Subsoil contaminated by hydrocarbons in an out-of-service oil distribution and storage station in Zacatecas, Mexico

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Abstract   A currently out-of-service oil distribution and storage station (ODSS) operated in Zacatecas, Mexico, from 1966 to 2000. At present, it is subject to a dismantling process. In 2000, a project, focused mainly on the characterization of the soil contamination in the ODSS, was required, and the convenience of carrying out a health risk assessment (HRA) to determine the required cleaning-up-levels was stated. The study concluded that the ODSS soil was contaminated mainly by gasoline and diesel, showing the presence of methyl-tertbutylether (MTBE), benzene, toluene, ethylbenzene, and xylene (BTEX). Nine of the 16 polycyclic aromatic hydrocarbons (PAHs) identified by the US Environmental Protection Agency (EPA) as priority hydrocarbons were found in the ODSS subsoil. Selected metals were also considered in the evaluation. The geo-accumulation indexes proposed by Muller for Fe, Pb, V, and Zn showed values characteristic of no geo-accumulation. The HRA suggested the reduction of three PAHs, [benzo (a) anthracene, benzo (a) pyrene, and benzo (b) fluoranthene], and vanadium.

Keywords BTEX · Health risk assessment · Metals · PAH · TPH · Zacatecas · Mexico

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Introduction

A currently out-of-service oil distribution and storage station (ODSS) operated in Zacatecas, Mexico, from 1966 to 2000. At present, it is subject to a dismantling process. Zacatecas is a Mexican state with important mining activities. In 1990 Zacatecas produced metallic products such as (in tons): Au, 0.58; Ag, 800.228; Cd, 13; Cu, 13,283; Pb, 54,052; Zn, 80,818, as well as non-metallic products, i.e. kaolin, 8,600; talc, 909; and wollastonite, 10,618 (Consejo de recursos minerales. Estado de Zacatecas 1991).

The site is in a zone with a very dry climate, at 2,420 m above sea level, and with no exploitable aquifer. Climate in the zone is semi-dry. The annual average temperature for the period 1965–1995 was 15.3 °C. The city lies over a geohydrological unity constituted mainly of rheolites, calcareous turfs, lutites, sandstone, limestone, schists, and in a lesser proportion by basalts, andesites, and small intrusive bodies. Due to the clayey composition of the rock, it is considered as a low permeability unit, without possibilities for economic water extraction (Secretaria de Programacion y Presupuesto 1979).

The soil at the ODSS was contaminated by gasoline and diesel, therefore, total petroleum hydrocarbons (TPH), BTEX, PAHs, and MTBE were present. Some metals were noted probably as a result of storage and distribution activities.

The Instituto de Ingeniería (UNAM) was required to carry out a project focused mainly on the characterization of the soil contamination and the application of a HRA in the ODSS. This paper establishes the distribution and extent of subsoil contamination (by hydrocarbons and metals), as well as the cleaning-up levels based on a health risk assessment.

Materials and Methods

Description of the site

ODDS soil is a low permeability clay with a bulk density of 1.7 g/cm^3, total porosity of 0.38, organic carbon fraction of 0.0074, hydraulic conductivity of 8.6×10^{-4} cm/s, and pH of 7.8. (Iturbe and others 2000).

Soil sampling procedure

Soil samples were taken at 42 points distributed all over the ODSS area. Samples were taken at 0.9 m below ground level, they were extracted with pneumatic perforation equipment, with a 900 kg_f.m/s motor, variable speed, and 1,379 N/cm^2 working pressure. A helicoidal 0.0762-m tube was employed for drilling. For sampling, a 0.6-m-long and 1.5-m-diameter tube screwed on both sides was used, and it was driven into the soil at the bottom of a borehole by means of a 63.5 hammer having a free ball of 760 mm similar to that used in a standard penetration test (SPT). This tube is divided longitudinally in two pieces. Inside there is an aluminum tube where the sample is accumulated. In that way, there is no contact between the soil and air. Samples were stored at low temperature (4 °C) until they were analyzed. At each sampled point, explosivity was measured by means of a Cosmos XP-311 APHA system. The parameters evaluated in the soil samples were TPH, MTBE, tertamyl methyl ether (TAME), BTEX, and the 16 PAHs considered as priority pollutants by EPA [acenaphtene, phenanthrene, fluoranthene, fluorene, anthracene, indeno (1,2,3-cd) pyrene, acenaphtylene, naphthalene, pyrene, benzo (a) anthracene, benzo (a) pyrene, benzo(a)fluoranthene, benzo (g,h,i) perylene, benzo (k) fluoranthene, chrysene and dibenzo (a,h) anthracene]. Four metals were also measured: Fe, Pb, V, and Zn. To determine the background concentrations, five samples were taken from uncontaminated soil outside the ODSS. In some samples, Cd and Cr were also evaluated.

No water samples were taken because of the lack of an exploitable aquifer in the zone.

PAHs and BTEX content in Mexican liquid fuels

To investigate some PAHs and BTEX concentrations in Mexican fuels, samples of PEMEX Magna gasoline (available since the 1990s), Gasoil (industrial fuel currently out-of-use), and PEMEX Diesel (currently available) were analyzed. Magna and Diesel were purchased in a service station. Gasoil was kindly donated by Instituto Mexicano del Petroleo (IMP) (Mexico).

Analytical methods

Soil samples were evaluated in accordance to EPA analytical techniques: EPA 418.1 for TPH; EPA 6010 for Cd, Cr, Fe, Pb, V, and Zn; EPA 8240 for hydrocarbons (i.e. diesel and gasoline, MTBE and BTEX). PAHs were analyzed using the EPA 8100 method. Fuels were analyzed using the EPA 8260, and 8270 for BTEX, and PAHs, respectively.

Health risk assessment

The HRA was carried out using the Risk Based Corrective Action (RBCA) Tool Kit for Chemical Releases VI.2 software (GSI 1998). Neither TPH nor diesel and gasoline were included in the HRA, since only chemical compounds and no mixtures of them are considered in this method. Even though more contaminants were analyzed in all samples, not all of them were present. For this reason, only PAH, MTBE, benzene, ethylbenzene, toluene, xylene and zinc were considered for the HRA. Lead and iron were not considered for the RBCA model as no reference doses, nor cancer slope factors (CSF) were available. Because of the absence of an aquifer, only soil was considered as contaminated media, and the migration mechanisms involved were volatilization to outdoor air, soil erosion, and subsequent wind transportation. Exposure routes considered were soil ingestion, inhalation of vapors and soil particles, as well as soil dermal contact. Two kinds of receptors were defined: on-site receptors (within the contamination source) and off-site receptors (away from the contamination source). On-site receptors are the ODSS workers, and the off-site receptors are people living in the ODSS surroundings (a perimeter of about 50 m wide). On-site receptors were evaluated as commercial land use, considering also construction workers' activities. The off-site receptors were evaluated as residential land use. In accordance with the American Society of Testing Materials (ASTM) (GSI 1998), the individual risk considered as acceptable for each chemical compound present at the study area was 1×10^{-6} for class A and B carcinogenic compounds [benzene, benzo (a) anthracene, benzo (a) pyrene, benzo (b) fluoranthene, dibenzo (a,h) anthracene and indeno (1,2,3,c-d) pyrene]. The total accumulated risk considered as acceptable was 1×10^{-5} . For non-carcinogenic compounds (all other contaminants) it was considered that the hazard quotient (HQ) and the hazard index (HI) had acceptable values of 1.0. When applying the model, degradation was not considered because off-site receptors are quite close to the contamination source, so it was necessary to make it more restrictive.

