

1 Estimation of smokers' exposure to mercury from combustible tobacco products, based on the  
2 approach used in food consumers' exposure estimation.

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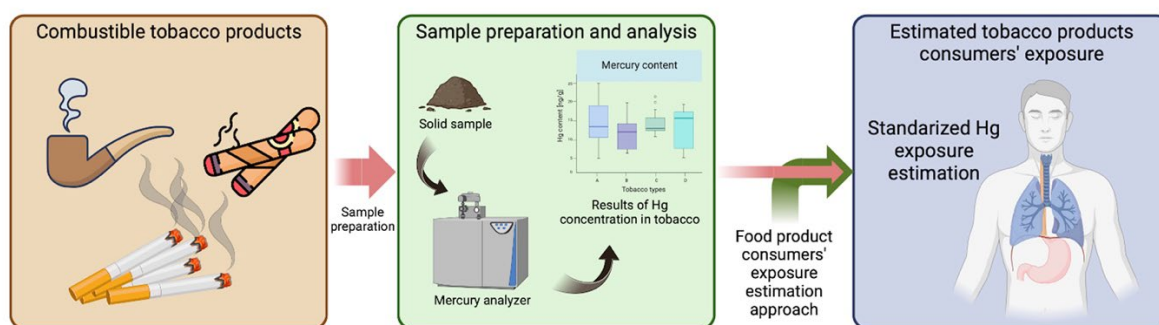
12 Keywords:

13 Tobacco, risk assessment, cigar, bidi, pipe tobacco, cigarette

## 14 Abstract

15 Smoking has been known to mankind for centuries, but it is only in recent decades that much  
16 attention has been paid to the harmfulness of this habit. Mercury inhalation is particularly  
17 dangerous in this respect and smoking creates extremely favorable conditions for the emission  
18 and targeted delivery of this element into the lungs. Despite this fact, a lack of a clear method  
19 for estimating the exposure of tobacco consumers to mercury was identified. This work shows  
20 justification to transfer the approach of estimating food product consumers' exposure to  
21 estimate the exposure of combustible tobacco product consumers to this element. In addition,  
22 it was noted that researchers' attention is mainly focused on cigarettes, while the tobacco  
23 market has a wide range of combustible products. Therefore, in this work, the mercury  
24 content of cigars ( $8.45 \pm 0.18 - 41.02 \pm 0.20 \mu\text{g/kg}$ ), pipe tobaccos ( $8.03 \pm 0.52 - 25.48 \pm$   
25  $0.50 \mu\text{g/kg}$ ), bidis ( $14.93 \pm 0.47 - 31.79 \pm 0.26 \mu\text{g/kg}$ ) and cigarette tobaccos ( $14.22 \pm 0.71 -$   
26  $34.5 \pm 1.4 \mu\text{g/kg}$ ) was analyzed. This study demonstrates that smoking can contribute  
27 significant total mercury exposure to consumers', although it is unlikely to cause mercury  
28 poisoning regardless of other exposure sources.

## 29 Graphical Abstract



30

## 31 1. Introduction

32 Mercury poisoning is a well-known issue that has been detailed and described in the scientific  
 33 literature (Ibrahim et al., 2006; Langford and Ferner, 1999; Mielcarek et al., 2022; Ronda et  
 34 al., 2022; Rutkowska et al., 2014). The toxicity, biochemical properties, and cycling of  
 35 mercury in the environment depend on the concentration and chemical form of this element  
 36 (Ibrahim et al., 2006; Neathery and Miller, 1975; Rutkowska et al., 2014). It has been  
 37 discovered that in general, organomercurials are more harmful than inorganic forms  
 38 (Rutkowska et al., 2014). Mercury vapors are also highly poisonous (Beate et al., 2010).  
 39 Although Hg is a liquid under normal conditions (Ibrahim et al., 2006; Langford and Ferner,  
 40 1999), it has a high vapor pressure, compared to other metals, of up to  $1.71 \cdot 10^{-1}$  Pa at 20 °C  
 41 (Huber et al., 2006). This vapor pressure corresponds to a mercury content of 14.09 mg/m<sup>3</sup> in  
 42 ambient air under set temperature conditions (applying ideal gas law) (Huber et al., 2006).  
 43 This value is far beyond recommended maximum volatile Hg concentrations established by  
 44 the organizations cited in this work (0.2 – 1.0 µg/m<sup>3</sup>) (Beate et al., 2010; Fresquez et al.,  
 45 2015; Richardson et al., 2008). Furthermore, its vapor pressure increases exponentially rather  
 46 than linearly with increasing temperature (it roughly doubles every 10 °C) (Langford and  
 47 Ferner, 1999).

48 Environmental mercury sources can be both natural (e.g., volcanic eruptions and forest fires)  
 49 and anthropogenic (Langford and Ferner, 1999; Rutkowska et al., 2014; Shen et al., 2022;  
 50 Sommar et al., 2020). An example of an anthropogenic source of mercury is the use of plant  
 51 protection products containing organomercury compounds (Amin-Zaki et al., 1974; Dameron  
 52 and Harrison, 1998; Elhassani, 1982; Ibrahim et al., 2006; Neathery and Miller, 1975). It must  
 53 be mentioned that not only the toxicity of this metal and its compounds are a great danger, but  
 54 also its bioaccumulation (Ronda et al., 2022; Rutkowska et al., 2014). This effect is amplified

55 as the trophic level increases, in a process known as biomagnification (Langford and Ferner,  
56 1999; Rutkowska et al., 2014).

57 Tobacco (*Nicotiana Tabacum L.*) and other plant products (which are the first link in the food  
58 chain) are the primary sources of exposure to mercury. It has also been observed that Hg is  
59 mostly found in plants in the form of organometallic compounds (Rutkowska et al., 2014) so  
60 it is expected that the organic form of Hg is the most prominent one in tobacco. Therefore, the  
61 risk of mercury contamination of food products should not be underestimated, especially  
62 given the number of recorded cases of severe poisoning and death (Amin-Zaki et al., 1974;  
63 Ibrahim et al., 2006; Langford and Ferner, 1999; Rutkowska et al., 2014). A prominent  
64 example is the infamous "Iraq poisoned grain disaster" of 1971, in which over 6000 people  
65 were poisoned by methylmercury after eating bread produced from contaminated wheat flour  
66 (Amin-Zaki et al., 1974; Bakir et al., 1980; Ibrahim et al., 2006).

