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Organic contaminants in the groundwaters of a lignite-bearing basin from northern Greece

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ABSTRACT

The aim of this study is to identify potential toxic or environmentally relevant organic compounds in the aquifers of the Amynteo hydrogeological basin and to investigate a possible link of the identified organic contaminants with the Pliocene Amynteo lignites. For these purposes, 10 groundwater samples were collected from this area. A sequential liquid–liquid extraction procedure was applied and all extracts were analyzed by gas chromatography and gas chromatography–mass spectrometry (GC–MS) by means of a non-target screening approach. The results of the GC–MS analyses of the extracts are presented and discussed in this work. The identified organic compounds with a potential environmental relevance are: 2,2,4-trimethyl-1,3-pentanediol diisobutyrate, triacetine, isopropyl palminate, isopropyl myristate, tributyl-, triethyl- and trioctylphosphates, N,N-dibutyl formamide, methyl dihydrojasmonate, nonylphenols and bumetrizole. However, all these organic micropollutants can derive either by anthropogenic emissions (plasticizers, industrial pollutants, pesticides, etc.) or by contaminations from the pump and the borehole structure itself. Noteworthy, coal-derived organic molecules (such as anthracene, fluorene, pyrene, phenanthrene, etc.) have not been detected. Hence, an influence of coal deposits to the groundwater quality is considered negligible.

Keywords: Organic pollutants; Groundwaters; Liquid–liquid extraction; GC–MS; Raman; Coal; Greece

1. Introduction

Groundwater use represents 42% of the total demanded hydraulic resources in Greece including 36% in agriculture, 5% in public supply and 1% in self-supplied industries, while in some cases nearly 100% of the drinking water requirements are met from groundwater [1]. A wide range of organic contaminants are present in groundwaters, which originate from various sources (industrial, municipal, agricultural, surface water exchange, etc.). Despite the aforementioned significance of groundwaters for Greece, only limited information is published regarding the organic contamination of groundwaters [1].

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Besides, a large number of coal-bearing geological basins exist in Greece, which are exploited by opencast mining and feed nearby lignite-fired power stations. The contribution of lignite to the total electric power output of the country exceeds 60% [2]. The pumped groundwater is used either for irrigation or for the drainage of the open-pit lignite mines. However, the organic pollutants originating from aquifers within lignite deposits are accused for endemic diseases such as Balkan Endemic Nephropathy (BEN) [3,4]. Thus, there is an additional interest and environmental concern for the organic contamination assessment of these groundwaters.

The aim of the present study is to identify potential toxic or environmentally relevant organic compounds present in the aquifers of Amynteo lignite-bearing basin, Northern Greece. A possible link of the identified organic contaminants with the Pliocene Amynteo lignites, i.e. whether leaching of lignite seams transferred organic micropollutants in the groundwater, is also investigated. It should be noted that the publications regarding organic pollutants of groundwaters from Greece are scarce, and there has not been a similar study related to organic contamination in the groundwaters of this area so far.

2. Description of study area

Most Greek lignite deposits are located in the Florina–Ptolemais–Kozani basin, a large intensively exploited area, in Northern Greece. The elongated intermontane Florina–Ptolemais–Kozani basin is a NNW–SSE trending graben, which extends over a distance of 250 km from Bitola, in the Former Yugoslavian Republic of Macedonia to Servia, southeast of Kozani, Greece. Within this basin, Pliocene lignite beds alternate with marls, clays and sands. There is a great variance in the thickness of the overburden, intermediate and floor rocks as well as in the thickness of lignite seams. The average thickness of the overburden is approximately 260 m and of the lignite beds approximately 20 m [2].

The Amynteo hydrogeological basin has a total surface of 228 km^2 and belongs to the aforementioned coal-bearing basin [5,6]. Numerous wells are located in the area, some of them employed for the drainage of the Amynteo open-pit lignite mine. The pumped groundwater is mainly used for irrigation.

3. Materials and methods

About 10 groundwater samples were collected from 10 irrigation wells of the study area (Fig. 1). Sampling sites were chosen in a way to cover the whole district. Before sampling, each well was purged. Glass bottles of 1 l were used to collect each water sample, which were filled to the top so that no headspace was present. A multiparameter probe MPS-K16 by SEBA Hydrometrie was employed for the *in situ* measurements of pH, electrical conductivity (EC) and total dissolved solids (TDS). The samples were stored in glass bottles in the dark at a temperature of approximately 4°C and were transferred in a portable fridge to the Laboratories of the Institute of Geology and Geochemistry of Petroleum and Coal, RWTH University, Aachen, Germany. Prior to extraction, water samples were filtered through precleaned filters (0.45 μm pore size) in order to remove suspended particulate matter from the aqueous phase.

