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Sampling and analytical methods for assessing the levels of organic pollutants in the atmosphere: PAH, phthalates and psychotropic substances: a short review

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Abstract This short review presents the procedures used to monitor PAHs, phthalates and psychotropic substances in the air, and the results of some measurements made in Italy and abroad. Organic contaminants are characterized by a variety of physical and chemical properties, including aggregation phase, concentration level, and life time. This variety widens the spectrum of procedures developed to assess their occurrence in the environment and biota, but prevents the complete speciation of the "organic fraction" of air, waters and particulates, and attention is paid to a few substances. The progress in health sciences stimulates the concern on contaminants and the development of new instrumental apparatuses and methods; new chemicals are continuously identified or recognized as capable of injuring the environment and organisms. Persistent organic pollutants and persistent biologically active toxicants are subject to regulation and extensively measured by means of standard procedures. For instance, polycyclic aromatic hydrocarbons, polychlorobiphenyls and polychlorodibenzodioxins are recovered from air through phase partition, thermal desorption or solvent extraction, then separated and detected through GC–MS or HPLC–MS procedures. By contrast, dedicated methods must be still optimized to monitor candidates or possible candidates as emerging organic pollutants, e.g. phthalates, flame retardants and perfluoroalkanes. Also, psychotropic substances appear of potential concern. Legal and illicit substances are commonly detected in the urban air besides waste and surface waters. If nicotine, caffeine and cocaine will result to enough persistence in the air, their monitoring will become an important issue of global chemical watching in the next future.

Keywords Perfluoroalkanes · PAH · Phthalates · Psychotropic substances · Organic contaminants

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Introduction

Looking to technical literature, a number of articles, books and monographs deal with organic pollutants and their characterization in environmental matrices. Thousands of compounds exist that affect all sectors of our world and impact on the living organisms and man. Clean air contains ca. 2 ppm of volatile hydrocarbons, many of which of natural origin (methane, isoprene and terpenes), while petroleum and fuel gas residues as well as pesticides, additives, plasticizers, fragrances and pharmaceuticals pollute inhabited and industrial areas (Hester and Harrison 1995). Both airborne particulates and emissions consist of organic matter in percentages ranging from 20 to 80 % (Seinfeld and Pankow 2003); it is a complex mixture of non-polar hydrocarbons (i.e. alkyl, aryl and polynuclear compounds) and polar substances, namely oxygenated (organic acids, phenols, alcohols and carbonyls) and halogenated (dioxin-like, perfluorinated) products, compounds of sulphur, nitrogen and phosphor, and metal organics (Turpin et al. 2000; Fraser et al. 2002; Alves 2008). Organics affect also waters and soils, characterizing both the surface and depths of Earth (Lake et al. 1979; Mai et al. 2002; Nadal et al. 2004).

Two complementary approaches, which can be called "deductive" and "inductive", are followed to chemically characterize the environment. The former one consists of

studying a few compounds, previously selected. This is the case of polynuclear aromatic hydrocarbons (PAHs) associated to aerosols or of fluorotelomer alcohols dispersed in surface waters. When that occurs, the chemical and physical properties of matrices and compounds are known, which favours the setup of reliable procedures for determining the analyte concentrations. The second approach is based on the chemical screening of a matrix extract, performed through general use methods that enrich the analytes and, conversely, cut off most potential analytical interferences. Through the first way, the target substances are determined with high accuracy, precision and sensitivity in well-characterized matrices. This approach looks like a tool subdued to several purposes, e.g. to evaluate the contamination degree of the environment, implement the environmental legislation, verify the effectiveness of detoxification processes and assess the health risk. The second approach is rather uncommon and a bit uncertain, but improves the knowledge of our world, providing background information for dedicated studies of new toxicants, new key compounds and new chemical kinetics.

Occurrence of organic pollutants in the environment and analytical approach

Focusing on the atmosphere, most persistent organic pollutants (POPs) and emerging organic contaminants (EOCs) partition between gas and particulate phases; moreover, organics tend to accumulate on the fine and ultra-fine particles, although exceptions and peculiarities exist. Therefore, to assess the true impact of substances on organisms and materials both vapours and size segregated particulate fractions must be collected and analysed separately. Nonetheless, investigations are usually focussed on only one substrate (e.g. PM_{10}). Except for acidic and basic substances, semi-volatile organics have no group-specific sorbents (e.g. XAD-2). Thus, they are enriched as a whole from air, leaving the task of removing interferences to sample handling and instrumental analysis. Airborne particulates are collected onto inert membranes (Teflon or quartz) by operating at high or medium volume conditions (ca. 70 or 1.0–2.3 m^3/h, respectively). The analytes are recovered from substrates by operating the soxhlet, microwave, ultrasonic bath or accelerated solvent extraction using polar solvents or mixtures. Thermodesorption/cryofocusing has found some applications, as the step following the vapour recovery from SPME cartridges exposed to atmosphere, or direct transfer of an aerosol aliquot into a micro-chamber acting as injector (Bates et al. 2008). With regard to compound identification and quantification, key points are neutrality, polarity, hydrophobicity and chemical stability. These properties influence the choice of the separation devices (columns, traps, cartridges and bio-accumulators), of gas, liquid or ion chromatography techniques adopted for analysis, and of the detection systems (flame ionization, electron capture, mass spectrometry (MS), fluorimetry and electrochemistry). In particular, various MS techniques have been adopted for this purpose: quadrupole and ion trap (EI), tandem (MS–MS), time-of-flight, high-resolution and triple quadrupole mass spectrometry. Each of them presents advantages and limitations depending on the nature of the analytes. For instance, flame ionization (FID) coupled to gas chromatography (GC) was the first tool to detect PAHs; thanks to low cost, ease use and wide linearity, it was the choice technique of the reference method for benzo[*a*]pyrene in urban air (IME 1994). Nevertheless, FID was soon replaced by mass spectrometry detection (MSD) owing to poor selectivity and impossibility of using perdeuterated homologues as reference or surrogate standards. Ion trap MS does not offer better performances than quadrupole MS, unless the tandem mode is applied to dirty matrices. As soon as GC–HRMS or high-performance liquid chromatography with fluorescence detection (HPLC-FD) has been adopted to perform instrumental analysis, the cleanup step included in the methods has been cut. Long-exposure diffusive samplers have been patented, suitable to collect semi-volatile organics from air. Nevertheless, their use is restricted to vapours of persistent substances like PAHs and PCBs (Söderström et al. 2005; Klánová et al. 2006; Tuduri et al. 2012). Filter/cartridge sets formally collect all PAHs and POPs from air, although only sampling trains encompassing denuders and filters seem capable of discriminating vapours from particulate contaminants (Gundel et al. 1995; Tsapakis and Stephanou 2003). Polyurethane foam (PUF), charcoal, polyvinylbenzene resins (XAD), reversed-phase surface modified membranes and silicone gum are adopted as cartridge sorbents or coated on high-efficiency denuders (Table 1).

Neutral highly polar chemicals are important components of the solvent-extractable organic fraction of particulates, looking both to mass percentage and long-term toxicity (Fabiani et al. 2008). Nevertheless, they gained the concern of scientists later than non-polar *n*-alkanes and low-polar PAHs due to the hard identification and quantification. In fact, the highly polar fraction looked as a very complex mixture of chemicals often occurring at low trace levels, prone to decomposition and unable to provide specific signals suitable for identification through gas chromatography coupled with common detectors. Derivatization could be a useful tool, but not for all analytes. On the other hand, HPLC was insufficient until various hiphenated MS techniques were developed. The availability of high-resolution detectors improved the characterization of environmental matrices by providing the identification of unexpected substances like flame retardants, insecticides and drugs, and reducing the limit of detection of compounds by orders of magnitude.