Results and discussion

TPH, BTEX, diesel and gasoline concentrations in subsoil

Figure 1 shows the TPH distribution in the ODSS, using the Rockworks 3D program. TPH was considered as an indicator of hot-spot contamination. As noted, there are three main zones where TPH concentrations are high. The first one corresponds to sampling points 1–6. Point 3 has the highest concentration (almost 25 g/kg). This is the area where the mobile-tanks were filled, and frequently leakage draining problems were reported. The second one extends around sampling points 9–15, which correspond to the railway, where also frequently draining problems occurred. Sampling points 17, 18, 19, and 28 confines the third zone. This zone corresponds to the ODSS wastewater treatment plant.

TPH concentrations in the ODSS soil ranged from 88 to 24,970 mg/kg with an arithmetic average of 2,702±5,208 mg/kg. Regarding the diesel fraction, it was present in 18 of the 46 points in a range of 11–688 mg/kg (average: 1,835±178 mg/kg). Gasoline fraction was found in 15 sampled points with an average of 833±1,324 mg/kg (range of 2.5–4,642 mg/kg). Regarding the BTEX compounds, it is relevant that benzene, toluene, ethylbenzene, and xylene were found in a rough proportion of 1:9:4:13. Benzene was found in the range of 0.01–0.77 mg/kg (average
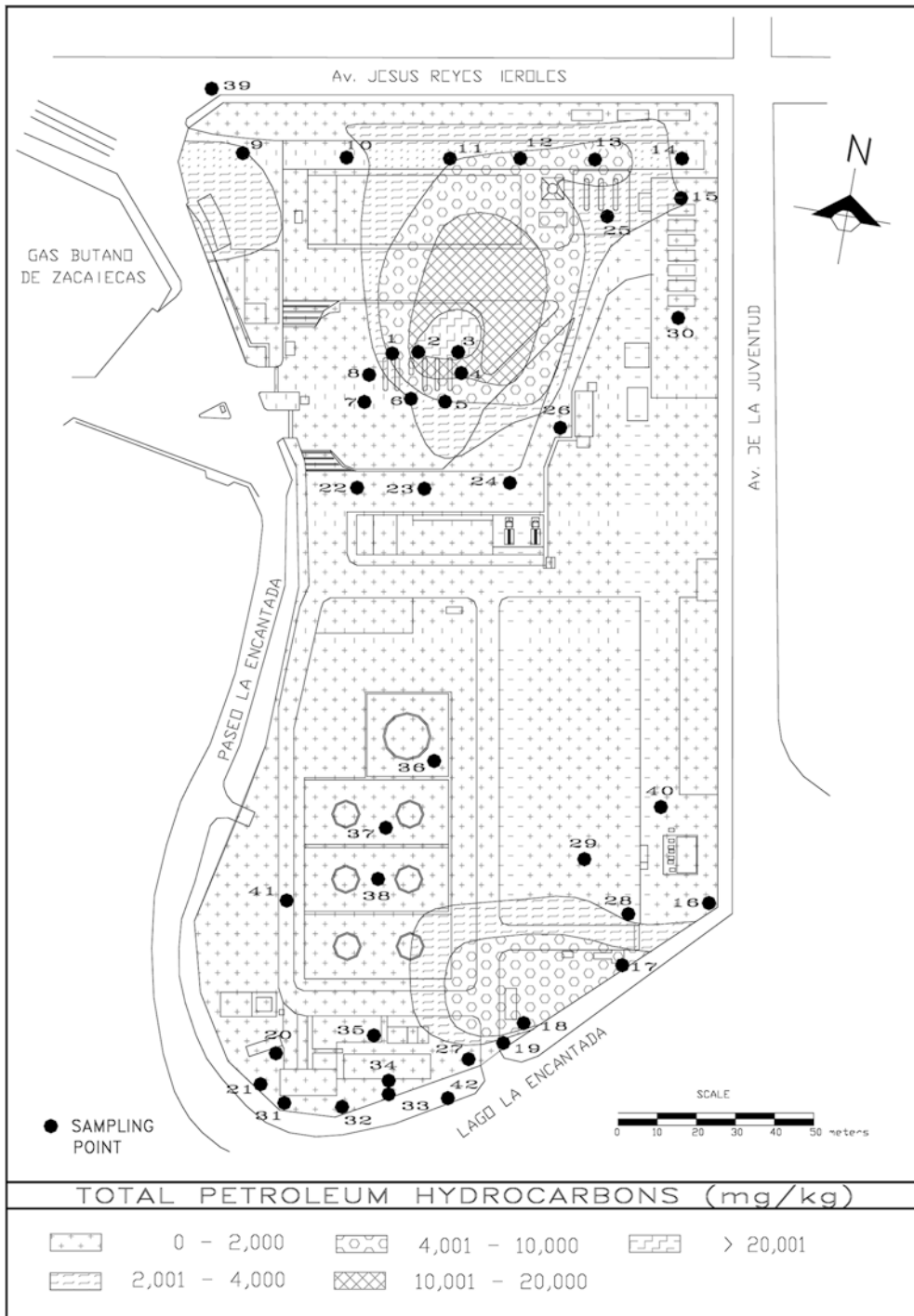
of 0.24±0.2 mg/kg). Toluene was found in the range of 0.08–8.8 mg/kg, with an average of 2.1±3.2 mg/kg. Ethylbenzene was found in the range of 0.01–100 mg/kg, (8±26.8 mg/kg). Finally, xylene (mixture of σ-, m-, and p-xylene) was found in the range of 0.13±229 mg/kg (average of 28±61 mg/kg). MTBE, the most commonly used fuel oxygenating compound was found in only 4 of the 46 sampled points, in a range of 0.04–0.3 mg/kg, (0.17±0.14 mg/kg). TAME was not found in any of the sampled points.

Even though a HRA was carried out to obtain soil clean levels, the Interim Remediation Criteria (IRC) for soils, suggested by Procuraduria Federal de Protección al Ambiente, Mexico (PROFEPA 2000) were also considered for comparative purposes. The IRC are not legislation levels, but only suggestions to work with when remediation of a given soil is on course. In the case of the compounds not considered by the IRC, values suggested by EPA or a specific US State were used (Bournicore 1996). Regarding the TPH average value, it was 1.35 times the goal value suggested by IRC (2,000 mg/kg). The diesel fraction is 0.2 times the goal value (2,000 mg/kg), while gasoline fraction is 1.67-fold the IRC goal value of 500 mg/kg. In the case of MTBE, it was found 0.0017 times the value proposed for the State of Massachusetts,

i.e. 100 mg/kg (Bournicore 1996). BTEX were always found in values under the goal value. Benzene is 0.0048 times the legislated value of 50 mg/kg, toluene is 0.021 the goal value of 100 mg/kg, ethylbenzene is 0.016 times the goal value of 500 mg/kg, while xylene is 0.227 times the proposed value of 100 mg/kg. Benzene, toluene, and xylene goals were suggested by PROFEPA (2000), while the ethylbenzene goal is regulated for the State of Massachusetts (Bournicore 1996).

PAHs distribution

Figure 2 presents a PAHs distribution map, where it is clear that there are three zones where PAHs were encountered. The first corresponds to sampling points 1–8, in the mobile-tanks' zone. The second one corresponds to the railway area (sampling points 10–15). The third one is around sampling point 16, near to the ODSS wastewater treatment plant. As noted, these areas coincide with the TPH contaminated zones.