A Thermo Scientific DXR Raman Microscope with two laser beams, one at 780 nm and another at 532 nm, was employed for the identification of the suspended particles. The power value of the sample irradiation was ranging from 1 to 12 mW. The average spectral resolution in the Raman shift range of 100–3,000 cm^{-1} was 5 cm^{-1} (grating 400 lines mm^{-1}, spot size 2 μm). Raman images were obtained using the 50× and 100× objectives of the confocal microscope. The number of exposures and the time of exposures were ranging from 10 to 120 exposures and from 0.5 to 10 s exposure time.

A sequential liquid–liquid extraction procedure was applied to approximately 1,000 ml aliquots of the groundwater samples, dichloromethane (DCM) and dichloromethane after acidification to pH 2 with hydrochloric acid. About 50 ml of solvent were used for each extraction step. Thereafter, the organic layers were concentrated to approximately 1 ml by rotary evaporation at room temperature under reduced pressure and dried by filtration over 1 g of anhydrous granulated sodium sulphate. The analytical results of the nonpolar and polar extracts are presented in this study. Prior to Gas Chromatography (GC) and GC/MS analyses, all extracts were further concentrated down to 50 μL at room temperature under ambient pressure.

Gas chromatographic analyses were carried out on a Carlo Erba 6000 vega series two gas chromatograph, equipped with a ZB5 capillary column (30 m × 0.25 mm IDX0.25 μm film). Flow velocity of the carrier gas (hydrogen) was 25 cm s^{-1}. The GC oven was programmed from 60 to 310°C at a rate of 3°C min^{-1}, after 3 min at the initial temperature. The injection was carried out on a split/splitless injector at 310°C, splitless time was 60 s. Detection was conducted by a flame ionization detector. GC/MS analyses were carried out with a Finnigan Trace MS mass spectrometer linked to