Excellent reviews have been published on EOC analysis in waters (Richardson 2009) and in the atmosphere (Xie and

Table 1 Block diagram of techniques used for measuring organic contaminants including PAHs, phthalates and psychotropic substances

Volatilization degree	Collection	Extraction/recovery	Cleanup/separation	Instrumental analysis
Semi-volatile compounds (or gaseous fraction)				
Neutral (PAHs and phthalates)	Cartridges (PUF, XAD, charcoal, Tenax and silicone)	Organic solvent (sonication, soxhlet); TD/CF	CC (on alumina, silica gel, florisil); SPE	GC–MSD/FID/ECD; HPLC-UV/FD/MSD
Neutral (PAHs and phthalates)	SPME (silicone phases)	TD/CF	CC (+ derivatization, if necessary)	GC-MSD/FID/ECD; HPLC-UV/FD/MSD
Neutral (PAHs and phthalates)	Denuder (XAD, charcoal and silicone)	Org. solvents (ASE, sonication, soxhlet)	CC (+ derivatization, if necessary)	GC-MSD/FID/ECD; HPLC-UV/FD/MSD
Acids	Cartridges (basic/neutral sorbents), alkaline filters	Water; solvent partition; head space	(derivatization needed for GC analysis)	GC-MSD/FID/ECD; HPLC-UV/FD/MSD IC
Bases (nicotine and cocaine)	Cartridges (acidic/neutral sorbents); acidic filters	Water; solvent partition; head space	(derivatization needed for GC analysis and used also with HPLC)	GC-MSD/FID/ECD; HPLC-UV/FD/MSD IC
High-boiling compounds (or particulate fraction)				
Neutral (PAHs and phthalates)	Quartz or Teflon filters	Org. solvent (ASE, sonication, soxhlet, MWD). TD/CF	CC (on alumina, silica gel, florisil); SPE; (derivatization)	GC-MSD/FID/ECD; HPLC-UV/FD/MSD
Bases (nicotine and cocaine)	Quartz or Teflon filters	Organic solvent (sonication, soxhlet); TD/CF	(derivatization needed for GC analysis and used also with HPLC)	GC-MSD/FID/ECD; HPLC-UV/FD/MSD

ASE accelerated solvent extraction, *CC* column chromatography, *MWD* microwave digestion, *PUF* polyurethane foam, *TD*/CF thermodesorption/cryofocusing

Ebinghaus 2008), while several papers analyse specific classes of compounds, e.g. organic phosphates, flame retardants with special focus on polybrominated diphenyl ethers, and fragrances. Even much richer is literature concerning polychlorodibenzodioxins/furans, polychlorobiphenyls and organochloride pesticides.

The focus of this short review encompasses three groups of pollutants, i.e. PAHs, phthalate esters and drugs, which enjoyed different concerns along the last 30 years. In fact, PAHs belong by far to most known chemicals and are recognized as toxicants. Phthalates are principally used to modulate the polyvinyl chloride strength and flexibility. Apart from a number of industrial processes, phthalate esters occur in personal care, medical and consumer products (Petersen and Breindahl 2000; Rahman and Brazel 2004). Phthalate esters are ubiquitous in the environment; on the other hand, they are endocrine disruptors, mutagenic and probable promoters of obesity (Shaffer et al. 1945; International Agency for Research on Cancer 1982; USDHHS 1993; Bornehag et al. 2004; Martino-Andrade and Chahoud 2010; La Merrill and Birnbaum 2011; Silva et al. 2004; European Commission 2001, 2005). Their investigations in the environment are relatively recent and overall restricted to indoor air (Fromme et al. 2004; Wormuth et al. 2006). Drugs (both illicit and legal) are acquiring only today the concern that they probably merit (Cecinato and Balducci 2007; Balducci et al. 2009; Viana et al. 2010, 2011). Among psychotropic substances, nicotine has a peculiar importance with regard to pollution of indoor environments, owing to the recognized impact of tobacco smoke on human health (FDA 1996; WHO 2008, 2009, 2011). By contrast, very few studies have been focussed till now on the presence of nicotine, caffeine and the corresponding by-products in open air, and the environmental data available appear very scarce, compared to the worldwide diffusion of these substances.

Most PAH investigations focus their objectives on the high-boiling fraction since most of them are recognized as probable or possible carcinogens. Since measurements are made for health preservation purposes, the focus is on breathable or fine particulates, although some attention is paid also to settled dust. HPLC-FD and GC–MS are the techniques of choice for this purpose (Winberry et al. 1988). The use of low-bleed and inert GC phases allows to extend the study to high molecular weight congeners, e.g. dibenzo/naphthopyrenes and fluoranthenes (Menichini and Merlo 2012). Both positive and negative artefacts are known of the PAH measurements (e.g. the adsorption of PAH on soot/filter surfaces or conversely their volatilization, and the PAH decomposition induced by oxidants); thus, dedicated procedures and tools are adopted to minimize them (e.g. ozone scrubbers).

A number of PAH derivatives have been found more toxic than parent compounds due to presence of methyl-, nitro- or halogen substituents in the molecule (Konig et al.

1983; Allen et al. 1997; Durant et al. 1996; Hannigan et al. 1998).

Nitro-PAHs are potent mutagens, not requiring enzymatic activation to display their toxicity. As important components of old-engine diesel vehicles, they occur in the air as a consequence of either direct emission or photochemical reactions. In Italy, nitro-PAH measurements were made since 1994 (Liberti et al. 1984; Fuoco et al. 1999; Cecinato et al. 1998). Accounting for small percentages of PAHs, nitro-PAHs required sensitive and selective detectors to be identified and quantified. Thus, GC-NICI-MSD (Di Filippo et al. 2009), GC-MSMS or HPLC-FD after reduction and derivatization has been adopted.

As for oxygenated PAHs, four main categories have been investigated, namely phenols/diols (e.g. 2-naphthol, 9-hydroxyphenanthrene and 1-hydroxypyrene), ketones or quinones (9H-fluorene-9-one, anthracene-9,10-dione, 7H-benz[*de*]anthracene-7-one and benz[*a*]anthracene-7,12-dione), carboxyalhehydes (napthalene-1-carboxaldehyde, pyrene-1-carboxaldehyde) and oxygenated heterocyclics (e.g. xanthene and xanthone, naphthofuranes). Dedicated studies on oxygenated PAHs made between 1983 and 1998 (Ramdahl 1983; Cretney et al. 1985; Kamens et al. 1989; Strandell et al. 1994; Oda et al. 1998) and, more recently, by Rosario Sienra (2006), Park et al. (2006), Albinet et al. (2007), and Tsakapis and Stephanou (2007), were based overall on characterization through GC–MSD, however, HPLC-MSMS was proposed by Delhomme et al. (2008). A review of Walgraeve et al. (2010) discuss most results in this topic.

As for airborne phthalates, they were first enriched from air at high aspiration flow either onto quartz/glass fibre filters (dust) or polyurethane foam (vapours). Solvent extraction was operated in soxhlet by using benzene/methanol 4:1, hexane/diethyl ether 9:1 or dichloromethane as solvent (Thuren and Larsson 1990; Xie et al. 2006); afterward, the dried residue was processed through column chromatography (silica). The phthalates were eluted with the neutral polar fraction and characterized through capillary gas chromatography coupled with mass spectrometric detection, EI-SIM mode. Deuterated homologues acted as internal reference compounds. Recently, airborne phthalates were measured in Nanjing, China (Wang et al. 2008) after a dedicated procedure was optimized including alkyl phenols (Xie et al. 2006). The positive-ion chemical ionization was applied to phthalates and organophosphates in indoor dust. Special attention was paid to avoid the volatilization from polyurethane foam cartridges and filters, by reducing the sampling period to 12 h (Bergh et al. 2010).

The analytical procedures optimized for monitoring psychotropic compounds were substantially derived from those applied for drugs and their metabolites or by-products in aqueous media, with the exception of sampling (Zaromb et al. 1993). At this regard, cocaine, cannabinoids and heroin exist predominantly as particles, whilst nicotine, caffeine and amphetamines are expected to partition between gaseous and particulate phases, although the true respective percentages remain unknown (Häger and Niessner 1997; Lai et al. 2008). Psychotropic substances were investigated in the frame of an extensive characterization of organic aerosols including PAHs, *n*-alkanes and oxy-PAHs (Cecinato et al. 2009; Ladji et al. 2009). Cocaine was detected at concentrations as low as 0.005 ng/m^3 (limit of detection, LoD, equal to 0.001 ng/m^3), while the three cannabinoids identified in aerosols (i.e. cannabinol, cannabidiol and Δ^9-tetrahydrocannabinol) were determined only when their sum exceeded 0.01 ng/m^3 (LoD~0.003 ng/m^3 for each of them). The procedure comprised the sample collection at 55 m^3/day, solvent extraction in soxhlet, fractionation on alumina column and GC-MSD (EI, SIM) analysis. Better analytical performances were obtained by applying HPLC-MSD and/or derivatization to cannabinoid analysis (Postigo et al. 2008, 2009; Balducci et al. 2009). HPLC-MSD allowed also to verify the occurrence of traces of amphetamines and heroin in the air of Spain at a few picogram levels.

