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Review

Environmental impact and human health risks of air pollutants near a large chemical/petrochemical complex: Case study in Tarragona, Spain

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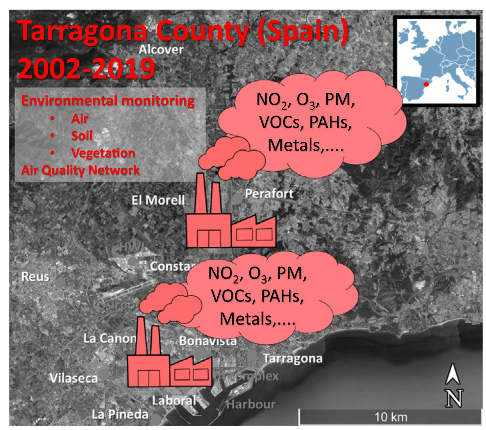
HIGHLIGHTS

- The largest chemical/petrochemical complex of Southern Europe is placed n Tarragona County, Spain.
- A number of toxic air pollutants are emitted by the facilities located in the complex.
- The available information on various pollutants in environmental matrices is here reviewed.
- Epidemiological/ecological studies are required to prevent human health adverse effects.

GRAPHICAL ABSTRACT



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ABSTRACT

Chemical industries and oil refineries are known emission sources of environmental contaminants, such as metals/metalloids, polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs) and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), among others. Based on the toxicological potential of these pollutants, harmful health effects can be expected for the population living near these facilities. One of the largest chemical/petrochemical complexes in Europe is located in Tarragona County (Catalonia, Spain). In the last two decades, a number of investigations aimed at assessing the environmental impact of air pollutants potentially emitted by this industrial complex have been carried out. The present paper is a review of the available scientific information on the levels of air pollutants related with the activities of this chemical/petrochemical complex. Although there are currently some data on the environmental burdens of metals/metalloids, PAHs, VOCs and PCDD/Fs, there is an evident lack of specific biological monitoring studies on human health. Taking into account the amount of chemicals released to air and their toxicity, it is essential to perform an in-depth analysis of the current health status of the population living in Tarragona County.

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Contents

1. Introduction

Since more than 50 years ago, one of the largest chemical/petrochemical complexes in Europe -and the largest in Southern Europe- is placed in Tarragona County (Catalonia, Spain). A petroleum refinery, together with an important number of chemical and petrochemical industries, is located in that area. From the very beginning, there has always been some concern over the possible adverse health effects for the population living in the neighborhood of this industrial complex. The concern notably increased from January 14, 2020, in the wake of the tragedy originated by the explosion in a reactor of the company IQOXE. The incident later extended to a cistern of ethylene oxide, causing three deaths and various wounded, as well as major material damage. The magnitude of this explosion had a direct impact on the people's concern, not only because of the fear to another possible accident, but also for the potential health consequences of living in the vicinity of an industrial complex, where a number of toxic pollutants are being continuously emitted. Since 2002, our laboratory has been assessing the health risks of various environmental pollutants for the population living in the neighborhood of this chemical/petrochemical complex. In the last two decades, we have obtained a considerable amount of data on the environmental levels of the analyzed contaminants. Other authors have also reported information on air pollutants. In order to definitively establish whether local residents can be affected by the chronic exposure to these contaminants, we have just started an extensive study aimed at evaluating the potential adverse effects for the population living near the chemical/petrochemical complex. As a preliminary step, we have carefully reviewed the available scientific information on the concentrations of various environmental pollutants in the area. The results are here presented. Data on some pollutants obtained from the Air Quality Network existing in this area, which should be useful for conducting health risk evaluations, are also reviewed. Information corresponding to the recent lockdown due to the COVID-19 is also discussed.

2. Environmental studies performed in the vicinity of the chemical/petrochemical complex of Tarragona County

In 2002, our laboratory performed a large monitoring study aimed at evaluating the environmental impact and potential human health risks associated to exposure of a number of micropollutants (Nadal et al., 2004a, 2004b; Schuhmacher et al., 2004). The investigation, which was the first of these characteristics in Tarragona County, was based on the sampling of soil and vegetation, which were used as long- and short-term environmental monitors, respectively. Samples of both matrices were collected in several areas close to chemical and petrochemical industries, as well as in urban sites. For comparison purposes, additional samples were also collected at reference points, located far away of the industrial emissions. The study included the analysis of several environmental pollutants, which were potentially emitted by those industries: heavy metals, polycyclic aromatic hydrocarbons (PAHs), as well as polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs) and polychlorinated naphthalenes (PCNs). Target metals/metalloids were the following: arsenic (As), cadmium (Cd), chromium (Cr), mercury (Hg), manganese (Mn), lead (Pb), and vanadium (V). For most metal concentrations no significant differences were noticed according to the area of sampling. However, V in soils and vegetation, and Cr in soils, were significantly increased in the industrial areas with respect to background zones (Nadal et al., 2004a). Reference samples were collected in presumably unpolluted zones, located at >30 km from the industrial areas (Schuhmacher et al., 2004).

According to the human health risk assessment, the ingestion of As and the inhalation of Cr in the industrial zone were identified as potentially relevant exposure pathways leading to an increase of cancer risks. In that study, we concluded that attention should be paid to As, Cr and V. Recently, González et al. (2021) reviewed the scientific literature on the occurrence of As and V in the vicinity of petrochemical complexes all over the world, considering environmental matrices (i.e., air, dust, sediments, soil, and water) and also biological samples (i.e., blood, hair, and urine). In general terms, the levels of As and V in environmental matrices showed important fluctuations according to the area of study. Moreover, As and V concentrations in urine samples from subjects living in petrochemical areas were higher than those found in individuals living further. A correlation between urinary V levels and air concentrations was also found (Chen et al., 2017).

The concentrations of PAHs and a number of polychlorinated compounds (PCDD/Fs, PCBs and PCNs) were also analyzed in the same samples of soil and vegetation collected in 2002. All these organic chemicals showed the same soil pattern, with higher concentrations in the industrial and urban/residential areas, and lower levels in the chemical/petrochemical area and the reference sites (Nadal et al., 2004b; Schuhmacher et al., 2004). Differences were statistically significant for the sum of PCDD/Fs and PCBs, but not for PCNs and PAHs. In vegetation, the highest values of PAHs were found in samples collected in residential/urban areas (Nadal et al., 2004b), while no significant differences were observed in any of the three groups of polychlorinated compounds (Schuhmacher et al., 2004).

These data were used to assess human health risks derived of the exposure to PCDD/Fs for adults living in two different zones (industrial and residential) of the same area of study (Tarragona County, Catalonia, Spain), comparing risk values according to the socioeconomic status of the population (Nadal et al., 2004c). Although environmental exposure was higher for the population living in the neighborhood of the industrial area (mainly lower socioeconomic group subjects), upper socioeconomic group populations were more exposed to PCDD/Fs, considering together the direct and indirect (dietary) routes of exposure. The results of the first monitoring program were also used to elaborate a GIS-based risk map of the chemical/petrochemical area, considering a multichemical perspective. The risk map was developed taking into account the soil concentrations of 7 heavy metals, 16 PAHs, 17 PCDD/Fs and 7 PCB-congeners, as well as the potential risk of each one of these pollutants. For it, a specific Hazard Index (HI) was derived from bibliographic data on their persistence, bioaccumulation and toxicity (Nadal et al., 2006). Subsequently, the HI was improved by applying probabilistic tools, combining self-organizing maps (SOM) and Monte Carlo analysis. In general, the deterministic and probabilistic HIs followed a similar pattern. In both cases, PCBs and light PAHs showed the highest and lowest HIs, respectively (Nadal et al., 2008).

In 2005, a 5-year monitoring program aimed at evaluating the temporal trends of the levels of the same environmental pollutants (heavy metals, PAHs, PCDD/Fs, PCBs and PCNs) in soil and vegetation samples, was initiated. In the period 2002–2005, V and PCNs significantly increased their concentrations in soils, especially in the samples collected in the chemical/petrochemical area (Nadal et al., 2007). Unlike the previous survey, only Cd and Pb showed significantly higher concentrations in the chemical/petrochemical zone, while no significant differences were found for the remaining elements and the organic pollutants. As part of this monitoring program, two new environmental surveillance surveys were again performed in 2007 and 2009. As a novelty, the airborne concentrations of the same micropollutants were determined. Moreover, the air profile of the same chemicals was compared to those found in soil and vegetation. Interestingly, the concentrations of Cr in soil samples, as well as V levels in vegetation samples collected near the oil refinery, were significantly higher than those found in background zones. Moreover, a significant and progressive increase of V concentrations was also noted. In air, a detailed study of the 7 carcinogenic PAHs and V suggested a relatively higher impact on the chemical/petrochemical and urban areas (Nadal et al., 2009). Similar PAH concentrations were reported by Ras et al. (2009b), who analyzed the airborne levels of these compounds in urban and industrial areas of Tarragona County. A gas/particle partitioning study was carried out, confirming that most hydrocarbons were in the gas phase. Phenanthrene was the most abundant compound of the 16 US EPA priority PAHs, with a contribution range of 32–44%. In a subsequent study, the same researchers analyzed the contents of 18 PAHs in 153 matched samples of atmospheric air and particulate matter from three sampling locations of Tarragona County. Higher levels were reported at low-temperature periods, with higher individual PAH concentrations observed in the gas phase, especially for the most volatile PAHs (Ramírez et al., 2011). These authors also estimated the lifetime lung cancer risk due to PAH inhalation and assessed the contribution to the total risk by PM_{10}, total suspended particles, and gas phases (Cuadras et al., 2016). For that purpose, the airborne levels of 18 PAHs were determined in separate phases from two different sites across Tarragona County. The gas phase accounted for the most significant contribution to the total risk (>60%), while BaP-bound PM_{10} accounted for a small contribution of the total risk (10%). Considering this low contributive value, it was suggested that BaP-bound PM_{10}, which was being used as an indicator of the risk by PAHs exposure, should be replaced. An alternative would be to consider both, gas and particle phases, when analyzing PAHs and evaluating the associated human health risks.

