HUMAN HEALTH RISK ASSESSMENT OF EXPOSURE TO ENVIRONMENTAL POLLUTANTS IN THE CHEMICAL / PETROCHEMICAL INDUSTRIAL AREA OF TARRAGONA (CATALONIA, SPAIN)

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SUMMARY

Summary

Since more than 30 years ago, one of the most important chemical/petrochemical complexes in Southern Europe is located in Tarragona (Catalonia, Spain). A big oil refinery (Repsol/YPF) is placed in the zone, together with a number of chemical and petrochemical industries. Among them, a PVC production facility, a chlor-alkali plant, a municipal solid waste incinerator (MSWI), and the only hazardous waste incinerator (HWI) of Spain are located in the area. Moreover, the local environment is also influenced by the presence of a highway and several roads with an important traffic density. In recent years, public concern over possible adverse health effects for the population living near the industrial complex has increased. In response to this concern, in 2002 we initiated a wide survey to determine the current levels of various inorganic and organic pollutants in the area. The health risks derived from the exposure to those contaminants by the local population were also assessed.

In the winter of 2002, samples of soils and vegetation (chards) were collected in several locations of the chemical and petrochemical industrial complex of Tarragona. Additional samples were obtained in Tarragona downtown as well as in some residential suburbs. Finally, a few samples were collected in presumably unpolluted zones outside the direct influence of the chemical industries. Concentrations of arsenic (As), cadmium (Cd), chromium (Cr), mercury (Hg), manganese (Mn), lead (Pb), and vanadium (V) were determined in those samples. In turn, the levels of polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs), polychlorinated biphenyls (PCBs), polychlorinated naphthalenes (PCNs), as well as polycyclic aromatic hydrocarbons (PAHs) were also determined in the same samples.

Soils collected near the chemical complex and in urban/residential areas showed the highest concentrations for all the chemicals analyzed. In turn, the levels in soil samples obtained in the petrochemical and unpolluted areas were notably lower. With respect to heavy metals, this difference was statistically significant only for Cr and V. High levels of Pb were found in urban soils, which was probably due to the fact that leaded gasoline was largely used in the past. In relation to organic compounds, the difference of concentration between the first group of samples (chemical and residential) and the second one

(petrochemical and unpolluted) was significant for PCDD/Fs and PCBs, while for PCNs and PAHs they did not reach the level of statistical significance. However, the levels of all pollutants in soil were clearly lower than the maximum allowed concentrations established by the Catalan and Spanish governments.

With regard to chard samples, no significant differences were observed for any of the pollutants, excepting V. In fact, V was the only chemical where significant differences were registered in both environmental monitors, soils and chards. Consequently, it can be considered that Tarragona is impacted by some degree of pollution by this metal. Relatively high levels of PAHs were found in vegetation samples collected in residential areas, remarking traffic as an important PAH emission source. Although the difference was not statistically significant, PCDD/F concentrations in chards were higher in unpolluted zones than in industrial and residential areas. Therefore, it can be thought that long-range transport and/or uncontrolled emission sources play an important role in the environmental levels of these pollutants.

Surprisingly, low levels of PAHs were found in spite of the presence of an important oil refinery. Therefore, an experiment was carried out in order to study the influence of the local environmental conditions on the degradation of these pollutants. Specifically, PAH photodegradation was studied simulating Atlantic (low temperature and solar radiation) and Mediterranean (high temperature and UV radiation) environments. It was found that both variables, temperature and UV-B dose, might have a synergistic effect over PAH degradation.

To characterize the degree of pollution in Tarragona and to determine possible “hot spots”, two kinds of classificatory tools were used. Kohonen’s Self-Organizing Map (SOM) and Principal Component Analysis (PCA) were applied for heavy metals and organic pollutants, respectively. Some sampling locations in the south-western corner of the chemical area, and in Tarragona downtown, were identified due to relatively high levels of pollution. In fact, the presence of a chlor-alkali plant in the chemical area as an important emission source, particularly of Hg and chlorinated compounds, would be a reasonable explanation why higher concentrations were found in the chemical area respect to the petrochemical zone. Moreover, the predominant wind regime (from North) and the height of stacks and torches of the oil refinery would make easy the dispersion of pollutants potentially emitted by this source and the deposition far away.

Health risks due to the exposure to heavy metals and PCDD/Fs by the local population were also assessed. With respect to metals, since levels were clearly lower than US EPA Preliminary Remediation Goals (PRG) and the Hazard Quotients (HQ) were under 1, current concentrations do not pose relevant non-carcinogenic risks. However, a certain number of cancer cases could derive from As ingestion (due to the low As levels established by US EPA) and Cr inhalation (according to the assumption that Cr^{+6} is 1/6 of the total chromium).

Human health risk assessment of PCDD/F exposure was carried out according to the socioeconomic status of the population. Subjects living near the industrial area may be more environmentally exposed to PCDD/Fs because of the comparatively higher levels in air and soil. In turn, because of the dietary PCDD/F ingestion, indirect exposure may be more important for high socioeconomic individuals living in Tarragona downtown. In fact, environmental exposure would only mean less than 2% of the total exposure. Overall, people of residential areas result more exposed to PCDD/Fs. However, non-carcinogenic and carcinogenic risks associated to that exposure would be assumable.

To study the global state of pollution in the area of Tarragona, a SOM-based Integral Risk Index was developed. Inorganic and organic pollutants were ranked according to different properties of persistence, bioaccumulation, and toxicity. Subsequently, a risk map of the zone was designed as the spatial representation of this Index with a Geographic Information System (GIS).

Although the risk by heavy metals and organic pollutants is not notable, continuous measurements of these and other pollutants in the industrial and urban Tarragona are remarkably advisable. Likewise, some efforts should be done to reduce the environmental levels of As, Cr, and V.

Resum

Des de fa més de 30 anys, està implantat a Tarragona un dels complexos químics/ petroquímics més importants del sud d’Europa. Una gran refineria de petroli (Repsol/YPF) hi opera, conjuntament amb un important nombre d’indústries químiques i petroquímiques. Entre elles, hi destaquen una fàbrica de producció de PVC, una de tractament de clor, una incineradora de residus sòlids urbans (IRSU) i l’única planta incineradora de residus industrials (IRI) de l’Estat. Així mateix, la presència d’una autopista i diverses carreteres densament transitades influeix el medi ambient de la zona. En els darrers anys, ha augmentat la preocupació pública envers els possibles efectes adversos que el complex industrial podria tenir per a la salut de la població resident a Tarragona. En resposta, el 2002 vam iniciar un important estudi per tal de determinar els nivells de diversos contaminants orgànics i inorgànics a l’àrea. Així mateix, també s’avaluaren els riscos per a la salut derivats de l’exposició a aquells agents químics per part de la població local.

A l’hivern de 2002, es van recollir mostres de sòls i vegetació (bledes) en diversos punts dels complexos industrials químic i petroquímic de Tarragona. Es van agafar mostres addicionals tant al centre urbà de Tarragona com en diversos barris residencials. Finalment, es van prendre mostres en zones presumiblement no contaminades, fora de l’àrea d’influència directa de les indústries avaluades. En totes les mostres, es van determinar les concentracions d’arsènic (As), cadmi (Cd), crom (Cr), mercuri (Hg), manganès (Mn), plom (Pb) i vanadi (V). Per altra banda, també s’hi analitzaren els nivells de policlordibenzo-p-dioxines i furans (PCDD/Fs), bifenils policlorats (PCBs), naftalens policlorats (PCNs) i hidrocarburs aromàtics policíclics (PAHs).

Els sòls recollits en el complex químic i les àrees urbana/residencial presentaren les concentracions més elevades per a tots els contaminants analitzats. Així mateix, els nivells en sòls de les àrees petroquímica i no contaminada foren substancialment menors. Respecte als metalls pesants, aquesta diferència només fou estadísticament significativa per al Cr i el V. També es trobaren altes concentracions de Pb en sòls urbans, probablement a causa de la utilització fins fa poc d’aquest element com a additiu en benzines. Quant als compostos orgànics, la diferència entre el primer grup de mostres (àrees química i residencial) i el segon (zones petroquímica i no contaminada) fou

significativa per a les PCDD/Fs i els PCBs, mentre que en el cas dels PCNs i els PAHs no es va assolir el nivell de significació estadística. No obstant això, els nivells de tots els contaminants en sòl foren clarament menors a les concentracions màximes permeses en les legislacions catalana i espanyola.

Respecte a les mostres de bleda, no es van trobar diferències significatives per a cap dels contaminants, llevat del V. De fet, el V fou l'únic agent químic del que es registraren diferències significatives en ambdós monitors ambientals, sòls i bledes. En conseqüència, es podria considerar que Tarragona presenta un cert grau de contaminació per part d'aquest metall. En zones residencials, s'observaren nivells relativament alts de PAHs, remarcant el trànsit com una important font d'emissió d'hidrocarburs. Malgrat que la diferència no fou significativa, les concentracions de PCDD/Fs en bledes foren més elevades a l'àrea no contaminada que a les zones industrial i residencial. Per tant, es podria pensar que el transport a llarga distància i/o les fonts d'emissió incontrolades juguen un paper important en els nivells mediambientals d'aquests contaminants.

Les concentracions de PAHs foren sorprenentment baixes malgrat la presència d'una important refineria de petroli. Així, es va dur a terme un experiment per tal de determinar la influència de les condicions locals ambientals sobre la degradació d'aquests compostos. Concretament, es va estudiar la fotodegradació de PAHs enfront 2 ambients: un Atlàntic (baixa temperatura i radiació solar) i un Mediterrani (alta temperatura i radiació UV). Es va concloure que ambdues variables podrien tenir un efecte sinergètic en la degradació de PAHs.

Per tal de caracteritzar el grau de pol·lució a Tarragona i determinar possibles "punts contaminats", es van utilitzar dos tipus d'eines classificatòries. El mapa auto-organitzatiu de Kohonen (SOM) i l'anàlisi de components principals (PCA) es van aplicar als nivells de metalls pesants i compostos orgànics, respectivament. S'identificaren alguns punts del sud-oest del complex químic, i del centre urbà de Tarragona, pels seus alts nivells de contaminació. De fet, la presència d'una planta de producció de clor com a font d'emissió, particularment de Hg i compostos clorats, seria una explicació raonable de per què es trobaren concentracions més elevades a l'àrea química respecte a la petroquímica. Així mateix, el règim de vents predominant (vent del nord) i l'altura de les torxes i xemeneies de la refineria facilitarien la dispersió de contaminants potencialment emesos, i la deposició lluny del focus.

També és va dur a terme un anàlisi dels riscos per a la salut de la població derivats de l'exposició a metalls pesants i PCDD/Fs. Respecte als metalls, les actuals concentracions no suposen un augment rellevant dels riscos no cancerígens, ja que els nivells foren clarament inferiors als marcats per l'agència de protecció mediambiental americana (US EPA) i els Quocients de Risc (HQ) calculats van ser menors d'1. No obstant, un cert nombre de casos de càncer podria derivar de la ingesta d'As (degut als baixos nivells d'As establerts per l'US EPA) i inhalació de Cr (car es va assumir que el Cr^{6+} era 1/6 del crom total).

L'avaluació de riscos per a la salut de l'exposició a PCDD/Fs es dugué a terme en funció del nivell socioeconòmic de la població. Els habitants de l'àrea industrial podrien estar més ambientalment exposats a les PCDD/Fs, a causa dels comparativament més alts nivells en aire i sòl. Per altra banda, l'exposició indirecta seria més important per als residents del centre urbà de Tarragona a causa de la ingesta de PCDD/Fs a través de la dieta. De fet, l'exposició directa suposaria menys del 2% del total. Globalment, els habitants de les àrees residencials estan més exposats a les PCDD/Fs. De tota manera, els riscos cancerígens i no cancerígens associats a aquesta exposició són assumibles.

Per tal d'estudiar l'estat integral de contaminació a l'àrea de Tarragona, es desenvolupà un Índex de Risc Integral en base al SOM. Així, es va elaborar un *ranking* dels diversos contaminants orgànics i inorgànics en funció de les seves propietats de persistència, bioacumulació i toxicitat. Posteriorment, es va dissenyar un mapa del risc de la zona mitjançant la representació espacial de l'Índex amb un Sistema d'Informació Geogràfica (GIS).

Tot i que el risc per metalls pesants i contaminants orgànics no és significatiu, fóra molt recomanable dur a terme mesures continuades del nivells d'aquests i altres contaminants en les àrees industrials i urbanes de Tarragona. Així mateix, caldria fer un esforç conjunt per tal de reduir els nivells ambientals d'As, Cr i V.

Resumen

Desde hace más de 30 años, está implantado en Tarragona uno de los complejos químicos/ petroquímicos más importantes del sur de Europa. Una gran refinería de petróleo (Repsol/YPF) opera, conjuntamente con un importante número de industrias químicas y petroquímicas. Entre ellas, destacan una fábrica de producción de PVC, una de tratamiento de cloro, una incineradora de residuos sólidos urbanos (IRSU) y la única planta incineradora de residuos industriales (IRI) del Estado. Asimismo, la presencia de una autopista y diversas carreteras densamente transitadas influye en el medio ambiente de la zona. En los últimos años, ha aumentado la preocupación pública respecto a los posibles efectos adversos que el complejo industrial podría tener para la salud de la población residente en Tarragona. En respuesta a ello, en 2002 iniciamos un importante estudio con el fin de determinar los niveles de diversos contaminantes orgánicos e inorgánicos en el área. Asimismo, también se evaluaron los riesgos para la salud derivados de la exposición a aquellos agentes químicos por parte de la población local.

En invierno de 2002, se recogieron muestras de suelos y vegetación (acelgas) en diversos puntos de los complejos industriales química y petroquímica de Tarragona. Se cogieron muestras adicionales tanto en el centro urbano de Tarragona como en diversos barrios residenciales. Finalmente, se recogieron muestras en zonas presumiblemente no contaminadas, fuera del área de influencia directa de las industrias evaluadas. En todas las muestras, se determinaron las concentraciones de arsénico (As), cadmio (Cd), cromo (Cr), mercurio (Hg), manganeso (Mn), plomo (Pb) y vanadio (V). Por otro lado, también se analizaron los niveles de policlorodibenzo-p-dioxinas y furanos (PCDD/Fs), bifenilos policlorados (PCBs), naftalenos policlorados (PCNs) e hidrocarburos aromáticos policíclicos (PAHs) en las mismas muestras.

Los suelos recogidos en el complejo químico y las áreas urbana/residencial presentaron las concentraciones más elevadas para todos los contaminantes analizados. Asimismo, los niveles en suelos de las áreas petroquímica y no contaminada fueron sustancialmente menores. Respecto a los metales pesados, esta diferencia sólo fue estadísticamente significativa para el Cr y el V. También se encontraron altas concentraciones de Pb en suelos urbanos, probablemente debido a la utilización en el pasado de este elemento como

aditivo en gasolinas. En cuanto a los compuestos orgánicos, la diferencia entre el primer grupo de muestras (áreas química y residencial) y el segundo (zonas petroquímica y no contaminada) fue significativa para las PCDD/Fs y los PCBs, mientras que en el caso de los PCNs y los PAHs no se alcanzó el nivel de significación estadística. Sin embargo, los niveles de todos los contaminantes en suelo fueron claramente menores a las concentraciones máximas permitidas en las legislaciones catalana y española.

Respecto a las muestras de acelga, no se encontraron diferencias significativas para ninguno de los contaminantes, exceptuando el V. De hecho, el V fue el único agente químico del que se registraron diferencias significativas en ambos monitores ambientales, suelos y acelgas. En consecuencia, se podría considerar que Tarragona presenta un cierto grado de contaminación por este metal. En zonas residenciales, se observaron niveles relativamente altos de PAHs, remarcando el tráfico como una importante fuente de emisión de hidrocarburos. Aunque la diferencia no fue significativa, las concentraciones de PCDD/Fs en acelgas fueron más elevadas en el área no contaminada que en las zonas industrial y residencial. Por tanto, se podría pensar que el transporte a larga distancia y/o las fuentes de emisión incontroladas juegan un papel importante en los niveles medioambientales de estos contaminantes.

