC-B	poly-(1,2-dihydro-2,2,4-trimethylquinoline)	26780-96-1	158/ 330	19.2
Target	TMQ-C	poly-(1,2-dihydro-2,2,4-trimethylquinoline)	26780-96-1	158/ 266	16.9
Target	OHBT	2-hydroxybenzothiazole	934-34-9	151/ 123	13.7
Target	ABT	2-aminobenzothiazole	136-95-8	150	13.2
ISTD		d12-benzo(a)antracene		240	17.7
ISTD		d12-perylene		264	20.9
ISTD		d10-pyrene		212	16.1

2.4. Rubber composition

The samples were analyzed for styrene butadiene rubber (SBR) and butadiene rubber (BR) following the Pyrolysis GC-MS methodology developed by Rødland et al. [57] with modifications (Table 5), and for Natural rubber (NR) following the methods described in ISO-TS-21396 [58]. Samples were analyzed with a Multi-Shot Pyrolyzer (EGA/-PY-3030D) equipped with an Auto-Shot Sampler (AS-1020E) (Frontier lab Ltd., Fukushima, Japan) coupled to gas chromatography mass spectrometer (GC/MS) (5977B MSD with 8860 GC, Agilent Technologies Inc., CA, USA).

Calibration for SBR+BR was performed using SBR1500 (Polymer Source Inc., Canada) in solution (chloroform, Sigma Aldrich) and all samples were spiked with an ISTD (deuterated polybutadiene, d6-PB, in chloroform solution). Calibration was made by adding 1, 5, 20, 60, 120 and 140 µg of SBR1500 solution in a single pyrolysis cup. Seven different marker compounds for SBR and BR were monitored: *m/z* 78 for benzene (B), *m/z* 118 for α-methylstyrene (MS), *m/z* 117 for ethylstyrene (ES), *m/z* 91 for butadiene trimer (Bt), *m/z* 54 for 4-Vinylcyclohexene (4-VCH), *m/z* 104 for styrene butadiene dimer (SB) and *m/z* 91 for styrene butadiene trimer (SBB). Quantification of SBR+BR was performed using

Table 3

Method description for analysis of selected organic components using cryo-trap thermal desorption pyrolysis gas chromatography mass spectrometry.

Equipment	Parameters	Settings
Micro-furnace Pyrolyzer (EGA/ PY-3030D)	Thermal desorption	100 °C (hold 0.20 min) → (20 °C/ min) → 350 °C (hold 0.30 min)
	Interface temperature	300 °C
Cryo-trap (MJT-2030E)	Temperature	-196 °C (during thermal desorption)
GC conditions	Column	Ultra-Alloy®− 50 precolumn (1 m, 0.25 mm I.D., 1.0 µm film thickness) connected to a Ultra-Alloy® 5 capillary column (30 m, 0.25 mm I.D., 0.5 µm film thickness) (Frontier Lab)
	Injector port temperature	300 °C
	Column oven temperature program	40 °C (hold 2 min) → (20 °C /min) → 320 °C (hold 14 min)
	Carrier gas	Helium, 1.0 mL/min, constant linear velocity
MS conditions	Ion source temperature	230 °C
	Ionization energy	Electron ionization (EI); 70 eV
	Scan range	29 to 600 *m/z*

Table 5

Method description for rubber analysis using pyrolysis gas chromatography mass spectrometry.

Equipment	Parameters	Settings
Micro-furnace Pyrolyzer (EGA/ PY-3030D)	Furnace temperature (pyrolysis)	700 °C
	Interface temperature	300 °C
	Pyrolysis time	12 s (0.20 min)
GC conditions	Column	Ultra-Alloy®− 50 precolumn (1 m, 0.25 mm I.D., 1.0 µm film thickness) connected to a Ultra-Alloy® 5 capillary column (30 m, 0.25 mm I.D., 0.5 µm film thickness) (Frontier Lab)
	Injector port temperature	300 °C
	Column oven temperature program	50 °C (hold 2 min) → (5 °C /min) → 190 °C (hold 0 min) → (20 °C /min) → 300 °C (hold 2 min)
	Carrier gas	Helium, 1.0 mL/min, constant linear velocity
MS conditions	Ion source temperature	230 °C
	Ionization energy	Electron ionization (EI); 70 eV
	Scan range	50 to 350 *m/z*

the combined peak heights of the four markers B, MS, ES and Bt, normalized by the internal standard (d6-Pb) (calibration curve $R^2 = 0.99$). Calibration of NR was performed using synthetic cis-polyisoprene (Polymer Source Inc., Canada) in solution (chloroform, Sigma Aldrich) and internal standard (d6-PB, in chloroform solution). Calibration was made by adding 1, 5, 10, 30, 60, 100, 140 μg of NR solution to in a single pyrolysis cup. Two marker compounds for NR were monitored: *m/z* 67 for isoprene and *m/z* 68 for dipentene. The peak height of dipentene, normalized by d6-PB was used for quantification (calibration curve $R^2 = 0.969$).

All tire samples were analyzed in triplicates. Tires were cut according to the description in 2.1 and stored in the lab for < 24 h prior to analysis. On the same day as the analysis, the tire piece was taken out with tweezers and placed on clean aluminum foil. From this piece of tire tread, three tire particles were cut using a ceramic scalpel. The particles were cut in an elongated shape and similar size. Each particle was inserted into pyrolysis cups and weighed on a microbalance. All tire particles were between 0.110 and 0.328 mg. Quality control (QC) samples (20 μg SBR1500 standard solution) were used to evaluate the performance of the PYR-GC/MS through the analysis run and analyzed for every 10–15 samples. Blank samples (no cups) were run before all QC samples to monitor potential carry-over from previous samples.

2.5. *Statistical analysis*

All boxplots were created in RStudio [59], R version 4.2.3 (2023), using the ggplot2-package [60] (gplot2_3.3.3). Analysis of Variance (ANOVA) was performed in RStudio using the car-package [61] and the dplyr-package [62]. The assumption of normal distribution of residuals was tested using an Andersen-Darling normality test. The assumption of equal variance was tested using Levene's Test of Homogeneity of Variance. Whenever this assumption was not met, Welch's one-way ANOVA was used. The statistically significant level was set to p = 0.05.

