Health Risk Assessment of Zone 7 Contaminated with Benzene in the Environmental Liability Generated by the “March 18th Ex-Refinery” in Mexico City

Evaluación del riesgo a la salud en la zona 7 contaminada con benceno del pasivo ambiental generado por la “Ex-refinería 18 de marzo” en la Ciudad de México

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Abstract

Benzene is a constituent of oil regarded as a potential carcinogen, and therefore a dangerous compound. Its risk increases when spills occur, added to the effect of gravity and high mobility, it’s infiltrated into the ground, reaching the phreatic area until dissolved, contaminating the water. The objective of this research was to evaluate the health risk of environmental liabilities caused by the contamination with benzene in the “Ex-refinery March 18” in Mexico City. For twenty years were carried out remediation work –which started since 2008– and today this space has been converted into a recreational park. This environmental liability is divided into seven zones for purposes of remediation, although in this case only was considered the 7 zone. It also, took into account only the concentration of this hydrocarbon (average, percentil 75 and 95) present in the soil. The results, –from a total of 642 samples from 122 soil profiles–, before the remediation –biospray with vapor extraction–, showed a health risk by depth between 1.2 to 7.2 m, from 1.69E–07 to 1.2 1.25E–05 m to 4.8 m, which coincides with the phreatic level of aquitard, was the place where the highest level of health risk is present. After remediation, the measurements yielded 4.07E–07 to 1.2 m and 3.85E–07 to 4.8 m. These values indicate that the mass of benzene before decontamination exceeded the risk considered acceptable, 1.0E–06 at a depth of 4.8 m; after that, reductions below the acceptable risk were achieved, which shows that the remnant hydrocarbon does not represent a health risk.
Introduction

Oil industrial production has been related to soil contamination, among which we face the problems of decomposition of hazardous materials and wastes, as well as related accidents in handling them. Large volumes of soil and groundwater become contaminated even by releasing small amounts of highly toxic organic compounds, which in many cases exceed the maximum acceptable limits. It is estimated that in Mexico all activities related to the oil industry are the major contributors to the environmental degradation, and basic petrochemicals are the largest contributors to pollution. Contaminated sites are defined as those where there has been deposition, burial or disposal of chemicals or wastes, related to industrial, commercial, agricultural or domestic activities (Salinas, 1997; Quadri y Proven-cio, 1994).

There are two types of contaminated sites:

1) so-called “environmental liabilities”, large sites with pollution problems caused by industrial use of land and improper handling of hazardous wastes, and
2) those sites which were contaminated by environmental emergencies and were brought into view as soon as they occurred (SEMARNAT, 2008).

All accidental leakages where dangerous materials and wastes are involved generate hazardous contaminated sites (soil and water), and are known as environmental emergencies. These accidents always involve some risk to the environment or to the people’s health. According to statistics obtained from the Federal Attorney for Environmental Protection (PROFEPA, 2011), each year in Mexico approximately 550 environmental emergencies related to hazardous materials and wastes are presented.

In 2004, there were identified 297 contaminated sites with hazardous materials or wastes. Among of them, 119 were ranked and prioritized according to the risk level to human health and the environment, 12 more sites were considered rehabilitated or in process of rehabilitation, the rest were not ranked. By April 2008, registered contaminated sites increased approximately by 12%, up to 333 locations, including the “Ex-refinery March 18th”, located in the north of Mexico City (SE- MARNAT, 2008).

The situation gets worse when leakages involve carcinogenic, mutagenic or teratogenic pollutants. One of the most hazardous crude oil compounds known for its carcinogenic toxicity is benzene, which is used as raw material in the production of compounds such as phenol, styrene, and cyclohexane. The USEPA (2007) has reported that benzene is considered a non-chlorinated...
organic compound and is integrated into the group of benzene, toluene, ethylbenzene, xylene (BTEX), components, which are usually found in soil remediation projects (Alves et al., 2010; Testa and Winegardner, 1991).

