Air concentrations of trace elements in a municipality under the influence of Tarragona petrochemical complex: Human health risks.

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ABSTRACT

One of the largest petrochemical complexes of southern Europe is located in Tarragona County (Catalonia, Spain). Despite environmental monitoring is routinely conducted in the area, the long-term occurrence of airborne trace elements has been poorly investigated. In the present study, the concentrations of arsenic (As), cadmium (Cd), chromium (Cr), nickel (Ni), lead (Pb) and vanadium (V) were analyzed in air samples collected in El Morell, a town potentially impacted by the petrochemical. Air samples were simultaneously collected in the town of Cambrils, as a background site. Meteorological data and retro trajectories analysis were used to evaluate the impact of the petrochemical industry on the levels of trace elements in air. Subsequently, human health risks due to inhalation exposure to the trace elements were also assessed. Except for V, air concentrations were significantly higher near the oil refinery than the background levels. Human health risks were also estimated to be higher in the vicinity of the petrochemical complex. In turn, air inhalation of Pb and V was higher than their dietary intakes. The present data should be considered only as preliminary, since the sampling was taken during only three weeks, which is an insufficient period to extract reliable conclusions. Further long-term studies should be focused on assessing the influence of temporary variables, such as meteorological conditions and fugitive or sporadic emissions.

Keywords: Petrochemical industry, air, PM_{10}, trace elements, human health risks

1. Introduction

Air pollution is a major environmental problem, which affects human health worldwide. It is also considered one of the nine planetary boundaries that indicate the state of the Earth's health. According to the World Health Organization (WHO), outdoor air pollution was responsible of 4.2 million premature deaths in 2019 (WHO, 2023). In fact, even an association between environmental pollution and the spread and severity of viral infections, such as COVID-19, has been demonstrated (Domingo and Rovira, 2020; Domingo et al., 2020; Marquès and Domingo, 2022). Due to the air release of chemical pollutants, whose climate change contribution is certainly relevant, the petrochemical industry has become an issue of notable concern. Petroleum refining and chemical-associated industries emit a wide range of pollutants, such as volatile organic compounds (VOCs), particulate matter (PM), greenhouse gasses and polycyclic aromatic hydrocarbons (PAHs), among other contaminants (Mu et al., 2023; Thang et al. 2019; Ragothaman et al., 2017). In turn, metals and metalloids can also be potentially released into the environment, as result of these industrial activities (Nadal et al., 2004; Stigter et al., 2000). The exposure to these elements – even at low concentrations – may lead to adverse human health effects, including carcinogenic effects (IARC, 2012).

Nowadays, Tarragona County (Catalonia, NE Spain) hosts one of the largest petrochemical complexes in southern Europe. It is divided into two areas (north and south), which are located very close to populated areas. In February 14th of 2020, only one month before the COVID-19 lockdown started in Spain, an accident happened in the aforementioned petrochemical complex, with an explosion of an ethylene oxide plant. This incident exacerbated the growing concern of the inhabitants of Tarragona County about the potential hazards of living near the petrochemical complex. Moreover, the lack of a proper urban planning has allowed to the construction of several neighbourhoods and the expansion of the petrochemical industry by a distance of <400 m. After that serious accident, authorities claimed that the event did not generate any pollution episode. However, unfortunately no report has been so far published until now.

Data on air quality nearby Tarragona petrochemical complex is scarce. Most studies have focused on macro pollutants (i.e., PM_{10}, $PM_{2.5}$, NO_x, SO_2 and O_3), which are not specific of this type of industry, while they can be also originated from other emission sources (i.e., traffic, calefaction). The only compound that is derived directly from the petrochemical industries, being routinely measured in a few cabins is benzene (Rovira et al., 2021). In contrast, many other compounds that are also related to the petrochemical industries are not usually evaluated. This list includes ethylene oxide, a well-known carcinogen compound (US EPA, 2018) and 1,3-butadiene, a carcinogenic VOC, which was only analysed in Tarragona County in the period 2013-2017 (Gallego et al., 2018).On the other hand, previous studies in the area found that environmental levels in soil, vegetation, and air of arsenic (As), cadmium (Cd), chromium (Cr) and vanadium (V) were higher around the petrochemical complex than in the control areas that were not influenced by those industrial activities (Nadal et al., 2004, 2009, 2011). However, there is a lack of data on the air levels of these trace elements (As, Cd, Cr, Ni, Pb and V) covering a large geographic area, or long monitoring periods around the zone. In a recent review, we found that As and V levels in environmental and biological matrices, although highly variable, were higher in the vicinity of these facilities than in the background areas (Gonzalez et al., 2021a).

The present study was aimed at determining the airborne levels of various trace elements (As, Cd, Cr, Ni, Pb and V) near the petrochemical complex of Tarragona, being the results compared with data from a background area. Meteorological data and back trajectories were additionally analysed, whereas human health risks derived of air inhalation were also assessed.

2. Materials and methods

2.1. Sampling

In the present study, two sampling sites were considered. On one hand, El Morell (41º11'26"N; 1º12'48"E), which is one of the closest municipalities to the industrial area. On the other hand, Cambrils (41º04'37"N; 1º03'22"E), which is located 20 km away from El Morell, was considered as background. This last municipality was chosen as a control area due to its distance from the petrochemical industry and its wind direction, which mainly comes from the North-South axis (Domínguez-Morueco et al., 2017). Sampling sites are depicted in Figure 1.