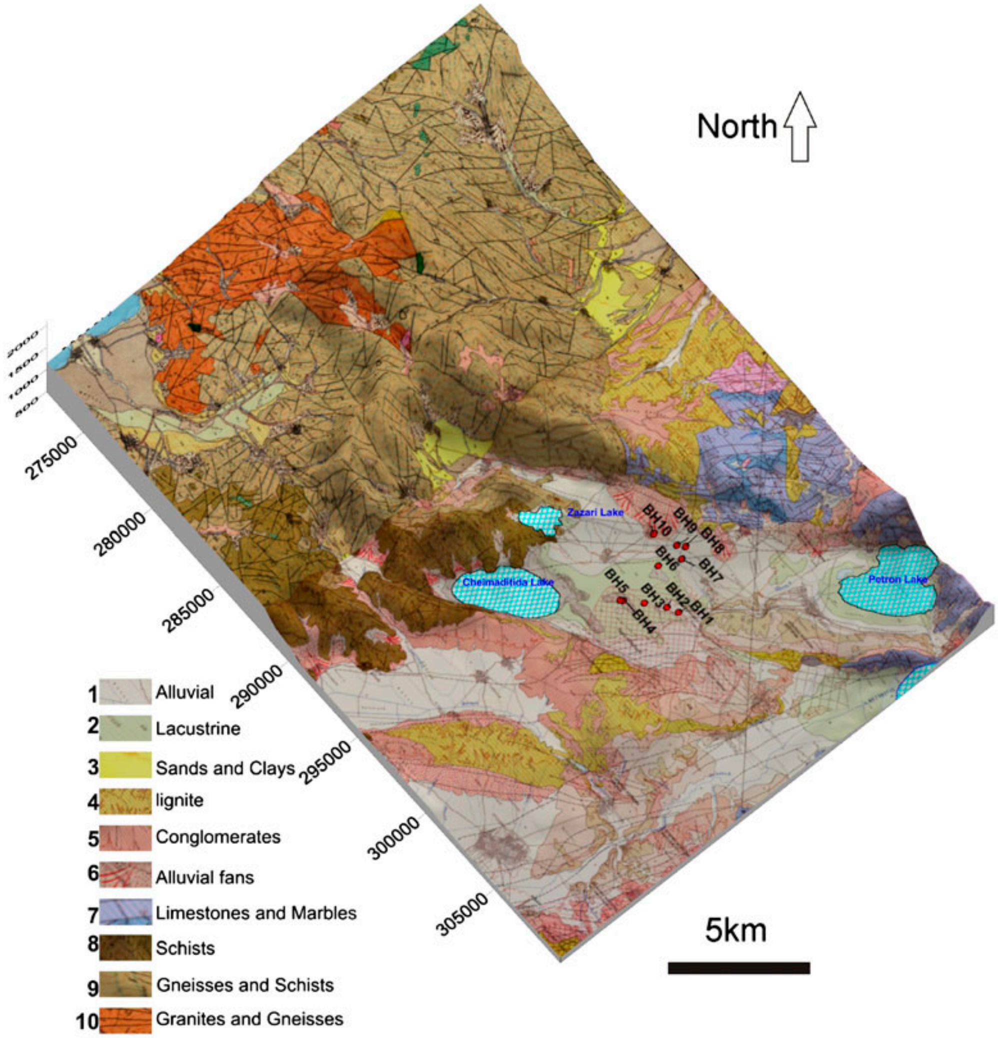

Fig. 1. Simplified geological map of the Amynteo lignite-bearing basin (Northern Greece), showing the 10 sampling sites of groundwaters [7].

a Carlo Erba HRGC 5160 gas chromatograph, employing the same conditions used for GC analysis.

4. Results and discussion

The main physicochemical characteristics of the analyzed groundwater samples are shown in Table 1. The pH values vary between 7.1 and 7.6, indicating a slightly alkaline environment. The EC ranges between 607 and 7,362 $\mu S\ cm^{-1}$ and correlates well with the TDS values, having a range between 407 and 4,932 $mg\ l^{-1}$, respectively. These values imply that the hardness of the groundwater samples varies significantly. In addition, Table 1 includes the macroscopic features of the suspended particles, which were trapped during filtering of the samples before proceeding to the organic pollutants analysis. Sand, clay and lignite particles are clearly observed, notwithstanding the presence of algae in one sample (BH4) and the almost clear waters of samples BH1 and BH2.

The presence of suspended lignite particles in the analyzed groundwaters is evident both macroscopically (Table 1) and under Raman microscope observation. The Raman spectra of a suspended lignite particle (Fig. 2) show the characteristic bands at 1,350 and 1,571 cm^{-1}. The Raman band at 1,350 cm^{-1} has been attributed to defects present in structural units and disordered carbonaceous structures, while a band at 1,571 cm^{-1} has been related to the 1,580 cm^{-1} band of graphite which has been assigned to the E2 g carbon–carbon in-plane stretching vibration [8].

Table 1
Physicochemical parameters of the ten groundwater samples (EC = electrical conductivity; TDS = total dissolved solids)

Sampling site ID	Longitude	Latitude	Water level (m)	Borehole depth (m)	EC (μS cm^{-1})	TDS (mg l^{-1})	pH	Macroscopic determination of suspended particles
BH1	21.6370	40.6468	90	160	1,469	984	7.2	Negligible
BH2	21.6309	40.6445	68	100	1,293	866	7.4	Negligible
BH3	21.6208	40.6382	5	65	7,362	4,932	7.2	Quite a few—clay and lignite
BH4	21.6124	40.6321	60	135	3,807	2,551	7.2	Quite a few—clay, algae and lignite
BH5	21.6114	40.6314	34	185	4,242	2,842	7.3	A few—clay
BH6	21.6085	40.6533	8	95	2,454	1,644	7.3	Many—sand, clay and lignite
BH7	21.6138	40.6628	19	135	910	610	7.5	A few—clay and lignite
BH8	21.6094	40.6673	17	110	625	419	7.5	Quite a few—sand and clay
BH9	21.6056	40.6648	4	85	607	407	7.6	Quite a few—sand and clay
BH10	21.5927	40.6603	7	90	1,314	880	7.1	A few—sand, clay and lignite