Following with the periodical surveillance program, samples of soil and vegetation (*Piptatherum* sp.) were again collected in 2009, and the levels of the same micropollutants were analyzed (Nadal et al., 2011a). Urban soils usually presented the highest concentrations of PCDD/Fs, PCNs and PAHs, confirming that traffic is an important emission source of these pollutants. The contamination profile was very similar to that found in the background (2002) study, since samples collected in zones of the complex, and in urban/residential zones, showed the highest concentrations of PCBs, PCNs and PAHs while the minimum values corresponded to the background sites. In addition, substantially higher levels of PAHs and some metals were found in vegetation samples collected in the chemical/petrochemical complex. The concentrations of those chemicals in soils were used to calculate the human environmental exposure to PCDD/Fs, PCBs, PCNs and PAHs, according to the methodologies developed by the US EPA (Nadal et al., 2011a). Because food consumption is the main route of human exposure to these chemical contaminants, the aggregate/cumulative environmental exposure to heavy metals, PAHs, PCDD/Fs, PCBs and PCNs was also compared with the dietary intake of these pollutants by the population living in the same zones (Linares et al., 2010). It meant a global analysis of the results, as human health risks were assessed from a multipollutant and multi-route perspective. Although no significant additional non-carcinogenic and carcinogenic risks were observed, it was concluded that the development of alternative methodologies of risk assessment -by considering synergistic/antagonistic effects according to the target organ or mode-of-action- was necessary. Current toxicological research is focused on the application of physiologically-based pharmacokinetic (PBPK) modeling, which simulates the time course distribution of a substance in the human body (Fàbrega et al., 2014). However, the US EPA suggests that the biochemical and mathematical relationships among biomarkers, exposures, and internal dose need to be also evaluated. Furthermore, linking exposure to health effects using a system biology approach is yet another future challenge (Silins and Högberg, 2011). In any case, the use of biomarkers and human biomonitoring are essential to evaluate the combined and aggregate exposure to chemicals present in mixtures.

Multimedia models are useful tools to estimate the chemical fate of organic chemicals in environmental systems (Diamond et al., 2001). Considering the notable density of chemical industries and urban emission sources of PAHs in the area, Domínguez-Morueco et al. (2016) estimated the emissions, fate and transport of PAHs in Tarragona County by applying the Multimedia Urban Model (MUM-Fate). The MUM-Fate is a Level III steady-state fugacity model consisting of seven bulk media compartments. The model was parameterized according to the environmental conditions of Tarragona County. It was used to back-calculate emissions from measured air concentrations of 6 individual PAHs (naphthalene, anthracene, phenanthrene, fluoranthene, pyrene and benzo[*a*]pyrene). The PAH estimated emissions by all the stationary and mobile sources were 42 t/year, with phenanthrene showing the greatest value (16 t/year). The results provided a first approximation of the emissions and fate of PAHs in Tarragona County. Another specific study of benzo[*a*]pyrene (BaP) was conducted -by using modeling and field-based data- to estimate the levels and geographical distribution of BaP in air and soils in a time series between 1996 and 2015 (Domínguez-Morueco et al., 2019). Because of the scientific concern of the climate change impact on the concentrations of persistent organic pollutants (POPs) and other chemical contaminants (Nadal et al., 2015), the regional distribution of atmospheric and soil BaP levels in the period 2031–2050 was also estimated under the more extreme climate change scenario RCP 8.5. Based on the projections, it was concluded that the current EU air limit for BaP (1 ng/m^3) will not be reached in 2050. However, there will be an increase in the life-time risk of lung cancer in Tarragona County (Domínguez-Morueco et al., 2019).

A multi-component environmental monitoring study of five classes of semi-volatile organic compounds (SVOCs), including not only PAHs and PCBs, but also synthetic musks (SMs), brominated flame retardants (BFRs) and hexachlorobenzene (HCB) in samples of soil and vegetation, was conducted by Domínguez-Morueco et al. (2018). PAHs were mainly associated with the presence of a nearby highway and several roads with heavy traffic, as well as the presence of chemical industries. PCBs prevailed in the chemical area in both matrices, probably associated with the presence of two sub-electrical stations located in the neighborhood. In turn, SMs were more abundant in background areas, suggesting an influence of the personal care products derived from beach-related tourism on Tarragona County coast. As an alternative to the most common environmental monitors, soil and vegetation, Domínguez-Morueco et al. (2017) carried out a comparative investigation of the suitability of using passive air samples (PAS) and lichen transplants (*Ramalina fastigiata*) to evaluate the pollution by PAHs in different zones of Tarragona County. The highest concentrations of PAHs in both passive monitoring tools were found in the vicinity of the oil refinery. In fact, a significant positive linear correlation was observed between the concentrations of low molecular weight PAHs in lichens and the amounts accumulated in passive air samples, suggesting that lichens might be used to monitor gas-phase PAHs.

Although the environmental occurrence of POPs and heavy metals has been extensively studied in Tarragona County, the presence of other environmental pollutants has not been neglected. Since volatile organic compounds (VOCs) are closely associated to the industrial emissions, in recent years a number of investigations have focused on this group of chemicals. Ras et al. (2009a) analyzed the concentrations of VOCs in ambient air in samples collected at urban and industrial sites of Tarragona County. Data from 192 air samples were collected from May to October 2007 at six air pollution measurement stations, being determined the levels of 65 VOCs, some of them ozone precursors. One year later, the same researchers updated this information by analyzing the airborne concentrations of VOCs for a year at urban and industrial areas from the same area (Ras et al., 2010). The most abundant compound in all samples, either urban or industrial, was i-pentane. Moreover, point and simultaneous emissions of ethylbenzene, xylenes, styrene and toluene were detected in the industrial zones, near the facility where these compounds were produced.

The risk associated to inhalation of VOCs by the population living near the chemical/petrochemical complex of Tarragona County was also characterized (Ramírez et al., 2012). None of the quantified VOCs showed average concentrations exceeding their chronic reference concentrations. Therefore, non-carcinogenic health effects were not expected as a result of this exposure. By contrast, the global average cancer risk due to exposure to VOCs in the zone was well above the threshold levels set by the World Health Organization (WHO) and the United States Environmental Protection Agency (USEPA).

Taking into account that benzene is carcinogenic to humans, it is one of the VOCs more frequently monitored in ambient air. In the EU, an annual threshold of 5 μg/m^3 is set to protect human health. Recently, Notario et al. (2020) reported atmospheric benzene measurements in the main metropolitan and industrial areas across Spain from 2014 to 2017. Annual mean levels ranged between 0.3 and 2.4 μg/m^3, with an hourly maximum value of 112 μg/m^3 in Tarragona County. This concentration differed by almost one order of magnitude with respect to those found in Spanish urban areas (e.g., 12 μg/m^3 in Sevilla and Barcelona urban stations), and twice the second largest recorded in the industrial area of Aviles (Asturias) (60 μg/m^3). Interestingly, industrial stations were pointed out to reach concentrations of one order of magnitude greater than urban sites (Notario et al., 2020).

Another VOC of notable concern for the population of Tarragona County is 1,3-butadiene, another carcinogenic compound. The early life exposure to 1,3-butadiene has been associated to an increased risk of acute lymphocytic leukemia (Symanski et al., 2016). 1,3-butadiene can be emitted to the atmosphere from several sources, but especially by petrochemical industries (Gallego et al., 2018a). In the period 2013–2017, several monitoring campaigns were conducted in twelve Catalan urban areas (including five near to the Tarragona County chemical/petrochemical complex) in order to determine 1,3-butadiene concentrations in outdoor air (Gallego et al., 2018a). Sampling points near the petrochemical facilities showed the highest average levels and the maximum 24 h concentrations of 1,3-butadiene. These same researchers also carried out a comparative study of the relative performance of active and passive sampling methods for the analysis of 1,3-butadiene in outdoor air (Gallego et al., 2018b). It was concluded that Radiello® samplers might be used for baseline 1,3-butadiene levels, whereas multi-sorbent bed tubes would be advisable when relevant episodes are expected. In addition, these authors also validated a commercially available metal oxide semiconductor gas sensor for the activation of a VOCs sampler when episodic events of nuisance/odorous annoyance occur. For that purpose, air VOC concentrations in daily 24 h samples and daily episodic samples collected over a period of 14 days (January–February 2019) were simultaneously measured in El Morell, a little town near the Tarragona chemical/petrochemical complex (Gallego et al., 2019).

