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1 **Consistency between air and biological monitoring for assessing polycyclic**
2 **aromatic hydrocarbon exposure and cancer risk of workers**

3

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11 **Abstract**

12 *Background:* Atmospheric levels of polycyclic aromatic hydrocarbons (PAHs) have been monitored in
13 many companies since 1940. Because of the use of respiratory protective equipment (RPE) and
14 cutaneous absorption, the measurement of urinary 1-hydroxypyrene (1-OHP), metabolite of pyrene
15 (Pyr), and, more recently, 3-hydroxybenzo[a]pyrene (3-OHBP), metabolite of benzo[a]pyrene (BaP),
16 has been carried out to assess PAH exposure and estimate health risks.

17 *Objectives:* This study aimed to investigate the agreement between 523 air and biological levels recorded
18 in the Exporisq-HAP database by taking into account the effectiveness of RPE.

19 *Methods:* The agreement/consistency between 523 air and biological exposure levels was assessed by
20 estimating and comparing the probability of exceeding French limit values (LVs) for both BaP and 3-
21 OHBP and ACGIH LV for 1-OHP, respectively. PAH airborne levels (w PAHs) were weighted by an
22 assigned protection factor (APF) depending on the type of mask worn by workers, while urinary 1-OHP
23 concentrations were adjusted with the w BaP/ w Pyr ratio of each industrial sector (w_{adj} 1-OHP).

24 *Results:* Within occupational groups, there was an overall agreement between airborne PAH levels and
25 urinary biomarker concentrations. A clear dichotomy was found between “petroleum-derived” and
26 “coal-derived” groups, with much higher exposures in the latest group despite the use of RPEs by two-
27 thirds of the workers. The type of RPE varied from one plant to another, which underlines the importance
28 of taking into account their effectiveness. The analysis of urinary 3-OHBP was not relevant for low
29 PAH exposure levels. In addition, this biomarker underdiagnosed the exceedance of LV relative to BaP
30 levels for 6% of “coal-derived” groups.

31 *Conclusions:* The use of urinary w_{adj} 1-OHP seemed to be more protective to assess the exceedance of
32 LVs than those of urinary 3-OHBP and air w BaP, but adjustment of the 1-OHP concentration by the
33 BaP/Pyr ratio requires air sampling due to highly variable ratios observed in the studied occupational
34 groups.

35

36 **Keywords**

37 Polycyclic aromatic hydrocarbons; exposure assessment; occupational limit values of benzo[a]pyrene;
38 1-OHP; 3-OHBP; health risk; respiratory mask

39 1. Introduction

40 Polycyclic aromatic hydrocarbons (PAHs) are a family of ubiquitous compounds resulting from the
41 incomplete combustion of fossil fuels or organic matter. In addition to environmental exposure to
42 tobacco smoke, vehicle engine exhaust and district heating emissions, PAH exposure can be encountered
43 in many occupational contexts, where they are mainly emitted as byproducts derived from coal or
44 petroleum distillation. Millions of workers are exposed to PAHs, such as road pavers, aluminum, silicon,
45 or electrode production workers, but exposures differ greatly from one industrial sector to another (IARC,
46 2010; Marczynski et al., 2009). The number of French workers exposed to PAHs was estimated
47 to be between 2 and 4 million (Arnaudo et al., 2012; Petit *et al.*, 2020). PAHs are associated with the
48 occurrence of different types of cancers, among which respiratory cancers are the most common (IARC,
49 2010). In France, for the year 2000, it was estimated that nearly 3% of lung cancers in men were
50 attributable to occupational PAH exposure (Boffetta et al., 2010). While numerous particulate PAHs are
51 classified as probably carcinogenic to humans by the European Chemicals Agency (ECHA, 2016) and
52 possibly carcinogenic by the International Agency for Research on Cancer (IARC), benzo[a]pyrene
53 (BaP) is the only PAH classified as a known human carcinogen (IARC, 2010).

54 To reduce the incidence of respiratory cancers, atmospheric PAH concentrations have been monitored
55 in many companies since 1940 to ensure that available occupational exposure limit values (OELs) are
56 not exceeded. However, discrepancies between OELs exist depending on the country and organization
57 (SCOEL, 2016). Assessment of airborne levels alone may not always provide a complete picture of
58 exposure because many industries rely on the use of respiratory protective equipment (RPE) to control
59 exposure (Unwin et al., 2006). Very few studies take into account their effectiveness for assessing PAH
60 exposure and estimating health risk. In addition, although workers are mainly exposed to PAHs via
61 inhalation, skin contamination is another important PAH absorption pathway (Bourgart et al., 2019;
62 Fustinoni et al., 2010).

63 Biological monitoring is a more recent approach that takes into account all uptake pathways and the use
64 of personal protective equipment. Because pyrene (Pyr) (both gaseous and particulate forms) is one of
65 the most abundant PAHs in mixtures, monitoring of its urinary metabolite, 1-hydroxypyrene (1-OHP),
66 was developed first and became the gold standard for estimating internal PAH exposure over the past

67 30 years (Jongeneelen, 2001; SCOEL, 2016). More recently, the analysis of 3-hydroxybenzo[a]pyrene
68 (3-OHBaP), an urinary metabolite of BaP, has been developed but requires a more sensitive analytical
69 technique than 1-OHP due to levels that are 1,000 to 10,000 times lower (Barbeau et al., 2011). Various
70 biological limit values (BLVs) or guidance values (GVs) have been proposed for these two biomarkers
71 by several organizations (ACGIH, 2017; Nikolova-Pavageau *et al*, 2018). In addition, to account for
72 different relative proportions of Pyr and BaP in PAH mixtures encountered in various industrial sectors,
73 it was proposed to adjust the 1-OHP BLV for different Pyr/BaP ratios in a specific exposure context
74 (ACGIH, 2017). Indeed, the BEI published by ACGIH considered a Pyr/BaP ratio of 2.5 that was
75 observed in coke oven plants but should be adjusted to other industrial environments. While air and
76 biological monitoring approaches are complementary, many questions remain unanswered regarding
77 their ability to assess the exceedance of existing OELs or BLVs to estimate PAH health risk.
78 The objective of this study was to investigate the consistency between biological and airborne
79 monitoring by taking into account the effectiveness of respiratory protection.

80

81 **2. Materials and methods**

82 **2.1 Data selection**

83 Since 1998, the Exporisq-HAP (E-HAP) database has prospectively recorded individual atmospheric
84 PAH levels and urinary metabolite concentrations of workers exposed to PAHs. For each worker, data
85 on age, smoking habits, job activities and RPE were collected. This database has been the subject of
86 several previous publications (Maître et al., 2018; Petit et al., 2017).

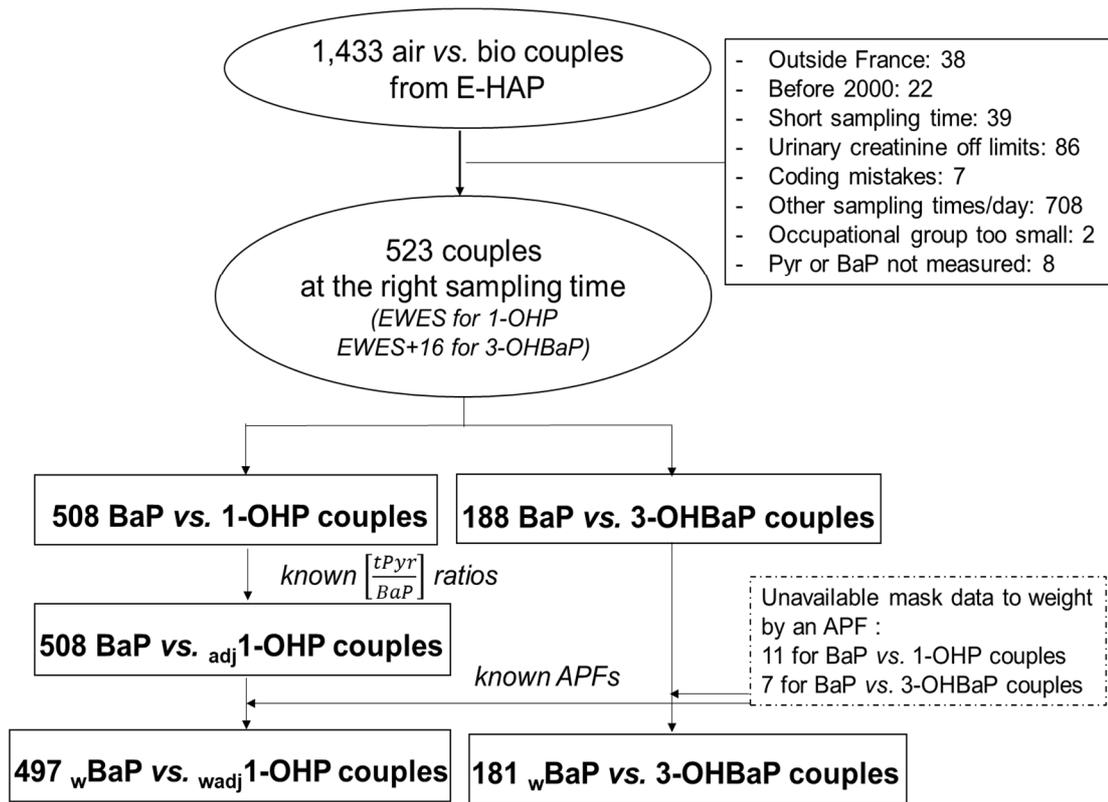
87 In the present study, only individual airborne and urine samples collected on the same working day were
88 selected. These two associated samples are referred to as “air vs. biocouple” or simply “couple”
89 throughout this manuscript. Only couples with the analysis of urinary 1-OHP measured at the end of the
90 work week-end of the shift (EWES) or of urinary 3-OHBaP at EWES plus sixteen hours (EWES+16)
91 were considered. Occupational activities outside of France or before the year 2000 (no gaseous PAH
92 samples), samples with a short sampling duration < 2 h, samples with urinary creatinine outside the
93 tolerable limits (< 0.3 g. L⁻¹ or > 3 g. L⁻¹), or samples with coding errors were excluded.

94 A total of 1,433 air vs. biocouples collected in 12 industrial sectors were found in the E-HAP database
95 (Fig. 1). Overall, 910 couples were excluded, mainly (78%) couples that were not sampled on the days
96 and moments of interest (Fig. 1). A total of 523 couples sampled in 98 plants between 2006 and 2019
97 were included in the present study. Among them, 508 air vs. biocouples included a measure of 1-OHP
98 (BaP vs. 1-OHP couples) and 188 of 3-OHBaP (BaP vs. 3-OHBaP couples). For 173 subjects, there were
99 measures of BaP, 1-OHP and 3-OHBaP.