Las concentraciones de PAHs fueron sorprendentemente bajas a pesar de la presencia de una importante refinería de petróleo. Así, se llevó a cabo un experimento para determinar la influencia de las condiciones locales ambientales sobre la degradación de estos compuestos. Concretamente, se estudió la fotodegradación de PAHs en 2 ambientes: uno Atlántico (baja temperatura y radiación solar) y uno Mediterráneo (alta temperatura y radiación UV). En él se concluyó que ambas variables podrían tener un efecto sinérgico en la degradación de PAHs.

Con el fin de caracterizar el grado de polución en Tarragona y determinar posibles “puntos contaminados”, se utilizaron dos tipos de herramientas clasificatorias. El mapa auto-organizativo de Kohonen (SOM) y el análisis de componentes principales (PCA) se aplicaron a los niveles de metales pesados y compuestos orgánicos, respectivamente. Se identificaron algunos puntos del suroeste del complejo químico, y del centro urbano de Tarragona, por sus altos niveles de contaminación. De hecho, la presencia de una planta de producción de cloro como fuente de emisión, particularmente de Hg y compuestos clorados, sería una explicación razonable de porqué se encontraron concentraciones más elevadas en el área química respecto a la petroquímica. Asimismo, el régimen de vientos predominantes (viento del norte) y la altura de las antorchas y chimeneas de la refinería facilitarían la dispersión de contaminantes potencialmente emitidos, y la deposición lejos del foco.

También se llevó a cabo un análisis de los riesgos para la salud de la población derivados de la exposición a metales pesados y PCDD/Fs. Respecto a los metales, las actuales concentraciones no suponen un aumento relevante de los riesgos no cancerígenos, ya que los niveles fueron claramente inferiores a los marcados por la agencia de protección medioambiental americana (US EPA) y los Cocientes de Riesgo (HQ) calculados fueron menor de 1. Sin embargo, un cierto número de casos de cáncer podría derivar de la ingesta de As (debido a los bajos niveles de As establecidos por la US EPA) e inhalación de Cr (ya que se ha asumido que el Cr^{6+} era 1/6 del cromo total).

La evaluación de riesgos para la salud por exposición a PCDD/Fs se llevó a cabo en función del nivel socioeconómico de la población. Los habitantes del área industrial podrían estar más ambientalmente expuestos a las PCDD/Fs, debido a los comparativamente más altos niveles en aire y suelo. Por otro lado, la exposición indirecta sería más importante para los residentes del centro urbano de Tarragona a causa de la ingesta de PCDD/Fs a través de la dieta. De hecho, la exposición directa supondría menos del 2% del total. Globalmente, los habitantes de las áreas residenciales están más expuestos a las PCDD/Fs. De todos modos, los riesgos cancerígenos y no cancerígenos asociados a esta exposición son asimilables.

Para determinar el estado integral de contaminación del área de Tarragona, se desarrolló un Índice de Riesgo Integral basado en el SOM. Así, se elaboró un *ranking* de los diversos contaminantes orgánicos e inorgánicos en función de sus propiedades de persistencia, bioacumulación y toxicidad. Posteriormente, se diseñó un mapa del riesgo de la zona mediante la representación espacial del Índice con un Sistema de Información Geográfica (GIS).

Aunque el riesgo por metales pesados y contaminantes orgánicos no es significativo, sería muy recomendable llevar a cabo medidas continuas de los niveles de estos y otros contaminantes en las áreas industriales y urbanas de Tarragona. Asimismo, sería necesario un esfuerzo conjunto con el fin de reducir los niveles ambientales de As, Cr y V.

INTRODUCTION

During the last two centuries, industrialization has played a key role in the pace of society progress. Until around mid-20th century only the positive side of industries was seen: the economy of every country grew parallelly to its industrial capacity. However, people began to realize that most of those facilities released to the environment great amounts of substances, some of them potentially dangerous. The introduction of these chemicals could mean a serious hazard not only for the environment and the living organisms, but also for the human health of populations living close to emission sources. Among the chemicals of concern, a special emphasis on heavy metals has been put by scientists. As much as the knowledge about these elements has been increasing, consciousness to reduce/eliminate their release has been also going up. Likewise, the list of dangerous substances has been enlarged, mainly thanks to the technical capacity of detecting trace amounts of different compounds.

Perception of general public around the potential adverse health effects of industries are usually in relation with the capacity of production and extension of the facilities. This means that larger a company is, more it may pollute. In consequence, the debate about the convenience of those facilities is continuous in those places where big industrial poles are located. Among the huge variability of industries, petroleum refineries are usually established in large extensions of territory. Moreover, because of the production process, plumes are sometimes identified arising from their stacks and torches.

According to the production capacity, the most important industrial complex of Spain is located in Tarragona (Catalonia). Besides an important number of chemical companies, a big oil refinery has been regularly operating for more than 30 years. Since these chemical and petrochemical facilities are potential sources of pollution, the public concern over possible adverse health effects has been increasing in recent years. In response to it, we carried out a wide survey focused on establishing the levels of different heavy metals and organic compounds in the area of Tarragona, and assessing the health risks derived from exposure to those chemicals.

Industrial environmental impact

Petrochemical industries

The determination of trace chemicals content in crude oils has been a widely used practice, carried out mainly by petrochemical industries, as a way to know the purity grade of the materials that are being purified (Ali et al., 1983). Among heavy metals, vanadium (V) has been pointed out, by far, as the major contributor (Duce and Hoffman, 1976). Vanadium contamination may occur as fallout from refining operations and burning of residual oils (Hope, 1997). However, it has been also suggested that other trace elements, such as arsenic (As) and chromium (Cr), can be directly released to air by the oil industry (Stigter et al., 2000). Moreover, a number of organic compounds may be also emitted from different production processes, the storage tanks and the waste areas (Cetin et al., 2003), as well as to be released to air through stacks and torches. Significant amounts of organic aerosols, such as volatile organic compounds (VOC), have been detected in air surrounding petrochemical refineries wideworld (Cetin et al., 2003; Lin et al., 2004; Yassaa and Cecinato, 2005). In turn, since significant higher levels of polycyclic aromatic hydrocarbons (PAHs) have been found in ambient air of oil refineries (Tsai et al., 1995), it has been suggested that air monitoring programs carried out near petrochemical complexes should incorporate measurements of PAH levels (Koos et al., 1991; Wilson et al., 1991). In addition, chlorinated compounds, such as polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs), have been identified during catalyst regeneration of a refinery reforming process (Thompson et al., 1990). However, insufficient data are still available to evaluate the importance of oil refineries as PCDD/PCDF sources (Beard et al., 1993). Finally, notable levels of polychlorinated biphenyls (PCBs) have been also found in ambient air near petroleum refineries (Lee et al., 1996).

In a reduced scale, discharges of oil derivates to soil and water by petroleum industries may be an important source of pollution for the closer environment. As an example, notable concentrations of PAHs have been identified in soils, water and sediments collected near oil refineries (Iturbe et al., 2004; Kilemade et al., 2004; Tolosa et al., in press).

On the other hand, since workers of oil refineries may be exposed to a large variety of organic chemicals, health surveillance programs of petrochemical workers (mainly epidemiological studies) have been carried out in order to assess whether or not these potential exposures could mean adverse health effects (Mehlman, 1992). There is a great controversy on the results, but some investigations have indicated that occupational exposure might play a key role in the development of certain cancers (Barberino et al., 2005). An excess risk from lung, bladder and non-melanotytic skin cancers, as well as non-Hodgkin's lymphoma has been identified for some workers, suggesting that exposure to PAHs and related chemicals could be associated with an increased risk of cancer (Consonni et al., 1999; Lo Presti et al., 2001; Ugnat et al., 2004). In addition, exposure to gasoline has been related with an increased risk of kidney cancer (Pukkala, 1998).

Human health effects of petrochemical industries have also been controlled carrying out epidemiological studies of the population living in the vicinity of such potential sources of pollution. Results from these investigations were even more unclear than that done with workers as subjects. Since some studies have failed to find a direct link between the presence of oil refineries and the development of adverse health effects by the local population (Wong and Foliart, 1993; Pekkanen et al., 1996; Neuberger et al., 2003), large controversies still exist around this topic. However, it is also true that some investigations have reported correlations between both factors. It has been demonstrated that communities located around petrochemical complexes sometimes argue about perception of annoying chemical odors derived from those industries (Taylor et al., 1996; Luginaah et al., 2000; 2002). In addition to odors, other acute symptoms such as eye irritation, nausea, and throat irritation have been identified in populations environmentally subjected to the potential impact of petrochemical industries (Yang et al., 1997). As one of the groups of population most sensitive to exposure, important incidence of petroleum manufacturing plants has been reported in children. Statistically significant excesses of leukemia, as well as bone, brain, and bladder cancers have been identified (Pan et al., 1994; Knox and Gilman, 1997). Likewise, a positive correlation has been reported between petrochemical air pollution and adverse pregnancy outcome (preterm delivery) (Yang et al., 2002). In adults, moderate increases in risk for bladder and lymphohematopoietic neoplasms have been detected in subjects living near petrochemical industries (Gottlieb et al., 1982; Wilkinson et al., 1999; Belli et al., 2004). Some evidence of increased incidence of lung cancer, particularly in women, has been also detected (Bhopal et al., 1998). Other cancers of the respiratory tract (i.e., buccal cavity and pharynx), as well as cardiovascular diseases have been positively associated to non-occupational exposure to petrochemical emissions (Kaldor et al., 1984).

Other industrial sources

In chemical and petrochemical complexes, there are multiple potential sources of pollution according to the typology and amount of chemicals released to the atmosphere. Therefore, the incidence on human health of chemical industries, apart from that of oil refineries, is expected to be notable. Although epidemiological studies around other kind of industries are sometimes inconclusive, the possibility that these industries can mean adverse health effects in locally exposed populations cannot be discarded. Thus, some concern still remains concerning the environmental and human health impact of old incinerators, vinyl chloride plants and metal smelters, among others.

Chemicals of concern

POPs

In the 2001 Stockholm Convention on Persistent Organic Pollutants (POPs), a global treaty for the regulation of these pollutants was signed (Bilcke, 2002). POPs are hazardous compounds characterized by a high persistence in the environment, bioaccumulation in the body burden, toxicity, and capacity to travel long distances from where they are released (long-range transport). The Stockholm treaty aims to promote both the reduction and prohibition of a list of 12 POPs, commonly identified as “dirty dozen”. Among them, PCDD/Fs as well as PCBs were included. In turn, new compounds, such as polychlorinated naphthalenes (PCNs), were proposed to be included in further revisions.

PCDD/Fs

PCDD/Fs commonly known as dioxins and furans, comprise a large group of chemical compounds of high environmental interest. They include a family of 210 congeners, which are differentiated according to their number and position of chlorine atoms. Among them, 75 are dioxins (PCDDs), and the remaining 135, are furans (PCDFs). Dioxin and furan molecules are based on 2 aromatic rings of benzene linked by two or one oxygen atoms, respectively. The general structure of both groups of compounds is depicted in Figure 1.

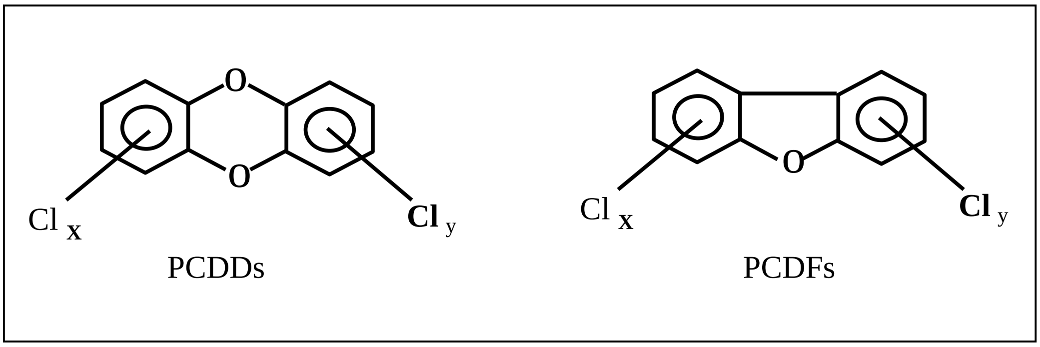

Figure 1. General chemical structure of PCDDs and PCDFs

Properties

Toxicity

PCDD/Fs are usually found in the environment as mixtures of several congeners, whose individual toxicity can vary in a 1000-folder magnitude. In order to evaluate this toxicity, a toxicity equivalency factor (I-TEF) was linked to each congener by international convention (US EPA, 1989b; Kutz et al., 1990). It was established that the 17 congeners containing a Cl atom in the positions 2, 3, 7 and 8 of the molecule were the most hazardous in terms of human health effects. Among these 17 congeners, in which 7 dioxins and 10 furans are included, 2,3,7,8-TCDD was identified as the most toxic. The I-TEF value for all the 17 congeners was referred to the toxicity of 2,3,7,8-TCDD, to which was assigned a TEF of 1. In 1998, new TEF (WHO-TEF) were redefined by the WHO for the 2,3,7,8-substituted compounds, while new factors were also assigned to some specific PCBs (Van Leeuwen et al., 2000). Both I-TEF and WHO-TEF are summarized in Table 1. Since the remaining 193 congeners present comparatively a very low toxicity, their contributions in the chemical mixture were considered to be negligible. Consequently, a TEF=0 was established for these compounds. In order to express PCDD/F concentration, Toxic Equivalents (TEQ) are calculated as the summation, for all the congeners, of the value obtained multiplying the respective TEF by the individual concentration, according to the following equation:

$$TEQ = \Sigma \left(TEF_i \cdot C_i \right)$$

Where TEF_i is the toxic equivalence factor (marked by NATO or WHO) for each congener, and C_i is its individual concentration in the mixture.

Health effects

Since mid-eighties of the 20th century, the US EPA has being studying the PCDD/Fs carcinogenicity on the basis of a plausible mechanism involving the highly conserved aryl-hydrocarbon receptor (AhR), animal models, and human data from industrial exposures and accidents (Baccarelli et al, 2004). In its last draft report, dioxins are classified by US

EPA as Group B2 (sufficient evidence in animals, insufficient evidence in humans) when considered alone, but complex mixtures of dioxin and related compounds (i.e., chlorophenols and phenoxyherbicides) are considered “likely to be carcinogenic to humans” (Group B1). Likewise, it is also mentioned that 2,3,7,8-TCDD is best characterized as “carcinogenic to humans” (US EPA, 2000a). In fact, carcinogenicity of 2,3,7,8-TCDD was studied on the basis of four cohort studies of herbicide producers (Fingerhut et al., 1991; Manz et al., 1991; Saracci et al., 1991; Flesch-Janys et al., 1995) and one cohort of residents in a contaminated area from Seveso, Italy (Bertazzi et al., 1989b; Bertazzi et al., 1989a). In 1997, the International Agency for Research on Cancer (IARC, 1997) also included 2,3,7,8-TCDD in the Group 1 of carcinogenicity (agents with sufficient evidence of being carcinogen for humans). However, other PCDDs and PCDFs failed to be considered carcinogens, and they were included in the Group 3 (not classifiable as carcinogens to humans).

Table 1. I-TEF and WHO-TEF for each of the 17 PCDD/F congeners

Congener	**I-TEF**	**WHO-TEF**
2,3,7,8-TCDD	1	1
1,2,3,7,8-PeCDD	0.5	**1**
1,2,3,4,7,8-HxCDD	0.1	0.1
1,2,3,6,7,8-HxCDD	0.1	0.1
1,2,3,7,8,9-HxCDD	0.1	0.1
1,2,3,4,6,7,8-HpCDD	0.01	0.01
OCDD	0.001	**0.0001**
2,3,7,8-TCDF	0.1	0.1
1,2,3,7,8-PeCDF	0.05	0.05
2,3,4,7,8-PeCDF	0.5	0.5
1,2,3,4,7,8-HxCDF	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1
1,2,3,7,8,9-HxCDF	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.01
OCDF	0.001	**0.0001**

In bold, dissimilarities between I-TEF and WHO-TEF

2,3,7,8-TCDD carcinogenicity is multiorgan. Increases of risk for lung cancer, soft-tissue sarcoma and non-Hodgkin lymphoma have been found in several cohort studies. Other associated pathologies are malignant neoplasms, digestive system cancers and multiple myeloma (IARC, 1997). Actually, the strongest evidence for the carcinogenicity of 2,3,7,8-TCDD is for all cancers combined, rather than for any specific site (Kogevinas, 2000).

