

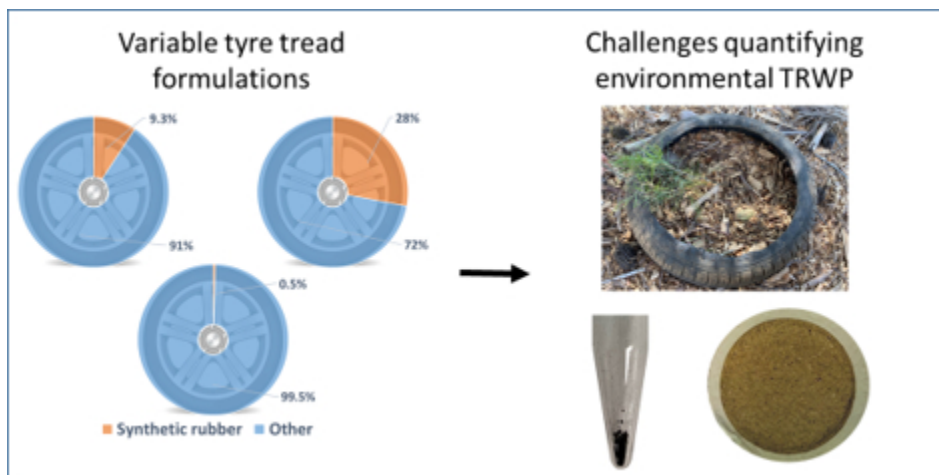
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TOC Art

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1 Challenges with quantifying tyre road wear particles – Recognising the need for further
2 refinement of the ISO technical specification

3
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11
12 **Abstract**

13 Environmental monitoring data on tyre road wear particles are vastly limited compared to other
14 microplastics, primarily due to analytical challenges with quantification. Recently, two ISO technical
15 specifications have been released using Pyrolysis GC-MS for quantification. However, these methods
16 have major assumptions including that the content of natural and synthetic rubber in tyre tread is
17 constant across formulations, and that the pyrolysis products chosen are selective. This study analysed
18 a wide range of commercially available tyres from Australia and Norway, using Pyrolysis GC-MS to test
19 these assumptions. The %mass of synthetic rubber in tyres (n=39) was highly variable ranging <0.05
20 to 28% when using the ISO recommended pyrolysis product 4-vinylcyclohexene. Content varied
21 between brands and models, demonstrating that formulations are highly variable and unknown. The
22 styrene butadiene dimer and trimer pyrolysis products were also assessed, and the calculated
23 synthetic rubber content was higher, had an even greater variability, and no correlation with
24 concentrations calculated using 4-vinylcyclohexene. Using the ISO method has the potential to
25 underreport environmental concentrations of TRWP by at least a factor of five, suggesting the
26 specification requires further refinement, and there is an immediate need for large-scale analysis of
27 commercial tyre treads and assessments of suitable pyrolysis products.

28
29 **Introduction**

30 Tyre road wear particles (TRWP) are a significant contributor to the total environmental burden of
31 plastic debris^{1, 2}, yet are vastly underrepresented in environmental assessments of plastic pollution.
32 TRWP are formed through abrasion of vehicle tyres on road surfaces during driving, accelerating and
33 braking. Their composition is a mixture of natural and synthetic rubber so they are considered a source
34 of microplastic to the environment.³ Tyres have been estimated to release up to 12% of their mass to
35 the environment over their lifetime⁴ and are one of the primary sources of microplastics to the
36 environment⁵, estimated to contribute 5-10% of the total plastic burden in the oceans which is second
37 only to discarded plastic debris.³ Annual emissions of tyre wear for different countries have been
38 estimated to be between 0.2 to 5.5 kg/capita*year.⁶

39 The presence of TRWP in the environment is of high concern due to their occurrence in a size range
40 that is easily digestible by organisms and reports of ecotoxicological effects.^{6, 7} It is also estimated that
41 0.1-10% of TRWP released into the environment is airborne, providing an inhalation risk to human
42 health.⁶ Further concern arises from the chemicals that are incorporated in the tyre material, with

43 potential to leach into the surrounding environment. These include of a range of metals and organic
44 additives that are used in the tyre production process, including vulcanisers.^{7, 8} These chemical
45 additives have demonstrated toxicity to aquatic species at environmentally relevant concentrations.^{6,}
46 ^{9, 10} Sorption of organic compounds to tyre material may also provide another source of contaminant
47 transport and exposure to the surrounding environment.^{11, 12}