Of the 16 PAHs listed by EPA, 9 were found in the ODSS soil. The total PAHs concentration was in the range of ND (non-detected) to 27 mg/kg (2.8±2.8 mg/kg). Pyrene was present in 11 of the 46 sampled points in a range of 0.1–9.8 mg/kg, with an average of 3.6±3.2 mg/kg. Anthracene was found in nine of the sampled points, in the range of 0.16–9.32 mg/kg, with an average of 2.6±2.8 mg/kg. Naphthalene was also found in nine of the sampled points in a range of 0.13–6.6 mg/kg. Fluoranthene was present in only four points, in concentrations between 0.25–1.2 mg/kg (0.8±0.3 mg/kg). In lesser amounts, the next PAHs found in three samples was benzo (b) fluoranthene, in an average concentration of 6.4±0.9 mg/kg (in a range of 0.5–2.3 mg/kg). The next PAHs encountered was phenanthrene in a range of 0.9–3.1 mg/kg (1.7±1.3 mg/kg). Benzo (a) anthracene was present in three samples in an average of 2.7±3.4 mg/kg, in the range of 0.76.7 mg/kg. Benzo (a) pyrene was found only in two sampled points, in the range between 0.8–1.4 mg/kg (1.1±0.5 mg/kg). Dibenzo (a,h) anthracene was also present in two points, in the range of 1.4–1.9 mg/kg (1.7±0.3 mg/kg). Finally, indene (1,2,3-cd) pyrene was found in only one sampling point in a concentration of 0.4 mg/kg.

Total PAHs concentration is not considered by IRC (PROFEPA 2000), nor by EPA (Bournicore 1996); regarding specific compounds the situation is as follows: anthracene was found 0.1395 times the proposed value for superfund sites of 1 mg/kg (Bournicore 1996). Naphthalene was found in average 0.0274 times the goal value of the State of Massachusetts (100 mg/kg, Bournicore 1996). Indene (1,2,3-cd) pyrene was found 0.46 times the goal value of 0.9 mg/kg for superfund sites (Bournicore 1996). Fluoranthene was found 0.86 times the goal value of 7.5 mg/kg established by the IRC (PROFEPA 2000). Dibenzo (a,h) anthracene (Bournicore 1996) was 18.8 times the goal value of 0.09 mg/kg established for superfund sites. Pyrene was 0.0016 times the goal value of 2,300 mg/kg also established for superfund sites (Bournicore 1996). Phenanthrene was 0.0007 times the goal value of 2,500 mg/kg. Fluoranthene was 0.0002 times the goal value for the State of Massachusetts (3,100 mg/kg,

Bournicore 1996) and benzo (a) anthracene was 0.366 times the 7.5 mg/kg goal value established by IRC (PROFEPA 2000).

Table 1 shows PAHs found in the ODSS soil, together with a group of physical-chemical properties, legislation values (i.e. EPA limits), and toxicity values; PAHs are presented in ascending order according to the number of rings. The number of points where a specific aromatic compound was encountered is indicated in every case. The most important fact is that pyrene was found in a total amount of almost 40 mg/kg. Naphthalene was found in a total amount of 24.6 mg/kg at nine points (20%). Anthracene was also encountered at nine points, in a total amount of 23.85 mg/kg (19%). The rest of the PAHs appeared in 1–4 sampled points in total amounts between 0.41 and 8.2 mg/kg. Specifically, PAHs with two rings appeared in 1.63% of the total, while the ones with three rings appeared in 4%. On the other hand, PAHs with four rings, the most abundant type, were present in 42.7%, and the five-ring PAH type represents 13.5% of the total PAHs. Finally, the six-ring PAHs were found in 0.33% of the total PAHs. It is observed that more than 50% of the compounds are heavy PAHs (four or more rings).

Guerin (1999) reported the bioremediation of aged tar residues in soil, and he found 15 PAHs with concentrations between 17–422 mg/kg. Specific PAHs and percentages were as follows: naphthalene (1.8%), acenaphtylene (7.5%), acenaphtene (4%), fluorene (6.5%), phenanthrene (17.9%), anthracene (6.5%), fluoranthene (10.9%), pyrene (9.9%), benzo (a) anthracene (4%), chrysene (3.2%), benzo (bkf) fluoranthene (5.3%), benzo (a) pyrene (3.2%), dibenzo (a,h) anthracene (1.0%), indeno (1,2,3-cd) pyrene (0.8%), and benzo (ghi) perylene (1.5%). Regarding the number of aromatic rings, the distribution was as follows: two-ring PAH, 18.8%; three-ring PAH, 41.4%; four-ring PAH, 28%; and five- to six-ring PAHs, 11.8%. As noted, the PAH distribution of these aged tar residues in soil is quite different from the ODSS' PAH distribution.

At this point, it is important to remark that PAHs have different physical-chemical properties, which lead to different toxicological features, and hence to diverse environmental limits established by national and worldwide organizations. In an attempt to elucidate why the specific PAHs mentioned before have the fixed proportions shown in the ODSS soil, a first analysis of those data can be proposed: the PAHs present in the ODSS soil have two to six aromatic rings. The number of aromatic rings in the compounds makes a difference in their characteristics. Lighter PAHs (three or fewer rings) are more volatile, more hydrophilic, and more biodegradable than heavier PAHs. Therefore, light and heavy PAHs have different water solubility degrees, octanol-water partition coefficient (Kow), organic carbon coefficient (Koc), and specific resistance to biodegradation, as shown in Table 1. Other important information shown in the same table are the molecular weights (MW). For this set of PAH, MW ranged from 128–278. Some PAHs have the same MW value, but a quite different spatial distribution. In Table 1, log Kow is the logarithm of the octanol-water partition coefficient for
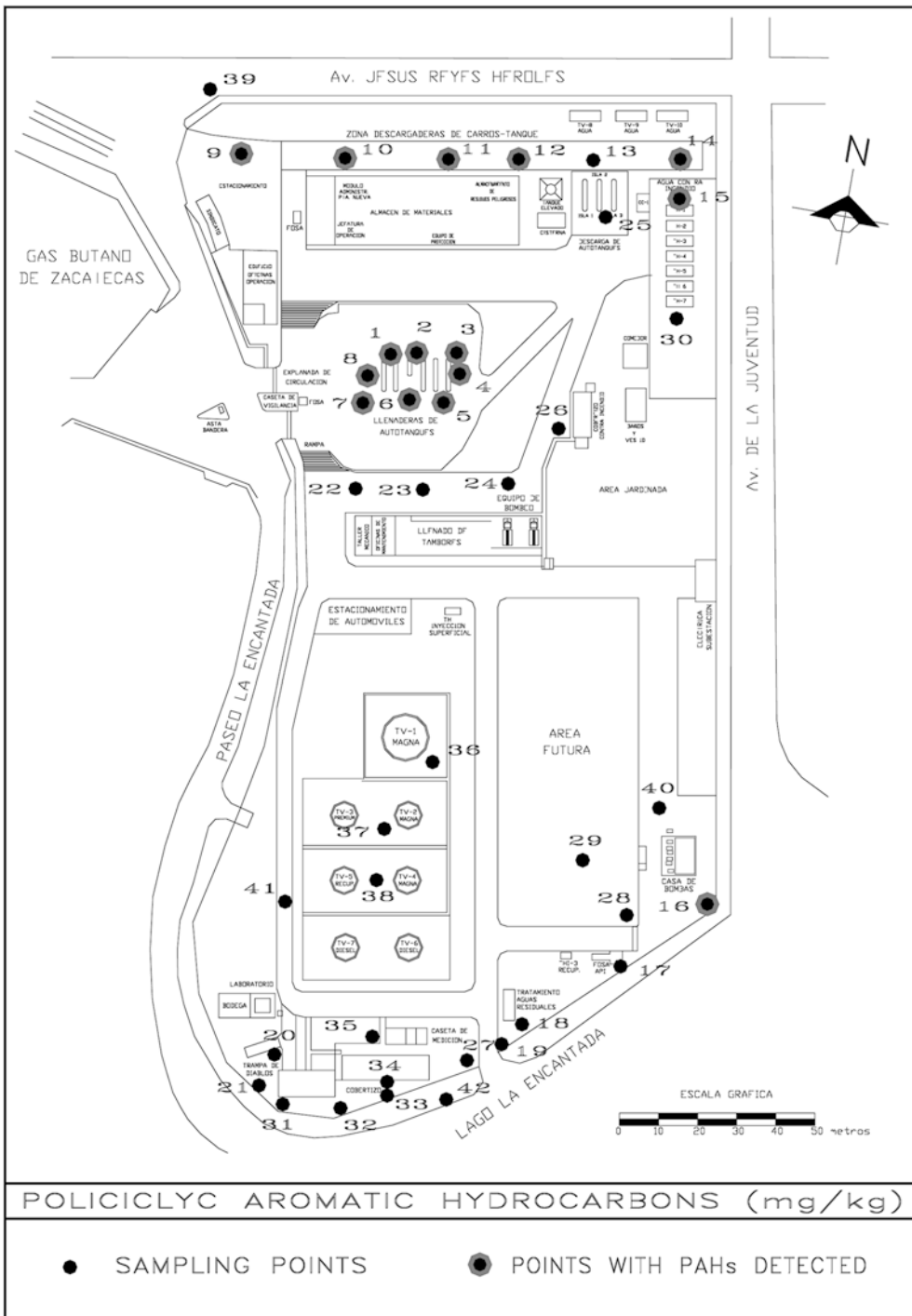
Fig. 2
Polycyclic aromatic hydrocarbon distribution at the ODSS