The US EPA has also established an oral slope factor (or carcinogenic potency) of $1.5 \cdot 10^{5}$ kg·day/mg as a risk estimation following ingestion of 2,3,7,8-TCDD. Slope factors for dermal and inhalation pathways exposures are $3 \cdot 10^{5}$ and $1.16 \cdot 10^{5}$ kg·day/mg, respectively (US EPA, 1999). Nevertheless, instead of the slope itself, an upper-bound (i.e., the 95% upper confidence limit) on this value is generally used, because it is a statistically more stable number. Thus, US EPA (2000a) suggests the use of $1 \cdot 10^{-3}$ kg·day/pg ($1 \cdot 10^{6}$ kg·day/mg) as an estimator of the upper-bound cancer risk for both background intakes and incremental intakes above background.

In spite of the huge number of investigations aimed in determining whether PCDD/Fs, in general, and 2,3,7,8-TCDD, in particular, are carcinogenic, there is still much uncertainty surrounding this issue. In this sense, some authors have criticized that, although experimental data are still very inconclusive, 2,3,7,8-TCDD was designated as a Group 1 carcinogen (Cole et al., 2003).

With respect to non-cancer effects, acute exposure to PCDD/Fs can cause a variety of harmful effects over the reproductive, developmental, immunological, and endocrine systems (ATSDR, 1998; Sweeney and Mocarelli, 2000). The most commonly observed and studied effect of exposure to 2,3,7,8-TCDD in humans is chloracne (Reggiani, 1980; Geusau et al., 2001; Sterling and Hanke, 2005). Other pathologies are hepatotoxicity, neurotoxicity, and cardiotoxicity (Birnbaum and Tuomisto, 2000).

Neither a Reference Concentration (RfC) nor a Reference Dose (RfD) for 2,3,7,8-TCDD has been established up now by the US EPA. However, non-cancer effects may be evaluated through the comparison with the tolerable daily intake (TDI) marked by the WHO. The most up-to-date surveys indicate a TDI for PCDD/Fs ranging from 1 to 4 pg/kg body weight (Van Leeuwen et al., 2000), and a tolerable weekly intake (TWI) of 14 pg/kg body weight (European Commission, 2001).

Bioaccumulation

PCDD/Fs can bioaccumulate very easily in the human body because they present a high solubility in lipids. The high hydrophobicity is characterized by an extremely low level of water solubility, ranging from 7.9 to 483 ng/l (Mackay et al., 1992). PCDD/F retention by lipids is also linked to biomagnification of dioxins and furans in the food chain, whose final step is human diet. Gastrointestinal and dermal absorption factors for 2,3,7,8-TCDD are 0.5 and 0.03, respectively (US EPA, 1999). In turn, maximum values of 63% were reported studying PCDD/Fs absorption through the digestive tract.

With regard to biological half-life, great differences between humans and other species of mammals have been observed. Thus, whereas a TCDD half-life between 5.8 to 11.3 years has been established in humans (Olson, 1994), a range of 10 to 30 days has been noted in rodents (IARC, 1997). In their investigations, Hays et al. (1997) assumed an elimination that follows a first-order kinetics, and a half-life of 25 days and 7.5 years in rats and humans, respectively.

Persistence

PCDD/Fs are very persistent in the environment. These compounds can be adsorbed very easily by particles present in air, soils and sediments, because they present a high value of octanol/water partition coefficient (K_{ow}) and organic carbon partition coefficient (K_{oc}). Ranges of K_{ow} and K_{oc} for the 2,3,7,8-substituted congeners are $1.26 \cdot 10^6$-$1.58 \cdot 10^8$ and $5.16 \cdot 10^5$-$6.50 \cdot 10^7$, respectively (Mackay et al., 1992). This powerful absorption makes mobilization as negligible (WHO, 2003). With respect to degradation processes, photolysis and microbial decomposition have been pointed out as the most influent mechanisms of PCDD/F loss, specially in air but also in vegetation (Podoll et al., 1986; Niu et al., 2004). Even though, very high half-lives have been suggested in all environmental compartments (Sinkkonen and Paasivirta, 2000). Normally, a general increase in the tropospheric lifetime with the degree of chlorination has been found (Atkinson, 1991).

Long-range transport

Although some PCDD/Fs have complex structures, their capacity to be adsorbed by air particulate matter lets them travel great distances. It affects environments located far away from the emission sources. Thus, although PCDD/Fs are semi-volatile compounds with relatively low vapor pressures, they can undergo long-range transport (Lohmann and Jones, 1998). In this context, it has been noted that most PCDD/F emissions tend to be transported beyond 100 km from where they were released (Lohman and Seigneur, 2001). High tropospheric lifetimes of particle-bound PCDD/Fs are another positive factor which favors long-range transport and subsequent deposition (Atkinson, 1991). Even in Arctic environments, PCDD/Fs have been detected in several abiotic and biotic compartments (Oehme et al., 1996; Ayotte et al., 1997; Braune and Simon, 2003).

Sources of PCDD/Fs

PCDD/Fs are unintentional byproducts of combustion processes, involving chlorine (Fiedler, 1996). Two great groups of sources, which release dioxins and furans into the environment, have been traditionally identified: regulated and non-regulated/diffuse.

The first set includes municipal solid, hazardous and clinical waste incinerators, as well as cement kilns and power generation plants (Alcock et al., 2001). Historically, municipal solid waste incinerators (MSWI) were the main PCDD/F emitters. In 1993, the UK inventory of dioxins and furans specified that MSWI contributed up to 80% of the emissions (Alcock et al., 1999). However, in recent years important legislation efforts aimed in regulating PCDD/F emissions by incinerators, have produced a dramatic reduction of the contribution percentage of these PCDD/F sources. In fact, trends indicate a general decrease from late 60s/early 70s (Alcock and Jones, 1996), although it was not until a few years later that legislation about emission control of PCDD/Fs started to be applied. As an example, in 1998, Alcock et al. (1999) noted a diminution of 30-50% of the amount of dioxins and furans released by MSWI. In turn, US EPA considered in 2005 that, for the first time, MSWI were not the most important contributors of PCDD/Fs into the environment. In fact, in 1987 and 1995, the leading source of PCDD/F emissions to the

U.S. environment was municipal waste combustion. However, in 2000 MSWI dropped to the third ranked source, and was substituted by burning of domestic refuse in backyard burn barrels (US EPA, 2005).

The second group of sources comprises both non-regulated and diffuse sources. Among them, vehicle emissions, domestic coal/wood combustion, and natural and accidental fires are the most important. Some studies indicate the possibility that these latter sources are becoming more important as PCDD/Fs inputs into the environment. Other potential secondary sources are landfill flare combustion, accidental combustion of PCBs in electrical equipment and re-entering through contaminated sewage sludge application (Fiedler, 1996; Alcock et al., 2001). Large uncertainties still remain around the amount of PCDD/Fs released to the environment (Duarte-Davidson et al., 1997). Thus, primary and secondary sources have been estimated in contributing 30-86% and 13-70%, respectively, of the total PCDD/Fs emitted to the atmosphere. (Alcock et al., 2001).

PCBs

Polychlorinated biphenyls (PCBs) are a family of ubiquitous organic pollutants, with a similar chemical structure to PCDD/Fs (Figure 2). They are made up of a biphenyl nucleus (dual-ring of benzene) with 1-10 chlorine atoms. According to the different degree of chlorination, there are up to 209 congeners (numerated from 1 to 209), which in turn may be *ortho*-, *meta*- or *para*-, if chlorine atoms are located in positions 2 and 6, 3 and 5, or 4. Moreover, coplanar PCBs include all *non-ortho*- and *mono-ortho*-PCBs, with a planar configuration (this is to say, that both benzene rings occupy the same plane).

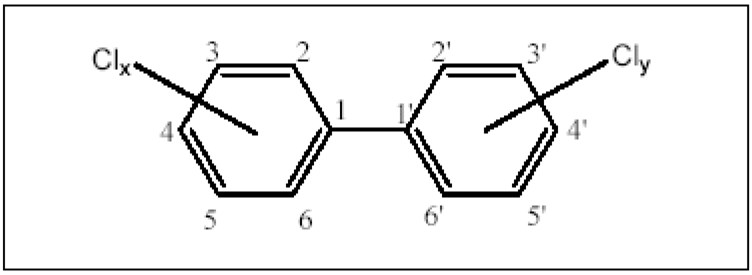

Figure 2. Chemical structure of PCBs

Properties

Toxicity

Just like dioxins, PCBs are found in the environment as mixtures of congeners. Although PCBs toxicity has not been so widely studied as that of PCDD/Fs, it has been known that some PCB congeners may have a similar toxicity mechanism. In fact, 12 of these PCB congeners have been identified as “dioxin-like”. A TEF value has been assigned to them, which is related to 2,3,7,8-TCDD toxicity. WHO-TEF for these “dioxin-like” PCBs range from 10^{-5} to 0.1, corresponding to PCB-167 and PCB-126, respectively.

With regard to cancer effects, PCBs have been classified as probably carcinogenic to humans, being included in Groups 2A and 2B by IARC (1987) and US EPA (1999), respectively. Although there is extensive conclusive of PCB carcinogenicity in animals, data regarding human cancer toxicity is still limited (ATSDR, 2000d). PCBs are absorbed through skin, lungs and gastrointestinal tract, and they are transported through the blood stream to liver, various muscles and adipose tissue, where they accumulate (Cogliano, 1998). Results of some epidemiological studies in workers suggest that exposure to PCB may induce liver cancer and malignant melanoma (Borja et al., 2005). Because of uncertainty in PCB carcinogenicity, the US EPA has established 3 different upper-bound oral slope factors applied to PCB mixtures: 2.0, 0.4 and 0.07 kg·day/mg according to if the risk is high, low or lowest, respectively (US EPA, 1999).

High exposure to PCBs can have other important non-cancer effects such as chloracne or liver damage (hepatitis). Likewise, PCBs may affect nervous system development and impair cognitive function, and induce neurobehavioral disorders in children (Tilson et al., 1998; Winneke et al., 2002). An oral reference dose has only established for some specific PCB mixtures (known as Aroclors): $7 \cdot 10^{-5}$ and $2 \cdot 10^{-5}$ kg/mg/day for Aroclor #1016 and #1254, respectively. Aroclors are commercial mixtures of PCBs, which contain a number of PCB congeners in a specific proportion (ATSDR, 2000d).

Bioaccumulation

PCBs are very hydrophobic compounds with a high lipid solubility. Therefore, they tend to accumulate in fatty tissues. Log K_{ow} of tri- to hepta-PCBs ranges from 5.6 to 7 (Mackay et al., 1992). Since the lipid bioaccumulation is a characteristic feature of PCBs, as it happens with PCDD/Fs, biomagnification of the food chain becomes an important process, enhancing the toxicological effects in the living organisms. In fact, dietary intake (specially of fish) has been pointed out as the major source/exposure pathway to PCBs in humans (Llobet et al., 2003a; DeCaprio et al., 2005). On the other hand, dermal absorption has been reported to be a minor pathway, with retention factors ranging from 4 to 14 % (Mayes et al., 2002).

There is still a wide divergence about the biological half-lives of PCB congeners. It is thought that commercial mixtures of PCBs may have mean half-lives in the human body ranging from 2 to 6 years (Shirai and Kissel, 1996). However, if PCB congeners are assessed individually, this value may vary enormously. For example, the half-life of PCB-153 was estimated in 12.4 years, whereas that of PCB-28 was estimated to be 1.4 years (Brown Jr, 1994).

Persistence

PCBs are very persistent in the environment. Because of their physical and chemical properties, PCBs tend to be adsorbed to particles in air, soil and sediments. Although atmosphere is the environmental compartment where PCBs are more quickly degraded, half-lives between 2 and 6 years have been suggested (Sweetman and Jones, 2000; Meijer et al., 2003), according to the chlorination degree. Photodegradation has been considered an important loss mechanism in air (Lin et al., 1995). In water, PCBs are adsorbed to particulate matter, and remain there for a number of years (Gouin et al., 2004). Finally, because PCBs have a high affinity to be strongly attached to soils and sediments, they act as sinks or reservoirs. Long half-lives have been observed in these media, specially for the most weighted compounds (Ayris and Harrad, 1999; Sinkkonen and Paasivirta, 2000).

Long-range transport

Since the physico-chemical properties of PCDD/Fs and PCBs are similar, PCBs also have the capacity to be adsorbed by air particulate matter, and therefore, to travel long distances. Thus, PCBs have been detected in air and other environmental matrices in remote areas such as Arctic and high mountains, where no local sources are present (Corsolini et al., 2002; Dawn Pier et al., 2002; Evenset et al., 2004; Grimalt and van Drooge, in press).

Sources

Unlike PCDD/Fs, the release of PCBs into the environment is not accidental, and there are no known natural sources of these pollutants. Their properties of thermal stability, non-flammability and high electrical resistivity have made that, for several decades, PCBs were extensively used in a wide range of industrial applications, such as dielectric fluids in transformers and large capacitors, pesticide extenders, plasticisers in sealants, lubricants for turbines and pumps, and in the formulation of cutting oils for metal treatment (Borja et al., 2005). Some of these applications resulted in direct or indirect releases into the environment due to inappropriate disposal, accidental spills, leaks from industrial facilities, and fires in PCB-containing products (Vallack et al., 1998). As far as it is known, there is still considerable uncertainty with respect to the relative importance of different industries as sources of PCBs (Breivik et al., 2004). Incineration processes of different kinds of waste (municipal solid, hazardous and medical) have been identified of being PCB releasers to air (Alcock et al., 1998), although it is also certain that well-controlled modern combustion plants emit low levels of PCBs (Dyke et al., 2003). Finally, additional sources of PCB emissions include landfill sites, steel and iron reclamation facilities, and environmental sinks of past PCB contamination.

Although PCB production in most countries was banned in the 1970s and 1980s, there is still an important amount of these pollutants in the environment, of which one third is circulating (Vallack et al., 1998). However, current PCB levels are much lower than those found in samples collected in the late 1960s, when a peak of concentration was registered (Harrad et al., 1994; Harner et al., 1995).

PCNs

Polychlorinated naphthalenes (PCNs) are a family of ubiquitous pollutants present in different environmental compartments (Falandysz, 1998). Specifically, 75 different congeners can be labeled as PCNs, structurally characterized by presenting from one to eight chlorine atoms bound to the naphthalene di-benzene ring (IPCS, 2001). The general chemical structure of these chlorinated compounds is depicted in Figure 3. Physical and chemical properties of PCNs are very similar to those of PCBs. They are hydrophobic and very stable chemically and thermically. Moreover, they have good electrical insulating properties and low flammability (Falandysz, 1998; Holoubek et al., 2000).

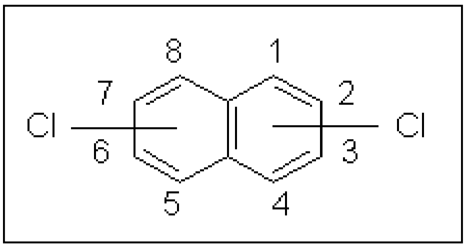

Figure 3. Chemical structure of PCNs

Properties

Toxicity

The literature regarding PCN toxicity is rather scarce. However, it has been well determined that, just like other POPs, their action mechanism of toxicity comes basically from their capacity to activate the aryl hydrocarbon receptor (AhR) (Blankenship et al., 2000). According to episodes of human intoxication, effects following exposure to PCNs might include chloracne, carcinogenesis, teratogenesis, and even lethality (Hayward, 1998). Nevertheless, the appearance of PCNs together with other chlorinated organic compounds, such as PCDD/Fs and PCBs, could have overestimated the potential of PCN harmful effects (Blankenship et al., 2000).