100

101 Fig.1 here

102



104

105 **Fig 1:** Flow-chart of the data selection step

106 E-HAP: Exporisq-HAP database, EWES: end of work week - end of shift, EWES+16: end of work week
 107 - end of shift plus 16 hours, Pyr: pyrene, BaP: benzo[a]pyrene, APF: assigned protection factor
 108 depending on the type of mask worn by the worker, couples: association of a PAH air sample with a
 109 urinary PAH metabolite sample performed in parallel on the same day for a given worker (BaP vs. 1-
 110 OHP couples: association of a BaP sample and an EWES 1-OHP sample, BaP vs. 3-OHBaP couples:
 111 association of a BaP sample and an EWES+16 3-OHBaP sample, BaP vs. adj 1-OHP couples: association
 112 of a BaP sample and an EWES 1-OHP sample adjusted for real $\left[\frac{tPyr}{BaP}\right]$ ratios, wBaP vs. wadj 1-OHP couples:
 113 association of a BaP sample weighted by an APF and an EWES 1-OHP sample adjusted by the weighted
 114 $wBaP/w_{pyr}$ ratio, wBaP vs. 3-OHBaP couples: association of a BaP sample weighted by an APF and an
 115 EWES+16 3-OHBaP sample).

2.2 Urinary biomarker concentrations and atmospheric PAH levels

The urinary 1-OHP and 3-OHBP concentrations were measured by liquid chromatography with fluorescence detection (LC-Fluo) since 2000 and 2007, respectively (Barbeau *et al.*, 2011). The limits of quantification (LoQ) ranged from 0.02 $\mu\text{g. L}^{-1}$ to 0.1 $\mu\text{g. L}^{-1}$ for 1-OHP and from 0.05 ng. L^{-1} to 0.2 ng. L^{-1} for 3-OHBP. Values below the LoQ were replaced with random values ranging from 0 (excluded) to the LoQ.

Regarding airborne levels, gaseous and particulate PAHs were collected using a polypropylene cassette holding a 37-mm-diameter quartz filter connected in series to an XAD2 tube according to the NF X43-294 standard, which is recommended in France (AFNOR 1995). PAHs were measured by LC-Fluo. The LoQ for BaP, gaseous pyrene (gPyr) and particulate pyrene (pPyr) was 0.05 ng.sample^{-1} . The sum of pPyr and gPyr, corresponding to total pyrene (tPyr), was calculated, as well as the tPyr/BaP ratio. The toxic equivalent BaP (BaPteq6) was calculated using PAHs classified as carcinogenic 1A or 1B by the EU and associated with their toxic equivalence factors (TEFs). A total of six particulate PAHs were included in the BaPteq6 calculation, namely, BaP, dibenzo[a,h]anthracene (DahA), benzo[a]anthracene (BaA), benzo[b]fluoranthene (Bbf), benzo[k]fluoranthene (BkF), and chrysene (Chr). The French INERIS recommended TEFs were used for the BaPteq6 calculation (Doornaert *et al.*, 2003) (Eq. 1).

$$BaPteq6 = \sum_{i=1}^n (C_i \times TEF_i) = [BaP] \times 1 + [DahA] \times 1 + 0.1 \times ([BaA] + [Bbf] + [BkF]) + [Chr] \times 0.01 \quad [1]$$

where C is the concentration of a given PAH congener designated by the letter i .

2.3 Occupational groups

Monitoring campaigns were performed in several industrial sectors using either products derived from coal, from petroleum or from products emitting combustion fume. Sectors were subdivided into similar activity groups according to the job description and workplace studies.

The distribution of airborne PAH levels and urinary biomarker concentrations were assessed in each of these occupational groups (industrial sectors and job activities) that included at least five air vs. biocouples. Following the same approach as in a previous work (Petit *et al.*, 2017), the geometric standard deviations (GSDs) of atmospheric levels and urinary concentrations were determined to assess

144 the exposure variability within occupational groups. The groups were considered similar exposure
 145 groups (SEGs) for a given PAH or biomarker if its GSD concentration was ≤ 3 .

146

147 **2.4 Respiratory protective equipment**

148 RPEs were classified into four groups depending on the nature of the filtering media (FFP2/3 or P2/3
 149 particle filtering masks and A/ABEK gas masks with cartridges). Table 1 presents the mask group, with
 150 the mask and cartridge type considered for each group as well as the considered efficiency against PAHs.

151

152 **Table 1:** List of mask groups

Mask group	Mask and cartridge type	Efficiency
Gas masks	FFR with A or ABEK cartridge	gPAH
	EHPR with A or ABEK cartridge	gPAH
Particulate masks	FFR with FFP2 or FFP3 cartridge	pPAH
	EHPR with P2 or P3 cartridge	pPAH
Combined masks	FFR with A or ABEK cartridge and FFP2 or FFP3 cartridge	gPAH and pPAH
	EHPR with A or ABEK cartridge and P2 or P3 cartridge	gPAH and pPAH
SAR	Supplied-air respirator	gPAH and pPAH

153 Note: EHPR: elastomeric half face piece respirators, FFR: face piece respirator, SAR: supplied-air
 154 respirator.

155

156 To take into account the efficiency of RPEs worn by workers, airborne PAH levels were weighted by
 157 an APF, as recommended by the French Department of Labor and the French National Institute for
 158 Research and Safety (INRS) (Ministère du Travail, 2009). When information about RPE was missing,
 159 air vs. biocouples were excluded from the analysis to calculate weighted PAH levels. The weighted
 160 levels are indicated by a “w” preceding the considered PAH throughout this manuscript as follows:

161 w_{BaP} , w_{Pyr} ...

162 The APF used for weighting PAH levels was presented in Table 2. For instance, for workers wearing a
 163 “particulate mask”, an APF of 10 was assigned to particulate PAHs and an APF of 1 to gaseous PAHs.
 164 Thus, the levels of particulate PAHs were divided by 10 while those of gaseous PAHs remained the
 165 same.

166

167 **Table 2:** Assigned protection factor used for the weighted level calculation depending on the type of
 168 mask worn

Type of mask worn	APF for pPAHs	APF for gPAHs	pPAH levels	gPAH levels
No mask	1	1	Unchanged	Unchanged
Gas mask	1	10	Unchanged	Divided by 10
Particulate mask	10	1	Divided by 10	Unchanged
Combined mask	10	10	Divided by 10	Divided by 10
SAR	250	250	Divided by 250	Divided by 250

169 Note: APF: assigned protection factor, gPAHs: gaseous PAHs, pPAHs: particulate PAHs, SAR:
 170 supplied-air respirator.

171

172 *2.5 Assessing health risk within occupational groups*

173 To assess health risk within occupational groups, the CEN 689 recommendations (AFNOR, 2019) were
 174 followed using the exceedance fraction of limit values (LVs) (i.e. OEL or BLV). According to this
 175 standard, health risk is considered high if more than 5% of the concentrations of the group exceed the
 176 LV (corresponding to the 95th percentile of the concentration distribution equal to or higher than the
 177 LV). By contrast, the risk is considered low when less than 0.1% of the concentrations exceed the LV
 178 (corresponding to the 99.9th percentile equal to or higher than the LV). When the LV is located between
 179 the 95th and 99.9th percentiles of the concentrations, health risk conclusions are impossible to
 180 determine/reach.

181

182 For BaP, two different OELs were considered: the OEL recommended by the French National Health
 183 Insurance Fund (OEL_{CNAM}) set at 150 ng.m⁻³ (Nikolova-Pavageau et al, 2018) and the OEL used in
 184 several European countries (Sweden, Switzerland, Poland) (OEL_{EU}) set at 2000 ng.m⁻³ (SCOEL, 2016).
 185 These OELs were applied to the BaP, _wBaP (BaP levels weighted by an APF) and BaP_{teq6}
 186 concentrations. To our knowledge, no OEL has been published for pyrene.

187

188 For 1-OHP, the BLV recommended by the ACGIH (BLV_A) set at 2.5 µg/L (ACGIH, 2017) adjusted to
 189 the airborne tPyr/BaP ratio was used. However, instead of comparing 1-OHP levels to several BLV_A

190 (based on their respective tPyr/BaP ratios), it was more convenient to use a BLV_A of 1 µg. L⁻¹ and
 191 compare it with 1-OHP levels adjusted by the BaP/tPyr ratio (_{adj}1-OHP) as follows (Eq.2):

$$192 \quad \textit{adj}1OHP = 1OHP \times \left[\frac{BaP}{tPyr} \right] \quad [2]$$

193
 194 To determine the usefulness of integrating APF for PAH exposure, the analyses were also performed
 195 with weighted airborne levels, which means that the weighted _{adj}1-OHP (_{wadj}1-OHP) was calculated by
 196 adjusting the 1-OHP concentration to the weighted _wBaP/_wtPyr ratio of the air vs. biocouple and
 197 comparing it to a stated weighted BLV_A of 1 µg. L⁻¹ (Eq.3), as follows:

$$198 \quad \textit{wadj}1OHP = 1OHP \times \left[\frac{wBaP}{wtPyr} \right] = 1OHP \times \left[\frac{wBaP}{wgPyr + wpPyr} \right] \quad [3]$$

199
 200 For 3-OHBaP, the French guidance value proposed by INRS (BLV_{INRS}) set at 0.97 ng.g⁻¹ creatinine
 201 (equivalent to 0.40 nmol.mol⁻¹ creatinine) was considered (Nikolova-Pavageau et al, 2018). This
 202 reference concentration, measured at the beginning of the shift on the 5th day of exposure, is assumed to
 203 result from atmospheric BaP exposure of 150 ng.m⁻³ (OEL_{CNAM}) over the work week.

204
 205 For the analysis using an APF to calculate weighted BaP levels (_wBaP) and weighted _{adj}1-OHP (_{wadj}1-
 206 OHP) concentrations, 497 _wBaP vs. _{wadj}1-OHP couples were included, and 181 _wBaP vs. 3-OHBaP
 207 couples (corresponding to 166 couples with a measure of both biomarkers) were included (Fig. 1).

208

209 **2.6 Consistency of BaP OEL_{CNAM} vs. BLV exceedances for couples**

210 The consistency of airborne OEL_{CNAM} and urinary BLV exceedances was analyzed on the scale of the
 211 air vs. biocouples. A total of 4 situations were considered: an exceedance of the OEL_{CNAM} alone, an
 212 exceedance of the BLV alone, an exceedance of both LVs or no exceedance at all. The last two situations
 213 corresponded to consistent conclusions regarding LV exceedances.

214 For BaP vs. _{adj}1-OHP couples, the OEL_{CNAM} exceedance of the BaP level was compared to the BLV_A
 215 exceedance of _{adj}1-OHP levels. The same analysis was conducted with weighted levels. For BaP vs. 3-

216 OHBaP couples, the OEL_{CNAM} exceedance of BaP and $wBaP$ levels was compared to the BLV_{INRS}
217 exceedance of 3-OHBaP.

218

219 **2.7 Software**

220 Analyses were performed using R version 4.1.1 for Windows 10®.

221

222 **3. Results**

223 **3.1 Air vs. biocouple characteristics**

224 Among 523 couples, 218 workers (42%) were involved in 15 plants of 6 “coal-derived” sectors, namely,
225 coke production, silicon production, aluminum production, carbon product manufacturing, steel foundry
226 and railroad maintenance. The remaining 305 workers from 83 plants were exposed to petroleum
227 distillates or combustion fumes in 4 “petroleum-derived” sectors, namely, combustion processes, the
228 handling of lubricating oils, engine exhaust emissions, and bitumen (Table 3). Combustion processes
229 were included in the “petroleum-derived” sector due to the similarly relatively low PAH exposure levels
230 that are usually found in these sectors.

