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Polychlorinated biphenyls in contaminated soil samples evaluated by GC–ECD with dual-column and GC–HRMS ☆

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ABSTRACT

We present and compare results obtained from the analysis of polychlorinated biphenyls (PCBs) of a limited number of contaminated soil samples collected in three areas of Basilicata region (south of Italy). The levels of PCBs were evaluated by using two analytical methods: (i) parallel dual-column gas-chromatography with dual electron capture detectors (GC–ECD) and (ii) gas-chromatography coupled to high-resolution mass spectrometry (GC–HRMS) via electron impact ionization (EI) in the multiple ion monitoring mode (MIM, two ions per compound). Two extraction methods prior to sample cleanup were also examined: microwave-assisted extraction (MAE) and ultrasonic-assisted extraction (UAE). The MAE was the extraction procedure adopted using acetone/*n*-hexane (1:1, v/v) as it is mainly characterized by higher sample throughput and allowed reduced consumption of organic solvents. While extraction and analysis of spiked soil samples showed the applicability of both methods, systematic differences between the results were obtained for the sum of PCBs as a result of some non-detected congeners by GC–ECD compared with GC–HRMS. Indeed, high resolution MS using EI mode (electron energy 40 eV) with a resolving power of 10,000 provides additional information about the contamination pattern. The GC–ECD screening of 11 soil samples led to just one sample non-compliant to as it was close to the guide value for soils fixed by the Italian legislation (i.e., 60 ppb for private or urban soil). Using GC–HRMS, the amount of all PCBs found ranged from 5.4 to 127 ppb with five soil samples non-compliant to the guide value. The number of identified congeners ranged from 1 to 9 and 9 to 18 using dual-column GC–ECD and GC–HRMS, respectively.

1. Introduction

Polychlorinated biphenyls (PCBs) are a class of synthetic organic compounds with general chemical formula $C_{12}H_{10-n}Cl_n$ with n ranging between 1 and 10; as a consequence 209 different configurations or congeners are possible. PCBs can be also categorized by degree of chlorination. The term "homolog" is used to refer to all PCBs with the same number of chlorines (e.g., trichloro-biphenyls), and homologous with different patterns are referred to as isomers. Each PCB congener is named according to the positions of chlorine substitution on the two rings of biphenyl and it is identified with a number from 1 to 209 (Ballschmiter and Zell, 1980).

The chemical stability of these synthetic compounds accounts for their persistence in the environment, and a congener-specific approach to PCB analysis is required in order to calculate the toxic potential of a mixture of PCB taking into account that there are enormous differences in the toxicity of PCB congeners (van den Berg et al., 1998). Interest in the toxicological effects of PCBs has been focused on a small group of planar congeners, which are referred to as coplanar PCBs (Tanabe, 1988). Coplanar PCBs have a close structural similarity to that of the tetrachlorodibenzo-*p*-dioxins, because toxicity correlates strongly with such structures, the toxicity of PCB mixtures may result from the presence of such compounds (called PCB dioxin-like). The toxicity of PCB mixtures is mainly due principally to a small group of non-*ortho* and mono-*ortho* substituted congeners (Tanabe, 1988) such as the congener 3,3′,4,4′,5,5′-hexachloro biphenyl (PCB 169). The concentration of non-*ortho* and mono-*ortho* substituted congeners in PCB extracts are generally low compared to those of other congeners. For this reason, it is of the utmost importance that a very sensitive method for the determination of the dioxin-like congeners is available. In this respect, capillary column GC has made possible to achieve lower detection limits and better separation of individual PCB congeners for quantification (Mullin et al., 1984; Newman et al., 1999; Frame, 1997), although complete separation of all congeners on a single column has not yet been achieved (Duebelbeis et al., 1989). The commonly used capillary columns (DB-5, DB-1701, SE-54, SIL-8, SP-2330 and

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CP-SIL-9) provide poor or no resolution for the following sets of congeners: 15/18, 28/31, 49/52, 77/110, 84/90/101, 118/149, 138/163/164, 105/132/153, 170/190 and 182/187 (Schantz et al., 1993; Liem, 1999). Nevertheless, the trend is toward congener-specific analysis by capillary GC. Recent advances include analytical methods that are able to quantify individual PCB congeners. EPA method 1668 (Revision A) is the current methodology used to determine individual PCB congeners in water, soil, sediment, and tissue by GC and high resolution mass spectrometry (HRMS) (US EPA, 1999k).

The determination of PCBs in soils is a difficult task owing to a series of problems, such as their low concentration (ppb to ppq) and simultaneous occurrence of a large number of other interfering compounds frequently found at much higher concentrations. In addition, soil is a heterogeneous sample matrix also considered as a complex matrix differing significantly in composition. Overcoming all these analytical problems is only possible with the application of a rigorous extraction and cleanup schemes. Several researchers have compared a range of techniques for the extraction of organic pollutants from environmental matrices (Saim et al., 1997; Sporring et al., 2005; Herbert et al., 2006; Fidalgo-Used et al., 2007). The choice of extraction technique is frequently decided upon based on initial capital cost, operating cost, simplicity of operation, amount of organic solvent required and sample throughput. The range of approaches currently available makes the selection of the most appropriate extraction technique difficult. In this paper, two extraction techniques are compared for their effectiveness to extract PCBs from contaminated soil, i.e. ultrasonic-assisted extraction and pressurized microwave-assisted extraction.

High-resolution capillary gas chromatography (GC) coupled with electron capture detection (ECD) or mass spectrometry (MS) systems have been the reference methods for determination of trace level of polychlorinated biphenyls (PCBs) in various environmental matrices for decade (Mullin et al., 1984; Morosini et al., 1993; Porte and Albaiges, 1993; Chen and Ling, 1994; Rahman et al., 1995; Colombo et al., 1997; Ruus et al.; 1999; Easton et al., 2002; Bordajandi et al., 2003; Sapozhnikova et al., 2004; Burreau et al., 2004; Schmid et al., 2005; De Saeger et al., 2005; Verenitch et al., 2007; Zhang et al., 2007). Here, we provide a comparison for congener-specific PCB analysis in soil samples with special emphasis on the capabilities and limitations associated to a parallel dual-column GC with electron capture detection (GC–ECD) and GC with high resolution mass spectrometric detection (GC–HRMS). As expected, high resolution MS detection provided confirmation of different congeners. The method applied here allows the chromatographic separation of at least 20 congeners (PCB n. 77, 123, 118, 114, 105, 126, 167, 157, 180, 169, 170, 28, 52, 101, 81, 153, 138, 128, 156 e 189), including both dioxin-like congeners and those with no dioxin-like activity.