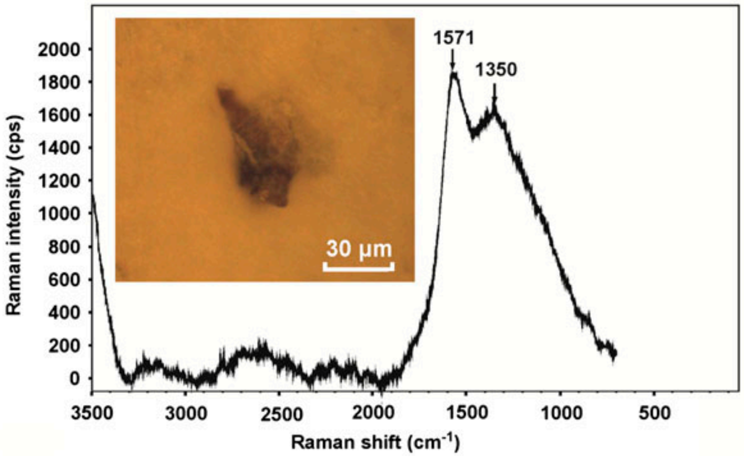

Fig. 2. Raman spectra and photomicrograph of a characteristic lignite suspended particle showing the characteristic bands at 1,350 and 1,571 cm^{-1}.

The results of the GC and GC/MS analyses of the DCM extracts are presented in Figs. 3–5. It should be noted that in our study, a non-target screening approach has been applied; hence only qualitative information are given.

The most significant identified organic compounds in terms of environmental concern are shown in Fig. 3, which is the gas chromatogram of the DCM extract of sample number 4. Very similar chromatograms were obtained by GC analyses of all other samples. The organic molecules presented in Fig. 3 are triacetin, 2,2,4-trimethyl-1,3-pentanediol diisobutyrate (TXIB), isopropyl palmitate, phthalates and squalane.

Under careful processing of the GC/MS results, some specific compounds were revealed. The assignment of the obtained mass spectra to specific molecules is shown in Figs. 4 and 5. In particular, the TXIB, tributyl phosphates and N,N-dibutyl formamide are shown in Fig. 3 and methyl dihydrojasmonate, bumetrizole and nonyl phenols are presented in Fig. 4. A synopsis of the most significant compounds found in the DCM extracts of the samples of our study is shown in Table 2.

The identified organic compounds with a potential environmental relevance are: TXIB, triacetine, isopropyl palminate, isopropyl myristate, tributyl-, triethyl- and trioctylphosphates, N,N-dibutyl formamide, methyl dihydrojasmonate, nonylphenols and bumetrizole.

TXIB is used as a plasticizer for the manufacture of PVC and vinyl plastics, and its medium toxicity to fish was indicated in previous reports [9].