48 Compared to other plastics in the environment, such as marine plastic debris, little is understood
49 about the occurrence and fate of TRWP in the environment. This is largely due to ongoing analytical
50 challenges with environmental monitoring of TRWP, and as a result data on environmental
51 concentrations is rare.⁶ TRWP have been identified and quantified in environmental samples using a
52 range of methods from microscopic identification of individual particles (e.g. scanning electron
53 microscopy energy dispersive X-ray spectroscopy) to using marker chemicals such as benzotriazoles
54 (vulcaniser accelerators) and zinc to quantify mass of TRWP in a sample.^{6, 13} These methods are
55 unreliable for quantification as microscopy methods will only identify particles within a certain size
56 range with limited characterisation of composition of particles, and marker chemicals may have
57 competing sources in the environment or leach from the TRWP over time.¹⁰ Alternatively, TRWPs have
58 been quantified using marker compounds produced by the thermal destruction of the polymers in the
59 tyre tread themselves, a process known as pyrolysis. Pyrolysis coupled to gas chromatography flame
60 ionization detection (GC-FID) has been used in the analysis of tyre polymers in environmental samples
61 since the 1960s, but more recently pyrolysis coupled to GC-mass spectrometry (Pyr-GCMS) has been
62 developed as a more selective and sensitive quantification method.⁴

63 Following the research from Kreider et al.¹⁴ and Unice et al.^{4, 15}, the International Organization for
64 Standardization (ISO) has published two technical specifications (ISO/TS 21396:2017(E) and ISO/TS
65 20593:2017(E)) for quantifying TRWP in soil/sediment and air with Pyr-GCMS.^{16, 17} The ISO methods
66 use marker compounds formed from the pyrolysis of natural rubber (NR) and synthetic rubber namely
67 styrene butadiene rubber (SBR) and butadiene rubber (BR), in the tyre tread. However, a number of
68 assumptions are made in the methodology for quantifying TRWP concentrations. For instance, the
69 method assumes that the pyrolysis products formed are specific for rubber polymers (no competing
70 sources), and that the total mass of synthetic + natural rubber in all tyre tread is constant. The ISO
71 method uses the assumption that total rubber content is 50% of the mass of the tread and that
72 passenger tyres contain 44% SBR+BR and truck tyres contain 45% NR.⁴ These compositions are pivotal
73 in calculating the total mass of TRWP in an environmental sample, and while obtained from only a few
74 examples of tyre formulations^{8, 18, 19} the list is not exhaustive and formulations will likely vary between
75 manufacturer and model¹⁹, information which is not generally disclosed by manufacturers.²⁰ It is
76 worth noting that these ISO methods are technical specifications, and by definition intended to
77 address work still under technical development, providing the means for feedback and refinement,
78 with the aim of eventually being republished as an International Standard.²¹

79 The European TRWP Platform, which includes a multi-sectorial stakeholder roundtable including Tyre
80 corporate members and National Associations, stated in their most recent report that one of the key
81 priorities in this field of research is to “develop and agree on a scientific methodology to empirically
82 study TRWPs in the environment”.²² The Platform includes members of the Tire Industry Project, a
83 consortium of 11 tyre companies that contributed to the development of the ISO methods, and the
84 recognition that further method development is required, supports the need for continued validation
85 and refinement of these ISO technical specifications.

86 The current study aimed to assess the Pyr-GCMS methods listed in the technical specifications ISO/TS
87 21396:2017(E) and ISO/TS 20593:2017(E) for quantifying TRWP in environmental samples, with the
88 aim of providing further assessment for continued refinement of the specifications. The analytical

89 methodology was repeated with tyre tread from a wide range of commercially available tyres in
90 Australia and Norway to test the above assumptions, and further identify and discuss immediate
91 challenges in quantifying TRWP in environmental samples.

92 **Materials and Methods**

93 Chemical details

94 Reference standards of the polymers SBR 1500, polyisoprene (PI), deuterated polybutadiene (d_6 -PB)
95 and deuterated polyisoprene (d_8 -IP) were purchased from Polymer Source Inc. (Dorval, Canada).
96 Further details on the polymer standards, including isomer contents are provided in Table S1. Liquid
97 chromatography grade dichloromethane (DCM) and liquid chromatography grade chloroform were
98 purchased from Merck (Darmstadt, Germany).

