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Original Article

Occupational Exposure to Metals in Shooting Ranges: A Biomonitoring Study

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A B S T R A C T

Background: Lead (Pb) exposure in shooting ranges has been reduced by various measures such as jacketed ammunition and lead-free primers. Nevertheless, this may lead to exposure to other metals, potentially resulting in adverse health effects.
Methods: In a cross-sectional study, 35 subjects from seven different shooting ranges were studied: four shooting instructors, 10 police officers, 15 Special Forces, and six maintenance staff members. Metals and metalloids were determined in blood and urine by inductively coupled plasma–mass spectrometry.
Results: The concentrations of most elements did not differ significantly between groups or compared to reference values, except for Sb and Pt in urine and Pb in blood. Mean values for Sb were considerably higher in urine from the Special Forces (0.34 μg/L), the maintenance staff (0.13 μg/L), and shooting instructors (0.32 μg/L) compared to the police officers before shooting (0.06 μg/L) and a Belgian reference value (0.04 μg/L). For Pt, the Special Forces showed higher mean urinary concentrations (0.078 μg/L) compared to a Belgian reference value ($<$0.061 μg/L). Mean values for blood lead were markedly higher in the Special Forces (3.9 μg/dL), maintenance staff (5.7 μg/dL), and instructors (11.7 μg/dL) compared to police officers (1.4 μg/dL). One instructor exceeded the biological exposure index for blood Pb (38.8 μg/dL).
Conclusion: Since both Pb and Sb were found to be higher in shooting range employees, especially among frequent shooters, it is advisable to provide appropriate protective equipment, education, and medical follow-up for shooting range personnel in addition to careful choice of ammunition.

1. Introduction

Shooting ranges are used for occupational and recreational training in many countries. In the past decades, various studies have evaluated metal exposure from ammunition [1–19], with a focus on lead, as demonstrated in a recent review [20]. Nowadays, however, lead exposure has been reduced by measures such as better ventilation systems, jacketed ammunition, and lead-free primers [21]. Nevertheless, the question arises if the focus on lead does not cause other metals and metalloids such as copper, antimony, zinc, and arsenic to be present in high concentrations in ammunition, potentially resulting in adverse health effects [2,12,22].

So far, studies using metal air sampling in shooting ranges have not shown any metal level exceeding the occupational exposure limits, which is reassuring [2,12,13]. Nevertheless, in several studies, the particle size of some metals released by firing was found to be in the nano-range [2,12,13,16,17]. Consequently, respiratory and systemic effects resulting from deposition in the lungs cannot be excluded.

We undertook this biomonitoring study to investigate the presence of different metals and metalloids in blood and urine originating from ammunition. We included different shooting ranges used by police officers and groups of workers with presumably different types and intensities of exposure.

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2. Materials and methods

2.1. Study design and selection of shooting ranges and participants

In Belgium, around 80 or 90 shooting ranges are used by police officers for training. We selected seven of these shooting ranges to obtain a range of representative ranges in location and type of bullet trap. The included ranges had been in operation since 1980–2008, accommodating between 20 to 120 shooters per day. The types of bullet traps were escalator ($n = 4$), granulate rubber ($n = 2$), and Venetian ($n = 1$), and the approximate area of shooting spaces ranged from 180 m^2 to 420 m^2. The number of lanes varied from four (in five ranges) and six and 12 in two. None of the shooting ranges were used for recreational shooting; all were used exclusively for the training of police officers with shooting range 1 being also used by military personnel and customs officers and shooting range 4 and 6 also by Special Forces. Five of the shooting ranges provided a specific type of 9 mm ammunition, but users regularly brought their own ammunition, resulting in different types of ammunition with different compositions used in every shooting range. Composition information of the provided ammunition was limited to the following: 9 mm ammunition with a lead bullet totally covered by copper and a NON-TOX primer (=not containing antimony, barium, or lead) in shooting range 1 and 9 mm ammunition with a bullet totally made of copper in shooting ranges 2, 3, and 4.

In a cross-sectional design, we studied groups with presumably different degrees of exposure. In the seven selected shooting ranges, we invited all shooting instructors to participate in the study ($n = 4$). We also invited the maintenance/cleaning staff of these ranges ($n = 4$), but to increase the number, we also recruited two maintenance staff members responsible for cleaning bullet traps from other police shooting ranges in the country. We also invited 15 members of the Special Forces to participate because their counter-terrorism tasks make them practice several times a week in shooting ranges. A group of general police officers having shooting training only a few times a year was also included, mainly to serve as a control. In the latter participants, we measured metals before and after a training session in shooting range 1 with the provided ammunition of this range.