2. Experimental

2.1. Reagents and chemicals

A set of two mixtures Mix-1 and Mix-2 containing a total of 20 congeners of established identity was used to study and compare results obtained using different detection methods. Each mixture contains a group of 9 and 11 PCBs; Mix-1 and Mix-2, respectively, were purchased from Dr. Ehrenstorfer Laboratories (Augsburg, Germany) at 10 ng/μL each component in iso-octane. The compositions of the two mixtures, using the IUPAC numbering system, are: Mix-1: PCB n 77, 123, 118, 114, 105, 126, 167, 157, 180, 169, 170, and Mix-2: PCB n 28, 52, 101, 81, 153, 138, 128, 156, 189. Perfluotributylamine (PFTBA or FC43) and all solvents (methanol, hexane, toluene, acetone) were analytical grade and purchased from Sigma–Aldrich (Buchs, Switzerland). The polychlorinated biphenyls (PCBs) included in this study were used to prepare a 'working standard' in hexane with 100 μg/L of PCBs, on average. This solution was used to prepare diluted standard solutions and spike uncontaminated soil samples to the required concentration. A soil sample was analyzed to confirm the absence of PCBs in order to used it as standard blank soil. Spiked dried soil samples were prepared by adding appropriate volumes of the PCBs concentrated stock solution to portion of soils. The spiked samples as well as the unknown soil samples were allowed to stand for 24 h to air-dry and extracted by MAE (and UAE) thereafter.

2.2. Apparatus and chromatography

For the GC–ECD analysis of PCBs, an Autosystem (XL Perkin–Elmer) consisting of an autosampler, a split–splitless injector and equipped with two ^{63}Ni electron capture detectors (ECDs) was used. Aliquots of the standard mixtures or soil extracts were injected in two parallel coupled columns, a 60 m × 0.25 mm, 0.25 μm 5%-phenyl–95%methylpolysiloxane (Zebron-5, Phenomenex) and a 60 m × 0.25 mm, 0.25 μm 50%-phenyl–50%methylpolysiloxane (Zebron-50, Phenomenex). The columns were installed in the GC oven together. The ECD system was operated at 325 °C and make up flow 30 mL/min. All the operating conditions of GC–ECD are summarized in Table 1. Total run time was 45 min. The volume of sample was 1 μL, injected in splitless mode. Helium (99.999% purity) was used as carrier gas. Identification of PCB congeners was solely based on their retention times (t_R) which were established from the analysis of authentic PCB standard solutions. Verification of correct t_R assignment for samples analyzed by GC–ECD was made from the analysis of a replicate sample spiked with known amounts of the 20 target PCB congeners.

The GC–MS analysis of PCBs was carried out on the DFS high resolution MS system coupled to a TRACE GC Ultra™ gas chromatograph equipped with a split/splitless injector. Samples were injected using the TriPlus™ Autosampler (ThermoScientific). The injection volume was 1 μL of each soil sample extract or standard mixture. The analytical column used was a J&W Scientific DB-5 fused silica capillary column (Folsom, CA, USA), a 5%-phenyl–95%-methylsiloxane with 30 m length, 0.25 mm of internal diameter and 0.25 μm of film thickness. The mass spectrometer source temperature was set at 250 °C, with the interface line at 290 °C (see operating conditions summarized in Table 1). The DFS mass spectrometer was setup in the multiple

Table 1
Operating conditions of GC–ECD and GC–HR-MS

Item	GC–ECD (dual-column)	GC–HRMS
Inlet liner	Quartz or glass wool packed liner or equivalent material	Quartz or Glass wool packed liner or equivalent material
Column	Dual-column: Zebron-5 and Zebron-50 both 60 m × 250 μm d.i., 0,25 μm film thickness	J&W Scientific DB-5 (30 m × 250 μm d.i., 0.25 μm film thickness)
Carrier gas	Helium gas (99.999%)	Helium gas (99.999%)
Detector	ECD at a temperature of 325 °C	HR–MS operating in the EI mode (electron energy 40 eV). Resolution = 10000; acquisition mode: multiple ion monitoring with two ions per compound. Transfer line temperature: 290 °C
Flow mode	Constant pressure mode at 28 psi	Constant flow at 0.9 ml/min
Injection mode and injector temperature	Splitless mode 250 °C, splitless time: 2.0 min	Splitless mode at 250 °C, splitless time: 1.0 min
Oven temperature	100 °C → 250 °C (25 °C/min, hold time 2 min) → 290 °C (1.5 °C/min) → 310 °C (15 °C/min, hold time 9 min)	75 °C (hold time 2 min) → 150 °C (15 °C/min) → 270 °C (2.5 °C/min hold time 7 min)

ion monitoring (MIM) mode at a resolution of 10,000 (10% valley definition) for achieving maximum sensitivity possible. Perfluorotributylamine (PFTBA or FC43) was used as a reference compound to provide the inherent lock and cali masses. These reference masses are monitored scan-to-scan to insure the highest mass precision, stability and ruggedness necessary for routine target compound analysis on a high resolution mass spectrometer. The two most abundant native isotope ions, $[M]^+$ and $[M+2]^+$ or $[M+2]^+$ and $[M+4]^+$, of known relative abundance were monitored for each homologue series (see Table 2).

The effective resolution was constantly monitored on the reference masses and documented in the data files for each MIM window. The optimization of the electron energy on the instrument is critical in obtaining the best results. On the DFS instrument used for the demonstrated measurements, an electron energy of 40 eV provided optimum sensitivity (US EPA, 1999k). During the optimized procedure, the best instrument performance was achieved by autotuning the ion source on the FC43 reference mass m/z 414 with a resolution setting of 10,000.

2.3. Soil sample pretreatment

After discarding any foreign objects such as sticks, leaves and rocks, the soil samples were air-dried at room temperature to constant weight for 48 h on hexane-rinsed aluminum foil, ground to a fine powder and passed through a 2-mm soil sieve before extraction. Spiked soil samples were prepared by adding appropriate volumes of PCBs concentrated stock solution to a 5.0 ± 0.1 g or 50.0 ± 0.1 g soil portion for microwave-assisted or ultrasonic-assisted extraction, respectively. The spiked samples as well as the unknown soil samples were extracted by ultrasound-assisted extraction and microwave-assisted extraction.