99 Tyre sample details and preparation

100 Samples of new tyre tread ($n=31$) were obtained directly from the manufacturer in Norway and
101 included 18 different models of passenger tyres and 13 models of truck tyres. Samples of worn tyre
102 tread ($n=8$) were donated from a private residence in Australia and included 7 different models of
103 passenger tyres and 1 truck tyre, details in Table S2.

104 The tyre tread was sub-sampled using a scalpel that was pre-cleaned with DCM, removing a fragment
105 1-2 mg in size and immediately placed in a sample (pyrolysis) cup (Eco-Cup LF, Frontier Laboratories,
106 Japan). The sample cup was weighed, then spiked with 76 μg of d_6 -PB as an internal standard prior to
107 analysis.

108 Sample analysis

109 Australian samples were analysed at the Queensland Alliance for Environmental Health Sciences
110 (QAEHS, UQ, Australia) and the Norwegian samples at the Norwegian Institute for Water Research
111 (NIVA, Norway) with the same model multi-shot micro-furnace pyrolysers (EGA/PY-3030D) equipped
112 with auto-shot samplers (AS-1020E, Frontier Lab Ltd., Fukushima Japan). The pyrolysis methods were
113 based on the method in Okoffo et al.²³ and specific details are listed in Table S3. To validate
114 comparability of the two methods, 13 Norwegian tread samples (10 passenger and 3 truck tyre tread)
115 were analysed at both institutes, with acceptable agreement in calculated synthetic rubber
116 concentrations, Figure S1 and discussed further in the Results.

117 Indicator pyrolysis products for tyre tread

118 Tyre tread contains a blend of synthetic rubbers, including styrene butadiene rubber (SBR) and
119 butadiene rubber (BR), and natural rubber (NR).^{4,19} Following the ISO methods, the pyrolysis product
120 4-vinylcyclohexene (VCH), a dimer of both SBR and BR, was monitored for quantifying the mass of
121 SBR+BR in samples, Table 1. The ISO method was also followed for preparation of isoprene rubber and
122 deuterated isoprene solutions to monitor NR, however these standards were not successfully
123 dissolved in chloroform following the ISO procedure. Therefore, calibration curves were not prepared
124 for analysis of NR, and the dipentene (DP) pyrolysis product was monitored for qualitative
125 identification of NR only.

126 A calibration curve for SBR+BR was prepared following the procedure in the ISO method, using SBR
127 1500 as a surrogate for SBR+BR, with concentrations ranging 1 to 100 μg . The calibration was linear
128 over this range with $R^2 > 0.994$.

129 The SBR+BR pyrolysis products of styrene butadiene hybrid dimer (SB) and hybrid trimer (SBB) were
 130 also monitored to compare quantification of SBR+BR concentration with different pyrolysis products.
 131 These products were chosen due to being the next abundant to VCH and styrene²⁴ and may have less
 132 competing sources than VCH.²⁵ d₆-PB was used as an internal standard to recovery correct
 133 concentrations of VCH, SB and SBB. To calculate the concentration of SBR+BR from the VCH pyrolysis
 134 product concentration, a correction factor of 0.9 was applied, as outlined in the ISO method. This is
 135 suggested to correct for the difference in styrene content between SBR 1500 used in the calibration
 136 curve of 23.5%, and the suggested SBR formulation used in the tyre industry of 15%: $(1-0.235) / (1-$
 137 $0.15) = 0.9$. For the SB and SBB pyrolysis products, which are formed from SBR and not BR, a correction
 138 factor of 1.57 $(0.235/0.15)$ was applied to calculate the SBR+BR concentration.

139 *Table 1. Pyrolysis marker compound details as identified in Tsuge et al.*²⁴

Tyre marker	Pyrolysis Product	Abbr.	Associated IS	Monitored ions (m/z)	Retention Time* (min)	LOD (µg)
SBR	4-vinylcyclohexene	VCH	d ₆ -PB	54, 79, 108	4.42	0.5
	SB hybrid dimer (C ₁₂ H ₁₄) (Benzene, 3-cyclohexen-1-yl) ²⁶	SB	d ₆ -PB	104, 158, 91	9.09	5
	SBB hybrid trimer (C ₁₆ H ₁₂)	SBB	d ₆ -PB	104, 91	11.00	1
d ₆ -PB	d ₆ 4-vinylcyclohexene	d ₆ -VCH	--	60	4.33	--
NR	Dipentene (Qualitative only)	DP	--	68, 136	6.56	--

140

141 QA/QC

142 As further confirmation that the pyrolysis was efficient (complete decomposition of the tread particle),
 143 one tyre (C2) was further tested by triplicate analyses of three different masses (0.1, 1 and 2mg) with
 144 pyrolysis hold times of both 12s and 24s. All masses and pyrolysis times resulted in consistent VCH
 145 concentration (46 ± 6 µg/g, Table S4), indicating the method was efficient.