231 Most workers (99%) were men with a median age of 41 years. The proportion of smokers was the same
232 in the “coal-derived” and “petroleum-derived” sectors, with an average of 37% (Table 3). Data for
233 smoking habits were missing for only 2% of the population.

234 The efficiency of RPE against gaseous and particulate PAHs varied greatly from one sector to another.
235 There were only 2% missing mask data, with the exception of steel foundries, where data were missing
236 for 44% of workers (Table 3). More than 50% of the workers involved in “coal-derived” sectors were
237 wearing an effective RPE against particulate PAHs (“particulate mask” or “combined mask”). Nearly
238 as many were wearing effective RPE against gaseous PAHs (“gaseous mask” or “combined mask”),
239 while 26% did not wear any RPE. These respective proportions were 9%, 6% and 86% in “petroleum-
240 derived” sectors; however, there were two exceptions. In railroad maintenance, no worker wore a RPE,
241 and for the combustion processes, approximately 40% of the workers wore a “particulate mask”. Only
242 6 workers involved in silicon production or carbon product manufacturing wore a SAR.

243 The 188 BaP vs. 3-OHBaP couples represented only one-third of the 523 air vs. biocouples, but their
244 overall characteristics were the same (data not shown). For these couples, no data were available for
245 coke production. In addition, none of the workers wore a “gas mask”, whereas the “particulate mask”
246 proportion was slightly greater (21% of workers), mainly due to aluminum production, for which all
247 workers wore such masks. Similar proportions of data were missing among these couples regarding
248 smoking habits (2%) and the type of mask worn (4% corresponding to the steel foundry).

249 **Table 3:** Distribution of air vs. biocouples for each occupational sector depending on smoking status
 250 and mask type

Industrial sectors	Number of plants	Number of workers	Number of smokers	Mask type				
				None	P	G	Combined	Unknown
"Coal-derived" sectors	15	218 (42%)	81 (37%)	56 (26%)	59 (27%)	39 (18%)	57 (26%)	7 (3%)
Coke production	1	40	17 (42%)	12 (30%)	1 (2%)	27 (68%)	0	0
Silicon production	5	67	24 (36%)	11 (16%)	14 (21%)	0	42 (63%)	0
Aluminum production	2	32	18 (56%)	2 (6%)	13 (41%)	12 (38%)	5 (16%)	0
Carbon product manufacturing	4	57	11 (19%)	25 (44%)	22 (39%)	0	10 (18%)	0
Railroad maintenance	1	6	2 (33%)	6 (100%)	0	0	0	0
Steel foundries	2	16	9 (56%)	0	9 (56%)	0	0	7 (44%)
"Petroleum-derived" sectors	83	305 (58%)	112 (37%)	263 (86%)	20 (7%)	11 (4%)	7 (2%)	4 (1%)
Combustion processes	8	17	4 (24%)	7 (41%)	5 (29%)	3 (18%)	2 (12%)	0
Handling of lubricating oils	5	44	12 (27%)	40 (91%)	1 (2%)	0	0	3 (7%)
Engine exhaust emissions	43	117	36 (31%)	89 (76%)	14 (12%)	8 (7%)	5 (4%)	1 (1%)
Bitumen	27	127	60 (47%)	127 (100%)	0	0	0	0
TOTAL	98	523	193 (37%)	319 (61%)	79 (15%)	50 (10%)	64 (12%)	11 (2%)

251 *Note:* air vs biocouples: association of an air sample and a urinary sample performed on the same day,
 252 at the end of shift (for 1-OHP analysis) or at the end of shift plus 16 hours (for 3-OHBP analysis).
 253 P: "particulate mask", G: "gaseous mask", combined: association of a gaseous cartridge and particulate
 254 filter (or air-supplied respirator), unknown: information not available.

255

256 *3.2 Comparison of airborne PAH levels and urinary biomarker concentrations within* 257 *occupational groups*

258

259 *3.2.1 BaP vs. 1-OHP couples*

260 Among the "coal-derived" sectors, 4 to 6 different job activities were identified for each sector (Table
 261 4), with the exception of the steel foundry where all workers were heating attendant masons, and the
 262 railroad maintenance consisting of 6 workers replacing creosote-impregnated wood in railroad ties. In
 263 the "petroleum-derived" sectors, there was one single job activity (chimney sweeper) in combustion
 264 processes and 9 job activities in engine exhaust emissions.

265 For the 508 BaP vs. 1-OHP couples, gPyr levels were rarely below the LoQ, with the exception of
 266 combustion processes (29%) and vehicle drivers (73%). Nearly 20% of the pPyr and BaP levels were

267 below the LoQ in the “petroleum-derived” sectors, while their levels were always quantifiable in the
268 “coal-derived” sectors.

269 The levels of particulate PAHs (pPyr and BaP) were approximately 300 times lower in “petroleum-
270 derived” sectors (BaP geometric mean (GM) of 0.5 ng.m⁻³) than in “coal-derived” sectors (BaP GM =
271 186 ng.m⁻³), while the levels of gPyr were only 20 times lower. Among “petroleum-derived” sectors,
272 combustion processes and some activities of engine exhaust emissions (working in closed environments
273 and waste management drivers) stood out with slightly higher levels of pPyr and BaP. The highest PAH
274 levels were measured in coke production (GM = 102 ng.m⁻³, 1370 ng.m⁻³ and 1500 ng.m⁻³ for gPyr, pPyr
275 and BaP, respectively), and a maximum of BaP GM at 2320 ng.m⁻³ was found for furnace battery
276 cleaning-up.

277 The median tPyr/BaP ratio was 4 times higher in “petroleum-derived” sectors than in “coal-derived”
278 sectors. Indeed, this ratio was above 2.5 in most “petroleum-derived” job activities and even above 20
279 in bitumen, whereas it was mainly below 2.5 in “coal-derived” sectors, with the exception of steel
280 foundry and railroad maintenance, where it exceeded a value of 8.

281 For 1-OHP, the only values below the LoQ were found for 6 workers involved in bitumen roofing. The
282 GM of 1-OHP concentrations was 9 times lower in “petroleum-derived” sectors than in “coal-derived”
283 sectors, with GM of 0.08 and 0.70 μmol.mol⁻¹ creatinine, respectively. The highest levels were once
284 again found for the activity of furnace battery cleaning-up in coke production (GM = 3.92 μmol.mol⁻¹
285 creatinine). Some activities were associated with high levels of 1-OHP considering the corresponding
286 airborne concentrations, such as anode production in aluminum production or raw carbon extrusion in
287 carbon product manufacturing. Workers involved in railroad maintenance had particularly high levels
288 of 1-OHP (GM = 1.52 μmol.mol⁻¹ creatinine) in parallel with relatively high levels of both gPyr (GM =
289 42 ng.m⁻³) and pPyr (GM = 31 ng.m⁻³), while BaP levels remained very low (GM = 8.4 ng.m⁻³).

290 **Table 4:** Airborne BaP levels at the end of week and urinary 1-OHP concentrations on the same day at the end of shift for multiple occupational groups

Occupational groups	Airborne PAH														Urinary 1-OHP						
	N	GM	gPyr			pPyr			BaP			tPyr/BaP				- 95th GSD <LoQ					
Industrial sectors Job activities			95th (ng.m ⁻³)	GSD	<LoQ (%)	GM	95th (ng.m ⁻³)	GSD	<LoQ (%)	GM	95th (ng.m ⁻³)	GSD	<LoQ (%)	Med	5th	95th	GM	95th (μmol.mol ⁻¹)	GSD	<LoQ (%)	
"Coal-derived" sectors	209	31	675	7.1	0%	272	17 290	8.8	0%	186	6 780	9.3	0%	1.5	0.7	10	0.70		4.83	3.3	0%
Coke production	40	102	527	3.7	0%	1 370	11 870	4.5	0%	1 500	9 060	3.4	0%	1.1	0.6	1.8	1.42		4.87	2.3	0%
Coke pusher	6	107	319	5.8	0%	1 230	3 910	7	0%	1 290	3 520	5.7	0%	1.1	0.8	1.3	0.79		1.38	1.7	0%
Furnace door settings	5	34	174	4	0%	769	3 990	6.1	0%	851	3 070	4.4	0%	1.1	0.7	1.3	0.83		2.29	2	0%
Furnace battery cleaning-up	7	195	341	1.7	0%	2 310	4 270	1.6	0%	2 320	4 920	1.6	0%	1.1	0.7	1.5	3.92		9.51	1.9	0%
Watchman	6	185	594	3.1	0%	1 860	16 320	5.2	0%	1 730	9 770	3.7	0%	1.3	0.8	1.7	1.02		1.86	1.6	0%
Mason	9	137	1 040	3.7	0%	1 360	10 760	4.8	0%	1 570	9 370	3.5	0%	1	0.6	1.9	1.72		3.42	2	0%
Silicon production	63	38	1 550	8.5	0%	676	50 420	13	0%	364	7 040	10	0%	1.7	0.8	8	0.56		8.75	4.7	0%
Paste loading in the composite electrode	12	34	181	4.1	0%	840	3 020	2.2	0%	774	3 260	2.5	0%	1.1	0.8	2.3	0.36		2.09	4.8	0%
Casing welding of the composite electrode	12	72	874	3.5	0%	1 040	5 710	3.3	0%	1 000	4 990	3.6	0%	1.1	0.7	2.5	0.38		1.03	2.2	0%
Manufacture	11	11	487	4.8	0%	44	642	5.3	0%	22	80	2.9	0%	1.7	1	21	0.21		0.68	2.7	0%
Annual maintenance (cold furnace)	12	62	1 100	9	0%	2 140	42 140	12	0%	634	7 690	7.5	0%	3.5	1.6	9.3	2.06		9.87	3.9	0%
Hot furnace maintenance	7	37	1 540	11	0%	3 010	66 040	66	0%	749	21 430	40	0%	6.4	2.1	7.8	1.97		10.1	6.5	0%
Aluminum production	32	19	142	3.3	0%	148	690	3.8	0%	80	353	3.9	0%	2.3	1	6.8	0.75		2.14	2.2	0%
Maintenance of paste tower and furnace	6	12	21	1.8	0%	171	510	2.1	0%	99	195	1.7	0%	1.8	1	4.5	0.73		1.7	2.2	0%
Ramming: furnace restoration	13	38	155	4.1	0%	182	504	2.1	0%	104	283	2.2	0%	2.3	1.2	6.2	0.52		1.11	2	0%
Anode baking	6	9.8	16	1.6	0%	32	74	1.8	0%	21	54	2.1	0%	2.2	1.3	2.6	0.73		1.73	2.1	0%
Anode production – paste tower	7	12	35	2.8	0%	336	10 870	7.5	0%	126	10 760	10	0%	3.3	1.1	9.1	1.54		3.01	1.6	0%
Carbon product manufacturing	53	32	324	4.4	0%	83	640	3.5	0%	96	1 130	4.1	0%	1.3	0.5	6.1	0.57		4.33	3	0%
Raw carbon cathode extruding	20	50	343	3.8	0%	135	497	2.1	0%	175	951	2.3	0%	0.9	0.5	6.9	0.57		1.59	2.2	0%
Raw graphite cathode extruding	11	13	81	2.5	0%	53	141	2.3	0%	69	218	2.4	0%	1	0.5	2.8	0.49		0.84	1.6	0%
Cathode graphitization	5	14	92	3.2	0%	25	62	2.4	0%	18	59	4.1	0%	2	1.2	8	0.28		0.44	2	0%
Laboratory analysis	6	33	1 010	9.3	0%	75	4 900	13	0%	68	3 820	13	0%	1.7	1	3.1	0.37		1.15	2.9	0%
Railroad maintenance (replacing creosote-impregnated wood ties)	5	42	54	1.2	0%	31	48	1.4	0%	8.4	15	1.6	0%	9.1	5.9	14	1.52		2.68	1.7	0%
Steel foundries (heating attendant mason)	16	1.5	12	9.3	6%	45	964	4.8	6%	9.2	95	4.6	0%	8.2	1.2	13	0.36		0.78	2	0%
"Petroleum-derived" sectors	299	1.3	26	5.2	6%	1.5	57	9.9	21%	0.5	14	7.7	24%	6.4	0.8	142	0.08		0.48	3.1	2%
Combustion processes	17	0.2	0.7	3.3	29%	4.3	66	8	29%	3	65	10	6%	1.8	0.6	5.4	0.1		0.33	2.1	0%
Chimney sweeper	5	0.2	0.5	3.3	20%	19	118	4.5	20%	8.8	58	3.9	0%	2	1.6	3.3	0.09		0.18	1.7	0%
Handling of lubricating oils	44	1.3	7.3	3.4	2%	2.7	24	5	14%	0.7	10	5.6	11%	6.4	1.8	50	0.1		0.28	2.1	0%
Undercutting	5	0.4	0.6	1.6	0%	0.06	0.2	2.7	100%	0.06	0.2	4.3	60%	5.3	3.4	45	0.08		0.13	1.5	0%
Turning	22	1.2	2	1.7	0%	3.2	4.3	1.3	0%	0.3	0.6	2.1	9%	12	5.9	104	0.09		0.28	2.2	0%
Discharge mold	10	4.7	25	3.4	0%	5.2	27	3.9	0%	4.7	13	2.4	0%	3.2	1.1	4.2	0.18		0.36	1.7	0%
Vehicles	7	0.8	4.6	5.9	14%	8.4	23	2.8	14%	3	7.2	2.5	0%	3.7	2.1	3.9	0.08		0.17	1.7	0%
Engine exhaust emissions	117	0.7	8	4.4	9%	1.1	61	12	22%	0.7	13	8.1	21%	3.7	0.4	45	0.07		0.34	2.8	0%
Mechanic of light vehicles	16	0.5	2.2	2.6	0%	0.3	4.9	6	31%	0.9	7.6	3.5	0%	1.3	0.3	4.2	0.09		0.19	1.8	0%
Technical control of light vehicles	7	0.5	1.6	2.3	0%	0.6	10	4.9	0%	0.3	4.2	4.8	14%	4	1.9	16	0.04		0.1	1.9	0%