Redundancy analysis (RDA) and principal component analysis (PCA) were conducted in Canoco 5.12 [63]. The significance level in the RDA is derived by Monte Carlo permutation tests (9999 permutations

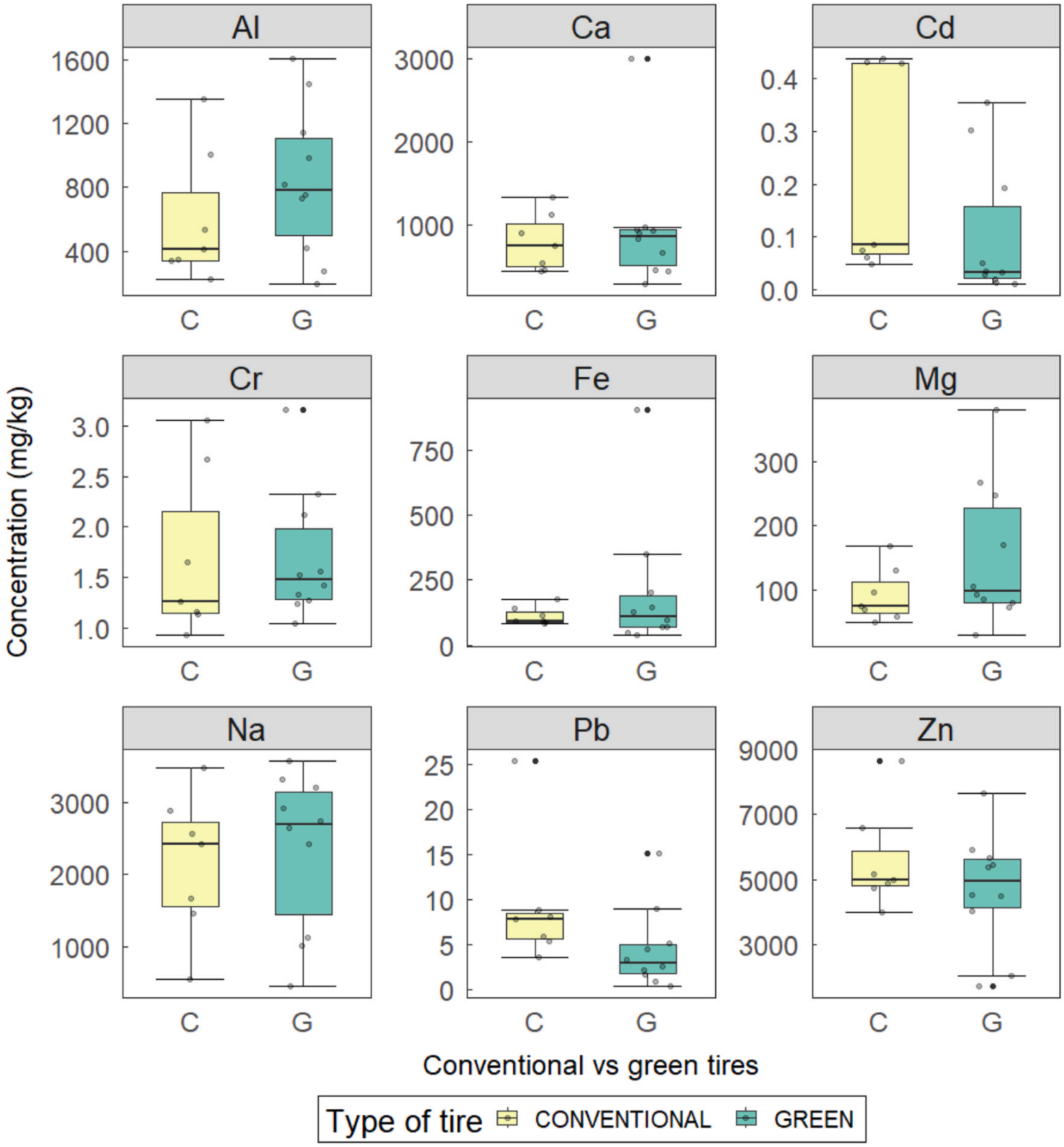

Fig. 2. Boxplot of selected metal levels in conventional (C) and green (G) tires, showing the actual sample values as dots, median value as the line across the box and whiskers representing the 75th percentiles of the dataset.

performed). For all tests, $p < 0.05$ is set as the level of significance.

3. Results and discussion

3.1. Metal composition

Of the 61 investigated metals, 7 metals had concentrations >LOD (SI Table S1) in less than 50 % of the samples and was therefore discarded from the dataset. Of the remaining 54 metals, a large variation in concentration was observed, with the highest average concentration from zinc (Zn, 5050 ± 1710 mg/kg, average ± standard deviation), sodium (Na, 2270 ± 1030 mg/kg), calcium (Ca, 876 ± 618 mg/kg), aluminum (Al, 739 ± 453 mg/kg), iron (Fe, 166 ± 204 mg/kg) and magnesium (Mg, 128 ± 93 mg/kg) (Fig. 2, Tables S2, S6, S7). The results also show the presence of rare earth elements such as lanthanum (La, 0.496 ± 0.444 mg/kg) and cerium (Ce, 0.637 ± 0.552 mg/kg) in lower concentrations. The rare earth metal neodymium (Nd), however, was found in variable amounts across all the tires, from 0.0809 mg/kg up to 35.5 mg/kg (SI Table S6), suggesting differences in the use of Nd in the catalyzation of polybutadiene used for the different tires [64].