67 Tobacco is one of the most extensively produced plants. According to the "Statista" website,  
68 the annual world production of tobacco ranged between 6 and 8 million tons from 1990 to  
69 2019 (M. Shahbandeh, 2021). Such level of production stays in response to equally great  
70 market demand (Le Foll et al., 2022). Every year, millions of tons of tobacco are being  
71 smoked in a variety of places (corresponding to the dispersion of consumers) (Le Foll et al.,  
72 2022). As mentioned above, combustion processes (e.g., fossil fuels or forest fires) are  
73 significant sources of mercury emissions into the environment (Rutkowska et al., 2014;  
74 Sommar et al., 2020). Therefore millions of tons of burnt tobacco can be considered to have a  
75 moderate contribution to natural sources of Hg emissions to the environment worldwide (Le  
76 Foll et al., 2022). In addition, human exposure as a result of smoking combustible tobacco  
77 (CT) products is likely to be significant because it is direct and targeted at the lungs, where  
78 volatile mercury is well absorbed (Beate et al., 2010; Ibrahim et al., 2006; Langford and  
79 Ferner, 1999).

80 Native Americans smoked tobacco centuries before Europeans discovered it in the 15th  
81 century (Musk and De Klerk, 2003). It was rapidly globalized (Musk and De Klerk, 2003) and  
82 is popular in numerous countries (Le Foll et al., 2022) and vast spectrum of forms to this day.  
83 Among those, traditional pipe tobaccos, cigarettes, and bidis / biris / beedis (common in India  
84 filter-free tobacco products comparable to cigarettes wrapped in tendu (*Diospyros*  
85 *melanoxylon*) (Lal, 2012) leaves instead of tobacco or tissue paper (Verma et al., 2010),  
86 known under, at least, three different names (Lal, 2012; Le Foll et al., 2022; Verma et al.,  
87 2010; Watanabe et al., 1987)) were studied in this work. Even though the market offers a  
88 wide range of tobacco products, researchers' attention is frequently drawn to selective

89 cigarettes (Verma et al., 2010). Consumers of all CT products are exposed to a wide range of  
90 hazardous chemicals in tobacco smoke, including volatile mercury. Its toxicity results mainly  
91 due to its ability to accumulate in body tissues (Ibrahim et al., 2006; Langford and Ferner,  
92 1999; Rutkowska et al., 2014) particularly the brain (Ibrahim et al., 2006; Langford and  
93 Ferner, 1999). Poisoning can cause diseases such as Minamata disease (caused by MeHg)  
94 (Inoue et al., 2012; Voegborlo and Akagi, 2007) or mad hatter disease/erethism (caused by  
95 free Hg vapor) (Ibrahim et al., 2006; Steckling et al., 2011).

96 Noteworthy is the sensitive route of tobacco smoke delivery, i.e. through the respiratory  
97 system, which is highly vulnerable to mercury vapor absorption (Langford and Ferner, 1999).  
98 Other important aspects are the conditions in CT products during consumption. Mallock et al.  
99 discovered that tobacco embers can reach temperatures of 700-950 °C (Mallock et al., 2019),  
100 and it must be remembered that smoking requires air circulation inside the products. Similar  
101 conditions are found in Mercury Analyzer MA3000 supplied by Nippon Instruments  
102 Corporation (NIC Japan), employed in this research, where the temperature in the  
103 decomposition furnace reaches 850 °C for Hg release. This condition promotes Hg release  
104 into the smoke stream.

105 CT products contamination is important for medical and environmental sciences according to  
106 its adverse health effect and vast number of consumers globally (Le Foll et al., 2022). The  
107 approach described in this paper suggests broadening an already interdisciplinary issue in the  
108 field of food chemistry, as there are similarities in tobacco and food product consumption.  
109 Furthermore, the lack of new studies on the total Hg content in non-cigarette CT products was  
110 indentified. There is also a lack of a standards outlining maximum permitted mercury  
111 concentration in tobacco, analogous one used in food products (Milatou et al., 2020). This  
112 justifies a thorough investigation into the determination of mercury concentrations in these  
113 products.

114 The study aimed to apply the food-product Hg exposure estimating method to evaluate the  
115 mercury exposure from cigars which are becoming increasingly popular among smokers  
116 (Corey et al., 2014; DeSantis and Morgan, 2003; Kowitt et al., 2020), and other tobacco  
117 products, i.e.: pipe tobaccos, cigarettes and bidis. The analyses of rare CT products that have  
118 been carried out are extremely important and provide new information. In addition, an  
119 approach was applied for estimating consumer exposure to mercury, which has so far only  
120 been used for food products (Milatou et al., 2020).



## 121 2. Materials and methods

### 122 2.1. Sampling

123 The cigars used in this study were obtained from two Internet retailers available in Poland.  
124 Pipe tobaccos and cigarettes were purchased in Gdansk (a city in northern Poland) at a local  
125 tobacco store. Bidis were bought in Rajkot, located in the western province of India, Gujarat.  
126 To compare cigar tobacco and other CT products the analyses from a previous paper was  
127 extended, and all results were used to test suggested in this research approach. For that, 37  
128 cigars, 4 shredded pipe tobaccos, 5 bidis, and 5 cigarette samples were analyzed. The previous  
129 research was extended with additional 4 shredded pipe tobaccos and 6 cigarette tobaccos. All  
130 samples were purchased in 2021-2022.

131 Cigars represented four origins (The Republic of Nicaragua, The United Mexican States, The  
132 Dominican Republic, and The Republic of Cuba) and reflected the whole range of varieties  
133 (small cigars, cigarillos, large machine-made cigars, and large handmade cigars) and prices. It  
134 makes them the most varied tobacco samples in this study. Since cigars are frequently made  
135 from "blends" (a mixture of tobaccos from different origins), only those whose tobacco had a  
136 homogeneous origin (according to information provided by the store) were chosen for  
137 analysis. Eleven brands of cigarette tobaccos, eight pipe tobaccos, and five bidis were also  
138 analyzed. During the process of selecting samples for analysis, a lack of information on the  
139 origin of the tobacco used in the preparation of cigarettes, bidis, and pipe tobaccos was  
140 observed. The explanation for this status quo might be that producers keep their recipes for  
141 tobacco mixtures secret. Except cigarettes with cigarette filters and papers (and a few small  
142 filter cigars), all of the tested products were fully made from plant leaves and just this  
143 material was used for the analysis.