Since the inhalation of particulate matter (PM) has been linked to serious adverse health effects, PM analysis has been also conducted in Tarragona County. Sánchez-Soberón et al. (2019) separately determined the content of coarse ($PM_{10-2.5}$), accumulation mode ($PM_{2.5-0.25}$), and quasi-ultrafine ($PM_{0.25}$) particulates in air samples collected inside twelve educative centers of Tarragona County during two seasons (cold and warm). A chemical characterization of the different PM fractions was conducted, being also evaluated the respiratory and digestive risks for children. Health risks were below the safety thresholds, with fine fractions being the main risk contributors. Recently, Rovira et al. (2020) assessed the impact to human health of air pollutants through the integration of different technics: data statistics (spatial and temporal trends), population attributable fraction using AIRQ+ model developed by the WHO, and burden of disease using Disability-Adjusted Life Years (DALYs). Air levels of PM_{10} and $PM_{2.5}$, as well as data on the levels of SO_2, NO, NO_2, O_3, H_2S, benzene, CO, benzo(*a*)pyrene and metals, obtained between 2005 and 2017 from the air quality monitoring network across Tarragona County, were temporally and spatially assessed. Interestingly, $PM_{2.5}$-associated lung cancer, ischemic heart disease, stroke and chronic obstructive pulmonary disease were above the WHO threshold limits, with DAYLs calculated at 240 years (Rovira et al., 2020). Previously, Nadal et al. (2011b) had used the data from the same network of surveillance and prevention of atmospheric contamination to generate a risk map of the same area by applying geographic information system (GIS) and fuzzy logic tools. This tool was subsequently applied to the case-study of the chemical/petrochemical complex of Tarragona County by generating risk maps.

Although petrochemical complexes and oil refineries are well known sources of a wide range of environmental pollutants, the number of epidemiological and ecological studies aimed at assessing the potential harmful health effects of living near these facilities is quite limited. In a recent review, Domingo et al. (2020) concluded that leukemia and other hematological malignancies are the main types of cancer observed in populations living close to petrochemical industries. In addition, a high incidence of lung and bladder cancer, as well as an excess mortality of bone, brain, liver, pleural, larynx and pancreas in individuals living near oil refineries, was also found. Furthermore, adverse health outcomes other than cancer were also reviewed (Marquès et al., 2020). An increase in the prevalence of asthma and other respiratory problems in children and adults, as well as reproductive outcomes in pregnant women, were associated to living in the surroundings of petrochemical complexes. Based on this, the authors recommended to conduct all the necessary studies for each specific area with the aim to take the appropriate measures to significantly reduce the levels of air pollutants and their adverse health effects.

Unfortunately, epidemiological information regarding the potential health effects of air emissions by the chemical/petrochemical complex of Tarragona County is not currently available. The only single investigation on this topic was conducted by Rovira et al. (2014), who evaluated the association between residential proximity to the chemical/petrochemical complex of Tarragona County and the prevalence of asthma, respiratory symptoms and lung function in children. Although a higher prevalence could not be proved, respiratory hospitalizations and nocturnal cough were related to short-term exposures to air pollutants. Anyhow, the same authors pointed out that other clinical and subclinical respiratory health effects in the area should be investigated (Rovira et al., 2014). In the scientific literature, there is abundant information regarding the effects of general ambient air pollution on pregnancy and birth outcomes (Segal and Giudice, 2019; Marquès et al., 2020; Gómez-Roig et al., 2021). Some of these studies have explored the relationship between residential proximity to oil and gas wells and birth outcomes in urban and rural areas (Tran et al., 2020). However, information on the effects for pregnant women living near petrochemical complexes is much more limited. Furthermore, none of these investigations were conducted in Tarragona County, so adverse health outcomes of prenatal exposure in this area remain unexplored.

Table 1
A summary of studies performed in Tarragona County in the last two decades, with information on sampling year, environmental monitors and analyzed pollutants.

Reference	Year	Soil						Vegetation						Air							
		Heavy metals	PAHs	PCDD/Fs	PCBs	PCNs	Others	Heavy metals	PAHs	PCDD/Fs	PCBs	PCNs	Others	Heavy metals	PAHs	PCDD/Fs	PCBs	PCNs	VOCs	PM	Others
Nadal et al., 2004a	2002	X						X													
Nadal et al., 2004b	2002		X						X												
Schuhmacher et al., 2004	2002			X	X	X				X	X	X									
Nadal et al., 2007	2005	X	X		X	X		X	X		X	X									
Nadal et al., 2009	2007	X	X	X	X	X		X	X	X	X	X		X	X	X	X	X			
Nadal et al., 2011a, 2011b	2009	X	X	X	X	X		X	X	X	X	X									
Ramírez et al., 2011	2008–2009														X						
Domínguez-Morueco et al., 2018	2016		X		X		SMs, BFRs, HCB		X		X		SMs, BFRs, HCB								
Domínguez-Morueco et al., 2017	2014–2015														X[a]						
Ras et al., 2009b	2007														X				X		
Ras et al., 2009a	2007																		X		
Ras et al., 2010	2007																		X		
Notario et al., 2020	2014–2017																		Benzene		
Ramírez et al., 2012	2008–2009																		X		
Sánchez-Soberón et al., 2019	2018																			X	
Rovira et al., 2020	2005–2017													X					Benzene	X	SO_2, NO, NO_2, O_3, H_2S, CO
Nadal et al., 2011a, 2011b	2009																			X	SO_2, NO_2, O_3, H_2S, CO
Gallego et al., 2018a	2013–2017																		1,3-Butadiene		
Gallego et al., 2019	2019																		1,3-Butadiene		

PAHs: polycyclic aromatic hydrocarbons; PCDD/Fs: polychlorinated dibenzo-*p*-dioxins and dibenzofurans; PCBs: polychlorinated biphenyls; PCNs: polychlorinated naphthalenes; PM: particulate matter; SMs: synthetic musks; BFRs: brominated flame retardants; HCB: hexachlorobenzene.
[a] Comparison with lichen transplants.

Table 2
Air quality monitoring stations in Tarragona County region considered in present study.

Station	Coordinates UTM 31 North	Altitude (m)	Pollutants	Bg
Alcover	347665, 4571462	238	SO_2, NO_2, H_2S, O_3, CO	RI
Bonavista	348300, 4553400	39	SO_2, NO_2, H_2S, PM_{10}, $PM_{2.5}$	SI
Constantí	350550, 4557690	56	SO_2, NO_2, H_2S, O_3, Bz, PM_{10}, $PM_{2.5}$, metals, B[*a*]p	SI
El Morell	350185, 4561472	60	Bz (since 2017)	RI
Laboral	349010, 4552030	5	SO_2, NO_2, H_2S, Bz, PM_{10}, $PM_{2.5}$	SI
La Canonja	347116, 4553232	40	Bz (since 2017)	RI
La Pineda	347803, 4549885	5	Bz (since 2017)	SF
Perafort	352230, 4561950	97	SO_2, NO_2, H_2S, Bz	RI
Reus	342355, 4557402	102	SO_2, NO_2, H_2S, O_3, Bz, PM_{10}, CO, metals	ST
Sant Salvador	352405, 4558155	57	SO_2, NO_2, H_2S, Bz	ST
Tarragona	352474, 4553482	13	SO_2, NO_2, H_2S, O_3, Bz, PM_{10}, $PM_{2.5}$, CO, metals	UT
Vila-seca	344920, 4553050	41	SO_2, NO_2, H_2S, O_3, Bz, PM_{10}, $PM_{2.5}$, metals	SM

Bz: benzene; B[*a*]p: benzo(*a*)pyrene; metals: As, Cd, Ni, and Pb.
In background (Bg), the first letter indicates use of soil; S:suburban; R: rural; U:urban; while the second letter indicates sources influence: T: traffic; I: industrial; M: mix.

Since 1998, a pre-operational surveillance program of a hazardous waste incinerator (HWI) located in Constantí, near the oil refinery, was initiated (Marquès et al., 2018). This program was based on the periodical determination of the contents of PCDD/Fs and heavy metals in environmental samples and food collected in the surroundings of the facility, as well as the analysis of a number of biomonitors from the local population. Breast milk, adipose tissue and plasma were used to monitor any changes of PCDD/Fs body burdens, while human hair, autopsy tissues and total blood were chosen as biomonitors of heavy metals (García et al., 2021). In the most recent biomonitoring campaign, performed in 2017–2019, a significant decrease of PCDD/Fs levels in the three evaluated monitors, compared with data from the baseline (1998) survey, was registered (Nadal et al., 2019; Schuhmacher et al., 2019; García et al., 2021). This reduction in the body burdens of PCDD/Fs was in agreement with their dietary intake, which significantly reduced between 1998 and 2018 (González et al., 2018). With respect to