Environmental EOC measurements

PAHs were detected in aerosols since 1950 (Waller 1952; De Maio and Corn 1996; Gordon and Bryan 1973; Gordon 1976). PAH measurements have been carried out everywhere, including polar and remote regions (Fellin et al. 1996; Ciccioli et al. 1994, 1996; Halsall et al. 1994; Khalili et al. 1995; Alves et al. 2001; Yassaa et al. 2001; Chang et al. 2004). In Italy, the first spotty measurements of airborne PAHs were made in the late 1960s (Zoccolillo et al. 1972). In the 1990s, investigations were made in many cities experiencing different degrees and types of pollution (Menichini 1992; Ferrovie dello Stato 1990) (see Table 2). Chemical characterizations were carried out by means of capillary GC-FID; reversed-phase HPLC-UV/FD was used only to reprocess congeners not resolved by GC phases.

A big impulse to investigations on PAHs was provided by environmental legislation (IME 1994; GURI 1999). Indeed, starting from 1994, the Authorities of Italian Regions must monitor particulate PAHs in the principal 15 Italian cities and implement policies aimed to reduce or maintain the yearly average concentration of benzo[*a*]pyrene (BaP) below 1.0 ng/m^3. Two more recent decrees have modified this *concentration limit* into *air quality target* and extended the measurements to seven *carcinogenic* PAHs in urban and rural localities, in order to assess the average exposition of population to this category of pollutants (GURI 2007, 2010). Nowadays, the 1.0 ng/m^3 target is

Table 2 Atmospheric concentrations (nanograms per cubic metre) of *carcinogenic* PAHs, detected in Italian cities during winter 1990 (Ferrovie dello Stato 1990)

Northern Italy	Aosta	Turin	Milan	Udine
BaA	7.4	2.7	3.5	4.3
BbjkF	10.5	8.0	14.7	9.3
BaP	9.8	3.7	4.3	5.0
IP	9.8	7.8	20.2	10.4
DBahA	3.4	5.3	3.6	1.4
Central Italy	Pisa	Ascoli Piceno	Terni	Rome
BaA	1.7	1.1	2.9	1.2
BbjkF	4.7	2.8	13.1	2.7
BaP	3.5	0.9	3.5	1.8
IP	8.3	3.9	10.6	2.8
DBahA	0.4	0.1	1.5	0.5
Southern and Insular Italy	Naples	Taranto	Cosenza	Catania
BaA	9.2	7.2	0.3	1.2
BbjkF	17.5	10.9	0.8	2.7
BaP	9.0	3.4	0.3	1.8
IP	13.1	11.3	0.5	2.8
DBahA	2.8	0.7	0.1	0.5

BaA benz(*a*)anthracene, *BbjkF* benz(*b*/*j*/*k*)fluoranthenes, *BaP* benzo(*a*)pyrene, *IP* indeno (1,2,3-cd)pyrene, *DBahA* dibenz (*a*,*h*)anthracene

usually reached in Italy, although important exceptions exist for areas hosting heavy industry concentrations like steel plants, refineries and harbours (e.g. in Taranto and Trieste). The PAH concentrations are declining since 20 years; nonetheless, BaP often exceeds 1.0 ng/m^3 in winter, despite the annual average is lower (see Table 3).

First restricted to PAH measurements, the investigations have been recently addressed to five major goals, i.e.: (1) to determine airborne PAHs in remote or developing regions (Bin Abas et al. 2004; Fanou et al. 2006; Pozo et al. 2009; Ladji et al. 2009; Sofowote et al. 2010; Callen et al. 2011; Amador-Muñoz et al. 2011); (2) to improve the knowledge of the PAH toxicity apart from cancer promotion, assess the "relative toxic potency" of each congener compared to BaP and dioxin and evaluate the true exposition of humans to PAHs (Rosario Sienra 2006; Villalobos-Pietrini et al. 2006; Srogi 2007; Martorell et al. 2010; Wei et al. 2011); (3) to assess the relative contributions of emission sources to the airborne PAH budget (Li and Kamens 1993; Gogou et al. 1996; Schauer et al. 1996; Cass 1998; Sharma et al. 2007); (4) to implement environmental legislations (EPA 1999; EC 2001; Ravindra et al. 2008); and (5) to know the partition of PAHs between gas and particulates, and their distribution along the aerosol size fractions. Worth mentioning are also the development of new procedures and instrumentations (Klanová et al. 2006; Liu et al. 2007; Li et al. 2010; Costa Menezes et al. 2011), and investigations in indoor environments, e.g. in work places and offices, houses, churches, schools and shops, both in the presence and absence of tobacco smokers (Li and Ro 2000; Lodovici et al. 2004; Ding et al. 2007; Lu et al. 2008; Mannino and Orecchio 2008; Delgado-Saborit et al. 2011; Titcombe et Simcik 2011).

According to measurements made before 2000, in Italy the semi-volatile nitronaphtalenes were the most abundant nitro-PAHs, while toxic nitrofluoranthenes and nitropyrenes ranged from 10 pg/m^3 to ca. 1 ng/m^3 (Ciccioli et al. 1996; Cecinato 2003). By contrast, nowadays single NPAH concentrations exceeding 0.1 ng/m^3 are unusual (Di Filippo et al. 2010). As for oxygenated PAHs, the concentrations in the atmosphere range from a few picograms up to tens of nanograms per cubic metre (Park et al. 2006; Albinet et al. 2007; Walgraeve et al. 2010). Unfortunately, no measurements have been made till now in Italy.

The occurrence of phthalate esters in the air at concentrations exceeding 300 ng/m^3 was reported by Thomas in 1973 and Cautreels et al. in 1977 (Table 4). In the same years, the use of gas chromatography coupled with electron capture detection was proposed as an alternative to flame ionization since ECD appeared selective and high responding vs. both halogenated and poly-oxygenated molecules (Giam et al. 1975), whilst MS instruments were much more expensive. Phthalates were identified in dusts of Antarctica and Himalaya. Both vapour and aerosol fraction were investigated over the North Sea (Xie et al. 2005) and extensively measured in Chinese cities, where total airborne concentrations ranged from ≈60 to ≈2,200 ng/m^3 (Wang et al. 2006). Unlike other contaminants, the highest phthalate values were observed in summer, and this finding was associated to volatilization from substrates. Despite the ubiquitous occurrence of phthalates in the atmosphere (Staples et al. 1994), the concern about these substances is overall restricted to indoor environments (Rudel et al. 2003; Fromme et al. 2004; Geiss et al. 2009), where concentrations are much higher than in open air (Table 4). In general, phthalates looked just as interfering

Table 3 Atmospheric concentrations (nanograms per cubic metre) of *carcinogenic* PAHs in Rome and Milan, Italy

Inter-year modulations	Rome[a]	Rome[a]	Rome[b]	Rome[b]	Rome[c]	Rome[d]
Year	1986	1991	1994	1997	2005	2009
BaA	0.6	0.4	1.2	0.6	0.4	0.4
BbjkF	4.2	2.7	4.3	2.7	1.6	1.3
BaP	1.3	1.1	1.1	0.7	0.6	0.4
IP	3.4	1.7	4.5	1.4	0.7	0.5
DbahA	0.3	0.2	0.6	0.4	0.1	<0.1
Year time modulations	Milan, 2000–01[e]		Rome, 2004[c]		Rome, 2010–2011[f]	
Year time	Winter	Summer	Winter	Summer	Winter	Summer
BaA	2.6	0.1	1.0	<0.1	0.86	0.1
BbjkF	7.0	0.4	3.9	0.5	3.7	0.3
BaP	2.3	0.1	2.0	<0.1	1.4	0.1
IP	3.6	0.1	2.6	0.1	1.2	0.1
DbahA	1.2	<0.1	0.3	<0.1	0.3	<0.1

BaA benz(*a*)anthracene, *BbjkF* benz(*b*/*j*/*k*)fluoranthenes, *BaP* benzo(*a*)pyrene, *IP* indeno (1,2,3-cd)pyrene, *DBahA* dibenz (*a*,*h*)anthracene

[a]Menichini 1992

[b]Cecinato et al. 1998

[c]Cecinato and Balducci 2007

[d]Cecinato et al. 2010

[e]Cecinato et al. 2003

[f]Cecinato et al. 2011

compounds of *true* pollutants. Teil et al. (2006) compared the phthalate burdens of the air and rain water, and more recently Weschler et al. (2008) included indoor settled dust. The phthalate metabolites in humans have been studied by Koch et al. (2003, 2007) and Calafat et al. (2004).

