Sediments Contaminated by Non-Polar Extractable Substances and Health Risks

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1Abstract: - The article deals with the assessment of non-carcinogenic health risks resulting from the contact of persons with bottom sediments contaminated by non-polar extractable substances. The sediments were taken in the river bed up and downstream from the premises of former chemical factory which had processed oil products. The concentration of non-polar extractable substances in the sediment was determined through infrared spectrometry. There were assessed the non-carcinogenic health risks of random ingestion and dermal contact with contaminated sediment for the population of 3 to 6 years old children, adults and the employees carrying out sanitation works.

Key-Words: - environmental burden, non-polar extractable substances, non-carcinogenic risk, oil products, sediment.

1 Introduction
More intensive activities of human society aimed at reaching higher standard of living are bringing a number of negative externalities. Increasing environmental burden belongs to significant externalities, which are frequently discussed by public as well as professionals. Contaminated soil, rock environment, hydrosphere and atmosphere represent a serious problem in the protection of ecosystems, health of human population and it often prevents the area from being used and regional activities from being developed.

Requirement for considerable amount of financial resources for clearing the relict environmental burdens on the one hand and the limited resources on the other hand need an integral system of analysing and decision making during the remedy of the environment aimed at maximal effectiveness [1].

The primary principle is to find the socially acceptable level of ecological and health risk while proceeding from the fact that reaching the “zero risk” is not always necessary from he viewpoint of public health and the environment [2]. The second principle on which the process is based is the analysis and remediation of burden with regard to the assumed exploitation of the territory [3]. It means that only realistic scenarios are assessed as far as the spread of contamination, health hazards and damage to natural resources are concerned. It is necessary to identify the real level of risk on the basis of risk analysis and give priority to the reduction of such burdens, which represent an acute and unacceptable risk to human health and ecosystems [4].

There are many contaminants that represent relict ecological burdens. Non-polar extractable substances (NES) belong to significant pollutants not only in the Czech Republic, but also in other parts of the world [5].

2 The Analysis of Current State
The NES may be originated mainly by the exploitation, transport and washing of oil, the processing of oil and coal, the production, storing and use of oil and coal products. It may also be produced by plants, animals and microorganisms. Legislation does not reflect this fact and all NES are considered to be xenobiotics regardless of their origin and bonds in matrix [6].

The NES are substances isolated from the sample by a low-polar medium (some freons, tetrachlorethylene, CO₂) and depleted of more polar components through sorption on a suitable sorbent (silica gel, florisil). The extract includes hydrocarbons together with non-polar and low-polar halogen hydrocarbons, oxygen, sulphur and nitrogen compounds. A partial sorption of aromatic hydrocarbons may occur when using a sorbent of too high activity. Then the NES are determined by a suitable analytical method. The level of presence of oil substances in the environment is usually connected with the occurrence of NES. Oil products are defined as hydrocarbons and their compounds, especially gasoline, benzene and its derivatives, Diesel oil, kerosene, heating oil and tar oil. The substances of kinematic viscosity higher than 100 mm² s⁻¹ at a temperature 50°C are not considered to be oil substances [7].

Other authors classify NES into the substances of petrogenic origin, i.e. substances from oil, coal, lignite, etc., and the substances of biogenic origin, i.e. those originated through biological processes [8]. The latter include, besides others, the substances in plants and the products of their transformation in natural environment.
including the compounds originated by the activities of soil and water microorganisms. The substances of anthropogenic origin are mentioned as well [6, 9].

Oil substances released into the environment infiltrate soil due to gravitation and they penetrate collector as far as the impermeable aquifer. Their low mixability with water causes their concentration on the surface of ground water and possible migration considerably far from the area of contamination [5].

Oil substances negatively affect sensory characteristics of water already at marginal concentrations. The threshold concentration of odour is given by the chemical composition of oil contaminants. Isoalkanes and aromatic hydrocarbons are extra sensory efficient [10]. They have bioaccumulative capability, so they may negatively affect taste and odour of meat of aquatic animals [11].

