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Isocyanatocyclohexane and isothiocyanatocyclohexane levels in urban and industrial areas and possible emission-related activities

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Abstract

Isocyanatocyclohexane and isothiocyanatocyclohexane are becoming relevant compounds in urban and industrial air, as they are used in important amounts in automobile industry and building insulation, as well as in the manufacture of foams, rubber, paints and varnishes. Glass multi-sorbent tubes (Carbotrap, Carbopack, Carboxen) were connected to LCMA-UPC pump samplers for the retention of iso- and isothiocyanatocyclohexanes. The analysis was performed by automatic thermal desorption (ATD) coupled with capillary gas chromatography (GC)/mass spectrometry detector (MSD). TD-GC/MS was chosen as analytical method due to its versatility and the possibility of analysis of a wide range of volatility and polarity VOC in air samples. The method was satisfactory sensitive, selective and reproducible for the studied compounds. The concentrations of iso- and isothioisocyanatocyclohexanes were evaluated in different urban, residential and industrial locations from extensive VOC air quality and odour episode studies in several cities in the Northeastern edge of Spain. Around 200–300 VOC were determined qualitatively in each sample. Higher values of iso- and isothiocyanatocyclohexane were found in industrial areas than in urban or residential locations. The concentrations ranged between n.d.−246 and n.d.−29 $\mu g\,m^{-3}$ for isocyanatocyclohexane and isothiocyanatocyclohexane, respectively, for industrial areas. On the other hand, urban and residential locations showed concentrations ranging between n.d.−164 and n.d.−29 $\mu g\,m^{-3}$ for isocyanatocyclohexane and isothiocyanatocyclohexane, respectively. The site location (urban or industrial), the kind and nearness of possible iso- and isothiocyanatocyclohexane emission activities (industrial or building construction) and the changes of wind regimes throughout the year have been found the most important factors influencing the concentrations of these compounds in the different places.

Keywords: Isocyanatocyclohexane; Isothiocyanaotcyclohexane; VOC; Air quality; Immission level; TD-GC/MS; Ambient air

1. Introduction

The application of air analysis based in TD-GC/MS to perform urban and industrial air quality and

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odour episodes studies has permitted us to detect iso- and isothiocyanatocyclohexane, simultaneously with other 300 chemical compounds. These poorly studied nitrogen organic compounds in outdoor air samples have nowadays a significant occurrence in urban and industrial air samples. Iso- and isothiocyanatocyclohexane have been recently included for the first time as target compounds in outdoors VOC analysis, due to their high occurrence in air samples (Ribes et al., 2007). The objective of the present study was to determine reference concentration levels of these recent atmospheric pollutant compounds in different urban and industrial areas.

Iso- and isothiocyanates are widely used in the manufacture of flexible and rigid polyurethane foams, rubber, adhesives, resins, sealants, coatings such as paints and varnishes, drugs, pesticides and elastomers (Streicherm et al., 2000; Gromiec et al., 2002; Skowroń, 2005). In particular, cyclohexane isocyanate and isothiocyanate are being increasingly used in the automobile industry (Gadd and Kennedy, 2003; Woskie et al., 2004; Boulter, 2006) and building insulation materials, having a significant occurrence in urban and industrial air samples (Ribes et al., 2004; Laping and Sullivan, 2004).

These compounds are used in a wide range of industrial activities and can be released into the environment through direct emissions, during industrial productive processes, as well as through indirect emissions, during application processes (e.g. building construction, painting, varnishing) or evaporating from the insulation materials used in building construction.

There are no references about recognised or suspected health hazards of long-term exposure to iso- and isothioisocyanatocyclohexanes. However, this does not mean that these substances are not harmful (New Jersey Department of Health and Senior Services, 2000), as some data are lacking for their safety assessment (EPA, 1998). On the other hand, it is recognised that acute exposure to isocyanates may lead to burning sensation, cough, laboured breathing, sore throat and induced asthma if inhaled (Chan-Yeung and Malo, 1995; Malo et al., 1999). It can also cause redness of the skin, watering eyes and blurred vision (IPCS, 1999). Exposure to iso- and isothioisocyanatocyclohexanes could have long-term effects on human health, for this reason, these compounds have been included in the US Federal Regulatory Program List to determine the aspects of their exposure in human safety, as they are thought to be hazardous if inhaled (OSHA, 2006).

The aim of this study was to evaluate the concentrations of iso- and isothioisocyanatocyclohexanes in different urban, residential and industrial locations in cities around the Northeastern edge of Spain. The cities included in the study are Vacarisses, Terrassa (Fig. 1), Banyoles (Fig. 2), Sitges, La Canonja, Constantí, Benicarló and Barcelona. Each city has different characteristics and they are located significantly far from each other. Possible iso- and isothioisocyanatocyclohexanes emission-related activities are also different in each place. It has to be noted that there is an important lack of knowledge of outdoors Spanish concentrations of VOC, and consequently of iso- and isothioisocyanates, generated by industrial and urban activities. Hence, iso- and isothiocyanatocyclohexanes may be found in a wide range of concentrations.

2. Materials and methods

2.1. Chemicals and materials

Standards of isocyanatocyclohexane and isothiocyanaotcyclohexane (98%) were obtained from Aldrich (Milwaukee, WI, USA). Perkin-Elmer glass tubes (Pyrex, 6 mm external diameter, 90 mm long), unsilanised wool and Carbotrap (20/40 mesh), Carbopack X (40/60 mesh) and Carboxen 569 (20/45 mesh) adsorbents were obtained from Supelco (Bellefonte, PA, USA).

