

# Exposure to PAH Compounds Among Cokery Workers in the Oil Shale Industry

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The exposure of Estonian cokery workers to polynuclear aromatic hydrocarbons at an oil shale processing plant was assessed by occupational hygiene and biomonitoring measurements. To assess the external dose of exposure to polynuclear aromatic hydrocarbons, pyrene and benzo[a]pyrene concentrations were measured from the breathing zone of workers during a workshift. Skin contamination with pyrene and benzo[a]pyrene was assessed by skin wipe sampling. As a biomarker of exposure to polynuclear aromatic hydrocarbons and as an integral of all possible absorption routes of pyrene, 1-hydroxypyrene concentration was measured from post-shift urine samples. Eighteen percent of the personal air samples exceeded the Finnish threshold limit value of benzo[a]pyrene (10 µg/m<sup>3</sup>). Mean values for benzo[a]pyrene and pyrene were 5.7 µg/m<sup>3</sup> and 8.1 µg/m<sup>3</sup>, respectively. Based on skin wipe sample analyses, the skin contamination was also obvious. The mean value of benzo[a]pyrene on the samples collected after the shift was 1.2 ng/cm<sup>2</sup>. In control samples, benzo[a]pyrene was not found. The mean value of urinary 1-hydroxypyrene concentration was 6.0 nmol/mmol creatinine for the exposed workers and 0.5 nmol/mmol creatinine for the controls. This study showed the usefulness of 1-hydroxypyrene as an indicator of internal dose of polynuclear aromatic hydrocarbons. We concluded that the cokery workers at the Kohtla-Järve plant are exposed to high concentrations of polynuclear aromatic compounds. — *Environ Health Perspect* 104(Suppl 3):539–541 (1996)

Key words: polynuclear aromatic hydrocarbons, coke production, industrial hygiene, biomonitoring, 1-hydroxypyrene

## Introduction

Estonia is one of the leading countries in the world where oil shale is used for petrochemical purposes. Oil shale processing has its start in the beginning of this century and has grown to include production of refined end products as well as raw materials for different fields of the chemical

industry (1). Cokery workers are exposed to a complex mixture of gaseous and particulate contaminants. There is sufficient evidence that occupational exposure causes an excess of skin and lung cancers among coke oven workers (2). The most extensively studied compounds that have adverse health effects in the cokery environment are the polynuclear aromatic hydrocarbons (PAHs) (3). Most of the mutagenic and carcinogenic PAHs are known to exist in the particulate phase (4). At the top of coke ovens, 35 to 200 µg/m<sup>3</sup> of pyrene and 14 to 69 µg/m<sup>3</sup> of benzo[a]pyrene (B[a]P) have been reported in air particulates (5). In a Swedish cokery, the amount of 14 analyzed PAH compounds was 6 to 570 µg/m<sup>3</sup>, of which 0.5 to 2.5% consisted of B[a]P (6). Recently in a modern Finnish cokery, the amount of B[a]P in the vicinity of the coke battery ranged from 2.7 to 3.8 µg/m<sup>3</sup> (7). Repeated measurements at

a cokery have shown that the PAH profile remains relatively constant (5).

Personal exposure to PAH compounds has been assessed in many different occupational environments. Ares (8) recommends that PAHs in the gas phase and those adsorbed on the air particulates be collected simultaneously. Absorption through the lungs has traditionally been considered the most important route of exposure; however, in many workplaces, absorption through skin may also be an important route of exposure. This is demonstrated in therapeutic as well as occupational exposure cases (9–12). VanRooij et al. (13) have demonstrated as high as 74 ng/cm<sup>2</sup> of pyrene and 55 ng/cm<sup>2</sup> of B[a]P on the skin of cokery workers. Considerable contamination was also noticed under the protective clothing. VanRooij et al. have also stated that approximately 75% of the total pyrene dose and 51% of B[a]P dose is absorbed through skin (13).

The markers of internal dose are important because they reflect the amount of the compound that has been absorbed into the body through all absorption routes (14). Several biomarkers have been tested for the assessment of occupational PAH exposure. The most important restrictions in these methods have been unselectivity and low sensitivity (15,16). In many occupational hygiene studies 1-hydroxypyrene has been shown to be a sound marker for PAH exposure (17–19).

