



Research article

Inventory of primary emissions of selected persistent organic pollutants to the atmosphere in the area of Great Mendoza

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ABSTRACT

The setting up of a country or region-based inventory is considered a crucial step toward the elimination of worldwide persistent organic pollutants (POPs) contamination. Moreover, the need of comparable emission inventories at city or region level is widely recognized to develop evidence-based policies accounting for the relation between emissions and institutional, socio-economic and demographic characteristics at small scale level.

Due to the low spatial and temporal resolution of the available measurements, highly variable air concentrations of several POPs have been observed in Latin American and Caribbean countries. This paper presents a high resolution spatially disaggregated atmospheric emission inventory for selected POPs in order to assess the environmental fate of some of these compounds in a finer resolution. As study case we estimated releases to air of POPs in a typical mid-size urban conglomeration in Argentina. Inventoried compounds were total polychlorinated biphenyls (PCBs), total polybrominated diphenyl ethers (PBDEs), total dichlorodiphenyltrichloroethane (DDT) on a sum basis, hexachlorobenzene (HCB) and dioxins and furans (PCDD/Fs), for which emissions were estimated in 0.92 kg/year, 1.65 kg/year, 4.2E–02 kg/year (total sum of congeners), 0.86 kg/year and 4.4E–02 kg/year respectively, values that are in accordance with the geographic and economic context. Although emitting sources are quite varied, there are very clear trends, particularly in relation to open burning of municipal solid waste and agrochemical use as major contributors. Overall, the inventory provides valuable data for the analysis of the heterogeneity of POP emissions and the necessary inputs for air quality modeling.

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1. Introduction

Persistent organic pollutants (POPs) are chemicals that are recognized for their high stability, their susceptibility to high long-range atmospheric transport, their potential to bioaccumulate in the food chain, and their inherent toxicity to wildlife and human beings [46]. The setup of a country or region-based POP inventory is considered a crucial step toward the elimination of worldwide POPs contamination. Moreover, identification of the emission sources of POPs in the environment is essential to establish the quantitative

factor in source–receptor relationships, and to reduce environmental burdens profitably [5]. Furthermore, reducing primary emissions would also lead to the reduction of secondary loadings of POPs, since these are supported by primary atmospheric emissions and would bring the benefit of reduction in local, regional, and global concentrations.

In this respect, the Toolkit for Identification and Quantification of Releases of Dioxins, Furans and Other Unintentional POPs has been used by some countries in Latin America to develop national release inventories as required by Article 5 (Measurements) and Article 15 (Reporting) of the Stockholm Convention [17], including an early PCDD/PCDF inventory compiled for releases in Argentina [32]. Although these official emission data present a general picture of emissions of individual POP substances in quantitative terms, no spatial distribution (i.e.: on a grid system) is reported.

While international effort has been put into developing harmonized inventories at global or regional scale [8,9,13,20,25], substantial differences have been observed by comparing different

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inventory estimates with measurements at city or local levels in Latin America and Caribbean countries [4,7,21,41,42,50]. Moreover, model simulations applied to this region appear to perform poorly for specific rural or urban sites, since they rely on emission inventories that fail to properly represent the accurate spatial distribution of the sources [6,41].

In that sense, there is an evident need for highly reliable spatial disaggregated maps that improve the information on POPs emission at local scale and provide proper input data for environmental models; both essential to establish more accurate exposure assessments and to improve possible control measures.

The present study is a methodological approach applied to the development of a spatially-distributed, high-resolution emissions inventory for selected POPs based on anthropogenic sources. As a case study, we used local information to generate a comprehensive inventory in order to understand the extent of POPs emissions to air from major sources in a typical mid-size urban conglomeration in Argentina. Since there is an increasing concern in Latin America about sustainable development strategies, an immediate priority is to reduce atmospheric emissions mainly related to thermal processes, agriculture and urban activities. Hence, dibenzo-p-dioxins/furans (PCDD/Fs), total polychlorinated biphenyls (PCBs), total polybrominated diphenyl ethers (PBDEs), total dichlorodiphenyl-trichloroethane (DDT) on a sum basis, and hexachlorobenzene (HCB) were inventoried to provide support to environmental fate assessment, highlighting the main differences between the inventories performed in other regions and the local particularities of the sources. The spatial allocation of emissions was made using source-based spatial surrogates from available basic data to avoid problems arising from different level of disaggregation, both in quantity and quality. Moreover, we quantified and assessed the magnitude and spatial extent of these primary POPs releases to the

atmosphere by using a methodological procedure that can be applied to any region allowing the compilation of a consistent regional inventory.

2. Materials and methods

2.1. Study area

Great Mendoza is the most important urban area in the region of Cuyo and the fourth in population of Argentina (1.7 million inhabitants in 2010). The conurbation is located in the west-central part of the country, in a region of foothills and high plains, on the eastern side of the Andes, between 32° and 37° 35'S, and 66° 30' and 70° 35'W.

The constructed area of about 16,700 km² extends in an irregular manner to the northeast, east and south, since the Andes Range prevents the city from growing to the west.

The surrounding area is a productive river oasis and one important wine region, accounting for nearly two-thirds of the country's entire wine production. Other important crops (mainly for the Argentine market) are apples, pears, tomatoes, onions, plums, olives, cherries, peaches and quince.

Great Mendoza is located in a semiarid region, with low relative humidity (<50%), and very low precipitation rates (230 mm yr⁻¹), with rain mainly occurring during Austral summer months. The closeness of the Andes Mountains has a strong influence on local meteorology and air quality, characterized by a day–night variation due to a typical valley–mountain circulation [40].

For the inventory purpose, the study area was divided into 8100 grid cells with 1 × 1 km² spatial resolution, covering the 11 different departments (Fig. 1).