2.4. Ultrasonic-assisted extraction method and clean-up with GPC

The ultrasonic-assisted extraction has been applied for the extraction of PCBs from various solid environmental samples (Moret et al., 2001; Martens et al., 2002). One reason for applying acoustic energy is that it enhances soil washing. The predominant

Table 2
Ions used for the quantification of PCBs under high resolution in the multiple ion monitoring mode

MIM window no. (time window)	Reference masses (FC43)[a] L = lock mass; C = cali mass	Target masses m/z	Ion identification	Compound	MIM cycle times (intensity, dwell time ms)
1-mono-PCB, di-PCB (10.00–14.00 min)	168.988 (L), 213.990 (C)	188.039 (*n*)[b]	M+2	^{35}Cl-1-PCB	0.50 s (L/C : 20, 3 ms, n:1, 64 ms)
		190.037 (*n*)	M	^{37}Cl-1-PCB	
		222.000 (*n*)	M+2	^{35}Cl-2-PCB	
		223.997 (*n*)		^{37}Cl-2-PCB	
2-di-PCB, tri-PCB (14.00–16.00 min)	213.990 (L), 313.983 (C)	222.000 (*n*)	M	^{35}Cl-2-PCB	0.50 s (L/C: 40, 2 ms; n:1, 92 ms)
		223.997 (*n*)	M+2	^{37}Cl-2-PCB	
		255.961 (*n*)	M	^{35}Cl-3-PCB	
		257.968 (*n*)	M+2	^{37}Cl-3-PCB	
3-tri-PCB, tetra-PCB, penta-PCB (16.00–20.00 min)	213.990 (L), 351.980 (C)	255.961 (*n*)	M	^{35}Cl-3-PCB	0.60 s (L/C: 30, 2 ms; n:1, 71.00 ms)
		257.968 (*n*)	M+2	^{37}Cl-3-PCB	
		291.919 (*n*)	M	^{35}Cl-4-PCB	
		301.963 (*n*)	M+2	^{37}Cl-4-PCB	
		325.880 (*n*)	M+2	^{35}Cl-5-PCB	
		327.878 (*n*)	M+4	^{37}Cl-5-PCB	
4-tetra-PCB, penta-PCB, hexa –PCB (20.00–25.00 min)	289.922 (L); 413.977 (C)	291.919 (*n*)	M	^{35}Cl-4-PCB	0.60 s (L/C: 30, 2 ms; n:1, 71.00 ms)
		301.963 (*n*)	M+2	^{37}Cl-4-PCB	
		325.880 (*n*)	M+2	^{35}Cl-5-PCB	
		327.878 (*n*)	M+4	^{37}Cl-5-PCB	
		359.842 (*n*)	M+2	^{35}Cl-6-PCB	
		361.839 (*n*)	M+4	^{37}Cl-6-PCB	
5-penta-PCB, hexa -PCB, hepta-PCB (25.00–34.50 min)	313.983 (L); 413.977 (C)	325.880 (*n*)	M+2	^{35}Cl-5-PCB	0.60 s (L/C: 30, 2 ms; n:1, 71.00 ms)
		327.878 (*n*)	M+4	^{37}Cl-5-PCB	
		359.842 (*n*)	M+2	^{35}Cl-6-PCB	
		361.839 (*n*)	M+4	^{37}Cl-6-PCB	
		393.803 (*n*)	M+2	^{35}Cl-7-PCB	
		395.800 (*n*)	M+4	^{37}Cl-7-PCB	
6-hexa -PCB, hepta-PCB, octa-PCB (34.50–36.50 min)	313.983 (L); 463.974 (C)	359.842 (*n*)	M+2	^{35}Cl-6-PCB	0.60 s (L/C: 30, 2 ms; n:1, 71.00 ms)
		361.839 (*n*)	M+4	^{37}Cl-6-PCB	
		393.803 (*n*)	M+2	^{35}Cl-7-PCB	
		395.800 (*n*)	M+4	^{37}Cl-7-PCB	
		427.764 (*n*)	M+2	^{35}Cl-8-PCB	
		429.761 (*n*)	M+4	^{37}Cl-8-PCB	
7-hepta-PCB, octa-PCB, nona-PCB (36.50–40.00 min)	413.977 (L); 463.974 (C)	393.803 (*n*)	M+2	^{35}Cl-7-PCB	0.60 s (L/C: 30, 2 ms; n:1, 71.00 ms)
		395.800 (*n*)	M+4	^{37}Cl-7-PCB	
		427.764 (*n*)	M+2	^{35}Cl-8-PCB	
		429.761 (*n*)	M+4	^{37}Cl-8-PCB	
		461.725 (*n*)	M+4	^{35}Cl-9-PCB	
		465.719 (*n*)	M+6	^{37}Cl-9-PCB	
7-octa-PCB, nona-PCB, deca-PCB (40.00–62.00 min)	463.974 (L); 501.971 (C)	427.764 (*n*)	M+2	^{35}Cl-8-PCB	0.40 s (L/C: 40, 3 ms; n:1, 150.00 ms)
		429.761 (*n*)	M+4	^{37}Cl-8-PCB	
		461.725 (*n*)	M+4	^{35}Cl-9-PCB	
		465.719 (*n*)	M+6	^{37}Cl-9-PCB	
		495.686 (*n*)	M+2	^{35}Cl-10-PCB	
		497.683 (*n*)	M+4	^{37}Cl-10-PCB	

[a] FC43 or PFTBA, Perflourotributylamine used as mass calibrant.
[b] *n* means native isotope.

mechanisms for this washing are mechanical, and include abrasion of suspended soil in slurries leading to surface removal of the contaminants, and improved solvent leaching of contaminants from the interior of particles (Timothy et al., 2004).

Sonication involves the use of sound waves to stir the sample immersed in the organic solvent. Briefly, energy in the form of acoustic sound waves, in the ultrasound region above 20 kHz, is used to accelerate mass transport and mechanical removal of analytes from the solid matrix surface by a process called "cavitation". This consists of the formation and implosion of vacuum bubbles trough the solvent, thus creating microenvironments with high temperatures and pressures (estimated up to 5000 °C and 100 MPa) (Priego-Capote and Luque de Castro, 2004). This mechanical effect of ultrasound induces a greater penetration of solvent into solid materials and improves mass transfer leading to an enhancement of sample extraction efficiency.