As PCDD/Fs and PCBs, PCNs generally appear under the form of mixtures of congeners. In order to characterize PCN toxicities, TEF values have been established for some congeners. It has been found that PCNs are from 3 to 6 orders of magnitude less toxic than PCDD/Fs, and their relative potency is similar to that of many PCBs (Van den Berg et al., 2000). Among them, some hexaCN congeners are the most potent, with a TEF of 0.002 (Blankenship et al., 2000). However, because of the lack of sufficient reliable data, PCNs toxicity has been categorized only for a few congeners (Kannan et al., 2001; Eljarrat and Barcelo, 2003).

Bioaccumulation

Biomagnification ability of PCNs is, in principle, quite important as it may be concluded from their relatively high octanol-water constant. Log K_{ow} ranges from 3.90 to 8.3, and it is specially significant for hexa- and heptaCN homologues (Harner and Bidleman, 1998). Bioaccumulation experiments have mainly focused on determining bioconcentration factors (BCF) in several aquatic species (Domingo, 2004), where BCF values of 20,000 have been exceeded (Opperhuizen et al., 1985; Crookes and Howe, 1993). It is thought that PCNs tend to biomagnify in the food chain, and they finally accumulate in some human fluids and tissues (Hanari et al., 2004).

Persistence

Data about PCN residence time in water, soils and sediments are very limited. In fact, half-lives have only been reported for mono- and di-CN, which ranged from 38 to 104 days (Crookes and Howe, 1993). In conclusion, although from the similar behavior of PCNs respect to other POPs, those compounds might be considered very persistent in the environment, insufficient evidence is currently available at this moment.

Long-range transport

During the preparation of the United Nations-Economic Commission for Europe Convention on Long-Range Transboundary Air Pollution Protocol on Persistent Organic Pollutants (UN-ECE LRTAP-POPs Protocol) of 1998, PCNs were not included in the “dirty dozen” list because of a lack of adequate data (Van de Plassche et al., 2002). However, scientific knowledge acquired in recent years has made PCNs to become a candidate to enlarge the list of chemicals to be restricted (Domingo, 2004). Harner et al. (1998) carried out the first survey about PCN levels in Arctic air. In turn, PCN concentrations were recently reported in two Swedish background air sampling stations located close to the polar circle (Egebäck et al., 2004).

Sources

Emissions from thermal processes, specially in winter, are one of the most important pathways of PCN entrance into the environment (Takasuga et al., 2004). PCNs have been found in flue gas and fly ash of different MSWI in Spain and Germany, respectively (Schneider et al., 1998; Abad et al., 1999). In Canada, combustion sources accounted around 54% of the total PCN release to air (Helm and Bidleman, 2003). Chlor-alkali processes have been also marked as important environmental sources of PCNs (Jarnberg et al., 1993; Kannan et al., 1998). Other sources are the use of technical PCB formulations whose production of PCNs as by-product was estimated in 169 tons (Yamashita et al., 2000).

Historical peak residues for PCNs are different according to their chlorination degree. The highest input for penta- and hexaCNs occurred prior to 1944, whereas peaks for tetraCNs and triCNs delayed until 1950s and around 1970, respectively (Meijer et al., 2001). However, significant increasing trends observed for several congeners associated with combustion sources suggest that combustion related sources are more important now than they were in the past (Meijer et al., 2001). In addition, a lack of a decline in PCN concentrations from the early 1990s until 2001 has been reported, in contrast to declining levels of PCBs over the same period (Lee et al., 2005b).

PAHs

Polycyclic aromatic hydrocarbons (PAHs) are environmental pollutants, with a chemical structure of two or more fused aromatic rings. Although PAHs are basically formed by carbon and hydrogen atoms, some heterocyclic aromatic hydrocarbons can contain nitrogen, sulfur, chlorine and oxygen (Stefanova et al., 2002). The PAH family comprises around 660 substances indexed by the National Institute of Standards and Technology (Sander and Wise, 1997), of which a 5% occur naturally in the environment (Grimmer, 1983). Among them, the US EPA identified a list of 16 PAHs as priority pollutants to be controlled due to the effects these might have on the human health and the environment (Table 2). They rarely appear individually, but forming PAH-containing mixtures.

Table 2. PAHs established by the US EPA as priority pollutants.

Hydrocarbon	*Molecular Weight*
Naphthalene	128.2
Acenaphthylene	152.2
Acenaphthene	154.2
Fluorene	166.2
Phenanthene	178.2
Anthracene	178.2
Fluoranthene	202.3
Pyrene	202.3
Chrysene	228.3
Benzo(a)anthracene	228.3
Benzo(k)fluoranthene	252.3
Benzo(b)fluoranthene	252.3
Benzo(a)pyrene	252.3
Indeno(123-cd)pyrene	276.3
Dibenz(ah)anthracene	278.4
Benzo(ghi)perylene	276.3

Importance of PAHs as organic pollutants

Since all PAHs do no fulfill accomplish with the requirements of persistence, bioaccumulation, toxicity, and long-range transport, they are not considered POPs. In consequence, PAHs were not included in the “dirty dozen” list in the Stockholm Convention on POPs. Moreover, since their release is unintentional, some reasons arise around the real possibility to eliminate or even reduce the amount of these compounds released to the atmosphere. However, according to United Nations-European Committee (UNECE) Protocol, PAHs should have been included in that list since they are chemicals whose releases must be prevented or minimized.

Toxicity

Health effects of PAHs have been largely studied, especially in the last years. However, the complete knowledge about PAH toxicity is still uncertain, since every single compound may show different human health effects. Thus, although tumorigenicity and carcinogenicity of individual PAH and PAH-containing mixtures have been widely investigated in experimental animals, evidence on carcinogenicity in humans is weak (Hammerle et al., 1994). Benzo[a]pyrene (B[a]P) has been, until now, the individual compound which more attention has received. Numerous studies have concluded that exposure to B[a]P and PAH mixtures containing this compound could induce cancerigen effects. Several experimental studies carried out in rodents have demonstrated that individual subjects developed skin, lung, stomach and liver cancer following PAH-containing mixture exposure (Lavoie et al., 1987; Horikawa et al., 1991). Some PAHs have been reported to suppress immune reaction in rodents as a previous step of cancer induction (White Jr. et al., 1985). On the other hand, epidemiological studies have detected an increase in lung cancer in humans occupationally exposed to coke oven emissions and cigarette smoke, presumably containing large amounts of PAHs (ATSDR, 1995; Armstrong et al., 2004). In consequence, B[a]P was classified as a probable human carcinogen (Group B2) by the USEPA (2002) and as probably carcinogenic to humans (Group 2A) by the IARC (1983). A value of 7.3 $(\text{mg/kg/day})^{-1}$ has been defined as the oral cancer slope factor for B[a]P (US EPA, 1999). Besides B[a]P, only other 6 PAHs else have been considered to be carcinogenic. All these (benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenzo[a,h]anthracene, and indeno[1,2,3-c,d]pyrene) have been included in the Group B2 by the US EPA (US EPA, 2002). In turn, apart from B[a]P, the IARC has only considered benzo[a]anthracene as a probable carcinogenic agent (Group 2A), while the remaining 5 just reached the consideration of possible carcinogenic agents (Group 2B).

Because PAH exposure is always through PAH-containing mixtures, some investigations have been performed in order to estimate how toxic a mixture of hydrocarbons might be. Specifically, a PAH TEF-based approach, similar to PCDD/Fs I-TEF, has been developed. In this case, toxicity of each individual compound is compared to that of B[a]P, which receives a TEF=1. Concentration is then expressed in B[a]P-equivalents (BaP-eq). Table 3 shows the BaP-TEF for different PAHs, estimated by various investigators.

Non-cancer effects following chronic exposure to PAHs include eye irritation, photophobia and skin disorders (dermatitis and keratosis), as well as disorders in the respiratory system and fibrosis. Although immunotoxicity and developmental toxicity have not been so deeply studied as carcinogenicity in both humans and animals, they could be important toxic endpoints (Winker et al., 1997; Karakaya et al., 2004). However, it must be taken into account that no deaths have been reported from short-term occupational exposures in humans (Muller et al., 1997).

Table 3. Values of BaP-TEF according to various studies.

PAHs	*(Thompson et al., 1990)*	*(US EPA, 1993)*	*(Nisbet and LaGoy, 1992)*	*(Larsen and Larsen, 1998)*
Naphthalene	-	-	0.001	-
Acenaphthylene	-	-	0.001	-
Acenaphthene	-	-	0.001	-
Fluorene	-	-	0.001	-
Phenanthrene	-	-	0.001	-
Anthracene	-	-	0.01	0.0005
Fluoranthene	-	-	0.001	0.05
Pyrene	0.081	-	0.001	0.001
Chrysene	0.0044	0.001	0.01	0.03
Benzo(a)anthracene	0.145	0.1	0.1	0.005
Benzo(k)fluoranthene	0.066	0.01	0.1	0.05
Benzo(b)fluoranthene	0.14	0.1	0.1	0.1
Benzo(a)pyrene	1	1	1	1
Indeno(123-cd)pyrene	0.232	0.1	0.1	0.1
Dibenz(ah)anthracene	1.11	1	5	1.1
Benzo(ghi)perylene	0.022	-	0.01	0.02

Bioaccumulation

Although all PAHs have a similar chemical structure, their physical and chemical properties can vary enormously. Octanol-water partition coefficients, which give an idea of the capacity of accumulation in a living organism, range from 3.37 to 6.75, corresponding to naphthalene and dibenzo(ah)anthracene, respectively. In general terms, only the most weighted PAHs have a relatively high bio-accumulation potential, with bioconcentration factors (BCF) up to 100,000 (IPCS, 1998). By species, some organisms, such as fish and higher invertebrates, bioaccumulate low amounts of PAHs because they can easily metabolize them (Edlund, 2001). However, some metabolites may be toxic as well (Simioli et al., 2004). The lack of biomagnification potential for some PAHs is one of the reasons why PAHs are not considered POPs, and therefore, included in the list of chemicals to be restricted.

Persistence in the environment

PAH volatility is highly dependent on the molecular weight. In the atmosphere, light PAHs are frequently found free due to their low vapor pressure, whereas larger molecular weight compounds are mostly adsorbed onto particular matter. In aquatic compartments, in spite of their low solubility, only low molecular weight PAHs can sometimes be found dissolved in water. Most of them are almost exclusively bound to particulate matter. Likewise, reported half-lives in the environment differ notably according to the PAHs under analysis. In air, lower molecular weight PAHs undergo photodegradation quite quickly in front of sunlight. In water, as well as soil and vegetation, photolytic processes of degradation are partly substituted by microbial activity which decompose PAHs into more elemental compounds (Wammer and Peters, 2005). In sediments, biodegradation is the most important PAH degradation pathway. In spite of all the above, PAHs with 4 or more rings present a long persistence in the environment in general, and in soils and sediments in particular.

Long-range transport

The physical and chemical properties of PAHs make them suitable candidates for dispersion by long-range atmospheric transport (Aamot et al., 1996; Brun et al., 2004). The atmosphere is the main medium of transport for PAHs. Adsorption on air particulate matter is the main travel pathway in air. However, some light hydrocarbons travel as vapor because of their high volatility. Consequently, not only lower molecular weight, but also heavy particle-bound PAHs, can travel long-distances and deposit far away from where they are released. Thus, some PAHs levels have been detected in remote areas of the planet such as the Arctic, in air (Prevedouros et al., 2004; Hung et al., 2005), sediments and biota (Sericano et al., 2001).

Sources

PAHs are formed as byproducts of incomplete combustion processes. Primary natural sources of airborne PAHs are forest fires and volcanoes (ATSDR, 1995; Wilcke, 2000). However, in recent decades, anthropogenic sources have become more important contributors of PAH release to the atmosphere. Unlike chlorinated compounds, residential burning of wood has been pointed out as the most significant pathway of PAH entrance into the environment, specially in northern and forested countries (Boström et al., 2002; Mandalakis et al., 2005). The use of coal in domestic burning has been also identified as a major contributor to total PAH emissions, and the biggest single emitter of B[a]P (Lee et al., 2005a). Other anthropogenic stationery sources include power generation, incineration and petrochemical manufacturing (Edwards, 1983; ATSDR, 1995). Water and soil pollution by PAHs are basically the result of atmospheric deposition, although refinery effluents, oil spills and automotive exhaust can also contribute (ATSDR, 1995). Mobile sources account approximately a 20% of the total PAH released to the atmosphere, being vehicular exhaust from gasoline and diesel-powered engines the most important contributors (Dunbar et al., 2001). PAH emissions from traffic become really important in urban and suburban areas (Glaser et al., 2005). In indoor air, one of the most important exposure pathways is direct and environmental tobacco smoke. An exposure to carcinogenic PAHs and B[a]P of 5 μg/packet and 0.4 μg/packet has been reported (Kaiserman and Rickert, 1992; Menzie et al., 1992).

Heavy metals

The exposure to some heavy metals has been associated to a huge variety of adverse health effects, including cancer. Moreover, although some elements are essential for humans, they can be dangerous at relatively high exposure levels (Domingo, 1994). Considering their potential toxicological importance, arsenic (As), cadmium (Cd), chromium (Cr), mercury (Hg) and lead (Pb) must be especially taken into account. Other elements such as manganese (Mn) and vanadium (V) must be also bore in mind if presumably high concentrations are expected in a specific area.

Arsenic

Arsenic (As) is an element classified as a metalloid, since it presents metal and non-metal properties. It occurs naturally in the Earth’s crust, with levels ranging between 2 and 5 mg/kg (ATSDR, 2000a). Primary natural sources of As released to the atmosphere are wind-blown dirt and volcanoes, but contributions of natural sources are largely exceeded by anthropogenic sources. Pesticides and fertilizers application in agriculture is one of the most important entrance pathways of As into land, primary, and water, indirectly (Dich et al., 1997; Basu et al., 2001). Air releases of As include coal and wood combustion, metal mining and smelting, and waste incineration.

Arsenic can be found in 2 different species: inorganic and organic. While inorganic As appears as As_2O_3, As_2O_5 or AsH_3, and it is the most toxic form, organic As occurs through biotransformation carried out by different organisms as a detoxification way, and it is fairly less harmful than inorganic form (Pongratz, 1998).

Non-occupational exposure to As is basically due to food intake. Fish and shellfish are the foodstuffs with a higher content of this element. Fortunately, the percentage of organic As (usually as arsenobetaine) over total As concentration is notably higher in comparison to inorganic As (Fattorini et al., 2004).

Arsenic and As compounds have been recognized as carcinogenic to humans (Group I), on the basis of sufficient evidence (IARC, 1987). Epidemiological studies have revealed an association between high arsenic concentrations in drinking water and increased incidences of skin cancers (Rossman et al., 2004). Likewise, a positive correlation has been established between inhalation to arsenic and lung cancer. This element has been also convincingly associated to development of lung, liver, kidney and bladder cancers (Huff et al., 2000). Oral and inhalation slope factors have been established in 1.5 and 15 $(mg/kg/day)^{-1}$ (US EPA, 2000b). Non-carcinogenic effects following an exposure to As include skin disorders as well as problems in the nervous and cardiovascular systems. The estimated Reference Dose (RfD) for chronic and subchronic oral exposures is $3 \cdot 10^{-4}$ mg/kg/day.

Cadmium

Cadmium (Cd) is a widespread element naturally found in the Earth's crust (ATSDR, 1999a; Pinot et al., 2000). Mineral weathering, volcanoes and forest fires are the main natural sources. However, it has been estimated that worldwide anthropogenic emissions of cadmium exceed natural ones by a factor close to ten (Elinder, 1992). Coal, wood and oil combustion, waste incineration and metal production have been found the most important anthropogenic sources of Cd released to the atmosphere. In soils, the main Cd pathway is through application of phosphate fertilizers. Leaching from polluted soils and industrial discharged effluents contribute to cadmium pollution in the aquatic compartment.