2.2. Dust samples

Dust was collected in October and November 2014 by placing polystyrene petri dishes (Falcon, 150 mm × 150 mm) for 4 to 8 weeks in six of the seven included shooting ranges. The petri dishes were placed on the ground (preferable in a protective container) to exclude differences because of height. They were placed 10 meters in front of the target where they hardly hindered shooters. Two control petri dishes were placed in a residential building and in a work office. The samples were analyzed by the Division of Soil and Water Management of the KU Leuven in December 2014. The collected dust was first weighed on a microbalance, digested with 1 mL concentrated nitric acid, boiled, and then diluted to 10 mL with a 1% HNO_3 solution, and the concentrations of 29 elements were measured by inductively coupled plasma–mass spectrometry (ICP-MS) as previously described [23].

2.3. Biomonitoring samples

Urine and blood samples from all participants were collected, between 27th of February and 27th of March 2015. All the samples were collected on site by the same researcher, on a Friday to obtain end of workweek samples (except for 3 subjects). Questionnaires were obtained from all participants to obtain information on age, sex, length of service, smoking behavior, diet, hobbies, recreational shooting, other forms of known metal/lead exposure, and details on exposure and the use of protective equipment in shooting ranges. Questionnaires were filled in on the day of the (first) sample collection. In the 10 police officers, urine and blood samples were obtained on the Friday preceding their training and a week later again on Friday, i.e. one day after the training session of a few hours. Blood was taken from a brachial vein using a vacutainer and collected in Becton Dickinson K_2-EDTA-tubes. Blood could not be taken from one maintenance staff member. A spot sample of urine was collected in a plastic cup and immediately poured into a sterile polystyrene container of about 30 mL. To avoid contamination, participants were asked to wash hands before sampling and to take off working clothes from the shooting range.

After collection, both urine and blood samples were stored in a domestic freezer at $-20°C$. When all samples had been obtained, they were sent by courier to the Louvain Centre for Toxicology and Applied Pharmacology (Université Catholique de Louvain, Belgium) for a blinded analysis by means of ICP-MS of 25 and eight metals and metalloids in urine and blood, respectively, as previously described [24]. Details of analytical procedures can be found in Supplementary Tables 1 and 2. Creatinine was also determined, and samples with creatinine values below 0.3 g/L were excluded, when considering creatinine-corrected values [27].

2.4. Ethical aspects

All participants were informed about the design and purpose of the study and were free to participate. Confidentiality was guaranteed. Written informed consent was obtained from every participant. The study was approved by the Ethics Committee of the University Hospitals Leuven.

2.5. Statistical analysis

Microsoft Excel 2010, SPSS Statistics 22 and GraphPad Prism 6 were used for database management and statistical analysis. The level of significance was set at $p < 0.05$ (two-sided).

In dust, only samples with elements for which at least half the samples had concentrations above the limit of quantification (LOQ) were retained for analysis. For concentrations below LOQ, half of LOQ was assigned for statistical calculations. The results from the six shooting ranges were compared with those from the control locations by means of the Mann–Whitney test.

For urine samples, we used reference values for the Belgian nonoccupationally exposed population defined by Hoet et al [24] and the available biological exposure index (BEI) [25] (Supplementary Table 1). For the blood samples, P50 and P95 from a recent study concerning 2000 residents in Northern France [26] as reference values and the available BEI were used [25] (Supplementary Table 2). For concentrations below limit of detection (LOD) for urine and LOQ for blood, half of LOD/LOQ was assigned for statistical calculations.

For both blood and urine concentration values, nonparametric tests were used because data could not be assumed to be normally distributed. In the cross-sectional analysis, data from all groups were compared by means of Kruskal–Wallis test, followed by Dunn's test. In the police officers, the results before and after shooting were compared by means of a Wilcoxon matched-pairs signed rank test. The correlation between biomonitoring data and metals in dust were assessed by a Spearman correlation.

3. Results

The characteristics of the study population are summarized in Table 1. None of the shooters stated to wear protective respiratory equipment. Respiratory protection, safety goggles, and gloves were stated to be used by four, two, and all six maintenance staff members, respectively. Two of them declared not having to clean bullet traps. The four maintenance staff members of the initially included shooting ranges reported cleaning the shooting range every morning for a couple of hours (daily dry and wet cleaning for two participants; dry cleaning every day and wet cleaning once a week for two participants). The two maintenance workers from the added shooting ranges declared working during 8 hours per day, mostly cleaning bullet traps, but they did not specify how. Only three participants (one Special Force and two instructors) stated to practice recreational shooting. All police officers and three out of four instructors indicated that they used only 9 mm ammunition. One instructor and all Special Forces stated to use 5.56, 7.62, and 0.308 ammunition in addition to 9 mm.