The procedure for sonication-assisted extraction was done according to the method 3550B (US EPA) approved by EPA. Extractions were performed in triplicate. Ultrasonic-assisted extractions were performed with a Vibra Cell VC 600 Sonicator (Sonics and Material, Danbury, CT). The uncontamined soil sample was spiked with a mixture of PCB standard such that the final spiked concentration was 1 ppb of target analytes. The soil, 50 g, was wetted with ca. 1 mL water before 1.5 mL acetone/g (solvent A) of soil was added and then homogenized in a Zoppas CU 56 mixer for two minutes before adding 100 mL of *n*-hexane (solvent B) together with 15 g of sodium chloride and shaken vigorously for two min. Then, the samples were sonicated for 3 min. Anhydrous Na_2SO_4 powder was added to remove water and 100 mL of the organic phase was transferred to a round bottom flask and evaporated to dryness by rotary evaporation (at 35 °C) and reconstituted in 7 mL of ethyl acetate/cyclohexane (1/1, v/v) and filtered on a 0.45μm PTFE filter. UAE of PCBs from soil samples was carried out using different solvent mixtures (solvent A/solvent B), i.e. acetone/*n*-hexane (0.75/1, v/v), acetone/dichloromethane (1/0.75, v/v), dichloromethane/*n*-hexane (1/0.75, v/v). After UAE the sample went through the clean-up procedure. Gel-permeation chromatography was employed as clean-up procedure and adapted from the method published by Jira (2004) to remove higher molecular weight compounds from the sample. Only the wasting and collecting times were changed, to 0–20 and 20–35 min, respectively. For GPC, a LC glass column with an i.d. of 25 mm, length 30 cm was filled with 50 g of Bio-Beads S-X3 (200–4000 mesh). The GPC (dedicated sample clean up system, Lab Service Analytica) was carried out with a solvent mixture of cyclohexane/ethyl acetate (1/1, v/v) and a flow rate of 5 mL/min. The eluate was evaporated to dryness by rotary evaporation and reconstructed in 1 mL of *n*-hexane.

In this vein, an official EPA method (Method 3640A GPC Cleanup) has been approved for the purification of organic extracts from solid environmental samples (US EPA). Normally, this method is most efficient for removing high boiling materials that condense in the injection port area of a gas chromatograph or the front of the GC column. This residue will ultimately reduce the chromatographic separation efficiency or column capacity because of adsorption of the target analytes on the active sites. GPC, operating on the principal of size exclusion, will not usually remove interference peaks that appear in the chromatogram since the molecular size of these compounds is relative similar to the target analytes. Separation cleanup techniques, based on other molecular characteristics (i.e., polarity), must be used to eliminate this type of interference.

2.5. Microwave-assisted extraction method and clean-up with SPE

To shorter extraction times and reduce solvent consumption is possible working at elevated temperatures, i.e., above the boiling point of the solvent. Thereby, the extraction process is facilitated due to increased analyte desorption and diffusion from the solid matrix. The microwave-assisted extraction (MAE) utilizes the energy of microwaves to cause molecular movement and rotation of liquids with a permanent dipole leading to a very fast heating of the solvent and the sample. Several applications utilizing MAE for the extraction of PCBs from solid samples have been published (During and Gath, 2000; Criado et al., 2005; Bartolomé et al., 2005). Microwave-assisted extractions were performed with an ETHOS E Touch Control Microwave Solvent Extraction Labstation (Milestone Corporation, Monroe, CT) with maximum power of 1000 W. In order to efficiently extract target PCBs from solid samples using MAE, the ideal solvent should be selected and extraction temperature and duration should be optimized (Liu et al., 2004). The solvent was selected based on high solvent polarity (i.e., dipole moment); in fact the microwave extraction is based on using microwave energy to heat solvents that are in contact with solid samples and to partition compounds of interest into the solvent. The nature of the solvent is of the great importance in MAE: it should selectively and efficiently solubilize the analytes of the sample but, at the same time, it should absorb the microwaves without leading to a strong heating, so as to avoid eventual degradation of the analyte compounds (Jassie et al., 1997). Thus, it is common practice to use a binary mixture (e.g., hexane-acetone, 1/1, v/v) where only one of the solvent is absorbing microwaves.

Preliminary testing was completed to ascertain which extraction solvent(s)/cocktail(s) resulted in greatest recovery of the target compounds from a soil sample. Two solvent mixtures of acetone/*n*-hexane (1/1, v/v) and methylene chloride/*n*-hexane (1/1, v/v) were tested to this goal. The uncontamined soil sample was spiked with a mixture of PCB standard such that the final spiked concentration was 1 ppb of target analyte. We selected an extraction temperature of 115 °C as suggested in the US EPA's Standard Operating Procedure for microwave-assisted extraction of soils and sediments for trace organic compounds (US EPA). The soil, 5 g, was loaded into the extraction cylinders and 30 mL of a mixture acetone/*n*-hexane (1/1, v/v) or methylene chloride/*n*-hexane (1/1, v/v) was added; the extraction temperature was 115 °C (1000 W) and programmed as follows: from room temperature ramp to 115 °C for 10 min, with the final temperature held for 20 min. After cooling, the sample was filtered on silica gel/anhydrous sodium sulphate (1/2, w/w) and the soil sample was washed three times with 15 mL of the same solvent mixture and the supernatants were combined. The silica gel was heated in an oven at 130 °C overnight and cooling down in a desiccator to room temperature before using. Sodium sulphate anhydrate in ceramic dish was ashed at 450 °C for 5 h, cooled and stored in a desiccator till use. The supernatants were combined, then evaporated by rotary evaporation to nearly 1 mL, which was then subjected to solid phase extraction (SPE) as clean up procedure. Use of Florisil (0.5 g/3 mL) SPE column enables removal of compounds from polar to highly polar, including lipids. After conditioning with 10 mL of *n*-hexane and sample loading, the analytes were drop-wise eluted with 10 mL of *n*-hexane. The eluate was evaporated to dryness by rotary evaporation and reconstituted in 1 mL of *n*-hexane. 200 μL of the final residue was transferred to GC–ECD vials with microvolume glass inserts for the analysis. Excluding the chromatographic run, the whole pretreatment procedure takes about 3 h.

3. Results and discussion

3.1. Extraction and clean-up of PCBs from soil samples

The particular PCB congener, as well as the type of soil, amount of organic matter, and amount of moisture, affect how readily and how strongly PCBs are adsorbed into soils and sediments. The performance of an analytical methodology can be enhanced if a

selective extraction procedure is employed that directly decreases or eliminates interfering substances in the extract. The composition of extraction solvent and the extraction system were examined. A comparison of recovery between by MAE extraction and UAE, using two and three selected mixtures, respectively, of organic solvents, was performed (see below). At the beginning, to achieve efficient extraction of target compounds from soil samples by MAE, the optimal extraction solvent needs to be selected, the polarity of which matches that of the tested compounds. Two solvent mixtures were evaluated for the extraction efficiency of the tested compounds at a nominal concentration of 1 ppb, i.e., acetone/*n*-hexane (1/1, v/v), and dichloromethane/*n*-hexane (1/1, v/v). Using acetone/*n*-hexane (1/1, v/v) the extraction efficiency values were more satisfactory and in the range 65–97% with an intra-day CV% varying from 2.5% to 6.5% ($n=3$) and an inter-day CV% always less than 11%, (three days, $n=3$) for all compounds; therefore such a mixture was chosen as the best solvent mixture for MAE extraction.