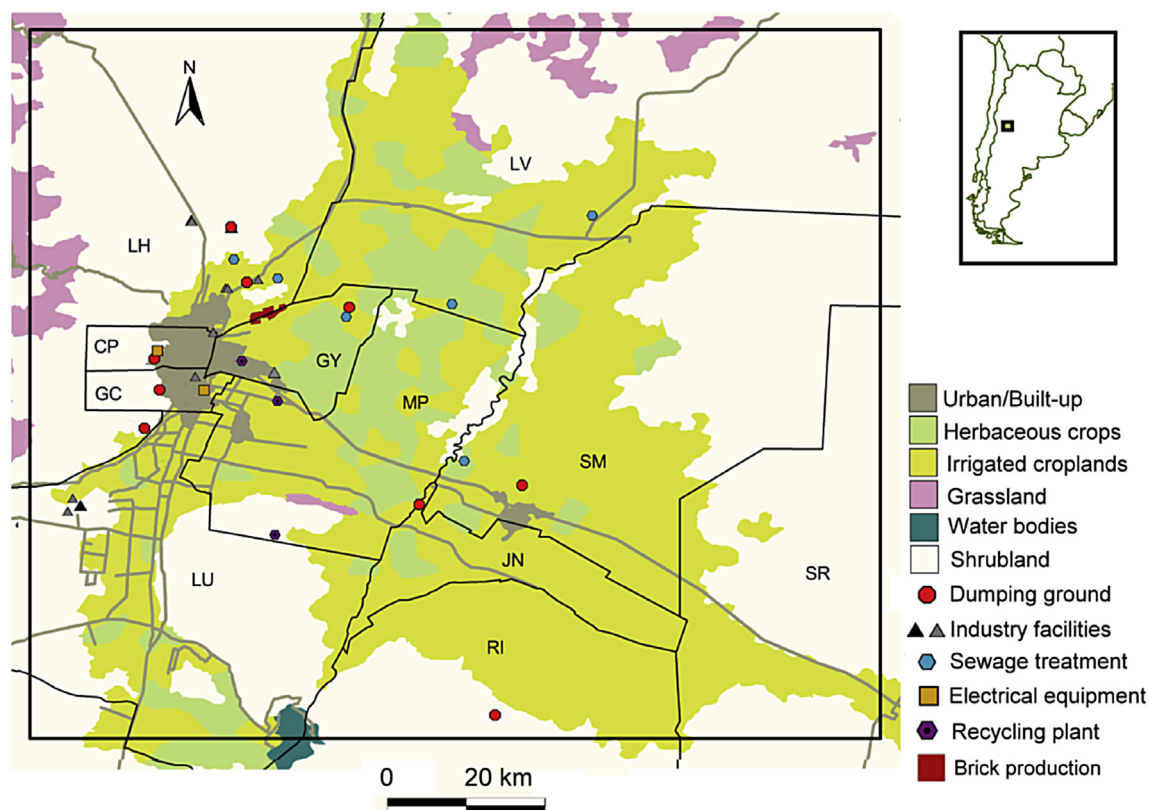


Fig. 1. Great Mendoza land use features and location of main POPs sources. Black solid lines represent interdepartmental boundaries: Capital (CP), Godoy Cruz (GC), Guaymallén (GY), Maipú (MP), Junín (JN), San Martín (SM), Rivadavia (RI), part of Luján de Cuyo (LU), Lavalle (LV), Las Heras (LH) and Santa Rosa (SR).

Major industrial sources are located in two industrial areas in the periphery of the city to the SW and the north edge, while the agro and food production is mostly located on the east side. Minor manufacturing facilities are dispersed in small industrial districts near the urban center. Several active urban waste disposal sites are situated in the periphery or integrated in suburban areas.

2.2. Source categories and data sources

Due to the fact that one of the main objectives of the creation of a POPs emissions inventory is its use for making decisions, a clear delimitation of individual sources and source categories becomes essential. The anthropic sources identified in the study area are listed in Table 1, and they are detailed in the sections below. We follow the categories listed under the Stockholm Convention Annex C Part II and Part III [45].

2.3. Methods for estimating POPs emissions

With the aim to ensure accuracy of the estimations calculated, the inventory was performed using two main methodologies, from the data available. A “bottom-up” methodology was used in specific sources, such as industrial sources, disposal and treatment of waste, and transformers, in which case there were data of activity levels or whose estimation was possible using the information available. On the other hand, a “top-down” methodology was used for area sources, including the application of agrochemicals and the use of electrical equipment with BFRs, for which there are available data at a regional level and a lesser level of disaggregation. There are numerous precedents in other countries that serve as references of this study [3,14,54,58]) where both approaches were used.

In this study, only selected POPs primary emissions were estimated, without congener differentiation. Since the congener composition is normally very variable and because of the limited information on speciated emission factors for the atmospheric emissions of PCBs, PBDEs, PCDD/Fs and DDT (or only restricted to range of them) we didn't report any emission profiles to air, and present total releases to air on a sum basis.

In all cases, the final calculation of emissions (E) was performed using the procedure proposed by the United Nations Environment Programme under Article 5 of the Stockholm Convention, according to which an emission factor (F: potential emission of a given substance per reference unit of a product or compound) and a temporal level of activity (A: values of consumption or production) are used for a known source, according to the equation [45]:

$$E = F \times A \quad (1)$$

Emission factors have been identified from various sources, such as publications, reports from environmental agencies and the private sector related to industrial activities. The estimation of the level of activity of each sector is detailed in subsequent sections. For detailed estimates of emissions, see supplementary material.

2.3.1. Waste incineration

2.3.1.1. Medical waste incineration. In the study area, the burning of waste generated in pharmacies, hospitals, health centers and drugstores is performed in a plant located north of the urban center. Those facilities have a system of pyrolytic thermal destruction of waste where 4.5 t/day of medical waste are incinerated, making it a source of PCBs, HCB and PCDD/PCDF to the atmosphere. Like other processes of incineration, a characteristic emission factor was used [14,45] (Table S1).

2.3.2. Ferrous and non-ferrous metal production

2.3.2.1. Coke production. An oil refinery, located in the Petrochemical Pole, produces 1.88E06 t coke/year [22]. Coke is produced from hard coal or brown coal by carbonization (heating under vacuum) in “coke ovens” at approximately 1000 °C in the absence of air. These conditions promote the formation of PCDD/PCDF. The plant has afterburner and dust removal equipment, and the emission factor was selected according to this [45] (Table S2).

2.3.2.2. Other non-ferrous metal production (ferroalloys). In the study area, there are also potential sources of unintentional POPs (HCB, PCBs and PCDD/PCDF) due to the production and subsequent treatment of ferroalloys [2,45]. In Mendoza, there is one plant located in a Petrochemical Pole south of the urban center, which is

Table 1

Source categories for the atmospheric emission inventory.

Source group	Source category	PCBs	PBDEs	DDT	HCB	PCDD/Fs
1. Waste incineration	c. Medical waste incineration	x			x	x
2. Ferrous and non-ferrous metal production	b. Coke Production				x	x
	j. Other non-ferrous metal production (Ferroalloys)	x			x	x
3. Heat and Power generation	a. Fossil Fuel power plants	x	x			x
	e. Domestic heating (fossil fuels)					x
4. Production of mineral products	a. Cement production				x	x
	c. Brick production				x	x
	d. Glass production					x
5. Transport	a. 4-Stroke engines					x
	c. Diesel engines					x
6. Open burning process	b. Waste burning and accidental fires	x	x		x	x
7. Production and use of chemicals and consumer goods	e. Other chlorinated and non-chlorinated chemicals					
	e.1 Polypropylene Production		x			
	e.2 Paint Production	x				
	e.3 Use of BFR in plastic of vehicles		x			
	e.4 Use of BFR in plastic of electrical appliances		x			
	f. Petroleum refining					x
9. Disposal and landfill	b. Sewage and sewage treatment		x			
	e. Waste oil treatment	x				
10. Contaminated sites and hotspots	c. Application of pesticides and chemicals.			x	x	x
	f. Use of PCBs					
	f.1 Transformer in use	x				
	f.2 Transformer stockpiling	x				
	l. Dumps of Wastes/Residues from Source Groups 1–9		x			

dedicated to the manufacture of ferroalloys (25,000 t/year) using electric arc furnace technology for the treatment of primary metals and scrap metal. Although the emitted POPs are present in the form of traces, this type of industry generates a large amount of waste gases, and emissions can be significant [2]. Typical emission factors for the available technology are depicted in Table S3.