In the petri dishes collected from the shooting ranges, the weight of dust ranged from 0.39 mg to 11.14 mg (after removal of visible bullet fragments or wood in some). In Supplementary Table 3, results (expressed in flux) are shown for the most important elements in different locations. The flux ratio of Cu, Sn, Sb, and Pb was higher in all shooting ranges when compared to the two control locations. Shooting range 1 and 6 showed higher flux ratios of Zn and Pb, respectively, compared to other ranges. The flux ratio of Ti was markedly higher in shooting ranges 1, 4, and 6. As shown in Fig. 1, the concentrations of metals in settled dust varied widely (by two orders of magnitude) among the six shooting ranges. Nevertheless, the median concentrations of all measured elements were higher in settled dust collected in the shooting ranges than in settled dust collected in two offices, with fold ratios ranging from 2 (for Mo) to more than 100 (for Pb); the concentrations in settled dust samples from shooting ranges did not overlap with those from the control samples in the case of Cu, Sn, Sb, and Pb. For Pb, a median of 278.6 μg/g dust (range 23.4–2167.7 μg/g dust) was found in dust collected from the shooting ranges, as compared to an average of 139.9 μg/g dust in the control office environment.

3.1. Biomonitoring

3.1.1. Urine samples

Results of the urine samples with and without correction for creatinine are shown in Table 2. Creatinine concentration was below 0.3 g/L in six urine samples, and these samples were excluded for creatinine-corrected analysis. All 45 urine samples had concentrations below LOD for Be and In. In general, the concentrations found in our subjects were similar or somewhat above the reference values for the nonoccupationally exposed Belgian population [24]. Only for Te, mean concentrations higher than the upper reference limit were observed in all groups before and after correction for creatinine. Consistent differences between groups were found for Sb, Pt, and Pb (Fig. 2(A–C)), both with and without correction for creatinine. Special Forces had higher values for Sb and Pt than police officers. Pb in urine was significantly lower among the police officers than all other three groups. Ti was significantly lower in Special Forces and maintenance members than in police officers after correction for creatinine. U was higher in Special Forces than in police officers, but not after creatinine correction. Ni was lower in maintenance staff members compared to police officers after correction for creatinine.

Comparing urine concentrations in police officers before and after shooting showed differences only for Se after creatinine-correction (a decrement from a mean of 42.5 μg/g creat to 36.5 μg/g creat; $p = 0.03$) (Fig. 3A).

No correlations were found between metal concentrations in urine and dust.

3.1.2. Blood samples

For Co, Pd, Tl, and U, all 44 samples had concentrations below LOD. Other results are shown in Table 3. For Mn, Cd, and Hg, mean values were comparable to the reference P50 [26]. For Pb on the other hand, all mean values were above the reference P95 with one instructor being above the BEI with a blood lead value of 38.8 μg/dL. Distribution of Pb in blood for the study population is shown in Fig. 2D. Only Pb showed significant differences between groups, with all three groups having higher concentrations than the control police officers.

Comparison before and after shooting for lead showed a minimal—yet significant—increment from a mean of 1.41 μg/dL–1.47 μg/dL (Fig. 3B).

No correlations were found between metal concentrations in blood and dust.

4. Discussion

To our knowledge, this is the first biomonitoring study investigating metals other than lead among people working in shooting ranges. Most of the 27 measured elements were within concentrations expected for the Belgian or northern French general adult population [24,26]. However, Sb, Pt, and Pb exceeded these concentrations in some participants and will be discussed in the following sections.

4.1. Shooting ranges

The fact that the included shooting ranges differed in location and type of bullet trap can be seen as a strength. Important to note is that none of the included shooting ranges was used for recreational purposes, which could be a disadvantage since exposure to lead is potentially higher in recreational shooting ranges [8]. On the other hand, the scope of this study was to examine occupational exposure and, therefore, not including recreational shooting ranges can be seen as a plus. A limitation of the study, on the other hand, is the high variability of the ammunition used in the ranges and the

Table 1
Characteristics of study participants

Parameter	SPF ($n = 15$)	Maintenance staff members ($n = 6$)	Instructors ($n = 4$)	Police officers ($n = 10$)	Total ($n = 35$)
Men no. (%)	15 (100%)	5 (83.3%)	4 (100%)	8 (80%)	32 (91.4%)
Smokers no. (%)	1 (6.7%)	2 (33.3%)	1 (25%)	1 (10%)	5 (14.3%)
Age in years—mean (sd)	34.8 (7.9)	40.4 (7.4)	52.2 (9.7)	44.5 (13.3)	40.5 (11.1)
Years of service in current job—mean (sd)	11.4 (1.9)	7.33 (4.9)	10.25 (7.3)	20.8 (15.0)	13.3 (10.8)
Number of hours in shooting range					
Per week—mean (sd)	5.3 (2.6)	21.3 (13.4)	19.0 (14.3)		
Per year—mean (sd)				10 (5.2)	

SPF, Special Forces; sd, standard deviation.