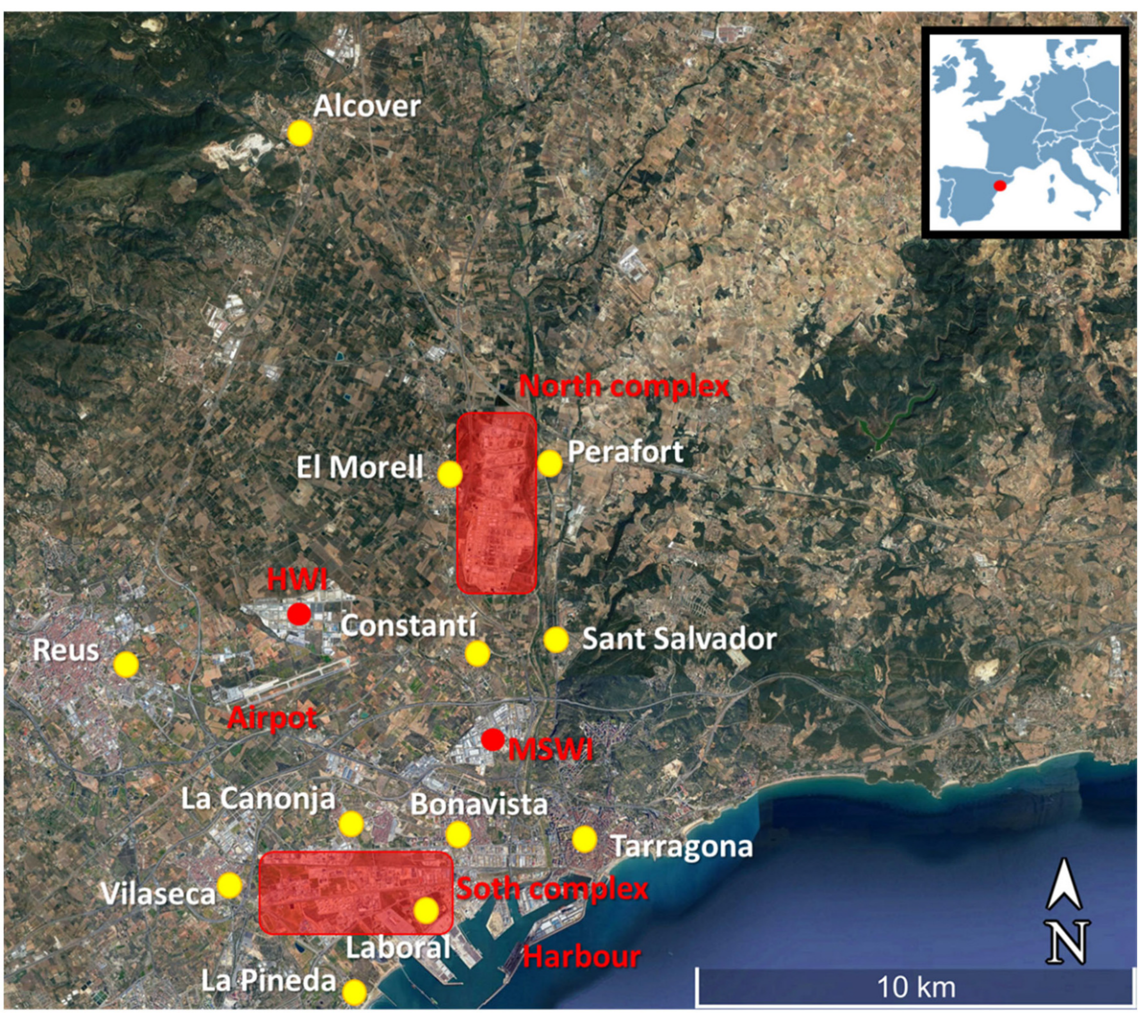

Fig. 1. Main industrial emission sources (red) and air quality monitoring stations (yellow dots) in Tarragona County.

Table 3
Mean annual concentrations of air pollutants levels measured by the Air Quality Network (AQN) of Tarragona County.

Pollutant	Station	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019
NO_2	Alcover	10	11	12	12	12	11	11	12	10	10	12	9	10	8	10
	Constantí	24	18	18	14	20	17	17	11	16	17	19	18	17	16	18
	Perafort	17	13	13	14	15	15	13	14	12	11	11	11	10	9	10
	Reus	21	22	19	17	23	23	21	20	19	18	19	19	18	18	18
	Bonavista	26	28	27	23	20	23	23	22	19	20	24	20	22	21	18
	Tarragona	30	26	32	28	30	29	26	26	24	23	25	23	23	22	22
	Sant Salvador	30	24	24	26	25	24	25	25	22	21	22	19	19	17	18
	Laboral	24	22	25	24	26	27	23	19	19	20	21	21	22	20	18
	Vila-seca	26	24	25	22	22	22	23	22	19	20	22	20	21	18	17
SO_2	Alcover	6	5	7	4	6	4	5	4	2	2	3	3	3	3	3
	Constantí	4	3	5	5	7	6	4	2	2	2	5	5	4	5	5
	Perafort	5	4	7	4	3	3	4	3	3	2	2	2	2	2	2
	Bonavista	4	4	4	3	3	2	3	2	1	3	3	3	3	3	3
	Tarragona	4	3	4	3	3	2	2	2	2	2	2	2	2	2	2
	Sant Salvador	7	5	8	4	4	3	4	3	3	2	2	2	3	2	3
	Laboral	8	4	4	3	5	3	3	2	2	2	2	2	2	2	2
	Vila-seca	2	2	2	2	2	2	2	2	2	2	2	3	3	3	2
	Reus	6	3	3	2	3	3	–	1	–	–	–	–	–	–	–
O_3	Alcover	–	67	68	55	65	69	69	70	73	69	70	69	71	68	73
	Constantí	49	53	53	56	51	56	57	55	58	55	57	56	56	57	54
	Reus	47	47	52	54	57	59	53	58	63	59	58	56	57	61	62
	Tarragona	52	52	49	51	51	53	51	53	56	52	53	52	55	56	58
	Vila-seca	56	54	50	51	55	56	55	57	58	54	56	54	58	56	57
PM_{10}	Constantí	41	43	35	33	22	17	22	24	19	18	23	20	20	22	20
	Reus[a]	–	–	–	–	28	24	26	24	20	24	25	22	21	19	18
	Reus	43	42	36	36	29	23	28	–	–	–	–	–	–	–	–
	Bonavista[a]	–	–	–	–	28	25	28	18	–	16	22	17	19	19	19
	Bonavista	36	40	36	35	29	20	23	22	18	19	22	21	21	19	20
	Tarragona	36	41	32	31	28	23	24	22	17	19	–	–	22	20	22
	Laboral	41	36	31	30	26	21	24	23	17	20	21	20	21	19	21
	Vila-seca[a]	–	–	–	–	32	27	28	23	–	17	25	17	20	18	18
	Vila-seca	52	41	34	32	28	21	26	27	20	21	27	27	24	23	22
$PM_{2.5}$	Constantí	–	–	–	12	13	11	13	14	12	11	15	11	11	10	10
	Bonavista	–	–	–	–	16	15	15	11	9	11	13	10	11	11	11
	Tarragona	–	–	15	13	14	10	11	15	13	12	–	–	–	–	–
	Laboral	–	–	–	9	12	11	12	14	12	11	15	11	12	10	10
	Vila-seca	–	–	–	–	18	16	17	14	10	12	16	11	13	12	11
H_2S	Alcover	1.2	1.4	1.6	1.3	1.0	1.1	1.0	1.1	1.0	1.1	1.2	1.3	2.0	1.7	2.3
	Constantí	1.2	2.2	3.1	2.1	3.5	1.7	2.0	1.9	1.7	1.7	1.9	1.8	1.9	2.1	1.4
	Perafort	1.5	1.3	1.1	1.8	1.5	2.0	1.3	1.4	1.3	1.3	1.5	1.5	1.4	1.4	1.5
	Reus	1.2	1.3	1.5	1.1	1.1	1.1	1.0	1.1	1.1	1.4	1.2	1.1	1.2	1.1	1.2
	Bonavista	1.2	1.3	1.1	1.4	1.7	1.6	1.5	1.5	1.6	1.9	1.8	1.8	1.6	1.8	1.4
	Tarragona	1.1	1.2	1.9	2.3	1.9	1.8	1.4	1.4	1.6	1.6	2.0	1.9	2.0	2.0	2.7
	Sant Salvador	1.7	1.6	1.7	1.5	1.8	1.5	1.3	1.3	1.7	1.2	1.2	1.2	1.3	1.3	1.3
	Laboral	2.6	2.2	1.5	1.4	1.4	1.3	1.5	1.5	1.5	1.5	1.6	1.8	2.0	1.5	2.6
	Vila-seca	1.1	1.5	1.3	1.2	1.4	1.7	1.4	1.4	1.2	1.3	1.2	1.5	1.4	1.3	1.3
B[*a*]P	Constantí	–	–	–	0.16	0.12	0.11	0.13	0.2	0.18	0.18	0.18	0.16	0.16	0.15	0.16
	Reus	–	–	–	0.15	0.27	0.17	–	–	–	–	–	–	–	–	–
	Vila-seca	–	–	–	0.17	0.12	–	–	–	–	–	–	–	–	–	–
Benzene	Constantí[a]	6.2	4.4	3.9	4.9	5.0	3.7	2.1	1.5	2	1.5	1.7	1.2	1.6	1.8	1.4
	El Morell	–	–	–	–	–	–	–	–	–	–	–	–	2.8	2.0	2.4
	La Canonja	–	–	–	–	–	–	–	–	–	–	–	–	2.9	1.7	2.6
	Perafort[a]	–	–	–	–	–	–	–	–	0.8	0.8	0.7	0.7	0.7	0.9	0.7
	Perafort	–	–	–	–	1.3	1.0	1.0	0.8	1.2	–	–	–	–	–	–
	Reus	1.1	1.3	1.0	0.9	0.8	0.7	1.1	0.8	0.8	1.1	1.1	1.1	1.0	0.8	0.7
	Tarragona	1.2	1.2	1.1	1.0	0.9	0.9	1.2	0.9	0.9	1.1	1.1	1.1	1.1	0.8	0.9
	Sant Salvador	1.1	1.3	1.2	–	1.1	–	1.0	0.7	–	–	–	–	1.0	0.8	0.8
	Laboral	–	2.1	2.3	2.0	1.6	1.8	1.8	1.6	1.3	1.5	1.5	1.2	1.6	1.2	1.1
	Vila-seca	–	–	–	–	–	–	–	–	–	–	–	1.0	0.9	0.7	0.9
	La Pineda	–	–	–	–	–	–	–	–	–	–	–	–	3.6	2.9	2.5
As	Constantí	0.9	1.2	2.0	1.3	0.5	0.5	0.5	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
	Reus	0.9	1.2	2.0	1.3	0.5	0.5	0.5	0.6	0.6	0.6	0.6	–	–	–	–
	Tarragona	1.1	1.1	2.0	1.3	0.5	0.5	–	–	–	–	–	–	–	–	–
	Vila-seca	1.3	1.2	2.1	1.3	0.6	0.5	0.5	0.5	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Cd	Constantí	3.0	2.8	2.0	1.1	0.1	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	Reus	3.0	2.6	2.2	1.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	–	–	–	–
	Tarragona	3.0	2.7	2.0	1.1	0.1	0.1	–	–	–	–	–	–	–	–	–
	Vila-seca	3.0	3.0	2.0	1.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Ni	Constantí	5.6	7.4	4.5	4.4	2.9	3.2	3.3	3.7	2.7	3	2.8	2.6	2.7	2.6	2.6
	Reus	5.8	7.7	6.6	4.6	3.1	2.9	2.4	3.6	2.8	2.8	3.2	–	–	–	–
	Tarragona	4.8	7.0	4.3	4.2	3.9	2.3	–	–	–	–	–	–	–	–	–
	Vila-seca	9.9	11.1	5.6	5.3	4.1	5.8	6.7	4.9	8.2	4.1	6.5	3.8	5.2	4.3	3.8
Pb	Constantí	–	12.4	11.3	7.7	3.3	3.5	5.1	4.8	4.2	3.5	3.4	3.0	2.5	3.0	2.8
	Reus	–	11.4	10.6	6.9	3.1	3.6	3.0	4.2	3.6	3.7	4.1	–	–	–	–
	Tarragona	–	10.2	10.5	7.0	3.8	4.5	–	–	–	–	–	–	–	–	–
	Vila-seca	–	12.0	10.5	6.4	3.3	4.7	4.9	3.8	4.7	3.8	4.3	3.6	3.7	2.8	3.1