2.2. Sampling

Isocyanatocyclohexane and isothiocyanatocyclohexane were dynamically sampled connecting the custom packed glass multi-sorbent cartridge tubes (Carbotap 20/40, 70 mg; Carbopack X 40/60, 100 mg and Carboxen 569 20/45, 90 mg) to an air collector pump sampler specially designed in our laboratory. The pump sampler was equipped with inert captation line and high precision total volume measurement. Other characteristics include 10 calibration flow levels, high flow stability, very low breakthrough values and inexistent tube contamination during pre-activation processes (Roca et al., 2003; Ribes et al., 2007).

Field air samples were taken in urban, residential and industrial sites in cities around the Northeastern Spanish edge, including Catalonia and the Valencian Community. Two hundred and thirteen

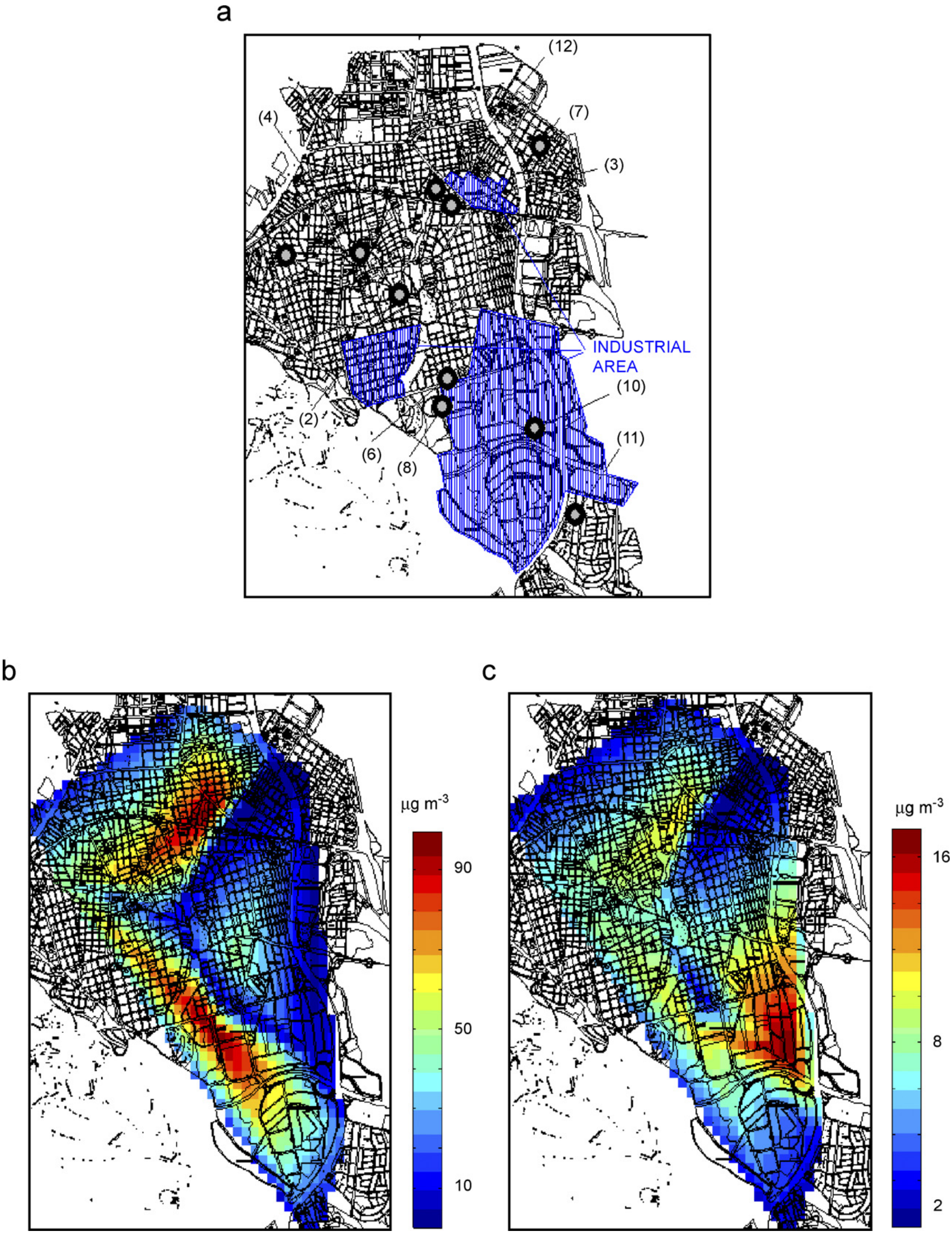

Fig. 1. Maps of Terrassa. Industrial areas and sampling points (a), average isocyanatocyclohexane concentrations ($\mu g\,m^{-3}$) (b), and average isothiocyanatocyclohexane concentrations ($\mu g\,m^{-3}$) (c).

