Assessment of occupational exposure to PAHs in a coke-plant by biological monitoring

G. Assennato, L. Bisceglia & G. de Nichilo
Department of Internal Medicine and Public Health, University Of Bari, Italy

Abstract

In 2002 a criminal law case was filed by the General Prosecutor in Taranto, accusing the management of the second largest steel plant in Europe of criminal misbehaviour in the industrial hygiene procedures at the batteries 3 through 6 of the coke oven plant. Some of the authors were appointed by the Taranto prosecutor to assess occupational exposure to concentrations of a wide range of volatile coal tar pitch compounds.

The present project aims at validating the biological monitoring of carcinogen (namely PAHs) exposure by performing environmental monitoring at the same time. Personal air samples of the workers were taken during the morning shift. The job activities were recorded by occupational physicians. On the same days, spot urine samples before and after the shift were collected to determine 1-hydroxypyrene as internal dose biomarker. Confounding factors, such as diet and smoking habits, were checked by means of a questionnaire. The PAH concentrations in the breathing zone air of coke-oven workers ranged from 20.40 mg/m³ to 76.68 mg/m³, with a median of 30.00 mg/m³. The concentration of 1-OHP in the pre-shift samples ranged from 0.01 µmol/mol creat to 1.32 µmol/mol creat with a median of 0.33, and in post-shift from 0.01 µmol/mol creat to 31.04 µmol/mol creat, with a median of 2.41. The correlation between total PAH and 1-HOP levels has been calculated, showing a correlation coefficient r = 0.31 (p<0.05).

The low correlation is partly due to variation in the working practices during environmental sampling, resulting in lower environmental exposure as well as to the poor sampling and analytical procedures used by the subcontracting industrial hygiene firm. The study shows that biological monitoring is more reliable then environmental monitoring in the assessment of occupational exposure to PAHs.

As a consequence of our survey, the management decided to shut off the batteries under study.

Keywords: PAHs, urinary 1-hydroxypyrene, ambient monitoring, biological monitoring, exposure assessment.
1 Introduction

In 2002 a criminal law case was filed by the General Prosecutor in Taranto, accusing the management of the second largest steel plant in Europe of criminal misbehaviour in the industrial hygiene procedures at the batteries 3 through 6 of the coke oven plant. Some of us were appointed by the Taranto Prosecutor to assess occupational exposure to concentrations of a wide range of volatile coal tar pitch compounds.

The Coke Oven Plant under study is situated close to the city of Taranto. The metropolitan area of Taranto has been defined by WHO area at high environmental risk because of the presence of several large industries and elevated rates for all-causes mortality and all cancer mortality, higher than regional mortality rates, especially for lung cancer [11].

The ILVA plant has been built up between 1960 and 1975: its extension is 150 Km² with 50 km of roads, 200 km of railways and 190 km of conveyer belts. There are more than 10,000 of employees. In the ILVA plant the fuel for the blast furnaces is provided by coke, produced in the coke oven plant.

The coke oven plant consisted of 12 batteries.

The present study concerns batteries indicated as 3-4 and 5-6, constructed respectively on 1964 and 1970. Each couple of batteries consists of 90 ovens. There are critical aspects in functioning of these batteries, due to their old age, characterized by frequent interruptions of production cycle and technical failures. As it is well known, coke production is classified into group 1 by IARC and several polycyclic compounds contained in coke oven emissions are known to be human carcinogens [1, 6]

In compliance with the Italian law on safety and health at work, occupational exposure to carcinogens in work environments has to be assessed: the Occupational Health Service of the ILVA plant has been implementing carcinogen exposure monitoring tools, by integrating ambient and biological monitoring.

The present study aimed at evaluating of PAH exposure in the coke plant through simultaneous air and biological monitoring; validating biological data by ambient monitoring; estimating a risk profile for health workers.

2 Methods

Air monitoring was performed by an external industrial hygiene firm. The Occupational Medicine Division of Bari University performed the biological monitoring and data analyses.

The survey was carried out with two-days campaigns of monitoring to evaluate external and internal exposure to PAH.

Air monitoring provided for two mobile stations situated on the charging car and on the pushing car for the sampling of air on the whole battery, for a last of 2 hours, for each measured parameters; area sampling was carried out with stations at top side on stairway side and banister side, pushing side, thermal inversion; personal breathing zone air samples were collected for each couple of battery
from a worker in each shift, selected by job-title. The air sampling was conducted for two hours.

Air samples were taken and analysed according to the NIOSH method n. 5506.

Such a plan aimed at evaluating air pollution in the workplace, characterizing coke emissions in terms of PAH profiles and defining individual level of exposure [15].

A questionnaire to evaluate potential confounding factors was administered by occupational physicians to collect information about smoking habits, consumption of grilled meat, work absence in the days before the monitoring.