Mechanic of heavy trucks	9	0.8	5.1	2.4	0%	3.8	24	5.7	0%	1	6.5	5.8	11%	3.9	1.4	80	0.05	0.2	4.8	0%
Technical control of heavy trucks	7	0.2	0.4	1.5	14%	0.2	0.4	1.7	29%	0.6	16	7.6	14%	1	0.1	4.7	0.03	0.03	1.3	0%
Vehicle driver	11	0.07	0.7	4.1	73%	0.2	2.7	5.3	73%	0.2	1.3	4.4	36%	2.3	0.4	6.5	0.04	0.19	3	0%
Use of 2-Stroke and 4-Stroke engines	12	3.5	25	4.1	0%	8	40	3.5	0%	2.3	13	2.8	0%	4.5	3	25	0.12	0.36	2.1	0%
Generator system maintenance	10	2.4	7.7	2.5	0%	3.5	45	6.9	10%	1	5.5	7.7	10%	3.9	2.2	76	0.09	0.2	2.1	0%
Working in closed environment (tunnel)	10	2	25	5.1	10%	31	174	6.6	10%	3.6	40	8.1	10%	10	1.9	219	0.11	0.36	2.8	0%
Waste management driver	21	0.6	5.1	2.6	0%	0.6	190	13	24%	0.2	161	18	57%	8.6	1.2	45	0.09	0.61	3.3	0%
Bitumen	121	3.3	41	4.4	2%	1.3	37	10	21%	0.3	7.8	6.6	33%	22	1.9	457	0.09	0.51	3.9	5%
Roofing	15	2.4	93	7.4	13%	2.3	38	7.2	13%	1.2	97	11	27%	3.6	1.4	18	0.02	0.42	8.7	40%
Road paving with hot bitumen	85	3.5	40	4.5	0%	2	69	9.2	14%	0.3	4.3	5.4	32%	27	2	518	0.1	0.48	2.9	0%
Road paving with warm bitumen in tunnel	19	3.5	8.6	2.5	0%	0.2	1	6	47%	0.1	2.4	6.5	37%	28	2.7	466	0.16	0.62	3	0%

291

292 *Note:* The occupational groups are subdivided into two main categories: "coal-derived sectors" using coal products and "petroleum-derived sectors" exposed to
 293 petroleum distillates or organic combustion. Groups in bold correspond to occupational sectors and those in grey to job activities (the sum of the job activity
 294 samples is not necessarily equal to the number of samples in their given sector, as groups of "extreme" size (either inferior to 5 samples, or very close to the
 295 number of samples in the sector) are not shown here.

296 pPyr: particulate pyrene, tPyr: total pyrene (sum of particulate and gaseous pyrene), BaP: benzo[a]pyrene, 1-OHP: 1-hydroxypyrene, LoQ: limit of quantification,

297 N: number of samples, GM: geometric mean, 5th: 5th percentile, 95th: 95th percentile, GSD: geometric standard deviation (in bold: ≤ 3, normal: 3-6, in italic: >

298 6), Med: median.

299 3.2.2 *BaP vs. 3-OHBaP couples*

300 Regarding the 188 BaP vs. 3-OHBaP couples (Table 5), airborne BaP levels were very low in
301 “petroleum-derived” sectors, with 30% of the values below the LoQ. This proportion rose to 60% when
302 handling lubricating oils. A maximum BaP GM of 8.8 ng.m⁻³ was found for chimney sweepers. The
303 levels in “coal-derived” sectors were almost 300 times higher than in “petroleum” sectors as they were
304 for BaP vs. 1-OHP couples. The BaP levels in silicon production, aluminum production and carbon
305 product manufacturing were 10 to 50 higher than those found in the steel foundry and railroad
306 maintenance.

307 For 3-OHBaP, approximately 70% of the values were below the LoQ in most “petroleum-derived”
308 sectors. Conversely, these values were rare in “coal-derived” sectors, affecting less than 20% of the
309 couples, with the exception of railroad maintenance (40%). In this last group, as well as in the steel
310 foundry, relatively low levels of both BaP (GM < 10 ng.m⁻³) and 3-OHBaP (GM < 0.05 nmol.mol⁻¹
311 creatinine) were recorded. In contrast, the highest 3-OHBaP concentrations were measured in carbon
312 product manufacturing (GM = 0.19 nmol.mol⁻¹ creatinine), while those of silicon production were
313 almost twice as low. These results were not consistent with airborne BaP levels, which were 3 times
314 higher in silicon production (GM = 309 ng.m⁻³) than those recorded for carbon product manufacturing
315 (GM = 94 ng.m⁻³).

316 **Table 5:** Airborne BaP levels at the end of week and urinary 3-OHBaP concentrations on the same day at the end of shift plus 16 hours for multiple occupational
 317 groups

Occupational groups	N	Airborne BaP				Urinary 3-OHBaP			
		GM	95th (ng.m ⁻³)	GSD	<LoQ (%)	GM	95th (nmol.mol ⁻¹)	GSD	<LoQ (%)
Industrial sectors									
Job activities									
"Coal-derived" sectors	101	103	3 550	7.9	0%	0.12	2.08	5	6%
Silicon production	32	309	8 070	9.9	0%	0.11	1.81	4.8	3%
Paste loading in the composite electrode	5	429	1 500	4.3	0%	0.09	1.43	5.5	0%
Manufacture	5	28	89	4.4	0%	0.04	0.15	3.3	0%
Annual maintenance (cold furnace)	10	426	6 890	7.2	0%	0.12	1.39	4	10%
Aluminum production	11	124	313	1.7	0%	0.08	0.36	4.9	18%
Ramming: furnace restoration	7	147	372	1.8	0%	0.11	0.36	4.7	14%
Carbon product manufacturing	46	94	1 300	4.7	0%	0.19	2.54	4.7	2%
Raw carbon cathode extruding	19	182	976	2.3	0%	0.21	2.08	3.7	0%
Raw graphite cathode extruding	9	47	188	2.9	0%	0.09	0.21	2.9	11%
Railroad maintenance (replacing creosote-impregnated wood ties)	5	7.7	14	1.5	0%	0.02	0.09	5.8	40%
Steel foundries (heating attendant mason)	7	6	155	7.3	0%	0.04	0.13	2	0%
"Petroleum-derived" sectors	87	0.4	16	9.6	30%	0.01	0.09	3.9	69%
Combustion processes	10	2.7	47	10	10%	0.01	0.05	3.8	70%
Chimney sweeper	5	8.8	58	3.9	0%	0.008	0.05	5.4	60%
Handling of lubricating oils (undercutting)	5	0.06	0.2	4.3	60%	0.1	0.23	2.7	20%
Engine exhaust emissions	22	0.3	3.5	4.4	23%	0.01	0.05	3.2	77%
Mechanic of light vehicles	5	0.6	1.7	2.7	0%	0.01	0.01	1.5	60%
Technical control of light vehicles	6	0.2	0.4	2.3	17%	0.007	0.02	3.9	100%
Bitumen	50	0.3	12	11	34%	0.01	0.07	3.8	70%
Roofing	17	1	90	10	29%	0.02	0.07	2.4	76%
Road paving with hot bitumen	22	0.2	6	10	41%	0.008	0.06	4.7	68%
Road paving with warm bitumen in tunnel	11	0.2	1.7	8.8	27%	0.008	0.05	3.8	64%

318

319 *Note:* The occupational groups are subdivided into two main categories: "coal-derived sectors" using coal products and "petroleum-derived sectors" exposed to
 320 petroleum distillates or organic combustion. Groups in bold correspond to occupational sectors and those in grey to job activities (the sum of the job activity
 321 samples is not necessarily equal to the number of samples in their given sector, as groups of "extreme" size (either inferior to 5 samples, or very close to the
 322 number of samples in the sector) are not shown here.

323 pPyr: particulate pyrene, tPyr: total pyrene (sum of particulate and gaseous pyrene), BaP: benzo[a]pyrene, 3-OHPBaP: 3-hydroxybenzo[a]pyrene, LoQ: limit of
324 quantification, N: number of samples, GM: geometric mean, 5th: 5th percentile, 95th: 95th percentile, GSD: geometric standard deviation (in bold: ≤ 3 , normal:
325 3-6, in italic: > 6), Med: median.