Nowadays, both tobacco smoking and illicit substances reach the size of global problems involving health, security, economy, ethics and policy (European Monitoring Centre for Drugs and Drug Addiction 2009; Italian Police 2009; Central Intelligence Agency 2008; United Nations Office on Drug and Crime 2009). Nevertheless, scarce attention is paid to the presence and aftermaths of psychotropic substances in the environment. Till now, nicotine has been widely studied only indoors, whilst measurements of other drugs have been made solely outdoors (Michael et al. 1996; Schorp et al. 2002; Nebot et al. 2005; Sureda et al. 2009). Illicit substances have been listed within the emerging pollutants (Richardson 2009) since they have been ascertained to affect the surface and waste waters (Castiglioni et al. 2006; Boleda et al. 2007; Postigo et al. 2008, 2009; van Nuijs et al. 2009; Mari et al. 2009). Quantitative relationships have been observed between the contents of cocaine, Δ^9-tetrahydrocannabinol and heroin metabolites in waste waters, and the drug prevalence estimated at local and

Table 4 Concentrations of phthalate esters (nanograms per cubic metre) observed in outdoor and indoor air

City	Location	DEP	DBuP	DEHP	BzBuP	Ref.
Hamilton, ON (Canada)	Outdoor	–	~700	~300	–	Thomas 1973
Antwerp, Belgium	Outdoor	–	24–74	29–132	–	Cautreels et al. 1977
College Station, TX (USA)	Outdoor	–	–	30–70	–	Giam et al. 1975
Paris, France	Outdoor	2–25	3–64	6–36	1–13	Teil et al. 2006
Stockholm, Sweden	Outdoor	<47–510	80–760	223–520	3–110	Bergh et al. 2010
Yamato, Japan	Outdoor	–	<50	<100	–	Toda et al. 2004
Yamato, Japan	Indoor	–	<100–780	<100–200	–	Toda et al. 2004
Nanjing, China	Outdoor	1–10	29–78	7–37	0.1–2.0	Wang et al. 2008
Nanjing, China	Outdoor	1–4	5–27	4–15	0–3.0	Wang et al. 2008
Cape Cod, MA (USA)	Indoor	–	52–1,100	59–1,000	31–480	Rudel et al. 2003
Berlin, Germany	Indoor	807	1,083	191	37	Fromme et al. 2004
Berlin, Germany	Cars	n.d.–1,400	n.d.–1,630	n.d.–3,656	–	Fromme et al. 2004
Thessaloniki, Greece	Outdoor	n.d.	0.13–2.4	4.6–45	0.04–0.98	Salapasidou et al. 2011
Thessaloniki, Greece	Outdoor	n.d.	1.2–3.4	n.d.–6.5	0.11–0.80	Salapasidou et al. 2011
Portland, OR (USA)	(Vapours)	104±77	271±113	944±918	59±36	Ligocki and Pankow 1989
Portland, OR (USA)	(Aerosols)	30±14	51±43	1,876±1,467	20±20	Ligocki and Pankow 1989
Tokyo, Japan	Indoor	90–190	110–600	40–230	n.d.–100	Otake et al. 2001

DEP diethyl phthalate, *DBuP* dibuthyl phthalate, *DEHP* di(2-ethylhexyl) phthalate, *BzBuP* benzylbutlyl phthalate, *n.d.* lower than the limit of detection of the applied method

national scales (Bones et al. 2007; Zuccato et al. 2008; Domènech et al. 2009). By contrast, the measurements in open atmospheres have been started later since the atmospheric contamination induced by drugs is supposedly negligible. For instance, the studies focussed on tobacco smoking consider tar and gaseous toxicants in spite of nicotine (IARC 1982), and caffeine is practically disregarded. Moreover, only in 2007 and 2009 was the ambient air contamination by cocaine, cannabinoids and heroin clarified (Cecinato et al. 2007; Postigo et al. 2008). Nonetheless, legal and illicit psychotropic substances affect the whole world. Nicotine and caffeine can reach 100 and 30 ng/m^3, respectively, while illicit substances sometimes exceed 1 ng/m^3 and are often much more abundant than known toxicants, e.g. BaP and organic halogenides.

Till now, only two extensive studies have been carried out about this topic, namely the *PSALM* and *AriaDrugs* projects (Cecinato et al. 2010; Department for Anti-Drug Policies of the Italian Presidency of Ministers' Council DPA 2010). As parts of *PSALM*, launched by CNR-IIA and based upon the voluntary participation of Regional Agencies for the Preservation of the Environment, two in-field campaigns were conducted in January and June 2009 in 38 Italian localities (see Table 5). *AriaDrugs*, funded by DPA, consists of continuous measurements carried out over 1 year in eight Italian big cities. Numerous outcomes and information were drawn from the former project, and even more are expected from *AriaDrugs*, whose end is scheduled for 2012. In particular, the variables potentially influencing the drug burdens in the air (e.g. meteorology, levels of oxidants and soot) will be evaluated, and the chance of deriving chemical indicators for the illicit drug abuse will be explored. Nevertheless, the health impact on populations will be elucidated only if long and extensive programmes will be implemented in regions of drug production, trafficking and consumption (European Monitoring Centre for Drugs and Drug Addiction 2009).

Conclusions

On the basis of the renewed general concern, PAHs merit to be regarded again as "emerging contaminants", going beyond the sheer monitoring in the atmosphere. It is quite surprising, for instance, that the influence of oxidants on atmospheric PAHs, although known, remains insufficiently studied, although tests conducted on artificial matrices or in artificial conditions have displayed quite conflicting results. Special attention would be paid to assess the real exposition to PAHs of the entire population or selected categories, taking into account reliable emission factors from human activities and natural events, as well as point and diffusive sources. In this regard, widely shared methods suitable to evaluate the various forms of toxicity induced by PAHs on humans are necessary to uniform legislation and epidemiological approach across the world (Collins et al. 1998).

In our opinion, phthalate esters will gain more environmental concern in the next future. Due to variety of uses they find in consumer and industrial products, favoured by their ability to modulate chemical and physical properties according to needs and by low production costs, it looks very hard their replacement with equivalent materials. Nevertheless, the degree of contamination reached in the environment, the knowledge of their toxicity and the persistence in the environment will lead community to develop phthalate-free technologies.

As for psychotropic substances, several questions are still waiting for answers, namely:(1) what are the predominant sources of environmental pollution at local and regional scales; (2) how persistent are psychotropic substances in

Table 5 Average contents (nanograms per cubic metre) of cocaine, cannabinoids and benzo(*a*)pyrene in the air of Italian cities in 2009 (Cecinato et al. 2011)

Period	Winter				Summer			
City	CO	CBs	BaP	CO/BaP	CO	CBs	BaP	CO/BaP
Turin	0.15	0.06	1.6	~0.1	0.05	0.05	0.02	~1.0
Milan	0.39	0.28	2.0	~0.2	0.09	0.08	0.09	~1.0
Bologna	0.09	0.11	0.5	~0.2	0.05	0.05	0.07	~0.7
Florence	–	–	–	–	0.01	0.25	0.04	~0.3
Rome	0.10	0.54	0.8	~0.10	0.04	0.05	0.08	~0.5
Jesi	0.03	X	0.7	~0.04	0.02	X	0.05	~0.4
Naples	–	–	–	–	0.03	0.20	0.02	~1.5
Bari	0.03	0.04	0.3	~0.1	0.01	X	0.01	~2.0
Rende	0.02	0.3	1.4	~0.01	0.01	0.03	0.01	~0.1

The cocaine/benzo(*a*)pyrene concentration ratios are also reported

CO cocaine, *CBs* Δ^9-tetrahydrocannabinol + cannabinol + cannabidiol, *BaP* benzo(*a*)pyrene, *X* detected but not quantified (<0.01 ng/m^3)

the atmosphere, and how much the aerosols are representative of total burdens affecting the environment; nicotine in particular seems worth of more extensive studies in open air; (3) how realistic is the attempt of deriving drug prevalence indicators from the environmental monitoring; and (4) what are the detrimental effects induced by drugs and their by-products on human health, in particular on non-consumer people.