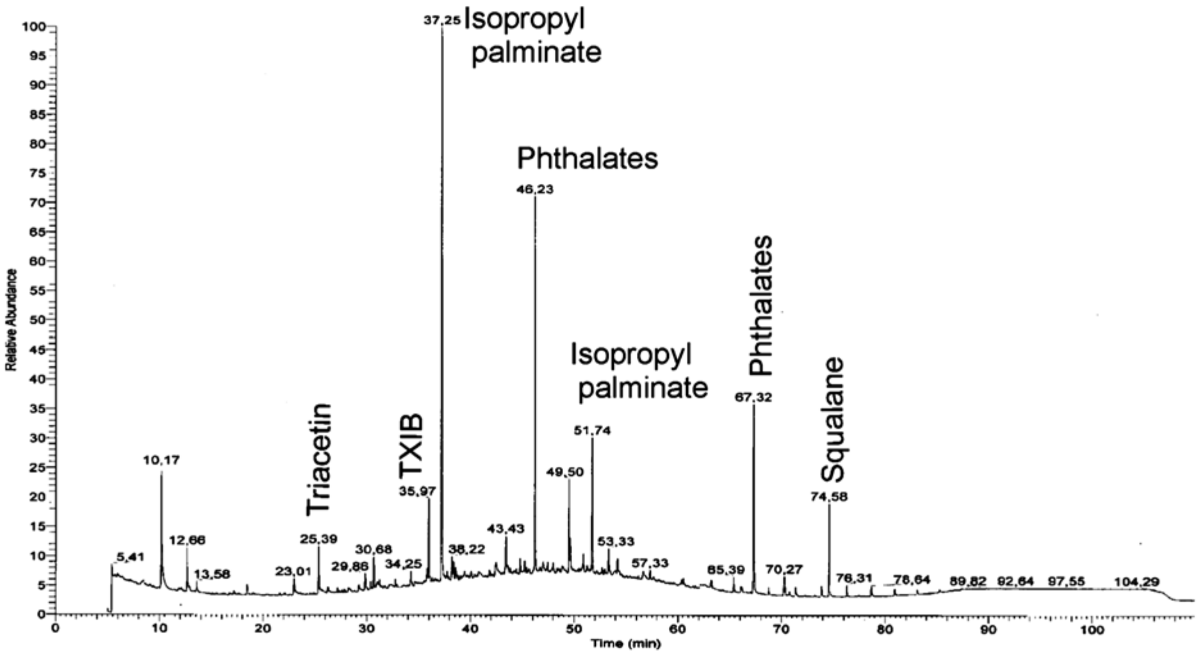

Fig. 3. Gas chromatogram of the DCM extracts of the groundwater sample number 4. Specific organic compounds are assigned on the chromatogram (Triacetin, TXIB, Isopropyl palminate, Phthalates and Squalane).

Triacetin was detected in most of the studied samples. It is a known contaminant in propellant and industrial wastewaters as well as in surface water [9]. It is mainly used as a cellulosic plasticizer in the manufacture of cigarette filters, plasticizer for laminating resins, vinylidene polymers and copolymers. It is also used as a solvent and carrier in pharmaceutical preparations, in the compounding of perfumes and flavors, as well as an ingredient for printing inks and useful reagents in textile dyeing, and the manufacture of photographic films. Therefore, it can be suggested to act as a potential indicator for these industrial processes.

Triethyl phosphate was detected in several extracts of our samples. It is used as an industrial solvent, plasticizer for resins, plastics, gums, fire-retarding agent, defoamer and raw material for insecticides [9].

Nonyl phenols, which are used as detergents, and bumetrizole, which is used in cosmetics, were detected only in sample number 9 and are indeed frequently found in groundwaters [10].

Likewise, methyl dihydrojasmonate, which is used for flavors and fragrances, and isopropyl palminate and isopropyl myristate, which are used in cosmetics and personal care products, were found in several samples of our study [11].

Phthalates, which were present in all of our samples, are very common organic compounds [12] with a versatile use (plastics etc.). Phthalates and other water-extractable organic compounds, originating from aquifers within Pliocene lignite deposits have been accused for the so-called BEN [3,13]. However, in our study, we imply that the identified phthalates have an anthropogenic origin (e.g. plastic parts within the borehole) and cannot be considered as originating from lignites.

Compounds such as cycloalkanes/alkenes, steranic structures, mono-aromatic and polyaromatic terpanes, polycyclic aromatic hydrocarbons, aromatic amines and N-, S-, and O-containing heterocyclic compounds are often related to leachates from lignite deposits [4,14–16]. Many of these compounds have attached oxygen-based functional groups (hydroxy-, phenol-, keto- and methoxy), and some of them contain heterocyclic nitrogen or amino groups, structural features that could make them nephrotoxic and carcinogenic. None of the aforementioned compounds were encountered in the DCM extracts of our samples.

In conclusion, all these organic micropollutants could have been derived either by anthropogenic emissions (plasticizers, industrial pollutants, pesticides, etc.) or could be contamination from the pump and the borehole structure itself. Noteworthy, coal-derived organic molecules have not been detected, such as anthracene, fluorene, pyrene, phenanthrene, etc. [15,16]. Hence, an influence of coal deposits to the groundwater quality is considered negligible.