In January and February of 2021, air samples were simultaneously collected in both locations (El Morell and Cambrils) during three consecutive weeks. Five 24-h samples were weekly collected, four of them during weekdays and one in the weekend

(Sunday). Up to 30 air samples were obtained, 15 for each sampling site. As described elsewhere, samples of air particulate matter of <10 µm of diameter (PM_{10}) were collected in quartz fibre filters (QFF) using a high-volume sampler TE-6070-DV (Tisch Environmental, Cleves, OH, USA) (Rovira et al., 2018). Total air volume ranged between 1700 and 1800 m^3 per sample. QFF were properly stored in a cold dry place at room temperature until subsequent analysis.

Meteorological data were acquired from two stations belonging to the Catalan Meteorological Services (Meteocat, 2023), which are located near to the sampling sites (Table S1, Supplementary Materials). Temperatures in Cambrils (background area) ranged from 2 to 24.5 ºC, while in El Morell (influenced area) they were within -1 and 23.7 ºC. The accumulated rainfall during the sampling period was 9.1 and 7.2 mm in the background and influenced areas, respectively. Finally, predominant wind directions in the background area were NE, while in the influenced area they came from W, NW and N directions.

2.2. Chemical analysis

The analytical methodology to analyse the concentrations of trace elements in PM_{10} samples was previously described (Herrero et al., 2020). In brief, QFF were subjected to an acid digestion; four replicates of an eighth part (6.3 cm^2) of each QFF were digested with HNO_3 (65% Suprapur, E. Merck, Darmstadt, Germany) in a hot block at 103 °C. Subsequently, trace elements (As, Cd, Cr, Ni, Pb and V) were analysed by inductively coupled plasma spectrometry (ICP-MS). Blanks and control samples, as well as reference materials, were used to check the accuracy of the instrumental methods. Recovery rates varied between 97%, for Ni, and 103%, for V, with a deviation between duplicates below 5%.

2.3. Retro trajectories analysis

The Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model, which was developed by NOAA Air Resources Laboratory's (Rolph et al., 2017; Stein et al., 2016), was applied to calculate 24-hour back-trajectories during the air sampling period, at 1-hour time resolution (Rovira et al., 2018). The objective of back-trajectories was to establish a correlation between airborne trace elements and the potential emissions from the oil refinery. To achieve this, the number of retrotrajectories that cross the petrochemical complex before reaching the sampling points have been recorded for each sampling day.

2.4. Human exposure and health risk assessment

The exposure through air inhalation and its associated risk assessment were assessed according to previously validated methodologies (Domingo et al., 2017; Rovira et al., 2016), which were based on US Environmental Protection Agency (US EPA). Exposure through air inhalation was estimated with the following equation:

(1)

$$exp_{inh} = \frac{C_{air} x IR x EF}{BW x 365}$$

where C_{air} is the concentration of the trace element (in ng/m^3), IR is the inhalation rate (20 m^3/day), EF is the exposure frequency (in day/year), and BW is the body weight (70 kg).

Additionally, the inhalation exposure concentration (EC_{inh}) was calculated to characterize the health risks, using the following equation:

(2)

$$EC_{inh} = \frac{C_{air} x ET x EF x ED}{AT x 365 x 24}$$

where ET is the exposure time (24 hours/day), EF is the exposure frequency (350 day/year), ED is the exposure duration (30 years) and AT is the average time of exposure duration (30 or 70 years for non-cancer or cancer risk, respectively). Non-carcinogenic (HQ) and carcinogenic risks (CR) were separately estimated. On one hand, the non-carcinogenic risk was calculated as follows:

(3)

$$HQ_{inh} = \frac{EC_{inh}}{RfDi}$$

where, EC_{inh} is the inhalation exposure concentration (in ng/m^3) and the RfDi is the inhalation reference dose (in ng/m^3). On the other hand, carcinogenic risk was calculated with the following equation:

(4)

$$CR_{inh} = EC_{inh} X IUR$$

where IUR is the inhalation unit risk (in m^3/ng).

Toxicological values, such as IUR and RfDi, were obtained from the US EPA Risk Assessment Information System (RAIS, 2023). To conduct the risk assessment in a conservative scenario, some assumptions were done for As and Cr. Since the hexavalent chromium (Cr(VI)) is the carcinogenic form, one sixth of the total Cr was assumed to be Cr(VI). In turn, total As was assumed to be as inorganic As (Sánchez-Soberón et al., 2015).

2.5. Data treatment

Data analysis was performed by means of the statistical package SPSS (Version 28.0). The Levene test was used to compare the homogeneity of the variances. Subsequently, ANOVA or the Kruskal-Wallis tests were used to compute significant differences. Correlation between organic compounds was conducted with Pearson's correlation test. Statistical significance was set at $p < 0.05$. Concentrations below the limit of detection (LOD) were considered to be one-half of that limit (<LOD = ½ LOD).

3. Results and discussion

3.1. Temporal trend of trace elements in PM_{10} samples

Daily levels of trace elements in both locations (background and influenced) are depicted in Figure 2. In January 24, an intense short rainy event caused a power failure that hampered the collection of one sample in the background location, Therefore, data from that day were excluded from the statistical analysis.