every PAH. In the case of the nine compounds found on the studied site, the log Kow values ranged between 3.37 (naphthalene) and 6.80 [dibenzo (ah) anthracene]. The organic carbon partition coefficient (Koc) for organic compounds correlates the partition coefficient (soil–water) (Kd) and the organic carbon fraction (foc) in a given soil, as follows (La Grega and others 1994):

$$Kd = Koc \; foc \tag{1}$$

where

Kd   soil–water partition coefficient (ml/g),

foc   organic carbon fraction of the considered soil (mg carbon/mg soil), and

Koc   organic carbon coefficient.

For the PAHs addressed in this study, Koc has values from 1.4×10^4 (anthracene) to 5.5×10^6 (benzo (a) pyrene). The ionization potential (IP) values shown in Table 1 were taken from Marquez-Rocha and others (1997), and the rest were determined from the worldwide web (NIST 2001). The values of IP have been correlated with the capabilities of the PAHs in the formation of deoxyribonucleic acid

Table 1
Some PAHs physical-chemical, legislation and toxicity characteristics

Compound	Molecular weight[a] (g/gmol)	Num of rings[a]	Solubility in water[a] (mg/l at 25 °C)	Log Kow[b]	Koc[b] (ml/g)	IP[c] (eV)	EC$_{50}$[c] (mg/l)	USEPA limits[e] (mg/kg)	Total amount found in ODSS	No. of sampling points in ODSS
Pyrene	202	4	0.1300	4.88	3.8E04	7.72	47.91	2,300	40	10
Naphthalene	128	2	31.0	3.37	Not reported	8.25	0.71	100	25	9
Anthracene	178	3	0.0500	4.45	1.4E04	7.55	7.39	19	24	9
Benzo (a) anthracene	228	4	0.0020	5.60	1.4E06	7.48[g]	0.73[d]	2.60	8	3
Benzo (k) fluoranthene	252	5	0.0008	6.06	5.5E05	–	–	2.6	6	1
Phenanthrene	178	3	1.1000	4.46	14E04	7.95[g]	0.48[d]	2,500	5	3
Benzo (b) fluoranthene	252	5	0.0015	6.06	5.5E05	–	–	–	5	3
Dibenzo (ah) anthracene	278	5	0.0005	6.80	3.3E06	7.59	–	0.09	3.4	2
Fluoranthene	202	4	0.2600	4.90	3.8E04	7.84[g]	0.83[d]	3,100[f]	3	4
Benzo (a) pyrene	252	5	0.0030	6.06	5.5E06	7.12	58.49	0.26[f]	2	2
Chrysene	228	4	0.0020	5.61	2.0E05	8.01	0.92[d]	–	0.85	1
Indene (1,2,3,a,c) Pyrene	276	6	0.0620	6.50	1.6E06	–	–	0.9	0.41	1

[a] From Eriksson and others (2000)
[b] From La Grega and others (1994)
[c] Ionization potential from Marquez-Rocha and others (1997). Microtox EC$_{50}$ from Marquez Rocha and others (1997)
[d] Johnson and Long (1998)
[e] USEPA. Bournicore (1996)
[f] From USEPA IX Region. Bournicore (1996)
[g] From NIST (2001)

(DNA) adducts, i.e., with the genotoxicity. The IP values for the PAHs found in this study are in the range from 7.12 eV (benzo (a) pyrene) to 825 eV (naphthalene). Another interesting parameter shown in Table 1 is toxicity. The median lethal dose (EC$_{50}$), in mg/l, is the concentration of a given compound which causes a 50% diminution in a fixed biological system with respect to a control group. The EC$_{50}$ values can be measured using a broad range of methods, namely the use of fish, algae, microscopic invertebrates, mixed bacterial consortia, specific bacteria, etc. One of the simplest and more common methodology is the Microtox system.

Note that the higher the EC$_{50}$ value for a given compound, the lower its toxicity. Hence, from Table 1, it is concluded that the most toxic PAH compound is phenanthrene (0.48 mg/l), and the least toxic is benzo (a) pyrene (58.5 mg/l). Unfortunately, the EC$_{50}$ values were not available for all the nine PAHs present in the site. The PAH concentration values listed by EPA (in three cases by EPA Region IX) according to Bournicore (1996) are also shown in Table 1. As observed, the levels allowed for PAHs in soils range from a few hundredths of milligrams [0.09 mg/kg for dibenzo (ah) anthracene] to thousandths of milligrams (3,100 mg/kg for fluoranthene). All the available data (i.e., total amount of PAHs found in ODSS, number of point samples, physical-chemical characteristics, norms, toxicity values, etc.) were compared, in order to find significant relationships among the variables. None of the physical-chemical properties, the toxicological or legislation data showed any correlation to the total amount of PAHs found in the ODSS soil.

Explosivity measurements

Soil samples for explosivity measurements were taken at different depths, always in the range of 0.45–1.2 m. The 38 points were distributed as follows: points 23 and 28 at 0.45 m depth; points 8, 9, 12–15 and 27 at 0.75 m depth; point 10 at 0.8 m depth; points 11, 25, and 26 at 0.85 m depth; points 35 and 36 at 0.90 m depth; points 1, 16–18 and 34 at 1.0 m depth; points 5–7, 20, 32, 37, and 38 at 1.1 m depth; points 3, 4, 19, 21, 22 and 30 at 1.20 m depth; point 31 at 1.30 m depth, and points 2, and 3 at 1.50 m depth.