The metal concentrations in this study are consistent with those measured in previous studies [65–67], although some variations were observed. One of the most importantly known metal present in tires for its toxicity is Zn [68,69]. The highest metal concentration in both green and conventional tires came in fact from Zn, with levels ranging from 1720 to 8660 mg/kg, (5050 ± 1710 mg/kg) across all tires, in agreement with previous studies reporting levels of this element between 3000 to 10,000 mg/kg [65–67]. Different types of tires and brands, as well as variation in analytical methods may be the reason for these differences. The average concentration of Zn was highest in the “conventional” tire (5580 ± 1370 mg/kg), however no significant difference between the “conventional” and the “green” tires was observed (ANOVA $p = 0.259$, SI Fig. S8). The same trend was observed for the other metals, although the average concentration was slightly higher in “green” tires for the metals Na (2350 ± 1090 mg/kg), Ca (940 ± 767 mg/kg), Al (837 ± 472 mg/kg), Fe (205 ± 263 mg/kg), Mg (153 ± 112 mg/kg) and Cu (3.64 ± 5.32 mg/kg) (Table S2). The second highest concentration of Zn was found in the “green” bike tire made with dandelion rubber (7640 mg/kg, SI Table S6). In addition, the bike tire had the highest concentrations for Ca (3010 mg/kg), Fe (905 mg/kg), Mg (381 mg/kg) and Cr (3.2 mg/kg) (SI Table S6). The concentration of these metals in the tires seems extremely variable also considering their relative concentration in the different samples: a correlation matrix shows limited significant correlations (Fig. S9). Generally, the presence of Na is negatively correlated with the abundance of other trace elements, while there is a weak positive correlation among Fe, Cu, Pb and Cd concentrations. This may be due to the different compounds added to fillers by different producers. Comparing the concentration of metals in the present tires to other plastic materials, some metals (e.g., Fe and Cu) are found at comparable levels, whereas other metals (e.g., Cr, Zn, Cd, Pb) are found in significantly higher concentrations, indicating tires as an important source of metals among plastic materials. It is worth mentioning that data on metal concentrations in environmental plastic is still fragmentary [66,70].

Testing the variation of all metals with redundancy analysis (RDA) and grouping the tires in “conventional” and “green”, explained 0.00 % of the observed variation and was not significant ($p = 0.5885$, SI Fig. S10), demonstrating that there is not a different composition between the tires based on being a “green, sustainable” option or a “conventional” tire considering the metals investigated. On the other hand, grouping the tires by season (summer, winter) and including the bike tire option, 36 % of the observed variation in metal concentrations could be explained ($p = 0.0001$, SI Fig. S11). As many of the metals in highest concentration also were found to be high in the bike tire, this indicates an important contribution from this type of tire to the total observed data variability. An additional RDA was therefore run without the bike tire, whereas now summer and winter tires could explain only 7.7 % ($p = 0.0178$, SI Fig. S12) of the variation in metal concentrations. This suggests that also grouping the different tires by their seasonal use is not sufficient to explain all the observed variation across the different tire brands and types tested in this study, and that metal composition variability is not strongly affected by any of the factors considered here (environmental label and season).

3.2. Organic composition

Before analysis of tire particles, a screening of the selected organic compounds using standard compounds in solution was tested to investigate which compounds could reliably be detected using this analytical approach. This resulted in the selection of ABT, OHBT, HMMM, DPG, 6PPD, 6PPD-Q and two variants of TMQ (TMQ-A and TMQ-B).

Of the initial list of organic compounds screened for in this, only three compounds were present in all tire samples, with highest concentrations of 6PPD (13 ± 7.3 μg/mg), followed by TMQ-B (3.6 ± 2.1 μg/mg) and TMQ-A (2.0 ± 1.5 μg/mg) (Table 6). Neither 6PPD-Q, DPG, ABT or OHBT were detected in the tire samples (Tables S5 and S6). High levels of DPG, 6PPD, 6PPD-Q and TMQ have previously been found in tunnel wash water [22] and in runoff from artificial football turfs and a tire recycling site [27], however these studied applied LC/MS methods to measure these compounds in leachates. In contrast to previous studies investigating leachates and environmental samples, only low levels of 6PPD-Q (<LOD) were found in this study). 6PPD-Q is a transformation product from 6PPD, induced by ozonation and oxidation, processes

Table 6
Summary statistics (average, standard deviation (STD), median, minimum (MIN), maximum (MAX) and number of samples (n) for selected organic compounds: N-(1,3-dimethylbutyl)-N’-phenyl-p-phenylenediamine (6PPD), 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ-A and TMQ-B). Statistics presented for all tire samples (n = 17) and grouped by “conventional” tires (n = 7), “green” tires (n = 9), summer tires (n = 9) and summer tires (n = 7). Unit for all compounds: μg/mg.

ALL TIRES	**6PPD**	**TMQ-A**	**TMQ-B**
AVERAGE	13	1.9	3.6
STD	7.3	1.5	2.1
MEDIAN	10	1.6	3.3
MIN	2.8	0.10	0.71
MAX	33	5.0	6.8
n	17	17	17
CONVENTIONAL	**6PPD**	**TMQ-A**	**TMQ-B**
AVERAGE	8.7	1.9	4.6
STD	4.5	0.8	1.4
MEDIAN	7.4	1.6	4.8
MIN	2.8	1.0	2.5
MAX	16	3.5	6.5
n	7	7	7
GREEN	**6PPD**	**TMQ-A**	**TMQ-B**
AVERAGE	16	2.0	2.9
STD	7.7	1.9	2.3
MEDIAN	13	1.7	2.0
MIN	8.8	0.1	0.71
MAX	33	5.0	6.8
n	9	9	9
SUMMER	**6PPD**	**TMQ-A**	**TMQ-B**
AVERAGE	16	1.9	3.2
STD	8.0	1.8	2.1
MEDIAN	16	1.6	2.1
MIN	6.2	0.1	0.91
MAX	33	5.0	6.3
n	9	9	9
WINTER	**6PPD**	**TMQ-A**	**TMQ-B**
AVERAGE	8.4	1.9	4.4
STD	3.2	1.3	2.3
MEDIAN	8.5	1.6	4.8
MIN	2.8	0.15	0.71
MAX	13	3.7	6.8
n	7	7	7

which can be strongly accelerated in the environment. The tires used in this study were all new tires stored in a cool, dry basement with no daylight, and all samples were cut from a deeper layer of the tire tread which had not been exposed to air or light prior to analysis. Thus, it is not expected to find a high level of 6PPD-Q in these samples. Previous studies have also reported high concentrations of the polymer cross-linking agent HMMM in river water receiving road runoff [17,71,72] and in tunnel wash water [22] using LC-MS and GC/MS analysis, suggesting tires as the main source. In addition, different benzothiazoles have also been found in tunnel wash water [22,27,73] such as benzothiazole-2-sulfonic (BTSA), 2-methylthiobenzothiazole (MTBT), 2-phenylbenzothiazole (PhBT), 2-aminobenzothiazole (ABT) and 2-hydroxybenzothiazole (OHBT), also applying LC-MS analysis. These compounds were not found in this present study. This may be due to a different extraction process and analytical technique deployed in this study (e.g. cryo-trap thermal desorption) compared to previous studies. However, cryo-trap PYR-GC/MS was found to be less suitable for detecting HMMM and benzothiazoles in tire particles. In addition, 2-OHBT have been found as transformation products related to hydrolysis of 2-mercaptobenzothiazole (MBT) and oxidation of benzothiazole (BT) [73], which could explain why it has been found in high concentrations in water samples and not found in the pure tire particles.