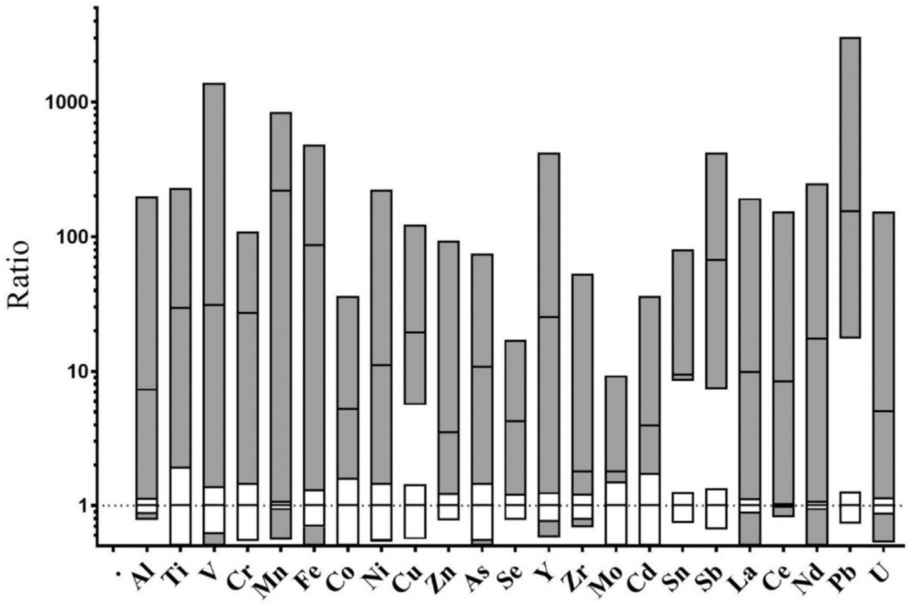

Fig. 1. Metal elements in settled dust from shooting ranges. Settled dust was sampled by placing petri dishes for 28 to 50 days in six shooting ranges (gray bars) and in two control location (office and residential building) (white bars). The concentrations of metals in dust are presented in the electronic supplement (Supplementary Table 3). In the figure, data are expressed as the ratio of the measured value with respect to the average value obtained in the control environment (defined as 1 on the y-axis). The horizontal lines inside the gray bars are medians.

lack of information on the composition of some ammunition, thus making it difficult to link dust and biomonitoring results to the ammunition.

4.2. Population

In total, 35 persons participated of which 25 belonged to a "continuously" exposed group and 10 to a "control" group with only occasional exposure. If we compare the number of participants with other studies in shooting ranges in which biomonitoring (for lead) took place, 35 participants are rather average. The total number of participants in previous studies varied from two [4] to 367 [10]. In most studies with larger numbers [8,10,11], the included participants were occasional shooters rather than shooting range employees, whereas our study included shooting range personnel, although fewer than in the recent study of Park et al [19]. In contrast to the latter study, we included maintenance staff which is also a strength of our study because this group is often forgotten when studying shooting ranges.

4.3. Dust results

The petri dish method was chosen because of its low cost and organizational convenience [28]. This method has been used previously for dust collection for measurement of metals, i.e. for lead [28–30] and cadmium [31]. Disadvantages of the petri dish technique are contamination, the long time period needed to achieve results, and the small amounts of collected dust [28,29]. Since time was not a problem in our study and because we expected to obtain more dust than in a house setting, we chose this technique. However, in the different shooting ranges, a great variance in dust quantities was obtained. With hindsight, the petri dish method was not the ideal technique for this study because we also collected wood and bullet fragments in some petri dishes. The higher flux ratio of Ti in shooting ranges 1, 4, and 6 might be explained by the use of other calibers than 9 mm in these ranges because military personnel or Special Forces practiced there in addition to police officers. Drawing more conclusions between dust results and ammunition exposure in the ranges is, however, difficult because of the aforementioned limitation. The fact that we could not find a significant correlation between dust results and biomonitoring results is likely due to the limited number of shooting ranges and of biomonitoring samples per shooting range.

4.4. Biomonitoring results

The advantage of biomonitoring in comparison with external measurement such as air sampling is the inclusion of all uptake routes (inhalable, dermal, and oral). A disadvantage is the possibly complex interpretation of results because of the various sources and intensity of exposure.

4.4.1. Urine samples

Six urine samples were too diluted (creatinine concentrations below 0.3 g/L) and thus left out for creatinine-corrected analysis. This led to only four maintenance staff members and seven police inspectors before and after shooting who could be evaluated regarding urine samples with correction for creatinine. All the elements determined in the urine samples, except for Ti, could be compared to the recently defined reference values for the Belgian adult population [24]. The samples in our study were analyzed in the same laboratory as in the cited study, supporting the comparison with these reference values.