The biological marker of exposure was urinary 1-hydroxypyrene, the hydroxylated metabolite of pyrene: several authors have reported an increased urinary excretion of this metabolite in the urine of subjects exposed to mixtures of PAHs [9]. As the proportion of pyrene in airborne mixtures of PAHs from different sources does not vary greatly, it was suggested that the concentration of hydroxypyrene in urine might be used as biological indicator of overall exposure to PAHs [2, 4, 10, 13]. The determination of urinary 1-hydroxypyrene was performed according to the Jongeneelen method [8].

Descriptive analyses were performed on both environmental and biological data: geometric mean, median and range were used to describe the distribution of data, in consideration of the skewed distribution. After log transformation, t-tests were used to compare groups under study. Spearman correlation coefficients were used to investigate the relationship of urinary 1-HOP concentrations and total PAH and pyrene concentrations.

3 Results

Table 1 shows the results of area sampling on the charging car: the German technical guiding concentration (TRK) for benzo(a)pyrene in the area near the ovens in coke plants of 5µg/m³ was exceeded in 11 samples of 16.

<table>
<thead>
<tr>
<th>Battery 3-4</th>
<th>Area Sampling</th>
</tr>
</thead>
<tbody>
<tr>
<td>09:20 a.m. 15:01-02</td>
<td>16:10 p.m. 16:25-02</td>
</tr>
</tbody>
</table>

Table 1: Results of area sampling on the charging car.

As for the biological monitoring, 105 workers were involved in the survey, 55 in battery 3-4 and 50 in battery 5-6.

The comparison between air and biological data according to job-title highlights that the workers most exposed to PAH were those occupied at the top side area of the coke oven plant, table 2. Concentrations of hydroxypyrene
according to batteries belonging and to job-title are presented: again, top side workers showed highest values, with concentration in 3-4 battery more elevated than battery 5-6. Overall concentrations ranged between 0.005 and 31.04µMol/Molcreat.

Table 2: Ambient PAHs data and Urinary 1-HOP levels according to job-title.

<table>
<thead>
<tr>
<th>Job-Title</th>
<th>PAH\textsubscript{t} (µg/m\textsuperscript{3})</th>
<th>Pyrene (µg/m\textsuperscript{3})</th>
<th>1-HOP\textsubscript{pre} (µMol/Mol\textsubscript{creat})</th>
<th>1-HOP\textsubscript{post} (µMol/Mol\textsubscript{creat})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standpipe Operator</td>
<td>30.54</td>
<td>2.66</td>
<td>5.4</td>
<td>14.6</td>
</tr>
<tr>
<td>Topside worker</td>
<td>73.26</td>
<td>6.58</td>
<td>5.6</td>
<td>15.4</td>
</tr>
<tr>
<td>Coke-Guide operator</td>
<td>67.11</td>
<td>1.32</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Door Operator</td>
<td>56.25</td>
<td>5.19</td>
<td>2.4</td>
<td>3.8</td>
</tr>
<tr>
<td>Charging-Car Operator</td>
<td>32.46</td>
<td>0.50</td>
<td>1.4</td>
<td>3.4</td>
</tr>
</tbody>
</table>

We reported levels of the biological marker according to personal characteristics, namely smoking habit, consumption of grilled meat, work absence 1, 2 or 15 days before the survey, table 3.

Table 3: Urinary 1-HOP levels according to personal characteristics.

Log transformation of data was carried out to normalise the distribution and t-tests were performed to compare groups under study. Statistical significant differences were observed between hydroxypyrrene concentrations of workers belonging to battery 3-4 vs battery 5-6, with battery 3-4 values higher; according to job-title, top side workers showed concentration of the biomarker significantly higher than others workers.
No statistical significance in difference between smokers vs. non-smokers were found and neither according consumption of roasted meat and work absence.

A correlation analysis was carried out to investigate the relation of urinary hydroxypyrene concentration measurement in the same workers one year apart: Spearman correlation coefficient has been found equal to 0.52. When we investigated the correlations between ambient and biological data we found weak relations.

Our biological data were very similar to the hydroxypyrene concentrations found in another Italian Coke plant, where Spearman coefficient for PAH and pyrene was 0.83, table 4 [3].

Table 4: Biological data according to job-title in two different Italian coke plants.

<table>
<thead>
<tr>
<th>Job-Title</th>
<th>1-HOP&lt;sub&gt;post&lt;/sub&gt; (Mean ±SD)&lt;sup&gt;1&lt;/sup&gt; ($\mu$mol/mol&lt;sub&gt;creat&lt;/sub&gt;)</th>
<th>1-HOP&lt;sub&gt;post&lt;/sub&gt; (Mean ±SD)&lt;sup&gt;2&lt;/sup&gt; ($\mu$mol/mol&lt;sub&gt;creat&lt;/sub&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standpipe</td>
<td>14.6 ± 4.67</td>
<td>9.46 ± 4.83</td>
</tr>
<tr>
<td>Top side</td>
<td>15.4 ± 3.96</td>
<td>12.87 ± 8.32</td>
</tr>
<tr>
<td>Coke Guide</td>
<td>2.5 ± 2.03</td>
<td>2.57 ± 2.02</td>
</tr>
<tr>
<td>Door Operator</td>
<td>3.8 ± 2.19</td>
<td>2.52 ± 0.68</td>
</tr>
<tr>
<td>Charging Car</td>
<td>3.4 ± 3.08</td>
<td>4.33 ± 1.80</td>
</tr>
</tbody>
</table>

<sup>1</sup> Taranto Coke Plant
<sup>2</sup> Piombino Coke Plant (correlation PAH and PYR/1-HOP: r=0.83)

This finding could strengthen the fact that we were in presence of ambient data of scarce accuracy, whereas the biological data were reliable.

