HUMAN HEALTH RISK ASSESSMENT BY EXPOSURE TO HEAVY METALS IN A CONTAMINATED SOIL BY OIL SPILL

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ABSTRACT

Significant amount of petroleum may cause serious damage in the environment by accidents and/or releasing effluents of petrochemical industries. Although metals are not the main pollutants present in this type of contamination, they might contribute for human health risk. The objective of this work is to assess the human health risk caused by the exposure to fifteen metals present in a soil contaminated by crude oil. In addition, the concentration of these metals in leached and in solubilized fractions was compared with the maximum concentration allowed by ABNT (1987) in order to estimate the potential groundwater impact. The studied metals were: antimony, arsenic, barium, cadmium, lead, cobalt, copper, chromium, mercury, molybdenum, nickel, silver, selenium, vanadium and zinc. These metals were analyzed by atomic absorption spectrometry. The methodology of human health risk assessment used was the recommended by USEPA (1989). The results of leaching and solubilizing tests showed that all metals concentrations were lower than maximum limits established by ABNT, showing that these metals do not offer contamination risk to groundwater, therefore not offering risk for population by groundwater ingestion. The exposure pathways studied were oral and dermal contact with the contaminated soil applied to close population (children and adults). In the human health risk assessment, the exposure pathway that resulted in higher hazards of non-carcinogens and risks of carcinogens effects in the population (children and adult) was dermal contact with soil. The main pollutants in both distinct exposure pathways were arsenic and antimony. When non-carcinogens and carcinogens effects in children and adults were evaluated, the values of hazard index and risk were higher than the target values, 1 and 1x10^-4, respectively. Finally, it may be concluded that although metals are not considered the main pollutants present in a compartment contaminated with petroleum, they can offer considerable risk of carcinogens and hazard of non-carcinogens effects.
INTRODUCTION

The relationship between the intensity of the environmental pollution and the potential risks to human health can be assessed by human health risk assessment methodology proposed by USEPA (1989). This methodology allows expressing human health risk as comparable numeric estimates, which permits to establish priority of impacted areas, as well as the evaluation of remediation techniques.

In addition, the methodology proposed by USEPA was developed to facilitate general population to understand the results. They are susceptible to systematic evaluation, which can be put to the disposition and discussed deeply by the involved social actors, guaranteeing the indispensable linking between the technical quality and the methodology of assessment committed with the business efficiency close to the society.

Therefore, the objective of this work is to estimate potential human health risk by ingestion and dermal contact with a soil contaminated by oil spill, according to USEPA methodology and in addition evaluate the concentration of fifteen metals in leaching and solubilizing fractions.

EXPERIMENTAL

Soil sampling and metals analysis were carried out as described by Lima, 2004. The concentrations of fifteen metals (antimony, arsenic, barium, cadmium, cobalt, copper, chromium, lead, mercury, molybdenum, nickel, silver, selenium, vanadium and zinc) in leaching and solubilizing fractions were determined according NBR10005 and NBR10006 Rules, respectively.

The USEPA (1989) human health risk assessment methodology is composed of four stages: 1) Elaboration of a qualitative conceptual model, which considers sources and pollutants of potential concern, their fates, transport and transference among environmental multimedia, exposure pathways and critical toxic effects; 2) Exposure assessment that involves quantifying the estimated intake of dose of the contaminant by human receptors for each route of exposure identified in the qualitative assessment; 3) Toxicity assessment, which involves the classification of the potential toxic effects of chemical, mainly in carcinogenic and non-carcinogenic compounds, and; 4) Risk characterization, which summaries and combines outputs of the exposure and toxicity assessments to characterize baseline risks, both in quantitative expressions and qualitative statements. Baseline risks are risks that might exist if no controls were applied at a site.
In this work was considered children and adults for two human exposure pathways: ingestion and dermal contact with soil.

The exposure equations used to determine the intake of dose of contaminants via ingestion and dermal contact with soil, considering a chronic exposure, at screening level, were derived from ATSDR (1989) and are summarized below, respectively.

\[
IR = \frac{(CC \times CR \times AF \times EF \times 10^{-3})}{BW} \quad (1)
\]
\[
DC = \frac{(CC \times A \times EF \times BF)}{BW} \quad (2)
\]

Where:

- \(IR\) = contaminant ingestion rate (mg.kg\(^{-1}\).day\(^{-1}\))
- \(CC\) = contaminant concentration (mg.kg\(^{-1}\))
- \(CR\) = soil consumption rate (g.day\(^{-1}\)) (1.00E-01 for children and 5.00E-02 for adults)
- \(AF\): Absorption factor (unitless) (1 for children and adults)
- \(EF\) = exposure factor (days.year\(^{-1}\)) (356 days per year, for all cases)
- \(BW\) = body weight (15kg for children, 70kg for adults)
- \(DC\) = Soil dermal contact dose (mg.kg\(^{-1}\).day\(^{-1}\))
- \(A\) = Total soil adhered (kg.day\(^{-1}\)) (5.25E-03 for children and 9.40E-03 for adults)
- \(BF\) = Biodisponibility factor (unitless) (1 for children and adults)