No significant difference in 6PPD, TMQ-A and TMQ-B concentrations was found by grouping the tires as “green” and “conventional” tires (RDA 9.5 %, $p = 0.067$) or by season (summer, winter) and bike tire (RDA 3.62 %, $p = 0.2785$). However, there was a significant difference in 6PPD concentration levels between tires categorized as “green” and “conventional” (ANOVA, $p = 0.023$, Fig. 3A), with the average concentration higher in the “green” tires (16 ± 7.8 μg/mg) compared to the “conventional” tires (8.7 ± 4.5 μg/mg). No significant difference in 6PPD levels was found when categorizing the tires by season and bike tire (ANOVA, $p = 0.259$, Fig. 3B). Although leaching capacity and transformation patterns were not considered in this study, the higher concentration of 6PPD in “green” tires could be related to higher release of 6PPD-Q to the environment, thus underlining the potential impact of these environmentally friendly and sustainable tires on the local environment. As 6PPD-Q has been found to cause acute mortality among selected aquatic species [74], there are now ongoing efforts to regulate the use of 6PPD in tires, especially in the US [75]. However, as no known substitute chemical for 6PPD has been proposed yet, it is likely that 6PPD will still be present in commercial tires for some time.

3.3. Rubber composition

The amount of both synthetic and natural rubbers varied between the different tires, with the average concentration of SBR+BR at 285 ± 102 μg/mg and of NR 99 ± 117 μg/mg across all tires (Table 7). The highest concentration of SBR+BR was in the winter tire CT1 (368 μg/mg) and the lowest was in CT12 (17 μg/mg, Table S1). The bike tire BT, although marketing the presence of the newly developed NR from dandelions, also had detectable levels of SBR+BR (77 μg/mg). However, NR were the main rubber found in BT and was the highest NR concentrations measured (408 μg/mg). Three tires (CT8, CT9, CT13, all marked as “green” tires) contained detectable levels of NR. The total rubber concentration (SBR+BR+NR) was surprisingly consistent in this study (38 ± 7 %), including those with no NR detected. This suggests that the total amount of rubber needed in tires is not significantly different between types of tires, whereas more marked differences are due to the type of rubber used. However, as only 17 tires were tested in this study, there are uncertainties related to these statements and a higher number of tires should be tested to understand the variations better. A previous study by Rødland et al. [57] using the same markers and similar PYR-GC/MS method found larger variation in the SBR+BR concentrations among 31 different tires, from 115–682 μg/mg, with an average of 32 ± 13 % only including SBR+BR. However, this study also included heavy vehicles (HV) whereas this current study only includes personal vehicles (PV). Rauert et al. [76] have also reported large variations in SBR+BR, from < 0.05 % to 20 % (average: 9.3 %, $n = 31$) using PYR-GC/MS, and in the method by Unice et al. [77] the sum of SBR+BR and NR in tire tread is estimated at 50 % across all tires, however, both of these studies used a different marker for SBR+BR (4-vinycyclohexene) compared to this study. Using worldwide production data on elastomers for tire use, Eisentraut calculated that the SBR+BR concentration in a whole tire should 11.3 % [78], which is closer to the average concentrations reported by Rauert et al. [76].

When comparing the rubber concentrations between “green” and “conventional” tires, there were no significant differences between them for either SBR+NR (ANOVA, $p = 0.65$) or NR (ANOVA, $p = 0.706$). However, grouping the tires by season (summer, winter non-studded, winter-studded) and the bike tire, both SBR+BR and NR

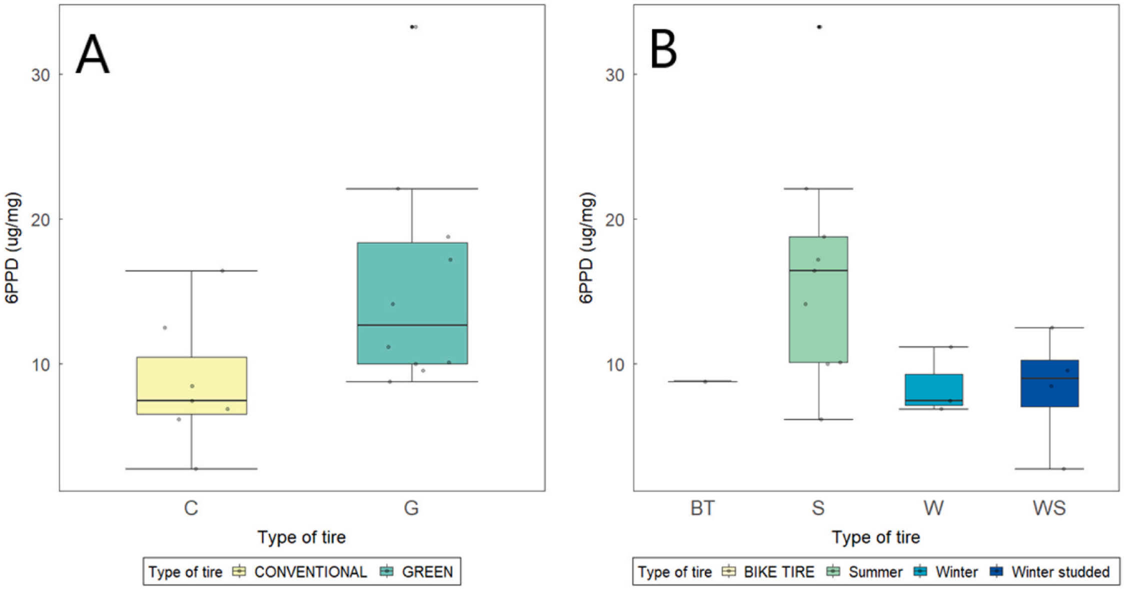

Fig. 3. **A)** Concentration of 6PPD in “green” tires compared to “conventional” tires. Significant difference was observed between the groups (ANOVA ($p = 0.023$). **B)** Concentration of 6PPD in tires grouped by season. No significant difference was observed between summer tires (S), winter non-studded tires (W), winter studded tires (WS) or bike tires (BT) (ANOVA, $p = 0.259$).