### 144 2.2. Sample treatment

145 Prior to mercury analysis with the use of the cold vapor atomic absorption spectrometry (CV-  
146 AAS) technique, some necessary steps for sample preparation were applied. It included  
147 sampling, drying, homogenizing, determination of water content, and proper storage. The  
148 entire procedure was carried out while the unique characteristics of the evaluated material  
149 were kept under consideration.

150 Since tobacco leaves are wrapped concentrically around the cigar axis during manufacturing  
151 (Langer et al., 1971), greater sample variability is expected to be in the cross, rather than the  
152 longitudinal, section. As a consequence, for the analysis, a "cigar slice" weighing 1-2 g was  
153 cut from the open part of each cigar (cigar foot). Each sample thus collected was dried in a  
154 laboratory dryer and homogenized in an agate mortar. Other products sampling was

155 performed analogously and included respectively picking for each brand: 4-5 random bidis,  
156 about 2.5 g of shredded pipe tobaccos, and three random cigarettes.

157 The next step was to determine the moisture content of the prepared samples. For this  
158 purpose, it was decided to choose the gravimetric method. As the determination of mercury  
159 content using the CV-AAS technique is carried out on dried samples, the determination of  
160 consumer exposure to toxic mercury on this basis is not correct. This is related to the fact that  
161 consumers smoke products containing a certain amount of water. Therefore, a conversion of  
162 the mercury content to the weight of the tobacco before drying ( $C_{w.w.}$ ) was applied using  
163 equation (1) used in comparable studies in the literature (Majewska et al., 2018; Milatou et  
164 al., 2020).

$$C_{w.w.} = C_{d.w.} \cdot \frac{m_{d.w.}}{m_{w.w.}} \quad (1)$$

165 Where  $C_{d.w.}$  is the mercury concentration in the dry tobacco ( $\mu\text{g}/\text{kg}$ ),  $m_{d.w.}$  and  $m_{w.w.}$  are dry  
166 and wet sample weights (g).

### 167 2.3. Instrumentation

168 Mercury Analyzer MA3000 supplied by Nippon Instruments Corporation (NIC Japan), which  
169 uses the technique of Direct Thermal Decomposition - Gold Amalgamation – Cold Vapors -  
170 Atomic Absorption Spectrometry (CV-AAS) was used for the analysis, and purified dry  
171 oxygen was used as the carrier gas.

172 Calibration was performed with calibration solutions diluted in L-cysteine. 0.001 % L-  
173 cysteine solution was made with the use of 10 mg of L-cysteine (Merck), 2 cm<sup>3</sup> of the  
174 certified reagent grade concentrated nitric acid, and deionized water. Hg standard of MS  
175 grade purity (Merck) at a concentration of 100 mg/dm<sup>3</sup> was used. By diluting 1 cm<sup>3</sup> of  
176 standard solution to 100 cm<sup>3</sup> with the L-cysteine solution, 1 mg/dm<sup>3</sup> stock solution Hg was  
177 achieved. Next, 7 calibration solutions were prepared and analysed in 3-4 repetitions,  
178 resulting linear calibration curve between the range of 1.0 to 8.0 ng ( $R^2 = 0.9972$ ). Calculated  
179 from the curve slope the limit of detection (LOD) and the limit of quantification (LOQ) were  
180 as follows, LOD = 1.5  $\mu\text{g}/\text{kg}$ , LOQ = 4.8  $\mu\text{g}/\text{kg}$ . Actually this values are method detection  
181 limit (MDL) and method quantification limit (MQL), as calibration curve was prepared in  
182 units of mass, and then calculated to units of content.

183 The analysis were performed with at least three repetitions. Samples were heated in a  
184 decomposition furnace to  $T=850$  °C for 4 min to cause thermal decomposition and release Hg  
185 from the sample. Glass tube with a gold deposit, called a “gold furnace”, was used to  
186 selectively absorb mercury from generated fumes (Au-Hg amalgam generation). The release

187 of mercury occurred due to the decomposition of Au-Hg amalgam at temperature  $T=600\text{ }^{\circ}\text{C}$   
188 carried out for 1 min. Hg analysis was performed with the use of spectrometric analysis  
189 (wavelength 253.7 nm).

190 This method is characterized by high selectivity (due to amalgam formation and measurement  
191 at the characteristic mercury wavelength) and repeatability. Among the advantages of the  
192 employed method, it is worth mentioning its "greenness" (it is practically solvent-free and  
193 does not need any aggressive additives). Millipore's Milli-Q<sup>®</sup> water purification system  
194 (USA) was used for the standard solution preparation.

195 The powdered samples were covered with "additive B" (Wako Pure Chemical Industries Ltd.;  
196 NIC Japan) in ceramic cuvettes.

197 Various drying methods for plant samples are proposed in the scientific literature (Hać et al.,  
198 2022; Ma et al., 2022; Polat et al., 2022). In this study, it was decided to use a laboratory  
199 dryer Redline by Binder. The Radwag WPS 30s moisture analyzer, the Protherm Furnaces  
200 PAF 120/12 muffle furnace, the freeze dryer (provided by Labconco), the desiccator, and a  
201 laboratory dryer were used. Karl Fisher titration was performed with 831 KF Coulometer by  
202 Metrohm.

203 Bidis homogenization was performed with an impact homogenizer instead of agate mortar  
204 because of the fibrousness of the wrapping tendu leaf that persisted even after the drying  
205 process. The powder samples obtained were kept at room temperature in Falcon<sup>®</sup>  
206 polypropylene containers. All weight measurements were taken with a professional analytical  
207 balance with a repeatability of 0.01 g (Radwag). A mercury standard—MSHG—at a  
208 concentration of  $100.10 \pm 0.43\text{ }\mu\text{g mL}^{-1}$  in 10% HCl was purchased from Inorganic  
209 Ventures, INC (USA). N-acetyl-L-cysteine was obtained from Sigma-Aldrich (Germany),  
210 nitric acid from J.T.Baker<sup>®</sup>, and Karl Fisher reagent for coulometric water determination from  
211 Aquastar<sup>®</sup>.