UAE was performed using acetone/*n*-hexane (0.75/1, v/v), acetone/dichloromethane (1/0.75, v/v) and dichloromethane/*n*-hexane (1/0.75, v/v). Using acetone/*n*-hexane (0.75/1, v/v) the extraction efficiency values were between 46% and 97% for all compounds and an intra-day CV% in the range from 3.5% to 7.2% ($n=3$) and an inter-day CV% less than 13%, (three days, $n=3$). Such a mixture was chosen as the best solvent mixture for UAE. Statistical significance between the two extraction procedures was evaluated using the two-tailed unpaired Student *t*-test (at the 95% confidence interval) on the values of the individual PCBs extracted from three replicate soil samples. In each case, the level of significance was determined and when this value was greater than 0.05, the hypothesis was accepted. Ultrasonic extraction of the dried homogenized soil sample using acetone/*n*-hexane (0.75/1, v/v) solvent mixture extracted comparable quantities of PCBs compared to the microwave-assisted extraction method using acetone/*n*-hexane (1/1, v/v). Statistical evaluation utilizing the unpaired Student *t*-test indicated no significant differences (p values > 0.05) between the individual PCB analyte values ($n=3$) extracted by ultrasonication and microwave-assisted processes. In addition, comparison of the precision of the procedures, by analysis of the relative standard deviation (RSD) of the PCBs extracted, showed no significant differences. MAE was selected because it reduces extraction time, uses small amounts of solvents (30 mL in MAE versus ca. 200 mL in UAE) and it is quite easy the sample clean-up procedure.

3.2. Gas chromatography with either ECD or EI–HRMS

In this section, two different detection modes ECD and HRMS with electron impact (EI) ionization upon GC separation are surveyed. The capabilities and limitations associated with each detector, with special emphasis on the sensitivity and selectivity, are discussed. The PCB analysis were achieved using either a magnetic sector mass spectrometer HRMS or an ECD system with two ^{63}Ni electron capture sources. The results of the 11 soil samples investigated in terms of PCB contamination using a parallel dual-column GC–ECD were compared with those determined by GC–HRMS. To accurately compare results from the two different analytical methods, it is important to understand and identify the potential problems inherent to both.

ECD was specifically designed to have high sensitivity for halogenated compounds, and is easy to operate and maintain. These advantages along with the relatively low cost have been the reasons for its wide use as the detection method of choice for the analysis of low levels of halogenated contaminants. The main limitation of the electron-capture detection is the fact that it does not produce a specific signal to individual compounds, meaning that all analytes having the same number of chlorine atoms (i.e., PCB congeners) give rise to similar responses. Determination of compound-specific concentrations relies on good separation of the individual compounds of interest during chromatography. The identification of analytes is based exclusively on their retention time. As a result, any compound interfering or co-eluting with the target analytes can prevent accurate quantification of those analytes (Jones et al., 1991; Harrad et al., 1992). Often, the influences of matrix and other compounds may have a profound effect on the chromatography of target analytes. Thus, second column confirmation is used to minimize the misidentification and matrix interferences encountered during GC–ECD analysis (DeCaprio et al., 2000). The confirmation column was chosen with a slightly different polarity compared with the primary column, thus separating the target analytes and interferent peaks in different retention orders.

The development of capillary columns in GC allows the congener-specific determination of a number of PCB mixtures. In general, molecules elute from a GC column in order of decreasing volatility, that is, for chlorinated compounds, in order of increasing chlorine number. The twenty PCBs were selected because they include the main toxic together with the main reported congeners in the literature. Because the polarity of coplanar (or non-*ortho*) PCBs is usually greater than non-planar PCBs with the same chlorine number, coplanar PCBs could co-elute with non-planar with a higher chlorine number. To separate, detect and quantify PCBs with GC–ECD the 20 PCBs had to be divided in two mixture Mix-1 and Mix-2 (see Section 2). In Figs. 1B, C and 2B, C are shown the GC–ECD chromatograms for the two standard mixtures from *tri*- to *hepta*-CBs on a Zebron-5 and a Zebron-50 capillary column, respectively. This type of columns was chosen because fewer co-elutions of target analytes occur. On both columns the PCBs are eluted not absolutely in order of increasing chlorine number, for example the PCB 81, which is a tetra-CB is eluted after the 101, a *penta*-CB (Fig. 1, trace C).

A typical separation using the GC–HRMS method with chromatographic and MS parameters reported in Tables 1 and 2, respectively, of the standard mixture of twenty PCB at a 5 ppb is shown in Fig. 3.

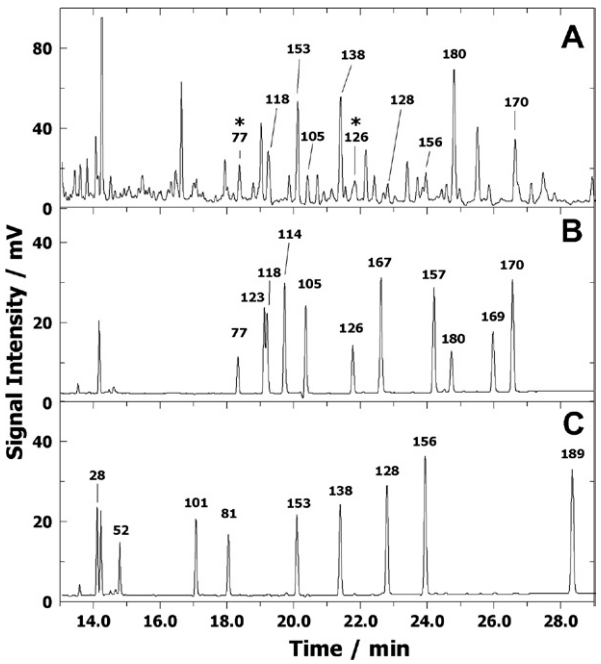

Fig. 1. GC–ECD chromatograms on the capillary column Zebron-5, 5%-phenyl–95%methylpolisiloxane, (60 m × 250 μm ID × 0.25 μm): (A) soil sample S224 (site no. 2); (B) PCBs standard mixture Mix-1 listed; (C) Mix-2. For experimental conditions see Table 1. Asterisk is used to select signal to be confirmed on the second column.