Inhalation is the main exposure pathway of Cd entrance into the human body. In fact, tobacco smoke seems to be an important contributor of this heavy metal, specially in indoor air. Average Cd levels in cigarettes range from 1 to 3 µg/kg (Massadeh et al., 2005). Gastrointestinal absorption hardly reaches 5% of the total intake, whereas absorption by lungs may be up to 50% (Robards and Worsfold, 1991). Cadmium is transported in the blood and widely distributed in the body, accumulating primarily in liver and kidneys (Goyer, 1991). Diet is another important way of exposure to Cd, mainly through ingestion of cereals, and fish and shellfish (Llobet et al., 1998). In fact, one of the most important episodes of food poisoning is the "Itai-Itai" syndrome (Japan). Population living near

Jintsu was poisoned after consumption of rice and drinking water with high concentrations of cadmium (Inaba et al., in press).

Acute exposure to Cd can cause fatality in humans. Exposure to lower amounts may cause gastrointestinal irritation, vomiting and diarrhea, if cadmium is ingested, or headache, chest pains, and pulmonary edema, if it is inhaled. An oral reference dose of $5 \cdot 10^{-4}$ mg/kg/day has been estimated for ingestion of this element. Cadmium has been linked to induce prostate and lung cancers in laboratory and epidemiological studies (Waalkes, 2000; Sahmoun et al., 2005). This element has been classified as carcinogenic to humans (Group 1) by the IARC, and probable human carcinogen (Group B1) by the US EPA. An inhalation slope factor of 6.1 $(\text{mg/kg/day})^{-1}$ has been estimated on the basis of respiratory tract cancer associated with occupational exposure (US EPA, 1999).

Chromium

Chromium (Cr) is a widespread element present in all environmental media (Shanker et al., 2005). Continental dust flux has been identified as the main natural source of exposure (ATSDR, 2000b). Volcanic dust and gas flux are minor natural sources of chromium in the atmosphere (Fishbein, 1981). However, anthropogenic sources have become very important in recent decades, and their contributions exceed notably those of natural sources. Chromium is released into the atmosphere mainly by anthropogenic stationary point sources, including gas, oil and coal combustion as well as metal industries (ATSDR, 2000b).

Chromium may appear in two forms: trivalent Cr(III), which is actually an essential nutrient to humans, and hexavalent Cr(VI), which is highly toxic. Inhalation is the main exposure pathway to Cr. Workers of steel and textile industries can be exposed to this element through inhalation of chromium-containing dust and fume, or through direct contact of Cr solutions. Since total chromium in mainstream cigarette smoke ranges 0.0002-0.5 µg/cigarette, tobacco smoke has been marked as another important way of exposure in indoor air (Rowbotham et al., 2000).

Hexavalent chromium has been classified as carcinogenic to humans (Group 1) by the IARC (1990), on the basis of different epidemiological studies showing sufficient evidence that exposure to Cr(VI) induces lung cancer. The US EPA (1999) has catalogued the hexavalent form of Cr as known human carcinogen, and subsequently, it has established an inhalation slope factor of 42 $(mg/kg/day)^{-1}$. A chronic exposure to Cr(VI) may produce non-cancer effects on the liver, kidney, gastrointestinal and immune systems. Moreover, harmful effects on skin (i.e., dermatitis, ulceration) can appear after dermal exposure to this metal. A value of $3 \cdot 10^{-3}$ mg/kg/day has been suggested as oral reference dose, based on the exposure at which no effects were noted in rats exposed to chromium in the drinking water.

Manganese

Manganese (Mn) is an ubiquitous element present in the environment. It occurs in soil, air, water, and food (ATSDR, 2000c). Anthropogenic sources of Mn include cement production plants, power plants, waste incineration, and combustion of fossil fuels.

In humans, Mn is an essential element for the human body for certain physiological functions (Torrente et al., 2005). Food intake is the main non-occupational exposure pathway. The estimated interval of Mn dietary intake is 2–5 mg/day for adults (Nkwenkeu et al., 2002; Bocio et al., 2005). Occupational exposure is basically through inhalation of dust. Chronic inhalation exposure of humans to manganese results, primarily, in effects on the nervous system (slower visual reaction time, poorer hand steadiness, and impaired eye-hand). Another important subsequent non-cancer effect is a syndrome called “manganism”, characterized by extrapyramidal dysfunction and neuropsychiatric (Zatta et al., 2003). When assessing risk from manganese in drinking water or soil, a RfD of 0.024 mg/kg/day is recommended (US EPA, 1999).

Mercury

Mercury (Hg) sources have both natural and anthropogenic origins. The main natural sources are volcanic activity and weathering of mercury-containing rocks. However, human activity developed during the last two centuries has significantly increased the average mercury level in the atmosphere (Mason et al., 1995). Coal and fossil fuel combustion, as well as waste incineration, mining and smelting, and industrial processes involving mercury such as chlor-alkali plants are important anthropogenic emission sources of Hg to air (ATSDR, 1999c; Conaway et al., 2005). In soils, the products that contribute mostly to Hg pollution are fertilizers, fungicides and municipal solid waste.

In the environment, Hg can be found as: a) elemental (Hg^0), b) divalent inorganic (Hg^{2+}), and c) organic mercury. Elemental mercury is the familiar form of this element, mainly used as indicator in thermometers, whose main feature is the fact of being liquid at a normal temperature. Mercury becomes inorganic when it combines with other elements, such as oxygen, sulphur and chlorine.

Mono methylmercury (CH_3Hg^+) is the mercury organic form, basically originated through biomethylation processes carried out by some marine microorganisms (bacteria, fungi and phytoplankton). Due to their physico-chemical properties and bioaccumulation capacity in the living organisms, mono mercurial organic compounds are the most toxic, causing very harmful effects in exposed populations (Booth and Zeller, 2005). Unfortunately, important precedent episodes regarding Hg pollution trough diet exist. The most important precedent occurred in Minamata (Japan) in 1950 and 60 decades. In those times, the Chisso chemical company (Japan) discharged a huge amount of waste effluents containing Hg, which was transformed to methylmercury and entered the food chain (Gochfeld, 2003). Fishermen and their families, whose diet was based on fish, were highly exposed to mercury. Death as well as development of very toxic effects in fishermen and their descendents were the consequences of that poisoning by organic Hg. The number of people who suffered the “Minamata disease” was established in around 3,000 dead and more than 10,000 sick. It is recognized one of the most important environmental pollution episodes of the 20th century (Eto, 2000).

Toxicity and absorption of Hg depend largely on its chemical form, as well as the entrance pathway to the body. Exposure to Hg^0 is usually occupational or may occur through use of dental amalgams fillings. Since lung retention is very high (Richardson, 2003), the main exposure pathway of this elemental form is inhalation. Through ingestion, inorganic salts of mercury are more toxic than the elemental form, and it is frequently found in drinking waters and soils, rather than in plants and animals (Lindqvist et al., 1991). Finally, methylmercury, as one of the most toxic forms of Hg, is the reference in terms of public health. Exposure to CH_3Hg^+ is oral, basically through fish consumption. It is easily absorbed in the digestive tract, being elimination hard. Therefore, it can accumulate in brain, liver and kidney.

Health effects resulting from a severe exposure to mercury depend on the chemical form of this element. On one hand, the primary health effect of methylmercury is impaired neurological development in infants and children. Other neurological effects found in exposed adult people are impairment of the peripheral vision, lack of coordination of movements, impairment of speech, hearing, and walking, as well as alterations in other body systems (Risher and Amler, 2005). Renal affections can be derived from chronic exposure to inorganic Hg. The US EPA has established an oral reference dose of $3 \cdot 10^{-4}$ mg/kg/day for mercury and its compounds. However, some differentiations have also been noted according to the chemical form. In consequence, the reference dose for methylmercury and elemental mercury has been established in $1 \cdot 10^{-4}$ mg/kg/day (oral) and $8.6 \cdot 10^{-5}$ mg/kg/day (inhalation), respectively.

Lead

Because of both, toxicological characteristics and dispersion in the environment, lead (Pb) has been one of the most studied heavy metals from a scientific point of view. Lead is formed naturally, but the main environmental pollution sources are anthropogenic. Among them, Pb emissions from vehicular traffic have been the most important pollution sources. Until late 20th century, Pb (as lead tetraethyl) was used an additive in gasoline. Due to harmful effects for human health, the US EPA banned the use of this kind of combustible in 1996 (ATSDR, 1999b). A few years later, the European Directive 98/70/CE on leaded gasoline prohibition was implanted in the European Union. Spain obtained a moratorium, and this kind of combustible was not definitively retired until 2001. In consequence, urban areas may be expected to be considerably polluted by Pb, especially in those developing countries where legislative measures have not been carried out yet.

Apart from use of leaded gasoline, other important anthropogenic sources of Pb released to the atmosphere are smelters, nonferrous foundries, and industries dealing with lead-containing products (ATSDR, 1999b). The incorrect use of batteries has been historically an important contribution of Pb to soils, although the concentration contained in these materials has been decreasing through years. Finally, this element has been largely used in different kinds of military ammunition, and scientific and medical equipment.

Elemental and inorganic compounds of lead are catalogued as possible carcinogenic agents in humans (Group 2B) by the IARC (1987). In turn, organic Pb is unclassifiable as to carcinogenicity to humans (Group 3). The health effects of Pb are mainly dependent on the developmental stage of exposure and magnitude of internal dose (Toscano and Guilarte, in press). The evidence shows that lead is a multitarget toxicant, causing effects in the gastrointestinal tract, hematopoietic system, cardiovascular system, central and peripheral nervous systems, kidneys, and immunological system (US EPA, 1999). In some patients, encephalopathy has been detected after acute exposure to Pb (Gordon et al., 2002).

Vanadium

Vanadium (V) is a heavy metal with a high presence in the environment. Vanadium is released naturally to air through the formation of continental dust, marine aerosols, and volcanic emissions. However, anthropogenic sources contribute to approximately 2/3 of the vanadium present in the atmosphere. Fossil fuels and coals contain important amounts of vanadium. Thus, combustion processes involving these materials release to air significant quantities of this element (Duce and Hoffman, 1976; Nriagu and Pacyna, 1988; Hope, 1997). Oil refining and burning of residual soils are other pollution entrance pathways of V into the atmosphere (Hope, 1997; Tudares, 1998). Unlike air, soil and water pollution is basically due to natural sources, such as weathering of rockbearing vanadium minerals, and wet and dry deposition from atmosphere.

Elemental vanadium does not occur naturally, but it is commonly present forming inorganic salts, such as vanadium pentoxide (V_2O_5) and sodium orthovanadate (Na_3VO_4). The toxicity of vanadium depends on its physico-chemical state, as well as on the human body circulating levels of this element (Domingo, 1996). Vanadium compounds are poorly absorbed through the gastrointestinal system (0.5-2% of dietary amount), but slightly more readily absorbed through the lungs (20-25%). It is now well established that vanadate (V^{+5}) and vanadyl (V^{+4}) may be reproductive and developmental toxicants in mammals (Domingo, 1996). Short-term localization occurs primarily in bone, kidneys, and liver (Roshchin et al., 1980). An oral reference dose has been recently established in $1{\cdot}10^{-3}$ mg/kg/day (US EPA, 2004).

Risk assessment

In recent decades, the interest about environmental issues has increased very quickly. Not only scientists, but also other active members of the society (i.e., politicians, industries, general public), have paid much attention in all aspects related to environment, in general, and environment protection, in particular. In this context, environmental pollution has been one of the fields where more efforts have been aimed to. Because of the lack of environmental consciousness and technical capacity, many industries released toxic substances to air, water and soil, for a number of years. As a first consequence, levels of pollution in areas surrounding industrial sites became much higher than *background* (unpolluted) zones. Recently, implementation of legislative measures carried out by public administrations has obliged to companies to improve their production processes in order to reduce the pollutant emissions. However, even though these measures are sometimes quantitatively quite restrictive, they are only focused on reducing the impact of an individual source of contamination, rather than aimed to control the integral state of the environment. It must be taken into account that industrial companies are rarely located isolately. Usually, they are in industrial sites together with many other facilities. Thus, these industrial complexes may include a large variety of potential sources of pollution which altogether can mean a significant entrance pathway of pollutants into the environment. On the other hand, in developed countries industries tend to be located close to city suburbs, so pollution may pose a potential risk for the population living near these facilities.

The concern resulting from the potential exposure to contaminants was the starting point to develop methodologies in order to evaluate the consequences that those might have over both the environment and human health. Among these methods, risk assessment has been one of the most widely used. Risk assessment is a formalized process for estimating the magnitude, likelihood, and uncertainty of environmentally induced health effects (Sexton et al., 1995). In 1983, the US National Research Council (NRC), in the so-called “Red Book”, defined a series of principles to be considered for human health risk assessment, and defined it as a process in which information is analyzed to determine if an environmental hazard might cause harm to exposed persons and ecosystems (NRC, 1983).

In addition to definition, NRC proposed a framework for human health risk assessment, which involved 4 basic steps (NRC, 1993):

a) *Hazard identification*

This step can be defined as the qualitative determination of whether or not a particular hazardous agent is associated with health effects of sufficient importance to warrant further scientific investigations. Different kinds of tools (QSAR, short-term toxicity test, etc.) are used in order to estimate the chemical damage of a single substance. When establishing the hazard from industrial sources, the chemicals are also identified according to measurements of amount and typology of emissions.

b) *Dose-response assessment*

This component is focused on examining quantitative relationships between the magnitude of the exposure (or dose) and the probability of occurrence of adverse effects in the population. Usually, dose-response assessment is based on extrapolations from data about laboratory animals, to which have been given high-doses of toxicant.

c) *Exposure assessment*

Exposure assessment may be defined as the quantitative determination of the extent of exposure of the population to the hazardous agent in question. Since they provide a real knowledge of the state of pollution of an area, data obtained in the environmental monitoring are commonly used as starting point.

d) *Risk characterization*

This fourth component can be defined as the description of the nature and magnitude of the risk, expressed in terms which are comprehensible to decision makers and the public. Information acquired in the previous 3 steps is integrated in order to communicate the overall meaning of, and confidence in, the hazard, exposure, and risk conclusions. Risk is expressed as a probability of suffering a particular kind of harm from a hazard to a specified group of population (Bennion et al., 2005). Moreover, qualitative and quantitative uncertainty related to risk must be also supplied.

As it has been seen, environmental monitoring is basic in order to carry out a correct evaluation of the exposure. Its aim is to determine quantitatively the concentration of pollutants in different media as a way to assess the impact of potential sources of contamination. Two approaches can be distinguished: biological and environmental monitoring. On one hand, human biomonitors, such as human milk, hair, adipose tissue, plasma and urine, may be used in surveillance programs. Although these may provide in a very realistic and direct way how population is exposed to pollution, they are very variable and highly dependent on personal characteristics, such as dietary habits, smoking, weight, etc., rather than on low-level environmental exposures (Paustenbach et al., 1997).

In contrast, the chemical analysis of the pollutant concentrations in different environmental compartments (i.e., air, soil, vegetation, sediments…) may be an interesting indirect methodology for human health risk assessment. Human exposure may be considered to occur through 2 routes: direct and indirect. Direct exposure is the sum of exposure to pollutants by direct pathways, such as air inhalation, dermal absorption or soil ingestion (US EPA, 1989a). In turn, pollutants can ultimately reach humans after crossing one or several paths, and they have been released by at least one intermediate (Rikken and Lijzen, 2004). For instance, contaminants can deposit in vegetation and, following the food chain, be ingested by animals. Finally, they can reach humans as a final step, through dietary intake, which should be considered consequently an indirect pathway of exposure. In fact, different studies have reported that food intake is the main exposure route to several pollutants for non-occupationally exposed populations (Capdevila et al., 2003; Hellström et al., 2004).