Benzene can infiltrate the body through the lungs, gastrointestinal tract and skin. When a high level of benzene concentration in the air occurs, in case of inhalation about half of benzene volume passes through the lungs and gets into the bloodstream. When benzene is found in foods or drinks, most part of benzene passes through the gastrointestinal tract and gets into the bloodstream. A small amount of benzene can infiltrate the body through the skin and also get into the bloodstream while skin has a contact with benzene or with the products containing benzene. Once it appears in the bloodstream, benzene travels through the body and can be stored temporarily in the bone marrow and fat tissues. (Toxicological Profile for Benzene, 2007; OSHA, 2003; IRIS, 2006).

Most investigations regarding the effects of long-term exposure of benzene were made on workers in facilities where this material is handled. Brief exposure (5-10 minutes) of a very high level of benzene concentration in the air (μg/m³ 1943000-6388600 [10000-20000 ppm]) may cause death. Lower levels of benzene concentration (μg/m³ 2236000-9583000 [700-3000 ppm]) may cause somnolence, dizziness, tachycardia, headaches, tremors, confusion and unconsciousness. In most cases, people will stop feeling these effects when they are not exposed anymore and when they start to breathe fresh air. The consumption of food or beverages with high level of benzene concentration can cause vomiting, stomach irritation, dizziness, somnolence, convulsions, tachycardia, coma and death. If benzene contacts the eyes it may cause irritation and even damage the cornea (Toxicological Profile for Benzene, 2007; OSHA, 2003; Toxicological Profile for Benzene, 2007; Wilbur, 2005; IRIS, 2006).

The USEPA has accepted the value of 5 ppb as a maximum level of benzene concentration in drinking water. The USEPA also set a goal to have the value of 0 ppb in drinking water and surface water such as rivers and lakes because the dangerous influence of benzene can cause leukemia. The USEPA has estimated the value of 10 ppb of benzene in drinking water or exposed in the air (0.4 ppb) over a lifetime can cause a risk of one additional cases of cancer per 1,000,000 persons (Toxicological Profile for Benzene, 2007; Wilbur, 2005).

The influence of benzene on health was defined by the results of investigations that have been reported (Mandiraciglu et al., 2011; McHale et al., 2011). However, it is very important to research environmental liabilities, which are a major factor in the revitalization of contaminated sites and it becomes even more important if we talk about the contaminated sites which are provided for recreation.

The world’s scientific community has published several studies related to the characterization of soil and groundwater in sites which were contaminated by the oil industry (Schneider et al., 2006). These researches provide an assessment of soil contamination of one refinery in Sao Paulo, Brazil, where the most feasible rehabilitation techniques are also evaluated. In that case, the soil was contaminated mainly by BTEX and affected the employees working in this refinery.

Another study on this subject (Li et al., 2005) presents an assessment of the health risk based in data obtained by mathematical modeling that allows determining contaminant concentrations in groundwater, and was applied in an oil contaminated site located in the West of Canada. Turczynowicz et al. (2001) applied a model of benzene diffusion inside the house basement. The investigation was performed in Australian houses in order to understand the behavior of benzene in confined sites and predict its influence on humans. Kreider et al., (2010) published a research work on a refinery in Illinois, USA, which was operated between 1977 and 2006 and an assessment of health risk to employees who worked at the refinery and were affected by benzene was made there.

Finally, there are a variety of studies of the efficiency of remediation techniques used in hydrocarbon contaminated sites, mainly in sites like refineries and fuel distribution stations (Aivalioti and Gidarakos, 2008, Clay, 2002; Margesin et al., 2003, O’Reilly and Thorsen, 2010). Iturbe et al. (2006) presented an assessment of health risk in an oil facility in Mexico, where TPH (total petroleum hydrocarbons) was the goal of study. Lesser and Saval (2000) investigated the characterization of oil pollution in clay soils in an “X” fuel storage and distribution station in Mexico. Iturbe and collaborators have made studies concerning the characterization of storage and distribution terminals in Puebla, Puebla (Iturbe et al., 1999), Zacatecas, Zacatecas (Iturbe et al., 2003a) and Morelia, Michoacán (Iturbe et al., 2003b). Navarro (2006) investigated the determination of the levels of soil sanitation in environmental liabilities, which show the level of exposure on Mexican individuals in sites contaminated with hazardous wastes.