#### 212 213 2.4. Calculation of health risks from consumption 214

215 Due to the lack of regulation of total Hg concentration in CT products, it was decided to use  
216 various maximum mercury level (MHgL) standards. In the present study, three cases were  
217 considered, as they may correspond to toxic mercury exposure due to the consumption of CT  
218 products, and these are as follows: dietary intake, occupational and non-occupational  
219 exposure.



220 The provisional tolerated weekly intake (PTWI) of inorganic mercury is one of the dedicated  
221 indicators for this element. It was established by the Joint FAO/WHO Committee on Food  
222 Additives, which had reduced its limit from 5  $\mu\text{g}/\text{kg}$  body weight (bw) to 4  $\mu\text{g}/\text{kg}$  bw at its  
223 72nd meeting in 2011 (Joint FAO/WHO Expert Committee on Food Additives. Meeting  
224 (74th : 2011 : Rome, 2012). It means that a  $\text{PTWI} = 280 \mu\text{g}/70 \text{ kg bw}$  per week can be  
225 established for an adult. The maximum limits of average dietary exposure to total mercury  
226 from foods other than fish and shellfish were even four times lower (1  $\mu\text{g}/\text{kg}$  bw per week)  
227 than PTWI (Joint FAO/WHO Expert Committee on Food Additives. Meeting (74th : 2011 :  
228 Rome, 2012; Milatou et al., 2020). This index is applied mainly to food products, i.e. dietary  
229 intake.

230 There are some similarities between food and CT consumption. Not only do the respiratory  
231 and digestive tracks share a first stage, but also the substances from consumed products in  
232 both cases eventually enter the bloodstream. The combustion step is analogous to the  
233 digesting step in the process of obtaining absorbable compounds. Nevertheless, CT products  
234 do not meet all the criteria for food products, which could limit the use of the PTWI index in  
235 their case.

236 According to the WHO's "*Air Quality Guidelines – Second Edition*" the lowest observed  
237 adverse effect limit (LOAEL) for volatile mercury occurs within a concentration of 15-30  
238  $\mu\text{g}/\text{m}^3$ , and the established time-weighted average (TWA) for mercury is 1  $\mu\text{g}/\text{m}^3$  within  
239 annual averaging time (World Health Organization, 2020). In the document  
240 "*Recommendation from the Scientific Committee on Occupational Exposure Limits for*  
241 *elemental mercury and inorganic divalent mercury compounds*" (European Commission  
242 2007) an exposure level of 0.02  $\text{mg}/\text{m}^3$  for an 8-hour TWA meets the criteria for a health-  
243 based occupational exposure limit (OEL) (Scientific Committee on Occupational Exposure  
244 Limits, 2007).

245 Assuming  $\text{MHgL} = \text{OEL}_{(t=8\text{h})} = 0.02 \text{ mg}/\text{m}^3$ , an estimate equivalent to the PTWI index for  
246 inhaled mercury vapor – an acceptable daily dose of mercury vapor ( $\text{ADD}_{\text{Hg v.}}$ ) – can be  
247 established. It is required to assume a daily inhalation ratio (DIR) [ $\text{m}^3$ ] for this purpose.  
248 Although the DIR value varies depending on age, gender, and other factors, the scientific  
249 literature indicates  $\text{DIR} = 20 \text{ m}^3$  for an adult (European Chemicals Agency, 2012). It is also  
250 important to note that approximately 80% (or more) of Hg vapor is absorbed by the lungs  
251 (Beate et al., 2010; Langford and Ferner, 1999). It must be remembered, that MHgL is  
252 calculated using standards for a specific time, therefore  $t$  in the following equation is the time



253 established for the used standard. Consequently, the estimated  $ADD_{Hg v.}$  value was calculated  
254 using the following equations (2 and 3).

$$ADD_{Hg v.} = MHgL \cdot \frac{DIR \cdot t}{24h} \cdot 0.8 \quad (2)$$

$$ADD_{Hg v.} = 0.02 \text{ mg}/\text{m}^3 \cdot \frac{20 \text{ m}^3 \cdot 8 \text{ h}}{24 \text{ h}} \cdot 0.8 = 0.106(6) \text{ mg} \quad (3)$$

255 According to equation 2, the calculated  $ADD_{Hg v.}$  is, in this example case, approximately  
256 0.107 mg. The use of this approach, however, has several limitations. To begin with, as  
257 previously mentioned, DIR is influenced by a variety of factors. Furthermore, the toxicity of  
258 mercury vapor is significantly greater for the developing brain of a fetus and a small child  
259 than for an adult, hence MHgL would be lower in these cases (Beate et al., 2010). Calculation  
260 in this study does not take into account the influence of occurring passive smoking or any  
261 susceptible subpopulations. For developing organisms like children or adolescents, a separate  
262 calculation should be performed, considering the specific toxicity impact on their organisms  
263 and different respiratory parameters (such as different DIR). Mercury vapor comes across one  
264 of its most toxic forms (Beate et al., 2010; Langford and Ferner, 1999), therefore, Table 3  
265 includes calculated  $ADD_{Hg v.}$  for other possible air permissible limits than the OEL.

266 A second indicator, the maximum permissible consumption of tobacco per day (MPCT),  
267 defined by equation (4), is required for further investigation and analysis of the data. In the  
268 scientific literature on mercury exposure in fish consumers, an analogous approach is used  
269 (Milatou et al., 2020).

$$MPCT = \frac{ADD_{Hg v.}}{C_{w.w.}} \quad (4)$$

270  $ADD_{Hg v.}$  depends on the chosen MHgL (e.g.  $OEL_{(t=8h)}$ ).

271 The maximum daily allowed consumption of tobacco is expressed in units of weight of  
272 tobacco that can be safely consumed daily to not cause Hg poisoning. It might be tough to  
273 utilize in its raw form; however, evaluating exposure in terms of burned tobacco weight  
274 seems to be the most practical and adaptable alternative.

### 275 3. Results and Discussion

276 Due to the current lack of information in the literature on the preparation of cigar tobacco  
277 samples for elemental analysis, this area was given special attention in this study. The  
278 analyzed material does not meet the criteria of a (fresh) plant as it contains substantially less  
279 water. Neither is it a dried or a pre-dried product. The specific CT product qualities, as well as



280 the smoke quality, are determined by the tobacco processing methods employed, such as  
281 curing or fermenting (Jensen and Parmele, 1950).