heavy metals, most trace elements did not show significant differences after 20 years (Esplugas et al., 2019, 2020), with the only exception of Ni in lung and Cr in both, kidney and bone from autopsied subjects, whose levels significantly increased (García et al., 2020). To the best of our knowledge, this is the only biomonitoring study performed in the area, being limited to the environmental impact of the HWI.

The studies performed in Tarragona County in the last two decades showing the year of the sampling, kind of environmental samples analyzed, and pollutants analyzed, are summarized in Table 1.

3. Air quality in the chemical/petrochemical area of Tarragona County

3.1. Standard data

Data on air quality in the area were obtained from the open data repository of the Department of Territory and Sustainability of the Autonomous Government of Catalonia (Gencat, 2021). The location and characteristics of the Air Quality Network (AQN) stations in Tarragona County are shown in Table 2, while the main emission sources and the location of the AQN stations are depicted in Fig. 1. The mean levels of air pollutants for each station – between 2005 and 2019 – are summarized in Table 3. In addition, the concentrations of air contaminants have been also depicted according to the specific location of the stations (urban, suburban and rural zones) (Fig. 2), as well as the closest emission sources (namely industrial, traffic and mix) (Fig. 3). For NO_2, a considerable effect of the urban environment and traffic was detected. Urban and other traffic-influenced stations showed higher levels of NO_2 than those registered in rural or industrial stations (Figs. 2 and 3). In general, a clear decreasing tendency was observed between 2005 and 2019. Neither mean annual levels nor hourly mean concentrations were higher than their respective European legal limits: 40 μg/m^3 and 200 μg/m^3, respectively. Similar differences and trends were also noted for PM_{10}. Thus, higher PM_{10} levels in traffic-influenced stations were observed, with a more pronounced decrease between 2005 and 2019. With the exception of some stations in 2005 and 2006, the annual mean PM_{10} limit (40 μg/m^3) and the daily mean PM_{10} threshold (<50 μg/m^3 for more than 35 times in a year) were not exceeded. However, the WHO air quality guidelines for PM_{10} and $PM_{2.5}$, whose annual mean is set at 20 and 10 μg/m^3, respectively, were systematically reached (WHO, 2006).

A different trend was observed for O_3, whose levels were higher in the rural zone of Alcover than in other urban and suburban stations. In that location, O_3 usually shows high concentrations due to the wind regimes blowing from the sea (form south to north), as wind transports NO_2 and VOCs from the urban and industrial areas. In addition, the presence of mountains in Alcover does not allow the dispersion of O_3 (Rovira et al., 2020; Jiménez and Baldasano, 2004). An increasing trend was observed between 2005 and 2019, which was possibly due to the reduction of PM_{10} levels. This decrease would be translated in a net increase of solar UV radiation, which eventually promotes an increase of O_3 synthesis (Li et al., 2011; Rovira et al., 2020). The O_3 objective value for the protection of the vegetation did not exceed the value of 18.000 μg/m^3·h in an average of 5 years (periods May–July). Since 2014, this objective was systematically unaccomplished in the station of Alcover, while values in Constantí station were close to that guideline. For the protection of human health, the daily maximum 8-hour average should not exceed a level of 120 μg/m^3 more than 25 times per year. Although this threshold was not exceeded, values were close to those found in the Alcover station. In addition, the daily maximum 8-hour average of O_3 reached the threshold set at 100 μg/m^3 by WHO (2006), every year in most stations. Several significant Pearson's correlations between airborne pollutant concentrations were found (Fig. 4). Positively significant ($p < 0.01$) Pearson's correlations were noted between NO_2 and SO_2, PM_{10}, $PM_{2.5}$, CO, benzene and Cd; between SO_2 and NO_2, PM_{10}, CO, benzene, As, Cd and Pb; and between PM_{10} and NO_2, SO_2, CO benzene As, Cd, Ni and Pb. However, O_3 showed a negatively significant correlation with several environmental contaminants (i.e., NO_2, SO_2, PM_{10}, CO, benzene, Ni and Pb).

None of the above-mentioned pollutants is a specific marker of the emissions of petrochemical industries. Unfortunately, 1,3-butadiene, which is an important pyrolysis product of crude oil and gas (Fukusaki et al., 2021)., as well as other VOCs different from benzene, are not routinely monitored in AQN stations. A number of emission sources such as all combustion processes, which include road traffic, domestic heating system or agricultural burning, among others, can emit these pollutants. However, for benzene -the only VOC analyzed in this AQN- all stations showed values quite below the legal annual limit, set at 5 μg/m^3. The only exception was the Constantí station, between 2005 and 2009 (3.9 to 6.0 μg/m^3), where benzene levels either exceeded or were close to that limit. Notwithstanding, in recent years (2017–2019) three new stations have been added to the AQN. These stations are placed in El Morell, La Canonja and La Pineda, nearby villages directly impacted by emissions of the chemical/petrochemical complex. These three stations, which only analyzed benzene levels during a 30% of the year, registered higher (2–3 times) concentrations than the others stations in the zone, being also below but near the annual legal limit (5 μg/m^3).

3.2. Data during the first COVID-19 lockdown

As in other areas (Tobías et al., 2020; Querol et al., 2021), during the Spanish full lockdown, occurred between March 16 and May 10, 2020, air pollution in Tarragona County dramatically diminished (unpublished data). Doubtless, it was due to the reduction of traffic density. Unfortunately, information regarding the potential changes in the activity of the chemical/petrochemical complex is not available. Therefore, it cannot be discerned whether this decrease was partly due to a decrease of the industrial activity. Anyhow, as they are considered as part of the essential sectors, most industrial companies did not decrease their activities. For example, for NO_2, a reduction of approximately 50% was noted in several air quality stations (Alcover, Constantí, Perafort, Reus, Tarragona, Sant Salvador and Laboral) compared with mean values registered between March and May in the last six years (2014–2019). In Vila-seca and Bonavista stations, which are close to the southern chemical/petrochemical complex, the reduction was 39%. It decreased from 19.5 μg/m^3 in the period March–May of the last six years to 12 μg/m^3 registered during the lockdown. Similarly, PM_{10} levels were also reduced by 30% during the lockdown, compared with the same 3-month period in the previous six years. The only exception was Vila-seca station, where PM_{10} increased in a 13% (20 and 18 μg/m^3 during the lockdown and the March–May period of the last six years, respectively). In turn, the reduction for O_3 was around 10% in Alcover, Reus, and Vila-seca. In Constantí and Tarragona stations, O_3 levels remained stable, with an increase of 1% and a reduction of 3%, respectively. Similar trends were observed for NO_2 and PM_{10} levels elsewhere, because of reduced traffic density (Tobías et al., 2020). Interestingly, an increase in O_3 concentrations was reported in some Spanish cities (Barcelona and Valencia), while in other cities (Lleida, Pamplona, Madrid and Zaragoza) O_3 levels reduced or kept similar (Briz-Redón et al., 2021).