146 Blank cups were run with every batch and target compounds were below detection limits in every
 147 blank. Limits of detection (LODs) were calculated as the concentration of a peak that is three times
 148 the noise level, Table 1. At least two ions were monitored for confirmation of each pyrolysis product,
 149 and the ratio of quantification ion to confirmation ion was monitored for interferences or matrix
 150 effects. The VCH and SBB ratios were within an acceptable variation of the mean ratio in the calibration
 151 standards ($\pm 14\%$ and $\pm 13\%$ respectively). The SB ratios had greater variability ($\pm 50\%$), which is
 152 influenced by the higher LOD of this pyrolysis product, with confirmation peaks close to the
 153 background noise level. Statistical analyses including regression analysis (95% confidence level), non-
 154 parametric comparison of means (Kruskal-Wallis H test) and Bonferroni corrected Mann Whitney U
 155 post-hoc test ($\alpha=0.015$) were performed with IBM SPSS Statistics version 25.

156 Results and Discussion

157 Calculation of SBR content in tyre tread

158 There was a large variation in concentrations of SBR+BR in the tyre tread samples, with % mass of
 159 SBR+BR in each tyre tread (calculated using VCH) ranging <0.05 to 28% (Figure 1, Table S5). In all tread
 160 samples the SBR+BR calculated content was well below the assumed SBR+BR mass of 44% in passenger
 161 tyres.⁴ There was a variability not just between brands, but also between models within brands, with
 162 a relative standard deviation (RSD) of 58% between all the tread samples. Furthermore, one tread

163 (Deli Tire) did not contain measurable concentrations of SBR+BR with VCH, SB and SBB pyrolysis
164 products all below LODs.

165 Interestingly, nine of the fourteen truck tyres contained the highest % compositions of SBR+BR (10-
166 28%, calculated from VCH). It had previously been assumed that truck tyres were 100% natural
167 rubber^{4, 27} or contained a higher proportion of NR as compared to passenger cars.²⁸ The one other
168 study to analyse truck tyres for SBR reported concentrations below detection limits in the 2 tyres
169 analysed, although they used thermal extraction and desorption GC-MS (TED-GC-MS) for analysis.²⁵
170 This study confirms that truck tyres can contain measurable concentrations of SBR+BR as a major
171 component of their formulation, and further demonstrates the high variability in formulations used
172 by tyre manufacturers.

173 DP (the pyrolysis product for NR) was detected in all samples, also with highly variable peak areas,
174 Figure S2. There was no statistical relationship ($n=21$, R^2 -adjusted=0.03, $p=0.22$) between normalised
175 peak areas of DP and VCH, indicating that an increased use of SBR+BR did not equal decreased use of
176 NR (keeping total content of SBR+BR+NR of 50% as assumed in the ISO method). The DP peak area in
177 the Deli Tire (where SBR+BR was below LOD) was not elevated compared to the other tyres, again
178 indicating that this tyre would have less than the assumed 50% mass of SBR+BR+NR in the tyre.

179 Using the pyrolysis products SB and SBB to calculate SBR+BR concentrations saw greater variability in
180 the calculated concentrations (%RSD of 62-69%), Table S5. In the majority of samples, concentrations
181 of SBR+BR were higher when calculated with SB or SBB, with a statistically significant difference
182 between all three groups as determined by Kruskal-Wallis H test ($H=37$, $p<0.001$) and Bonferroni
183 corrected Mann Whitney post hoc test ($p<0.012$). The reproducibility of replicate sub-samples of the
184 same tyre tread also varied (%RSD of 1-67% for the three pyrolysis products), suggesting a lack of
185 homogeneity of the rubber within the tyre itself. The replicate analyses at QAEHS and NIVA were more
186 reproducible than the variation within the tread itself and were highly correlated ($n=39$, R^2 -
187 adjusted=0.86, $p<0.001$), Table S6 and Figure S1. Quantifying using SB had greater variability but was
188 still within the variation observed in the tread samples themselves. However, this higher variability for
189 the SB pyrolysis product, its higher detection limit (and higher RSDs with the ion ratios), and that some
190 concentrations were unreasonably high at 100% SBR+BR content in the tyre tread, suggests it is not a
191 suitable product for quantification of SBR+BR concentration using this method.