2.3.3. Heat and power generation

2.3.3.1. Fossil fuel power plants. PCBs, PBDEs and PCDD/PCDF emissions have been verified in power generation and incineration processes [11,45,49]. In the study area, there is a power plant complex, with a total of 540 MW installed capacity. Although fuel composition is not accurately known, 79% of the power produced is generated by means of 45,400 t/year of light fuels, producing PCBs, PCDD/PCDF and PBDEs emissions. They were estimated with characteristic emission factors [11,45,49]; for cases in which emission controls are unknown, assuming worst-case scenarios (Tables S4 and S5).

2.3.3.2. Domestic heating (fossil fuels). In the study area, natural gas is used extensively for domestic heating and cooking. During the combustion process, PCDD/PCDF are unintentionally formed. It is assumed that reasonably well-operated and maintained ovens and stoves are employed in order to maximize heat output and ensure safety [45]. According to the information provided by the Local Regulatory Authority, 16,212 TJ are consumed annually for household heating and cooking. Details on the emissions estimations are presented in Table S6.

2.3.4. Production of mineral products

2.3.4.1. Cement production. Cement production is a unintentional source of HCB and PCDD/PCDF emissions, due to the kiln's feed material and the nature of process [3]. In the study area, there is a cement manufacturing plant located northwest of the urban center, whose kiln uses a mixture that includes hazardous waste and raw material as complement of fuels, in rotary kilns, with dust collector between 200 and 300 °C. For emission estimation purposes, a scenario where not always a co-combustion of alternative fuels was considered, and consequently, the generation of chlorinated products, like HCB and PCDD/PCDF, does not always occur. In this regard, although total production of cement for the year of reference was taken into account (736,000 t), a mean emission factor of $1.7E-04 \mu\text{g}/\text{t}$ cement was used for HCB instead of considering the worst case, as suggested by the Portland Cement Association of Canada, according to many studies performed in cement kilns [3]. In the case of PCDD/PCDF, as recommended in Ref. [45] for this type of technology, the default emission factor was used (Table S7).

2.3.4.2. Brick production. Very primitive brick kiln technology continues to be widely used in developing countries. In Mendoza, intermittent kilns with low efficiencies produce bricks in the traditional way without any abatement of emissions. The average annual production is $60E06$ brick/year, meaning $1.32E05$ t brick/year [29]. The use of fuel wood from unsustainably managed forest complemented by wastes with high calorific values (oil, tires, plastic) may promote higher emissions of PCDD/PCDF, PCBs and HCB, which were calculated using characteristic emission factors for this activity [27,45] (Table S8).

2.3.4.3. Glass production. In the considered domain, there is a glass manufacturing plant dedicated to the production of packaging, elaborating $6E08$ bottles/year, meaning $4.2E05$ t/year. The process involves mineral products and a wide range of other materials used to achieve properties such as color, clarity and for purification, resulting in the formation of chlorinated substances, especially

PCDD/PCDF. The plant operates with continuous furnaces and gases are cleaned with sorbents and electrostatic precipitators or fabric filters. The emission factor was selected according to the technology used [45] (Table S9).

2.3.5. Transport

POPs emissions from transport result from incomplete combustion of fuel in engines. Levels of unintentional POPs in exhaust gases from vehicles depend on many factors including the type of engine, maintenance and age, technologies of emission reduction (catalysts), type and quality of fuel, driving conditions and ambient conditions. The impacts assessment of the traffic activity on POPs releases to air is particularly relevant, especially when considering the growth in the number of cars. For the purpose of this atmospheric emission inventory, a simple methodology is used, where emission rates are considered a function of the engine characteristics and type of fuel. Thus, emission factors are given according to the type of combustion engine, the emission reduction technology applied (catalysts) the type of fuel [45]. Road transport calculations were divided into three main modes: 4-strokes engines (with/without catalytic converter) and diesel engines. Fuel consumption was estimated according to [36] (see detailed calculations in Table S10.)

2.3.6. Open burning process

2.3.6.1. Waste burning and accidental fires. Open burning of Municipal Solid Waste (MSW) is probably one of the most significant sources of POPs in developing countries [51] and still it is a common practice in the area, where the average generation is 1.18 kg MSW/habitants.day with a typical composition detailed in Table S11, according to local official reports. As stated in the Inter-governmental Panel on Climate Change [23], in South America, an average of 54% reaches controlled dumping sites, while the rest goes to clandestine waste dumping sites, of which there is no information, and consequently, they have not been considered in this study. Of the waste that reaches these controlled sites, there is a portion made up of paper, cardboard, glass and metal that is separated for reuse by informal workers. Part of the remainder (by 60%) is burnt to reduce its volume and to avoid sources of infection [23]. The burning is performed in the open air without use of appropriate equipment or any control over the emissions. From that information, it was calculated that 350 t MSW/day are burnt.

Given the wide range of experimental results and measuring at a global level and the lack of local measuring, HCB and PCBs emission factors characteristic of developing countries were used [3,14]. The PCDD/PCDF emission factor was taken from Ref. [45].

In the case of PBDEs a slightly different methodology was used because only plastic material containing BFRs emits this type of substances. Consequently, only the corresponding fraction of MSW was considered, which, according to studies, is about 30% of the total plastic waste [33], that is 15.9 Tn/day. For the estimation of emissions, the method proposed by Ref. [38] was used, whereby emissions of all PBDEs congeners are calculated in basis of DecaBDE. The emission factor used in this case refers only to the quantity of this congener, and the total amount is calculated using a relation DecaBDE/totalPBDEs (Tables S12 and S13).

2.3.7. Production and use of chemicals and consumer goods

2.3.7.1. Other chlorinated and non-chlorinated chemicals

2.3.7.1.1. Polypropylene production. Commercial mixtures of PBDEs for the production of polypropylene homopolymers and copolymers (120,000 t/year) are introduced in the study area, since they are added as additives to the polymeric mixture as flame retardants [1]. The estimation of direct emissions to the atmosphere in the production sector was previously performed by calculating

the additives stock (1 g additive/kg polymer, according to the producer's reports). Due to lack of information, the worst-case scenario involving the fact that the entire additive is PBDEs (Table S13) was assumed. A generic emission factor assuming a release to the atmosphere proportional to such stock was used [39].