The AQN of the Tarragona County is not specifically designed to monitor air pollutants derived from the emissions of industries located in the area. Instead, they are aimed at measuring general environmental contamination due to traffic and other fuel combustion activities. Although several efforts have been done in recent years in order to

Notes to Table 3:
All values are given in μg/m^3, excepting As, Cd, Ni and Pb, as well as B[*a*]P that are given in ng/m^3. B[*a*]P: benzo(*a*)pyrene.
[a] PM_{10} and benzene were analyzed by means of automatic measurement equipment.

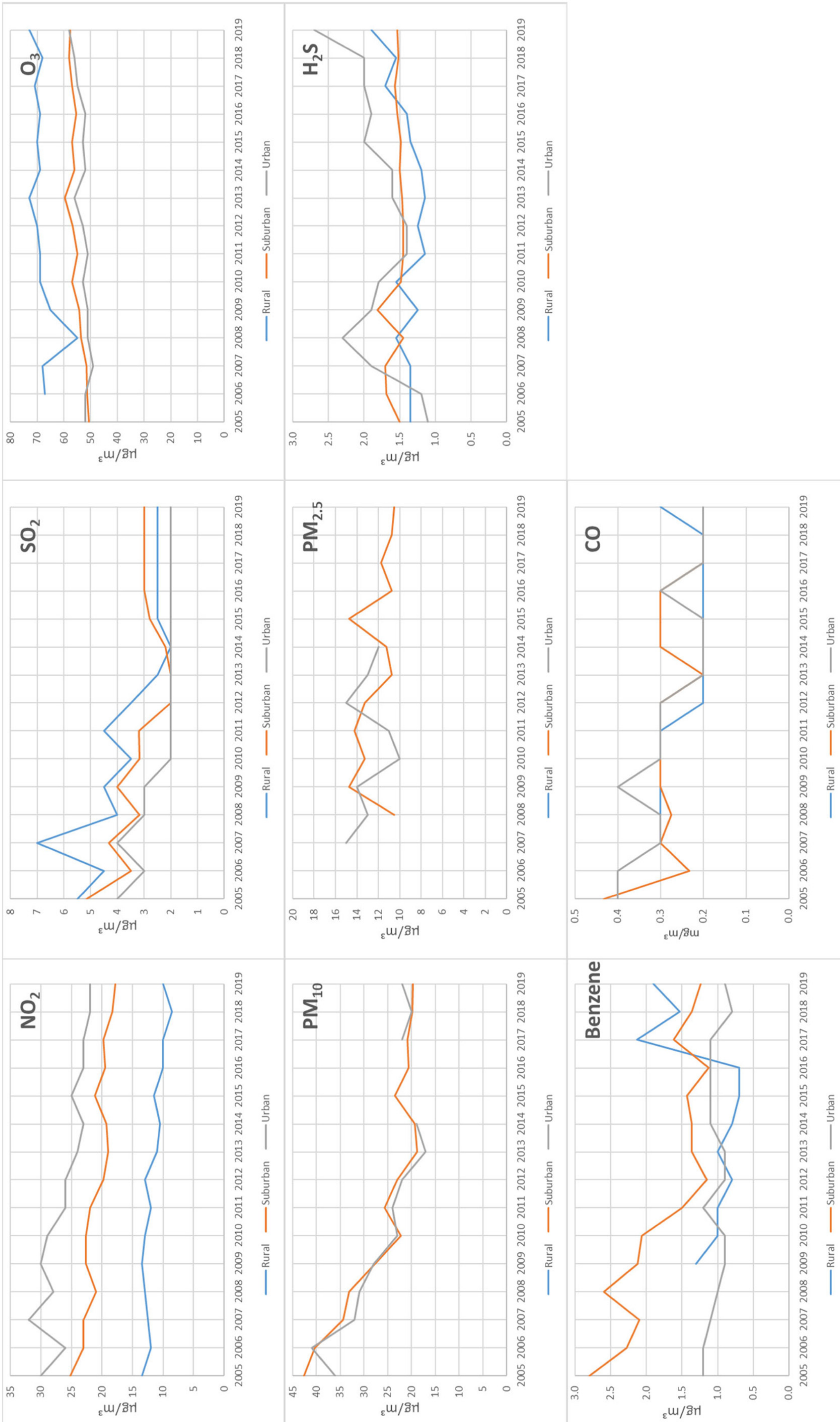

Fig. 2. Mean annual concentrations of air pollutants according to the location of each station (rural, suburban and urban) in Tarragona County. Data given from 2005 to 2019.

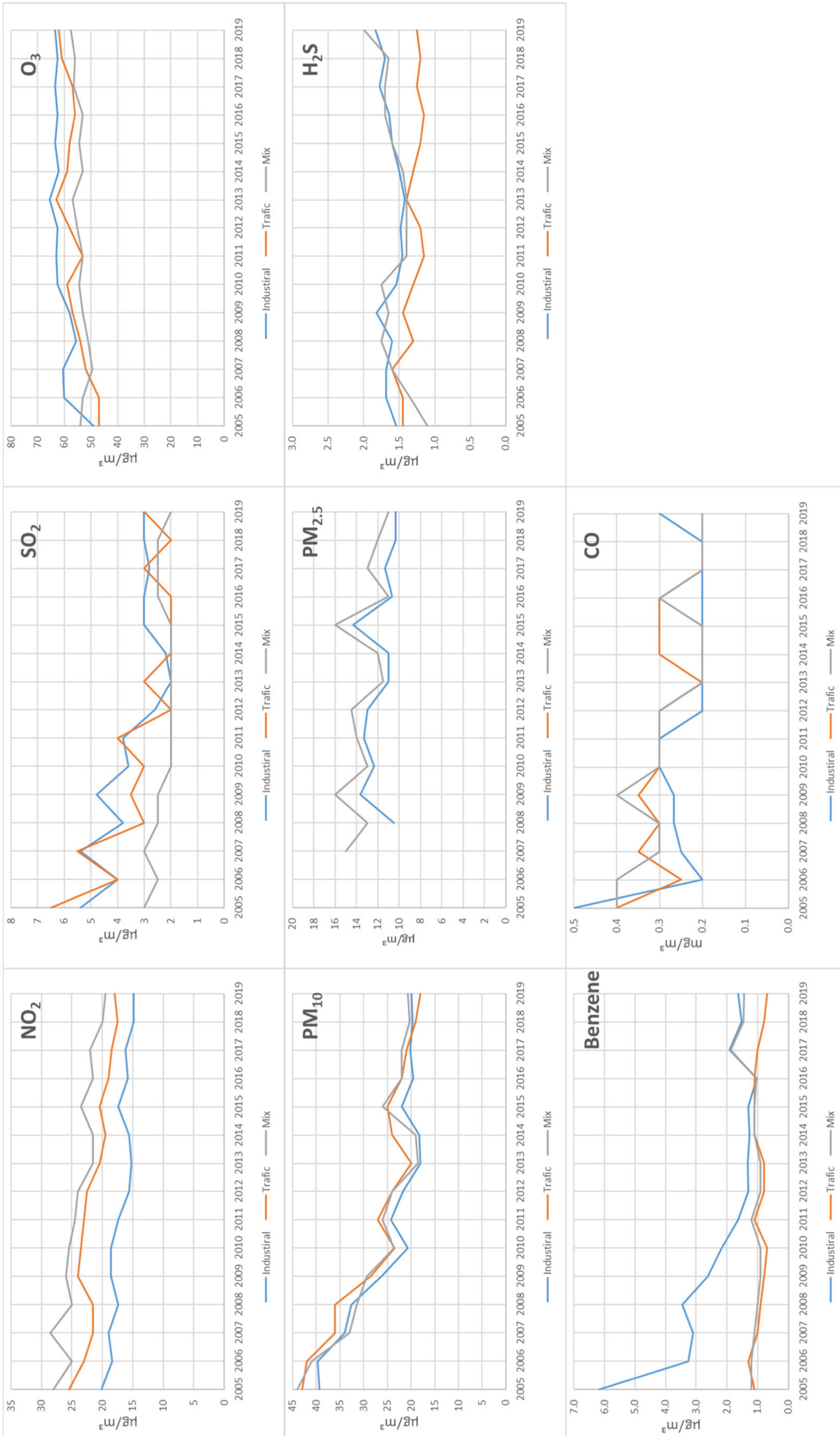

Fig. 3. Mean annual concentrations of air pollutants according to the emission sources (industrial, traffic or mixture (Mix)) in Tarragona County. Data given from 2005 to 2019.

