Biological monitoring of occupational exposure to polycyclic aromatic hydrocarbons in a prebake-anode aluminium plant.

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Introduction. Polycyclic aromatic hydrocarbons (PAH) are a class of chemical compounds, formed by incomplete combustion or pyrolysis of organic matter.[1] PAH are highly suspected to induce cancer in humans.[1] Sources of PAH exposure are environment, food and occupation, with the last exceeding by 2-3 orders of magnitude the other two in some workplaces.[2] In Greece, an estimated 13.000 workers are exposed to PAH, not including approximately 269.000 workers exposed to passive smoking and diesel exhaust.[3]

Aluminium production industry is among the working environments with the heaviest exposure to PAH.[4] Occupational exposure to PAH in aluminium workers has been associated with lung and bladder cancer.[5–9] The International Agency for Research on Cancer (IARC) classified several chemical substances, mixtures and productive processes relating to PAH (including aluminium production industry) as carcinogenic (class 1) or probably carcinogenic (class 2A) to humans.[10]

In order to estimate exposure and to assess the risk of side effects, monitoring methods have been developed. Coal tar pitch volatiles (CTPV) and benzo(a)pyrene (BaP) have been used as representative markers of airborne exposure to PAH and Threshold Limit Values were adopted.[11,12] Measuring external exposure, however, does not reflect the amount of carcinogen actually absorbed by an individual (called the “internal dose”). This is influenced by many factors, such as absorption by other routes (skin, ingestion), non-occupational exposure (smoking, food, environment, tar-containing shampoos) and metabolic host factors.[13] In order to estimate the total uptake of PAH, it was suggested that 1-hydroxypyrene, a metabolite of pyrene, in urine can be used as a biomarker of human exposure to PAH.[14]

The purpose of this study was: (1) to assess occupational exposure to PAH in workers at an aluminium production plant, in which the prebake anode process

is used; and (2) to estimate the influence of other factors in the urinary concentration of 1-hydroxypyrene.

Materials and methods.The study was performed at an aluminium primary production plant located in Central Greece. Thirty-two actively employed male workers (mean age: 47±7 years, range: 31-58 years) voluntarily participated in the study.Twenty-three of them were working in the anode production section, while the remaining nine belonged to a pot relining crew. Biological monitoring was conducted by taking a single urine sample from each worker after the end of the 8-hour shift of at least the third consecutive day of work. Personal breathing zone air samples (3-hour sampling) were collected for nine of the above workers as well. All subjects completed a questionnaire which investigated factors that could influence excretion of 1-hydroxypyrene, such as dermal exposure, use of protective equipment, dietary habits, smoking history and medications. Determination of urinary 1-hydroxypyrene was carried out with high-performance liquid chromatography whereas air samples were analyzed for 17 PAH by gas chromatography-mass spectrometry. Statistical analysis was carried out on SPSS® 10.0 statistical software. Both parametric and non-parametric tests were used, depending on the normality or not of data distributions. Results considered significant for p-values < 0,05 (two-tailed).

Results. Median urinary 1-hydroxypyrene concentration of exposed workers was 0,26 μmol/mol creatinine (range: 0,02-1,93). These values are considered relatively low. The suggested limit of high-level exposure (1,5 μmol/mol creatinine)[15,16] was marginally exceeded in three cases (Figure 1). 1-hydroxypyrene values were substantially higher among smokers (median=0.33 μmol/mol creatinine, n=15), but the difference between smokers and non-smokers (median=0.14 μmol/mol creatinine, n=17) was not statistically significant (t-test for log-transformed values: t=0.93, p=0.36). Although overall exposure was relatively low, workers in the raw production section of the anode plant had significantly higher values than the other workers (ANOVA: F=4.98, Tukey: p<0.05, Figure 2).

Total PAH concentration in air samples varied from 2.8 to 295.4 μg/m^3, whereas benzo(a)pyrene (BaP) values ranged from 0.05 to 0.99 μg/m^3, which is well below the threshold limit value applied in Greece (5 μg/m^3). Log-

transformed urinary 1-hydroxypyrene values were significantly correlated with BaP in air samples (Pearson correlation coefficient: $r=0.8$, $p<0.01$, $n=9$).

A multiple regression analysis was conducted to evaluate how well a number of factors theoretically related to PAH intake could predict 1-hydroxypyrene concentration in urine (dependent variable). Independent variables (predictors) included: age, hours of daily occupational exposure to PAH, dermal occupational exposure to PAH during the previous 3 days (0=no, 1=yes), number of cigarettes smoked per day and worksite (reference group: furnaces).There was a significant linear relationship between the dependent variable and the entire set of predictor variables, $F_{(7,24)}=4.758$, $p=0.002$. The sample multiple correlation coefficient was 0,762. Approximately 58% of variance of the dependent variable can be accounted for by the independent variables. Worksite (raw production), number of cigarettes, hours of exposure, and dermal exposure were found important for better prediction (Table 1).

Discussion. There was a low level occupational exposure to PAH at a prebake anode aluminium plant located in Greece. 1-hydroxypyrene values were among the lowest reported so far (Table 2).[17–20] Low level exposure to PAH at the specific environment could be attributed to the highly automated procedures involving closed processing systems and/or the use of protective equipment that decreases furthermore PAH uptake via inhalation or skin absorption.