From these 38 points, 20 (55.5%) did not show explosive characteristics. Eight points (22.2%) showed low to average explosivities (between 5 and 50%). Finally, the remaining ten points (27.7%) showed a 100% explosivity index. These points were 5, 10, 11, 13, 15, 17, 18, 20, 31, and 36. Note that these points correspond to the highest values for TPH, BTEX and metals, and are placed again in the three main polluted ODSS zones. Explosivity indexes can be used as an easy, cheap and quick method for determining the contamination profiles at a polluted site. Of course, these data must be confirmed through the direct analysis of soils for the quantification of the desired parameters (i.e., TPH).

Metals and geo-accumulation index

Figures 3 and 4 show the Fe and V distribution maps, respectively, drawn with the Rockwroks 3D software. As observed, Fe and V distribution profiles show concentrations ranging from 5,000 to almost 50,000 mg/kg for Fe and 20 to more than 200 mg/kg for V. Note that these
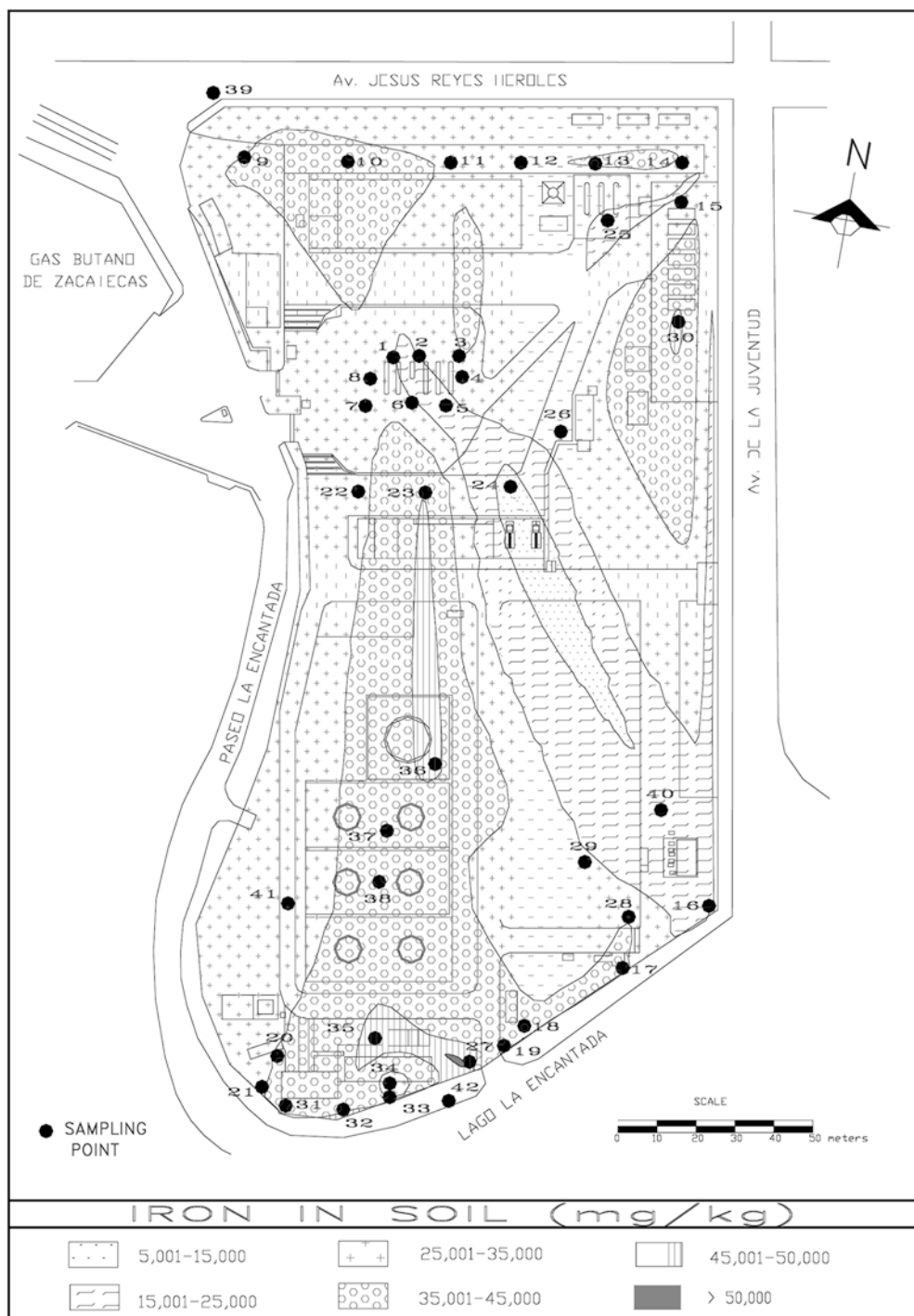
distributions (1) do not correlate with TPH or PAH distributions, and (2) they seem to be geologically determined. It is important to note that for a relatively small area (around 750×150 m) there is a high spatial variation on metal concentration. Fe and V distribution maps seem to be correlated.

Of the four metals evaluated in the ODSS soil samples, Fe was found in the highest concentrations. This element was present in the sampled points in concentrations between 8,396 and 51,536 mg/kg, with an average concentration of 32,040±10,436 mg/kg. Zn was the second element in

abundance, quite far from iron. Zinc was found in a range of 24.5–321.6 mg/kg (93±57 mg/kg). V was present in a range of 20.4–212.4 mg/kg (92±45 mg/kg). Finally, Pb was in the range 10.7–423.2 mg/kg (58.5±71 mg/kg on average).