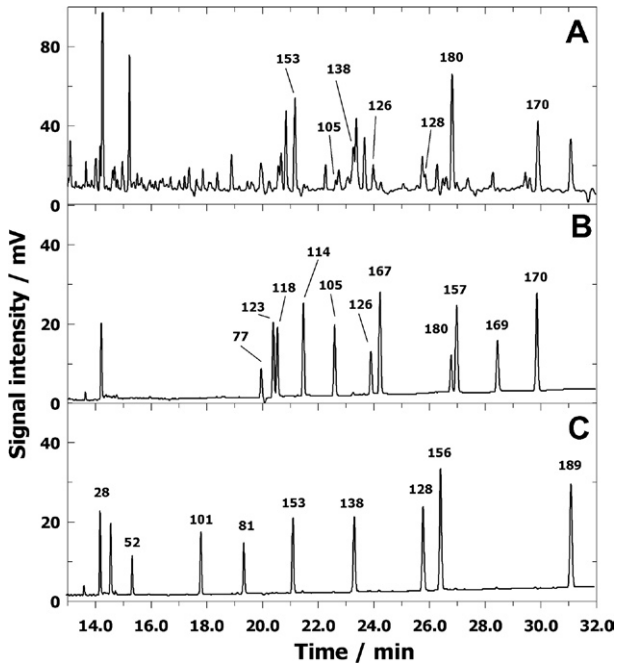

Fig. 2. GC–ECD chromatograms on the capillary column Zebron-50, 50%-phenyl–50%methylpolisiloxane, (60 m × 250 μm ID × 0.25 μm): (A) soil sample S224 (site no. 2); (B) the PCB standard mixture Mix-1 listed; (C) Mix-2. Only the occurrence of PCBs 153, 105, 138, 126, 128, 180 and 189 is confirmed with this capillary column.

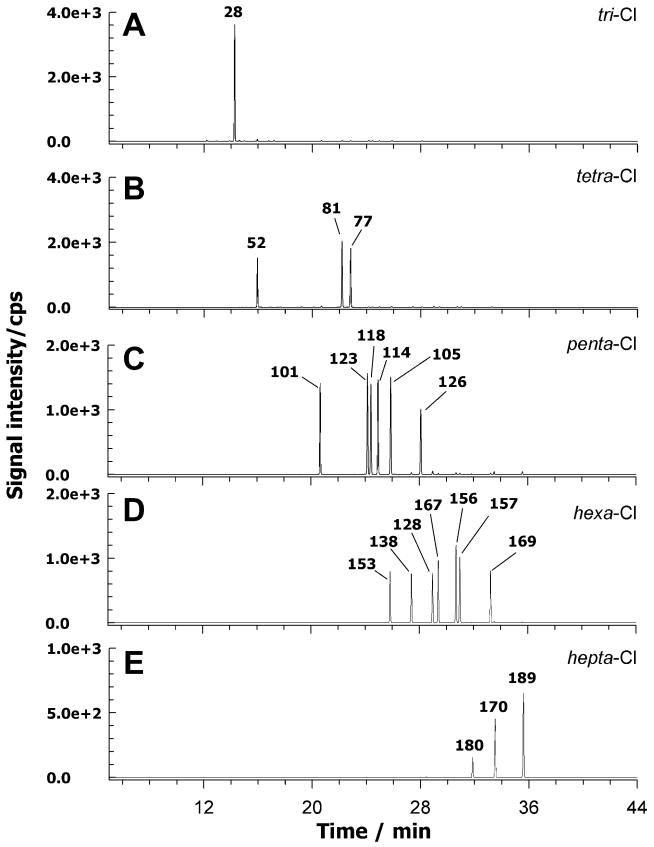

Fig. 3. Extracted ion chromatograms for a mixture of 20 PCBs (see Section 2) registered by GC–HRMS. The top traces show the selected ion chromatograms of the sum intensity of the $M^{\bullet+}$, $[M+2]^{\bullet+}$ and $[M+4]^{\bullet+}$. Ions from isomers containing three, four, five, six and seven chlorine atoms, respectively. Each peak in the selected ion chromatogram is identified by its IUPAC number. (A) *tri*-Cl, (B) *tetra*-Cl, (C) *penta*-Cl, (D) *hexa*-Cl and (E) *hepta*-Cl chromatograms of the same mixture at a concentration level of 5 ppb. For experimental conditions see Tables 2 and 3. Capillary column, DB-5 (5%-phenyl–95% methylpolysiloxane) 30 m × 250 μm ID × 0.25 μm.

A 1 μL of the standard mixture was injected in the splitless mode; a DB-5 column, was used to separate the twenty PCB congeners. Detection of all analytes was determined using electron impact ionization and high resolution MIM conditions; details of *m/z* values for PCBs detection are given in Table 2. No interference on the PCBs screening was found due to the highly specific MIM acquisition method. In most related studies using EI–MS the electron energy is either 70 eV or between 30 and 40 eV (Pirard et al., 2003). Here, the electron energy value was set at 40 eV in agreement with EPA suggestions (US EPA, 1999k). A sequence of 10 repeated injections measuring PCB masses of a 5 ppb PCB standard mixture was performed. The instrumental parameters were accurately optimized in order to obtain a mass resolution (R, 10% valley definition) of 10,000. In order to increase sensitivity of MIM mode the sum of the two most abundant peaks in the charged molecular cluster was accomplished. In Fig. 3 all the revealed peaks are well resolved and the chromatographic run is completed in less than 45 min.

3.3. Validation study

During the evaluation process, mixed samples of a hexane stock solution of both Mix-1 and Mix-2 were injected. Using the chromatographic conditions described above and summarized in Table 1, a comparison was made within the GC–ECD and GC–HR mass spectrometer. Twenty 6-point calibration curves were plotted as the peak area of analytes versus concentration and were linear in the range 1–100 ppb and 0.01–25 ppb, for GC–ECD and GC–HRMS, respectively; all measurements were done in triplicate. The accuracy of the method was demonstrated by recovery experiments described above. The limit of detection (LOD) of the investigated PCBs was evaluated using either the GC–ECD or GC–HRMS analytical methodologies. As expected, significant improvement in the LODs was obtained using the mass spectrometric detection; the estimated value, based on a signal to noise ratio of 3, was found to be in the range 0.01–0.04 ppb and 0.001–0.01 ppb when the GC–ECD and GC–HRMS were used, respectively. Although calculated LODs were very low, standards of those levels of concentration were excluded from calibration curve, considering the fact that these concentrations are considerably below the guideline set for the total content of PCB in soil dedicated to public green, i.e. 60 ppb (Italian Decret n. 152, 2006). The method limit of detection (MDL), as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero, was determined from analysis of an uncontamined soil sample in a given matrix containing the analyte at 1 ppb (US EPA SW-846, 2007); for the 20 individual compounds in our study MDL varied from 0.6 to 1.6 ppb, when the GC–ECD was used and from 0.01 to 0.05 ppb in the case of GC–HRMS. Quantification of PCBs was performed by external standard procedure. Calibration standards ranged from 1 to 200 ppb and from 0.01 to 25 ppb for GC–ECD and for GC–HRMS, respectively. In these ranges, a good linearity for ECD (correlation coefficient, $r \geqslant 0.9994$) and the MS ($r \geqslant 0.9996$) detectors was achieved.