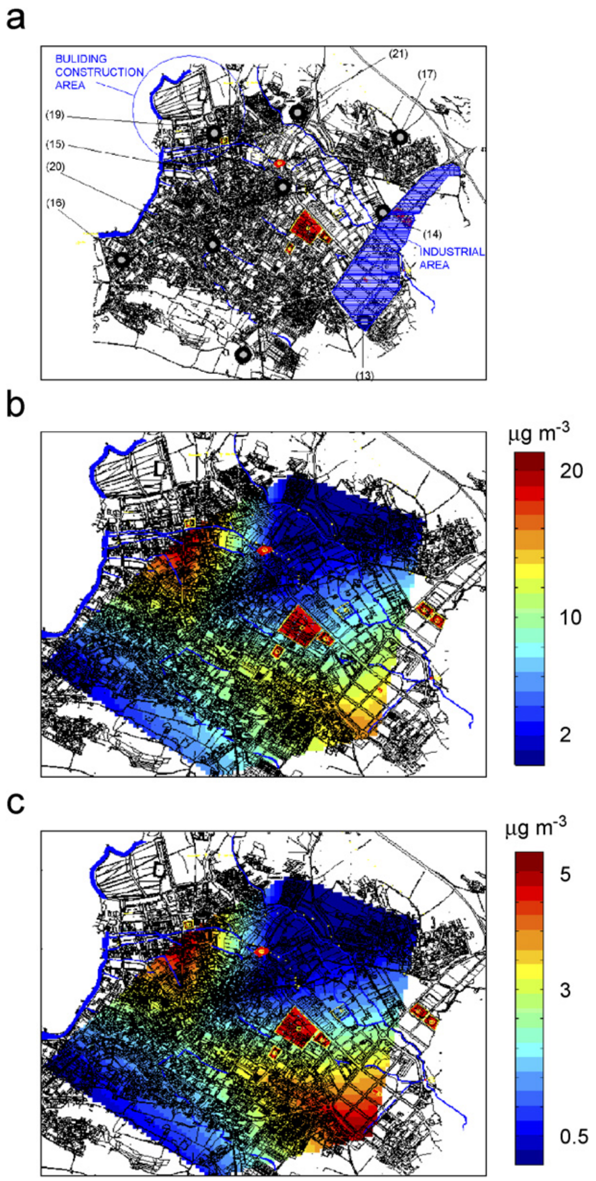

Fig. 2. Maps of Banyoles. Industrial areas, construction areas and sampling points (a), average isocyanatocyclohexane concentrations ($\mu g\,m^{-3}$) (b), and average isothiocyanatocyclohexane concentrations ($\mu g\,m^{-3}$) (c).

samples were taken during 24 h controls and during odour episodes between March 2002 and February 2007 (Table 1). Odour episodes were sampled when medium and high odour intensity and nuisance was percept by the inhabitants of the sites.

The majority of cities included in the study are similar in number of inhabitants, around 20,000–25,000. However, three of these places differ, having Terrassa and Vacarisses near 200,000 and 3000 inhabitants, respectively. Barcelona metropolitan area has nearly 3 million of inhabitants; however, the studied point is a low dense area of the city, as it is where the main universities are located. All cities have industrial activities near the urban sites, in some cases being a street the separation line between urban and industrial soil use (e.g. Point 6 located in Terrassa (Fig. 1)). In all these cases, industrial activities could have an impact in the urban tissue, depending on the annual wind regimes. On the other hand, Sitges can be considered as a residential area, having its industrial activity located far from its inhabited area.

2.3. Analytical instrumentation

The analysis of isocyanatocyclohexane and isothiocyanatocyclohexane was performed by automatic thermal desorption (ATD) coupled with capillary gas chromatography (GC)/mass spectrometry detector (MSD), using a Perkin-Elmer ATD 400 (Perkin-Elmer, Boston, MA, USA) and a Thermo Quest Trace 2000 GC (ThermoQuest, San Jose, CA, USA) fitted with a Thermo Quest Trace Finnigan MSD. The methodology is described elsewhere (Ribes et al., 2007). Briefly, thermal desorption of the sampling tubes was carried out at 300 °C with a flow rate of $50\,ml\,min^{-1}$ for 10 min (primary desorption), during which time the eluted compounds were swept from the tube to a cryofocusing trap (containing approximately 15 mg of Tenax TA and 15 mg of Carbotrap) maintained at −30 °C, applying a flow split of $4\,ml\,min^{-1}$. After a primary desorption, the cold trap was rapidly heated from −30 to 300 °C (secondary desorption) and then maintained at this temperature for 10 min. During the secondary desorption, the compounds were submitted to a flow split of $7\,ml\,min^{-1}$ and were injected onto the capillary column (DB-624, 60 m × 0.25 mm × 1.4 µm, provided by J&W, Folsom, CA, USA) via a transfer lined heated at 200 °C. The column oven temperature started at 40 °C for 1 min, increased to 230 °C at a rate of $6\,°C\,min^{-1}$ and then maintained at 230 °C for 5 min. Helium (99.999%, Air Liquide) carrier gas flow in the analytical column was approximately $1\,ml\,min^{-1}$ (1.4 bar).

Mass spectral data were acquired over a mass range of 20–300 amu. A 6 min solvent delay time was applied for standards analysis to avoid saturation of mass spectrometer detector.