Airborne concentrations of the analysed trace elements are summarized in Table 1. Mean, median and maximum levels during the sampling campaign were higher in El

Morell than in Cambrils, being Pb the element showing the highest mean concentrations (4.05 and 1.53 ng/m^3 in El Morell and Cambrils, respectively). It is well known that meteorology influences the levels of air pollutants. In fact, the lowest levels of trace elements were recorded in January 24, when the raining event occurred. Most trace elements presented higher levels in El Morell (influenced village) than in Cambrils (background), 0.28 vs. 0.14 ng/m^3 for As, 0.11 vs. 0.03 ng/m^3 for Cd, 1.32 vs. 0.40 ng/m^3 for Cr, 1.62 vs. 0.88 ng/m^3 for Ni and 4.05 vs. 1.53 ng/m^3 for Pb. For all these elements, interquartile range (IQR) showed no, or little overlaps. The only exception was V, which showed similar levels in both locations (0.69 vs. 0.47 ng/m^3) with overlapping IQR. This could be due to a potential high content of this element in petroleum and oil-derived products (Amorim et al., 2007). In general terms, individual daily levels were higher in El Morell than in Cambrils, with the exceptions of Ni, Cd and V, in January 21.

On the other hand, no significant differences were detected for any trace element between weekdays and weekends, considering both sampling sites together or individually. The only exception was As in El Morell. This element showed higher levels during weekdays than in the weekends (0.31 vs. 0.12 ng/m^3).

Some years ago, our laboratory performed a series of studies in the surroundings of the oil refinery of Tarragona County (Nadal et al., 2009). Although similar levels of As (0.12±0.08 ng/m^3) were found, air concentrations of Cr (2.19±0.28 ng/m^3) and V (9.10±6.97 ng/m^3) were higher than those found in the current survey. In contrast, lower levels of Cd (<0.05 ng/m^3) and Pb (1.22±0.29 ng/m^3) were then observed (Nadal et al., 2009). In Huelva (SW Spain), mean As concentrations of 6.2 ± 7.8 ng/m^3 were reported near a petrochemical industrial area (Fernández-Camacho et al., 2012), while in the surroundings of oil refineries in Thailand and Italy, As levels of 4.17 ± 4.95 ng/m^3 and 3.58 ± 3.53 ng/m^3 were reported (Boonkhao et al., 2017; Sortini et al., 2009). Anyway, As values reported in the scientific literature are generally higher than those found in the present study (mean levels of 0.28 ng/m^3 and 0.14 ng/m^3 in El Morell and Cambrils, respectively).

Regarding Cd, mean levels in air samples were 0.11 and 0.03 ng/m^3 in El Morell and Cambrils, respectively. According to the scientific literature, similar values have been reported in other industrial areas. Thus, Velasco et al. (2005) reported a Cd concentration of 0.008 ng/m^3 in a petrochemical area in Milan (Italy), while a similar value was observed in a Venezuelan industrial area (0.05 ± 0.02 ng/m^3) (Machado et al., 2008). In contrast, a higher mean Cd value was found in Venice (Italy) (53 ng/m^3) (Sortini et al., 2009).

In turn, a number of authors have reported Cr values within a range of 0.05-2 ng/m^3 in air nearby petrochemical industries (Machado et al., 2008; Velasco et al., 2005; Fernández-Camacho et al., 2012; Gaudry et al., 2008). Air concentrations in El Morell and Cambrils would fit within this range (mean concentrations of 1.32 and 0.40 ng/m^3, respectively).

In the current survey, the mean Ni concentrations were 0.11 and 0.03 ng/m^3 in El Morell and Cambrils, respectively. These values are slightly higher than those detected in an industrial area of Milan in Italy (0.031 ng/m^3), and at the Manizales landfill in Colombia (0.08 ± 0.03 ng/m^3) (Velasco et al., 2005; Machado et al., 2008). In contrast, Ni concentration in air near the petrochemical area of Huelva (SW Spain) was 3.7 ± 2.8 ng/m^3 (Fernández-Camacho et al., 2012), a higher value than that currently found in El Morell. Even higher concentrations were also found in a petrochemical area in Venice (Italy), reaching up to 12.2 ng/m^3 (Sortini et al., 2009).

Lead mean concentrations were 4.05 ng/m^3 in El Morell and 1.53 ng/m^3 in Cambrils, being both levels higher than those reported in the scientific literature. In a study conducted in Venezuela, the mean Pb concentration found in industrial areas was 1.13 ± 0.39 ng/m^3 (Machado et al., 2008), while in the city of Milan (Italy) the air concentration of Pb was 0.25 ng/m^3 (Velasco et al., 2005). In contrast, Storini et al. (2009) and Fernández-Camacho et al. (2012) found considerably higher mean values of Pb in other areas under the impacted of industrial emissions (18.1 and 14.4 ng/m^3, respectively).

The mean V concentrations found in the present study were 0.69 ng/m^3 and 0.47 ng/m^3 in El Morell and Cambrils, respectively. These levels are notably lower than those detected in previous studies conducted around petrochemical and/or industrial areas. For example, Soldi et al. (1996) detected mean V values of 14-20 ng/m^3 in a study carried out near a refinery in Milan (Italy), while Gaudry et al. (2008) found a similar concentration (15.98 ng/m^3) in a French industrial zone. In turn, a mean concentration of V of 8.45 ng/m^3 was found near a petrochemical complex in Taiwan (Boonkhao et al., 2017). On the other hand, in a study performed in urban and industrial areas in the east of Spain, Rodríguez et al. (2004) found concentrations of 2.16 and 6 ng/m^3, respectively, with a clear incidence of emissions by road traffic, while in the petrochemical area of Huelva, mean concentrations of V of 3.4 ± 3.2 ng/m^3 were reported (Fernández-Camacho et al. 2012).