Although these four metal concentrations have not been specifically reported for pristine soils in Mexico, there is a report of USA agricultural soil with Pb, Zn, Cd and Ni concentrations of 12.3, 56.5, 0.265 and 23.9 mg/kg, respectively (Holmgren and others 1993). On the other hand, another work makes reference to the characteriza-
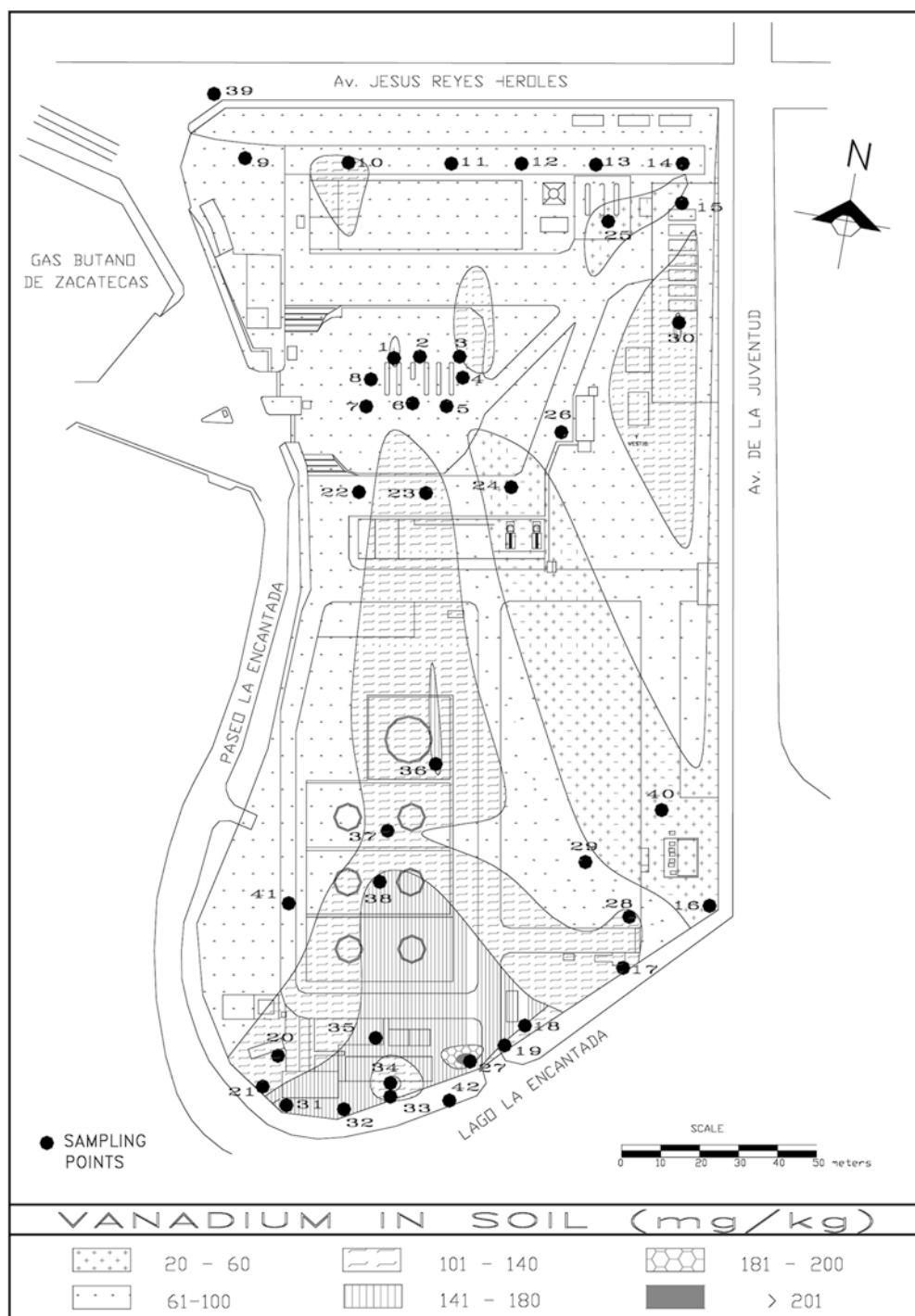
Fig. 4
Vanadium distribution at the ODSS

tion of a European soil. The values for these same metals were 50, 100, 1.5 and 50 mg/kg, respectively (Lorenz and others 1997). Finally, Murray and others (2000) found values of 5.43, 75.3, 497 and 489 mg/kg, for Cd, Ni, Pb, and Zn, respectively, in a railway yard in Montreal, Quebec. Thus, the metal concentration measured in the ODSS area are, in general, considerably higher than the mentioned metal concentrations, especially for iron.

In another study, Quiroz and Ilangovan (1999) reported the Pb, Zn, Cu, and Mn concentrations present in mineral soils along an Oak Forest vegetation gradient in Mexico City. They reported the metal concentrations at three different depths (0–0.20, 0.20–0.90, and >0.90 m). For the deeper samples (>0.9 m) the Pb, Zn, Cu, and Mn concentrations were in the ranges of 6.7–10.9, 35.1–18.7, and 233–422 mg/kg, respectively. As noted, the values for the ODSS uncontaminated soil show higher Pb concentrations, and lower Zn concentrations.

In fact, the metal concentrations measured are not alarming from the point of view of the environmental risk. It should be noted that metals can inhibit the biodegradation of organic compounds in a subsequent biological

process such as composting, bioventing, natural attenuation, or biostimulation. Amor and others (2001) reported that the biodegradation of monoaromatic hydrocarbons by *Bacillus* and *Pseudomonas* sp. was inhibited by Cd, Zn, and Ni. More specifically, *Bacillus* sp. k_i inhibition constant values (in mM) for toluene, ethylbenzene, and σ-xylene were in the range of 0.416–0.757, 0.403–0.431, and 0.606–0.690 in the presence of Cd, Zn, and Ni, respectively.

The metal concentrations found in the ODSS soil were compared to IRC (Pb and Zn) and EPA levels (Fe and V). Fe was found 1.28 times the goal value of 25,000 mg/kg for the superfund site (Bournicore 1996), while Pb was present 0.030 times the goal value of 1,500 mg/kg. Vanadium was 0.9254 times the proposed goal of 100 mg/kg for the State of Georgia (Bournicore 1996), and Zn was 0.0621 times the goal value of 1,500 mg/kg.

At this point, it is not clear if such high metal concentrations are geologically determined or were introduced to the environment by human activities. With the purpose of giving clues for that discussion, a comparison between the non-contaminated and the contaminated soil would be useful.

Table 2 shows the metal basal concentrations, calculated from two points where no hydrocarbon contamination was observed (points 39 and 42, denoted as A and B in Table 2), as well as from five points sampled outside the ODSS (points C to G in Table 2). The detection limits for every metal are included with comparison purposes.

Table 3 shows metal concentrations for earth crust, and igneous and sedimentary rocks obtained from Gülec and others (2001), and Taylor and McClennan (1985). These concentrations are compared with the basal concentrations found on ODSS soil.

In Table 2 it is observed that Cd, Cr, Fe, Pb, V, and Zn had values of 2±0.2, 91±15, 38,092±8,539, 62±38, 109±40, 165±110 mg/kg. Note the high standard deviation values, especially for Fe, Pb, V, and Zn.

The geo-accumulation indexes (I-geo) proposed by Müller (1969) are defined as

$$I - geo = \log_2(Cn/1.5\ Bn) \qquad (2)$$

where

Cn   is the analyzed metal concentration, and
Bn   is the background content for that metal.

The I-geo indexes were calculated for the ODSS soil metal obtaining the following values: Fe: −0.8346, Pb: −1.4821, V: −0.8210, Zn: −1.4071, which are indicative of no geo-accumulation, which means that metal concentrations found at the ODSS are due to natural causes; this result is consistent with the ODSS being located in a mining zone. Zhang and others(1999) reported values for the accumulation of different heavy metals in Nanjing, China, due to the existence of a highway, and a metal refinery. In particular, they found Pb I-geo of 0.12 due to the highway, Cr I-geo of 0.59, and 0.98, due to the highway and the metal refinery, respectively, and Pb I-geo of 0.13, due to the metal refinery. As noted, the Pb I-geo values are highest for this study. It is important to note that the contamination pathway in the work of Zhang and others (1999) is air, and not contaminated material deposition as in the present case.

Thuy and others (2000) investigated the distribution of heavy metals in urban, rural, agricultural, and industrial soils in Vietnam. They supposed the metal contents of rural soils to be the background level, and calculated the enrichment factor for the urban, agricultural, and industrial soils. From their data the I-geo indexes were calculated. For industrial soils I-geo values of 6.8439, −0.2692, and 1.488 for Pb, Cr, and Zn were determined, respectively. On the other hand, for urban soils, I-geo values of 0.3370, −0.6803, and 0.5293, for Pb, Cr, and Zn, were obtained. Finally for agricultural soils, I-geo values of −0.1890, −1.0716 and 0.4051, for Pb, Cr, and Zn, were calculated.