Table 1
Iso- and isothiocyanatocyclohexane concentrations ($\mu g\,m^{-3}$), wind impact frequencies and probable emission activities of the studied samples

City	Area type[a]	Point	Cyclohexane isocyanate ($\mu g\,m^{-3}$)	Cyclohexane isothiocyanate ($\mu g\,m^{-3}$)	Industrial activity distance (m)	Wind impact frequency[b] (%)	Type[c]	Date	Probable emission activity
Vacarisses	i	1	n.d.[d]–7.0	2.6–7.0	300	40	ep	March 2002	Plastic manufacturers
	i	1	n.d.	6.0	300	24	ep	October 2002	Plastic manufacturers
	i	1	n.d.	2.6	300	2	ep	November 2002	Plastic manufacturers
Terrassa	i	2	16–246	0.03–13	20	38–66	24-h	February 2004	Asphalt. Textile. Nuts toasting
	u	3	0.3–1.5	<lod	100	0–16	24-h	February 2004	Low level of building construction
	u	3	0.6–1.5	<lod	100	0	24-h	March 2004	Low level of building construction
	u	3	0.3	<lod	100	0	24-h	April 2004	Low level of building construction
	u	4	22–23	1.4–1.7	500	4–10	24-h	February 2004	Building construction. Industrial influence
	u	4	71–164	10.6–17.3	500	15–24	12-h	May 2004	Buildings construction. Industrial influence
	u	5	22.2–67	3.9–8.9	10	15–29	24-h	August 2003	Building construction
	i	6	0.3–10.4	0.1–1.2	300	4–19	24-h	June 2003	Painters. Secondary Aluminum
	i	6	0.4–8.4	<lod–0.6	50	0–38	ep	July 2003	Textile. Food industry
	i	6	8.2	0.5	800	56	ep	August 2003	Textile. Food industry
	i	6	38.1–104	3.6–24	300	36–96	24-h	April 2004	Painters. Metal Smelting Plant
	i	7	25	0.8	50	88	24-h	November 2003	Textile
	i	7	10–14.1	0.7–0.8	50	57	ep	November 2003	Textile
	i	8	97–131	9.0–10.7	50	32–48	24-h	June 2003	Textile. Food industry
	i	8	134	4.5	50	88	ep	July 2003	Textile. Food industry
	i	8	10–135	11.0–18.0	50	30–58	24-h	March 2004	Textile. Food industry
	r	9	<lod[e]–0.5	<lod	500	6	24-h	September 2003	Waste water treatment
	r	9	<lod	<lod	500	0	ep	September 2003	Waste water treatment
	i	10	5	18	25	66	ep	November 2003	Textile
	u	11	<lod	< lod	250	0	24-h	November 2003	Drugs. Resins. Rubber Coatings
	u	11	15.3–19.3	0.7–1.5	250	11–33	24-h	April 2004	Drugs. Resins. Rubber Coatings
	i	12	102	11	150	54	24-h	Jan. 2004	Textile. Automobile Mechanics

Banyoles	i	13	18.5–19.1	2.8–11.2	100	23–27	24-h	July 2004	Leather painting factory. Steel works
	i	13	10.3	2.1	100	13	ep	July 2004	Leather painting factory. Steel works
	i	14	13.3	3.2	200	31	24-h	July 2004	Tire recycle
	i	14	<lod –4.6	1.2–1.4	200	2–10	ep	September 2004	Tire recycle
	i	14	21	3.4	200	33	ep	November 2004	Tire recycle
	i	14	<lod	0.06	200	0	ep	December 2004	Tire recycle
	i	14	4.2–4.7	1.8–2.6	200	8–22	24-h	September 2005	Tire recycle
	u	15	0.6–1.6	0.20–0.24	200	12–27	24-h	October 2004	Food Industry. Low level of building construction
	u	15	0.6–2.0	0.2	200	9–16	24-h	November 2004	Food industry. Low level of building construction
	u	15	<loq–1.6	0.1–0.2	200	8–15	24-h	December 2004	Food industry. Low level of building construction
	r	16	<lod	<lod–0.02	1500	0–20	24-h	January 2005	Low level of building construction. Food industry: gelatin
	r	16	<lod–<loq[f]	<lod	1500	0–8	24-h	February 2005	Low level of buildings construction. Food industry: gelatin
	R	17	0.2–1.8	0.03–0.15	600	16–24	24-h	January 2005	Food industry: Beef slaughterhouse. Cleaning products
	u	18	8.5	0.7	400	14	24-h	January 2005	Secondary Aluminum
	u	18	3.9–5.1	0.6–1.0	400	6–10	24-h	January 2005	Smelting of recycled aluminum
	u	19	19.9–22.7	5.3–5.9	200	37–51	24-h	January 2005	Buildings construction
	u	19	22.1	5.1	200	38	24-h	January 2005	Buildings construction
	u	20	2.5	0.2	100	14	24-h	January 2005	Buildings construction
	u	20	17.8	4.8	100	10	24-h	February 2005	Buildings construction
	r	21	<lod	<lod	1000	9	24-h	February 2005	Not buildings construction. Food industry: gelatin
Sitges	r	22	18.3–28.7	n.d.	50	33	24-h	May 2003	Building construction activity
	r	22	n.d.	n.d.	50	40	24-h	September 2006	Building construction activity finished
La Canonja	i	23	55.3	8.6	500	31	24-h	August 2006	Petrochemical
	i	23	8.5–28.8	0.6–2.8	500	2–14	ep	August 2006	Petrochemical
Constantí	i	24	100.3–151.5	16.8–29.3	50	17–50	3-h	August 2006	Hazardous waste incineration
Benicarló	u	25	n.d.	0.89	500	25	ep	May 2006	Polyester resins plant
	u	26	n.d.	0.79	700	8	ep	May 2006	Furniture industry (stack emissions)
	u	26	0.98	2.00	700	17	24-h	May 2006	Furniture industry (stack emissions)
	i	27	2.4	1.4	800	25	ep	October 2006	Paints industry
	i	27	0.4–0.7	2.6–8.3	50	30–37	24-h	October 2006	Furniture industry (diffusive emissions)
	u	28	0.7–6.1	3.0–9.6	700	25–29	24-h		Furniture industry (stack emissions)