While niche-level researches appear reasonably suitable to tackle most emerging items, only large-scale programmes co-ordinated at international level can succeed in improving the general level of knowledge and, finally, the quality of our life.

References

Albinet A, Leoz-Garziandia E, Budzinski H, ViIlenave E (2007) Polycyclic aromatic hydrocarbons (PAHs), nitrated PAHs and oxygenated PAHs in ambient air of the Marseilles area (South of France): concentrations and sources. Sci Total Environ 384:280–292

Allen JO, Dookeran NM, Taghizadeh K, Lafleur AL, Smith KA, Sarofim AF (1997) Measurement of oxygenated polycyclic aromatic hydrocarbons associated with a size-segregated urban aerosol. Environ Sci Technol 31:2064–2070

Alves CA (2008) Characterisation of solvent extractable organic constituents in atmospheric particulate matter: an overview. Anais da Academia Brasileira de Ciências (Ann Brazilian Acad Sci) 80:21–82

Alves C, Pio C, Duarte A (2001) Composition of extractable organic matter of air particles from rural and urban Portuguese areas. Atmos Environ 35:5485–5496

Amador-Muñoz O, Villalobos-Pietrini R, Miranda J, Vera-Avila LE (2011) Organic compounds of $PM_{2.5}$ in Mexico Valley: spatial and temporal patterns, behavior and sources. Sci Total Environ 409:1453–1465

Balducci C, Nervegna G, Cecinato A (2009) Evaluation of principal cannabinoids in airborne particulates. Ana Chim Acta 641:89–94

Bates M, Bruno P, Caputi M, Caselli M, de Gennaro G, Tutino M (2008) Analysis of polycyclic aromatic hydrocarbons (PAHs) in airborne particles by direct sample introduction thermal desorption GC/MS. Atmos Environ 42:6144–6151

Bergh C, Torgrip R, Östman C (2010) Simultaneous selective detection of organophosphate and phthalate esters using gas chromatography withpositive ion chemical ionization tandem mass spectrometry and its application to indoor air and dust. Rapid Commun Mass Spectrom 24:2859–2867

Bin Abas MR, Rahman NA, Omar NYMJ, Maah MJ, Abu Samah A, Oros DR, Otto A, Simoneit BRT (2004) Organic composition of aerosol particulate matter during a haze episode in Kuala Lumpur, Malaysia. Atmos Environ 38:4223–4241

Boleda MR, Galceran MT, Ventura F (2007) Trace determination of cannabinoids and opiates in wastewater and surface waters by ultra-performance liquid chromatography–tandem mass spectrometry. J Chromatog A 1175:38–48

Bones J, Thomas KV, Paull B (2007) Using environmental analytical data to estimate levels of community consumption of illicit drugs and abused pharmaceuticals. J Environ Monit 9:701–707

Bornehag CG, Sundell J, Weschler CJ, Sigsgaard T, Lundgren B, Hasselgren M, Hägerhed-Engman L (2004) The association between asthma and allergic symptoms in children and phthalates in house dust: a nested case–control study. Environ Health Perspec 112:1393–1397

Calafat AM, Slakman AR, Silva MJ, Herbert AR, Needham LL (2004) Automated solid phase extraction and quantitative analysis of human milk for 13 phthalate metabolites. J Chromatog B 805:49–56

Callen MS, Lopez JM, Mastral AM (2011) Characterization of PM_{10}-bound polycyclic aromatic hydrocarbons in the ambient air of Spanish urban and rural areas. J Environ Monit 13:319–327

Cass GR (1998) Organic molecular tracers for particulate air pollution sources. Trends Anal Chem 17:356–366

Castiglioni S, Zuccato E, Crisci E, Chiabrando C, Fanelli R, Bagnati R (2006) Identification and measurement of illicit drugs and their metabolites in urban wastewater by liquid chromatography–tandem mass spectrometry. Anal Chem 78:8421–8429

Cautreels W, Van Cauwenberghe K, Guzman LA (1977) Comparison between the organic fraction of suspended matter at a background and an urban station. Sci Total Environ 8:1389–1399

Cecinato A (2003) Nitrated polynuclear aromatic hydrocarbons in ambient air in Italy. A brief overview. J Sep Sci 26:402–408

Cecinato A, Balducci C (2007) Detection of cocaine in the airborne particles of the Italian cities Rome and Taranto. J Sep Sci 30:1930–1935

Cecinato A, Ciccioli P, Brancaleoni E, Zagari M (1998) PAH and N-PAH in the urban atmosphere of Rome and Milan. Ann Chim 88:369–379

Cecinato A, Tomasi Scianò MC, Di Menno Di Buccchianico A (2003) Organic aerosols in the air of Milan. The IIA-CNR measurement campaign of 2000–2001. J Sep Sci 26:397–401

Cecinato A, Balducci C, Nervegna G (2009) Occurrence of cocaine in the air of the world's cities: an emerging problem? A new tool to investigate the social incidence of drugs? Sci Total Environ 407:1683–1690

Cecinato A, Balducci C, Budetta V, Pasini A (2010) Illicit psychotropic substance contents in the air of Italy. Atmos Environ 44:2358–2363

Cecinato A, Balducci C, Guerriero E, Sprovieri F, Cofone F (2011) Possible social relevance of illicit psychotropic substances present in the atmosphere. Sci Total Environ 412–413:87–92

Central Intelligence Agency (2008) The World Factbook 2008. https://www.cia.gov/library/publications/the-world-factbook/fields/2086.html. Accessed 20 Sept 2011)

Chang KF, Fang GC, Chen JC, Wu YS (2004) Atmospheric polycyclic aromatic hydrocarbons (PAHs) in Asia: a review from 1999 to 2004. Environ Pollut 142:388–396

Ciccioli P, Cecinato A, Brancaleoni E, Montagnoli M, Allegrini I (1994) Chemical composition of particulate organic matter (POM) collected at Terra Nova Bay in Antarctica. Int J Anal Chem 55:47–59

Ciccioli P, Cecinato A, Brancaleoni E, Frattoni M, Zacchei P, Miguel AH, De Castro Vasconcellos P (1996) Formation and transport of 2-nitrofluoranthene and 2-nitropyrene of photochemicalorigin in the troposphere. J Geophys Res 101-D14:19567–19581

Collins JF, Brown JP, Alexeeff GV, Salmon AG (1998) Potency equivalency factors for some polycyclic aromatic hydrocarbons and polycyclic aromatic hydrocarbon derivatives. Regul Toxicol Pharmacol 28:45–54

Costa Menezes H, ZdL C (2011) Determination of polycyclic aromatic hydrocarbons from ambient air particulate matter using a cold fiber solid phase micro-extraction gas chromatography–mass spectrometry method. J Chromatog A 1218:3300–3305

Cretney JR, Lee HK, Wright GJ, Swallow WH, Taylor MC (1985) Analysis of polycyclic aromatic hydrocarbons in air particulate matter from lightly industrialized urban area. Environ Sci Technol 19:397–404

De Maio L, Corn M (1996) Polynuclear aromatic hydrocarbons associated with particulates in Pittsburgh air. JAPCA 16:67–71

del Rosario Sienra MM (2006) Oxygenated polycyclic aromatic hydrocarbons in urban air particulate matter. Atmos Environ 40:2374–2384

Delgado-Saborit JM, Stark C, Harrison RM (2011) Carcinogenic potential, levels and sources of polycyclic aromatic hydrocarbon mixtures in indoor and outdoor environments and their implications for air quality standards. Environ Int 37:383–392

Delhomme O, Millet M, Herckes P (2008) Determination of oxygenated polycyclic aromatic hydrocarbons in atmospheric aerosol samples by liquid chromatography-tandem mass spectrometry. Talanta 74:703–710

Department for Anti-Drug Policies of the Italian Presidency of Ministers' Council DPA (2010) http://www.politicheantidroga.it/progetti-e-ricerca/progetti-dpa/sezione-5—epidemiologia-e-valutazione/55-ariadrugs/presentazione-.aspx. Accessed 3 Aug 2011

Di Filippo P, Riccardi C, Pomata D, Gariazzo C, Buiarelli F (2009) Seasonal abundance of particle-phase organic pollutants in an urban/industrial atmosphere. Water Air Soil Pollut 211:231–250