The effects of oil products are the function of their chemical composition. However, possible biological damage will also depend on the type and vulnerability of polluted ecosystem [5]. The release of oil substances will have a negative impact on organisms either through direct toxicity or through physical cover of water surface causing suffocation. The accumulation of oil substances on water surface cause the depletion of oxygen in water by transforming organic matter into inorganic compounds. The reduction of biodiversity is then caused by reduced populations of amphipods, which are important in food chain, and eutrophication [12]. It was also discovered that the contamination of water and soil by oil substances reduces the speed of photosynthesis and the production of aquatic and terrestrial biomass [13]. Soil contamination caused by oil deteriorates the yields of agricultural crops for even long time depending on the type and concentration of pollutant [14].

It is generally true that oil substances are toxic for living organisms and ecosystems because of the presence of polycyclic aromatic hydrocarbons (PAHs) [15], many of which are considered to be probable human carcinogens of B2 group [16]. Besides that the toxicity of oil substances, including PAHs, increases due to their exposure to the solar UV radiation causing the production of other highly toxic by-products through radical reaction and oxidation [17].

The effects of NES on human health differ depending on their composition and exposure. Health problems connected with the release of oil substances become evident by any combination of exposure pathways of contaminated food, contaminated water, emissions, and vapours. Oil substances generally show narcotic effects. There are known cases of acute peroral and inhalation poisoning. Percutaneous and mixed poisoning is rarer. The acute poisoning is characterized by the feeling of weakness, dizziness, headache, impaired consciousness and hypothermia. The contact of oil substances with skin may cause eczemas among sensitive people. Oil substances penetrate skin with difficulty and in case of single exposure there is usually no evidence of effects [16]. Poisoning of mammals is characterized by cerebral haemorrhage, pulmonary apoplexy, kidney and liver haemorrhage [18]. Aromates have the highest chronic effects resulting in haemato genesis failure. The symptoms of chronic poisoning include inflammation of air passages, skin tumefaction, enlargement of thyroidea among women, changes of mood, apathy, forgetfulness and manic depressive psychosis. The studies carried out on animals reveal negative impacts of oil products on lungs, liver, kidney and central nervous system [16].

The by-products of PAHs oxidation may increase the risk of mortality caused by infectious diseases [19] and reduce the reproduction capacity of exposed population [20].

Oil products contain components classified according to the U.S. EPA as A group human carcinogens (benzene) and B2 group probable human carcinogens with inadequate evidence (benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenz[a,h]anthracene, etc.) [16]. The exposure of mammals to oil hydrocarbons may affect genetic integrity demonstrated by carcinogenic, mutagenic and teratogenic effects and reproduction disorders [21].

Many organic components classified as NES according to prescribed procedure need not even be present in oil. The content of NES in some foods is not negligible either, although they do not behave as xenobiotics there [22].

The outcome of the NES content analysis is affected by the solubility of substances passing into extract, the polarity of substances passing into eluent and the applied analytical method. The gravimetric method is not suitable for low concentrations and with regard to the work technique it is not suitable for volatile substances either. The UV-spectrometry detects solely aromates for which it is very sensitive. The IR-spectrometry may determine the substances containing the carbon-hydrogen bonds while applying the standardized way of measuring within the range of 2900-3100 cm⁻¹. In case of incorrectly applied calibration even this method need not offer correct outcomes. In contrast to the IR-method the gas chromatography (GC) may better distinguish individual components of NES. On the other hand though, the substances of lower boiling point may escape to be noticed, although otherwise classified by other methods [23].

Until 2008 it was possible to apply the IR-spectrometry as the standard method for classifying the NES in the Czech Republic. The IR-spectrometry used R-113 freon (1,1,2-trichloro-1,2,2-trifluoroethane) as
3 Problem Solution

3.1 Applied Methods and Devices
The sampling of contaminated sediments from the bottom of selected stream was carried out in compliance with standards into a glass sample bottle of 0.2 dm³ capacity with tight inert cap [26]. Two sampling spots were chosen approximately 20 m up and down stream from the former chemical factory with the aim to assess the contribution of relict burden. The sampling was carried out during 8 weeks in July and August. Three samples were taken a week. The samples were distributed into a laboratory, put into a refrigerator and analyzed within 24 hours. Altogether there were 24 samples analysed at each sampling spot.