Table 1 (*continued*)

City	Area type[a]	Point	Cyclohexane isocyanate ($\mu g\,m^{-3}$)	Cyclohexane isothiocyanate ($\mu g\,m^{-3}$)	Industrial activity distance (m)	Wind impact frequency[b] (%)	Type[c]	Date	Probable emission activity
								September 2006	
	u	28	n.d.	n.d.	700	6	24-h	October 2006	Furniture industry (stack emissions)
	i	29	0.4–2.2	0.3–2.6	25	49	24-h	October 2006	Polyester resins plant
	u	30	5.1–8.2	8.5–14.5	250	20	24-h	October 2006	Furniture lacquer treatment
	u	31	0.3–0.8	1.2–6.8	500	40–45	24-h	September 2006	Furniture industry (stack emissions)
	u	31	3.1	18.2	800	50	ep	October 2006	Paints industry
	i	32	n.d.	n.d.	50	20	24-h	October 2006	Fragrances plant
Barcelona	u	33	7.7–9.9	7.3–7.9	20	78–88	24-h	May 2005	Building construction not started
	u	33	50.1–130.0	16.5–29.1	20	36–98	24-h	February 2007	Building construction

[a]Area type: i, industrial; u, urban; r, residential.
[b]Wind impact frequency of activities on control points.
[c]Sample type: ep, episode, 24-h, 24-hour.
[d]Non-detected.
[e]Below limit of detection.
[f]Below limit of quantification.

Qualitative identification of target compounds was based on the match of the retention times and the ion ratios of the target quantification ions and the qualifier ions (Xcalibur 1.2 validated software package) (Fig. 3). Quantification of field samples was conducted by the external standard method, with the qualifier ions 82 and 125, and 55 and 141, for isocyanatocyclohexane and isothiocyanaotcyclohexane, respectively. Standards were prepared in methanol and injected at 30 °C on the multi-sorbent tubes under an inert helium gas flow (100 ml min^{-1}) using a conventional gas chromatograph packed column injector. Tube loading lasted not less than 5 min (Ribes et al., 2007). The studied compounds exhibited linearity ranges (ng) of three orders of magnitude and showed reproducibilities (% relative standard deviation values) between 5% and 21%, accomplishing the EPA performance criteria (US EPA, 1999). Extreme precautions were established for quality assurance, injecting periodically blank samples and a known concentration of toluene.

All concentration values were normalised by temperature (273 °C) and pressure (760 mmHg).

3. Results and discussion

3.1. Isothiocyanatocyclohexane generation during the thermal desorption phase

NIOSH (2002) found that isothiocyanatocyclohexane could be generated as a cause of the interaction of carbon disulphide and cyclohexylamine in the thermal desorption stage during analysis. In order to check if the concentrations of isothiocyanatocyclohexane detected in the samples studied had been produced because of this interaction, the correlations between isothiocyanatocyclohexane, isocyanatocyclohexane and carbon disulphide