Lead concentrations were higher in Special Forces, maintenance staff members, and instructors compared with the control group. The mean urinary lead concentrations of the latter two groups exceeded the upper reference limits of the Belgian population. However, lead exposure is better assessed by measuring blood Pb, and this will be discussed below.

Antimony was significantly elevated in urine from the exposed group compared with the control group, persisting after correction for creatinine. The Special Forces showed the highest average values, but the highest value in an individual was found in a shooting instructor (at least without correction for creatinine). The

Table 2
Results of metals in urine (in μg/L and μg/g creatinine)

μg/L μg/g creat	Reference values P50 P50-creat	Reference values URL URL-creat	SPF Mean (sd) ($n = 15$) Mean (sd) ($n = 14$)	Maintenance Mean (sd) ($n = 6$) Mean (sd) ($n = 4$)	Instructors Mean (sd) ($n = 4$) Mean (sd) ($n = 4$)	Police officers (before shooting training) Mean (sd) ($n = 10$) Mean (sd) ($n = 8$)	Total Mean (sd) ($n = 35$) Mean (sd) ($n = 30$)
Creat (g/L)			0.85 (0.41)	1.10 (0.87)	0.93 (0.64)	0.77 (0.42)	0.87 (0.50)
Li	22.9 21.5	100 100	28.9 (10.9) 44.4 (26.9)	21.6 (22.8) 28.3 (17.7)	19.2 (17.3) 22.9 (14.2)	31.8 (29.0) 51.5 (32.8)	27.4 (19.9) 41.2 (27.2)
Al	2.17 2.04	15 10	1.86 (1.93) 2.27 (1.69)	1.21 (0.67) 1.54 (0.61)	1.77 (1.31) 2.70 (2.63)	1.22 (0.76) 2.05 (1.69)	1.56 (1.42) 2.16 (1.69)
Ti			32.57 (19.79) 39.76 (20.95)*	24.00 (11.22) 36.02 (17.08)*	38.60 (7.72) 60.65 (38.30)	43.84 (27.19) 75.28 (28.71)	35.01 (20.72) 51.52 (29.07)
V	0.248 0.221	1.5 2	0.408 (0.126) 0.556 (0.157)	0.369 (0.137) 0.457 (0.275)	0.321 (0.107) 0.459 (0.241)	0.311 (0.149) 0.532 (0.223)	0.364 (0.137) 0.523 (0.196)
Cr	0.134 0.109	0.55 0.35	0.217 (0.098) 0.285 (0.123)	0.176 (0.218) 0.204 (0.098)	0.190 (0.099) 0.249 (0.116)	0.171 (0.099) 0.262 (0.036)	0.194 (0.122) 0.263 (0.101)
Mn	<0.043	0.75 1	0.043 (0.047) 0.072 (0.114)	0.051 (0.072) 0.048 (0.027)	0.037 (0.032) 0.045 (0.022)	0.039 (0.029) 0.056 (0.025)	0.043 (0.045) 0.061 (0.079)
Co	0.184 0.199	1.8 1.3	0.335 (0.489) 0.392 (0.354)	0.165 (0.110) 0.170 (0.070)	0.229 (0.166) 0.261 (0.088)	0.175 (0.090) 0.233 (0.053)	0.248 (0.333) 0.302 (0.257)
Ni	2.05 1.79	6 5	2.67 (1.90) 3.49 (2.07)	1.64 (1.26) 2.07 (0.41)*	1.72 (0.85) 2.28 (1.00)	2.13 (0.97) 3.43 (1.07)	2.23 (1.49) 3.12 (1.63)
Cu	8.18 6.99	27 14	7.80 (3.47) 10.17 (3.73)	6.93 (5.73) 9.18 (2.59)	11.35 (5.74) 14.21 (4.37)	7.90 (4.15) 13.07 (4.16)	8.08 (4.33) 11.35 (4.04)
Zn	256 246	1620 770	273 (163) 363 (200)	249 (216) 377 (258)	221 (109) 304 (134)	282 (133) 483 (216)	266 (155) 389 (204)
As	14.1 13.7	300 260	25.7 (48.9) 32.9 (44.4)	30.7 (25.4) 32.1 (25.4)	10.7 (9.3) 24.0 (37.3)	18.8 (17.4) 31.3 (35.9)	22.9 (34.7) 31.2 (37.6)
Se	25.1 21.6	80 40	31.6 (13.1) 42.2 (11.1)	24.3 (18.1) 34.9 (16.5)	26.0 (10.0) 35.1 (15.6)	27.3 (17.2) 43.9 (10.1)	28.5 (14.7) 40.7 (12.1)
Mo	31.3 29.8	150 100	42.8 (36.1) 50.7 (24.9)	46.8 (58.9) 58.5 (32.0)	43.7 (26.2) 53.7 (20.6)	50.2 (35.4) 85.0 (43.3)	45.7 (38.1) 61.3 (33.1)
Cd	0.276 0.243	1.5 1	0.407 (0.219) 0.518 (0.181)	0.371 (0.239) 0.512 (0.192)	0.673 (0.629) 0.731 (0.420)	0.377 (0.178) 0.608 (0.205)	0.423 (0.283) 0.570 (0.229)
Sn	0.373 0.351	4 2.5	0.682 (0.708) 0.889 (0.874)	0.411 (0.521) 0.419 (0.252)	0.785 (0.644) 0.888 (0.326)	0.726 (1.046) 0.977 (0.755)	0.660 (0.766) 0.850 (0.727)
Sb	0.040 0.041	0.35 0.25	0.344 (0.198)* 0.471 (0.384)*	0.129 (0.177) 0.176 (0.175)	0.322 (0.435) 0.320 (0.341)	0.057 (0.037) 0.087 (0.025)	0.223 (0.234) 0.309 (0.332)
Te	0.153 0.137	0.4 0.5	0.700 (0.300) 0.937 (0.405)	0.448 (0.267) 0.682 (0.398)	0.535 (0.281) 0.662 (0.225)	0.482 (0.255) 0.781 (0.324)	0.576 (0.290) 0.825 (0.366)
Ba	1.91 1.86	9 8	3.59 (3.33) 6.32 (10.55)	1.01 (0.50) 1.74 (1.10)	3.35 (2.99) 4.00 (4.05)	3.24 (3.50) 3.79 (2.49)	3.02 (3.09) 4.77 (7.47)
Pt	<0.061	<0.061	0.076 (0.025)* 0.107 (0.045)*	0.041 (0.012) 0.053 (0.027)	0.052 (0.032) 0.069 (0.037)	0.041 (0.017) 0.064 (0.023)	0.057 (0.027) 0.083 (0.042)
Tl	0.211 0.179	0.6 0.5	0.328 (0.129) 0.451 (0.160)	0.185 (0.145) 0.254 (0.114)	0.260 (0.094) 0.393 (0.260)	0.214 (0.134) 0.345 (0.112)	0.263 (0.138) 0.389 (0.167)
Pb	0.872 1.780	4 3	1.716 (0.970)* 1.980 (0.703)*	3.530 (3.270)* 4.487 (3.074)*	7.867 (12.778)* 7.350 (10.380)*	0.669 (0.421) 1.132 (0.408)	2.431 (4.609) 2.804 (4.090)
Bi	<0.016	0.05 0.05	0.012 (0.009) 0.163 (0.008)	ALL UNDER LOD 0.011 (0.007)	0.013 (0.009) 0.017 (0.010)	0.014 (0.013) 0.026 (0.034)	0.012 (0.009) 0.018 (0.019)
U	<0.007	0.05 0.04	0.029 (0.009)* 0.041 (0.017)	0.019 (0.012) 0.029 (0.015)	0.023 (0.009) 0.032 (0.018)	0.018 (0.009) 0.029 (0.010)	0.023 (0.010) 0.035 (0.015)