2.3.7.1.2. Paint production. Various studies analyzing commercial pigments [19] have found traces of PCBs, specifically in azo and phthalocyanines, commonly used in the manufacture of paints, in a proportion that varies between 20 and 200 ng PCBs/g fresh pigment. PCBs emissions to the atmosphere from such source were calculated estimating the PCBs stock, considering the limit of 180 ng PCBs/g of pigment set by the USA standard. Furthermore, the average proportions of pigments in the dissolved solids, the quantity of solids in commercial paints and the proportion of pigments that are phthalocyanines were considered [10]. Emissions were divided among all paint manufacturers in the study area of Great Mendoza in Las Heras (LH) and Godoy Cruz (GC) districts, which have a total production of 5871 t/year (Table S14). Volatilization was calculated using a characteristic emission factor [14].

2.3.7.1.3. Use of BFR in plastic of vehicles. Among the wide range of materials containing BFRs, vehicle interiors are a major source. In order to estimate the stock of PBDEs used in automobiles, statistics of the number of vehicles in Argentina disaggregated by type were used, according to data provided by Argentina's National Registry of Motor Vehicle Property. The method suggested by the UNEP [47] was used as a reference for emission calculation according to which, cars manufactured or imported as from 2005 are considered PBDEs-free, as BFRs have no longer been used in vehicles since then. Approximately 63% of Argentina's 2011 vehicle fleet was registered prior to 2005 [36]. For emission calculations, the amount of PentaBDE congener used by type of vehicle was first estimated, which was then affected by one use-factor depending on the geographical location (0.05 for Latin America). Finally, the total amount of PBDEs contained in vehicle interiors was estimated through the proportion of PentaBDE/PBDEs (58%, Table S16). The emission factor used in this case was also extracted from the study conducted by Ref. [39].

2.3.7.1.4. Use of BFR in plastic of electrical appliances. The amount of PBDEs in electrical equipment in use was estimated using disaggregated data of electrical appliances present in Great Mendoza (TV sets, refrigerators, mobile phones, computers, land-line telephones) according to the statistics of Argentina's National Census 2010 (INDEC, National Institute of Statistics and Censuses). As with the vehicles, the method proposed by the UNEP [47] was used. The amount of plastic was determined by means of a weight percentage for each equipment type and the amount of OctaBDE congener present. The OctaBDE was assumed to be 35% of the PBDEs, amount from which the total was calculated. The emission factor used is also obtained from Ref. [39] (Table S17).

2.3.7.2. Petroleum refining. In Mendoza, there is an oil refinery located in a Petrochemical Pole south of the urban center, dedicated to the manufacture of combustibles and petrochemical substances. In the catalytic reforming process, that turns naphtha into high-octane gasoline, continuously regenerated catalysts are used, with the addition of chlorine and/or organochlorines, producing PCDD/PCDF releases to air from vent stacks and flares. At present, the refinery treats 371,250 t oil/year by catalytic reforming [22], which emit 0.02 µg PCDD/Fs/t oil [45] (Table S18).

2.3.8. Disposal and landfill

2.3.8.1. Sewage and sewage treatment. Several studies indicate that PBDEs may be released to the atmosphere from municipal wastewater plants [28]. In the domain considered, there are 7 sewage sludge treatment facilities, with different volumes of treated

effluents, according to the information provided by the Local Regulatory Agency, where a total 234,000 m³/day are treated. For the estimation of emissions (Table S19), it is necessary to determine the level of contamination of PBDEs effluents, for which a concentration of 29 pg PBDEs/m³ effluent was taken [31]. Final emission to the environment is proportional to the amount of PBDEs contained in it [28]. Consequently, emission factors for plants similar to the ones located in the region were used.

2.3.8.2. Waste oil treatment. There are PCBs treatment methods complying with industrial standards, electrical equipment containing materials with PCBs concentrations of at least 50 mg/kg, although this is particularly scarce in Mendoza. According to data provided by the Environmental Office of the Province of Mendoza, the amount of lubricating oil containing PCBs that is discarded by industrial equipment is 122.6 t/year and all of it is treated in a plant located south of the urban center (MP). The amount of PCBs in the material was assumed to be, taking a conservative perspective, 50 mg PCBs/kg oil. Total emissions (Table S20) were calculated with reported emission factors [16].

2.3.9. Contaminated sites and hotspots

2.3.9.1. Application of pesticides and chemicals. The inventory of POPs emissions resulting from the application of organochlorine pesticides was created using a "top down" approach based on a sectorial analysis of the application of agrochemicals in the study area, due to the fact that there are no official disaggregated data on the use of organochlorine pesticides. Generic official data showed that only dicofol is used, which contains DDT impurities, as well as PCNB (also known as Quintozene) and chlorothalonil, which contain a low percentage of HCB [30,43,48]. PCNB also contains high amounts of PCDD/PCDF and recent atmospheric release estimates suggest that contaminated pesticides are an important ongoing source of these substances to the environment [18]. This study presents the first consideration of pesticide use as a source of PCDD/PCDF in the atmosphere of Argentina.

The final estimation was performed taking into account the cultivated hectares, the typical applications for each type of crop (grapevines, fruits, some vegetables, in differentiated applications), the recommended dose, a number of maximum applications per cropping cycle, POPs concentration in the active ingredient, and an emission factor that takes both volatilization in each application and mode of use into account (Tables S21 and S22). The estimated annual averages of the application of organochlorine pesticides were verified against global official data on agrochemicals in order to ensure inventory consistency.

2.3.9.2. Use of PCBs

2.3.9.2.1. Transformer in use. The use of PCBs as dielectric fluids in transformers and capacitors has been banned in Argentina since 2001. According to the information provided by the power distribution company in the Province, the vast majority of transformers containing PCBs had been decommissioned by 2006. There is only one transformer in use containing this substance. Since the mineral oils previously used in transformers contained between 50 and 500 parts per million (ppm) of PCBs [16], the worst-case scenario was assumed and thus the higher value was considered. Total emissions are proportional to the total amount of PCBs in the transformer [24] (Table S23).

2.3.9.2.2. Stockpiling. In order to treat transformers having PCBs-contaminated oils, 30,000 L of this substance were temporarily stocked in a location in the Godoy Cruz Department (GC) until the end of the reference year of this inventory. Emissions are expected due to possible damage to the transformer's outer casing resulting in PCB-fluid leaking. As with the transformers in use, the

PCBs content was assumed to be of 500 ppm [16] and the emission factors established in Ref. [24] (Table S24) were considered.