Table 7

Summary statistics (average, standard deviation (STD), median, minimum (MIN), maximum (MAX) and number of samples (n) for styrene butadiene rubber and butadiene rubber combined (SBR+BR), natural rubber (NR), the total sum of rubbers (Sum rubbers) in µg/mg and the total sum of rubbers in %.

ALL TIRES	**SBR+BR**	**NR**	**Sum rubbers**	**Sum rubber %**
AVERAGE	285	98.6	381	38.1
STD	102	117	70.1	7.01
MEDIAN	302	57	377	38
MIN	17.3	0	223	22.3
MAX	392	408	493	49.3
N	17	17	17	17
CONVENTIONAL	**SBR+BR**	**NR**	**Tot-rubber**	**Rubber-%**
AVERAGE	299	112	406	40.6
STD	67.1	95.0	50.5	5.05
MEDIAN	294	95	397	40
MIN	189	7.11	357	35.7
MAX	392	268	493	49.3
N	7	7	7	7
GREEN	**SBR+BR**	**NR**	**Tot-rubber**	**Rubber-%**
AVERAGE	275	89.2	364	36.4
STD	123	135	78.9	7.89
MEDIAN	320	20	364	36
MIN	17.3	0	223	22.3
MAX	366	408	485	48.5
N	9	9	9	9
SUMMER	**SBR+BR**	**NR**	**Tot-rubber**	**Rubber-%**
AVERAGE	339	22.6	358	35.8
STD	30.9	32.5	35.9	3.59
MEDIAN	341	7	364	36
MIN	301	0	302	30.2
MAX	392	94.7	399	39.9
N	9	9	9	9
WINTER	**SBR+BR**	**NR**	**Tot-rubber**	**Rubber-%**
AVERAGE	245	152	397	39.7
STD	113	86.1	92.2	9.22
MEDIAN	282	177	397	40
MIN	17.3	8.40	223	22.3
MAX	368	268	493	49.3
N	7	7	7	7

concentrations were significant different between the groups (ANOVA, SBR+BR: $p = 0.020$, NR: $p = 0.00017$) (Fig. 4), which has not been reported in previous studies. In the study by Rødland et al. [57], no significant difference in SBR+BR concentration was found by grouping the tires as PV and HV or by seasonality. However, as the number of samples were higher in the previous study by Rødland et al. ($n = 31$) compared to this present study ($n = 17$), the observed significant difference might be also due to a lower number of samples.

3.4. Multivariate analysis

Using the different components analyzed in this study (metals, organic compounds, and rubbers) and multivariate techniques (redundancy analysis RDA, principal component analysis PCA), the relationship between different components was investigated for all tires and groups of tires.

A PCA applied using the concentrations of the metals (Zn, Ca, Cu, Cr, Cd, Fe, Mg, Al, Pb, Na), the organic compounds (6PPD, 6PPD-Q, TMQ-A and TMQ-B) and the rubbers (SBR+BR, NR) as inputs segregate the "conventional" tires cluster (Fig. 5, yellow color), while the "green" tires result widely spread considering principal components 1 and 2 (explaining 57 % of the total variance), demonstrating a large variability in additive and metal levels across different producers. The same variation and pattern are also seen if PCA analysis of metals and organic compounds are performed separately, in the PCA performed on the metal data (metals: 64 %, organic compounds: 94 %) (Figs. S13 and S14). If we only focus on the car tires and remove the bike tire (BT1) from the PCA, the grouping of green vs conventional tires (Fig. S15) shows the same general trends as seen in Fig. 5, and the variation explained by PC1 and PC2 is similar (52 %).

A PCA plot (Fig. 6) using different markers for SBR+BR and NR rubber demonstrates that the different tires are more likely to be similar to other tires with the same seasonal purpose, rather than being defined as environmentally friendly (Fig. 6, green color) or not (Fig. 6, yellow color) for components 1 and 2 (explaining 85 % of the variance). It also shows that there is a bias in the dataset, as most (70 %) of the "green" tires that was obtained on the commercial market were summer tires, whereas 71 % of the "conventional" tires were winter tires. This however was driven by the fact that to date "green" labelled tires available on market encompasses mostly products for the summer season.

To test if the variation observed could be attributed to various tire brands, an RDA analysis using metals, organic compounds and rubbers as response variables and the brands as explanatory variables was performed (Fig. 7). A weak (11 %) non-significant ($p = 0.1669$) correlation was observed, indicating a lack of relation between tire brands and chemical composition previously reported [65,79].

A significant correlation was observed between rubbers (SBR+BR, NR), metals and organic compounds using RDA (Fig. 8, $p = 0.0065$), where 19 % of the variation observed for the metals and organic compounds could be explained by the variation of SBR+BR and NR. While the relationship cannot be considered as very strong, it indicates that higher concentration of natural rubber is associated with higher concentration of metals and TMQ, whereas higher concentration of synthetic rubber is more related to higher concentrations of 6PPD and Na. Both metals and organic compounds are added to tires during the production process, some intentionally and some unintentionally (80), however, limited available information exists about how variation in both types and mass percentage of synthetic rubber and natural rubber could influence the presence of metals and organic compounds in tires. The results presented in this study indicate that changes in the rubber composition also come with potential trade-offs in chemical composition with a potential environmental relevance. If the efforts to replace natural rubber from rubber trees with the more sustainable rubber from dandelion or guayule leads to an increase of natural rubber in tires, the results from this present study suggest that these sustainable tires may also have higher concentrations of metals compared to tires with more synthetic rubber. More research is urgently needed on this topic.