In this study we examined the PAH exposure of cokery workers in an Estonian oil shale processing plant. Personal air sampling and skin wipe sampling were used to assess the external dose, and 1-hydroxypyrene was used as a biomarker of internal dose.

## Methods

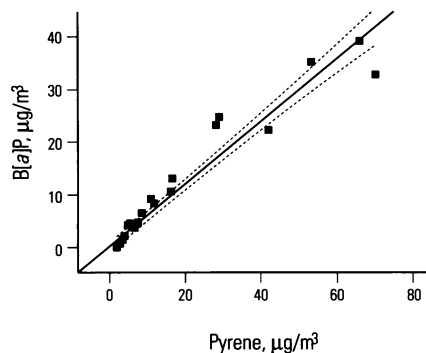
Forty-nine cokery workers from an Estonian oil shale plant at Kohtla-Järve and 10 controls from a nearby Iisaku village took part in this study. Sampling was conducted twice in the beginning of March 1994 and in September 1994. A detailed interview concerning work history, state of health, smoking habits, and other aspects relevant to the study preceded the sampling. Personal air sampling was made by portable pumps over the whole workshift. The air samples were collected onto a Teflon filter followed by XAD-2 adsorbent material. Skin wipe samples were taken before and after the workshift (only once

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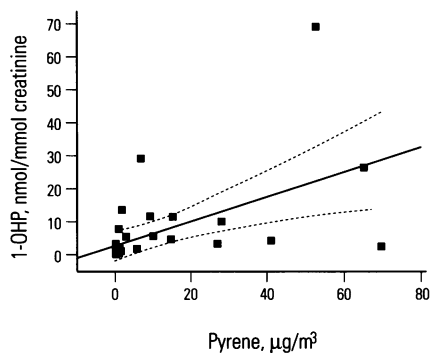
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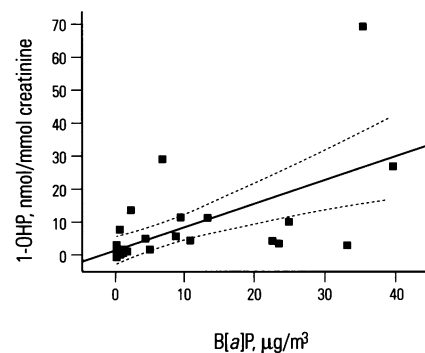
Abbreviations used: PAH, polycyclic aromatic hydrocarbon; B[a]P, benzo[a]pyrene; GM, geometric mean.



**Figure 1.** Correlation between pyrene and B[a]P measured in personal air samples of cokery workers. A linear regression with 95% confidence limits is shown.  $n=45$ ;  $r=0.97$ ;  $p=0.00$ .



**Figure 2.** Correlation between the pyrene concentration in personal air samples and urinary 1-hydroxypyrene (1-OHP). A linear regression with 95% confidence limits is shown.  $n=41$ ;  $r=0.56$ ;  $p=0.0002$ .



**Figure 3.** Correlation between the B[a]P concentration in cokery filter samples and urinary 1-hydroxypyrene (1-OHP). A linear regression with 95% confidence limits is shown.  $n=41$ ;  $r=0.63$ ;  $p=0.00001$ .

from the control) from the left inside wrist with a Smear Tab (SKC Inc., Eighty Four, PA). All samples were protected from sunlight and frozen immediately. National Institute of Occupational Safety and Health (NIOSH) standard 5506 was followed for the preparation of air and skin wipe samples. Analytes were desorbed in toluene and redissolved in methanol for analysis. High-pressure liquid chromatography (HPLC) equipment was Millipore Waters 717 Autosampler, 600-MS pump unit and 470 Scanning fluorescence detector (Millipore, Milford, MA). System control and data handling were done with a Millennium 2010 Chromatography Manager. 1-Hydroxypyrene (Aldrich Chemical Co., Milwaukee, WI) was determined from post-shift spot urine samples according to the method of Jongeneelen et al. (20).