Di Filippo P, Riccardi C, Pomata D, Buiarelli F (2010) Concentrations of PAHs, and nitro- and methyl-derivatives associated with a size-segregated urban aerosol. Atmos Environ 44:2742–2749

Ding YS, Ashley DL, Watson CH (2007) Determination of 10 carcinogenic polycyclic aromatic hydrocarbons in mainstream cigarette smoke. J Agric Food Chem 55:5966–5973

Domènech X, Peral J, Muñoz I (2009) Predicted environmental concentrations of cocaine and benzoylecgonine in a model environmental system. Water Res 43:5236–5242

Durant JL, Busby WF Jr, Lafleur AL, Penman BW, Crespi CL (1996) Human cell mutagenicity of oxygenated, nitrated and unsubstituted polynuclear aromatic hydrocarbons associated with urban aerosols. Mutat Res 371:123–157

Environmental Protection Agency (1999) US EPA Compendium of methods for the determination of toxic organic compounds in ambient air. US Federal Register, Compendium Method TO-13A, 1999, pp. 1–42

European Commission (2001) Ambient air pollution by polycyclic aromatic hydrocarbons (PAH) position paper. Office for Official Publications of the European Communities, Luxembourg, p 55

European Commission (2005) Restrictions on the marketing anduse of certain dangerous substances and preparations (phthalates in toys and childcare articles). Directive 2005/84/EC. Off J Eur Union L344:40–43

European Monitoring Centre for Drugs and Drug Addiction EMCDDA (2009) Annual Report 2009: the state of the drugs problem in Europe EMCDDA. Publications Office of the European Union, Luxembourg

Fabiani R, De Bartolomeo A, Rosignoli P, Morozzi G, Cecinato A, Balducci C (2008) Chemical and toxicological characterization of airborne total suspended particulate and PM_{10} organic extracts. Polycyc Aromat Comp 28:486–499

Fanou LA, Mobio TA, Creppy EE, Fayomi B, Fustoni S, Møller P, Kyrtopoulos S, Georgiades P, Loft S, Sannia A, Skov H, Øvrebø S, Autrup H (2006) Survey of air pollution in Cotonou, Benin—air monitoring and biomarkers. Sci Total Environ 358:85–96

Fellin P, Barrie LA, Dougherty D, Toom D, Muir D, Grift N, Lockhart L, Billeck B (1996) Air monitoring in the Arctic: results for selected persistent organic pollutants for 1992. Environ Toxicol Chem 15:253–261

Ferrovie dello Stato (1990) Trenoverde 2. Inquinamento atmosferico e acustico nei centri urbani. 2. Risultati analitici. Istituto Sperimentale FS Publ., Rome, p 192

Food and Drug Administration FDA (1996) Regulations restricting the sale and distribution of cigarettes and smokeless tobacco to protect children and adolescents; final rule. Fed Reg 61:44396–45318

Fraser MP, Yue ZW, Tropp RJ, Kohl SD, Chow JC (2002) Molecular composition of organic fine particulate matter in Houston, TX. Atmos Environ 38:5751–5758

Fromme H, Lahrz T, Piloty M, Gebhart H, Oddoy A, Rüden H (2004) Occurrence of phthalates and musk fragrances in indoor air and dust from apartments and kindergartens in Berlin (Germany). Indoor Air 14:188–195

Fuoco R, Ceccarini A, Onor M, Marrara L (1999) Analysis of priority pollutants in environmental samples by on-line supercritical fluid chromatography cleanup–cryo-trap–gas chromatography–mass spectrometry. J Chromatog A 846:387–393

Gazzetta Ufficiale della Repubblica Italiana GURI (1999) Law by Decree No. 351 released on August 4th, 1999 "Implementation of the 96/62/CE on air quality". Publ. in GURI No. 241, October 13, 1999

Gazzetta Ufficiale della Repubblica Italiana GURI (2007) Law by Decree No. 152 released on August 3, 2007 "Implementation of the 2004/107/CE Directive concerning arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air". Publ. in GURI No. 213, September 13, 2007, Supplement No. 194

Gazzetta Ufficiale della Repubblica Italiana GURI (2010) Law by Decree No. 155 released on August 13, 2010 "Implementation of the 2008/50/CE Directive concerning the ambient air quality and for a cleaner air in Europe". Publ. in GURI No. 216, September 15, 2010–Suppl. No. 217

Geiss O, Tirendi S, Barrero-Moreno J, Kotzias D (2009) Investigation on volatile organic compounds and phthalates present in the cabin air of used private cars. Environ Int 35:1188–1195

Giam CS, Chan HS, Neff GS (1975) Rapid and inexpensive method for detection of polychlorinated biphenyls and phthalates in the air. Anal Chem 47:2319–2320

Gogou AI, Stratigakis N, Kanakidou K, Stephanou EG (1996) Organic aerosols in Eastern Mediterranean: components source reconciliation by using molecular markers and atmospheric back trajectories. Org Geochem 25:79–96

Gordon RJ (1976) Distribution of airborne polycyclic aromatic hydrocarbons throughout Los Angeles. Environ Sci Technol 10:370–373

Gordon RJ, Bryan RJ (1973) Patterns in airborne polynuclear hydrocarbon concentrations at four Los Angeles sites. Environ Sci Technol 7:1050–1053

Gundel LA, Lee VC, Mahanama KRR, Stevens RK, Daisey JM (1995) Direct determination of the phase distributions of semi-volatile polycyclic aromatic hydrocarbons using annular denuders. Atmos Environ 29:1719–1733

Häger B, Niessner R (1997) On the distribution of nicotine between the gas and particle phase and its measurement. Aerosol Sci Technol 26:163–174

Halsall CJ, Coleman PJ, Davis BJ, Burnett V, Waterhouse KS, Harding-Jones P, Jones KC (1994) Polycyclic aromatic hydrocarbons in U.K. urban air. Environ Sci Technol 28:2380–2386

Hannigan MP, Cass GR, Penman BW, Crespi CL, Lafleur AL, Busby F Jr, Thilly WG, Simoneit BRT (1998) Bioassay-directed chemical analysis of Los Angeles airborne particulate matter using a human cell mutagenicity assay. Environ Sci Technol 32:3502–3514

Hester RE, Harrison RM (eds) (1995) Volatile organic compounds in the atmosphere. Royal Society of Chemistry, London, p 149. ISBN 978-0-85404-215-9

International Agency for Research on Cancer (1982) IARC monographs on the evaluation of carcinogenic risks to humans, vol. 29. IARC, Lyon, p 257, Suppl. No. 7

Italian Police (2009) Italian Police Annual Drug Report 2009. http://poliziadistato.it/articolo/14925-Relazione_Annuale_2008_della_Direzione_Centrale_per_i_Servizi_Antidroga. Accessed 4 Sept 2011

Italian Ministry of the Environment IME (1994) Ministry Decree released on November 25th, 1994 "Updating of the technical rules concerning the concentration limits and the precautionary and

warning levels regarding the atmospheric pollutants in the urban areas and indications for the measure of some pollutants referred in the Ministerial released on April 15th, 1994". Publ. in GURI, Suppl. No. 290, December 13th, 1994

Kamens RM, Karam H, Guo J, Perry JM, Stockburgerg L (1989) The behavior of oxygenated polycyclic aromatic hydrocarbons on atmospheric soot particles. Environ Sci Technol 23:801–805

Khalili NR, Scheff PA, Holsen TM (1995) PAH source fingerprints for coke ovens, diesel and gasoline engines, highway tunnels and wood combustion emissions. Atmos Environ 29:533–542

Klánová J, Kohoutek J, Hamplová L, Urbanová P, Holoubek I (2006) Passive air sampler as a tool for long-term air pollution monitoring: part 1. Performance assessment for seasonal and spatial variations. Environ Pollut 144:393–405

Koch HM, Gonzalez-Reche LM, Angerer J (2003) On-line clean-up by multidimensional liquid chromatography–electrospray ionization tandem mass spectrometry for high throughput quantification of primary and secondary phthalate metabolites in human urine. J Chromatog B 784:169–182

Koch HM, Müller J, Angerer J (2007) Determination of secondary, oxidised di-iso-nonylphthalate (DINP) metabolites in human urine representative for the exposure to commercial DINP plasticizers. J Chromatog B 847:114–125

Konig J, Balfanz E, Fncke W, Romanowsk T (1983) Determination of oxygenated polycyclic aromatic hydrocarbons in airborne particulate matter by capillary gas chromatography and gas chromatography/mass spectrometry. Anal Chem 55:599–603