	NO_2	SO_2	O_3	PM_{10}	$PM_{2.5}$	H_2S	CO	BaP	Benzene	As	Cd	Ni	Pb
NO_2	1.00	**0.83**	**-0.80**	**0.80**	**0.79**	-0.13	**0.87**	-0.18	**0.70**	0.48	**0.66**	**0.57**	**0.60**
SO_2	**0.83**	1.00	**-0.83**	**0.84**	**0.58**	0.20	**0.82**	-0.53	**0.81**	**0.67**	**0.78**	**0.55**	**0.67**
O_3	**-0.80**	**-0.83**	1.00	**-0.90**	-0.42	0.06	**-0.83**	0.16	**-0.80**	**-0.64**	**-0.81**	**-0.61**	**-0.71**
PM_{10}	**0.80**	**0.84**	**-0.90**	1.00	**0.57**	-0.01	**0.74**	-0.15	**0.86**	**0.70**	**0.94**	**0.86**	**0.91**
$PM_{2.5}$	**0.79**	**0.58**	-0.42	**0.57**	1.00	-0.05	**0.58**	0.18	0.19	0.29	0.33	0.47	0.44
H_2S	-0.13	0.20	0.06	-0.01	-0.05	1.00	-0.17	-0.17	0.25	0.20	-0.04	-0.17	0.07
CO	**0.87**	**0.82**	**-0.83**	**0.74**	**0.58**	-0.17	1.00	-0.28	**0.64**	0.34	**0.63**	0.42	0.41
BaP	-0.18	-0.53	0.16	-0.15	0.18	-0.17	-0.28	1.00	-0.37	0.03	-0.09	0.17	0.01
Benzene	**0.70**	**0.81**	**-0.80**	**0.86**	0.19	0.25	**0.64**	-0.37	1.00	**0.62**	**0.79**	**0.65**	**0.66**
As	0.48	**0.67**	**-0.64**	**0.70**	0.29	0.20	0.34	0.03	**0.62**	1.00	**0.75**	**0.57**	**0.86**
Cd	**0.66**	**0.78**	**-0.81**	**0.94**	0.33	-0.04	**0.63**	-0.09	**0.79**	**0.75**	1.00	**0.90**	**0.98**
Ni	**0.57**	**0.55**	**-0.61**	**0.86**	0.47	-0.17	0.42	0.17	**0.65**	**0.57**	**0.90**	1.00	**0.88**
Pb	**0.60**	**0.67**	**-0.71**	**0.91**	0.44	0.07	0.41	0.01	**0.66**	**0.86**	**0.98**	**0.88**	1.00

Fig. 4. Pearson's correlations between annual levels of pollutants in Tarragona County. Bold numbers indicate $p < 0.05$, while those bold and underlined indicate $p < 0.01$.

measure benzene concentrations in population nuclei closest to these facilities, it is still necessary to strength these efforts. Increasing the number and the spatial and temporal coverage of VOCs monitored, as well some metals/metalloids directly related with the activities of the chemical/petrochemical complex such as As or V (González et al., 2021), is essential in order to detect potential sporadic and operational episodes that could mean a negative impact for the health of the population living in the vicinity of the complex. Furthermore, a detailed study of pollutants released by chemical/petrochemical industries, irrespective of the obligatory nature of the environmental legislation, should be conducted. The geographical deployment of stations and the choice of target pollutants must take into account that one of the main objectives of air pollution surveillance networks is public health protection. Finally, the potential interactions among pollutants of regulated and non-regulated air pollutants should be also considered. In this particular case, a larger number of carcinogenic substances, including 1,3-butadiene as a specific target substance of petrochemical emissions, should be analyzed in AQN cabins. Currently, the available information relative to the environmental concentrations of carcinogenic substances, especially in air, is excessively short, and only limited to chemicals restricted by law. Moreover, the potential interactions among chemicals with the same toxic endpoints (e.g., cancer) are not considered at all.

4. Conclusions

Although the chemical/petrochemical complex of Tarragona County initiated its operations in the 1960s, an in-time exhaustive and continued control of air pollutants emitted by the important number of chemical and petrochemical industries located in the area has not so far existed, despite the potential health risks of most air chemicals. Only a few point scientific studies have been conducted, starting in 2002, more than 30 years after the complex started to operate. On the other hand, the AQN of Tarragona County only measures certain air contaminants and does not distinguish its origins (industrial, traffic, etc.). Importantly, potential serious adverse carcinogenic (Domingo et al., 2020) and non-carcinogenic (Marquès et al., 2020) health effects have been associated to living near large petrochemical complexes. In the current paper, all the available scientific information on the concentrations of air pollutants related with the activities in the chemical/petrochemical complex of Tarragona County has been reviewed. Taking into account the complexity of this issue, the lack of specific biological monitoring studies on human health, as well as the increasing concern by the population living near the chemical/petrochemical industries, it is essential to perform an in-depth analysis of the current health status of the population of Tarragona County.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

Briz-Redón, A., Belenguer-Sapiña, C., Serrano-Aroca, A., 2021. Changes in air pollution during COVID-19 lockdown in Spain: a multi-city study. J. Environ. Sci. 101, 16–26.

Chen, C.-H.S., Yuan, T.-H., Shie, R.-H., Wu, K.-Y., Chan, C.-C., 2017. Linking sources to early effects by profiling urine metabolome of residents living near oil refineries and coal-fired power plants. Environ. Int. 102, 87–96.