At screening level, the gastrointestinal absorption is assumed as total (100%). The predicted dose rate (IR) is compared to the reference dose (RfD) for non-carcinogens and to slope factor (sf) for carcinogens. The ratio of the predicted exposure to the RfD is the hazard quotient (HQ) and the product of the predicted exposure to the sf is the risk (R). The equations used to calculated HQ and R are shown bellow, respectively.

\[
HQ = \frac{IR}{RfD} \quad (3)
\]
\[
R = IR \times sf \quad (4)
\]

The hazard quotients associated with the different metals are added to produce a hazard index (HI). A HI less than 1 indicates that the predicted exposure is unlikely to pose potential human health risks. On the other hand, HI higher than 1 indicate potential adverse health effects. When evaluating the magnitude of HI at screening levels, indices
that are marginally different from 1, it is important to consider the sources of uncertainties. In relation to risk, it is expressed as a probability of a human to develop cancer.

Some metals analyzed do not have referenced dose values reported. In relation to metals that have referenced values reported, the RfD (mg kg\(^{-1}\) day\(^{-1}\)) are: Antimony, 4.0E-04; arsenic, 3.0E-04; barium, 7.0E-02; cadmium, 5.0E-04; mercury, 3.0E-04 (only for ingestion pathway); molybdenum, 5.0E-03; nickel, 2.0E-02; silver, 5.0E-03; selenium, 5.0E-03; vanadium, 7.0E-03; and zinc, 3.0E-01. For risk evaluation, only arsenic have slope factor, that is 1.5E+00 mg kg\(^{-1}\) day\(^{-1}\).

**RESULTS AND DISCUSSION**

Table 1 shows the metals concentrations in soil and in solubilizing and leaching fractions. Six of the fifteen metals evaluated presented concentrations higher than the referenced. As defined by CETESB (2001) a soil can be considered “clean” if all metals concentrations are lower than the referenced value. But it was not observed in the case studied. For arsenic, barium, lead, cobalt, nickel and silver the values analyzed were higher than the referenced. So, this soil can not be considered “clean”. In relation to metals in leaching and solubilizing fractions, none of them was higher than the established values.

Figure 1 shows the hazard indexes (HI) for children and adults by ingestion and dermal contact with soil. It can be observed that for both cases the values of HI corresponding to dermal contact were higher than those by ingestion of soil. In addition, the value of total HI was higher for children (5.54E+01) than for adults (2.10E+01). It means that for children the HI are more than fifty times and for adults more than twenty times higher than the referenced value (1.00E+00). In all cases the metals that contributed more for the results were antimony and arsenic.

In relation to risk analysis, the only metal that there is referenced value is arsenic. All the values of risk for, respectively, children and adult by ingestion (3.17E-04 and 3.40E-05) and by dermal contact (1.66E-02 and 6.39E-03) were higher than the maximum value established by USEPA (1989), that is 1.00E-06. When compared to referenced value established by CETESB (2001), that is 1.00E-04, only the scenario of soil ingestion by adult was lower than the allowed. It means that more than one person in ten thousand people probably will develop cancer by exposure to the soil investigated.
Table 1: Comparison between metals concentration in soil and referenced values

<table>
<thead>
<tr>
<th>Metal</th>
<th>Soil (mg.kg⁻¹)</th>
<th>Leaching (mg.L⁻¹)</th>
<th>Solubilizing (mg.L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CD¹</td>
<td>Ref. Value²</td>
<td>CD¹</td>
</tr>
<tr>
<td>Sb</td>
<td>&lt;25</td>
<td>&lt;0.5</td>
<td>-</td>
</tr>
<tr>
<td>As</td>
<td>31.7</td>
<td>3.5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Ba</td>
<td>236</td>
<td>75</td>
<td>78</td>
</tr>
<tr>
<td>Cd</td>
<td>&lt;4.0</td>
<td>&lt;0.5</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>Pb</td>
<td>40.5</td>
<td>17</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Co</td>
<td>522.5</td>
<td>13</td>
<td>-</td>
</tr>
<tr>
<td>Cu</td>
<td>29.1</td>
<td>35</td>
<td>-</td>
</tr>
<tr>
<td>Cr</td>
<td>14</td>
<td>40</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Hg</td>
<td>0.048</td>
<td>0.05</td>
<td>&lt;0.000002</td>
</tr>
<tr>
<td>Mo</td>
<td>18</td>
<td>&lt;25</td>
<td>-</td>
</tr>
<tr>
<td>Ni</td>
<td>20.5</td>
<td>13</td>
<td>-</td>
</tr>
<tr>
<td>Ag</td>
<td>1.3</td>
<td>0.25</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Se</td>
<td>&lt;50</td>
<td>0.25</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>V</td>
<td>7.5</td>
<td>275</td>
<td>-</td>
</tr>
<tr>
<td>Zn</td>
<td>47.6</td>
<td>60</td>
<td>-</td>
</tr>
</tbody>
</table>

¹ CD: Concentration determined as described in section Experimental; ² Referenced value established by CETESB (2001); ³ Maximum value determined by ABNT (1989).

Figure 1: Hazard indexes for each scenario evaluated.

DC: Dermal contact; Ing: Ingestion
ACKNOWLEDGMENTS
To MCT/CETEM for institutional and CNPq for financial supports.

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