2.3.9.3. Dumps of Wastes/Residues from Source Groups 1–9. Plastic recycling is an increasingly common practice that poses environmental risks due to the reemission of PBDEs included in the polymeric matrix, during dismantling and crushing operations, in the dust from the waste treatment equipment [38]. Plastic recycling plants (private and municipal) are identified as specific sources and the amount of material to be recycled is known (Table S25). PBDEs stock contained in the material to be recycled depends on the type of plastic and its use [61].

Regarding e-waste, in Mendoza there is a plant that treats 2 t/month of this type of waste. The amount of PBDEs was calculated considering that only 5% of e-waste contains BFRs as additive in an average concentration of 115 g/kg [61], which means 0.003 t/day of BFR-containing plastic treated in this site (Table S25). Emission factors for all cases were considered according to information reported by Ref. [38]; taking into account whether the process includes only dismantling or crushing as well.

3. Spatial allocation

In order to produce a spatial allocated emission inventory for input into air transport models, activity data with spatial resolution as detailed as possible must be collected. The methods for spatially disaggregating the estimated emissions into the 1 km × 1 km domain grid cells depend on the source characteristics. In that sense, Geographic Information Systems (GIS) were used to create maps and performing the allocation of emissions to geospatial data. The first step is to find proper spatial surrogates, which specify the fraction of the emissions released in a particular area and that should be allocated to a particular grid cell. For example, the

emissions from point sources, like large and small industrial facilities and open burning of MSW, are directly allocated into grid cells, where the sources are located based on their latitude and longitude information.

Since the emissions from PBDEs-containing electrical equipment are associated to population, the population density data was used as surrogate to aid in the spatial allocation of these emissions [34]. A GIS-based road network information and road types-based traffic flows as spatial surrogates were adopted for allocating vehicle-associated PBDEs emissions [34,35]. The spatial allocations of agro-related emissions are conducted based upon land use and associated surrogate data, such as crop type.

Polygon-based and line-based spatial surrogates are weighted using the variable value in the intersection of the line or area and the grid cell to the total value of the variable. For each source category, point and non-point source emissions were spatially distributed using the quantitative spatial surrogate data, detailed in Table 2.

4. Results

4.1. Total emissions

The POPs inventory, elaborated for the area of Great Mendoza during 2011, for the sources analyzed above, is presented in Table 3.

In order to prevent erroneous messages, all uncertainties involved in the calculation and in the data sets need to be accurately communicated in this study. In that sense, the confidence rating scheme of the United States Dioxin Inventory was used to characterize the quality of the emission estimation based on both the confidence of the emission factor and the activity level. The category ratings for the quantitative estimations are A (high

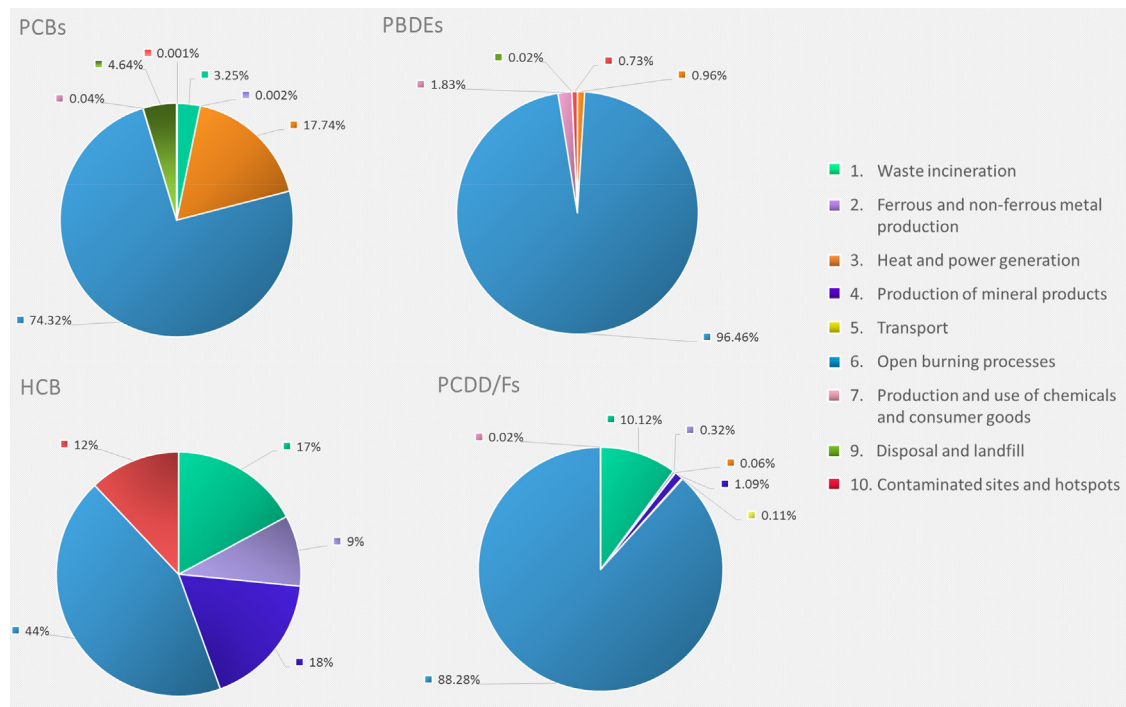
Table 2
Auxiliary surrogate variables used to spatially allocate emissions to air.

Source group	Source category	Spatial surrogates
1. Waste incineration	c. Medical waste incineration	Aerial photography + GIS tools
2. Ferrous and non-ferrous metal production	b. Coke Production j. Other non-ferrous metal production (Ferroalloys)	
3. Heat and power generation	a. Fossil Fuel power plants e. Domestic heating (fossil fuels)	
4. Production of mineral products	a. Cement production c. Brick production d. Glass production	Population density data + urban district maps + DMSP-OLS "Earth at night" satellite data Aerial photography + GIS tools
5. Transport	a. 4-Stroke engines c. Diesel engines	Population density by district + Road map + Annual Mean Daily Traffic (AMDT) + DMSP-OLS "Earth at night" satellite data GLOBCOVER2009 LULC Database + Aerial photography + GIS tools
6. Open burning process	b. Waste burning and accidental fires	Aerial photography + GIS tools
7. Production and use of chemicals and consumer goods	e. Other chlorinated and non-chlorinated chemicals e.1 Polypropylene Production e.2 Paint Production e.3 Use of BFR in plastic of vehicles	Population density by district + Road map + Annual Mean Daily Traffic (AMDT) + DMSP-OLS "Earth at night" satellite data Population density data + urban district maps + DMSP-OLS "Earth at night" satellite data + National census data on electrical equipment
9. Disposal and landfill	e.4 Use of BFR in plastic of electrical appliances f. Petroleum refining b. Sewage and sewage treatment	Aerial photography + GIS tools Aerial photography + GLOBCOVER2009 LULC Database
10. Contaminated sites and hotspots	e. Waste oil treatment c. Application of pesticides and chemicals. f. Use of PCBs f.1 Transformer in use f.2 Transformer stockpiling l. Dumps of Wastes/Residues from Source Groups 1–9	Aerial photography + GIS tools GLOBCOVER2009 LULC Database + Aerial photography + National Census data on pesticides + Crop distribution map Aerial photography + GIS tools

Table 3

Total POPs emissions to air in Great Mendoza in 2011. All emissions are in g/yr.