Determining the concentration of NES in the sediment was in compliance with national standards valid at that time as well [24]. The samples of bottom sediments were laboratory extracted in Soxhlet extractor with 1,1,2-trichloro-1,2,2-trifluoroethane and then the polar substances were removed batch wise with silica gel. Determining the concentration of NES itself was carried out with the help of Perkin Elmer FT-IR 1760 X IR-spectrometer with the limit of determination 20 mg of NES per one kilogram of dry matter. The findings were then analyzed and the arithmetic average determined.

The risk assessment itself was carried out in compliance with the valid legal regulation of the Czech Republic [26], which complies with the method proposed by the U.S. EPA [27] and at the same time adapts the exposure factors to national conditions.

3.2 Outcomes and Discussion
The area of interest is located in the bottom land of brook R on the south-east outskirts of the village S in the altitude 213.70-217.76 m. The surroundings of the chemical factory are mainly a residential area at present. The surrounding area may partially be used for recreation. There are 28 family houses near the south boundary and some of them have old private wells. The brook R running south is on the eastern side of the premises and on its left bank there are 40 family houses and a grocery. Southeast there is a garden centre and private gardens. North and west of the premises there are family houses as well, but as the groundwater flow is southeast it can be assumed that the environment will not be polluted. Drinking water is supplied by public water main. Some inhabitants use water from private wells as service water, though.

The area is the T2 warm climatic region. It is characterized by long, very hot and dry summer, short transition period of warm spring and autumn and short, mild and very dry winter with short duration of snow cover.

The area belongs to the Danube catchment area and the examined brook R is the stream of VI degree. It has to be mentioned that the monitored contaminated area is neither in the protective zone of groundwater source nor in the protective zone of surface source. The brook R is not a significant water stream in the area of interest.

The contamination of the area was caused by the operation of former chemical company D in 1938-1962. The production programme was based on distilling the coal tar and production of tar boards from pitch as the distillation residue. Coal tar was distilled in the central part of the premises, where individual distillation fractions were stored and passed to further processing by other national companies.

In general, every activity in the technological procedure of distillation of coal tar resulted in the leakage of coal tar into bedrock and then into surface and ground waters. Frequent accidents also contributed to the environmental pollution. Water management was the most serious problem of coal tar processing and production of tar boards at that time. Considerable amount of production waste waters was drawn into so called “phenol pond” and subsequently discharged into the brook R. That way further coal tar was released into the environment. After the company D finished its activity in 1962 the “phenol pond” was levelled by clinker and brick rubble. The residues of coal tar and soil contaminated by coal tar were not drawn and sanitation did not take place. The “phenol pond” became a permanent and significant source of environmental burden just as the contaminated saturated and non-saturated areas on the premises of the company and its surroundings with many pollutants among which NES were dominant.

After the chemical production was finished the area of former chemical company was used for the production of fibre and cardboard boxes without any sanitation till the mid 90-ies. After that the premises were hired to other companies for storing, car-repair and small furniture production.
During the privatization of the premises a contract on decontamination of the area was signed with the National Property Fund in 1994. After exploration work a protective sanitation pumping was carried out in 1996-1997, and a regular sanitation pumping continued in 1998-2002 in compliance with the contract documents [28]. There were approx. 216 m$^3$ of coal tar drawn and removed altogether. It was estimated by the contracted company that after the end of sanitation there were approx. 570 m$^3$ of coal tar remaining rock-bound in the area and 60 m$^3$ of mobile phase of coal tar in the saturated zone.

The building of horizontal drain in the axis of brook bed was a significant sanitation element. The drain captures and collects the free phase of coal tar and also functions as a hydraulic barrier reducing the spread of contamination. The drain is built on the right bank of the brook R. It consists of an open pit 193 m long and a system of horizontal drill holes 110 m long. The total effective length of drain is 239 m. The mined uncontaminated soil usually from the middle part of profile of drift soils were at first deposited at the functional area within the premises of former company D and then used for the filling of the drain. Other contaminated soil was transported and decontaminated “off site” on a biodegradation area.