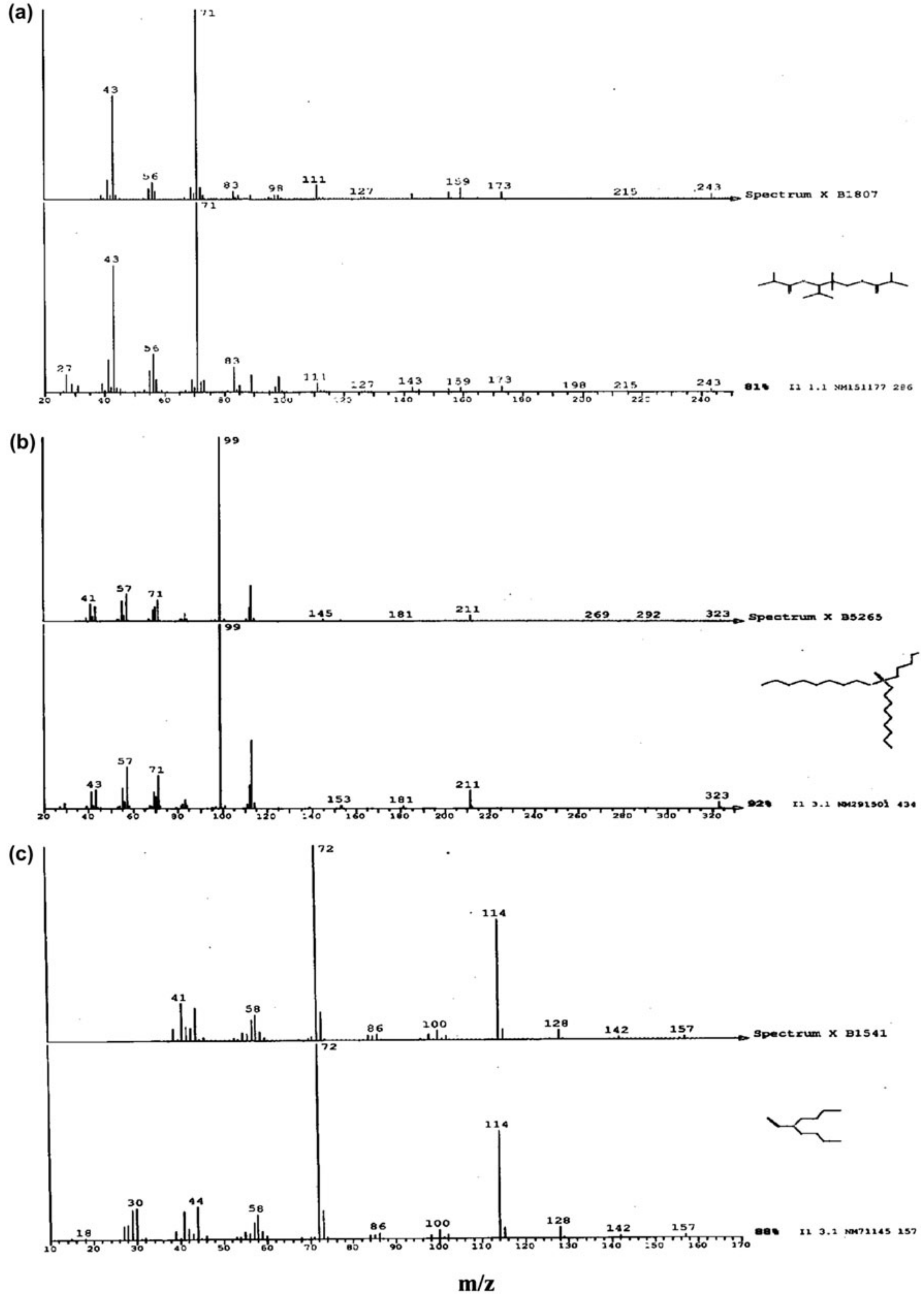

Fig. 4. Mass spectra assignment of specific organic molecules found in the GC–MS analysis of the DCM extracts of the groundwater samples: (a) TXIB, (b) Tributyl phosphate and (c) N,N-dibutyl formamide.