As it has been noted, it is imperative to adequately characterize variability and uncertainty in all the steps risk assessment process. In fact, this qualitative and quantitative characterization becomes critical in the fourth paradigm. Uncertainty and variability are related to heterogeneity inherit in the population and lack of total knowledge of the same, respectively (US EPA, 2001). Consequently, risk assessment must be performed since a probabilistic point of view, rather than by considering deterministic aspects. Monte-Carlo analysis has been increasingly used to adapt the necessity of including these aspects. This method has the advantage of allowing the analyst to account for relationships between input variables and of providing the flexibility to investigate the effects of different modeling assumptions (US EPA, 1997).

Risk assessment has been marked really as a procedure to link scientific information about potentially hazardous substances to the decision-making process, through which human exposures to these substances are regulated. A clear differentiation between the role of scientists (risk assessors) and decision makers (risk managers) in the evaluation process must be carried out (Williams, 2004). Risk assessment is just a part of risk analysis, which comprises 2 further steps: risk communication and risk management. Risk management is the subsequent stage where social, cultural, economic, and political issues are taken into account, and integrated to the evaluation process of risk. Finally, risk communication is the interactive exchange of information and opinions among individuals, groups and institutions.

The chemical/petrochemical complex of Tarragona, Spain

The geographic location of the city of Tarragona (Catalonia, Spain) has been crucial in the economic development of the zone throughout the history. Tourism and industrial activity have been, and still remain, two basic important axis on which the local economy has been held on. Already 2000 years ago, the city (then known as Tarraco) was strategically located in the Roman Empire, and its vital importance as manufacturer and exporter of products was widely recognized. During the 18th and 19th centuries, numerous industries raised in Tarragona, as well as in other neighbor urban nuclei (such as Reus, located at approximately 10 km). Notwithstanding, it was not until early 1960s that the industrial area of Tarragona started to become what it is today, with the constitution of the cradle of the actual AEQT (Chemical Companies Association of Tarragona). During that decade and the beginning of the following one, several important chemical companies (ASESA, Dow Chemical, BASF, Aragonesas, Aiscondel, Bayer, Messer Carburos…) settled down in the suburban area of Tarragona. In the mid-1970s, a big oil refinery (constituted later as Repsol) was inaugurated in the North complex. Since then, the number of companies established in the chemical/petrochemical complex of Tarragona has been continuously growing up (AEQT, 2004).

The industrial complex of Tarragona is one of the most important chemical/petrochemical areas in Southern Europe. In fact, according to the level of production, it is the most influent in Spain and it is ranked in the top 5 in all Europe. Its production capacity is approximately 18 million tones/year, including a wide range of products, such as chlor-alkali, propane, propilene, fuels, gasolines and derived products. With a global surface of 1190 ha, the industrial complex is divided into 2 zones: North and South (Figure 4).

The Northern zone is basically a petrochemical area, where the big oil refinery of Repsol/YPF is located. Repsol/YPF is a petrochemical, chemical and gas company, whose main production is the manufacturing of petroleum, as well as oil derivates, petroliferous products, liquid gases and natural gases. This facility has a production capacity of crude of 8,000,000 tones/year, and it has two stacks and two burning torches with a height of 110 m and 114 m, respectively. The Northern zone is complemented by Repsol Química (the chemical branch of the company aimed to production of polyethylene and polypropylene) and Dow Chemical (ethylene plant).

On the other hand, the Southern zone is basically composed by chemical industries. Production of some important facilities, such as Dow Chemical and BASF, includes chemicals related to plastics and derivates: polyethylene, polystyrene, as well as some synthesis gases. In the South-western corner of this pole, Aiscondel, an important plant of vinyl chloride monomer (VCM) and polivinyl chloride (PVC), is settled down together with other chlor-alkali plants (Aragonesas and Bayer). Moreover, in the Eastern side of the complex, Asesa, another crude refining plant of 1,400,000 tones/y operate.

Concurrently with the above described facilities, a municipal solid waste incinerator (MSWI) and a hazardous waste incinerator (HWI) are located near the village of Constantí. In addition, the area is crossed by a highway and several important roads supporting an intense traffic.

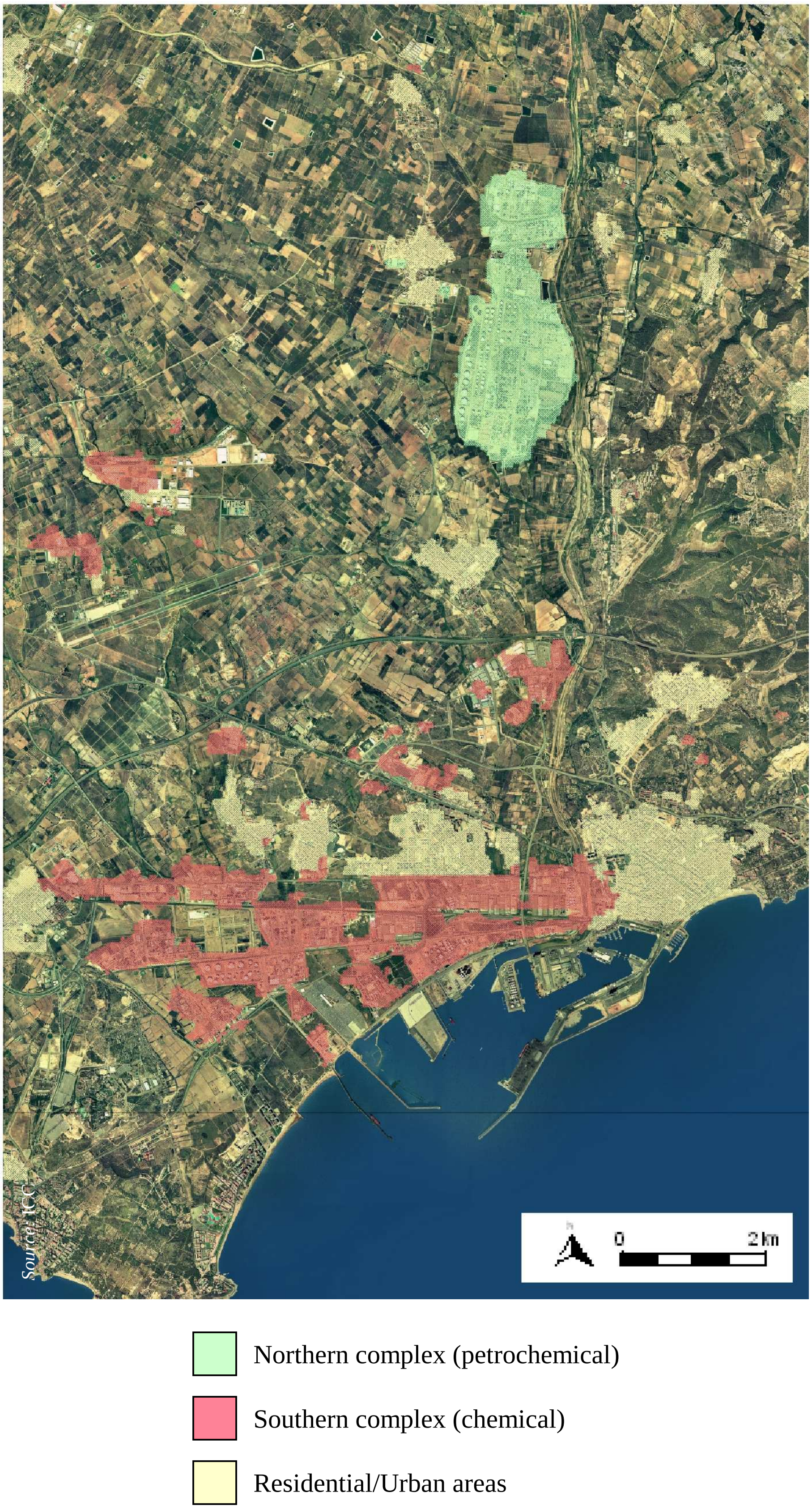

Figure 4. Chemical and petrochemical industrial complexes of Tarragona.

HYPOTHESES AND OBJECTIVES

Hypotheses

In the industrial area of Tarragona, different chemical and petrochemical facilities are located. It means that this area is subjected to emissions of a large number and variety of organic and inorganic pollutants. The exposure to these chemicals could mean a potential risk for human health of people living in the vicinity of the industries. The presence of two incinerators and several important roads are also two additional elements to be taken into account when assessing the potential health impacts for the local population.

Petroleum refineries are potentially important releasers of toxic substances such as PAHs. Considering that a big oil refinery has been operating for many years in Tarragona, notable concentrations of these compounds could be expected in the environment of the area under its direct influence. Since other important chemical companies are also established in the industrial complex, the presence and levels of PAHs as well as other inorganic (heavy metals) and organic (PCDD/Fs, PCBs and PCNs) pollutants in the surrounding environment could be even more significant.

However, previous investigations carried out near potential specific sources of PCDD/Fs and heavy metals, such as MSWI and cement plants, have shown that human exposure to these pollutants is mainly due to ingestion of foodstuffs, rather than due to direct emissions of these industries. Consequently, it is suggested that the influence of environmental levels of the above indicated pollutants in the chemical/petrochemical area of Tarragona could be minimal in comparison to exposure through food intake.

In conclusion, it is hypothesized that, considering the large amount of potential emission sources of pollution in the chemical/petrochemical complex of Tarragona, environmental levels of organic and inorganic pollutants might be very high in this zone. Likewise, a notable high risk might derive from an exposure to those pollutants by the local population.

Objectives

General objective

To assess the human health risks due to exposure to a number of metals, PCDD/Fs, PCBs, PCNs and PAHs for the population living near the chemical/petrochemical area of Tarragona.

Specific objectives

- To determine the concentration of 7 heavy metals (As, Cd, Cr, Hg, Mn, Pb and V) in soil and chard samples collected in industrial and residential areas of Tarragona.
- To determine the levels of PCDD/Fs, PCBs, PCNs and PAHs in the same samples.
- To characterize the most environmentally polluted zones by applying different classificatory tools.
- To determine the influence of local environmental conditions on the degradation of specific pollutants.
- To establish the exposure to those pollutants for the population living near the industrial area, as well as for those living in urban zones.
- To assess the human health risks due to exposure to PCDD/Fs and heavy metals.
- To elaborate a multichemical integral risk index and apply it for a number of pollutants.
- To design a map of risk of the chemical/petrochemical area of Tarragona based on an integral risk index.

MATERIALS AND METHODS

Sampling

In the winter of 2002, 24 soil and 12 wild chard (*Beta vulgaris*) samples were collected in various zones of Tarragona County (Figure 5). Soil and vegetation (chard) samples were selected for representing long- and short-term environmental monitors where pollutants are accumulated. Soil sampling points were chosen as follows: 15 in the industrial complex divided into industrial-1 (8 samples collected in the vicinity of chemical industries) and industrial-2 (7 samples collected near the Repsol/YPF oil refinery and petrochemical industries), 5 in urban (Tarragona downtown) and residential (several suburbs of Tarragona city) zones, and finally, 4 samples in presumably unpolluted sites (pesticides-free rural uncultivated land), located 30 km far away from the area of direct influence of all suspected sources of contamination. Every sampling point was selected depending on: 1) the location of potentially important focuses of contamination, 2) according to the possibility of getting meteorological data in the zone (in order to get a better understanding of the process of contaminants dispersion), and 3) bearing in mind the proximity to residential areas in which people might be affected by industrial emissions. Several subsamples were collected at the same time as bulk samples within approximately 10 m^2 in each sampling site. Duplicate soil samples were taken from the upper 3 cm of soil and kept in polyethylene bags. Once in the laboratory, samples were moved to aluminum foils in order to prevent adsorption by plastic. They were dried at room temperature until constant weight and sieved through a 2-mm mesh screen.

Chard samples were collected in 12 of the 24 sites in which soil samples were taken. Six samples were collected in the industrial zone (industrial-1 and industrial-2, indistinctly), 3 in the urban/residential zones, and 3 in unpolluted sites. Chards were about 20 cm high at the collection time. When samples were collected the weather was sunny. There was no precipitation at least during the 10 days previous to collection. Chard samples were obtained by cutting the aerial part of the plant, and subsequently packed in aluminum foils. They were dried at room temperature and shredded with a domestic shredder. Finally, samples were kept in a double aluminum foil, packed in labeled plastic bags, and stored at room temperature until analyses protected from the solar light.

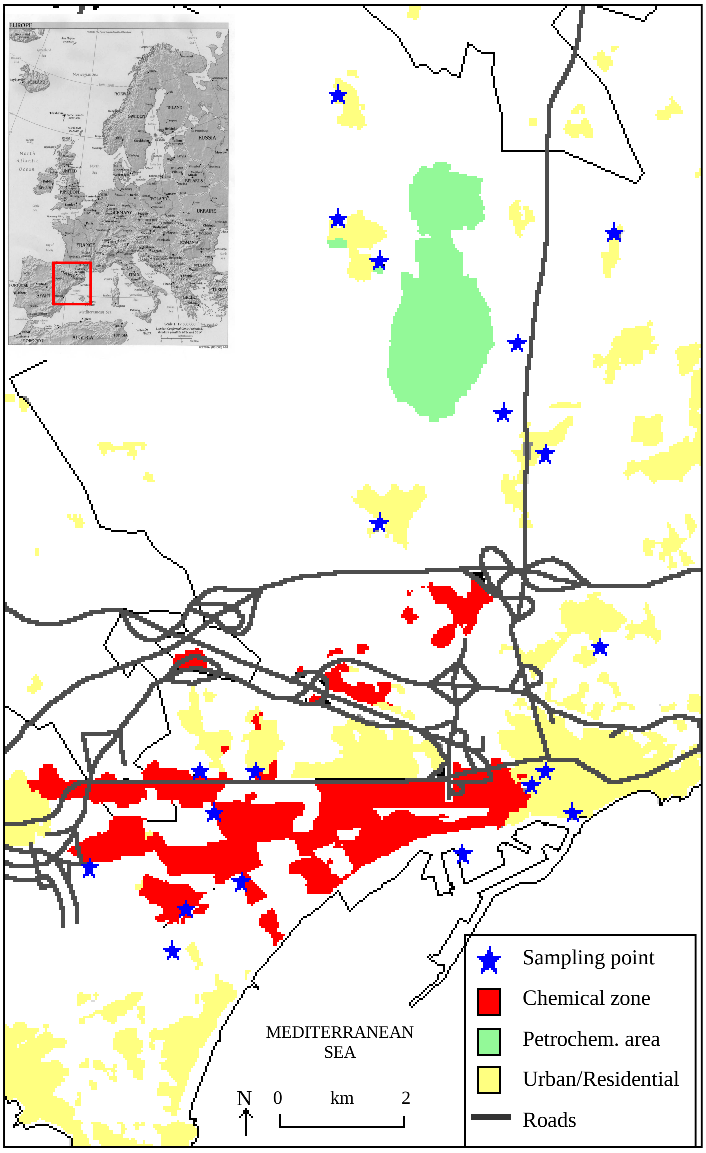

Figure 5. Sampling points in the area of study

Analytical procedure

Soil parameters

The values of pH and organic matter content of the soil samples were also determined. Fifteen grams of sample were dissolved in 15 ml of deionized water, and after mixing for 24 h the measurement of pH was done with a pH-meter. Organic matter content was evaluated according to the Loss on Ignition (LOI) method. Samples were dried in order to eliminate water content. Subsequently, they were heated for 2 h at 600ºC and the weight loss was assessed.

Heavy metals

Approximately 0.5 g of dried samples of soil or chard were treated with 5 ml of nitric acid (65% Suprapur, E. Merck, Darmstadt, Germany) in Teflon vessels for 8 h at room temperature. Subsequently, they were heated at 80ºC in a stove for 8 h. After cooling, solutions were filtered and made up to 25 ml with deionized water. Concentrations of As, Cd, Cr, Hg, Mn, Pb and V in soils were determined by inductively coupled mass spectrometry (ICP-MS, Perkin Elmer Elan 6000). In chard samples, the levels of As, Cd, Hg, Mn and Pb were measured using ICP-MS, while Cr and V concentrations were determined by atomic absorption spectrometry with graphite furnace atomization (Varian spectrophotometer, Spectra A-30) (Meneses et al., 1999). The accuracy of the instrumental methods and the analytical procedures was checked by duplication of the samples, as well as by using a reference material (Lobster hepatopancreas, NRC Canada, TORT 2), which was run up every 10 samples. The mean recovery rates were between 80% and 95%. The limits of detection (LOD) for metals in soils and chards were the following: 0.025 µg/g for Mn, Pb and Cd, 0.05 µg/g for Hg, and 0.1 µg/g for As. In turn, the detection limit for Cr and V was 0.25 µg/g in soils and 0.01 µg/g in chards.