192 Eisentraut et al.²⁵ also reported a similar variation in SBR content (55%) from analysis of 12 tyre
193 samples with TED-GC-MS. Instead of assuming tyre tread is 50% natural and synthetic rubber, they
194 took worldwide production tonnages of major elastomer tyre compounds and individual fractions
195 used for tyre production for all types of tyres, for an estimated average SBR content in tyre material
196 of 11.3%. This estimate is closer to the average SBR content in the 39 tyre samples analysed in this
197 study of 9.3%.

198 Although information is limited on tyre manufacturing, there are reported to be two general processes
199 for manufacturing tyre material, emulsion and solution, and they each have numerous recipes. The
200 solution process is particularly complex as it is difficult to produce consistent molecular weights and
201 degrees of branching in the polymer.¹⁹ Differences in the final polymer between formulations may
202 lead to the variations in concentrations of the dimer and trimer, as compared the VCH, observed in
203 these samples.

204 Furthermore, the butadiene monomer in SBR can exist in various geometric isomers including 1,2-
205 butadiene, and *cis*- or *trans*-1,4-butadiene. Formation of VCH has been shown to increase with the
206 amount of 1,4-butadiene present and decreases with the mass of 1,2-butadiene present.²⁹ and if the

207 tyre composition is different to the composition of the SBR 1500 standard (87% 1,4-butadiene and
208 13% 1,3-butadiene which forms 1,2-butadiene with polymerisation, Table S1) a variable VCH
209 concentration would result. Again, this information on tyre compositions is not known and ideally
210 would be obtained from the manufacturer, or could be determined in individual tyres from analysis of
211 different standards.^{30, 31}

212 *Implications*

213 Using the VCH ion to calculate the concentration of TRWP in tread and assumed SBR+BR content in all
214 tyres of 50% has the potential to underreport TRWP concentrations by at least a factor of 5, if using
215 the average SBR+BR content in tyres from this study of 9.3%. However, as the detected SBR+BR %
216 mass was as low as 0.5% in these samples, the method has the potential to underreport
217 concentrations by a lot more, demonstrating that the methods require additional development.

218 Market averages of SBR in tyre manufacture, as used in previous studies including the ISO method,
219 are likely to have changed and will keep changing over time with technological advancements. Further,
220 recent use of synthetic rubber in the manufacturing of tyres in Australia has been increasing due to
221 an increase in NR prices.²⁸ This adds further challenges to quantification as compositions are also likely
222 to vary over time as well as by formulation.

223 Unless specific information on tyre formulations are provided by manufacturers, large scale testing of
224 commercially available tyres is needed to further understand this variability. With more data, a
225 probability distribution of SBR+BR content could be determined, to aid quantification of TRWP mass
226 in a sample.

227 Further challenges that need to be researched and addressed as a priority include:

- 228 • Large scale surveys on synthetic rubber content in common commercially available tyres are
229 needed. This should include country/region specific assessments that target known tyre use
230 for that region (e.g. studded- and non-studded winter tires + summer tyres in Norway or all-
231 year tyres in Australia).
- 232 • Further assessments are needed on the most appropriate pyrolysis product/s for calculation
233 of SBR+BR content. The high variability between the three products assessed in this study
234 demonstrates the importance of selecting appropriate products for environmental
235 assessments. Testing tyre tread samples where the formulation has been disclosed would be
236 of benefit to provide more information on this. It may also be more appropriate to monitor a
237 range of pyrolysis products for multiple lines of evidence.
- 238 • The assumption that VCH, SB and SBB pyrolysis products are selective for tyre rubber needs
239 to be addressed. Other polymers with similar building blocks such as acrylonitrile-butadiene-
240 styrene (ABS) or styrene-butadiene-styrene block copolymer (SBS) will likely form the same
241 pyrolysis products, and the influence of this on environmental samples needs to be assessed.
242 For example, SBS is often used as a bitumen modifier in asphalt applied to roads.³²

243 Quantification of TRWP in environmental samples still requires further validation and assessment. The
244 current standard methods require reworking and with the continually increasing number of studies
245 reporting TRWP in environmental matrices, improved understanding and quantification methods are
246 required as a matter of urgency.