La Merrill M, Birnbaum LS (2011) Childhood obesity and environmental chemicals. Mount Sinai J Med 78:22–48

Ladji R, Yassaa N, Balducci C, Cecinato A, Meklati BY (2009) Annual variation of particulate organic compounds in PM10 in the urban atmosphere of Algiers. Atmos Res 92:258–269

Lai H, Corbin I, Almirall JR (2008) Headspace sampling and detection of cocaine, MDMA, and marijuana via volatile markers in the presence of potential interferences by solid phase microextraction-ion mobility spectrometry (SPME-IMS). Anal Bioanal Chem 392:105–113

Lake JL, Norwood C, Dimock C, Bowen R (1979) Origins of polycyclic aromatic hydrocarbons in estuarine sediments. Geochim Cosmochim Acta 43:1847–1854

Li CK, Kamens RM (1993) The use of polycyclic aromatic hydrocarbons as source signatures in receptor modeling. Atmos Environ 27:523–532

Li CS, Ro YS (2000) Indoor characteristics of polycyclic aromatic hydrocarbons in the urban atmosphere of Taipei. Atmos Environ 34:611–620

Li Z, Pittman EN, Trinidad DA, Romanoff L, Mulholland J, Sjödin A (2010) Determination of 43 polycyclic aromatic hydrocarbons in air particulate matter by use of direct elution and isotope dilution gas chromatography/mass spectrometry. Anal Bioanal Chem 396:1321–1330

Liberti A, Ciccioli P, Cecinato A, Brancaleoni E, Di Palo C (1984) Determination of nitrated-polyaromatic hydrocarbons (Nitro-PAHs) in environmental samples by high resolution chromatographic techniques. J High Resolut Chromatog Chromatog Commun 7:389–397

Ligocki MP, Pankow JF (1989) Measurements of the gas/particle distributions of atmospheric organic compounds. Environ Sci Technol 23:75–83

Liu LB, Liu Y, Lin JM, Tang N, Hayakawa K, Maeda T (2007) Development of analytical methods for polycyclic aromatic hydrocarbons (PAHs) in airborne particulates: a review. J Environ Sci 19:1–11

Lodovici M, Akpan V, Evangelisti C, Dolara P (2004) Sidestream tobacco smoke as the main predictor of exposure to polycyclic aromatic hydrocarbons. J Appl Toxicol 24:277–281

Lu H, Zhu L, Chen S (2008) Pollution level, phase distribution and health risk of polycyclic aromatic hydrocarbons in indoor air at public places of Hangzhou, China. Environ Pollut 152:569–575

Mai BX, Fu JM, Sheng GY, Kang YH, Lin Z, Zhang G, Min YS, Zeng EY (2002) Chlorinated and polycyclic aromatic hydrocarbons in riverine andestuarine sediments from Pearl River Delta, China. Environ Pollut 117:457–474

Mannino MR, Orecchio S (2008) Polycyclic aromatic hydrocarbons (PAHs) in indoor dust matter of Palermo (Italy) area: extraction, GC–MS analysis, distribution and sources. Atmos Environ 42:1801–1817

Mari F, Politi L, Biggeri A, Accetta G, Trignano C, Di Padua M, Bertol E (2009) Cocaine and heroin in waste water plants: a 1-year study in the city of Florence, Italy. Forensic Sci Int 189:88–92

Martino-Andrade AJ, Chahoud I (2010) Reproductive toxicity of phthalate esters. Mol Nutr Food Res 54:148–157

Martorell I, Perelló G, Martí-Cid R, Castell V, Llobet JM, Domingo JL (2010) Polycyclic aromatic hydrocarbons (PAH) in foods and estimated PAH intake by the population of Catalonia, Spain: temporal trend. Environ Int 36:424–432

Menichini E (1992) Urban air pollution by polycyclic aromatic hydrocarbons: levels and source of variability. Sci Total Environ 116:109–135

Menichini E, Merlo F (2012) Dibenzopyrenes, other PAHs with molecular weight 302, and selected carcinogenic PAHs seldom determined: identification and one year quantification in urban air. Int J Environ Anal Chem. doi:10.1080/03067319.2011.554979

Michael CM, Demetriou E, Kosmas V, Krashia A, Akkelidou D (1996) Nicotine levels in indoor athletic centres. Sci Total Environ 192:213–216

Nadal M, Schuhmacher M, Domingo JL (2004) Levels of PAHs in soil and vegetation samples from Tarragona County, Spain. Environ Pollut 132:1–11

Nebot M, López MJ, Gorini G, Neuberger M, Axelsson S, Pilali M, Fonseca C, Abdennbi K, Hackshaw A, Moshammer H, Laurent AM, Salles J, Georgouli M, Fondelli MC, Serrahima E, Centrich F, Hammond SK (2005) Environmental tobacco smoke exposure in public places of European cities. Tob Control 14:60–63

Oda J, Maeda I, Mori T, Yashuara A, Saito Y (1998) The relative proportions of polycyclic aromatic hydrocarbons and oxygenated derivatives in accumulated organic particulates as affected by air pollution sources. Environ Technol 19:961–976

Otake T, Yoshinaga J, Yanagisawa Y (2001) Analysis of organic esters of plasticizer in indoor air by GC-MS and GC-FPD. Environ Sci Technol 35:3099–3102

Park SS, Bae MS, Schauer JJ, Kim YJ, Cho SY, Kim SJ (2006) Molecular composition of $PM_{2.5}$ organic aerosol measured at an urban site of Korea during the ACE-Asia campaign. Atmos Environ 40:4182–4198

Petersen JH, Breindahl T (2000) Plasticizers in total diet samples, baby food and infant formulae. Food Addit Contam 17:133–141

Postigo C, de Alda MJL, Barcelò D (2008) Fully automated determination in the low nanogram per litre level of different classes of drugs of abuse in sewage water by on-line solid-phase extraction-liquid chromatography-electrospray-tandem mass spectrometry. Anal Chem 80:3123–3134

Postigo C, de Alda MJL, Viana M, Querol X, Alastuey A, Artiñano B, Barcelò D (2009) Determination of drugs of abuse in airborne particles by pressurized liquid extraction and liquid chromatography-electrospray-tandem mass spectrometry. Anal Chem 81:4382–4388

Pozo K, Harner T, Lee SC, Wania F, Muir DCG, Jones KC (2009) Seasonally resolved concentrations of persistent organic pollutants in the global atmosphere from the first year of the GAPS study. Environ Sci Technol 43:796–803

Rahman M, Brazel CS (2004) The plasticizer market: an assessment of traditional plasticizers and research trends to meet new challenges. Prog Polym Sci 29:1223–1248

Ramdahl T (1983) Polycyclic aromatic ketones in environmental samples. Environ Sci Technol 17:666–670

Ravindra K, Sokhi R, Van Grieken R (2008) Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation. Atmos Environ 42:2895–2921

Richardson SD (2009) Water analysis: emerging contaminants and current issues. Anal Chem 81:4645–4677

Rudel RA, Camann DE, Spengler JD, Korn LR, Brody JG (2003) Phthalates, alkylphenols, pesticides, polybrominated diphenyl ethers, and other endocrine-disrupting compounds in indoor air and dust. Environ Sci Technol 37:4543–4553

Salapasidou M, Samara C, Voutsa D (2011) Endocrine disrupting compounds in the atmosphere of the urban area of Thessaloniki, Greece. Atmos Environ 45:3720–3729

Schauer JJ, Rogge WF, Hildemann LM, Mazurek MA, Cass GR, Simoneit BRT (1996) Source apportionment of airborne particulate matter using organic compounds as tracers. Atmos Environ 30:3837–3855

Schorp MK, Leyden DE (2002) Distribution analysis of airborne nicotine concentrations in hospitality facilities. Environ Int 27:567–578

Seinfeld JH, Pankow JF (2003) Organic atmospheric particulate material. Ann Rev Phys Chem 54:121–140

Shaffer CB, Carpenter CP, Smyth HR Jr (1945) Acute andsub-acute toxicity of di-(2-ethylhexyl) phthalate with note upon its metabolism. J Ind Hygiene Toxicol 27:130–135

Sharma H, Jain VK, Khan ZH (2007) Characterization and source identification of polycyclic aromatic hydrocarbons (PAHs) in the urban environment of Delhi. Chemosphere 66:302–310