Organic compounds

PCDD/Fs, PCBs and PCNs

POP concentrations were determined in accordance to the German VDI 3499 and US EPA 1625 guidelines. Prior to extraction, dried samples were homogenized and spiked with a mixture of internal standards ($^{13}C_{12}$-labelled PCDD/Fs and PCBs). Subsequently, samples were extracted in a Soxhlet with toluene for 16 h. The clean-up procedure and fractionation of the crude extract was carried out by adsorption chromatography as a multi-step-clean-up, using consecutively a multilayer silica column (from top to bottom: sodium sulfate, silica, silica-sulphuric acid, silica, silica-potassium hydroxide, silica) and an alumina column. For chard samples, additionally, a 70 g BioBead-SX3- gel permeation chromatography column and gel permeation columns were used. The sample extract was concentrated by rotary vacuum evaporation, and dried with a nitrogen stream until a final volume of 10 µl. Prior to analysis, a ^{13}C-labeled standard was added to calculate recovery ratios. The cleaned extract was analyzed by high-resolution gas chromatography/high-resolution mass spectrometry (a Fisons CE 8000 gas chromatograph coupled with a VG Autospec Ultima system with electronic impact and a multiple ion detection mode, with a resolution > 10,000). PCNs were analyzed using a 60 m DB5ms-column. PCB and PCDD/F congeners were analyzed by a DB-XLB column. For analysis of PCDD/Fs, additional polar columns of a CP-Sil-88-type were used in order to confirm the obtained values for the lowest chlorinated congeners. The recovery rates of the analyzed POPs were in the range of 42-117%. Detection limits for tetra- and penta-CDD/F homologues were 0.05 ng/kg, whereas that for hexa- and hepta-CDD/Fs was 0.1 ng/kg. Finally, OCDD/Fs presented a LOD of 0.2 ng/kg. In addition, detection limit for all PCB congeners and PCN homologues was 0.10 ng/kg, in both soils and chards.

PAHs

PAH levels were determined according to US EPA method 8100. Soil and chard samples were firstly homogenized and subsequently spiked with deuterated d_{10}-fluorene and d_{10}-pyrene (Cambridge Isotope Laboratories), which acted as internal standards. Extraction step consisted on a Soxhlet with hexane/dichloromethane (1:1). As for soils, copper (Merck, Darmstadt, Germany) was added in order to eliminate its content of sulfur. The clean-up procedure was carried out by passing the extract through an alumina adsorption column (from top to bottom: sodium sulphate, alumina B – Super I activated overnight, and glass fiber). Hexane and a mixture of hexane/dichloromethane (1:1) were consecutively passed through the column as fractionation method. Naphthalene was recovered in the first fraction and the remaining 15 analyzed PAHs were found in the second one. Subsequently, all fractions were again evaporated with a rotavapor and concentrated with a gentle stream of purified N_2 to 40 µl.

Prior to injection, d_8-napthalene was added as an internal standard. The samples were analyzed by a gas chromatograph (Agilent 6890, Wilmington, DE, USA) equipped with a fused silica capillary column (HP-5: 30 m long, 0.25 mm i.d., 0.25 µm film thickness) and a Flame Ionization Detector (FID). The oven temperature started at 80ºC. It was then raised at 25ºC/min up to 160ºC. A new ramp of 3ºC/min was started until 300ºC, when the temperature was held for 5 min. The inlet mode chosen was splitless and helium as carrier gas (17.8 mL/min). Inlet and detector temperatures were 310ºC and 325ºC, respectively. In soils, mean recovery percentages were 76.2 and 90.0% for d_{10}-fluorene and d_{10}-pyrene, respectively. In chard samples, d_{10}-pyrene recovery reached a 98.9% although d_{10}-fluorene, behavior could not be determined because of the presence of an interfering peak. Detection limit for soils and chards was 2 ng/g (dry weight).

Data analysis

Statistical analysis of the results was carried out with the statistical package SPSS 11.0. In those samples in which a compound was not detected (ND), its concentration was assumed to be one-half of the limit of detection (ND = ½ LOD). Statistical significance of the differences was determined by one-way analysis of variance (ANOVA) for variables with normal distribution, and the Kruskal-Wallis test for those with no normal distribution. A probability of 0.05 or lower ($p<0.05$) was considered as significant.

Self-Organizing Map (SOM) application to heavy metals

Kohonen’s SOM is a special kind of Artificial Neural Network (ANN). It was originally proposed by Kohonen (1982), and it is based on an unsupervised competitive learning algorithm. That means that the training is entirely data-driven and the neurons of the map compete among them (Vesanto, 2000). SOM provides a projection of multidimensional data into a lower (usually two-) dimensional map, preserving the topology of the original data. In fact, SOM is a process based on *data mining*, which could be considered as a further step from the classic statistical tools. Although the objective of both SOM and traditional statistical methods is to classify large amounts of data by reducing the dimensionality of data, Kohonen’s map presents great advantages. The main difference is that SOM technique can construct models automatically without a priori knowledge of the data. In fact, unlike other methodologies, this unsupervised ANN deals very efficiently with non-linear and heterogeneous data. Likewise, the clustering procedure has been shown to be as good as (or even better than) that of other cluster analysis methods (Waller et al., 1998).

The Kohonen neural network consists of two layers: the input layer, connected to a vector of the input data set, and the output layer (or map), which is an array of nodes (also called neurons). The number of cells must be chosen before the learning process as the best compromise between representation clarity and computing time (Brosse et al., 2001). To interpret the results, SOM visualization process starts with the map itself. Each of the SOM nodes has a specific weight, allowing to cluster the original information (Espinosa et al., 2002). The weights associated to each node or neuron in a this twodimensional lattice are adjusted to cluster the original information. The map can also be divided into so many c-planes (component planes) as data variables, representing the variable contribution to each node in the map. SOM can be thought as a cake consisting of component layers. Each component plane is a horizontal layer of this cake, while each reference vector is a vertical slice (Nadal et al., 2004).

In order to establish the behavior of the different metals analyzed, as well as to characterize the most polluted areas by these elements, a SOM was executed. In this case, the chosen Kohonen's map was a rectangular grid of 35 virtual units (7 x 5 hexagons). Each, the learning and tuning phases, were broken down with 10 000 steps.

Principal Component Analysis (PCA) applied to organic pollutants

PCA was originally introduced in the early 1900s (Pearson, 1901; Hotelling, 1933), and it is one of the most popular multivariate analysis tools. The objective of PCA is to derive total variance of a set of multivariate data to a few new uncorrelated components (called principal components or PC), each of which is as a linear combination of the original variables. PCA involves assigning a score to each sample in each component, allowing a quick classification and a further easy visualization.

In the present study, PCA was used to establish the relationship of POP content in soils and chards according to the different zones of collection. Since behavior of chlorinated and non-chlorinated compounds can differ widely, two multivariate analyses were carried out: one for PCDD/Fs, PCBs and PCNs, and another one for PAHs.

Health risk assessment

Heavy metals

In order to assess non-carcinogenic risks, concentrations of all metals in soil were compared with the levels of metals considered as safe for people living in residential areas (Preliminary Remediation Goals or PRG) (US EPA, 2000b). Non-carcinogenic risks were also assessed by calculating the Hazard Quotient (HQ), defined as the relation between the predicted exposure and the oral reference dose (RfD_o). The criteria used for calculations were taken from US EPA (2000b). Predicted inhalation exposure to all elements was also calculated.

With regard to carcinogenic risks, the levels of those carcinogenic metals (As, Cd and Cr) were compared to PRG. Likewise, cancer risks through ingestion and inhalation were also assessed by multiplying the predicted exposure, on one hand, and the oral or inhalation slope factor, on the other hand.

PCDD/Fs

A probabilistic health risk assessment was carried out for PCDD/Fs. Specifically, a Monte-Carlo approach (by running Crystal Ball$^{©}$ 4.0 software) was done in order to take into account variability and uncertainty aspects of data.

Exposure assessment

To assess PCDD/F exposure, 2 different routes were considered:

1) Direct contact, including air inhalation, dermal absorption through soil and dust, and soil and dust ingestion.
2) Dietary exposure.

1. Direct exposure

All calculations were carried out according to previously reported equations (Nouwen et al., 2001; Domingo et al., 2002). The "worst scenario" hypothesis was raised in terms of absorption factor for ingested food (bioavailability of 100%), and exposure time to polluted air (24 h day^{-1}).

2. Dietary exposure

It was calculated taking into account the PCDD/F concentration for different food groups and the food ingestion rate for each of them. Data about PCDD/F levels in foodstuffs were obtained from a recent survey performed in our laboratory (Llobet et al., 2003b). In this survey, the daily intake of PCDD/Fs by the population of Catalonia was determined. On the other hand, data about food consumption depending on the socioeconomic level, were used to determine the dietary exposure to PCDD/Fs for the population living in suburbs (lower class) and residential zones (upper class) (Capdevila et al., 2000).

Risk characterization

Human health risks of PCDD/Fs were divided into:
a) Non-carcinogenic risk: assessed as Hazard Quotient, by comparing total exposure (sum up of direct and dietary exposure, in ng/kg/day) respect to tolerable dietary intake (TDI, in ng/kg/day).
b) Carcinogenic risk: by multiplying total exposure (ng/kg/day) by the carcinogenic slope factor (kg·day/ng).

All the Monte-Carlo parameter distributions for the calculations of direct and dietary exposure to PCDD/Fs, as well as human health risks, are included in Annex 1.

RESULTS AND DISCUSSION. ARTICLES

Article I

Nadal M, Schuhmacher M, Domingo JL

Metal pollution of soils and vegetation in an area with petrochemical industry

Science of the Total Environment 321: 59-69 (2004)

Article II

Schuhmacher M, Nadal M, Domingo JL

Levels of PCDD/Fs, PCBs, and PCNs in soils and vegetation

in an area with chemical and petrochemical industries

Environmental Science and Technology 38: 1960-1969 (2004)

Article III

Nadal M, Schuhmacher M, Domingo JL

Levels of PAHs in soil and vegetation samples from Tarragona County, Spain

Environmental Pollution 132: 1-11 (2004)

Article IV

Nadal M, Schuhmacher M, Domingo JL

Probabilistic human health risk of PCDD/F exposure: a socioeconomic assessment

Journal of Environmental Monitoring 6: 926-931 (2004)

Article V

Nadal M, Wargent JJ, Jones KC, Paul NG, Schuhmacher M, Domingo JL

Interlatitudinal comparison of the influence of UV-B

radiation and temperature over PAHs photodegradation

Submitted to *Atmospheric Environment*

Article VI

Nadal M, Kumar V, Schuhmacher M, Domingo JL

Definition and GIS-based characterization of an Integral Risk Index applied to a petrochemical area

Submitted to *Chemosphere*

RESULTS AND DISCUSSION. SUMMARY

Soil parameters

The mean pH of soils was 7.66 (7.03-8.22), while the mean content of organic matter in the 24 soil samples was 5.8% (2.6-9.5%). Significant Pearson correlations with organic matter were found for Pb ($p<0.01$) as well as for Hg and Cd ($p<0.05$). With regard to organic compounds, the organic matter content was only significantly correlated with PCBs and PCNs ($p<0.01$ and $p<0.05$, respectively).

Heavy metals

Article I: Nadal M, Schuhmacher M, Domingo JL
Metal pollution of soils and vegetation in an area with petrochemical industry
Science of the Total Environment 321: 59-69 (2004)

With regard to soils, samples collected in the industrial area presented the highest concentrations, for all the analyzed heavy metals, except for Pb. In turn, the levels of metals in the unpolluted soils were the lowest ones. However, the differences between both areas were statistically significant only for Cr (13.8 and 8.6 µg/g, respectively) and V (19.3 and 12.2 µg/g, respectively). On the other hand, Pb levels in the residential/urban zones were significantly higher than those observed in the unpolluted zone (66.1 and 14.6 µg/g, respectively).

In chard samples, significant differences of metal concentrations between the industrial and unpolluted areas were only found for V. In fact, vanadium was the only element where significantly higher levels were reported in both environmental monitors (soil and vegetation). That indicates that pollution by V is notable in the industrial area, in comparison to *background* levels.

The SOM application allowed to establish that the chemical area (industrial-1) presented a higher degree of pollution by heavy metals, respect to the petrochemical zone (industrial-2). Although in Article I all samples corresponding to both industrial areas (n=15) were considered as a whole, in Annex 2 a new Table has been added to present the results quantitatively according to the 4 areas of study (this is, splitting the industrial area into chemical and petrochemical zones). It is again noted that soil samples collected in the southern area showed higher levels of heavy metals, being this difference statistically significant for Cr and V.

Health risk assessment due to exposure to heavy metals

The comparison between metal levels in soils and the Preliminary Remediation Goals (PRG) let conclude that non-carcinogenic risks are not worrying either in the industrial zone or the residential area, since all values were well included in the safety interval. Likewise, although the Hazard Quotient (HQ), calculated from the predicted oral exposure, was higher in children than in adults, it did not exceed the safe value of 1 for any of the analyzed elements.

With respect to carcinogenic risks, only As levels in soils surpassed those marked as PRG, in both industrial and residential areas. Moreover, cancer risk derived from As ingestion was calculated in a higher value than 10^{-6} (considered as safe). Oral intake of arsenic is specially relevant for children living in residential zones, where a risk of $7.5 \cdot 10^{-6}$ was reported. Although As concentrations in soils found in a number of investigations worldwide are usually higher than those established as threshold by the US EPA (2000b), a serious effort should be done to reduce the environmental levels of this metal. On the other hand, concentrations of carcinogenic Cd and Cr were below the 100% of soil screening level, when they were compared to levels marked as PRG. Notwithstanding, inhalation of chromium slightly exceeded 10^{-6}, basically because of the assumption that Cr^{6+} (the carcinogenic form) meant 1/6 of the total chromium.

POPs

Article II: Schuhmacher M, Nadal M, Domingo JL
Levels of PCDD/Fs, PCBs, and PCNs in soils and vegetation in an area with chemical and petrochemical industries
Environmental Science and Technology 38: 1960-1969 (2004)

PCDD/Fs

In relation to soils, mean PCDD/F concentrations ranged from 2.65 ng I-TEQ/kg d.m. (chemical area) to 0.16 ng I-TEQ/kg d.m. (unpolluted sites). PCDD/F levels of the residential soils were one-half of those corresponding to the chemical area (1.31 ng I-TEQ/kg d.m.), while the samples collected near the oil refinery showed a closer concentration to blank (0.45 ng I-TEQ/kg d.m.). Significant differences in PCDD/F levels were noted between samples collected in the chemical and residential zones, and those obtained in the petrochemical and unpolluted areas. Except for 1,2,3,7,8,9-HxCDF, all the PCDD/F congeners showed significant differences between the chemical and petrochemical areas.

In chards, mean PCDD/F concentrations were 0.46, 0.33 and 0.54 ng I-TEQ/kg d.m. in the industrial, residential and unpolluted zones, respectively. No significant differences were observed for any of the congeners, homologues or TEQ, according to the area of collection. In fact, chards sampled in the unpolluted sites showed higher concentrations than those obtained in the other two areas.

PCBs

The profile of PCB concentrations according to the sampling area was very similar to that presented by PCDD/F. In soils, the highest PCB levels were found in the chemical and residential areas (12038 and 10342 ng/kg, respectively). In turn, samples collected near the oil refinery seemed to present notable lower concentrations of PCBs (1965 ng/kg). Finally, PCB concentrations in soils of the rural zone were significantly lower than those observed in the other areas under study (657 ng/kg). Significant differences in ΣPCB (7 congeners) levels were detected in the soils obtained in the chemical area respect to the samples collected in the petrochemical and rural zones.