For 13 of the 17 tires tested in this study, EU Tyre Label data was available and could be used to test if there is a relationship between the chemical composition and the scores for each tire in the label. The A-E ranking of rolling resistance and wet grip were changed to numeric for the RDA analysis (with A-E are converted as 5–1). For the noise level, the actual noise level (in dB) was applied instead. Only a weak relationship was found between the rubbers, the selected metals and the selected organic compounds, explaining 4.2 % (not significant, $p = 0.2821$), however the RDA plot (Fig. 9) indicates that there might be trends to discover between the different parameters used to evaluate tires for the EU Tyre Label. As an example, there is a trend seen in Fig. 9 indicating that both higher rolling resistance and increased wet grip are linked to higher levels of synthetic rubber and 6PPD. However, as this study had a limited number of tires samples and a limited number of organic compounds investigated, more research is needed to understand the link between the tire characteristics and the chemical composition, especially as decreasing of the rolling resistance has been extensively put on focus for the current "green tires" tested in this study. This is due to the current attention to a reduction of CO_2 emission from fuel consumption and the increasing driving range for electric vehicles. Although there is a weak correlation, this study indicates that the green tires (green dots) are associated with increased rolling resistance (Fig. 9). As there is limited openly available knowledge of how tire producers change tire formulations to adjust to the "tire triangle" (Fig. 1), there is also limited possibilities to risk assess what the future changes to this "triangle" will be in terms of environmental impact, especially with the upcoming focus on abrasion resistance due to Euro7 and the increasing focus on "green, sustainable tires". As the upcoming Euro7 only focuses on reduction in abrasion of tires, with no consideration of chemical composition, this

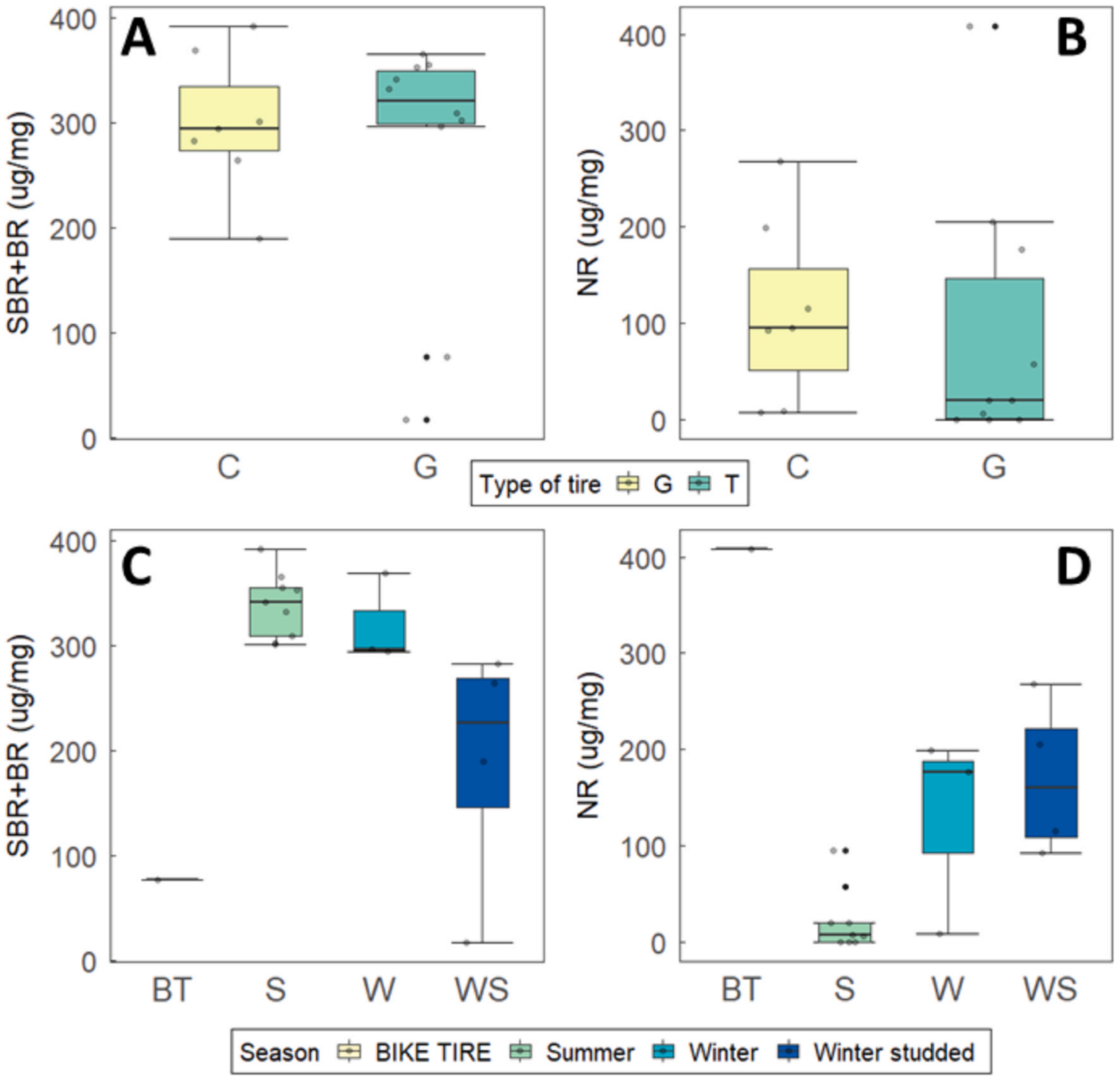

Fig. 4. A) Concentrations of styrene butadiene rubber and butadiene rubber (SBR+BR) in "conventional" tires compared to "green" tires. No significant difference between the groups were observed (ANOVA, p = 0.65). **B)** Concentrations of natural rubber (NR) in "conventional" tires compared to "green" tires. No significant difference between the groups were observed (ANOVA, p = 0.706). **C)** Concentration of SBR+BR in tires grouped by season. Significant differences between the groups summer (S), winter tires (W), winter tires studded (WS) and bike tire (BT) were observed (ANOVA, p = 0.00199). **D)** Concentration of NR in tires grouped by season. Significant differences between the groups were observed for BT, S, W and WS (ANOVA, p = 0.000174).

should be highlighted as a major limitation regarding regulation of the environmental impact of tires and tire wear particles.