Considering the metal concentrations present on natural parental rocks and the ones found on ODSS as shown in Table 3, it is likely that the metal basal levels could correspond to shale as parent rocks. The metal ranges for Fe, Cr, Zn, Pb, Cd, and V support this affirmation. In some way, these facts could support the idea that V is not a soil contaminant, but part of a geological conformation, where high levels of V, Fe, Zn, and Pb are present.

Relationships between compounds and fractions

With the purpose of finding new elements for discussion, the values of most of the contaminant compounds and fractions in the ODSS soil were fitted in order to determine

Table 2
Uncontaminated soil metal concentrations (basal level) and geo-accumulation indexes

	Cd (mg/kg)	Cr (mg/kg)	Fe (mg/kg)	Pb (mg/kg)	V (mg/kg)	Zn (mg/kg)
A	NA	NA	25,194	27	62	65
B	NA	NA	48,851	35	164	74
C	1.89	101.79	31,328	105	79	262
D	2.23	79.84	35,298	84	130	257
E	NA	NA	37,640	NA	82.25	NA
F	NA	NA	47,819	NA	136.83	NA
G	NA	NA	40,698	NA	NA	NA
Average	2	91	38,092	62	109	165
SD	0.2	15	8,539	38	40	110
I-geo	NC	NC	−0.8346	−1.4821	−0.8210	−1.4071
Detection limit	4.00	6.00	4.00	6.37	5.31	3.72

NA, not analyzed; NC, not calculated

Table 3

Upper crust, parent rocks, and ODSS subsoil basal metal concentrations. (Adapted from Gülec and others 2001)

Elements (mg/kg)	Upper crust (average) (mg/kg)	Igneous rocks (average) (mg/kg)				Sedimentary rocks (average) (mg/kg)			ODSS subsoil basal level
		Ultramafic rocks	Mafic rocks	Intermediate rocks	Felsic rocks	Shale	Sandstone	Carbonates	
Al	80,400	5,000	88,000	89,000	77,000	80,000	25,000	4,200	NA
Fe	35,000	99,000	86,000	59,000	27,000	47,200	9,800	3,800	25,194–48,851
Cr	35	2,000	200	50	25	90	35	11	80–102
Cu	25	20	100	35	20	45	–	4	NA
Zn	71	–	–	–	–	95	16	20	65–262
Pb	20	<1	8	15	20	20	7	9	27–105
Cd	0.098	–	–	–	–	0.3	–	0.09	1.9–2.2
Co	10	200	45	10	5	19	0.3	0.1	NA
V	56[a]	NR	NR	NR	NR	55–190[a]	NR	NR	62–164

[a]From Taylor and McCLennan (1985)
NR, not reported; NA, not analyzed

Table 4

Correlation among compounds and fractions in ODSS subsoil (r^2 values)

	TPH	Diesel	Gasoline	MTBE	Benzene	Ethyl-benzene	Toluene	Xylene	Fe	Pb	V	Zn	Tot PAH
TPH	–	0.6793	0.9497	0.6141	0.9439	−0.0993	0.7940	0.8489	−0.1539	0.7009	−0.1628	0.2469	0.5628
Diesel	–	–	0.6599	1	0.9689	−0.2935	−0.2580	0.5343	−0.1659	0.1889	−0.0492	0.1642	0.7955
Gasoline	–	–	–	0.8160	0.9286	NR	0.9287	0.9510	0.0852	0.4602	0.2015	−0.0394	0.2850
E	–	–	–	–	0.8419	–	0.9934	−0.6405	NR	NR	NR	NR	NR
Fe	–	–	–	–	–	–	–	–	–	0.0413	0.8037	0.1975	NR

NR, not reported

the correlation factor r^2, as a measure of the interrelation among parameters. Table 4 shows the correlation factor found for every comparison. Total TPH concentrations are related to gasoline, benzene, toluene, and xylene (r^2=0.9479, 0.9439, 0.7940 and 0.8489, respectively). Diesel fraction correlated well with benzene (r^2=0.9689), total PAHs (r^2=0.7955), and oddly, with MTBE (r^2=1). This could be related to the fact that gasoline (in 15 sampling points) and diesel (in 18 sampling points) are the main oil fractions present at the ODSS as contaminants. Metals did not correlate with diesel fraction. On the other hand, gasoline seems to be related to MTBE, benzene, toluene, and xylene (r^2=0.8160, 0.9286, 0.9287 and 0.9510, respectively). This sounds logical as MTBE and BTEX are gasoline components. Metals did not correlate with gasoline either.

Benzene and toluene are closely correlated with ethylbenzene (r^2=0.84 and 0.99, respectively), which would mean that they come from the same source (gasoline). Finally, Fe is closely correlated to V (r^2=0.8037), but not to Pb or Zn (r^2=0.0413 and 0.1975, respectively).

Regarding gasoil, diesel, and gasoline characterization, the following was found. No BTEX or PAHs were found above the detection limit of 0.01% vol for gasoil, and diesel. This fact shows the excellent quality of the Mexican commercial fuels. Only in the case of gasoline, were benzene, toluene, ethylbenzene, and xylene found in concentrations of 2.2, 3.09, 1.07 and 1.96% vol, respectively. This means a BTEX ratio of 2:3:1:2. Besides, naphthalene was found in a concentration of 0.03% vol. The rest of the PAHs were below 0.01% vol. As pointed out before, BTEX were found in the ODSS soil, in average concentrations of 0.24, 2.12, 8.05 and 27.72 mg/kg. The BTEX ratio was about 1:9:4:13. Differences between BTEX ratios in the Mexican gasoline and in the soil samples are due to different factors, among them: (1) BTEX physicochemical characteristics which allows different results in different soil profiles, (2) BTEX toxicological characteristics, which allow different biodegradation rates for every single compound, and (3) the gasoline analyzed for this study's purposes is the product currently commercialized, but the ODSS soil has been contaminated for decades with a series of gasoline products with different manufacturing procedures.

Regarding PAHs in gasoline, only naphthalene was found in the Mexican gasoline at a concentration of 0.03% vol. In the soil samples, naphthalene was at a concentration of 2.74 mg/kg. Pyrene, anthracene, benzo (a) anthracene, phenanthrene, benzo (b) fluoranthene, dibenzo (a,h) anthracene, fluoranthene, benzo (a) pyrene and indene were below the detection limit of 0.01% vol. Again, differences between gasoline and soil sample contents might be due to the three factors mentioned above.

Health risk assessment and cleaning levels

In Table 5, the risk values and the risk-based cleaning-up levels are summarized. Note that in accordance with the goal established in the material and methods section, benzo (a) anthracene, benzo (a) pyrene, benzo (b) fluoranthene, and dibenzo (a,h) anthracene exceeded the acceptable individual risk for the on-site receptors with residential land use. For the off-site receptors involved in temporary excavation activities, none of the chemical compounds exceeded the acceptable individual risk. The accumulated risk established previously as acceptable was exceeded only for on-site receptors with residential land use.

For vanadium, soil concentrations exceeded the risk-based cleaning level of 142 mg/kg, shown in Table 5. Regarding the outdoor exposure pathway, the ODSS did not exceed the individual risk or accumulated risk for carcinogenic compounds, and neither the HQ values nor HI on both the on-site and off-site receptors.