3.2. Correlation between trace elements in PM_{10} samples

Figure 3 shows the Pearson's correlations between the trace elements here analysed considering both locations together, and the influenced and background areas separately. When all samples were considered, significant correlations were detected for most of the pair-comparisons of the trace elements. However, when only El Morell samples (influenced) were considered, significant correlations were observed between the following pairs of elements: As-Pb (0.904), As-V (0.629), As-Ni (0.553), Cd-Cr (0.528), Cr-Ni (0.870), Cr-V (0.671), Ni-Pb (0.707), Ni-V (0.865) and Pb-V (0.762). It should be noted that, when only Cambrils samples (background) were considered, the correlation between As and V was not observed. It is well known that these two elements are directly linked to oil refineries emissions (González et al., 2021a). Therefore, this indicates that the presence of As and V in El Morell could be potentially originated from the same emission sources.

3.3. Retro trajectories

A total of 24 retro trajectories per day were simulated, one each hour, during the 15 days of the sampling period (Figure 4). These air trajectories were calculated backwards for a total of 24 hours. Consequently, during the sampling period of 15 days, we knew from where the air came from, with a time resolution of 1 hour. Although the current study is the longest surveillance study regarding trace elements in the area, only three of the days the retro trajectories from El Morell crossed the petrochemical complex (January 19 for 3 h, January 26 for 6 h, and February 4 for 19 h). In turn, none of the retro trajectories started in Cambrils crossed the petrochemical complex. This corroborates the adequacy of selecting Cambrils as a background site.

Unfortunately, there was not sufficient data to perform an statistical analysis. In February 4, El Morell presented high levels of As (0.48 ng/m^3), Ni (2.34) ng/m^3, Pb (7.86 ng/m^3) and V (1.81 ng/m^3). Additionally, in January 27, a day after the retro trajectories crossed the petrochemical complex, air samples from El Morell also showed high levels of As (0.48 ng/m^3), Ni (2.39 ng/m^3), Pb (6.68 ng/m^3) and V (0.66ng/m^3). Despite the low number of retro trajectories that crossed the petrochemical complex, the potential effect of other emission sources (e.g., diffusive) in El Morell cannot be neglected.

3.4. Air inhalation of trace elements

Table 2 summarizes the mean exposure to the analysed trace elements in El Morell (influenced) and in Cambrils (background) through air inhalation. Mean exposure to As, Cd, Cr, Ni, Pb and V in El Morell was estimated to be $7.7 \cdot 10^{-5}$, $3.0 \cdot 10^{-5}$, $3.6 \cdot 10^{-4}$, $4.4 \cdot 10^{-4}$, $1.1 \cdot 10^{-3}$ and $1.9 \cdot 10^{-4}$ mg/kg/day, respectively. In contrast, mean exposure in Cambrils was between 30% and 75% lower (for all trace elements) than in El Morell.

It is important to remark that only inhalation route was considered to estimate the environmental exposure. However, the role of other routes, such as soil ingestion or dermal absorption, should be also taken into account for a complete risk assessment. It must be reminded that food consumption is usually the main route of exposure to many of these trace elements for non-occupationally exposed populations (Linares et al., 2010). In a recent study, the dietary exposure to trace elements by the adult population of Tarragona was estimated in 85.5, 6.55, 301, 21.4 and 3.09 µg/day for As, Cd, Ni, Pb and V, respectively (González et al., 2021b). When compared to the current results, dietary intake was substantially higher than inhalation exposure for As, Cd and Ni. In turn, air inhalation of Pb and V was higher than the dietary intake in the area influenced by the petrochemical industry (Table 2). However, these results are in disagreement with other studies conducted in the same area, where authors concluded that the dietary intake was the main route of exposure to metals with a specific weight above 93% (Linares et al., 2010). These results reinforce the idea that environmental surveys should be conducted periodically around these hotspots, considering the intensive industrial activities around.

3.5. Risk characterization

Human health risks (non-carcinogenic and carcinogenic) derived from the inhalation of trace elements associated to PM_{10} were also assessed. Non-carcinogenic risks were calculated as the HQ between the exposure to a trace element and its inhalation reference level (RfDi) (Table 2), at which no adverse effects are considered. A HQ lower than one means that there is no risk of suffering adverse health effects, other than cancer.

In the current survey, all HQs were much lower than one, reaching an average level of 0.1% of the inhalation reference dose (HQ=0.01) (Table 3).

In turn, the carcinogenic risk is the probability of developing cancer. In this case, it is considered that zero risk does exist if an exposure to a carcinogenic agent has occurred. Generally, a CR lower than 10^{-5} is considered as acceptable, while a CR lower than 10^{-6} is considered as negligible. In the present study, the carcinogenic risks derived from the inhalation of As, Cd, Cr(VI) and Ni were assessed (Figure 5). The carcinogenic risk due to the inhalation to the trace elements was lower than 10^{-5}, only exceeding the limit of 10^{-6} for Cr(VI) in El Morell. For all the trace elements, higher levels of cancer risk were observed in El Morell than in Cambrils. Similar or slightly higher inhalation carcinogenic risks were reported by Linares et al. (2010) in the same area of study.