4. Conclusions

Based on the results presented in this study, more research is needed to investigate the full chemical composition of different types of tires, including those sold as "green, sustainable and eco-friendly friendly" options. The green tires that were tested in this study did contain the same levels of metals, organic compounds and similar types of rubbers as the group of "conventional" tires, which indicates that tires marketed as "green options" not necessarily are more environmentally friendly in terms of their chemical composition. This finding furthers the need for a standardized labelling system for tires that includes different aspects of "sustainability" to improve both transparency and ensure that customers can make conscious choices. For some compounds, including those of environmental and health concern (such as 6PPD), the "green" tires even had higher concentrations compared to the "conventional" ones. Thus, disproving the hypothesis in the first objective of this study, the levels of compounds associated with toxicity and environmental impact of the study were not significantly lower in the "green" tires compared to the "conventional" tires. However, in future research, a non-target approach using multiple analytical techniques should be used to further investigate if there are other compounds outside the selected and known compounds of this study that can be related to different types of tires, and potentially induce a higher environmental risk compared to those that are already known.

The classification of tires as either "green" or "conventional" did not correspond to any significant difference between the groups, thus disproving the hypothesis of the second objective. However, classifying the tires according to their seasonal use did explain a significant proportion of the observed variation. Using the EU Tyre Label classifiers, lower rolling resistance is indicated to be related to higher levels of both synthetic rubbers and 6PPD. To fully understand the link between the tire features and the chemical composition, more in-depth studies are needed.

The results of this study indicate the need to include chemical composition of tires when considering their environmental impact. The environmental impact from tires is not only related to CO_2 emissions or the use of sustainable raw materials. The environmental impacts from

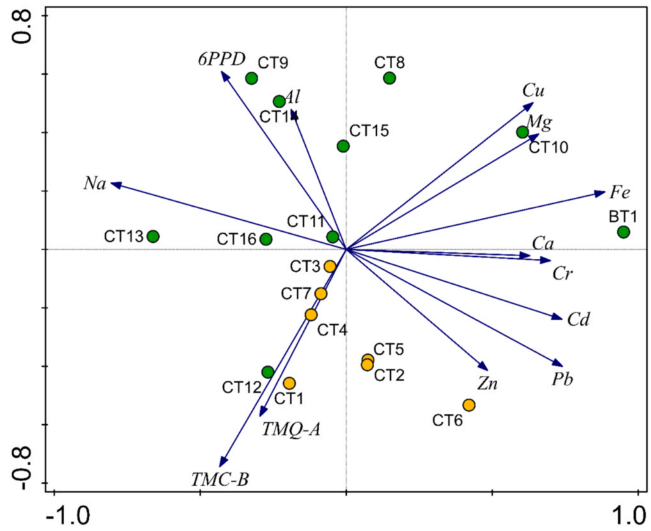

Fig. 5. Principal components analysis (PCA) of all tires using the concentration of metals (Zn, Ca, Cu, Cr, Cd, Fe, Mg, Al, Pb, Na), organic compounds (6PPD, TMQ-A and TMQ-B) and rubbers (SBR+BR, NR). Green dots are the "green" tires and yellow dots are the "conventional" tires. Principal components 1 and 2 explain 57 % of the total variation.

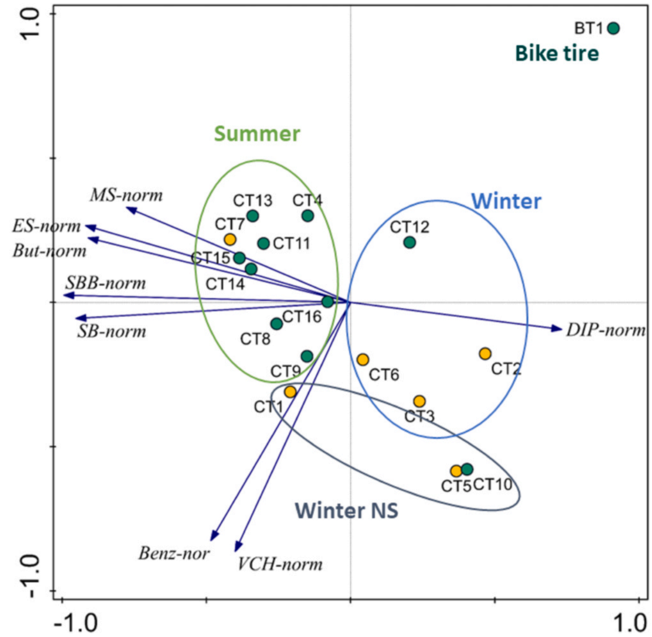

Fig. 6. Principal components analysis (PCA) of all tires using peak height of different markers for SBR+BR normalized by internal standard (d_6-PB): Benzene (Benz-norm), 4-vinylcyclohexene (VCH-norm), methylstyrene (MS-norm), ethylstyrene (ES-norm), butadiene dimer (But-norm), styrene butadiene dimer (SB-norm) and styrene butadiene trimer (SBB-norm), and the marker for NR normalized by d_6-PB: dipentene (DIP-norm). Green dots are the "green" tires and yellow dots are the "conventional" tires. Groups are depicted by circles: green (summer), blue (winter), grey (Winter non-studded, NS) and the bike tire (BT) as the outlier in the upper right corner. Principal components 1 and 2 explain 85 % of the total variation.