282 The water concentration in CT products varies, as shown in Table 1. Elemental analysis  
283 should be performed by comparing the results to a common reference point for all samples,  
284 i.e., dry weight. As a result, the drying process is an important step in sample preparation, in  
285 this case, to determine mercury concentration. Several different methods of drying samples  
286 were tested in this study.

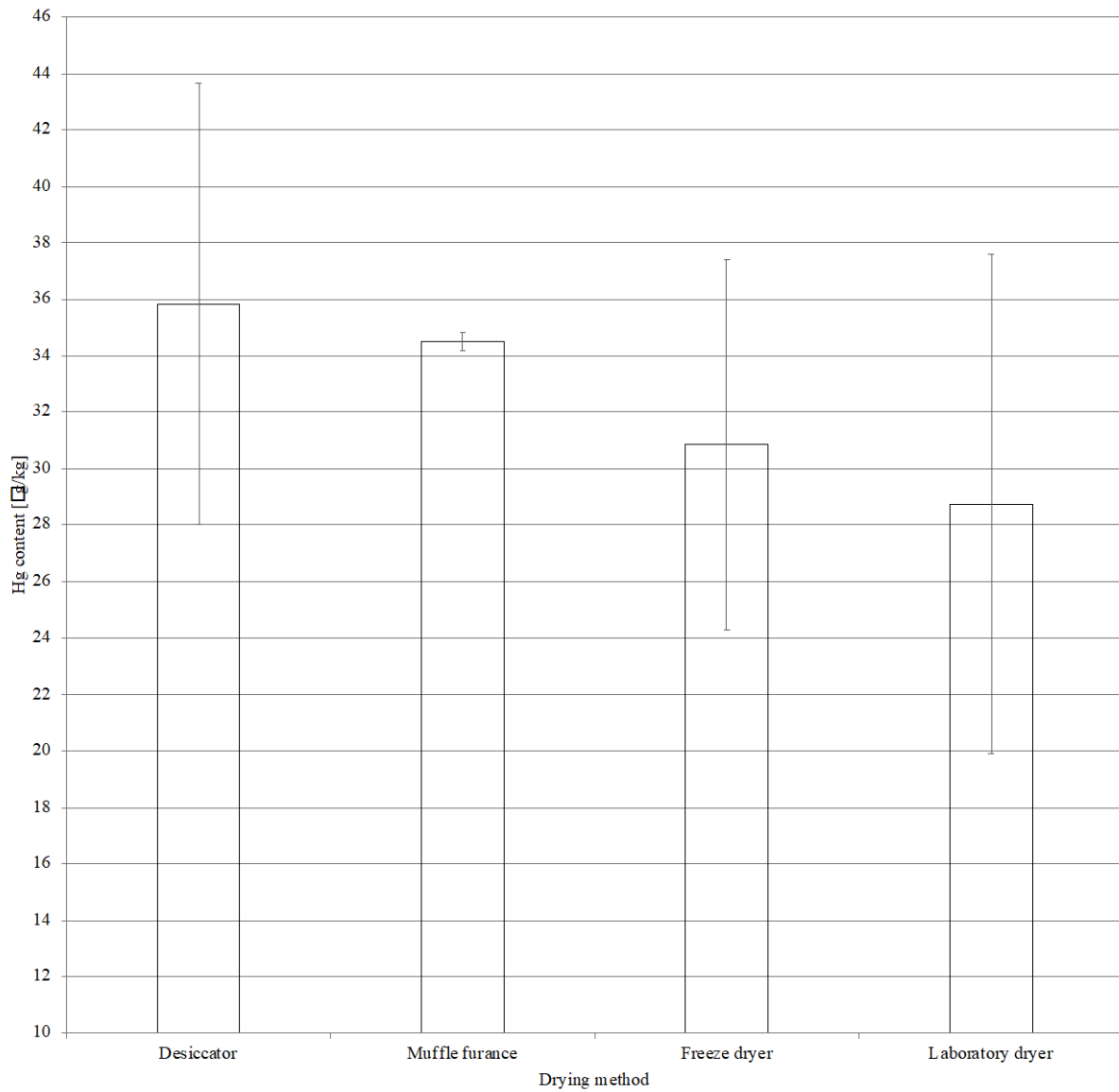
287 Table 1. Water content in cigars, determined within the gravimetric method using a variety of  
288 drying methods. All presented values are expressed in percentages.

Sample	Desiccator	Freeze-dryer	Muffle furnace [105°]	Moisture analyzer [120°]	Laboratory dryer [105°]
La Prueba No. 2	7.61	12.4	12.4	13.9	14.2
La Prueba No. 3	7.00	12.2	12.7	14.6	15.1
Guantanamera Puritos	5.42	9.28	9.86	14.3	12.3

289  
290 Moisture analyzers, which are commonly used in laboratories, appear to have limited utility  
291 as they usually can only dry one sample at a time. The aim of testing several drying methods  
292 was to determine which of the possible drying procedures gives the most similar results to  
293 those obtained using the moisture analyzer. The laboratory drier most closely met the  
294 expectations in this respect, and it also enabled the drying of several dozen samples  
295 simultaneously. As a result, it was decided to use this method, which was run for 24 h at 105  
296 °C (until a constant weight was obtained ~ 0.01g). A muffle furnace set to the same  
297 temperature as the laboratory dryer dried the tobacco samples with less efficiency. The inertia  
298 of a furnace at 105 °C might be large since it is typically employed at higher temperature  
299 ranges. As a result, the actual temperature at which the samples were dried was probably  
300 different. Furthermore, the laboratory drier has the advantage of supporting high temperatures  
301 in the drying process with air circulation.

302 It is important to note that at higher temperatures, tobacco products emit several volatile  
303 chemicals (WHO Study Group on Tobacco Production Regulation, 2012). Water contents  
304 reported by moisture analyzer, muffle furnace, or laboratory dryer might be overvalued. The  
305 conditions could theoretically also affect the evaporation of mercury from the sample, but it  
306 should be remembered that Hg is not expected to be present in the elemental form and the  
307 temperature range associated with drying does not correlate to that used in mercury analyzers.  
308 The drying process is therefore not expected to have a significant impact on the loss of Hg

309 from the sample, but this has been verified in the example of one cigar. As evidenced in  
310 Figure 1, the determined mercury contents of the samples dried within different methods,  
311 vary, but are in the range of their uncertainties.