SPF, Special Forces; LOD, limit of detection; URL, upper reference limit; sd, standard deviation.

URL, URL-creat, P50 and P50-creat defined by the study of Hoet et al [24] with URL defined as the upper limit of the 90% confidence interval of P97.5; for creatinine-corrected values, samples with creatinine <0.3 g/L were excluded.

* Significant when performing Kruskal–Wallis test, followed by Dunn's test, with police officers as controls.

fact that Sb could be found in ammunition is supported by the development of so called NON-TOX ammunition which does not contain Sb in the primer [17]. Little is known about the health effects of exposure to Sb. However, Sb is stated as a possible cause for the occurrence of pneumoconiosis [32]. A BEI has not been defined yet, but the concentrations found in our study appear to be relatively low because Bailly et al [33] showed that an airborne concentration of Sb of about 0.5 mg/m^3 leads to an increase in urinary Sb concentration of 35 μg/g creatinine during a shift, whereas our maximal measured concentration only amounts to 1.5 μg/g creatinine, (result not shown). Nevertheless, paying attention to Sb in shooting range employees and shooters is advisable.

Platinum was remarkably higher in Special Forces compared to all other groups. The only explanation for this observation is the presence of Pt in “special” ammunition possibly only used by Special Forces. This hypothesis is supported by the mention of the use of Pt in electric primers in an old patent [34]. Known health effects of (complex salts of) Pt are allergic reactions [35]. Pt concentrations in our study were not that elevated considering a mean value of 1.52 μg/L that was demonstrated in American residents in 1998 [36], which is much higher than our highest measured value (0.11 μg/L).