3.4. Analysis of contaminated soil samples

Figs. 1 and 2 provide the typical dual-column GC–ECD chromatograms on the capillary columns Zebron-5 and Zebron-50 respectively; the upper trace (A) in Fig. 1 is relative to a soil sample extract, traces (B & C) are relative to the standard mixtures Mix-1 and Mix-2, respectively. Each peak in the chromatogram is identified by its corresponding IUPAC number. The samples tested positive by GC–ECD on the first column (Zebron-5) required further confirmation on the second column (Zebron-50), the relatively lower polar column.

The use of parallel dual-column GC coupled to double ECD detectors was used to reduce the occurrence of false positive in environmental matrices. The soil samples were obtained from three sites of Basilicata (South of Italy). Most likely, PCBs were released to soil by wastes that had been spread over land or are due to leaks from inappropriate disposal in landfills.

The analysis of sample S224 (Fig. 1) revealed the presence of six PCBs, viz. 153, 138, 128, 180, 170 and one dioxin-like PCB, i.e. n. 105. The same analysis were performed on all soil samples and the results are given in Table 3. The total concentration values were evaluated as a sum of all PCBs revealed, which ranged between 0.6±0.1 to 62±6 ppb for the S479 and S50 soil samples, respectively. Concerning to congeners dioxin-like, only the PCBs 118 and 105 were revealed in extracts of soil samples from site n. 2, namely the S36AR, S231 and S233; the S224 contained only the PCB 105. The same soil samples were investigated by GC–HRMS. The identification of PCBs was based on the following criteria: (1) retention times of chromatographic peaks must be within the appropriate chromatographic windows; (2) simultaneous responses for the two masses monitored must be obtained; (3) signal-to-noise ratio must be greater than 3. A typical MIM chromatogram of the soil sample S224 (site n. 2) is showed in Fig. 4. Thirteen PCBs could be identified: n. 28, 52, 77, 101, 118, 105, 153, 138, 128, 167, 156, 180 and 170 of which six are dioxin-like PCBs (i.e., 28, 77, 118, 105, 167 and 156). Conceivably, the combination of exact mass measurement by the use of high-resolution mass spectrometry with chromatographic data (i.e., retention time and peak shape) gives extraordinary insight into the nature of the PCBs. Apart from the twenty indicator PCBs studied in this work, some of soil sample i.e. the S224 contains several others PCBs; in the MIM chromatogram of Fig. 4 the traces A, G and H are relative to *di*-, *octa*-, *deca*-PCBs that could in the future be quantified by the same method providing that these compounds are included in the standards. The analytical results for all soil samples analyzed by GC–HRMS are reported in Table 3. Consequently, a higher number of PCBs was found when GC–HRMS is employed and as a direct consequence a higher level of concentration of total PCBs was obtained. PCB concentrations (sum of all PCBs found) in the soil samples ranged from 5.4 to 127 ppb with GC–HRMS without using any fixed recovery correction factor.

When GC–ECD was employed there were only one sample, i.e. the S479 (site n. 3), in our study whose PCB total concentration was close to the guide value for soil dedicated to private or urban use, which is estimated to be 60 ppb (Italian Decret n. 152, 2006). With GC–HRMS three samples were found above to the guide value, i.e. S36AR, S479, S480 and two close to it, i.e. S224 and S233. The remaining six samples were still below the trigger value of 60 ppb. The congener pattern was characteristic for each sample: the number of total congener ranged from 1 to 9 when GC–ECD was employed and between 9 and 18 with GC–HRMS. About the number of dioxin-like congeners, with GC–ECD only four samples, nominally S36AR, S224, S231 and S233 showed the presence of PCBs dioxin-like, viz., n. 118 and 105 (boldface in Table 3). When GC–HRMS was employed a higher number of dioxin-like congeners (including the mono-*ortho*-PCBs) were identified in all samples analyzed. The calculated concentrations for the sum of PCBs was higher when using HRMS than the values given by ECD due to higher limit of quantification of ECD and to the high selectivity of high resolution mass spectrometry which allowed to identify a higher number of PCBs. The method can be further improved by including appropriate internal standard(s) in order to avoid differences between extraction efficiencies among different samples (work is in progress). In addition a quantification with the isotope dilution method would be useful to accurately determine PCBs in agree with EPA suggestion (US EPA, 1999k). However, quantification was not one of our first goals: we wanted to compare two analytical methods, i.e. GC–ECD and GC–HRMS for the determination of PCBs in soil samples.

4. Conclusions

Two different extraction methods were compared and was established that MAE is a better choice in terms of throughput considerations and lower solvent consumption. Such a microwave extraction method was then employed to explore the presence of PCBs in soil samples. Systematic differences between the results were obtained for the sum of PCBs which were generally due to some non-detected congeners in GC–ECD determinations, even employing a parallel dual-column. Such differences in the homolog and congener patterns were examined in detail by GC–HRMS and allowed to verify, in terms of total PCB concentration, that five samples were non-compliant with the Italian legislation guide value for soil. It is confirmed that GC–HRMS is a valuable tool in the national and EU policy of contaminants control as regards illegal PCBs and dioxin-like disposals in soils and environmental matrices.