Silva MJ, Barr DB, Reidy JA, Malek NA (2004) Urinary levels of seven phthalate metabolites in the U.S. population from the National Health and Nutrition Examination Survey (NHANES) 1999–2000. Environ Health Perspect 112:331–338

Söderström H, Hajšlovà J, Kocourek V, Siegmund B, Kocan A, Obiedzinski MW, Tysklind M, Bergqvist PA (2005) PAHs and nitrated PAHs in air of five European countries determined using SPMDs as passive samplers. Atmos Environ 39:1627–1640

Sofowote UM, Allan LM, McCarry BE (2010) Evaluation of PAH diagnostic ratios as source apportionment tools for air particulates collected in an urban-industrial environment. J Environ Monit 12:417–422

Srogi K (2007) Monitoring of environmental exposure to polycyclic aromatic hydrocarbons: a review. Environ Chem Lett 5:169–195

Staples CA, Peterson DR, Parkerton TF, Adam WJ (1994) The environmental fate of phthalate esters: a literature review. Chemosphere 35:667–749

Strandell M, Zakrisson S, Alsberg T, Westerholm R, Winquist L, Rannug U (1994) Chemical analysis and biological testing of a polar fraction of ambient air, diesel engine, and gasoline engine particulate extracts. Environ Health Perspect 102:85–92

Sureda X, Fu M, José López M, Martínez-Sánchez JM, Carabasa E, Saltó E, Martínez C, Nebot M, Fernández E (2009) Second-hand smoke in hospitals in Catalonia (2009): a cross-sectional study measuring PM2.5 and vapour-phase nicotine. Environ Res 110:750–755

Teil MJ, Blanchard M, Cherveuil M (2006) Atmospheric fate of phthalate esters in an urban area (Paris, France). Sci Total Environ 354:212–223

Thomas GH (1973) Quantitative determination and confirmation of identity of trace amounts of dialkyl phthalates in environmental samples. Environ Health Perspect 3:23–28

Thuren A, Larsson P (1990) Phthalate esters in theSwedish atmosphere. Environ Sci Technol 24:554–559

Titcombe ME, Simcik M (2011) Personal and indoor exposure to $PM_{2.5}$ and polycyclic aromatic hydrocarbons in the southern highlands of Tanzania: a pilot-scale study. Environ Monit Assess 180:461–476

Toda H, Sako K, Yagome Y, Nakamura T (2004) Simultaneous determination of phosphate esters and phthalate esters in clean room air and indoor air by gas chromatography–mass spectrometry. Anal Chim Acta 519:213–218

Tsakapis M, Stephanou EG (2007) Diurnal cycle of PAHs, Nitro-PAHs, and oxy-PAHs in a high oxidation capacity marine background atmosphere. Environ Sci Technol 41:8011–8017

Tsapakis M, Stephanou EG (2003) Collection of gas and particle semi-volatile organic compounds: use of an oxidant denuder to minimize polycyclic aromatic hydrocarbons degradation during high-volume air sampling. Atmos Environ 37:4935–4944

Tuduri L, Millet M, Briand O, Montury M (2012) Passive air sampling of semi-volatile organic compounds. Trends Anal Chem 31:38–49

Turpin BJ, Saxena P, Andrews E (2000) Measuring and simulating particulate organics in the atmosphere: problems and prospects. Atmos Environ 34:2983–3014

U.S. Department of Health & Human Services USDHHS Public Health Service, Agency for Toxic Substances and Disease Registry (1993) Toxicological profile for di(2-ethylhexyl)phthalate

United Nations Office on Drug and Crime UNODC (2009) World Drug Report 2009. United Nations Publications

van Nuijs ALN, Pecceu B, Theunis L, Dubois N, Charlier C, Jorens PG, Bervoets L, Blust R, Neels H, Covaci A (2009) Cocaine and metabolites in waste and surface water across Belgium. Environ Pollut 157:123–129

Viana M, Querol X, Alastuey A, Postigo C, de Alda MJL, Barcelò D, Artiñano B (2010) Drugs of abuse in airborne particulates in urban environments. Environ Int 36:527–534

Viana M, Postigo C, Querol X, Alastuey A, de Alda MJL, Barceló D, Artíñano B, López-Mahia P, García Gacio D, Cots N (2011) Cocaine and other illicit drugs in airborne particulates in urban environments: a reflection of social conduct and population size. Environ Pollut 159:1241–1247

Villalobos-Pietrini R, Amador-Munoz O, Waliszewski S, Hernandez-Mena L, Munive-Colına Z, Gomez-Arroyo S, Bravo-Cabrera JL, Frias-Villegas A (2006) Mutagenicity and polycyclic aromatic hydrocarbons associated with extractable organic matter from airborne particles PM_{10} in southwest Mexico City. Atmos Environ 40:5845–5857

Walgraeve C, Demeestere K, Dewulf J, Zimmermann R, Van Langenhove H (2010) Oxygenated polycyclic aromatic hydrocarbons in atmospheric particulate matter: molecular characterization and occurrence. Atmos Environ 44:1831–1846

Waller RE (1952) The benzpyrene content of town air. British J Cancer 6:8–21

Wang G, Kawamura K, Lee S, Ho K, Cao J (2006) Molecular, seasonal, and spatial distributions of organic aerosols from fourteen Chinese cities. Environ Sci Technol 40:4619–4625

Wang P, Wang SL, Fan CQ (2008) Atmospheric distribution of particulate- and gas-phase phthalic esters (PAEs) in a metropolitan city, Nanjing, East China. Chemosphere 72:1567–1572

Wei S, Liu M, Huang B, Bi X, Sheng G, Fu J (2011) Polycyclic aromatic hydrocarbons with molecular weight 302 in $PM_{2.5}$ at two industrial sites in South China. J Environ Monit 13:2568–2574

Weschler CJ, Salthammer T, Fromme H (2008) Partitioning of phthalates among the gas phase, airborne particles and settled dust in indoor environments. Atmos Environ 42:1449–1460

WHO (2008) Report on the global tobacco epidemic, 2008: the MPOWER package. WHO Press, Geneva, pp 1–342

WHO (2009) Report on the global tobacco epidemic, 2009: implementing smoke-free environments. WHO Press, Geneva, pp 1–568

WHO (2011) Report on the global tobacco epidemic, 2011: warning about the dangers of tobacco. Zuccato E., Chiabrando C (eds), WHO Press, Geneva, 1–164

Winberry WT Jr, Murphy NT, Riggan RM (1988) Method TO 13: Determination of benzo(*a*)pyrene and other polynuclear aromatic hydrocarbons PAHs in ambient air using gas chromatographic

GC and high performance liquid chromatographic analysis. Compendium of methods for the determination of toxic organic compounds in ambient air. EPAr600/4/89/018, 1988. Accessed 10 Apr 2012)

Wormuth M, Scheringer M, Vollenweider M, Hungerbühler K (2006) What are the sources of exposure to eight frequently used phthalic acid esters in Europeans? Risk Anal 26:803–824

Xie Z, Ebinghaus R, Temme C, Caba A, Ruck W (2005) Atmospheric concentrations and air–sea exchanges of phthalates in the North Sea (German Bight). Atmos Environ 39:3209–3219

Xie Z, Selzer R, Ebinghaus J, Caba A, Ruck W (2006) Development and validation of a method for the determination of trace alkylphenols and phthalates in the atmosphere. Anal Chim Acta 565:198–207

Xie Z, Ebinghaus R (2008) Analytical methods for the determination of emerging organic contaminants in the atmosphere. Anal Chim Acta 610:156–178

Yassaa N, Meklati BY, Cecinato A (2001) Chemical characteristics of organic aerosols in Algiers city area: influence of a fat manufacture plant. Atmos Environ 35:6003–6013

Zaromb S, Alcaraz J, Lawson D (1993) Detection of airborne cocaine and heroin by high-troughput liquid absorption preconcentration and liquid chromatography-electrochemical detection. J Chromatog A 643:107–115

Zoccolillo L, Liberti A, Brocco D (1972) Determination of polycyclic hydrocarbons in air by gas chromatography with high efficiency packed columns. Atmos Environ 6:715–720

Zuccato E, Castiglioni S, Bagnati R, Chiabrando C, Grassi P, Fanelli R (2008) Illicit drugs, a novel group of environmental contaminants. Water Res 42:961–968