Based on the results obtained, the proposed cleaning-up levels are (Table 5):

1. To reduce the benzo (a) anthracene levels from 6.7 to 0.55 mg/kg.
2. To reduce the benzo (a) pyrene concentration of 1.43 to 0.054 mg/kg.
3. Benzo (b) fluoranthene levels must be reduced from 1.4 to 0.0324 mg/kg.
4. Finally, due to the uncertainties about the nature of vanadium concentrations on the ODSS soil, it was decided to reduce V from 212 to 142 mg/kg.

Table 5
Risk and cleaning-up levels to reach at ODSS

Compound	Class	HQ Risk	Subsoil On-site (0 m) Residential	Construction workers	Outside air On-site (0 m) Residential	Construction workers	Off-site (120 m) Residential	Based-in-risk cleaning levels (mg/kg)
Anthracene	D	HQ Risk	1.9E -04	5.8E-05	–	–	–	3.0E+04
Benzene	A	HQ	1.0E-02	5.4E-03	2.6E-03	7.3E-03	2.6E-03	1.7E+00
		Risk	4.0E-07	6.9E-09	5.5E-08	5.2E-09	5.5E-08	
Benzo (a) anthracene	B2	HQ	–	–	1.0E-06	2.9E-06	1.0E-06	5.5E-01
		Risk	1.2E-05	2.1E-07	3.9E-08	3.7E-09	3.9E-08	
Benzo (a) pyrene	B2	HQ	–	–	2.3E-08	6.5E-08	2.3E-08	5.4E-02
		Risk	2.6E-05	4.5E-07	2.3E-07	2.1E-08	2.3E-07	
Benzo (b) Fluoranthene	B2	HQ	–	–	4.5E-07	1.3E-06	4.5E-07	5.5E-01
		Risk	4.3E-06	7.4E-08	1.7E-08	1.6E-09	1.7E-08	
Dibenzo (ah) anthracene	B2	HQ	–	–	7.8E-07	2.2E-06	7.8E-07	3.2E-02
		Risk	3.5E-05	6.1E-07	–	–	–	–
Ethylbenzene	D	HQ	4.3E-02	2.2E-02	8.7E-04	2.4E-03	8.7E-04	2.3E+03
		Risk	–	–	–	–	–	–
Fluoranthene	D	HQ	2.9E-04	8.8E-05	–	–	–	4.1E+03
		Risk						
Indene (1,2,3,c,d)	B2	HQ			8.2E-09	2.3E-08	8.2E-09	5.5E-01
Pyrene	–	Risk	7.6E-07	1.3E-08	3.4E-10	3.2E-11	3.4E-10	–
Methyl t-butyl	–	HQ	1.5E-03	7.8E-04	9.0E-06	2.5E-05	9.0E-06	1.9E+02
Ether	–	Risk	–	–	–	–	–	–
Naphthalene	D	HQ	9.8E-05	5.0E-05	1.8E-05	5.0E-05	1.8E-05	5.8E+04
		Risk	–	–	–	–	–	–
Phenathrene	D	HQ	1.0E-03	301E-04	–	–	–	3.0E+03
		Risk	–	–	–	–	–	–
Pyrene	D	HQ	303E-03	9.9E-04	–	–	–	3.0E+03
		Risk	–	–	–	–	–	–
Toluene	D	HQ	2.3E-03	1.2E-03	3.2E-04	9.1E-04	3.2E-04	3.4E+03
		Risk	–	–	–	–	–	–
Vanadium	–	HQ	1.5	2.1E-02	–	–	–	1.4E+02
		Risk	–	–	–	–	–	–
Xylenes (mixture of isomers)	D	HQ	5.1E-03	2.6E-03	3.5E-04	1.0E-03	3.5E-04	4.2E+04
		Risk	–	–	–	–	–	–
Zinc	D	HQ	3.2E-02	7.6E-04	–	–	–	9.9E+03
		Risk	–	–	–	–	–	–
HI	–	–	1.1E-01	5.6E-02	4.2E-03	1.2E-02	4.2E-03	–
Accumulated risk	–	–	7.9E-05	1.4E-06	3.4E-07	3.2E-08	3.4E-07	–

Areas and volumes to be treated

Based on the iso-concentrations obtained with the Rockworks 3D software, volumes to be treated were calculated (TPH concentrations over 2,000 mg/kg). For the area under the railway, a volume of 660 m^3, the area under the mobile-tanks, a volume of 702 m^3, for the A and B areas, a volume of 280 m^3 were proposed. These figures total 1,642 m^3 of soil to be treated. Soil washing and biopiles could be suitable technologies for cleaning the soil.

Conclusions

1. The ODSS soil is contaminated mainly by TPH, gasoline, diesel, MTBE, BTEX, and PAH.
2. TPH, PAH, and gasoline fractions are quite localized in three main zones. The first zone is where mobile-tanks were filled and frequent leaking problems were reported. The second zone corresponds to the railway, where frequent leaking problems occurred. The third zone is the ODSS wastewater treatment plant.
3. Nine of the 16 PAHs listed as priority contaminants by EPA were found in the ODSS soil. Neither the physical-chemical properties, nor the toxicology and legislation values available correlated with the total amount of PAHs found in the ODSS soil. Only the molecular weight, the number of aromatic rings and the EC$_{50}$ value correlated with the number of sampling points where PAHs were found in the ODSS.
4. The metal-based concentrations were calculated from two points inside the ODSS where no hydrocarbon contamination was observed as well as from five points sampled outside the ODSS. Cd, Cr, Fe, Pb, V, and Z showed values of 2.06, 90.82, 38,092, 62.46, 109, and 164,57 mg/kg, respectively, with high standard deviation values. According to a metal characterization for igneous and sedimentary rocks, the parent rock for this soil could be shale rocks. The geo-accumulation indexes proposed by Müller (1969) were calculated for the ODSS soil metal. The values of the I-geo for Fe, Pb, V, and Zn are −0.8346, −1.4821, −0.8210, and −1.4071, which are indicative of no geo-accumulation, which could mean that the metal concentrations found in ODSS soil are due to natural sources.
5. It is likely that total TPH concentrations are related to gasoline and BTEX. The diesel fraction correlated well with benzene, total PAH, and with MTBE. This correlation (benzene and MTBE vs. the diesel fraction) could be due to the fact that subsoil is contaminated with an old mixture of diesel and gasolines, and does not imply that diesel contained MTBE or benzene. Metals did not correlate with diesel fractions. On the other hand, gasoline seems to be related to MTBE, benzene, toluene, and xylene. This appears logical as MTBE and BTEX are gasoline components. Metals did not correlate with gasoline either. It seems that benzene and toluene are closely correlated with ethylbenzene, which would mean that these three compounds come from the same source (gasoline). Finally, Fe is closely correlated to V, but not to Pb or Zn.
6. Based on the HRA and the clean up levels determined, it is necessary to reduce the benzo (a) anthracene levels from 6.7 to 0.55 mg/kg, to reduce the benzo (a) pyrene concentration from 1.43 to 0.054 mg/kg, and benzo(b) fluoranthene from 1.4 to 0.0324 mg/kg. Finally, even though it is not likely that vanadium comes from contamination activities, the actual V level of 212 mg/kg should be reduced to 142 mg/kg.
7. The reduction of the three PAHs and V down to values suggested by the HRA, and the reduction of the TPH level under the IRC suggested level of 2,000 mg/kg, will allow the use of the old ODSS for other industrial uses in the short term.

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