Source group	Source category	PCBs	PBDEs	DDT	HCB	PCDD/Fs	Uncertainty
1. Waste incineration	c. Medical waste incineration	30			148.5	4.46	B
2. Ferrous and non-ferrous metal production	b. Coke production				1.13	0.06	A
	j. Other non-ferrous metal production (ferroalloys)	0.02			80	0.08	A
3. Heat and power generation	a. Fossil fuel power plants	164	15.8			4.9E–03	A
	e. Domestic heating (fossil fuels)					0.02	B
4. Production of mineral products	a. Cement production				125	0.44	B
	c. Brick production				29.7	0.03	C
	d. Glass production					0.01	B
5. Transport	a. 4-Stroke engines					9.7E–03	B
	c. Diesel engines					0.04	B
6. Open burning process	b. Waste burning and accidental fires	687	1589		376	38.9	C
7. Production and use of chemicals and consumer goods	e. Other chlorinated and non-chlorinated chemicals		16.8				C
	e.1 Polypropylene Production						D
	e.2 Paint Production	0.39					C
	e.3 Use of BFR in plastic of vehicles		6.1				C
	e.4 Use of BFR in plastic of electrical appliances		7.3				B
	f. Petroleum refining					0.01	B
9. Disposal and landfill	b. Sewage and sewage treatment		0.25				B
	e. Waste oil treatment	42.9					C
10. Contaminated sites and hotspots	c. Application of pesticides and chemicals.			42	104	2.44E–03	C
	f. Use of PCBs						
	f.1 Transformer in use	9.3E–03					C
	f.2 Transformer stockpiling	7.6E–04					C
	l. Dumps of Wastes/Residues from Source Groups 1–9		12.1				B
Total		924.32	1647.35	42.00	864.33	44.07	

**Fig. 2.** Contribution by sources to total emissions of HCB, PCBs, PBDEs, and PCDD/Fs.

confidence), B (medium confidence), C (low confidence) and D (non representative) [44].

4.2. Contribution by sources

Fig. 2 shows the percentage contributions of each source to the total emissions of each analyzed POP. The graph for DDT is not included since it only has one source of emission.

As it can be observed, the open burning of MSW appears as the main source, followed by waste incineration and power generation.

4.3. Spatial characteristics of POPs emissions in Great Mendoza

Fig. 3 shows the spatial distribution of the total emission of selected POPs in 2011 for the area of Great Mendoza, georeferenced in grid cells of 1 km × 1 km, in kg/year. As it can be observed, the emission distribution of compounds whose sources are the use of

organochlorine pesticides (DDT and HCB) is very similar to that of the area covered by crops and shown in the land use map in Fig. 1. For PCBs and PBDEs, the maps show more heterogeneity due to the wide range of emission sources.

PCDD/PCDF emissions to air are related to stronger industrial activities and in a lesser extent to population density, traffic activity and agro production. Particularly, high POPs emissions were estimated in zones with MSW open burning, which account for only 0.3% of the total land area, but to 75%, 44%, 97% and 88% of total atmospheric emissions of PCBs, HCB, PBDEs and PCDD/Fs respectively.

5. Discussion

For comparison purposes, Table 4 shows the results of emission inventories of other countries with different characteristics in terms of total population and GDP, as an indicator of the standard of living.

Per capita emissions of HCB in Mendoza are in the middle range of available studies in other regions. Our estimates for PBDEs and PCBs are lower than the atmospheric emissions in other countries (23–93% lower). PCBs and PBDEs emissions are particularly related to the existing stock of these substances and their historical consumption, which explains the variability of emissions in relation to other regions, such as Italy or Germany. Conversely DDT emissions are larger, possibly due to the fact that dicofol is banned or less used and Mendoza is a primarily agricultural region. PCDD/Fs emissions to air in Mendoza are much higher than in other countries. These differences can be explained by the importance of the regular MSW burning in the region, the main contributor to dioxins and furans emissions. Notice that our estimates are in the same order of magnitude that the ones presented officially for Argentina [32], but pared to our city-scale emission. Additionally, the methodological approach proposed in this manuscript uses different background information to better characterize the MSW open burning activities.