In our study, high mean tellurium concentrations were observed in urine. To our knowledge, Te is not used in ammunition, and we

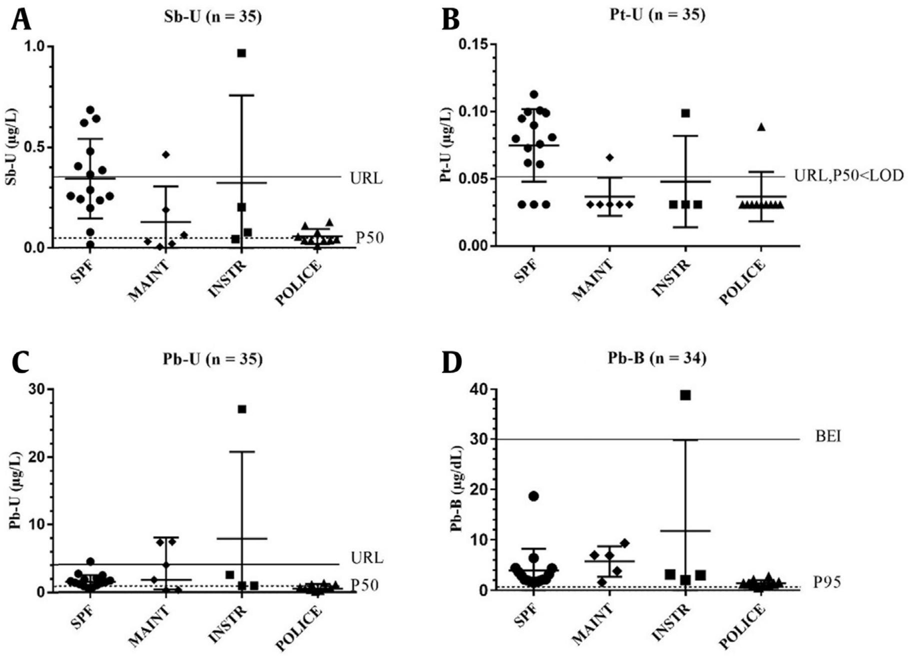

Fig. 2. Scatterplots. (A) Sb in urine. (B) Pt in urine. (C) Pb in urine. (D) Pb in blood. URL and P50 in urine defined by the study of Hoet et al [24] with URL defined as the upper limit of the 90% confidence interval of P97.5. P95 from the study in Northern France [26]. Black lines show mean and standard deviation.
SPF, Special Forces; MAINT, maintenance staff; INSTR, instructors; POLICE, police officers before shooting training; LOD, limit of detection; URL, upper reference limit; BEI, biological exposure limit [25].

cannot draw conclusions about these elevated values of Te in urine; neither can we draw conclusions about the observed lower titanium and higher creatinine-corrected uranium values in Special Forces and lower nickel values in maintenance members.

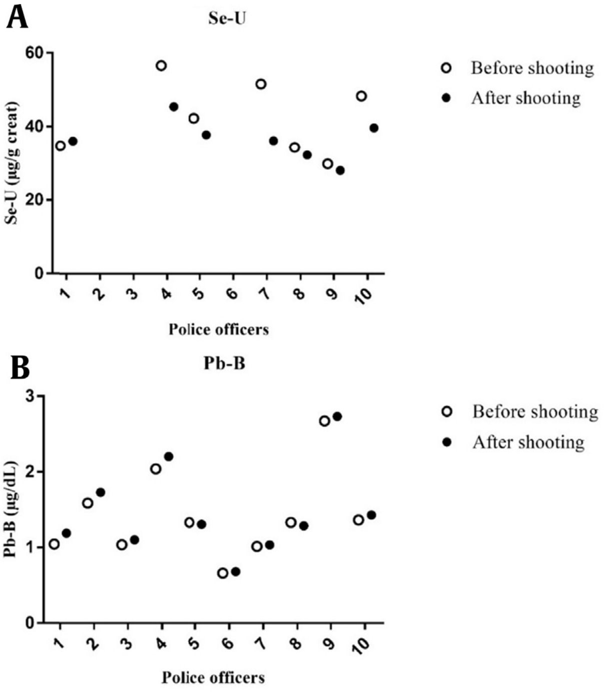

Fig. 3. Creatinine-corrected Se and Pb sampled before and after shooting. (A) Se in urine. (B) Pb in blood. Comparison of concentrations before and after a shooting session in police officers showed significant differences for Se in urine after creatinine-correction (a decrement from a mean of 42.5 µg/g creat to 36.5 µg/g creat; $p = 0.03$) and Pb in blood (an increment from a mean of 1.41 µg/dL to 1.47 µg/dL) when performing a Wilcoxon matched-pairs signed rank test; for creatinine-corrected values, samples with creatinine <0.3 g/L were excluded.

When comparing urinary values before and after shooting, a significant difference could be noted only for creatinine-corrected Se, which was decreased after shooting. A possible explanation for this finding will be discussed below.