Therefore, the goal of this study is to evaluate the health risk in zone 7 which is contaminated with benzene in environmental liabilities “Ex-refinery March 18th” in Mexico City, taking into consideration three different concentrations of benzene in the soil particles.
Case study and methodology

The site of this study is a part of the “Ex-Refinery March 18th” and has an area of 77.45 hectares. It is located in the Miguel Hidalgo locality in the northwest of Mexico City. On October 29th, 1930, the Mexican Oil Company El Aguila, SA, was authorized to install and operate the refinery in the Azcapotzalco locality of the Federal District. The Refinery “March 18th” began operations in 1933, which ended on March 18th, 1991 by decree of the Federal Government. For 58 years operations of refining, storage and distribution of oil were conducted, until the closure of refinery in 1991. During this period there were oil leakages that impacted the ground and the water.

The ex-refinery is divided into seven zones for its study. In each zone, the contamination was analyzed and determined, as shown in Figure 1. Zone 7 is the objective of the present study, which was contaminated by benzene due to a series of oil leakages; some of them were recorded during the operation of the refinery. In order to remediate the contaminated soil a combined technique of biospray and vapor extraction was applied during one and a half years. Physical and chemical properties of benzene are shown in Table 1.

The subsoil of the ex-refinery “March 18th” consists of five fine granular layers, disposed in a marginal lacustrine environment. The first layer is filled with materials of different origin and the rest four layers consist of original soil (Diaz, 2006). Although there are slight changes in the vertical and the horizontal directions, the subsoil structure remains essentially unified along the site. Table 2 shows the physical and chemical characteristics of the soil at different depths before remediation.

Figure 2 presents a cross section of the stratigraphy of the environmental liability previously characterized by contracted companies, which obtained an approximation of the soil types that forms the aquitard in order to understand the behavior of contaminants. The stratigraphy shows only the first 10 m of depth, because the maximal sampling depth was 7.2 m, where clay predominates in the subsoil of the ex-refinery. The low values of hydraulic conductivities show the presence of fine material that makes the water flow slow, which has direct influence to the retained contaminant concentrations.

Samples were taken from a maximal depth of 7.2 m, with intervals of 1.2 m. Thus, there are seven sets of concentrations that allow us to define the mass of the contaminant for each depth accordingly. The evaluation of the concentrations at each interval is performed by taking samples from 28 geo-referenced wells for each depth. In total 168 samples. After remediation of the site measurements of concentrations were made in 30 wells having 180 samples in the subsoil profile from 1.2 m to 7.2 m. Benzene quantitative determination was obtained by a column gas chromatography using mass spectrometry as indicated by NOM-138-SEMARNAT-/SS-2003. Reference method was EPA8260B 1996.
The health risk to people who are exposed to environmental contaminants is calculated as the product of the concentration of the chemical compound in the exposure area, the exposure dose and the toxicity of the chemical compound from equation 1:

\[ \text{[Risk]} = \text{[Exposure concentration]} \times \text{[Dose]} \times \text{[Toxicity]} \] (1)

It follows that the safe concentration in the exposure area can be calculated by solving the equation and specifying the acceptable risk. Equation 2:

\[ \text{[Limit of exposure concentration]} = \frac{\text{[Acceptable risk]}}{\text{[Dose]} \times \text{[Toxicity]}} \] (2)

Knowing the estimated concentration, the health risk can be obtained from equation 1. Knowing the acceptable risk – reported by USEPA – we can calculate the specific remediation level (SRL) as shown in equation 3:

\[ \text{[SRL]} = \frac{\text{[Acceptable risk]}}{\text{[Exposure factors]} \times \text{[Toxicity]}} \] (3)

When the exposure site is different to the site where the impact occurs, then these equations must be adjusted taking into account the cumulative effect of various phenomena of partition, dilution and attenuation that lower the compound concentrations during its transportation from the source point to the receptor. This contamination reduction takes place due to so-called natural attenuation factor (NAF), which is defined as the ratio of the concentration in the source to concentration in the point of exposure. Therefore, the health risk or the limit level of concentration in the source can be calculated using the following equation (4):

\[ \text{[Calculated risk]} = \frac{\text{[Concentration in source]} \times \text{[Dose]} \times \text{[Toxicity]}}{\text{[Natural attenuation factor]}} \] (4)

As mentioned above, the Natural Attenuation Factor (NAF) represents the cumulative effect of partition, dilution and attenuation phenomena for each route of exposure which reduce compound concentration during transport from source to recipient. Such NAF components can involve transfer factors through environmental media (soil-to-air volatilization or soil-to-water leaching) as well as lateral transport (air and groundwater dispersion).