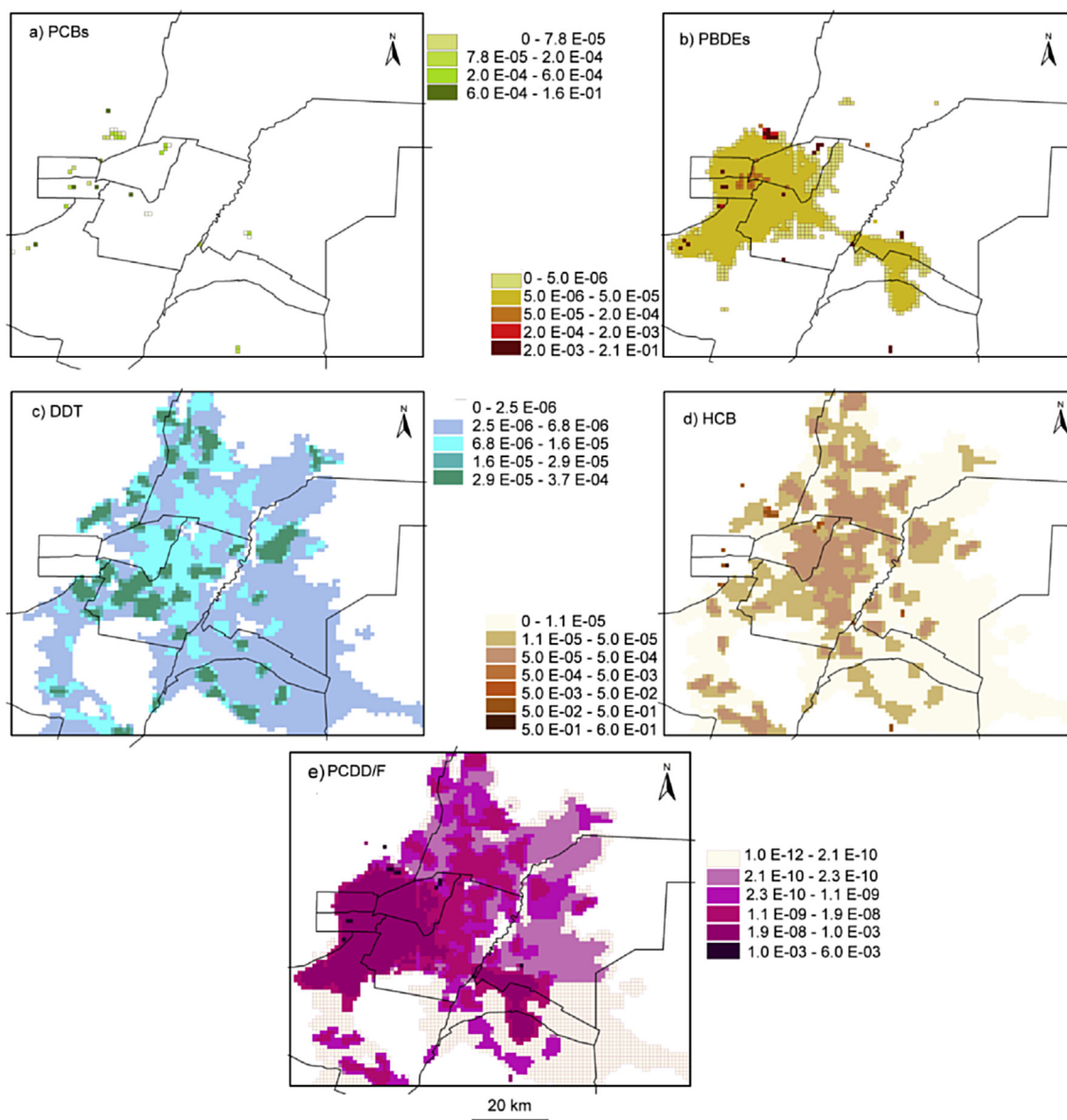


Fig. 3. POPs emissions in Great Mendoza (kg yr^{-1}): a) PCBs, b) PBDEs, c) DDT, d) HCB and e) PCDD/Fs.

Table 4(a and b) Emissions of the selected POPs per capita and per US\$ of GDP (<http://data.worldbank.org/>), according to this study and presented in the literature.

a)					
Pollutant	Study area	Year	Emission per capita [kg/10 ⁷ inhabitants]	Emission/GDP [kg/10 ¹¹ US\$]	References
PCBs	Mendoza	2011	9.9	5.5	This study
	California (US)	2011	95.5	18.4	[62]
	Spain	2011	7.0	2.2	[55]
	UK	2011	143.4	38	[57]
	Italy	2010	33.2	9.3	[15]
	Germany	2010	27.4	6.6	[15]
PBDEs	Mendoza	2011	17.60	12.85	This study
	Taiwan ^b	2008	22.83	7.66	[49]
	Japan ^c	2002	77.57	24.84	[38]
	Switzerland ^d	2010	333.42	44.89	[53]
	U.S. ^e	2007	136.11	28.32	[52]
DDT	Mendoza	2011	0.4	0.3	This study
	Spain ^a	2000	0.2	0.1	[30]
	U.S.	2007	0.0	0.0	[9]
HCB	Mendoza	2011	9.2	6.7	This study
	France	2011	2.5	0.6	[15]
	Ontario	2006	10.3	2.6	[62]
	UK	2011	4.5	1.2	[57]

b)					
Pollutant	Study area	Year	Emission per capita [g/10 ⁷ inhabitants]	Emission/GDP [g/10 ⁹ US\$]	References
PCDD/Fs	Mendoza	2011	469.3	342.7	This study
	U.K.	2011	32.2	7.7	[57]
	Colombia	2010	107.8	174.5	[63]
	Ecuador	2004	48.4	178.9	[60]
	Perú	2003	69.1	220.4	[56]
	Argentina	2001	234.6	268.7	[59]

^a Calculated with dicofol use.^b Only combustion sources.^c Only DBDE congener.^d Average of summer and winter seasons.^e Only from houses and garages.

A high correlation between pollutant emissions to the atmosphere and GDP was observed [26,37], particularly for those compounds which are most related to regional development, such as PCBs and PBDEs. In the case of the latter, the different BFRs consumption and use scenarios, related to a higher standard of living, explain the most significant differences in the emission patterns in certain regions of the study, such as European countries or the United States [12].

5.1. Uncertainty analysis

Although we used consistent methods in the estimation of emissions in order to avoid differences in the estimated releases to atmosphere that come from the methodological approach, uncertainties in the inputs can propagate through the emissions calculations. The inventory uncertainties are attributed to errors and simplifying processes or the omission of certain factors in the estimations of activity data and to errors associated with the emission factors.

Monte Carlo simulations were used to perform a detailed assessment of the uncertainties of calculated emissions to air for all POPs. Monte Carlo model inputs (activity data and emission factors) were treated as random variables described by a normal probability density function. In that sense, we ensured that the expected values for emission factors were accurately represented and 99.7% confidence intervals were as close to those quoted in the literature for the available local technology. Uncertainty information on activity data was assumed to normally

distribute with 99.7% confidence interval $\pm(10-40\%)$ of the mean, as suggested in Ref. [15]. The expected values and standard errors for the activity data were calculated using local survey data, as detailed in the previous sections. We assumed that there were no correlations since variables were not estimated from the same data sources. A value for each input was pseudo-randomly sampled from the normal distributions and the model was run to produce an output value. This process was repeated (20,000 runs) resulting in a set of emissions which form empirical distributions that describes the uncertainty. Further details are given in Tables S26–S30.

Fig. 4 shows the empirical distribution of the estimate of POPs emissions to air in 2011 for the Great Mendoza urban area. Emissions present a normal distribution for all POPs with similar skewness, with the exception of the HCB, that is less spread due to the reduced uncertainty in the emitting sources. The coefficient of variation for the emissions ranged from 16% to 37%. Table 5 shows a summary of the estimated emissions in a 99.7% of confidence interval. The inputs that most affected the uncertainty in emissions were similar for all POPs, although the order of importance varied slightly from one to another. The sectors Production and use of chemicals and consumer goods and Contaminated sites and hotspots display the largest coefficient of variation (20–16.7%) in the activity data, followed by Transport (18%) and Production of mineral products (13.6%).

The emission factor in the sectors Heat and Power generation and Open Burning Process had the largest impact on uncertainty for all emitted compounds from these sources.