326 **3.3 Comparison of airborne PAH and urinary biomarker GSDs within occupational groups**

327

328 Within each occupational group, the dispersion of urinary 1-OHP concentrations was usually lower than
329 that of atmospheric PAHs measured in parallel (Table 4). Indeed, at the industrial sector level, GSDs
330 were below 3 in 70% of the cases for 1-OHP concentrations but in only 10% of the cases for BaP, gPyr
331 and pPyr. At the job/activity level, lower GSDs were observed, with nearly 75% of GSDs below 3 for
332 1-OHP, and 40% for PAH levels.

333 The GSDs of gPyr, pPyr and BaP were similar to each other in “coal-derived” sectors, while gPyr GSDs
334 tended to be lower than the other two in “petroleum-derived” sectors and thus were closer to the 1-OHP
335 distribution GSDs.

336 The dispersion of 3-OHBaP concentrations was higher than that of 1-OHP but was again lower than that
337 of atmospheric BaP levels. Regardless of the occupational groups, most 3-OHBaP GSDs ranged from 3
338 to 6 and were in all cases below 6. Conversely, 40% of the BaP GSDs were above 6. Aluminum
339 production had higher 3-OHBaP GSDs than BaP GSDs.

340

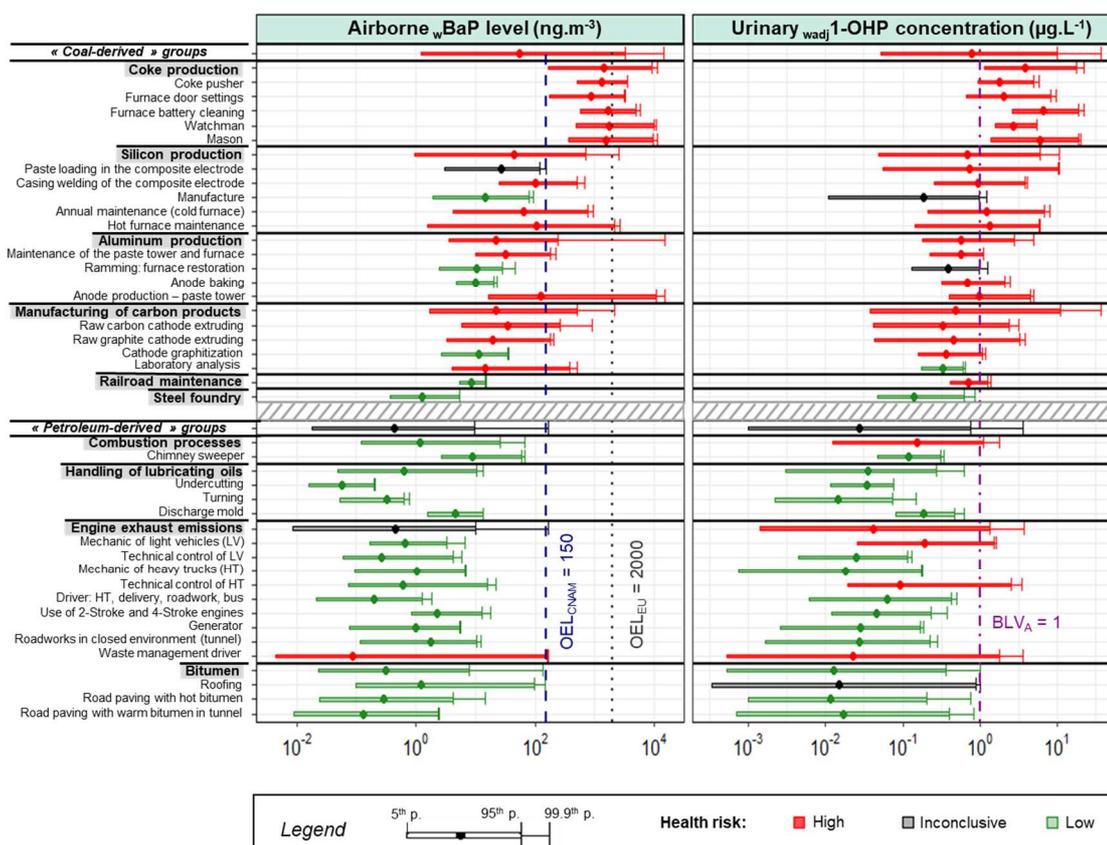
341 **3.4 Assessing health risk within occupational groups**

342 **3.4.1 $wBaP$ vs. $wadj1-OHP$ couples**

343 The distributions of airborne BaP concentrations weighted by APF ($wBaP$) and 1-OHP concentrations
344 adjusted by the $wBaP/wPyr$ ratio ($wadj1-OHP$) are presented within each occupational group in Fig. 2.
345 Both OEL_{CNAM} and BLV_A are represented to assess the health risk depending on their exceedance
346 fraction. The OEL_{EU} is also drawn for information.

347 The conclusions regarding the health risk were similar according to the exceedance fraction of OEL_{CNAM}
348 and BLV_A for 75% of the occupational groups. More precisely, every activity estimated at high risk
349 when using OEL_{CNAM} was also considered at high risk based on BLV_A , with the exception of the
350 laboratory analysis in carbon product manufacturing. Conversely, several activities estimated at high
351 risk when using BLV_A were estimated at low risk with OEL_{CNAM} , both in “petroleum-derived” and “coal-
352 derived” sectors.

353 In “petroleum-derived” sectors, only the activity of waste management drivers was estimated to be at
 354 high risk according to OEL_{CNAM} , while 20% of all job activities presented a high risk according to BLV_A .
 355 Conversely, in “coal-derived” sectors, health risk according to OEL_{CNAM} was high for all sectors, with
 356 the exception of the steel foundry and railroad maintenance. It was also high for all activities of coke
 357 production. When using BLV_A , health risk was considered high in all sectors, with the exception of steel
 358 foundries, and in most job activities.
 359 Overall, twice as many occupational groups were estimated to be at high risk when considering
 360 OEL_{CNAM} instead of OEL_{EU} . Coke production was the only sector considered at high risk when using
 361 OEL_{EU} , but three other “coal-derived” sectors could possibly be at risk, as the estimation was
 362 inconclusive. Conclusions were identical when considering $wBaP_{teq6}$ instead of $wBaP$.



363
 364 **Fig 2:** Distribution of weighted BaP levels and adjusted 1-OHP concentrations and health risk
 365 assessment within occupational groups
 366 $wBaP$: benzo[a]pyrene concentrations weighted by an assigned protection factor (APF) depending on
 367 the type of mask worn by the worker, $wadj$ 1-OHP: 1-OHP concentration adjusted by the weighted $wBaP$
 368 / w_{tPyr} ratio (w_{tPyr} corresponding to the sum of gaseous and particulate pyrene levels weighted by an

369 APF). Health risk was assessed depending on the exceedance fraction of the limit values (OEL_{CNAM} and
 370 BLV_A , respectively).

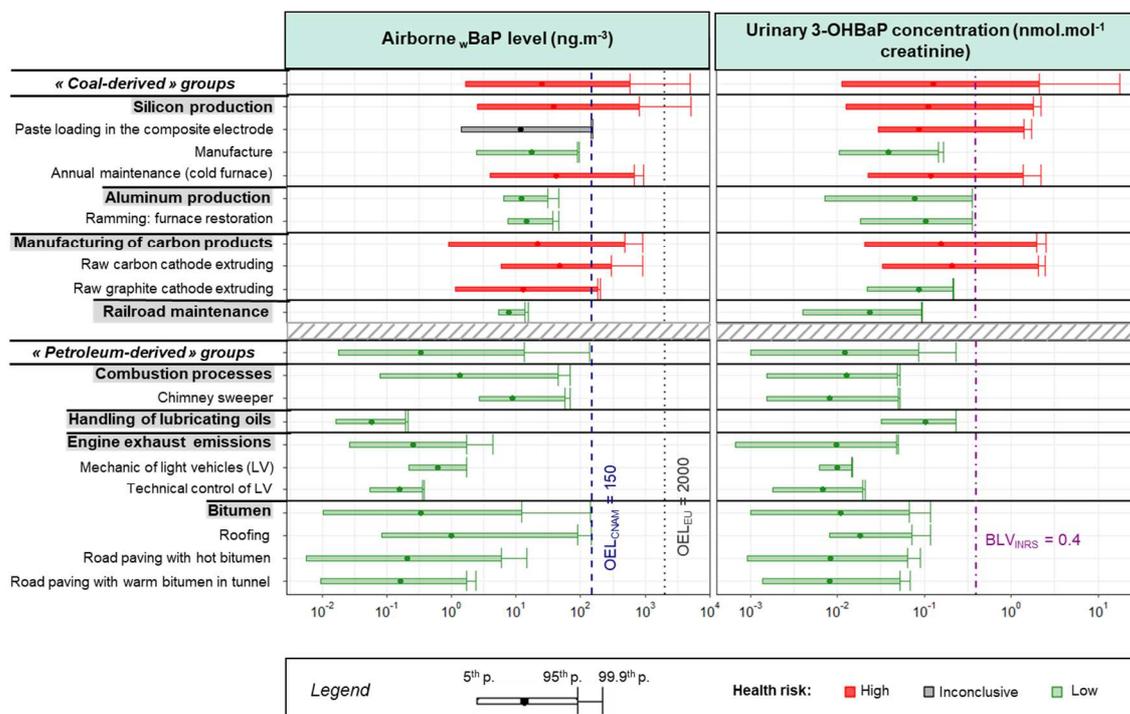
371

372 3.4.2 *wBaP vs. 3-OHBaP couples*

373 The distributions of $wBaP$ and 3-OHBaP within each occupational group are presented in Fig. 3 for the
 374 181 couples. The health risk was assessed by the respective exceedance fraction of OEL_{CNAM} and
 375 BLV_{INRS} . No data were available for the coke production and steel foundries.

376 The conclusions regarding health risk were identical according to OEL_{CNAM} and BLV_{INRS} for 90% of the
 377 occupational groups. Regardless of the LV considered, health risk was low for all “petroleum-derived”
 378 sectors and for two “coal-derived” sectors (railroad maintenance and aluminum production). All groups
 379 estimated at high risk according to BLV_{INRS} were also estimated at high risk (or inconclusive) with
 380 OEL_{CNAM} . Conversely, the activity of the extruding raw graphite cathode was estimated to be at high
 381 risk according to OEL_{CNAM} but not according to BLV_{INRS} .

382 According to OEL_{EU} , no group was estimated to be at high risk, and only silicon production could be at
 383 risk with an inconclusive estimation. Conclusions were identical when considering $wBaP_{teq6}$ instead of
 384 $wBaP$.



385

386 **Fig 3:** Distributions of weighted BaP levels and 3-OHBaP concentrations and health risk assessment
387 within occupational groups

388 $wBaP$: benzo[a]pyrene concentrations weighted by an assigned protection factor (APF) depending on
389 the type of mask worn by the worker, 3-OHBaP: 3-hydroxybenzo[a]pyrene concentrations. Health risk
390 is assessed depending on the exceedance fraction of the limit values (OEL_{CNAM} and BLV_{INRS} ,
391 respectively).