In these calculations, the value “dose” includes directly measured ingestion doses as well as estimated inhalation doses of vapors volatilized from the soil.
In all these calculations it is considered that chemical toxicity and dose are very conservative and therefore the SRL acceptable levels are estimated including large safety margins. The following equation (5) can be used to calculate the safe concentration in the environmental area:

\[
\text{Safe concentration in source} = \frac{\text{Acceptable risk} \times \text{Natural attenuation factor}}{\text{Dose} \times \text{Toxicity}}
\]

SEMARNAT’s Guide (2006) defines this safe concentration in the source as specific remediation level (SRL). The above equation presents the basis for the calculation of the SRL, similarly to the method used in SEMARNAT guide where the safe concentration value of each contaminant is based on the acceptable level of risk. Such value is typically 1.0E–06, meaning that the occurrence of one cancer case between one million of possible recipients is tolerable. Under this procedure, estimation of clean levels is simple but with many uncertainties since it does not take into account inherent variability related to different situations nor recipient diversity. It can be argued that there is any ethical justification to the acceptable risk concept, being no risk or zero risk the only one acceptable. In terms of remediation goals it would involve a total eradication of pollution from a site. Nevertheless, restoring its pristine conditions could lead to technical, economical or logistic difficulties, prolonging its sanitation indefinitely (Navarro, 2006; Collasius, 2006). The calculation of the SRL as a function of an acceptable level of risk has the advantage of allowing a direct comparison of site concentrations in order to determine areas that may require remediation according to the use of the area and to delineate the area to be remedied. On the other hand, if this equation is used to estimate the risk, it is necessary to use it for each measured point to delineate the area for remediation.

In order to calculate the health risk, a measured concentration at a specific point is needed; the SRL value estimated as described above (the calculations of risk and SRL are based on the same equation 6) can be used, considering the following proportion:

\[
\frac{\text{Calculated risk}}{\text{Acceptable risk}} = \frac{\text{Concentration in source}}{\text{Safe concentration in source}}
\]

The SRL represents the concentration of a specific compound in an environmental area (for example, soil or groundwater) that protects the receptor’s health for a determined active exposure route in a determined exposure point (EP). Therefore, it is necessary to calculate the SRL for each compound of interest (COI) in each environmental area in order to protect each present receptor (or the more sensitive receptor, if it is known) for each exposure route in the most reasonable exposure points.

The risk, which may be caused by permanent exposure to the contaminants present in a determined concentration in soil in a specific contaminated site, is normally calculated taking into account representative statistics of concentration in the area (for example, the arithmetic mean or the upper limit of the mean confidence). However, there an effort was made to be extremely conservative, when calculating the risk to people’s health which is caused by permanent exposure to the present contaminant concentration in each specific point (extreme case which will not hap-
pen under any condition of land usage). It is important to note that for horizons where concentrations above the SRL were detected at various depths in the same column of soil, the average concentrations were used. Below we present the calculation for benzene concentrations reported in the characterization study of the site, as well as the concentration measured at one point, concentration with percentile 75 and percentile 95.

In order to estimate the health risk represented by the presence of a benzene mass the following equation 7 is applied:

\[
\frac{\text{[Calculated risk]}}{\text{[Acceptable risk]}} = \frac{\text{[Concentration in source]}}{\text{[Calculated SRL]}}
\]

(7)

\[
\text{[Calculated risk]} = \frac{\text{[Concentration in source]}}{\text{[Calculated SRL]}} \times \text{[Acceptable risk]}
\]

Calculated risk:
Concentration in source (mg/kg)
SRLCal. (mg/kg) = calculated specific remediation level
Acceptable risk = 0.000001

The obtained result is a dimensionless number, which indicates the probability that a person will develop cancer or suffer non carcinogenic effects during his lifetime. For carcinogenic compounds, a value of 1.00E-6 has been set as acceptable risk (probability that one person in a million will develop cancer).