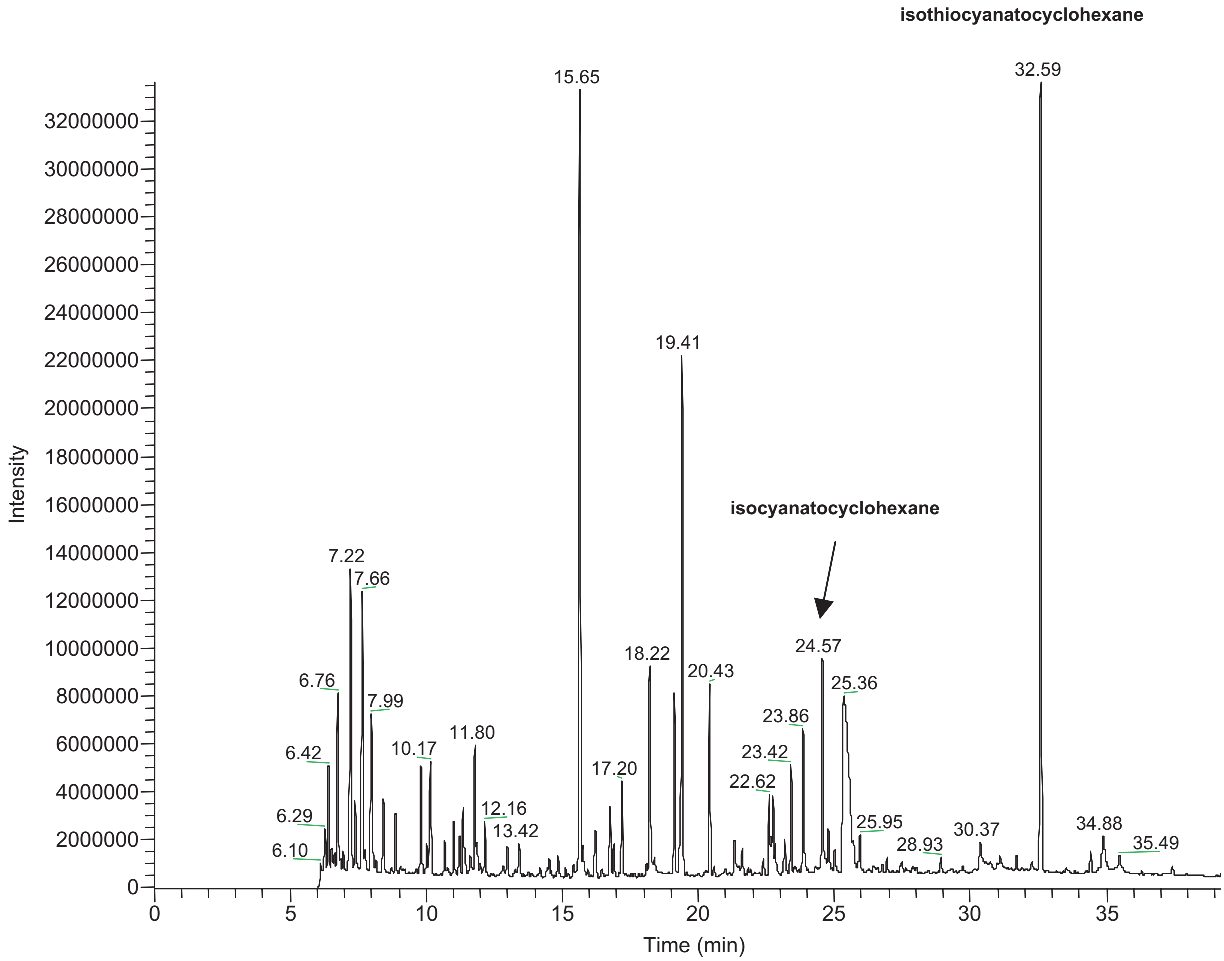

Fig. 3. Total ion chromatogram (TIC) in a 24 h control sample in an urban sample (Point 33, building construction activities).

concentrations form the main locations (Terrassa, Banyoles and Benicarló) have been studied. Only in the gas samples from Terrassa, a significant linear correlation has been obtained for the concentrations of isothiocyanatocyclohexane and carbon disulphide ($r^2 = 0.7864$, $p < 0.01$). Neither Banyoles ($r^2 = 0.0588$) nor Benicarló ($r^2 = 0.1443$) show significant correlations. However, good linear correlations have been observed between the concentrations of isothiocyanatocyclohexane and isocyanatocyclohexane, with $r^2 = 0.6110$ ($p < 0.01$), $r^2 = 0.8905$ ($p < 0.01$) and $r^2 = 0.6707$ ($p < 0.01$) in Terrassa, Banyoles and Benicarló, respectively. This observation seems to indicate a common origin for these two chemical compounds (iso- and isothiocyanatocyclohexane) in Banyoles and the main part of Terrassa and Benicarló, discarding the probability of being the source of isothiocyanatocyclohexane in the samples analysed its production during the desorption stage previous to the injection into the chromatograph.

3.2. Air concentrations

Air concentrations of isocyanatocyclohexane in all studied cities range between n.d. to a maximum value of 246 $\mu g\,m^{-3}$, found in an industrial location of Terrassa (Point 3, Fig. 2). On the other hand, isothiocyanatocyclohexane concentrations range from n.d. to 29 $\mu g\,m^{-3}$, found near the hazardous waste incineration facility of Constantí (Point 24, Table 1). Generally, higher concentrations of iso- and isothiocyanatocyclohexane are found in industrial areas than in urban and residential locations (Tables 2 and 3). To exemplify it, iso- and isothiocyanatocyclohexane average concentrations are represented in Fig. 1 (Terrassa) and Fig. 2 (Banyoles) using interpolation between concentrations at the air sampling points.

Table 2
Average (±standard deviation) concentrations of isocyanatocyclohexane ($\mu g\,m^{-3}$) in residential, urban and industrial locations in 24 h and odour episode samples

City	Residential		Urban		Industrial	
	24 h	Episodes	24 h	Episodes	24 h	Episodes
Vacarisses	–[a]	–	–	–	–	1.8±3.5
Terrassa	0.3±0.4	<lod[b]	34.6±46.1	–	72.9±72.6	22.9±45.1
Banyoles	1.0±1.1	–	7.8±8.7	–	12.0±7.2	12.0±8.3
La Canonja	–	–	–	–	55.3	18.7±14.4
Constantí	–	–	–	–	–	125.9±36.2
Benicarló	–	–	2.6±3.0	1.0±1.8	1.0±0.7	2.4
Sitges	23.5±7.4	–	–	–	–	–
Barcelona	–	–	44.6±48.1	–	–	–

[a]No sample.
[b]Below limit of detection.

Table 3
Average (±standard deviation) concentrations of isothiocyanatocyclohexane ($\mu g\,m^{-3}$) in residential, urban and industrial locations in 24 h and odour episode samples

City	Residential		Urban		Industrial	
	24 h	Episodes	24 h	Episodes	24 h	Episodes
Vacarisses	–	–	–	–	–	3.7±2.0
Terrassa	<lod	<lod	7.0±5.9	–	8.6±6.8	3.6±6.5
Banyoles	0.2±0.12	–	1.7±2.3	–	4.3±3.9	1.6±1.2
La Canonja	–	–	–	–	8.6	1.7±1.5
Constantí	–	–	–	–	–	23.1±8.8
Benicarló	–	–	6.0±4.3	6.6±10.0	2.9±2.6	1.4
Sitges	n.d.[a]	–	–	–	–	–
Barcelona	–	–	14.2±8.6	–	–	–

[a]Non-detected.

However, it has to be noted that some of the urban and residential samples from Barcelona and Sitges present high levels of the studied compounds as a consequence of the proximity of the sampling points to building construction activities (Table 1).