In chards, PCB concentrations did not differ significantly according to the area of collection. PCB levels ranged from 2503 to 2943 ng/kg, corresponding to the unpolluted and residential/urban areas, respectively. In these samples, ΣPCB concentrations were notably higher than those obtained in soils. Vegetation has also been remarked as a potentially important environmental sink following long-range transport.

PCNs

With respect to PCN levels in soils, samples of the chemical and urban areas showed also the highest concentrations (121 and 180 ng/kg, respectively), followed by the soils sampled in the petrochemical and unpolluted zones (70 and 32 ng/kg, respectively). However, these differences did not reach the level of statistical significance. The concentration of the octa-CN homologue was under the limit of detection for all samples.

ΣPCN concentrations in chards were not significantly different according to the zone of study. PCN levels were 214 ng/kg in the chemical/petrochemical zones, 172 ng/kg in the residential area, and 146 ng/kg in the rural zones. Neither hepta- nor octaCN were detected in any of the chard samples. On the other hand, tetra- and pentaCN concentrations in chards were higher than those found in soils.

PAHs

Article III: Nadal M, Schuhmacher M, Domingo JL
Levels of PAHs in soil and vegetation samples from Tarragona County, Spain
Environmental Pollution 132: 1-11 (2004)

With respect to the level of 16 PAHs in soil, samples of the chemical and residential zones were the most concentrated (1002 and 736 ng/g, respectively), while those corresponding to the petrochemical and unpolluted areas showed the lowest levels (166 and 122 ng/g, respectively). The same profile was obtained for the 7 carcinogenic PAHs: 397, 322, 70 and 37 ng/g for chemical, residential, petrochemical and unpolluted sites, respectively. Soils collected in the residential/urban areas presented a significant higher level of 4 individual PAHs respect to those obtained in the unpolluted zones. However, no significant differences were observed for the remaining 12 PAHs as well as for the summed concentrations of 16 PAHs and 7 carcinogenic PAHs.

In chards, samples collected in the residential area seemed to present the highest concentration of 16 PAHs, with a value of 179 ng/g. In turn, a value of 58 and 28 ng/g was detected in the vegetation samples taken in the industrial and unpolluted zones, respectively. For all the samples, the levels of the 7 carcinogenic PAHs as well as naphthalene were under their respective detection limits.

Health risk assessment due to exposure to PCDD/Fs

Article IV: Nadal M, Schuhmacher M, Domingo JL
Probabilistic human health risk of PCDD/F exposure: a socioeconomic assessment
Journal of Environmental Monitoring 6: 926-931 (2004)

Human health risks of PCDD/Fs were separately assessed for populations living near the industrial area and in Tarragona downtown, assuming that these populations belonged to lower and upper socioeconomic groups, respectively. With regard to direct exposure to PCDD/Fs, individuals living close to the chemical complex seemed to be more affected than those living in the urban center (mean values: $1.07 \cdot 10^{-5}$ and $4.66 \cdot 10^{-6}$ ng I-TEQ/kg/day, respectively). Among the exposure pathways, air inhalation was identified as the most important.

In relation to dietary exposure, people living in the residential zones seemed to show a slightly more elevated intake of PCDD/Fs, in comparison with the individuals residing in suburbs (mean values: $1.20 \cdot 10^{-3}$ and $1.01 \cdot 10^{-3}$ ng I-TEQ/kg/day, respectively). The reason might be due to the fact that these populations ingest more amount of products which contain, at the same time, higher concentrations of PCDD/Fs (i.e., fish, shellfish, and dairy products).

If both direct and indirect exposures to PCDD/Fs are considered together, the environmental exposure to these compounds only means a 1.05% and 0.39 % of the total, for the industrial and residential areas, respectively. Because dietary intake contribution is so important, the overall exposure to PCDD/Fs is higher for subjects living in the residential zones than for those residing in the suburbs adjacent to the chemical area (mean values: $1.21 \cdot 10^{-3}$ and $1.02 \cdot 10^{-3}$ ng I-TEQ/kg/day, respectively). However, these levels are clearly below the tolerable daily intake established by the WHO for PCDD/Fs.

With regard to the non-carcinogenic risks, the Hazard Quotient was under 1 for both groups of population. In turn, carcinogenic risks were between 10^{-4} and 10^{-6}, which can be considered as assumable because of the individual variability of the subjects. Thus, neither environmental nor dietary exposure to PCDD/Fs in both suburb and downtown would mean an additional health risk for the population living in these areas.

Influence of temperature and solar radiation on PAH photodegradation

Article V: Nadal M, Wargent JJ, Jones KC, Paul NG, Schuhmacher M, Domingo JL
Interlatitudinal comparison of the influence of UV-B radiation and temperature over PAHs photodegradation
Submitted to *Atmospheric Environment*

Environmental conditions may play a key role on degradation of PAHs. Among them, temperature and solar radiation are two of the most influent. It has been reported that an increase of temperature implies that PAHs degrade faster. In turn, photolysis has been found to be an important degradation process when those compounds are exposed to UV radiation. Considering these hypothesis, an experimental study was carried out in order to assess the joint effect of both, temperature and UV-B radiation, over PAH degradation.

A mixture of 10 single PAHs in tetradecane was exposed to 2 different simulated environments: Atlantic (low UV-B dose and temperature) and Mediterranean (high UV-B dose and temperature). Real data from Lancaster (North-West of England) and Tarragona (Catalonia, Spain) were used. Alternatively, a few samples were protected from sunlight in order to study the affection of other loss processes, such as volatilization.

As expected, PAH photodegradation rates depended widely on the molecular weight of each PAH. In fact, no loss along the experiment was found for PAHs with more than 5-rings. In contrast, naphthalene was the only compound suffering volatilization. In Tarragona simulated environment, half-lives of light PAHs ranged from 14 to 192 h for naphthalene and pyrene, respectively. In turn, in Lancaster, photodegradation rates ranged from 97 to 654 h corresponding to acenaphthene and fluoranthene, respectively.

A relevant loss of PAH concentrations was detected when both temperature and UV-B dose were high. Consequently, it seems that they have a synergistic effect over the degradation of these compounds. This synergism can have a great implication not only in PAH degradation in vegetation of specific areas, but also in long-range transport of PAHs.

Map of risk of the chemical/petrochemical area of Tarragona

Article VI: Nadal M, Kumar V, Schuhmacher M, Domingo JL
Definition and GIS-based characterization of an Integral Risk Index applied to a petrochemical area
Submitted to *Chemosphere*

In order to design a risk map of the industrial zone of Tarragona, an Integral Risk Index was previously developed. This Index was based on two parameters: a) a Hazard Index, defined as a ranking of a series of pollutants (heavy metals, PCDD/Fs, PCBs, and PAHs); and b) the concentration of each pollutant in soils collected in the area under study.

The Hazard Index was achieved by applying Kohonen's Self-Organizing Maps (SOM) to persistence, bioaccumulation and toxicity (PBT) properties of all the chemicals. As expected, the pollutants grouped in several clusters according to their similarities. With regard to the value itself, PCB congeners resulted to present the highest Hazard Index. Although they are not so toxic as PCDD/Fs, PCBs tend to bioaccumulate more easily in the body burden. In contrast, the most volatile PAHs were the less hazardous compounds among all the considered pollutants.

The risk map was designed by representing the spatial distribution of the Integral Risk Index in the industrial and residential areas of Tarragona by a Geographic Information System (GIS). The South-western corner of the chemical complex presented the highest relative risk, since notable amounts of PCBs, PCDD/Fs, PAHs, Pb and V had been found in soils. However, due to closeness to population, special attention should be paid by the risk managers to two other "hot spots": northern part of the chemical zone, and city downtown. In turn, the values of the Integral Risk Index were also calculated considering the legislative established maximum allowed concentrations of all the pollutants in soil. Since the current values were much lower than threshold, it might be concluded that, in principle, the current concentrations of the chemicals under study would not pose a significant risk over local population.

GENERAL DISCUSSION

In general terms, the concentrations of all the chemicals under study found in soil samples collected in the chemical and petrochemical complexes of Tarragona are similar to those previously reported in a number of industrial sites. In fact, relatively higher levels of some specific pollutants have been detected by different authors when studying the impact of oil refineries. In this context, Soldi (1996) found a vanadium concentration of 65-70 mg/kg in the first soil layer of an area affected by an Italian petroleum refinery. In turn, Bakker et al. (2000) reported a total concentration of PAHs of 300,000 ng/g in a soil sample collected at 50 m from an oil refinery in Belgium, whereas levels ranging between 3000 and 14000 ng/g were found in sampling points located at 1.3 to 4.2 km from the same source. In Annex 3, the concentrations of a series of pollutants in soils reported in various studies are summarized. It allows to compare them with the levels found in the present study.

It has been noted that PAH concentrations in soils, and mainly in vegetation, were surprisingly much lower than those that could be expected, according to the values found in the literature. In consequence, a further investigation was carried out in order to find out whether or not local environmental conditions of temperature and solar irradiation played a key role into PAH degradation. In fact, both variables seemed to show a synergistic effect over PAH photodegradation.

In the *Soil Quality Criteria*, the maximum allowed concentration in soils of a series of pollutants is established by the Catalan legislation (Busquet, 1997). Recently, the Spanish government has developed new guidelines to consider whether or not a specific soil is pollute, according to different soil uses (BOE, 2005). The levels observed for all the chemicals analyzed in soils collected in Tarragona were even lower than the most restrictive scenario. In Annex 4, legislative levels established by the Catalan and Spanish governments are summarized in detail.

The current levels of contaminants in chard samples were also in the low part of the range in comparison with previous investigations in urban and industrial sites. Recently, Bosco et al. (2005) reported remarkably higher mean concentrations of vanadium in pine needles collected near an important petroleum refinery in Sicily (64 mg/kg), with respect to those obtained in samples from urban and rural zones (22 and 13 mg/kg, respectively). With regard to PAHs, Bakker et al. (2000) observed a 16 PAH level of 8000 and 2000 ng/g in plantain and grass, respectively, sampled at 50 m of an oil refinery. At greater distances, PAH concentrations in plants ranged from 200 to 1900 ng/g, whereas urban levels of 8 PAHs ranged from 200 to 1700 ng/g (Bakker et al., 2001). These and other levels found in vegetation samples collected in different locations worldwide are presented in Annex 3.

On the basis of levels of inorganic and organic pollutants found in soils of Tarragona, a new methodology to assess the integral risk was developed. The Integral Risk Index may be a valid technique to be applied in zones potentially impacted by different kinds of contaminants. The display of this Index may be useful in order to create a risk map of specific areas.

CONCLUSIONS

1) An environmental monitoring program was carried out in the chemical and petrochemical industrial areas of Tarragona. The objective was to determine the current levels of a series of heavy metals and organic pollutants in soils and chards. Results may be useful not only to know the present global state of pollution of this zone, but also to establish a *starting point* for future surveys.

2) Concentrations of all metals (excepting Pb) in soil samples collected in the industrial area were higher than those corresponding to urban and unpolluted zones. However, that difference was statistically significant only for Cr and V. Urban soils registered a significantly higher level of Pb with respect to rural soils. Soil acts as a sink where a notable content of Pb is still present, basically because leaded gasoline has been largely used in the past. Since vanadium was the only element where significant differences were found in both soil and chard samples, it can be considered that Tarragona is impacted by some degree of pollution by this element. However, the V levels are notably lower than those found in other petrochemical areas.

3) The current concentrations of metals in soils are clearly below the Catalan soil quality guidelines. These concentrations would not pose a relevant non-carcinogenic risk, since the values of all them are remarkably lower than Preliminary Remediation Goals, while the calculated Hazard Quotients are below 1.

4) Some efforts should be focused on decreasing the levels of As and Cr, since the actual levels might induce a slight increase of carcinogenic risk for local population. This additional risk could be explained because of the low As levels marked by US EPA, as well as the assumption that Cr^{+6} is 1/6 of the total chromium.

5) SOM is a friendly chemometric tool with a great ability to classify data. In the present study, this ANN was useful to establish that samples collected in the chemical area were much polluted than those corresponding to the petrochemical zone.

6) Soils collected in the chemical and residential areas presented the highest concentration of POPs. In turn, the levels of these compounds near the oil refinery

and in unpolluted areas were significantly lower for PCDD/Fs and PCBs, whereas for PCNs they did not reach the level of statistical significance.

7) In chard samples, no significant differences were noted in POP levels according to the area of collection. However, PCDD/F levels were notably lower for those samples collected in presumably unpolluted areas, remarking the long-range transport and possible uncontrolled burning processes as essential in a short-term analysis. On the other hand, because of their physico-chemical properties, associated to their behavior as POPs, PCBs and the most volatile PCNs seemed to show higher concentrations in chards than in soils.

8) The current concentrations of POPs were relatively low when compared to previously reported levels in different industrial and urban areas.

9) The chemical and residential zones presented the highest values of 16 PAHs in soil, followed, by far, by the petrochemical and unpolluted areas. However, no significant differences were detected. In turn, the pattern of 7 carcinogenic PAHs was similar to that of the sum of 16 PAHs: chemical>residential>>>petrochemical>unpolluted.

10) Chard samples collected in Tarragona residential areas showed the highest concentrations of PAHs. Thus, it can be again concluded that urban areas are environments with remarkable PAH levels, whose most important contributor is traffic.

11) The contribution of high molecular weight PAHs to the total concentration was more important for soils collected near the oil refinery. Heavy PAHs, rather than volatile PAHs, have been more usually identified near their emission sources.

12) PAH levels in soils and chards were similar to those found in different industrial and urban areas around the world. Likewise, concentrations near the oil refinery were comparatively low when compared to other zones affected by petroleum industries. Since PAH levels were surprisingly low in spite of the presence of an important oil refinery, an experimental study was carried out in order to know the influence of

local environmental characteristics over PAH degradation. In fact, it was seen that when both, temperature and UV-B radiation, are high, a synergistic effect may disenchant a quick photodegradation of these compounds in biotic compartments.

13) People living near the industrial area may be more directly exposed to PCDD/Fs because of the higher concentrations of these pollutants in air and soil. On the other hand, indirect exposure to PCDD/Fs is more important for subjects living in Tarragona downtown because they ingest higher amounts of PCDD/Fs through the diet.

14) Environmental exposure to PCDD/Fs means less than 2% of the total exposure. In consequence, people of residential areas (which are supposed to belong to a higher socioeconomic group) result more exposed to PCDD/Fs. Air inhalation and intake of fish and shellfish are the main pathways of environmental and dietary exposure to PCDD/Fs, respectively.

15) The current exposure to PCDD/Fs in Tarragona would not mean an additional non-carcinogenic risk for the individuals living in the residential or in the industrial zones. Although carcinogenic risk derived from exposure to PCDD/Fs was above the upper bound $1 \cdot 10^{-6}$, it was clearly below the critic value of $1 \cdot 10^{-4}$, so it can be assumable.

16) Databases of environmental pollution due to different chemicals may be very useful to develop maps of risk. In the present study, two different methodologies (SOM and GIS) were assembled in order to construct an Integral Risk Index, and depict a global risk map of the industrial and residential areas of Tarragona. Soil concentration derived-risk in the chemical area resulted to be comparatively higher than in the petrochemical zone. The presence of a chlor-alkali plant, together with the wind regime and the height of the oil refinery stacks and torches, would help the deposition of pollutants in the chemical complex, rather than near the petrochemical area.

General conclusion

In spite of the magnitude of the industrialization in the area under evaluation, the current results suggest that chemical and petrochemical facilities located in the industrial complexes of Tarragona would not mean a relevant source of pollution by heavy metals and certain organic compounds. Moreover, the presence of these industries does not pose a notable risk for the health of the population living in the vicinity. However, a surveillance program is clearly advisable, while some efforts should be focused on reducing the environmental levels of specific elements (As, Cr and V).

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ANNEXES