## Results and Discussion

In the cokery, the pyrene concentration of the filter samples was 0.01 to 69.6  $\mu\text{g}/\text{m}^3$  and the B[a]P concentration was 0.02 to 39.6  $\mu\text{g}/\text{m}^3$ , with the mean values being 8.1  $\mu\text{g}/\text{m}^3$  and 5.7  $\mu\text{g}/\text{m}^3$ , respectively. In the control filter samples, the pyrene concentration was 0.001 to 0.004  $\mu\text{g}/\text{m}^3$  (mean 0.002  $\mu\text{g}/\text{m}^3$ ) and B[a]P was 0 to 0.005  $\mu\text{g}/\text{m}^3$  (mean 0.001  $\mu\text{g}/\text{m}^3$ ). No B[a]P was found from the XAD-2 samples and only minimal amounts of pyrene were detected. In 71% of samples ( $n=21$ ), less than 5% of the pyrene measured from filter

samples was found in XAD-2 material during the winter sampling. In the second sampling, less than 5% of the pyrene was found in 54% ( $n=24$ ) of XAD-2 samples. The outdoor temperature was approximately  $-20^\circ\text{C}$  during the winter sampling days, and it is known that temperature has a considerable influence on the occurrence of smaller PAHs in particulate or gaseous phase in the atmosphere (21). Correlation between pyrene and B[a]P concentrations was, however, very good (Figure 1). In a Finnish cokery study, B[a]P concentration in personal samples ranged from 1.4 to 2.5  $\mu\text{g}/\text{m}^3$  (7). In another recent study, topside cokery workers were exposed to 9.44 (geometric mean [GM])  $\mu\text{g}/\text{m}^3$  pyrene concentrations and to 5.85 (GM)  $\mu\text{g}/\text{m}^3$  B[a]P concentrations (19).

The measured contamination on wrist skin was 0.1 to 9.0  $\text{ng}/\text{cm}^2$  (mean 1.6  $\text{ng}/\text{cm}^2$ ) for pyrene and 0 to 7.4  $\text{ng}/\text{cm}^2$  (mean 1.3  $\text{ng}/\text{cm}^2$ ) for B[a]P. A clear skin contamination was demonstrated and, in most cases (60%,  $n=48$ ), the post-shift value was higher, although handwashing could not be controlled in all cases before sampling.

In this study, 1-hydroxypyrene was measured from post-shift samples of 49 exposed workers and 10 controls. Most of the studied subjects were smokers (75%). As showed by VanRooij et al. (22), smoking and dietary intake of PAH have an effect on the baseline excretion of

1-hydroxypyrene in urine (mean value 0.25  $\mu\text{mol}/\text{mol}$  creatinine for smokers). In our study, the controls excreted slightly higher levels of 1-hydroxypyrene, showing a mean of 0.5  $\text{nmol}/\text{mmol}$  creatinine (range 0.1–1.7  $\text{nmol}/\text{mmol}$  creatinine). However, the exposed workers showed clearly elevated levels of 1-hydroxypyrene in their urines. The 1-hydroxypyrene concentration was about 12 times higher (mean 6.0  $\text{nmol}/\text{mmol}$  creatinine, range 0.2–69.5  $\text{nmol}/\text{mmol}$  creatinine) than the local control population. Correlation between airborne pyrene and 1-hydroxypyrene was strong, showing an  $r$ -value of 0.56 (Figure 2). Correlation between B[a]P and 1-hydroxypyrene was even stronger, showing an  $r$ -value of 0.63 (Figure 3).

In this study we found that the cokery workers were exposed to high concentrations of pyrene and B[a]P. Results of biological monitoring are in an agreement with occupational hygiene measurements from the workplace atmosphere. Skin contamination and the importance of possible PAH exposure through the skin is obvious. Because of the big difference of 1-hydroxypyrene concentrations in controls compared to exposed workers and a strong correlation between occupational exposure to pyrene and urinary 1-hydroxypyrene level, we further concluded that environmental factors such as diet and smoking are buried behind high occupational exposures.

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