392

393 *3.5 Consistency of LV exceedances within couples*

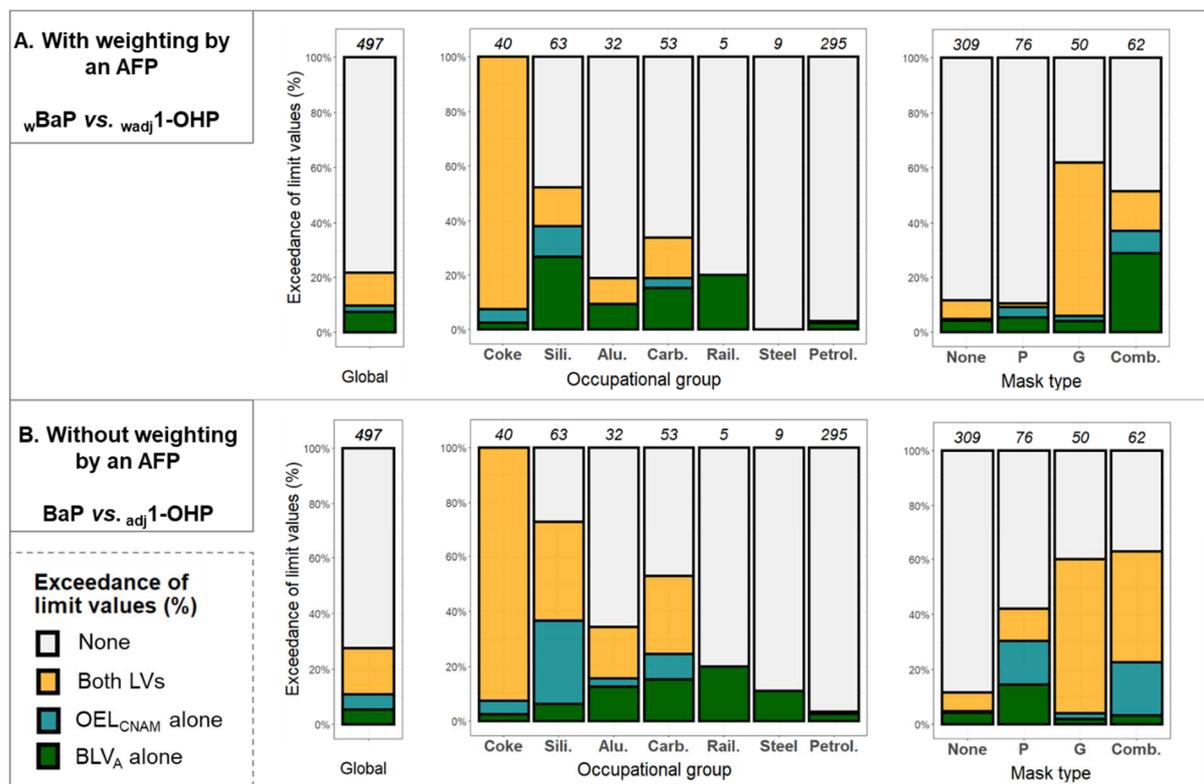
394

395 *3.5.1 $wBaP$ vs. $wadj1-OHP$ couples*

396 For each of the 497 couples, the OEL_{CNAM} exceedance of the $wBaP$ level was compared to BLV_A
397 exceedance of $wadj1-OHP$ and analyzed according to the occupational sector and mask type (Fig. 4A).

398 Regarding “petroleum-derived” sectors, no exceedance of OEL_{CNAM} or BLV_A was found for 97% of the
399 couples. An exceedance of OEL_{CNAM} alone was found for less than 1% of the couples, and an exceedance
400 of BLV_A alone for less than 3%. Conversely, the exceedances of OEL_{CNAM} and BLV_A were much less
401 consistent for “coal-derived” sectors. Only the levels in the steel foundry were consistent with no LV
402 exceedance, and in coke production where both LVs were exceeded in 90% of the cases. For the other
403 sectors, exceedances of BLV_A alone were observed in 9% of couples in aluminum production, 15% in
404 carbon product manufacturing, 20% in railroad maintenance and 27% in silicon production. The
405 exceedances of OEL_{CNAM} alone were related only to 4% in carbon product manufacturing, 5% in coke
406 production and 11% in silicon production.

407 Regarding mask type, when workers wore no mask, a “particulate mask” or a “gas mask”, the OEL_{CNAM}
408 exceedance of $wBaP$ was consistent with BLV_A exceedance of $wadj1-OHP$ for 90% of the couples (Fig.
409 4A). This was mainly due to an absence of LV exceedance in the first two cases, whereas more than
410 50% of the couples with a “gas mask” presented an exceedance of both LVs. For “combined masks”,
411 consistent results were found for only 60% of the couples, a quarter of which exceeded both LVs. While
412 the exceedances of OEL_{CNAM} alone were related to only 8% of the couples, those of BLV_A alone were
413 related to 29% of them.



415

416 **Fig. 4:** Consistency between the exceedances of the atmospheric limit value (OEL_{CNAM}) and the
 417 biological limit value (BLV_A) for BaP vs. adj1-OHP couples according to occupational sector and mask
 418 type, with or without weighting by an APF

419 A: with weighting by AFP = wBaP vs. wadj1-OHP couples, B: without weighting by AFP = BaP vs. adj1-
 420 OHP couples.

421 Couple: association of a PAH air sample with a urinary PAH metabolite sample performed on the same
 422 day for a given worker, wBaP: benzo[a]pyrene concentrations weighted by an assigned protection factor
 423 (APF) depending on the type of mask worn by the worker, wadj1-OHP: 1-OHP concentrations adjusted
 424 by the weighted wBaP/wtPyr ratio (wtPyr corresponding to the sum of gaseous and particulate pyrene
 425 levels weighted by an APF), adj1-OHP: 1-OHP concentrations adjusted by the nonweighted BaP/tPyr
 426 ratio, LV: limit value, OEL_{CNAM}: occupational exposure LV defined for BaP by the French CNAM,
 427 BLV_A: biological LV defined for adj1-OHP by the ACGIH, Sili: silicon production, Alu: aluminum
 428 production, Carb: carbon product manufacturing, Rail: railroad maintenance, Steel: steel foundry,
 429 Petrol: “petroleum-derived sectors, P: “particulate mask”, G: “gas mask”, Comb: “combined mask”.

430 3.5.2 *BaP vs. 1-OHP couples*

431 The same analyses were performed without taking into account the efficiency of the mask worn by the
432 workers, using non-weighted BLV_A for $adj1$ -OHP and OEL_{CNAM} for non-weighted BaP (Fig. 4B). The
433 results were the same as those of weighted levels for “petroleum-derived” sectors, coke production and
434 railroad maintenance. For the other “coal-derived” sectors, the exceedance of OEL_{CNAM} alone increased,
435 and the percentage exceeding both LVs was twice as high, with the exception of the steel foundry. While
436 the exceedance of BLV_A alone decreased from 27% to 6% in silicon production, it increased from 0%
437 to 11% in the steel foundry.

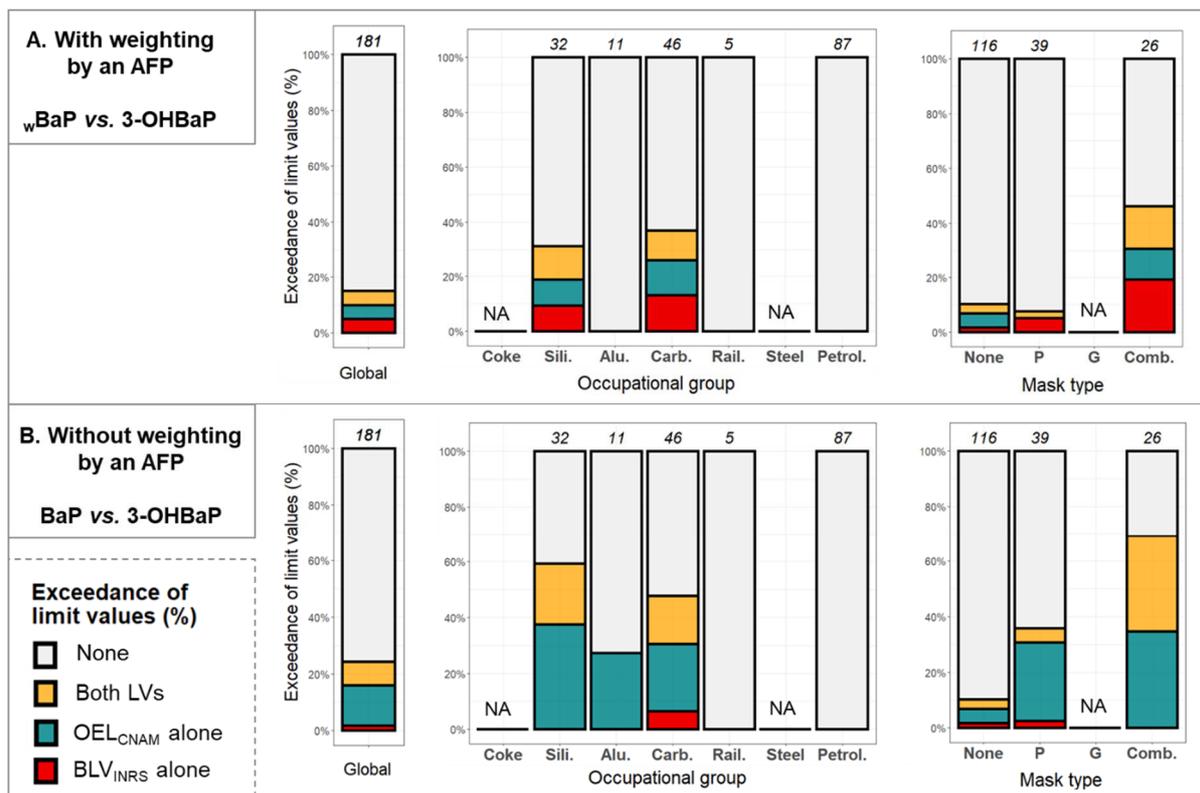
438 Without weighting by APF, the exceedances of BLV_A alone decreased from 4% to 2% for workers
439 wearing a “gas mask” (Fig. 4B). For those wearing a “particulate mask”, the exceedances of LVs
440 increased to approximately 15% for OEL_{CNAM} alone, BLV_A alone and for both LVs. For workers wearing
441 a “combined mask”, only 37% of couples did not exceed any LV. While the exceedance of OEL_{CNAM}
442 alone and the exceedance of both LVs more than doubled, the exceedance of BLV_A alone decreased
443 from 28% to 3% without weighting by APF.

444

445 3.5.3 *wBaP vs. 3-OHBaP couples*

446 Among the 181 couples for which BaP levels were weighted by an APF, OEL_{CNAM} and BLV_{INRS}
447 exceedances were consistent for 90% of the couples, with no LV exceedance for 85% of them. Only 5%
448 exceeded BLV_{INRS} alone and 5% exceeded OEL_{CNAM} alone (Fig. 5A). No data were available for the
449 coke production and steel foundries. No LV exceedance was found for “petroleum-derived” sectors,
450 railroad maintenance or aluminum production. Conversely, the results of 20% of the couples were not
451 consistent in silicon production and carbon product manufacturing, with as many exceedances of
452 BLV_{INRS} alone as of OEL_{CNAM} alone.