Despite being one of the longest studies of exposure to trace elements conducted in the petrochemical area here evaluated, the sampling period (three weeks) could not be enough to assess the complexity of several temporary variables (meteorology and fugitive and/or sporadic emissions). The meteorological variability during the year is a key parameter in environmental monitoring. In addition, specific episodes of pollutant emissions can lead to a change in the levels of trace elements in air. It should be taken into account that the spatial coverage of the present environmental monitoring should be more extensive in order to be able to properly evaluate the environmental exposure of the residents around the entire petrochemical complex. Therefore, a longer study covering a greater geographic extension would be necessary in order to obtain more representative results regarding human health risks of living near this petrochemical complex.

Finally, it should be emphasized that human exposure to the evaluated trace elements does not occur only through inhalation of air, but other direct (soil intake, dermal absorption, etc.) or indirect (diet) routes of exposure can be also certainly important for some of the analysed trace elements.

4. Conclusions

Trace elements (As, Cd, Cr, Ni, Pb and V) associated to PM_{10} were analysed in the surroundings of a petrochemical complex (El Morell, Catalonia, Spain) as well as in a background site (Cambrils). Significantly higher levels of most trace elements were found in El Morell when compared to Cambrils, with the exception of V, which was similar in both sampling locations. In turn, the exposure assessment showed that the air inhalation of Pb and V were higher than the dietary intake, being a relevant and unprecedented issue. Notwithstanding, non-carcinogenic risks were below one for all analysed trace elements in both sampling locations. Finally, cancer risks potentially derived from exposure to Cr(VI) exceeded the threshold of 10^{-6} in El Morell.

Although this is the longest study performed in this petrochemical complex, the sampling period (three weeks) seems not enough to assess the complexity of several temporary variables, such as meteorology, fugitive and/or sporadic emissions, or the presence of other emission sources in the area. A more complete campaign, in terms of length and covered geographic area, is required to address the role of seasonal variability and complexity in the final results.

Declarations

Credit author statement

Joaquim Rovira: Conceptualization, Investigation, Data collection, Samples Processing, Writing – original draft. **Neus González:** Writing – original draft. **Martí Nadal:** Writing – original draft. **José L. Domingo:** Writing – original draft. **Marta Schuhmacher:** Conceptualization, Supervision, Writing & Editing.

Conflict and/or 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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Table 1. Statistical descriptors of trace elements (ng/m^3) during the sampling campaign in both sampling zones: El Morell (impacted by the activities of the petrochemical complex) and Cambrils (background).

		n	Mean	SD	Median	IQR	Minimum	Maximum	*p*-value
As	**El Morell**	15	0.28	0.15	0.25	0.19-0.36	0.05	0.53	*0.005*
	Cambrils	14	0.14	0.08	0.13	0.07-0.18	0.04	0.36	
Cd	**El Morell**	15	0.11	0.12	0.06	0.04-0.12	<0.01	0.49	*0.003*
	Cambrils	14	0.03	0.03	0.02	<0.01-0.04	<0.01	0.09	
Cr	**El Morell**	15	1.32	0.62	1.20	0.97-1.36	0.52	2.71	*<0.001*
	Cambrils	14	0.40	0.24	0.35	0.23-0.44	0.18	1.05	
Ni	**El Morell**	15	1.62	0.74	1.35	1.00-2.15	0.81	3.18	*0.007*
	Cambrils	14	0.88	0.64	0.52	0.44-1.12	0.36	2.28	
Pb	**El Morell**	15	4.05	2.31	2.95	2.18-5.92	1.30	7.91	*<0.001*
	Cambrils	14	1.53	1.12	1.37	0.74-1.72	0.54	4.43	
V	**El Morell**	15	0.69	0.56	0.47	0.28-1.02	0.10	1.81	*0.253*
	Cambrils	14	0.47	0.40	0.32	0.23-0.50	0.11	1.36	

SD: Standard deviation, IQR: Interquartile range

Table 2. Mean inhalation exposure levels (mg/kg/day) in an influenced and a background sampling location.

	Air levels (ng/m^3)		**Inhalation exposure (mg/kg/day)**		**Inhalation intake (µg/day)**		**Dietary intake for adults (µg/day)**	**RfD_i (ng/m^3)**
	Inf.	**Bckg**	**Inf.**	**Bckg**	**Inf.**	**Bckg**	**González et al. (2021b)**	**USEPA (2023)**
As	0.28	0.14	$7.67 \cdot 10^{-5}$	$3.84 \cdot 10^{-5}$	5.39	2.68	85.5	15
Cd	0.11	0.03	$3.01 \cdot 10^{-5}$	$8.22 \cdot 10^{-6}$	2.66	0.58	6.59	10
Cr	1.32	0.40	$3.62 \cdot 10^{-4}$	$1.10 \cdot 10^{-4}$	2.52	7.67	NC	400
Ni	1.62	0.88	$4.44 \cdot 10^{-4}$	$2.41 \cdot 10^{-4}$	30.80	16.91	301	14
Pb	4.05	1.53	$1.11 \cdot 10^{-4}$	$4.19 \cdot 10^{-4}$	77.67	29.34	21.4	-
V	0.69	0.47	$1.89 \cdot 10^{-4}$	$1.29 \cdot 10^{-4}$	13.32	9.01	3.09	100

NC: Not calculated.
Inf.: Influenced by the petrochemical complex (El Morell). Bckg. Background (Cambrils)

Table 3. Hazardous quotients (HQ) associated to air inhalation of various trace elements in El Morell and Cambrils.