312  
313 Figure 1. Comparison of mercury contents in La Prueba No.3 cigar, dried with four drying  
314 methods (the error bars result from measurement repetition expanded uncertainty).

315 Methods that do not use high temperatures are more reliable for estimating the water content  
316 of these kinds of materials. Lyophilization, which employs low pressure, is one of these.  
317 Although such conditions protect compounds from oxidation and degradation, this technique  
318 also does not remove water from the sample selectively. This limitation is remedied by using  
319 a desiccator that uses a selective water sorbent. This process takes place at room temperature  
320 but is very time-consuming. Chromatographic methods are also used for determining moisture  
321 content (Zhou et al., 1998), although they are better applicable to liquid samples.

322 It should be noted that the results of the selecting optimum drying conditions process do not  
 323 reflect the real water content of the tobacco. Other substances may also evaporate during  
 324 drying, which is a trivial point. The goal, however, was to select the best, repeatable  
 325 procedure of sample preparation for elemental analysis. Although the Karl Fisher Titration  
 326 (KFT) method is recommended in the case of tobacco products (International Organization  
 327 for Standardization, 2021) it was decided not to use it in all samples, due to two reasons.  
 328 Firstly sample preparation included grinding, which had to be performed on dry samples, and  
 329 drying is also used in gravimetric moisture analysis, the use of gravimetric method allowed to  
 330 use same samples for elemental analysis and moisture analysis (dried within the same  
 331 method). Secondly, the exposure calculating method in this study does not require the  
 332 determination of real and precise water content in the sample. It was decided to perform a few  
 333 diagnostic KFT using two cigars, two pipe tobaccos, and two cigarette tobaccos. All six  
 334 samples were freshly purchased in April 2023 in Gdańsk, Poland. Results obtained with KFT  
 335 are presented in Table 2 and as can be seen, they are similar to those obtained with the  
 336 gravimetric method. It was decided to present results in Table 2 as ranges, as it was observed  
 337 that individual parts of cigars or individual tobacco ribbons from packages had different  
 338 content of water.

339 Table 2. Water content in diagnostic tobacco samples was determined using Karl Fisher  
 340 Titration.

Sample	Product	Water content [%]
VF	Cigar	6.46 – 11.2
Casa de Garcia	Cigar	6.00 – 12.3
Amphora Full	Pipe tobacco	14.6 – 18.7
Peterson Wild Atlantic	Pipe tobacco	14.5 – 18.3
LD	Cigarette tobacco	7.42 – 9.28
Camel	Cigarette tobacco	11.1 – 12.1

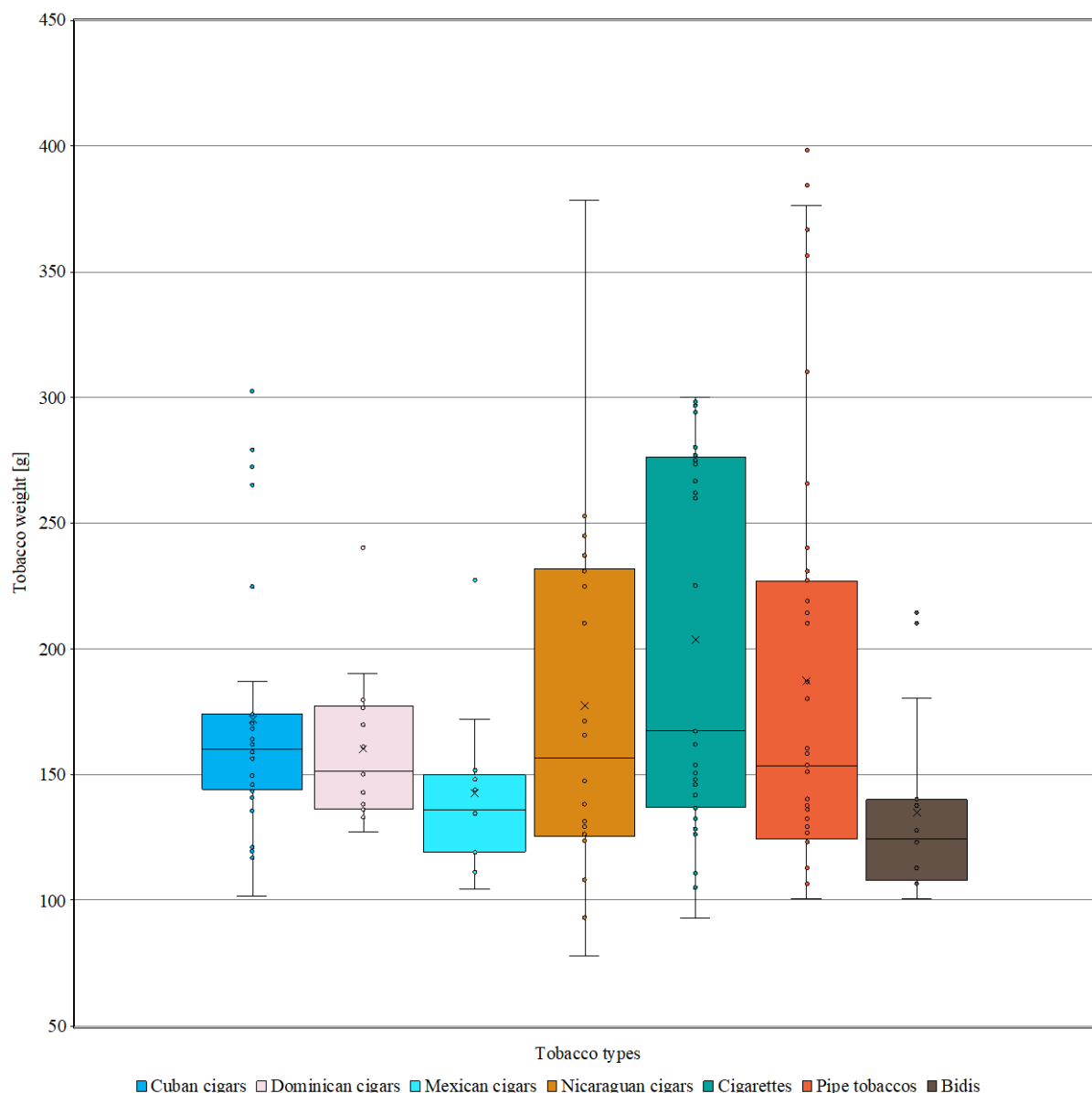
341  
 342 While it is usual practice in food chemistry to convert the mercury (or other heavy metals)  
 343 content in a sample's dry weight to the concentration in the wet weight (using eq. 1) (Milatou  
 344 et al., 2020), it was also successfully applied to tobacco (Majewska et al., 2018). This  
 345 demonstrates the scientific literature's attempts to un- or consciously recognize CT as food  
 346 products (to estimate consumers' exposure to toxins). In the context of its contamination,  
 347 selective designation of these products as food would allow for a more accurate assessment of  
 348 consumer exposure. The main advantage of the suggested approach is that determining the  
 349 precise moisture content becomes secondary. However, owing to the lack of data in this field,  
 350 it is nonetheless useful information.