4.4.2. Blood samples

In blood, significant differences were obtained only for lead, which was much higher in the continuously exposed group compared to the control group. These values were also much higher than those recently established in the general population of Northern France [26]. Although the purpose of our study was to assess metals other than Pb, the elevated blood lead levels still represent the most relevant finding in this study. One instructor showed a value above the BEI value of 30 µg/dL [25]. The fact that he had much higher blood lead levels than the other instructors might be due to more years in service or additional recreational shooting. Instructors who only recently got in service probably benefitted from the measures previously taken to reduce lead exposure, reflected in lower blood lead levels. Nevertheless the National Research Council [21] stated that lead could also have negative effects below the BEI, which is recently confirmed [20,37]. Laidlaw et al [20] stated that there is sufficient evidence that blood lead levels <10 µg/dL are associated with hypertension and decreased glomerular filtration, so we still advise attention to lead exposure in instructors. Important to note are the elevated blood lead levels in the maintenance staff members, even if all of them used gloves and four of them respiratory equipment. We think cleaning the bullet trap might be the biggest cause of lead exposure, but unfortunately, our maintenance group is too small to draw conclusions about the contribution of specific working methods or the effectiveness of personal protective equipment to lower blood lead levels. Nevertheless, like Park et al [19], we advise health surveillance for shooting range employees including periodically biomonitoring for lead in blood for cleaners and maintenance workers. Moreover, providing appropriate protective equipment for this group appears indispensable.

Table 3
Descriptive statistics of metals in blood (in μg/dL)

μg/dL	Reference values P50	Reference values P95	SPF Mean (sd) ($n = 15$)	Maintenance Mean (sd) ($n = 5$)	Instructors Mean (sd) ($n = 4$)	Police officers (before shooting training) Mean (sd) ($n = 10$)	Total Mean (sd) ($n = 34$)
Mn	0.77	1.30	0.66 (0.24)	0.79 (0.21)	0.65 (0.11)	0.76 (0.12)	0.71 (0.19)
Cd	0.04	0.17	0.02 (0.02)	0.04 (0.02)	0.04 (0.06)	0.02 (0.02)	0.03 (0.03)
H	0.17	0.51	0.13 (0.07)	0.10 (0.14)	0.09 (0.08)	0.17 (0.22)	0.13 (0.14)
Pb	0.18	0.49	3.91* (4.30)	5.71* (3.02)	11.74* (18.03)	1.39 (0.60)	4.36 (6.95)

SPF, Special Forces; sd, standard deviation; URL, upper reference limit.

P50 and P95 from the study in Northern France [26].

* Significant when performing Kruskal–Wallis test, followed by Dunn's test, with police officers as controls.

Finally, when comparing before and after a shooting session, a significant increment in blood Pb could be detected. The increase was minimal and clinically not relevant. Nevertheless, the change not only proves the sensitivity of the ICP-MS technique but also demonstrates that ammunition consisting of a lead bullet totally covered by copper and a NON-TOX primer apparently still causes a detectable lead exposure. It is surprising that we found a slight elevation for lead in blood and not in urine. We have no explanation for this phenomenon other than hypothesizing that the recent uptake of lead via inhalation was reflected in blood and not (yet) in urine. The much higher increments in lead after shooting training, as stated in the review on lead exposure in firing ranges [20], could be explained by the longer duration of training in their cited studies: i.e. a few days to weeks compared to only a few hours in our study. The fact that the concentration of Se in urine decreased while that of lead in blood augmented after shooting supports the findings of Pawlas et al [38], who showed an inverse relationship between levels of Pb in blood and Se in serum probably due to interaction of Pb with the antioxidant enzyme glutathione peroxidase.

In conclusion, this biomonitoring study reveals for several metals no significant excess in shooting range personnel or people whose work involves frequent shooting sessions. Among the 27 tested elements, however, antimony, lead, and, to a lesser degree, platinum deserve attention. Antimony and lead, both present in ammunition, were elevated in urine and in blood (lead) in shooting instructors and maintenance staff and in Special Forces who attend shooting trainings a few hours a week. Both metals could cause health concerns. Platinum was only elevated in urine from Special Forces. Since it can be found in some primers and ammunition, this possibly indicates inhalatory uptake of platinum released from ammunition.

We advise that shooting range personnel and frequent shooters should be informed of the possible uptake of metals and their potential health consequences. Besides, providing adequate protection equipment for working in shooting ranges is recommended, especially for maintenance staff. Health surveillance is indicated, both for education and for detecting possible health complaints. Biomonitoring for lead does not seem imperative for sporadic shooters, but it is recommended for employees working daily in shooting ranges. Last but not least, careful choice of ammunition is essential.

Conflict of interest

The authors have no conflict of interest to declare.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.shaw.2018.05.006.

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