The brook R was cleaned in the same length as the drain. The drift soil was removed in the depth of 0.4-0.5 m and this depth of cleaned brook was backfilled with macadam. Then the bottom of brook R was regulated into former profile with crushed limestone. Altogether there were approx. 855 tons of bottom sediments mined and transported for sanitation.

After the remedial intervention, during which a major part of mobile phase of coal tar was removed from the ground waters, the concentration of NES in surface water of brook R decreased to acceptable level. However, the rock-bound coal tar and very high concentrations of dissolved pollutants in ground waters remain in major part of the premises and partially cross the boundary south and eastward into a built-up area. Therefore it was decided to check which carcinogenic risks result from the current contamination for the local population and the staff carrying out the remedial works.

The risk assessment considered the arithmetic average of NES concentrations in bottom sediments detected down stream the former chemical factory $c_b = 320$ mg kg$^{-1}$. In order to assess the burden the concentration of NES was also monitored up stream the premises $c_a = 58$ mg kg$^{-1}$.

It is necessary to know the reference doses $RfD$ [$\mu$g kg$^{-1}$ day$^{-1}$] for the risk assessment of contaminants with threshold effect. The $RfD$ can be calculated according to the relation (1):

$$RfD = \frac{NOAEL \times UF \times MF}{1}$$  \hspace{1cm} (1)

where $NOAEL$ is the concentration of contaminant in case of which there are no observed adverse health effects, $UF$ is the aggregate uncertainty factor and $MF$ is the modification factor. The $UF = 10^6$ and $x \in 0 \land N$, where $N$ represents the symbol for the set of natural numbers expressing the number of uncertainties and $MF \in (1; 10)$ characterizes the uncertainties not included in the UF.

Regarding the fact that NES represent a wide mixture of substances neither NOAEL nor $RfD$ are published for them. The $RfD_{Or}$ values for random oral ingestion were found for the assessment of non-carcinogenic health risks of individual fractions of hydrocarbons and chemical individuums and they are presented in Table 1 [29].

<table>
<thead>
<tr>
<th>Substance/Fraction</th>
<th>Naphthalene</th>
<th>Phenol</th>
<th>C$_7$-C$_8$</th>
<th>C$<em>9$-C$</em>{10}$</th>
<th>C$<em>{11}$-C$</em>{12}$</th>
<th>C$<em>{13}$-C$</em>{16}$</th>
<th>C$<em>{17}$-C$</em>{21}$</th>
<th>C$<em>{22}$-C$</em>{35}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$RfD_{Or}$ [mg kg$^{-1}$ day$^{-1}$]</td>
<td>0.02</td>
<td>0.30</td>
<td>0.10</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
<td>0.03</td>
<td>0.03</td>
</tr>
</tbody>
</table>

The critical value of $RfD_{Or} = 0.03$ mg kg$^{-1}$ day$^{-1}$ was set for the risk analysis as it best characterizes the existing uncertainties. Following the legislation [30] the value of $RfD_{Der}$ for random dermal contact with the polluted sediment was calculated according to the relation (2):

$$RfD_{Der} = RfD_{Or} \times ABS_{Der}$$  \hspace{1cm} (2)

where $ABS_{Der} = 0.13$ is the absorption dermal factor for NES.