247

248

249 **Supporting Information**

250 The Supporting Information (SI) is available free of charge at:

251 SI contents include polymer reference standard details, tyre tread sample details, pyrolysis method
252 details (Tables S1-S3); analysis results (Tables S4-S6); comparison of analysis at QAEHS and NIVA
253 (Figure S1); comparison of VCH and DP normalised peak areas (Figure S2).

254

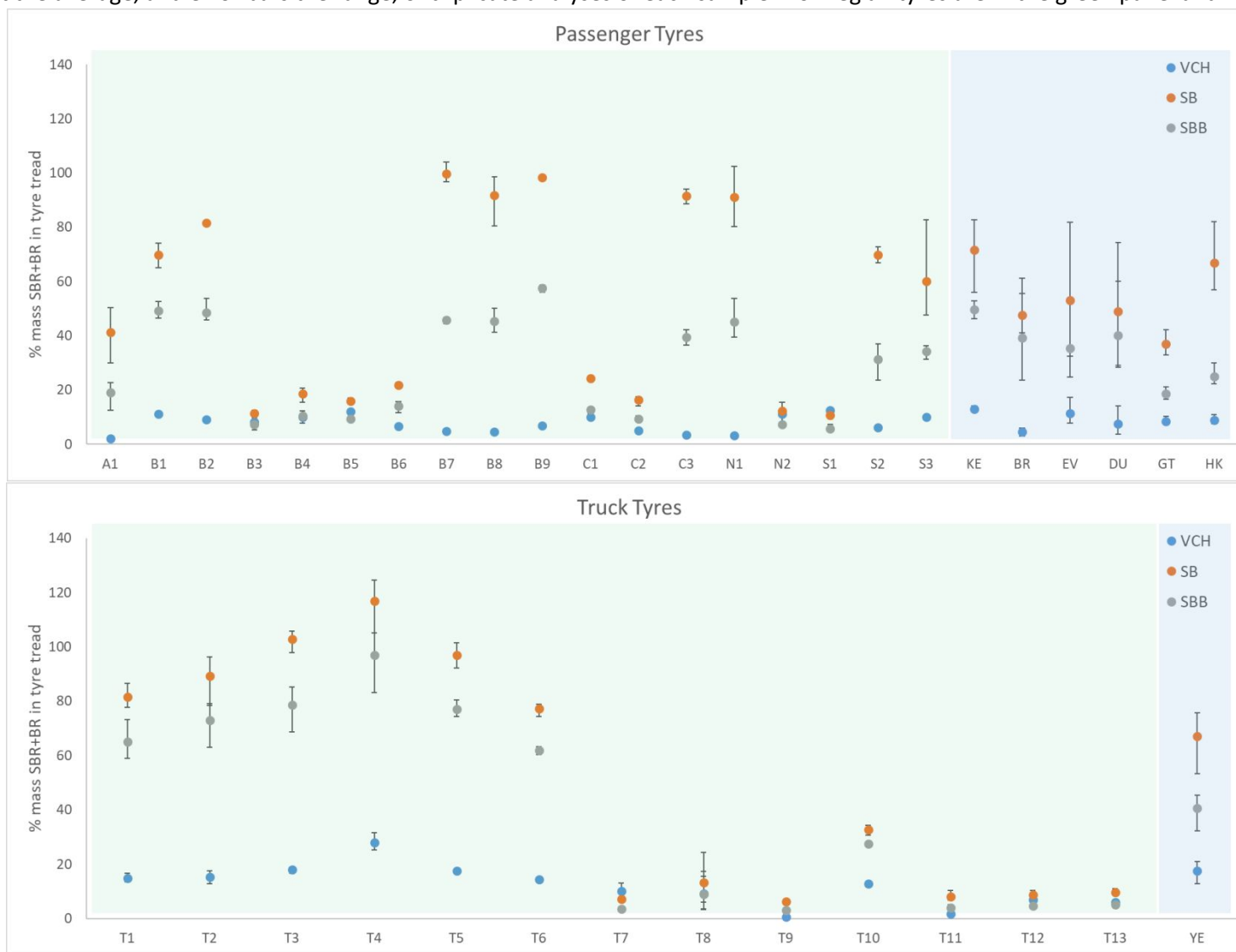
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261

262 Figure 1: Comparison of % mass of synthetic rubber in 24 passenger and 14 truck tyre tread samples, as calculated from VCH, SB and SBB pyrolysis products.
263 Points represent the average, and error bars the range, of triplicate analyses of each sample. Norwegian tyres are in the green panel and Australian in blue.

264



265

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