Isothiocyanatocyclohexane values are found in lower concentrations than isocyanatocyclohexane in the majority of samples analysed, except those from Benicarló, where values of isothiocyanatocyclohexane generally overtake values of isocyanatocyclohexane (Table 1; Table 4). These differing values correspond to points usually located far from construction building activities and near furniture industry manufactures. Some differences between Benicarló and the rest of the sampling points may explain the differences observed in iso- and isothiocyanatocyclohexane concentrations. Mainly, the fewer building activities developed in Benicarló and the higher distance of them of the sampling points, as it is generally observed that building activities are related to emissions of isocyanatocyclohexane, and the absence of potential isocyanato-related activities, such as drugs or plastic industry (Crossman, 1988). On the other hand, the most important isothiocyanatocyclohexane concentrations in Benicarló points are located near polyester resins, painters and furniture lacquer manufactures, activities that use isothiocyanatocyclohexane in their industrial processes. These observations are consistent with the higher isothiocyanatocyclohexane concentrations observed in respect to isocyanatocyclohexane. However, only a direct measurement in the emission sources could confirm their origin. The absence of a Spanish specific VOC control legislation leads to a lack of knowledge of industrial emitted compounds, as well as difficult an immission outdoor air quality control.

Table 4
Average (±standard deviation) of isocyanatocylohexane/isothiocyanatocyclohexane ratios

	Residential	Urban	Industrial
Vacarisses	–	–	1.0
Terrassa	–	10.7 ± 5.8	12.1 ± 8.4
Banyoles	7.8 ± 1.7	6.4 ± 3.2	4.0 ± 1.9
La Canonja	–	–	10.3 ± 3.9
Constantí	–	–	5.6 ± 0.6
Benicarló	–	0.4 ± 0.3	1.0 ± 0.9
Sitges	–	–	–
Barcelona	–	2.4 ± 1.5	–

Significant differences are not observed between the ratios of iso- and isothiocycanatocyclohexane in the different locations from the different cities, being the average ratio 7.4 ± 3.7, ranging from 2.4 to 12.1. These values may indicate that iso- and isothiocyanatocyclohexanes are released to the atmosphere in similar relative concentrations either in residential, urban or industrial areas, probably due to the distribution of use of these compounds in industrial- and building-related activities. However, Benicarló and Vacarisses values are lower that the ones found in the main locations, ranging from 0.4 to 1.0 (Table 4). As it has been explained previously, higher levels of isothiocyanatocyclohexane are found when specific activities using this compound in their processes are located in the zone; however, a final conclusion about this topic cannot be made as a more specific study evaluating iso- and isothiocyanatocyclohexane industrial emissions should be developed.

As it has been said before, in some urban places the concentrations of the target compounds may be related mainly to construction activities (e.g. Points 22 and 33, Table 1), but in other locations, the wind regimes are responsible of transporting these compounds from industrial locations to urban places, being the highest concentration of isocyanatocyclohexane found in an urban area (164 $\mu g\,m^{-3}$; Terrassa, Point 4, May 2004) influenced by an industrial facility (Fig. 1).

In industrial areas, notorious concentrations of the studied compounds are detected during episode sampling; however, 24 h control samples show higher concentrations (Tables 2 and 3). Air concentrations of iso- and isothiocyanatocyclohexane in industrial areas may be caused by emissions or releases from industrial processes, such as textile, painters, plastics, drugs, pesticides, resins, rubber and polyurethane elastomeric coating manufactures. Hence, the differences in concentrations and type of samples found between urban and industrial locations may reside in differences in quantities and utilisation of these compounds as well as differences in the wind regimes dominating in each season of the year.

3.3. City differences

3.3.1. Residential locations

Generally, residential locations present low levels of iso- and isothiocyanatocyclohexane (Tables 2 and 3). However, Sitges has to be highlighted

(Point 22, Table 1), where high levels of the target compounds were detected due to a building activity. These concentrations were not observed when the construction was over.

3.3.2. Urban locations

Barcelona and Terrassa present the highest concentrations of the studied compounds, nearly five times more concentrated than the other studied cities (Tables 2 and 3). The concentrations, however, are not similar in origin. Barcelona shows high concentrations of the target compounds as a result of a near building activity, whereas Terrassa present high concentrations of iso- and isothiocyanatocyclohexane in its urban tissue due to the nearness of industrial activities and its influence. The concentrations observed in Barcelona probably would decrease when the building would be finished, as it has been observed in other locations (Point 22, Table 1); however, the concentrations detected in Terrassa probably would remain similar throughout the years as the probable emission of these compounds are the industrial activities close to the city.

3.3.3. Industrial locations

Terrassa presents the highest concentrations of the studied compounds in 24 h controls in industrial locations (72.9 ± 72.6 and $8.6 \pm 6.8\,\mu g\,m^{-3}$ for iso- and isothiocyanatocyclohexane, respectively) (Tables 2 and 3). However, it has to be noted that La Canonja, and specially Constantí show high values of isocyanatocyclohexane during episode samplings, 18.7 ± 14.4 and $125.9 \pm 36.2\,\mu g\,m^{-3}$, respectively. La Canonja and Constantí are located near an important petrochemical area in Tarragona, having also Constantí a hazardous residues incineration facility.

3.4. Temporal trends

Temporal trends are observed in the distributions of the target compounds in air in some of the studied cities in 24 h control samples. Different concentrations of iso- and isothiocyanatocyclohexane through time may be consequence of changes in the sources of emission of these compounds, as it can be observed in two of the studied points.