To categorize the exposure level, an attempt was made by Jongeneelen and colleagues to propose a three-level benchmark guideline for urinary hydroxypyrene [/]. The first level of 0.24 for non-smokers and 0.76 for smokers represents the level of background exposure in general population, not occupationally exposed. The second level of 1.4 corresponds to the no biological effect level: under this level no genotoxic effects are expected. The third level of 2.3 is specific for coke oven workers: it corresponds to the US threshold limit value of 0.2 in the benzene soluble fraction and it is estimated to be associated to a relative risk of lung cancer of 1.3.

Applying these levels to our data according to battery belonging, we observed that 34% of workers in the battery 3-4 exceeded the third level while 15% in the battery 5-6; 50% in battery 3-4 and 22% in battery 5-6 exceeded the second level; 94% and 70% of non smokers workers exceeded the first level of 0.24 and 72% and 42% of smokers workers exceeded the level of 0.76, table 5.

We conducted this evaluation according to job-title: the mean and the standard deviation were compared to the benchmark level considered as population level. We assumed that the variance in the reference population was the same as the observed variance. We performed a z-test to investigate the
statistical significance of observed means versus population means corresponding to the three level proposed.

Table 5: Urinary 1-hop levels according to benchmark guideline for urinary 1-hydroxypyrene as biomarker of occupational exposure to polycyclic aromatic hydrocarbons.

<table>
<thead>
<tr>
<th></th>
<th>BATTERY 3-4 (n. 50)</th>
<th>BATTERY 5-6 (n. 55)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>2,16</td>
<td>1,60</td>
</tr>
<tr>
<td>Median</td>
<td>1,51</td>
<td>0,52</td>
</tr>
<tr>
<td>Range</td>
<td>0,16-22,76</td>
<td>0,005-31,04</td>
</tr>
<tr>
<td>&gt;2,3µMol/Mol Creat</td>
<td>34%</td>
<td>&gt;2,3µMol/Mol Creat</td>
</tr>
<tr>
<td>&gt;1,4µMol/Mol Creat</td>
<td>50%</td>
<td>&gt;1,4µMol/Mol Creat</td>
</tr>
<tr>
<td>&gt;0,24µMol/Mol Creat</td>
<td>94%</td>
<td>&gt;0,24µMol/Mol Creat</td>
</tr>
<tr>
<td>&gt;0,76µMol/Mol Creat</td>
<td>72%</td>
<td>&gt;0,76µMol/Mol Creat</td>
</tr>
</tbody>
</table>

With respect to the third level, the mean concentration of hydroxypyrene of top side workers of battery 3-4 was found significantly increased; as for the second level all workers of the battery 3-4 showed mean concentration of the biological indicator significantly elevated.

4 Discussion and conclusion

We observed high exposure to PAH in the coke oven plant, especially in battery 3-4 and in topside workers. No confounding effects were ascertained.

An examination of ambient data pointed out problems of quality of monitoring operations: the indications on quantity of the parameters that were collected have not been always respected and so in many samples the concentration of single PAH reported was under the detectable limit.

Prolonged time of manipulation of filters in the analysis phase, three or fourfold higher than indicated by NIOSH method, as reported by industrial hygiene experts, could have compromised the correct detection of PAH.

The time of sampling of two hours could not be representative of the entire shift: we observed significant variations of the concentrations in following samples.

Furthermore, PAH profiles showed a wider variability compared to other studies.

The feature of the weak correlation between ambient and biological data could be explained on one hand because air monitoring does not take into account ways of absorption different than respiratory route. The quantity excreted of metabolite in urine depends on metabolism and excretion routes of pyrene. The importance of the metabolic pathway of pyrene to hydroxypyrene in man has not yet been quantified [4]. So, dermal contribution, as well as ingestion contribution, to the total amount of internal exposure could be neglected [5, 16].

On the other hand, the problem of the reliability of ambient data could not be overlooked, as also the correlation between total PAH and pyrene was low.
Even in absence of validation by ambient monitoring, that generally represents the gold standard for the exposure assessment, relevant implications from the biological data could be derived by the Occupational Health Service of ILVA plant as the application of the biological monitoring to evaluate workers’ exposure may contribute significantly to risk assessment by allowing the estimation of the effectively absorbed dose.

An estimate of risk profile can be drawn as the third level of benchmark guideline was exceeded, significantly for top side workers of battery 3-4.

As a consequence of our survey, the management decided to shut off the batteries under study.

References