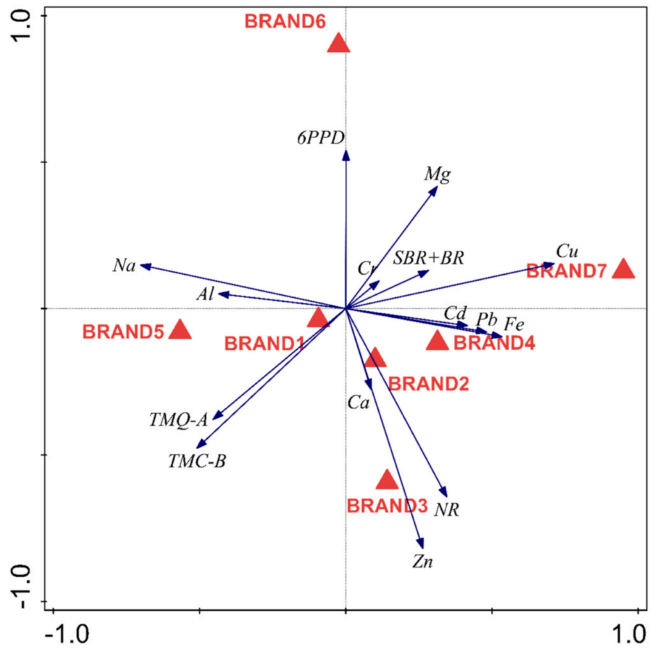

Fig. 7. Redundancy analysis (RDA) using the metals (Zn, Ca, Cu, Cr, Cd, Fe, Mg, Al, Pb, Na), organic compounds (6PPD, TMQ-A and TMQ-B) and rubbers (SBR+BR, NR) as response variables and the tire brands as the explanatory variables. Brands explained 11 % of the variation (not significant, $p = 0.1669$).

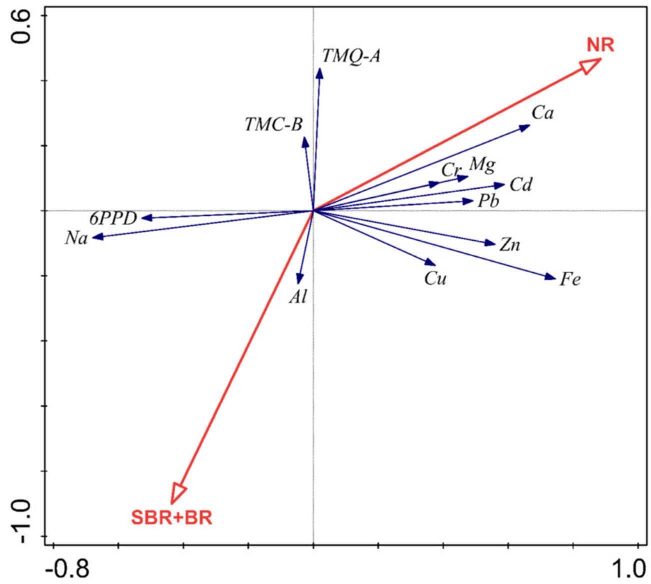

Fig. 8. Redundancy analysis (RDA) using the metals (Zn, Ca, Cu, Cr, Cd, Fe, Mg, Al, Pb, Na) and organic compounds (6PPD, TMQ-A and TMQ-B) as response variables and the rubbers (SBR+BR, NR) the explanatory variables. Rubbers explained 19 % ($p = 0.0065$) of the observed variation in metals and organic compounds.

direct effects of TRWP and their chemical additives on a local scale should also be considered when discussing sustainability and "green" options for vehicle transport. Future studies should continue to investigate the chemical composition of different types of tires, as well as including experiments simulating both abiotic stress factors (such as temperature, UV, mechanical stress) and biotic stress factors (such as fouling, microbial degradation) under controlled scenarios. In addition, leaching tests to monitor the potential variation in leaching capabilities from different tires should be included.

Environmental implications of this study

As several tire-related compounds have been found to cause severe negative impact in the environment and especially for aquatic organisms, it should be imperative that we observe less of these compounds in

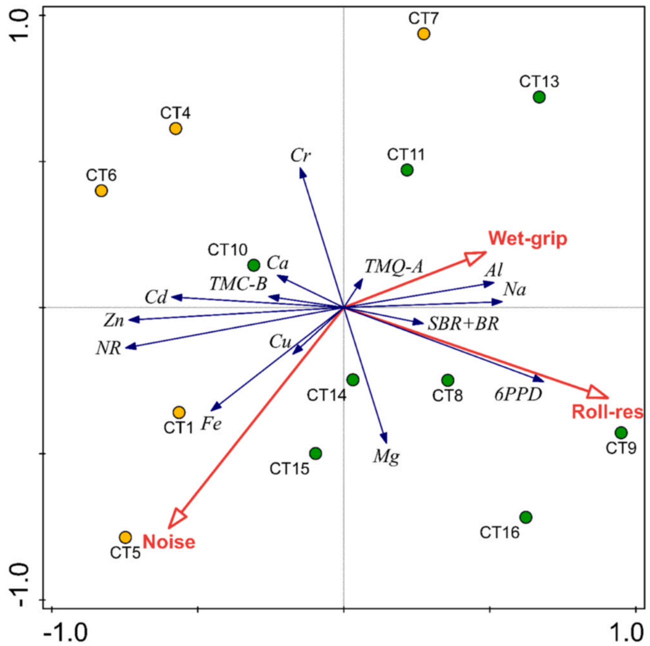

Fig. 9. Redundancy analysis (RDA) using the metals (Zn, Ca, Cu, Cr, Cd, Fe, Mg, Al, Pb, Na), organic compounds (6PPD, TMQ-A and TMQ-B) and rubbers (SBR+BR, NR) as response variables and the EU Tyre Label factors (rolling resistance, wet grip and noise) as explanatory variables. Rolling resistance, wet grip and noise explained 4.2 % ($p = 0.2821$) of the observed variation in metals, organic compounds and rubbers. Green dots depict “green tires”, and orange dots depict “conventional tires”.

tires that are being sold as better options for the environment. Our study demonstrates that such assumptions are wrong, and some of these “green” options even had higher levels of compounds that have been linked to toxicity, such as Cu, Cr, Al, and 6PPD. As such, these “green” tires are potentially just as hazardous to the local environment as “conventional” tires.

CRediT authorship contribution statement

Elisabeth Støhle Rødland: Writing – original draft, Visualization, Project administration, Formal analysis, Data curation, Conceptualization. **Gilberto Binda:** Writing – review & editing, Conceptualization. **David Spanu:** Writing – review & editing, Formal analysis. **Stefano Carnati:** Writing – review & editing, Formal analysis. **Laura Röhler Bjerke:** Writing – review & editing, Formal analysis. **Luca Nizzetto:** Writing – review & editing, Funding acquisition, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

This work was funded by the Research Council of Norway (grant 342628).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2024.135042.

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