Cuadras, A., Rovira, E., Marcé, R.M., Borrull, F., 2016. Lung cancer risk by polycyclic aromatic hydrocarbons in a Mediterranean industrialized area. Environ. Sci. Pollut. Res. Int. 23 (22), 23215–23227.
Diamond, M.L., Priemer, D.A., Law, N.L., 2001. Developing a multimedia model of chemical dynamics in an urban area. Chemosphere 44, 1655–1667.
Domingo, J.L., Marquès, M., Nadal, M., Schuhmacher, M., 2020. Health risks for the population living near petrochemical industrial complexes. 1. Cancer risks: a review of the scientific literature. Environ. Res. 186, 109495.
Domínguez-Morueco, N., Diamond, M.L., Sierra, J., Schuhmacher, M., Domingo, J.L., Nadal, M., 2016. Application of the Multimedia Urban Model to estimate the emissions and environmental fate of PAHs in Tarragona County, Catalonia, Spain. Sci. Total Environ. 573, 1622–1629.
Domínguez-Morueco, N., Augusto, S., Trabalón, L., Pocurull, E., Borrull, F., Schuhmacher, M., Domingo, J.L., Nadal, M., 2017. Monitoring PAHs in the petrochemical area of Tarragona County, Spain: comparing passive air samplers with lichen transplants. Environ. Sci. Pollut. Res. Int. 24, 11890–11900.
Domínguez-Morueco, N., Carvalho, M., Sierra, J., Schuhmacher, M., Domingo, J.L., Ratola, N., Nadal, M., 2018. Multi-component determination of atmospheric semi-volatile organic compounds in soils and vegetation from Tarragona County, Catalonia, Spain. Sci. Total Environ. 631-632, 1138–1152.
Domínguez-Morueco, N., Ratola, N., Sierra, J., Nadal, M., Jiménez-Guerrero, P., 2019. Combining monitoring and modelling approaches for BaP characterization over a petrochemical area. Sci. Total Environ. 658, 424–438.
Esplugas, R., Mari, M., Marquès, M., Schuhmacher, M., Domingo, J.L., Nadal, M., 2019. Biomonitoring of trace elements in hair of schoolchildren living near a hazardous waste incinerator-a 20 years follow-up. Toxics 7, 52.
Esplugas, R., Serra, N., Marquès, M., Schuhmacher, M., Nadal, M., Domingo, J.L., 2020. Trace elements in blood of the population living near a hazardous waste incinerator in Catalonia, Spain. Biol. Trace Elem. Res. 198, 37–45.
Fàbrega, F., Kumar, V., Schuhmacher, M., Domingo, J.L., Nadal, M., 2014. PBPK modeling for PFOS and PFOA: validation with human experimental data. Toxicol. Lett. 230, 244–251.
Fukusaki Y, Kousa Y, Umehara M, Ishida M, Sato R, Otagiri K, Hoshi J, Nudejima C, Takahashi K, Nakai S (2021) Source region identification and source apportionment of volatile organic compounds in the Tokyo Bay coastal area, Japan. Atmos. Environ. X 9: 100103.
Gallego, E., Roca, F.J., Perales, J.F., Gadea, E., 2018a. Outdoor air 1,3-butadiene monitoring near a petrochemical industry (Tarragona region) and in several Catalan urban areas using active multi-sorbent bed tubes and analysis through TD-GC/MS. Sci. Total Environ 618, 1440–1448.
Gallego, E., Teixidor, P., Roca, F.J., Perales, J.F., 2018b. Outdoor air 1,3-butadiene monitoring: comparison of performance of Radiello® passive samplers and active multi-sorbent bed tubes. Atmos. Environ. 182, 9–16.
Gallego, E., Folch, J., Teixidor, P., Roca, F.J., Perales, J.F., 2019. Outdoor air monitoring: performance evaluation of a gas sensor to assess episodic nuisance/odorous events using active multi-sorbent bed tube sampling coupled to TD-GC/MS analysis. Sci. Total Environ. 694, 133752.
García, F., Marquès, M., Barbería, E., Torralba, P., Landin, I., Laguna, C., Domingo, J.L., Nadal, M., 2020. Biomonitoring of trace elements in subjects living near a hazardous waste incinerator: concentrations in autopsy tissues. Toxics 8, 11.
García, F., Barbería, E., Torralba, P., Landin, I., Laguna, C., Marquès, M., Nadal, M., Domingo, J.L., 2021. Decreasing temporal trends of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in adipose tissue from residents near a hazardous waste incinerator. Sci. Total Environ. 751, 141844.
Gencat, Departament de Territori i Sosteniblitat de la Generalaitat de Catalanya, 2021. Avaluació de la qualitat de l'aire. http://mediambient.gencat.cat/ca/05_ambits_dactuacio/atmosfera/qualitat_de_laire/avaluacio. (Accessed 22 March 2021).
Gómez-Roig, M.D., Pascal, R., Cahuana, M.J., García-Algar, O., Sebastiani, G., Andreu-Fernández, V., Martínez, L., Rodríguez, G., Iglesia, I., Ortiz-Arrabal, O., Mesa, M.D., Cabero, M.J., Guerra, L., Llurba, E., Domínguez, C., Zanini, M.J., Foraster, M., Larqué, E., Cabañas, F., Lopez-Azorín, M., Pérez, A., Loureiro, B., Pallás-Alonso, C.R., Escuder-Vieco, D., Vento, M., 2021. Environmental exposure during pregnancy: influence on prenatal development and early life: a comprehensive review. Fetal Diagn. Ther. 48, 245–257.
González, N., Marquès, M., Nadal, M., Domingo, J.L., 2018. Levels of PCDD/Fs in foodstuffs in Tarragona County (Catalonia, Spain): spectacular decrease in the dietary intake of PCDD/Fs in the last 20 years. Food Chem. Toxicol. 121, 109–114.
González, N., Esplugas, R., Marquès, M., Domingo, J.L., 2021. Concentrations of arsenic and vanadium in environmental and biological samples collected in the neighborhood of petrochemical industries: a review of the scientific literature. Sci. Total Environ. 771, 145149.
Jiménez, P., Baldasano, J.M., 2004. Ozone response to precursor controls in very complex terrains: use of photochemical indicators to assess O_3-NO_x-VOC sensitivity in the northeastern Iberian Peninsula. J. Geophys. Res. D. Atmos. 109(D20309, 1–20.
Li, G., Bei, N., Tie, X., Molina, L.T., 2011. Aerosol effects on the photochemistry in Mexico City during MCMA-2006/MILAGRO campaign. Atmos. Chem. Phys. 11, 5169–5182.
Linares, V., Perelló, G., Nadal, M., Gómez-Catalán, J., Llobet, J.M., Domingo, J.L., 2010. Environmental versus dietary exposure to POPs and metals: a probabilistic assessment of human health risks. J. Environ. Monit. 12, 681–688.
Marquès, M., Nadal, M., Díaz-Ferrero, J., Schuhmacher, M., Domingo, J.L., 2018. Concentrations of PCDD/Fs in the neighborhood of a hazardous waste incinerator: human health risks. Environ. Sci. Pollut. Res. 25, 26470–26481.
Marquès, M., Domingo, J.L., Nadal, M., Schuhmacher, M., 2020. Health risks for the population living near petrochemical industrial complexes. 2. Adverse health outcomes other than cancer. Sci. Total Environ. 730, 139122.
Nadal, M., Schuhmacher, M., Domingo, J.L., 2004a. Metal pollution of soils and vegetation in an area with petrochemical industry. Sci. Total Environ. 321 (1–3), 59–69.
Nadal, M., Schuhmacher, M., Domingo, J.L., 2004b. Levels of PAHs in soil and vegetation samples from Tarragona County, Spain. Environ. Pollut. 132 (1), 1–11.
Nadal, M., Schuhmacher, M., Domingo, J.L., 2004c. Probabilistic human health risk of PCDD/F exposure: a socioeconomic assessment. J. Environ. Monit. 6 (11), 926–931.
Nadal, M., Kumar, V., Schuhmacher, M., Domingo, J.L., 2006. Definition and GIS-based characterization of an integral risk index applied to a chemical/petrochemical area. Chemosphere 64 (9), 1526–1535.
Nadal, M., Schuhmacher, M., Domingo, J.L., 2007. Levels of metals, PCBs, PCNs and PAHs in soils of a highly industrialized chemical/petrochemical area: temporal trend. Chemosphere 66 (2), 267–276.
Nadal, M., Kumar, V., Schuhmacher, M., Domingo, J.L., 2008. Applicability of a neuroprobabilistic integral risk index for the environmental management of polluted areas: a case study. Risk Anal. 28 (2), 271–286.
Nadal, M., Mari, M., Schuhmacher, M., Domingo, J.L., 2009. Multi-compartmental environmental surveillance of a petrochemical area: levels of micropollutants. Environ. Int. 35 (2), 227–235.
Nadal, M., Schuhmacher, M., Domingo, J.L., 2011a. Long-term environmental monitoring of persistent organic pollutants and metals in a chemical/petrochemical area: human health risks. Environ. Pollut. 159 (7), 1769–1777.
Nadal, M., Cadiach, O., Kumar, V., Poblet, P., Mari, M., Schuhmacher, M., Domingo, J.L., 2011b. Health risk map of a petrochemical complex through GIS-fuzzy integration of air pollution monitoring data. Hum. Ecol. Risk. Assess. 17, 873–891.
Nadal, M., Marquès, M., Mari, M., Domingo, J.L., 2015. Climate change and environmental concentrations of POPs. A review. Environ. Res. 143, 177–185.
Nadal, M., Mari, M., Schuhmacher, M., Domingo, J.L., 2019. Monitoring dioxins and furans in plasma of individuals living near a hazardous waste incinerator: temporal trend after 20 years. Environ. Res. 173, 207–211.
Notario, A., Gutiérrez-Álvarez, I., Adame, J.A., 2020. Atmospheric benzene measurements in the main metropolitan and industrial areas of Spain from 2014 to 2017. Atmos. Res. 238, 104896.
Querol X, Massagué J, Alastuey A, Moreno T, Gangoiti G, Mantilla E, Duéguez JJ, Escudero M, Monfort E, Pérez García-Pando C, Petetin H, Jorba O, Vázquez V, de la Rosa J, Campos A, Muñóz M, Monge S, Hervás M, Javato R, Cornide MJ (2021) Lessons from the COVID-19 air pollution decrease in Spain: now what? Sci. Total Environ. 779: 146380.
Ramírez, N., Cuadras, A., Rovira, E., Marcé, R.M., Borrull, F., 2011. Risk assessment related to atmospheric polycyclic aromatic hydrocarbons in gas and particle phases near industrial sites. Environ. Health Perspect. 119, 1110–1116.
Ramírez, N., Cuadras, A., Rovira, E., Borrull, F., Marcé, R.M., 2012. Chronic risk assessment of exposure to volatile organic compounds in the atmosphere near the largest Mediterranean industrial site. Environ. Int. 39 (1), 200–209.
Ras, M.R., Marcé, R.M., Borrull, F., 2009a. Characterization of ozone precursor volatile organic compounds in urban atmospheres and around the petrochemical industry in the Tarragona region. Sci. Total Environ. 407 (14), 4312–4319.
Ras, M.R., Marcé, R.M., Cuadras, A., Mari, M., Nadal, M., Borrull, F., 2009b. Atmospheric levels of polycyclic aromatic hydrocarbons in gas and particulate phases from Tarragona Region (NE Spain). Int. J. Environ. Anal. Chem. 89 (7), 543–556.
Ras, M.R., Marcé, R.M., Borrull, F., 2010. Volatile organic compounds in air at urban and industrial areas in the Tarragona region by thermal desorption and gas chromatography-mass spectrometry. Environ. Monit. Assess. 161 (1–4), 389–402.
Rovira, E., Cuadras, A., Aguilar, X., Esteban, L., Borràs-Santos, A., Zock, J.P., Sunyer, J., 2014. Asthma, respiratory symptoms and lung function in children living near a petrochemical site. Environ. Res. 133, 156–163.
Rovira, J., Domingo, J.L., Schuhmacher, M., 2020. Air quality, health impacts and burden of disease due to air pollution (PM_{10}, $PM_{2.5}$, NO_2 and O_3): application of AirQ+ model to the Camp de Tarragona County (Catalonia, Spain). Sci. Total Environ. 703, 135538.
Sánchez-Soberón, F., Rovira, J., Sierra, J., Mari, M., Domingo, J.L., Schuhmacher, M., 2019. Seasonal characterization and dosimetry-assisted risk assessment of indoor particulate matter ($PM_{10-2.5}$, $PM_{2.5-0.25}$, and $PM_{0.25}$) collected in different schools. Environ. Res. 175, 287–296.
Schuhmacher, M., Nadal, M., Domingo, J.L., 2004. Levels of PCDD/Fs, PCBs, and PCNs in soils and vegetation in an area with chemical and petrochemical industries. Environ. Sci. Technol. 38 (7), 1960–1969.
Schuhmacher, M., Mari, M., Nadal, M., Domingo, J.L., 2019. Concentrations of dioxins and furans in breast milk of women living near a hazardous waste incinerator in Catalonia, Spain. Environ. Int. 125, 334–341.
Segal, T.R., Giudice, L.C., 2019. Before the beginning: environmental exposures and reproductive and obstetrical outcomes. Fertil. Steril. 112, 613–621.
Silins, I., Högberg, J., 2011. Combined toxic exposures and human health: biomarkers of exposure and effect. Int. J. Environ. Res. Public Health 8, 629–647.
Symanski, E., Tee Lewis, P.G., Chen, T.Y., Chan, W., Lai, D., Ma, X., 2016. Air toxics and early childhood acute lymphocytic leukemia in Texas, a population based case control study. Environ. Health 15, 70.
Tobías, A., Carnerero, C., Reche, C., Massagué, J., Via, M., Minguillón, M.C., Alastuey, A., Querol, X., 2020. Changes in air quality during the lockdown in Barcelona (Spain) one month into the SARS-CoV-2 epidemic. Sci. Total Environ. 726, 138540.
Tran, K.V., Casey, J.A., Cushing, L.J., Morello-Frosch, R., 2020. Residential proximity to oil and gas development and birth outcomes in California: a retrospective cohort study of 2006–2015 births. Environ. Health Perspect. 128, 067001.
WHO, World Health Organization, 2006. WHO Air Quality Guidelines for Particulate Matter, Ozone, Nitrogen Dioxide and Sulfur Dioxide. Global Update 2005. Summary of Risk Assessment. World Health Organization Press, Geneva, Switzerland.