The second prerequisite for risk quantification is the exposure assessment. The aim is to assess the amount of chronic daily intake $CDI_{Or}$ [mg kg$^{-1}$ day$^{-1}$] for random ingestion and random dermal contact with contaminated bottom sediment $CDI_{Der}$ [mg kg$^{-1}$ day$^{-1}$] expressed by equations (3) and (4).

$$CDI_{Or} = c_b \times IR \times CF \times FI \times EF \times ED \times BW^{-1} \times AT^{-1}$$  \hspace{1cm} (3)

$$CDI_{Der} = c_b \times CF \times SA \times AF \times ABS_{Der} \times EF \times ED \times BW^{-1} \times AT^{-1}$$  \hspace{1cm} (4)
where \( c_b \) [mg kg\(^{-1}\)] represents the concentration of contaminant in the sediment acquired by measurement, \( IR \) [mg day\(^{-1}\)] rate of ingested sediment a day, \( CF = 10^6 \) [kg mg\(^{-1}\)] conversion factor for converting mg to kg, \( FI \in (0; 1) \) fraction of ingested soil from the contaminated sediments, \( EF \) [day year\(^{-1}\)] exposure frequency, \( ED \) [year] exposure duration, \( BW \) [kg] average body weight of given group of population, \( AT \) [day] time, during which the concentration of contaminant \( c_b \) in bottom sediment can be considered constant, \( SA \) [cm\(^2\) day\(^{-1}\)] exposed skin area per day, \( AF \) [mg cm\(^{-2}\)] adherent factor depending on the type of sediment and the exposed part of body and finally \( ABS \in (0; 1) \) is dermal absorption factor.

The hazard quotient \( HQ \) served to the characterization of non-carcinogenic risk. The \( HQ \) is expressed by equation (5). When \( HQ < 1 \), the risk is acceptable, when \( HQ \in (1; 4) \), the risk is tolerable and it is necessary to make decision whether to start sanitation, and when \( HQ > 4 \), the risk is unacceptable and it is necessary either to start sanitation works as soon as possible, or to evacuate population.

\[
HQ = \frac{CDI \times RfD^{-1}}{}
\]

The calculated values of \( CDI \) and \( HQ \) for selected exposure scenarios of random ingestion and dermal contact with contaminated soil are presented in Table 2. At the same time there is calculated the value of summary hazard quotient assuming that there is an additive effect of ingestion and dermal intake.

The presented findings have the following uncertainties, which mostly contribute to the overestimate of the assessed risk:

a) The detected concentrations of NES in the sediment include also NES of biogenic origin;

b) The validity of \( RfD \) and exposure scenarios for the calculation of \( CDI \) is assessed as “medium”;

c) The calculations of \( CDI \) in the risk analysis are based on the assumption that NES are fully absorbed in human organism, which is not very realistic in practice;

d) It is assumed that the NES components have additive effect, although they may show synergic as well as antagonic effects;

e) The interaction of NES with other contaminants is not considered.

### Table 2 The values of chronic daily intake and hazard quotients for the selected exposure pathways and scenarios

<table>
<thead>
<tr>
<th>Exposure scenario</th>
<th>Exposure pathway</th>
<th>Sum ( \Sigma HQ = HQ_{Or} + HQ_{Der} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Oral ( CDI_{Or} )</td>
<td>Dermal ( CDI_{Der} )</td>
</tr>
<tr>
<td>Sanitation worker</td>
<td>2.82E-03</td>
<td>9.39E-02</td>
</tr>
<tr>
<td>Adult</td>
<td>3.25E-04</td>
<td>1.09E-02</td>
</tr>
<tr>
<td>Children aged 3 - 6</td>
<td>3.04E-03</td>
<td>1.01E-01</td>
</tr>
</tbody>
</table>

### 4 Conclusion

It is obvious from the assessed values of summary hazard quotient \( \Sigma HQ \) for the assessed exposure scenarios that the public and sanitation workers non-carcinogenic health risks in the surroundings of former chemical factory resulting from the environmental contamination caused by NES are acceptable after the first phase of sanitation. Therefore it would be socially ineffective to continue in sanitation. However, before the final decision is taken it is necessary to assess also genotoxic risks resulting from probable occurrence of PAHs and their oxidation nox in the area.

The non-carcinogenic risks cannot be underestimated and the NES content in the surroundings of the premises should be monitored regularly. Besides that it is necessary to restore all technical measures, which were implemented in the first phase of sanitation with accent on subhorizontal drain and repeatedly remind people living near the premises of using water from private wells only as service water.

### References:


Recent Researches in Environment, Energy Planning and Pollution