**Results**

The distribution of the benzene plume in soil is shown in Figure 3, which takes into account the accumulation of benzene and its horizontally limited mobility due to the stratigraphy of the site, where the clay loam soil and the ground water level of aquitard significantly reduce its vertical mobility. Although benzene has been expanding during several years, its highest concentration is on the depth of 4.8 m, which coincides with the ground water level and is found in a free form.

Considering the worst case of two suggested scenarios, behavior of the health risk was analyzed with concentrations of percentile 95, which shows clearly that the health risk exceeds acceptable limits at depth 4.8 m and 7.2 m. This does not represent a risk to the civil population that may visit the contaminated site, because it is located at a depth in which a person does not have any direct contact with the contaminant. Besides, in the upper layer of soil there is a concrete slab that covers the contaminant and indirectly reduces the health risk. However, zone 7 has been rehabilitated because the characterization studies showed that the concentration of benzene exceeded the acceptable limits, and therefore there a combined method of vapor extraction and biospray was applied in order to remove pollutants which remain in the saturated zone in free form.

The facts described above allowed the remediation works of the site to be successfully achieving efficiencies between 92% and 99%. Remediation methods
used consisted on a combination of biospray and vapor extraction. The first one is an atmospheric air injection below of polluted zones, creating a microbubble screen, which removes both dissolved and adsorbed pollutants in non-saturated zone. This removal follows two ways: physical dragging of nutrient-charged air, and native bacterial stimulation. The second one is the bioventing inverse process, that is to say, the use of vapor extraction wells, so that it is possible to extract volatile and semivolatile fractions from adsorbed and absorbed hydrocarbons in the non-saturated zone; at the same time, atmospheric oxygen infiltration into subsoil is induced by this method, stimulating microbial activity. Figure 4 shows a behavior diagram of health risk of the remained mass of benzene.

Figure 4 shows the behavior of the health risk for benzene after remediation in three possible scenarios: average concentration, concentration with percentile 75 and concentration with percentile 95. In general for all three scenarios the reduction of health risk below the accepted level is clearly seen. Comparing with the worst scenario before rehabilitation as shown in Figure 5, it is seen that the risk is decreasing and reaching the values with low level of risk, which allows to be sure that there is no risk for people who visit the site. Increase of the health risk in the upper layers happens due to the technique used in rehabilitation, when after removing the benzene vapors, they were distributed and grown up, however, they do not exceed the maximal acceptable concentrations and this is clearly represented in the value of the calculated health risk.

The results obtained before the remediation works show the health risk by depth between 1.2 m and 7.2 m, from 1.69E-07 at 1.2 m and 1.25E-05 at 4.8 m, that coincide with the ground water level of aquitard where the highest level of health risk is reached. After the remediation works the obtained results show 4.07E-07 at 1.2 m and 3.85E-07 at 4.8 m. The results clearly show that benzene mass before remediation exceeded the acceptable risk of 1.0E-06 at depth of 4.8 m and after the remediation works the health risk decreased below this value. Although benzene can be dissolved in the saturated zone according to SEMARNAT, there is no indication of concentration data, meaning an insignificant remaining hydrocarbon mass and, hence, no virtual health risk.

Conclusions

The health risk in zone 7 contaminated with benzene in the environmental liability generated by the “Ex–Refinery March 18th” in Mexico City, using a technical guide in order to support the development of studies of environmental risk assessment of contaminated sites. It was found out that the health risk decreased and became lower than levels of acceptable risk after remediation. A benzene mass still remains in the soil, but does not represent any health risk to the people. Consequently, in the present time the zone 7 can be considered as a safe recreational area.

The SEMARNAT Technical Guideline was used to calculate health risk in this research. It was very useful, since it can be implemented in various environmental liabilities real cases to solve.

Combination of techniques –biospraying and vapor extraction–, along with our health risks results, provide considerable support to any initiative on risk minimization in this site.

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Health Risk Assessment of Zone 7 Contaminated with Benzene in the Environmental Liability Generated by the “March 18th Ex-Refinery” in Mexico City

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