	El Morell	**Cambrils**	**RfDi (ng/m^3)**
As	$1.8 \cdot 10^{-2}$	$8.9 \cdot 10^{-3}$	15
Cd	$5.3 \cdot 10^{-3}$	$1.4 \cdot 10^{-3}$	10
Cr	$1.3 \cdot 10^{-2}$	$3.8 \cdot 10^{-3}$	400
Ni	$1.7 \cdot 10^{-2}$	$9.4 \cdot 10^{-3}$	14
Pb	NA	NA	-
V	$7.0 \cdot 10^{-3}$	$5.0 \cdot 10^{-3}$	100

NA: not assessed because no reference dose was established at RAIS (2013)

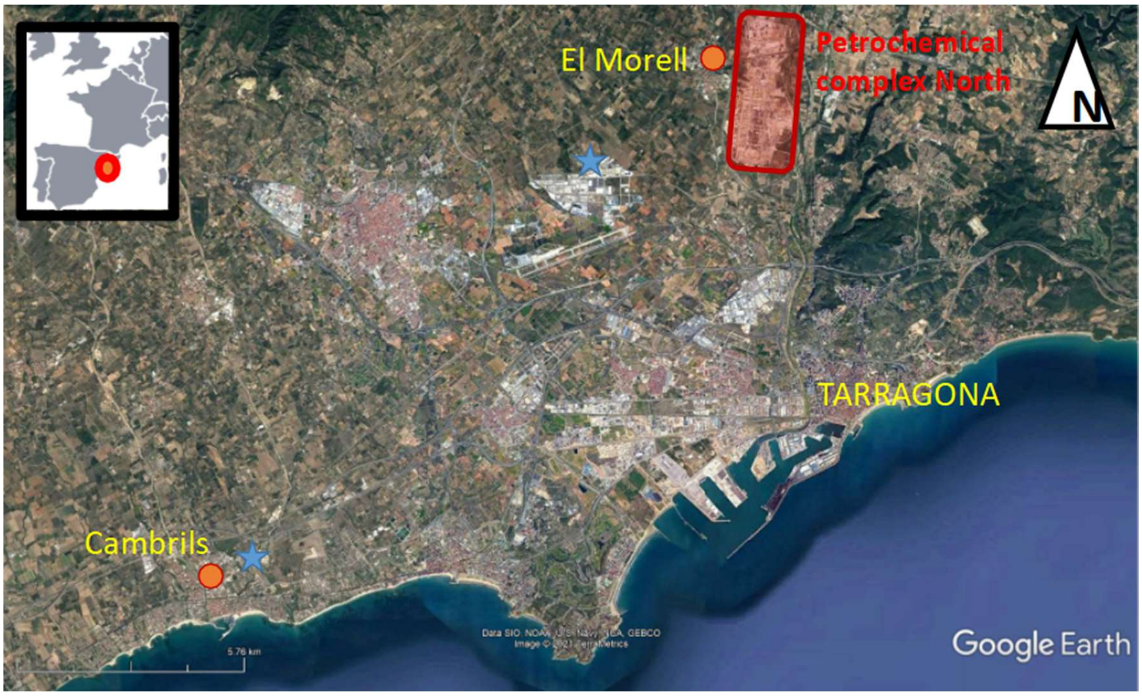


Figure 1. Area of study highlighting the sampling points: El Morell, influenced by the emissions of the petrochemical complex, and Cambrils, as background site. Blue stars indicate the location of meteorological stations.