In the residential location of Sitges (Point 22, Table 1), far from industrial influence sources, significant levels of isocyanatocyclohexane were found in May 2003. In that period of time, a building was being constructed just in front of the place where the samples were taken (50 m of distance). After 3 years (September 2006), the building was finished and the construction activity was over. In that period, the studied compounds were not detected, indicating that when the construction activity is finished, the release to the atmosphere of iso- and isothiocyanatocyclohexane also disappears, or decreases to a minimum. A similar behaviour was observed in Barcelona city (Point 33, Table 1), where concentrations of iso- and isothiocyanatocyclohexane were much higher in February 2007 than in May 2005. In May 2005, no special activities were being conducted in the nearness of the sampling point, whereas in February 2007 a building was being constructed at 20 m of distance of the studied point (Table 1). As it has been said before, iso- and isothiocyanatocyclohexane are used extensively as building insulation materials and coatings, such as paints and varnishes. When a building is being constructed, large amounts of these compounds are used and at the same time emitted to the atmosphere from the applied materials. Some time after the application of these products, the emissions form the materials decrease, as well as the concentrations in the surrounding air. Hence, urban levels of iso- and isothiocyanatocyclohexane may be relevant in city locations where urban growth is important.

On the other hand, different concentrations of iso- and isothiocyanatocyclohexane through time may also be consequence of changes in the distributions of wind regimes throughout the year seasons. Differences in the frequencies of winds that come from the industrial facilities nearby and impact on the studied points result in an increase of the target compounds concentrations in these points. However, some studied points show similar concentrations of the target compounds throughout the year. These similar concentrations may be explained by a similar percentage of impact of winds coming from the probable emission activities near the studied points (when focus and immission points are aligned with the wind direction). This case is observed in some locations in Terrassa and Banyoles. In Point 3 in Terrassa (Fig. 1), concentrations of iso- and isothiocyanatocyclohexane found in February 2004 and April 2004 are very similar, being also very similar the wind impact frequencies in the two dates, 0% and 0–16%, respectively. The same behaviour can be observed in Point 8, where the concentrations of the target compounds in June 2003 and March 2004 are similar, being the wind impact frequencies 32–48% and 30–58% for each month, respectively. In Banyoles (Fig. 2), Point 15 show very similar concentrations of the studied compounds in October and December 2004, with wind impact frequencies of 12–27% and 8–15%, respectively (Table 1). As it can be observed, the concentrations of the studied compounds in air in the different periods of the year when a sampling has been performed are similar in those cases where the percentages of impact of the industrial activities are also very similar.

On the other hand, different concentrations of the target compounds are observed in the same urban area in Terrassa (Point 11, Fig. 1) within 5 months of difference. Iso- and isothiocyanatocyclohexane concentrations (15.3–19.3 and 0.7–1.5 $\mu g\, m^{-3}$, respectively) were found in April 2004, whereas these compounds were below the limit of detection in November–December 2003. These higher concentrations are caused by a change in the wind regimes, being the wind impact frequencies of the industrial activities near the point an 11–33% in April 2004, whereas a 0% in November–December 2003 (Table 1, Fig. 1). The same trends are observed in Points 4 and 6. In Point 4, concentrations of the target compounds are nearly 10 times higher in May 2004 than in February 2004. The wind impact frequency increased from 4% to 10% in February 2004 to 15–24% in May 2004. In Point 6, the concentrations are also 10 times higher in April 2004 than in June 2003. The wind impact frequencies were 36–96% and 4–19% for June 2003 and April 2004, respectively (Table 1). In Benicarló (Point 28), the target compounds were detected in September 2006 (0.7–6.1 and 3.0–9.6 $\mu g\, m^{-3}$ for iso- and isothiocyanatocyclohexane, respectively) whereas they were below the limit of detection in October 2006. The wind impact frequencies were 25–29% and 6% in September and October 2006, respectively (Table 1).

Hence, higher concentrations of the target compounds in a point throughout the year are found when the wind impact frequencies coming from the probable emission activities are higher, releasing these activities iso- and isothiocyanatocyclohexane to the atmosphere during their industrial productive processes and/or waste deposition or incineration of these mentioned compounds.

4. Conclusions

In studies of outdoor air quality in several cities at the Northeast of Spain, it has been detected the presence of a new generation of the nitrogen compounds: cyclohexane isocyanate and cyclohexane isothiocyanate. Concentrations of iso- and isothiocyanatocyclohexane range from n.d.−246 to n.d.−29 $\mu g\, m^{-3}$, respectively. These compounds are present in all studied places, with the exception of the residential areas where no building construction activity is being performed. Usually, industrial areas show higher concentrations than urban or residential locations.

The site location (urban or industrial), the kind and nearness of possible iso- and isothiocyanatocyclohexane emission activities (industrial or building construction) and the changes of wind regimes throughout the year have been found the most important factors influencing the concentrations of these compounds in the different places. The main factor affecting the concentration level in residential areas seem to be building construction activities, because higher levels have been detected when the construction activities are being carried on whereas concentrations diminish when they conclude.

Nowadays, iso- and isothiocyanatocyclohexane are not included in the lists of chemical compounds in analysis protocols of urban air; they have only been registered in indoor workplaces (Gromiec et al., 2002; NIOSH, 2002). According to their probably health effects (not yet established in air, but regulated in food packing plastics; European Commission, 2002) and the results obtained from this work, which points out the non-negligible concentrations of these compounds in urban air, it could be interesting to include them in the list of chemical compounds that must be analysed in air quality studies. In air quality determination, these compounds must be taken into account according to their toxic character, although their human effects are nowadays still under evaluation (US EPA, 2006).

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