Table 3
Comparison of the results obtained by employing two methods GC–HRMS and dual-column GC–ECD for the analysis of PCBs in 11 soil samples of the Basilicata (Italy)

Detector		SITE no. 1			SITE no. 2						SITE no. 3	
		S14	S50	S129	S36AR	S224	S231	S233	SP44	SPX	S479	S480
ECD	C_{tot} (ppb)	20±1	0.6±0.1	11±1	58±2	54±1	27±1	53±1	10±1	2.0±0.1	62±6*	10±5
	Congeners	180, 170, 153, 138	138	180, 170, 153	**118**, **105**, 180, 170, 52, 101, 153, 138, 128	**105**, 180, 170, 153, 138, 128	**118**, **105**, 180, 170, 153, 138	**118**, **105**, 180, 170, 52, 101, 153, 138, 128	180, 170, 153	180	180, 170, 153, 138	180, 170, 153, 138
	Dioxin-like	–	–	–	2	1	2	2	–	–	–	–
HRMS	$C_{tot.}$(ppb)	24±1	5.4±0.5	22±4	116±2*	61±4*	40±6	63.4±2*	18±1	7.1±0.6	127±2*	72±2*
	Congeners	**118**, 180, 170, **28**, 52, 101, 153, 138, 128	**118**, 180, 170, **28**, 52, 101, 153, 138	**118**, **105**, 180, 170, **28**, 52, 101, 153, 138, 128	**118**, **105**, **167**, 180, 170, **28**, 52, 101, 153, 138, 128, 156	**77**, **118**, **105**, **167**, 180, 170, **28**, 52, 101, 138, 153, 128, **156**	**77**, **118**, **123**, **114**, **105**, **126**, **167**, 180, **157**, 170, **28**, 52, 101, 153, 138, 128, **156**, 189	**118**, **105**, **167**, 180, 170, **28**, 52, 101, 153, 138, 128, **156**	**118**, 180, 170, **28**, 52, 101, 153, 138, 128	**118**, 180, 170, **28**, 52, 101, 153, 138	**118**, **123**, 180, 170, **28**, 52, 101, 153, 138, 128	**118**, 180, 170, **28**, 52, 101, 153, 138
	Dioxin-like	2	2	3	4	6	10	5	2	2	3	2

* Sample of soils in which the total amounts of PCBs were non-compliant with the Italian legislation. PCBs in boldface identify dioxin-like congeners. Each soil sample was analyzed in triplicate (n=3).

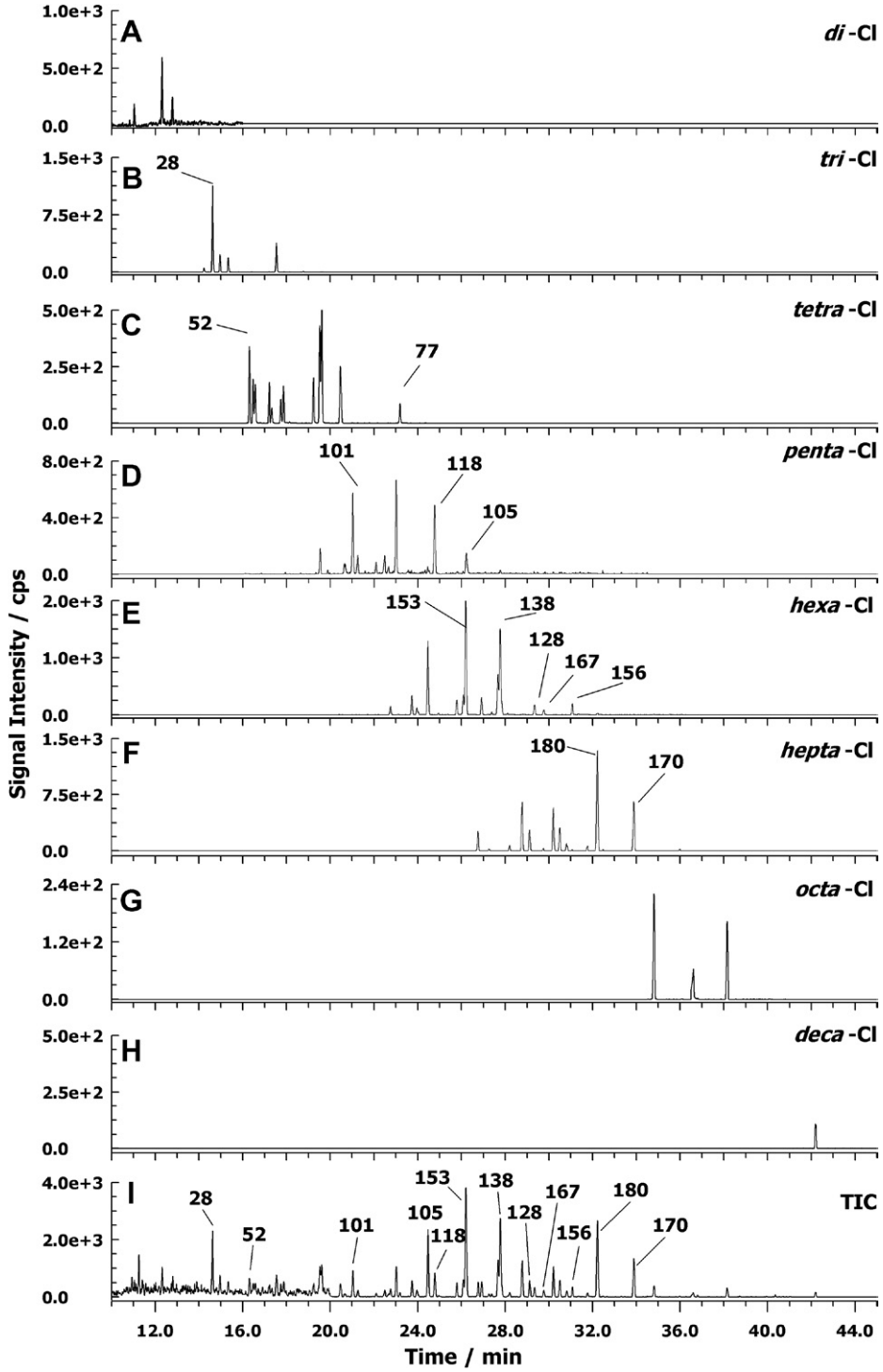

Fig. 4. Extracted ion chromatograms for the mixture of a soil sample S224 (site no. 2) registered by GC–HRMS. The top traces show the selected ion chromatograms of the intensity sum of the $M^{\bullet+}$, $[M+2]^{\bullet+}$ and $[M+4]^{\bullet+}$. Ions from isomers containing four, five and six chlorine atoms, respectively. Each peak in the selected ion chromatogram is identified by its IUPAC number. (A) *di*-Cl, (B) *tri*-Cl, (C) *tetra*-Cl, (D) *penta*-Cl, (E) *hexa*-Cl, (F) *hepta*-Cl, (G) *octa*-Cl, (H) *deca*-Cl and TIC chromatogram of the same sample. Capillary column DB-5 (5%-phenyl–95%methylpolisiloxane) 30 m × 250 μm ID × 0.25 μm.

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