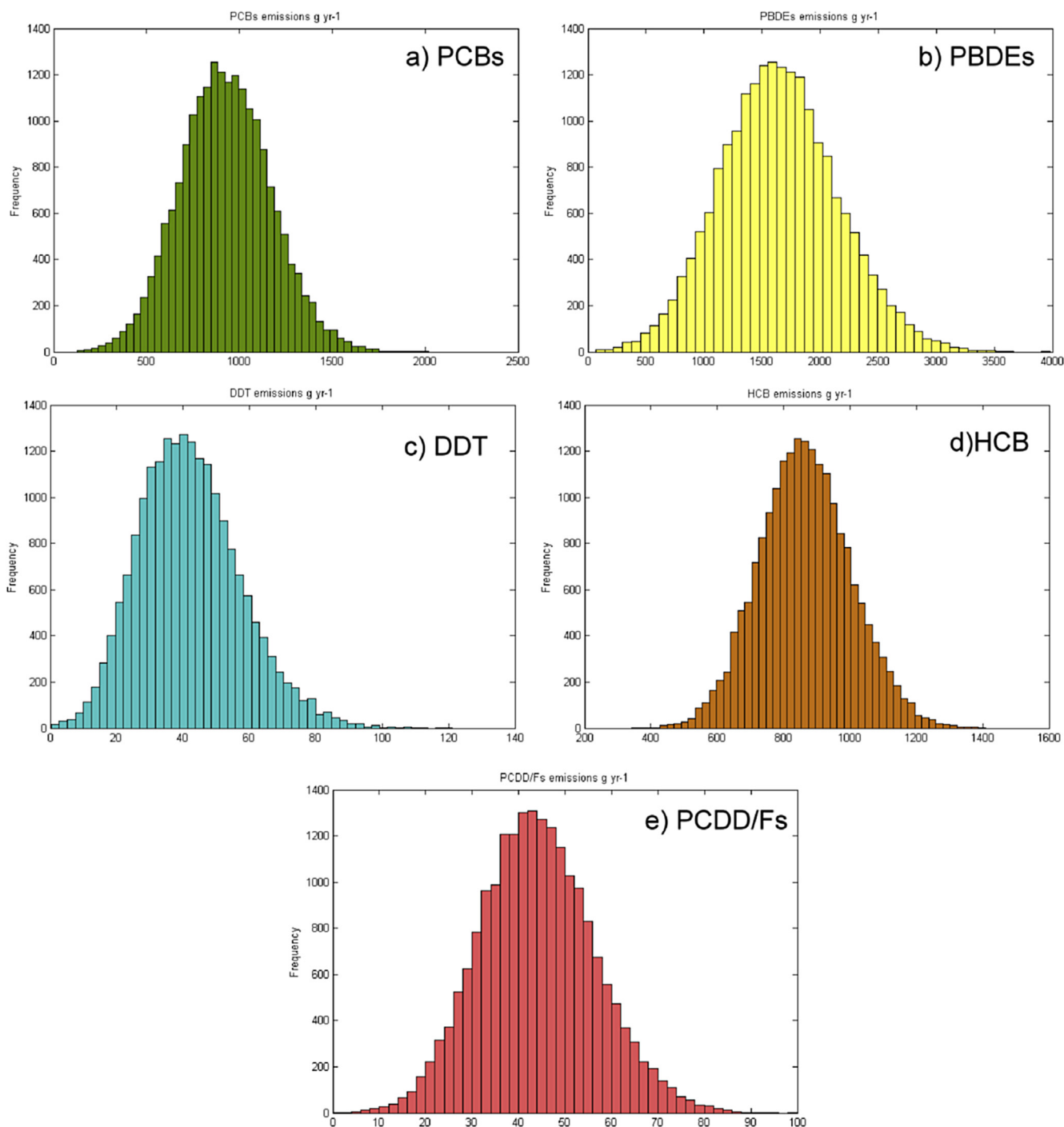


Fig. 4. Frequency distribution of the POP emissions to air in Great Mendoza, obtained with Monte Carlo simulations (20,000 runs) (g yr^{-1}): a) PCBs, b) PBDEs, c) DDT, d) HCB and e) PCDD/Fs.

Table 5

Summary of the annual emissions of POPs (g) estimated with Monte Carlo simulations.

	Mean	Standard deviation	Skewness	Coefficient of variation
HCB	864.8	138.8	0.120	16%
PCBS	925.3	243.7	0.137	26%
DDT	42.0	15.4	0.464	37%
PCDD/Fs	44.0	12.4	0.187	28%
PBDEs	1645.7	503.9	0.173	31%

6. Conclusion and recommendations

This work presents the first spatially explicit atmospheric POPs emissions in Argentina, based on high-resolution activity data. Calculated emissions for the year 2011 in the area of Great Mendoza were 0.92 kg for PCBs; 1.65 kg for PBDEs; $4.2\text{E}-02$ kg for DDT, 0.86 kg for HCB and $4.2\text{E}-02$ kg for PCDD/Fs. A novel aspect of our study is that we provide high-resolution emissions maps that constitute a basis for the management of POPs in accordance with

the Stockholm Convention as well as for data collection on contaminated sites and health risk assessment. For instance, at coarse spatial scales for activity data (e.g. national- or provincial-level) spatial variations within cities cannot be accurately accounted through atmospheric transport models. Using higher resolution data, such as city-level activity information, we were able to identify hotspots of POPs emissions and reveal the spatial heterogeneity of potential local sources and probably the influence of individual pollution episodes.

In spite of the regional differences, the estimations of POPs inventory for Mendoza seem to be reasonable within its geographical and economic context. However, the contribution by sectors to the total amount released to the atmosphere has certain distinctive features which should be highlighted:

1. The open burning of MSW in urban areas and their suburbs is the most significant source for compounds emitted for this activity. This poses a debate in relation to these practices, which although widely popular in the region, are not regulated by any local normative frame.
2. The estimated emissions seem to be consistent with the data on land use, which show the urban–rural gradients for each type of compound, according to their uses and emission sources. With regard to PBDEs, emissions are closely related to urban areas and their suburbs, mostly due to MSW burning, although the sources related to the use of BRF-containing products, directly affected with the degree of urbanization, are also relevant. In turn, organochlorine pesticides show a wide geographical distribution. The emission maps in Fig. 3 show the similarity with land use (Fig. 1), revealing the large area affected by this kind of activity. The different emission values are related to the type of crop in the area.
3. The estimated emissions of PCBs are directly associated to the estimated stock, which is much smaller than those of other more developed areas, where the production and use of this compound are far more significant.

In the future, we expect to validate the emissions calculated in this inventory. To further this purpose, we are currently working on the dispersion modeling of such emissions, which will be later compared with measurements taken in the area of interest. Additionally, field experiments or process-based models may help to better estimate local emission factors and reduce the uncertainties in these emission inventories.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.emcon.2015.12.001>.

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