351 In the scientific literature, consumer exposure to mercury from food products is stated as the  
 352 maximum safe weekly intake, which is comparable to the proposed MPCT index derived and  
 353 follows from the adopted standard. Previously, the OEL index was cited as an example of  
 354 MHgL. Because the result appeared to be significant, it was decided to pursue the more  
 355 stringent non-occupational regulatory exposure level (REL) (Richardson et al., 2008). The  
 356 standards referenced in numerous publications (Beate et al., 2010; Fresquez et al., 2015;  
 357 Richardson et al., 2008) were chosen and collected in Table 3, along with the calculated  
 358  $ADD_{Hg v}$  values (for  $t = 24h$  and  $DIR = 20 m^3$  (European Chemicals Agency, 2012)).

359 Table 3. Summary of the various RELs their official names and calculated  $ADD_{Hg v}$  factors

Organization	Author	Standard name	REL [ $\mu g/m^3$ ]	$ADD_{Hg v}$ . [ $\mu g$ ]
United States Environmental Protection Agency (US EPA) 2007	Beate et al. (Beate et al., 2010)	Reference Air Concentration (RfC)	0.3	4.8
Agency for Toxic Substances and Disease Registry (ATSDR) 1999	Fresquez et al. (Fresquez et al., 2015)	Minimal Risk Level	0.2	3.2
California Environmental Protection Agency (CalEPA) 2005	Richardson et al. (Richardson et al., 2008)	REL	0.9	14.4
World Health Organization (WHO) 2000	Richardson et al. (Richardson et al., 2008; World Health Organization, 2020)	Air Quality Guidelines as to the Annual Average Concentration	1.0	16.0

360 Figure 2 illustrates the results of the MPCT values as a boxplot for the ATSDR REL values. It  
 361 must be remembered, that calculation was performed only for the adult smokers population,  
 362 for who  $DIR = 20 m^3$ , and REL level was assumed as presented in Table 3. The samples were  
 363 divided according to tobacco kind and (for cigars) country of origin. Four cigar ash samples  
 364 were also analyzed, but the obtained results were scattered and on the borderline of LOQ and  
 365 even LOD.  $LOQ = 0.35 \mu g/kg$ ;  $LOD = 0.11 \mu g/kg$  were calculated from the different, lower  
 366 calibration curve. Based on these results, the ash was found to have negligible mercury  
 367 content.  
 368



369

370 Figure 2. The maximum daily allowable weights of tobacco consumption according to its

371 mercury content, were calculated using ATSDR REL values.

372 Based on the results of the study, it can be concluded that to exceed the permissible level of

373 Hg inhalation, a significant mass of tobacco would have to be consumed. To date, there have

374 been no reports in the literature about smokers commonly showing mercury poisoning

375 symptoms. The concentrations determination procedure is used to confirm that the element

376 content in CT, is in practice insufficient to directly and independently significantly expose

377 smokers. To overcome the most stringent  $ADD_{Hg v}$ , it would be necessary to consume at least

378 approximately 75 grams of tobacco per day (equivalent to about 130 cigarettes). It is unlike

379 that anyone, from a considered subpopulation, would smoke such an amount of tobacco.

380 Therefore it is unlike that tobacco smoking, separately from other potential sources, would  
381 cause mercury poisoning.

382 As can be seen in Figure 2, the three types of tobacco are characterized by elevated mercury  
383 content. These are bidi, cigarette tobacco, and Mexican cigars. The mercury results for these  
384 samples are concentrated at higher values. It is worth mentioning that these tobaccos are  
385 representing the cheapest groups among collected products. The greatest differentiation in Hg  
386 amount is observed for Nicaraguan cigars and pipe tobacco samples. Moreover, some pipe  
387 tobacco samples contain the lowest amounts of mercury among all samples in this study,  
388 however, simultaneously the sample with the highest mercury content was the Nicaragua  
389 cigar. Nevertheless, the last results might be considered an aberration.

390 As can be seen, the proposed approach is convenient to use because it allows a quick estimate  
391 of customer exposure based on their smoking habits. Therefore, the consideration of CT  
392 product consumers' Hg exposure, analogous to food product consumers, is justified. The lack  
393 of a standard or index of tolerable highest concentration for volatile mercury in inhaled  
394 products is, however, currently a significant disadvantage and limitation. In this study,  
395 calculations were based on limits for allowed air contamination that were appropriately  
396 adapted. Therefore, the establishment of official indices of acceptable Hg concentration in CT  
397 products is necessary for the correct determination of consumer exposure using the  
398 suggested approach.

399 Although the concentration of mercury in tobacco may not be life-threatening to consumers, it  
400 should be considered in the context of the high environmental pollution burden worldwide  
401 (Landrigan et al., 2018) and the diverse variety of substances contained in tobacco smoke  
402 (WHO Study Group on Tobacco Production Regulation, 2012), to which smokers are exposed  
403 to. There are three types of combined harmful effects documented in the literature:  
404 synergistic, antagonistic, and additive (Meynard et al., 2021). This indicates that toxins can  
405 have different impacts on humans when they react together than when they occur alone. This  
406 is exemplified by the established stronger than just additive adverse health effects of  
407 tobacco smoke and arsenic in humans (Ferrecio et al., 2013).

408 The necessity for the establishment of an index for the maximum permissible mercury content  
409 in CT products, as previously advocated, is made even more urgent by the fact that smoke is  
410 an additional source of mercury exposure for consumers. Although the concentration of Hg in  
411 the environment varies, tobacco contributes to total exposure for smokers and those around  
412 them (passive smoking). As a result, it is reasonable to expect that the value of such an index  
413 should be lower than the RELs used in this study. Moreover, the suggested approach gives the

414 possibility to standardize mercury exposure and use it to estimate total exposure. Such  
415 standardization gives also the possibility to estimate a budget for exposure and verify  
416 contribution of each component.