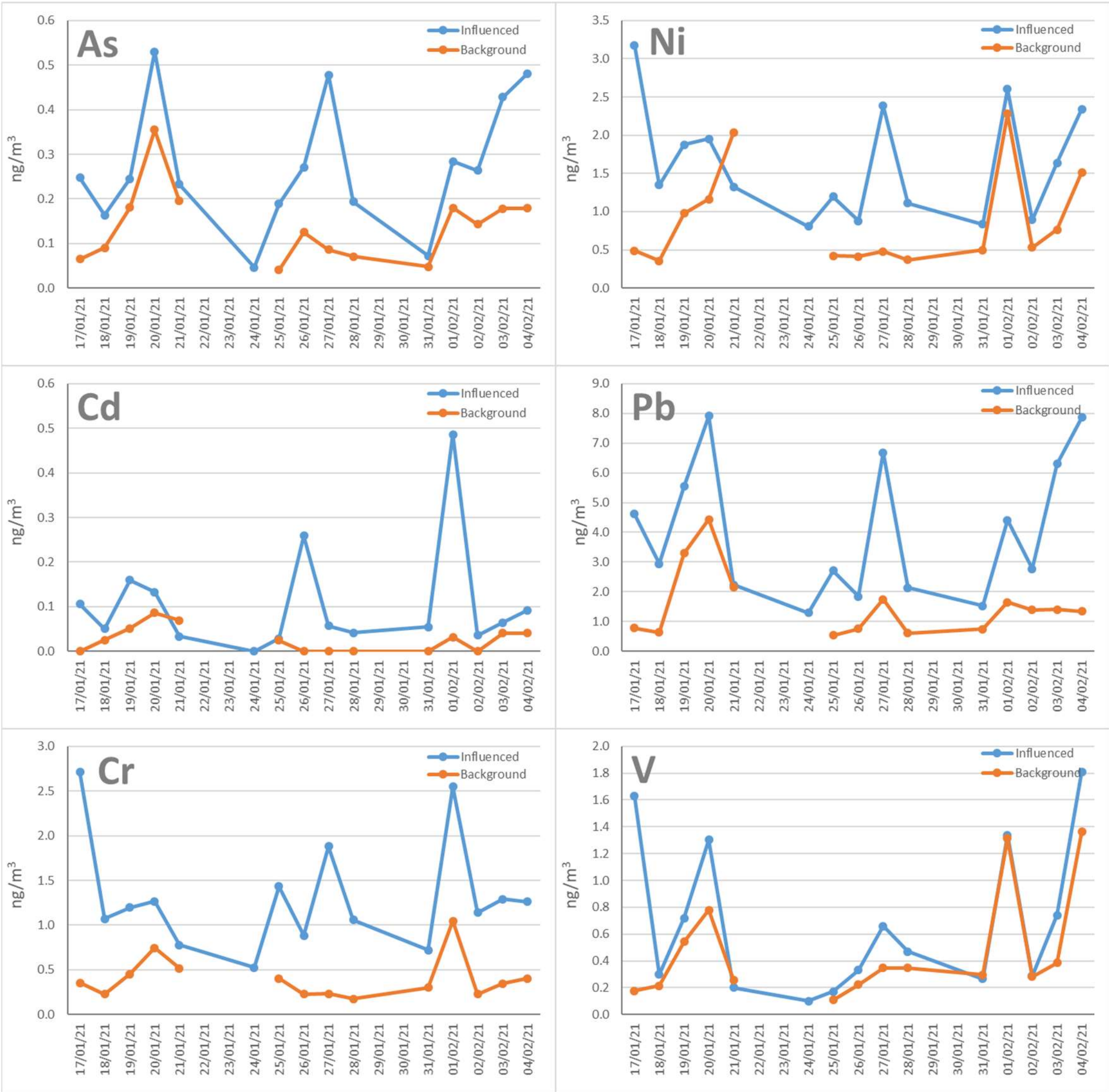
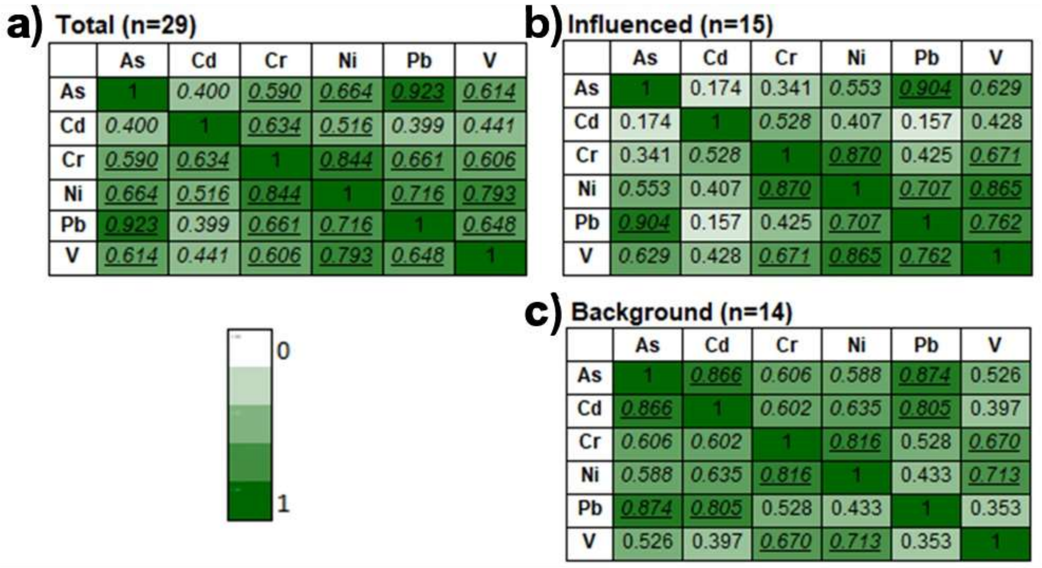


Figure 2. Temporal trends of trace elements levels associated to PM_{10} in both sampling points, influenced or not by the petrochemical complex activities, between January 17 and February 4, 2021. Dots indicate measured levels.



a) Total (n=29)

	As	Cd	Cr	Ni	Pb	V
As	1	0.400	0.590	0.664	0.923	0.614
Cd	0.400	1	0.634	0.516	0.399	0.441
Cr	0.590	0.634	1	0.844	0.661	0.606
Ni	0.664	0.516	0.844	1	0.716	0.793
Pb	0.923	0.399	0.661	0.716	1	0.648
V	0.614	0.441	0.606	0.793	0.648	1

b) Influenced (n=15)

	As	Cd	Cr	Ni	Pb	V
As	1	0.174	0.341	0.553	0.904	0.629
Cd	0.174	1	0.528	0.407	0.157	0.428
Cr	0.341	0.528	1	0.870	0.425	0.671
Ni	0.553	0.407	0.870	1	0.707	0.865
Pb	0.904	0.157	0.425	0.707	1	0.762
V	0.629	0.428	0.671	0.865	0.762	1

c) Background (n=14)

	As	Cd	Cr	Ni	Pb	V
As	1	0.866	0.606	0.588	0.874	0.526
Cd	0.866	1	0.602	0.635	0.805	0.397
Cr	0.606	0.602	1	0.816	0.528	0.670
Ni	0.588	0.635	0.816	1	0.433	0.713
Pb	0.874	0.805	0.528	0.433	1	0.353
V	0.526	0.397	0.670	0.713	0.353	1

Figure 3. Pearson's correlations between the trace elements considering: a) all samples, b) El Morell samples and c) Cambrils samples. On Italic, significant correlation at $p<0.05$. Underlined, significant correlation at $p<0.01$.