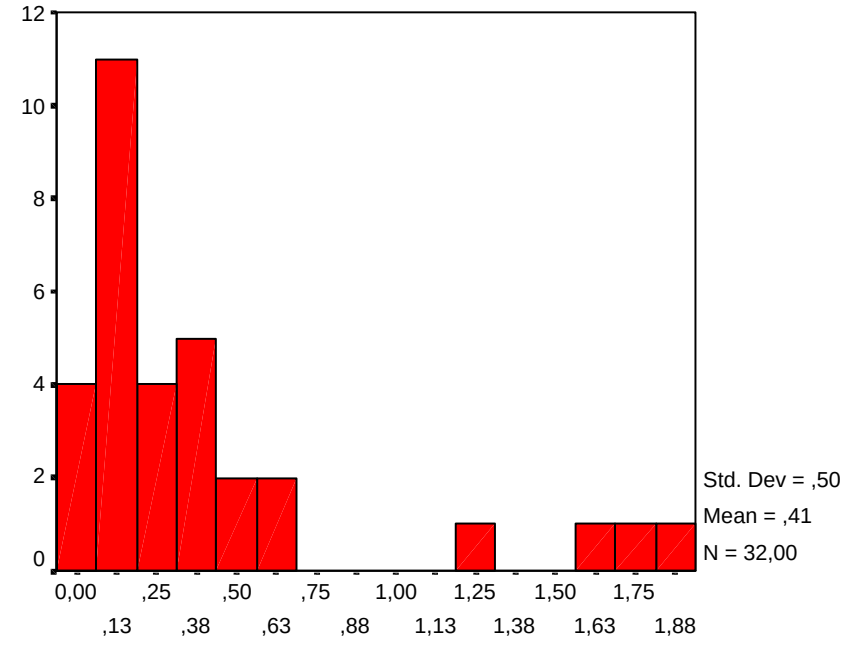

Figure 1. Distribution of 1-hydroxypyrene values in post-shift urine samples of exposed workers.

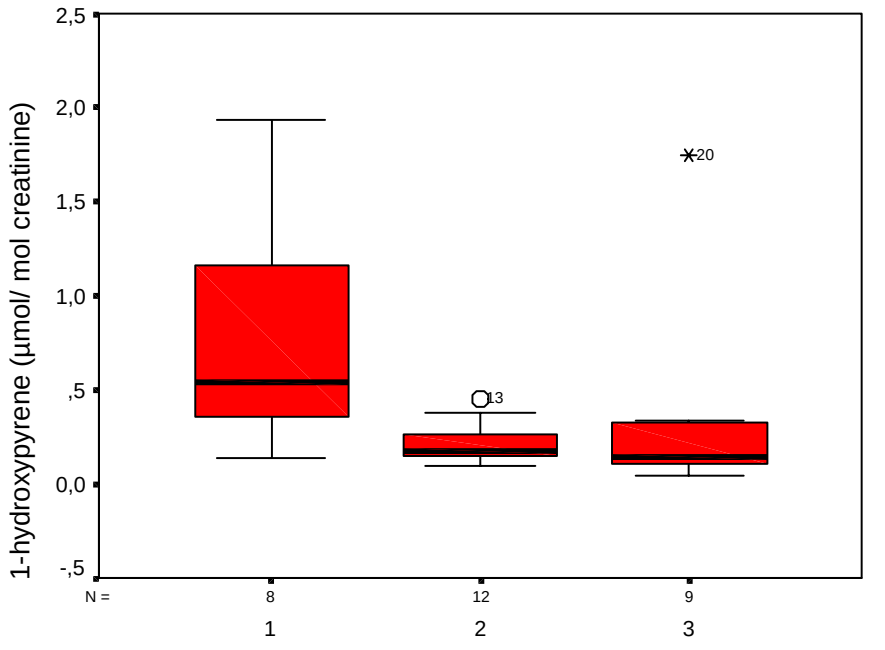

Figure 2. Urinary 1-hydroxypyrene values according to job position.

Table 1. Multiple regression analysis for post-shift 1-hydroxypyrene values in urine of aluminium workers (ln values, n=31).

Independent variables	**B**	**SE of B**	**b**	**p value (t-test)**
Age	-0,02	0,021	-0,134	0,350
Hours of daily exposure	0,261	0,098	0,395	0,014
Dermal occupational exposure	0,757	0,307	0,350	0,021
Number of cigarettes per day	0,029	0,010	0,406	0,011
Raw production	1,303	0,378	0,522	0,002
Pot reconsrtuction	0,071	0,372	0,030	0,850
Rodding section	0,176	0,657	0,039	0,791
Furnaces	-	-	-	-
Constant	-2,738	1,109	-	0,021

B = Unstandardized regression coefficient.
SE = Standard error of B.
b = Standardized regression coefficient.

Table 2. 1-hydroxypyrene levels in post-shift urine samples from workers at prebake-anode manufacturing plants.

Reference	**1-hydroxypyrene (µmol/mol creatinine)**
Tolos et al., 1990	2,67 (mean of 55 samples from 28 workers)
Van Rooij et al., 1992	0,98-13,1 (range, n=20)
Petry et al., 1996	0,5-61,8 (range of 30 samples from 6 workers)
Van Delft et al., 1998	0,11-7,38 (range, n=55)

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