417 It should be noted that the results presented in this paper represent actual data, but are used as  
418 a model to demonstrate the implementation of the proposed tobacco consumers' exposure  
419 estimation approach. It is assumed in this work that full thermal decomposition of mercury  
420 compounds occurs during smoking and that the Hg is fully emitted as a vapor into the smoke.  
421 However, it has been proven that in tobacco products, the temperature of the tobacco changes  
422 gradiently as it is smoked, resulting in an occurrence of a distillation zone (Mallock et al.,  
423 2019). Some mercury compounds likely evaporate before they decompose with the release of  
424 Hg, and the evaporated mercury compounds show different adverse health effects than  
425 mercury vapor alone (Langford and Ferner, 1999). Nevertheless, the approach proposed in  
426 this study can be applied to various elements as well as their compounds to calculate proper  
427 ADD. However, as aforementioned, it is important to always remember that the adverse health  
428 effect of various toxins is not necessarily additive.

429 Human urine, blood, and hair have been reported to be used as biomonitors for air  
430 contamination with Hg vapor (Beate et al., 2010). This fact was applied to calculate the  
431 conversion factors for Hg air contamination to its level in the urine/blood/hair of exposed  
432 humans. Also, an in vitro exposure to mercury vapor increased levels of this element in cut  
433 human head hair (Beate et al., 2010; Hać and Krechniak, 1993). It should be noted that  
434 smoking was considered an influencing factor in the population analyzed in the study by  
435 Beate et al. on reference concentrations of mercury vapor (Beate et al., 2010).

436 Approach presented and applied in this study uses estimated ADD<sub>Hg v.</sub> values for only one  
437 group of consumers, that can be considered as standard smokers. Meanwhile, there is a vast  
438 number of subpopulations, that differ within, environmental exposure (eg. employees of some  
439 industry branches), physical workers whose DIR factor may differ, adolescents and children,  
440 who might be more toxicologically sensitive, and possibly others. Therefore it is advisable to  
441 take into account subpopulations and their characterization while estimating exposure  
442 (European Chemicals Agency, 2012). For that purpose suggested approach can be used.

443 Despite numerous efforts to promote smoking cessation (Le Foll et al., 2022; WHO Study  
444 Group on Tobacco Production Regulation, 2012), significant tobacco production (M.  
445 Shahbandeh, 2021) and a high number of smoking-related deaths persist worldwide (Le Foll  
446 et al., 2022). In addition to attempts to reduce the number of tobacco users, the use of each  
447 cigarette as an air filter could be considered. Using mercury as an example, by placing a





448 health-neutral agent in the filter (Pauly et al., 1997), effectively immobilizing Hg vapor  
449 (Langford and Ferner, 1999), smoking would decontaminate (from this element) not only the  
450 smoke but also the ambient air. This would both relieve smokers' organisms and have a  
451 positive impact on the environment. The problem of collecting used contaminated filters  
452 could be obtained with any motivation system, such as deposit system. Price of cigarette  
453 package could be discounted for consumers giving back in settlement used filters. A single  
454 cigarette would have little impact on decontaminating the atmosphere, but a large number of  
455 them could help to eliminate Hg from the atmosphere and reduce its emissions from CT  
456 products. This approach can be considered inspired by a similar path occurring in nature:  
457 filtrating water mussels (Elliott et al., 2008). On the scale of a lake or sea, a single organism  
458 does not have a significant meaning, but thousands and millions of them do (Vaughn, 2018).

#### 459 4. Conclusions

460 The study demonstrates that implementing the same method to combustible tobacco products  
461 to estimate mercury exposure from food is feasible and convenient to use. Simultaneously,  
462 this is the first time such an approach has been used with CT. Its employment requires the use  
463 of an appropriate standard or index for the maximum permissible inhalation dose of volatile  
464 mercury for a specific subpopulation, providing a basis for its application. Because there are  
465 none, the most restrictive REL for airborne Hg pollution was adopted as an alternative  
466 strategy. Therefore, the urgent need to define a suitable index for combustible tobacco  
467 products, for a variety of subpopulations of smokers was identified.

468 Based on research, CT products alone are believed to be unlikely to cause mercury poisoning  
469 in smokers themselves (for standard, adult smokers population which was considered in this  
470 study), according to the MRL index provided by ATSDR. It should be noted, however, that  
471 more Hg sources in the human environment also affect their organisms, so exposures should  
472 be added up. Furthermore, a phenomenon known as the combined toxicity effect was  
473 described in the scientific literature, suggesting that the adverse health effect of volatile Hg  
474 could be exacerbated when it is mixed with other components of smoke. There is a lack of  
475 baseline studies of noncigarette CT products in the scientific literature, which must be  
476 performed and developed. As a result, further research is suggested in this area.

477 It is also advisable to extend the verification regarding the possible influence of the drying  
478 method on the loss of elements from the sample. For that purpose different drying methods  
479 can be used or different homogenization methods, i.e. eg. cryogenic grinding. Such an  
480 approach would eliminate possible Hg loss during drying and would eliminate the step of

481 recalculation mercury content from dry weight to wet weight. In further research, it is  
482 advisable to perform optimization of the drying method and if the increased temperature  
483 would be employed, a standard addition method might be useful. An important step towards  
484 estimating consumer exposure to toxic elements contained in CT is also to estimate their real  
485 distribution pathway to the human body. For this purpose, it is worth conducting a smoke  
486 analysis, which however is associated with some technical laboratory difficulties.

487 The method suggested in this study enables estimation of consumers' exposure to mercury  
488 from combustible tobacco products using the method used for food products consumers. Such  
489 computational method is however limited, so it advisable is to expand research including  
490 population studies with verification of bioavailability by the organism, speciation studies, and  
491 using it with a wider spectrum of elements.

492 Transferring the exposure estimation method used for food consumers to tobacco consumers  
493 has another key advantage. Applying the same estimation method to food and smoking allows  
494 further convenient estimation of total exposure. Such standardization provides new  
495 opportunities for further research.

496

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501

#### 502 **Conflict of interest statement**

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