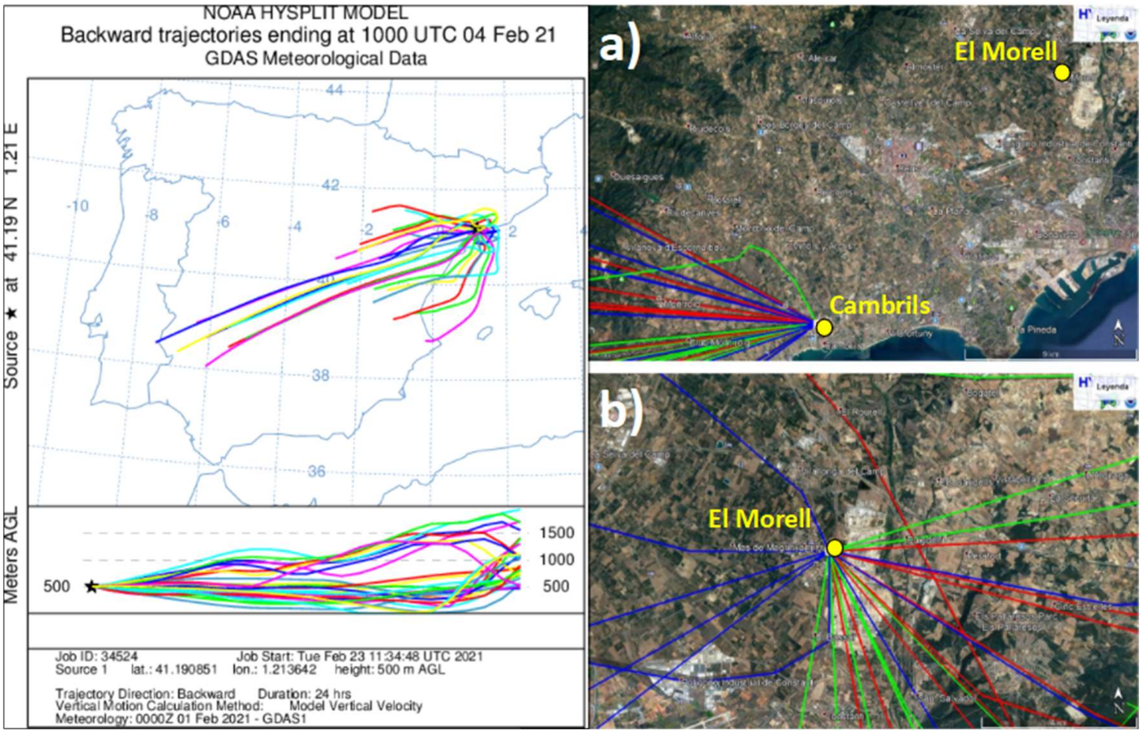


Figure 4. Retro trajectories in: a) background (Cambrils) and b) influenced (El Morell) sampling zones in February 4, 2021.

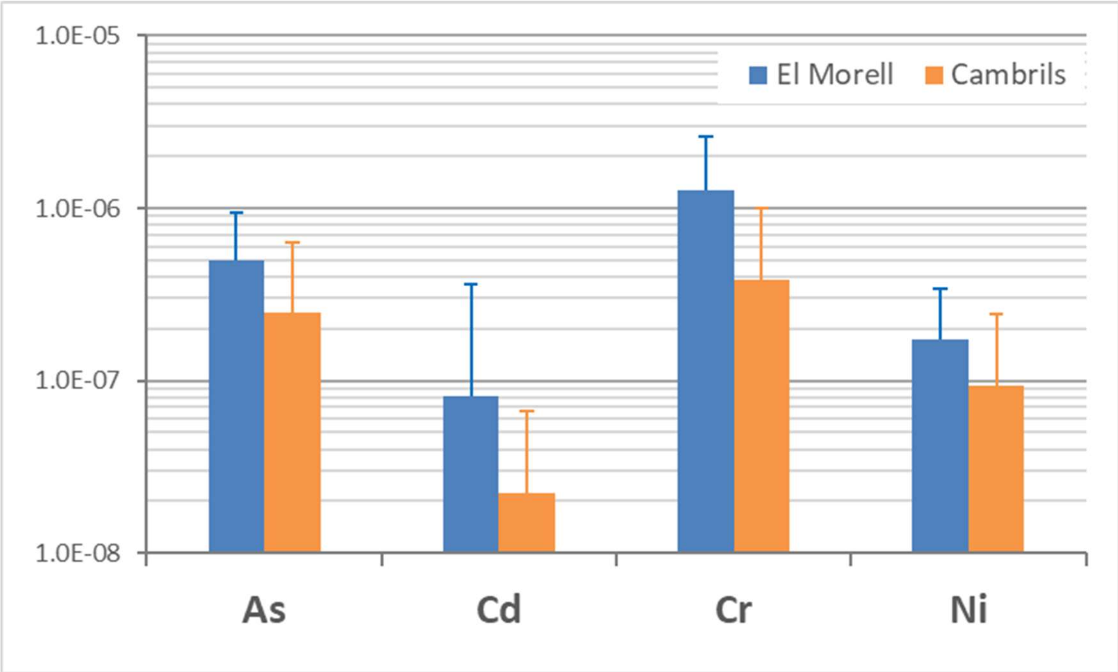


Figure 5. Cancer risks associated to the air inhalation of various trace elements in El Morell and Cambrils. Cr represent the risk for C(VI) assuming that Cr(VI) levels were equal to 1/6 of total Cr.