453 Regarding the mask type, the results were consistent for almost 95% of the workers wearing no mask or
454 a “particulate mask”, with few LV exceedances. However, 6% of workers not wearing any mask
455 presented an exceedance of OEL_{CNAM} alone. For workers wearing “combined masks”, the results were
456 consistent only for 70% of the couples, including 15% exceeding both LVs. In this group, 19% exceeded
457 the BLV_{INRS} alone, while 12% exceeded the OEL_{CNAM} alone.



458

459 **Fig. 5:** Consistency between the exceedances of the atmospheric limit value (OEL_{CNAM}) and the
 460 biological limit value (BLV_{INRS}) for BaP vs. 3-OHBP couples according to occupational sector and
 461 mask type, with or without weighting by an AFP

462 A: with weighting by AFP = wBaP vs. 3-OHBP couples, B: without weighting by AFP = BaP vs. 3-
 463 OHBP couples.

464 Couple: association of a PAH air sample with a urinary PAH metabolite sample performed on the same
 465 day for a given worker; wBaP: benzo[a]pyrene concentrations weighted by an assigned protection factor
 466 (APF) depending on the type of mask worn by the worker, LV: limit value, OEL_{CNAM}: occupational
 467 exposure LV defined for BaP by the French CNAM, BLV_{INRS}: biological LV defined for 3-OHBP by
 468 the French INRS, Sili: silicon production, Alu: aluminum production, Carb: carbon product
 469 manufacturing, Rail: railroad maintenance Steel: steel foundry, Petrol: “petroleum-derived” sectors, P:
 470 “particulate mask”, G: “gas mask”, Comb: “combined mask”, NA: no data available.

471 3.5.4 BaP vs. 3-OHBaP couples

472 When using OEL_{CNAM} for non-weighted BaP (Fig. 5B), the results were the same as those of weighted
473 levels for “petroleum-derived” sectors and railroad maintenance. The results were less consistent in the
474 3 other “coal-derived” sectors due to an increase in the exceedance of OEL_{CNAM} alone, reaching more
475 than 20% in carbon product manufacturing and aluminum production and almost 40% in silicon
476 production. Conversely, the exceedance of BLV_{INRS} alone decreased, and the percentage of couples did
477 not exceed any LV.

478 For workers wearing no mask, the results were the same regardless of whether the levels were weighted
479 (Fig. 5B). For those wearing a “particulate mask”, the exceedances of OEL_{CNAM} alone reached 30%
480 without weighting (instead of 0%), while the couples not exceeding any LV decreased by the same
481 percentage. For workers wearing a “combined mask”, only 31% of couples did not exceed any LV,
482 while an exceedance of both LVs and OEL_{CNAM} alone was found for 35% of the couples.

483

484 4. Discussion

485 This study aimed to investigate the consistency between biological and airborne monitoring by taking
486 into account the effectiveness of RPE. To achieve this goal, comparisons between airborne BaP exposure
487 levels and urinary metabolite concentrations were performed in different occupational groups (industrial
488 sectors and job activities).

489

490 4.1 Urinary metabolite selection

491 3-OHBaP was chosen because it is the main metabolite of the carcinogenic BaP, which has been shown
492 to be a specific and sensitive biomarker for determining the internal exposure to PAHs of workers in
493 different industries (Barbeau et al. 2014, 2015; Forster et al. 2008).

494 1-OHP was selected because it is the most widely used urinary PAH metabolite in occupational
495 environment, even though it reflects the absorption of particulate pyrene and especially gaseous pyrene,
496 a non-carcinogenic PAH (Barbeau et al. 2015, 2017; Gao et al. 2018; Ifegwu et al. 2012; Jongeneelen
497 2014).

498 Other urinary metabolites of gaseous PAHs have been used to assess environmental exposure but they
499 do not reflect carcinogenic PAH exposure and are strongly linked to individual behaviors (e.g., dietary
500 patterns, tobacco smoke...) and air pollution (Patel et al. 2021). Furthermore, 3-OHBaP and 1-OHP are
501 the only urinary PAH biomarkers with existing guidance/limit values.

502

503 4.2 Exposure levels within petroleum-derived sectors

504 Regarding “petroleum-derived” sectors, airborne BaP levels of workers exposed to asphalt and engine
505 exhaust fume (GM of 0.3 and 0.7 ng.m⁻³) were very low and from the same order of magnitude as
506 workers in Italy (mean of 0.3 ng.m⁻³) (Campo et al., 2006), but slightly lower than workers in the UK
507 (BaP of approximately 10 ng.m⁻³) (Unwin et al., 2006). However, the 1-OHP levels in both of these
508 studies were 2 to 3 times higher than ours (median of 0.7 µg.L⁻¹ vs. 0.3 µg.L⁻¹). This difference could be
509 due to a larger number of smokers or to less cutaneous protection for their workers. The “petroleum-
510 derived” groups presented a 95th percentile (P95) of 1-OHP at 0.5 µmol.mol⁻¹, equivalent to that of the
511 general population. Indeed, urinary concentrations ranged from 0.04 to 0.53 µmol.mol⁻¹ for smokers and
512 from 0.01 to 0.15 µmol.mol⁻¹ for nonsmokers in a French study (Lafontaine et al, 2006), while the P95
513 value was equal to 0.46 µmol.mol⁻¹ for smokers and 0.15 µmol.mol⁻¹ for nonsmokers in the NHANES
514 study (CDC, 2019). For 3-OHBaP, the large number of < LoQ values (70%) prevented the accurate
515 analysis of low PAH exposure levels. This result was consistent with the scarce literature regarding 3-
516 OHBaP in non-occupationally exposed subjects, with 30% of the values below the LoQ (Raponi et al.,
517 2017) and up to 80% for nonsmokers (Barbeau et al., 2011; Leroyer et al., 2010). Consequently, urinary
518 3-OHBaP analysis is not relevant for assessing low PAH exposures in “petroleum-derived” sectors.

519

520 4.3 Exposure levels within coal derived sectors

521 Regarding “coal-derived” sectors, the BaP and pyrene levels as well as the 1-OHP and 3-OHBaP
522 concentrations were consistent with previously published data as well as the very low proportion of 3-
523 OHBaP levels < LoQ (Förster et al., 2008). The highest airborne BaP levels (GM = 1.5 µg.m⁻³) were
524 found in coking plants and were in the same range as those of a large study conducted in the UK (Unwin
525 et al., 2006) and 2 times higher than those performed in Germany (median of 0.89 µg.m⁻³) (Förster et

526 al., 2008). The corresponding 1-OHP urinary levels found in our study (GM = 1.4 $\mu\text{mol}\cdot\text{mol}^{-1}$) were
527 similar to those of the UK study (Unwin et al., 2006) but 2 times lower than those reported in an
528 European study (Talaska et al., 2014). The differences between studies result from various job activities
529 and RPE efficiency but also from various coking plant features with a clear improvement over time,
530 with average levels divided by 10-fold in a few years (Pyy et al., 1997). Moreover, the sampling time of
531 day and the work week has a strong influence on biomarker levels. While the best sampling time for 1-
532 OHP was at EWES (Jongeneelen, 2014), that of 3-OHBaP was at EWES+16 because of its urinary
533 elimination delay (Barbeau et al., 2015; Lafontaine et al., 2004). However, urine samples were
534 sometimes collected only at the end of the shift for scheduling reasons (Talaska et al., 2014), which can
535 modify the results and explain the observed differences.

536 For aluminum production using prebaked anodes, the airborne BaP levels and the urinary 1-OHP
537 concentrations were also similar to those previously reported (Unwin et al., 2006) but were 10 times
538 lower than those found in the Netherlands before 1990 (VanSchooten et al., 1995). In this industrial
539 sector, PAH exposures have considerably decreased because of the change in the anode composition
540 and the disappearance of coal tar pitch from products used for pot relining. In the same way, the BaP
541 and pyrene levels measured in carbon product manufacturing were 15 to 22 times lower than those
542 measured 15 years earlier in Germany (medians of 1.5 and 2.2 $\mu\text{g}\cdot\text{m}^{-3}$, respectively), while the 1-OHP
543 and 3-OHBaP concentrations were 2 to 3 times lower (Förster et al., 2008). In steel foundries, the BaP
544 levels as well as the 1-OHP and 3-OHBaP concentrations were low, as previously reported (Campo et
545 al., 2016; Unwin et al., 2006). Compared with the other “coal-derived” sectors, railroad maintenance
546 presented a unique profile, as already pointed out (Hebisch et al., 2020; Unwin et al., 2006), with
547 particularly low BaP exposure associated with notably high 1-OHP urinary levels due to the absence of
548 worn RPE and a very high tPyr/BaP ratio.

549 While atmospheric levels of “coal-derived” sectors were 30 times higher for gPyr, 200 times higher for
550 pPyr and 300 times higher for BaP than those of “petroleum-derived” sectors, urinary biomarker
551 concentrations were only 10 times higher.

552

553 4.4 Variability of air and urinary levels

554 The variability of urinary concentrations of 1-OHP and 3-OHBaP was 1.5 to 3 times lower than those
555 of the atmospheric levels of gPyr, pPyr and BaP. For industrial sectors with less than 40% values of 3-
556 OHBaP below the LoQ, the GSD of 3-OHBaP was higher than that of 1-OHP, which could be explained
557 by fewer workers in each group. This lower variability in biological levels had already been pointed out
558 within a large cohort of Korean workers with a GSD of only 3.07 for 1-OHP concentrations (Koh et al.,
559 2020) and by several studies comparing biological and atmospheric variances (Lin et al., 2005;
560 Symanski and Greeson, 2002). The difference between air and biological levels could be explained by
561 the fact that urinary concentrations are averaged over several hours but also because 74% of workers
562 involved in “coal-derived” sectors wore a RPE. In “petroleum-derived” sectors, only 14% of workers
563 were wearing RPE, but PAH exposure was very low.

564

565 4.5 Pyrene/BaP ratio

566 In the present study, the airborne PAH proportions were found to be highly variable depending on the
567 occupational group—hence the atmospheric mixtures—with a tPyr/BaP ratio ranging from 0.6 to 28.
568 This variable composition was even more pronounced in two other French studies, with tPyr/BaP ratios
569 ranging from 2.3 to 274 in coal sectors (Lafontaine et al., 2004) and a global proportion of particulate
570 PAHs ranging from 1% to 32% (Maître et al., 2018). The PAH mixture composition (gas/particle
571 partitioning) depends on the source of emission and environmental conditions and is highly variable
572 from one source to another. The highest levels of particulate PAHs, carcinogenic PAHs and BaP were
573 found in coal derived sectors because of the raw material composition and the high temperatures
574 observed in these sectors. Indeed, a high temperature is associated with a higher proportion of particulate
575 PAHs within the emitted mixture as a result of the lower volatility of these compounds compared with
576 gaseous PAHs (Kim et al., 2013). To take into account the great variability of PAHs contained in
577 atmospheric mixtures, the urinary 1-OHP concentrations were adjusted in our study by the ratio of the
578 airborne concentration of BaP to that of total pyrene (BaP/tPyr ratio).

579

580 4.6 Respiratory protective equipment and assigned protection factors

581 The type of mask and its effectiveness in stopping gases or particles varied from one sector to another
582 but also from one company to another. In silicon production, carbon product manufacturing and steel
583 foundries, all the RPEs worn by workers were effective against particulate PAHs (and sometimes against
584 gases), while those worn by workers at coking plants were effective solely against gaseous PAHs. This
585 variability highlights the need to take into account the efficiency of RPE for assessing occupational
586 exposure and health risk of workers exposed to PAHs, as previously pointed out by several authors
587 (Crawford et al., 2014; Unwin et al., 2006). Because of the difficulty of collecting accurate information
588 about RPE and the technical complexity of atmospheric sampling, biological monitoring alone is often
589 preferred for assessing occupational health risk.

590 To assess health risk, the w BaP levels and the w tPyr/ w BaP ratios were calculated by weighting the
591 atmospheric levels with an APF depending on the type of mask worn by the worker. The APF values
592 chosen in this study corresponded to the French recommendations (Ministère du Travail, 2010) and were
593 in agreement with values published by other authors (Crawford et al., 2014). However, some authors
594 have recommended that the current half-mask APF should be reduced from 10 to 5 (Nicas and Neuhaus,
595 2004).

596

597 4.7 Health risk assessment

598

599 4.7.1 Choice of the relevant limit values

600 Due to the existence of different LVs and the lack of studies reporting a relationship between PAH
601 exposure and carcinogenic effects, the most protective value was used for assessing health risk.

602 For BaP and w BaP, French OEL_{CNAM} at 150 ng.m⁻³ was more protective than OEL_{EU} at 2,000 ng.m⁻³.

603 Indeed, the exceedance of OEL_{CNAM} and OEL_{EU} occurred for 14% and 4% of the couples, respectively.

604 This OEL_{CNAM} is used in Latvia and is very close to that of Australia set at 200 ng.m⁻³ (SCOEL, 2016).

605 In the same way, no BLV of PAH biomarkers derives from a dose/response relationship between the

606 hydroxylated metabolite levels and carcinogenic effects. The most commonly used BLVs in France were

607 established from an extrapolation of existing atmospheric OELs (Jongeneelen, 2001). Indeed, the

608 BLV_{INRS} of 3-OHBaP set up to 0.40 nmol.mol⁻¹ creatinine was proposed for concentrations measured at

609 the beginning of the shift on the 5th day of exposure and was assumed to result from atmospheric BaP
610 exposure of 150 ng.m⁻³ over the working week (Nikolova-Pavageau *et al*, 2018).

611 For 1-OHP, there was no French BLV, but ACGIH proposed adjusting the BLV_A established for coke
612 oven workers by the ratio of the airborne concentration of total pyrene to that of BaP (tPyr/BaP ratio)
613 (ACGIH, 2017).

614

615 4.7.2 Exceedance of limit values within occupational group

616 The health risk assessment with OEL_{CNAM} for _wBaP and the two BLVs (BLV_A and BLV_{INRS}) for _{wadj}1-
617 OHP provided the same conclusions in most cases. However, _{wadj}1-OHP seemed more protective than
618 _wBaP, since every group except one (due to one single worker exposed to particularly high PAH levels),
619 estimated to be at high risk with atmospheric OEL_{CNAM}, was also considered at risk with urinary BLV_A.
620 Moreover, several groups presented a high health risk according to _{wadj}1-OHP, while _wBaP levels were
621 below OEL_{CNAM}, probably due to dermal exposure. In contrast, most “petroleum-derived” groups
622 exposed to low BaP levels were considered at low risk based on _{wadj}1-OHP monitoring, suggesting a
623 satisfying specificity of this biomarker.

624 Regarding 3-OHBaP, a large number of values < LoQ were mainly found in “petroleum-derived”
625 groups, where _wBaP concentrations were below OEL_{CNAM}. The agreement of conclusions regarding LV
626 exceedances between 3-OHBaP monitoring and air monitoring was almost perfect for “coal-derived”
627 groups, but 3-OHBaP seemed less protective than _wBaP. Indeed, while raw graphite cathode extrusion
628 was estimated to be at high risk with _wBaP levels, the 3-OHBaP concentrations of 19 workers were all
629 below BLV_{INRS}.

630

631 4.7.3 Exceedance of limit values for each worker – comparison by occupational groups

632 The consistency between airborne and urinary LV exceedance for each worker was excellent for the
633 lowest (“petroleum-derived” sector) and the highest (coke production) exposure groups. For the other
634 “coal-derived” sectors, the results were inconsistent for 10% to 40% of the couples. In railroad
635 maintenance, there were many exceedances of BLV_A alone with the measure of _{adj}1-OHP (weighted or
636 not), whereas no exceedance of BLV_{INRS} alone was recorded. In this sector, dermal absorption accounted

637 for up to 90% of the internal dose (Jongeneelen, 2001), and BaP levels were 10 times lower than tPyr,
638 with nearly 60% in gaseous form. Thus, it is unclear whether these exceedances of BLV_A alone indicate
639 a better ability of $_{adj}1\text{-OHP}$ to reflect cutaneous exposure or if it is biased by the high proportion of
640 pyrene despite the adjustment.

641 When using $_{w}BaP$ and $_{wadj}1\text{-OHP}$ levels weighted by an APF, the risk of exceeding OEL_{CNAM} alone,
642 BLV_A alone and both LVs (BLV_A and OEL_{CNAM} , or BLV_{INRS} and OEL_{CNAM}) was globally lower than
643 that without weighting. However, in numerous “coal-derived” sectors, LV exceedances were still
644 frequent despite this weighting. Stratification by mask type is useful to understand them.

645

646 4.7.4 Exceedance of limit values for each worker – comparison by mask types

647 For workers using a “gas mask”, the exceedances of BLV_A and OEL_{CNAM} were approximately the same
648 with and without weighting, since BaP is not stopped by this type of mask and the filtered gPyr
649 represents only 10% of tPyr in atmospheric mixtures of “coal-derived” sectors. Those workers presented
650 a large number of parallel exceedances of both LVs, which were largely met in coke production, where
651 70% of the workers wore a “gas mask” and the rest wore no mask. This finding suggests the capacity of
652 $_{wadj}1\text{-OHP}$ to detect $_{w}BaP$ levels exceeding OEL_{CNAM} .

653 For “particulate masks”, the weighting drastically reduced all LV exceedances, as it affected both BaP
654 levels and the $_{w}BaP/_{w}tPyr$ ratios. In contrast, the weighting of this ratio did not affect the $_{wadj}1\text{-OHP}$
655 levels (hence the BLV_A exceedances) for workers wearing a “combined mask”, for which only OEL_{CNAM}
656 exceedances were reduced. Would the BaP levels not have been weighted, there would indeed have been
657 more than twice as many total exceedances of OEL_{CNAM} for “combined mask” and five times as many
658 for “particulate masks”, which would have greatly increased the considered occupational risk. Despite
659 the weighting, when workers wore a “combined mask”, the exceedances of both LVs were still high at
660 15%, indicating insufficient protection despite respiratory PPE. This phenomenon was especially
661 apparent in silicon production, for activities near furnace, and in carbon product manufacturing for raw
662 cathode extrusion. Furthermore, 10% of couples presented an exceedance of OEL_{CNAM} alone, which
663 could be due to insufficient respiratory protection or to an underestimation of the mask efficiency by the
664 APF value. However, when RPE was taken into account, exceedances of BLV_A or BLV_{INRS} alone existed

665 regardless of the mask type but in a much higher proportion when the worker wore a “combined mask”
666 (30% for BLV_A or 20% for BLV_{INRS}). This phenomenon could be explained by an APF that was too
667 high, as previously reported (Nicas and Neuhaus, 2004), or/and by an added skin absorption because
668 these exceedances of BLV alone were found in 3 industrial sectors with high exposure levels, low
669 tPyr/BaP ratios and frequent cutaneous exposure.

670 In fact, the exceedances of all LVs were particularly high for workers wearing a RPE, as the most
671 exposed workers were also the best protected. For high exposure levels, the use of biological monitoring
672 is thus justified to ensure that workers are properly protected and to take into account the cutaneous
673 exposure route. While using an APF allowed us to more accurately assess external and internal exposure
674 levels, it increased the points of uncertainty due to possible over- or underestimations of the protective
675 effect of the RPE. Among workers not wearing any RPE, no exceedance of OEL_{CNAM} alone existed for
676 the “ $w_{adj}1\text{-OHP}$ vs. $w\text{BaP}$ couples”, but 6% of the “3-OHBaP vs. $w\text{BaP}$ couples” presented an exceedance
677 of OEL_{CNAM} alone without a parallel exceedance of BLV_{INRS} . For these last couples, although the
678 maximum BaP reached 925 ng/m^3 , the corresponding 3-OHBaP concentrations ranged only from 0.04
679 to $0.33\text{ nmol.mol}^{-1}$. The BLV_{INRS} was directly derived from this OEL_{CNAM} , and the samplings were
680 indeed performed at the start of the 5th day shift as recommended (Nikolova-Pavageau et al, 2018),
681 eliminating all possible confounding factors. Thus, the measurement of urinary 3-OHBaP could lead to
682 underdiagnoses, a problem that was not encountered with $w_{adj}1\text{-OHP}$.

683 Finally, for the 166 couples with a measure of $w_{adj}1\text{-OHP}$ and 3-OHBaP, there were twice as few
684 exceedances of 3-OHBaP BLV_{INRS} than of $w_{adj}1\text{-OHP}$ BLV_A , and only two-thirds of the exceedances of
685 the BLV_{INRS} were associated with a parallel exceedance of the BLV_A .

686

687 **5. Conclusion**

688 This study highlights the importance of taking into account the effectiveness of RPE for assessing health
689 risk, although using an APF increased the degree of uncertainty due to possible over- or
690 underestimations of the protective effect of the RPE.

691 The urinary 3-OHBaP was not relevant for occupational groups with low PAH exposure levels and could
692 lead to underdiagnoses for assessing health risk, which has never been encountered with $w_{adj}1\text{-OHP}$.

693 This last biomarker seems to be more protective than 3-OHBaP and _wBaP but requires air sampling to
694 provide the BaP/tPyr ratio. However, the use of _{wadj}1-OHP has been shown to be faulty in the case of
695 very high pyrene proportions in PAH mixtures.

696 Given the complexity and cost of monitoring atmospheric levels, alternative approaches to simultaneous
697 airborne and urine sampling could be developed, such as the use of abacus/tables providing the best
698 weight to use for adjusting 1-OHP levels according to job activities and type of mask. Thus, there is a
699 need for further analyses and studies, particularly for modeling and studying the relationship between
700 biomarkers and air PAH levels in various industrial sectors.

701

702 *Declaration of competing interest*

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

705

706 *CRedit author statement*

707 **Mélodie Valière:** Conceptualization, Methodology, Software, Formal analysis, Investigation, Data
708 Curation, Writing - Original Draft, Visualization. **Pascal Petit:** Conceptualization, Methodology,
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713 Review & Editing, Supervision, Resources, Project administration.

714

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718

719 *Data availability statement*

720 The data and datasets generated during and/or analyzed during the current study are not publicly
721 available due to the confidential nature of data (individual measurements and monitoring performed in
722 plants).

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