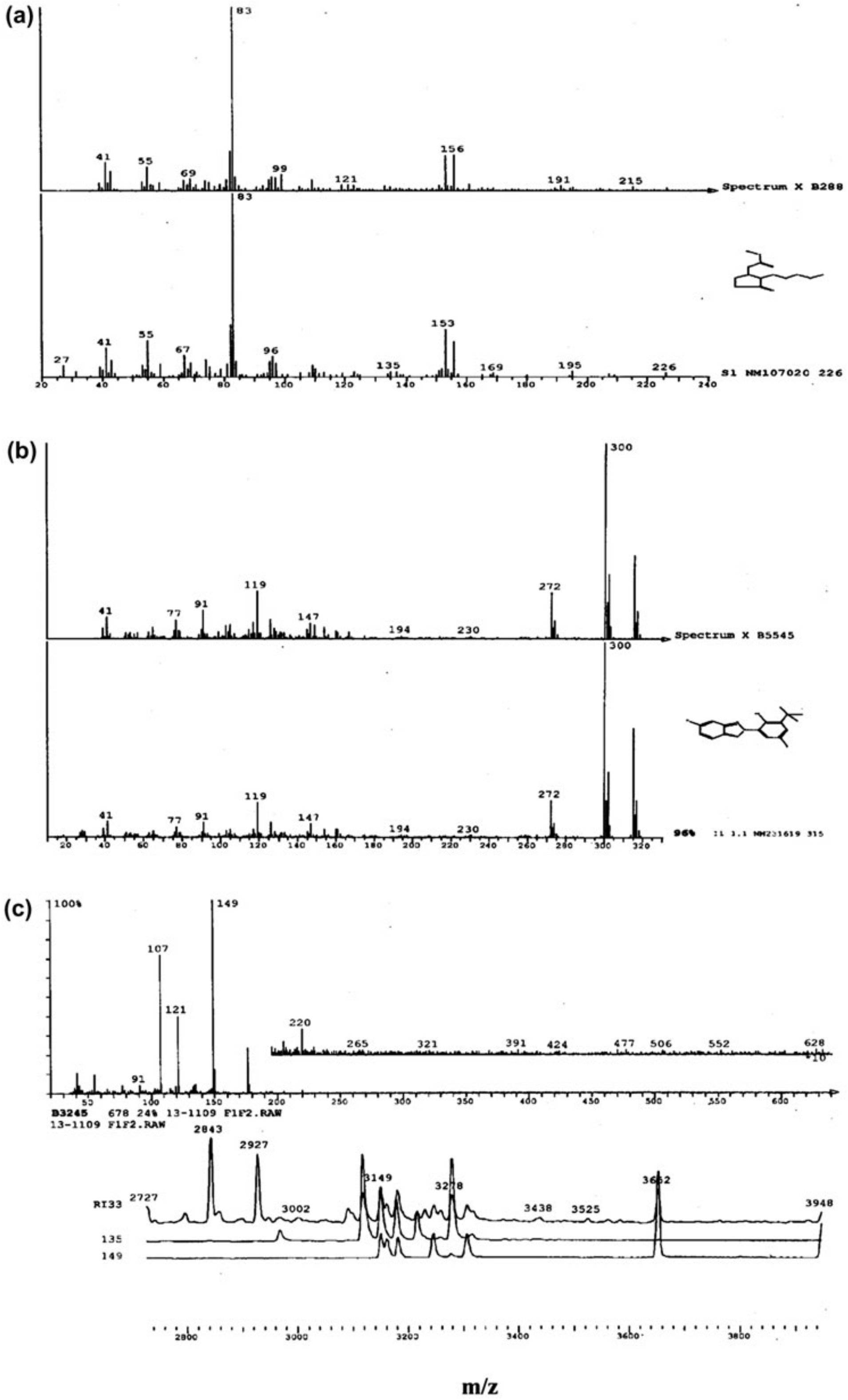

Fig. 5. Mass spectra assignment of specific organic molecules found in the GC–MS analysis of the DCM extracts of the groundwater samples: (a) Methyl dihydrojasmonate, (b) Bumetrizole and (c) Nonyl phenols.

Table 2
Abundance of organic pollutants in the groundwater samples of our study

	BH1	BH2	BH3	BH4	BH5	BH6	BH7	BH8	BH9	BH10
TXIB	+	+	+	+	+	+	+	+	+	
Triacetin			+	+		+	+		+	+
Isopropyl palminate		+	+	+	+	+	+			+
Isopropyl myristate						+				+
Tributyl-, triethyl- and trioctyl- phosphate		+			+				+	+
N,N-Dibuytl formamide			+			+	+			+
Methyl dihydro jasmonate						+				+
Nonylphenols									+	
Bumetrizole									+	

Notes: Some of the detected compounds are also known as: Bumetrizole = Uvazol 236, Tinuvin 326, Benazol PBK4, Lowitite 26, Hydroxybutylmethylphenylchlorobenzotriazole; TXIB = Propanoic acid, 2,2,4-trimethyl-1,3-pentanediol diisobutyrate, Kodaflex.

5. Conclusions

A non-target screening analysis of organic pollutants from the Amynteo coal-bearing basin is employed in the present study. The leaching of organic molecules from the lignite beds to the groundwater aquifers was investigated. The identified organic compounds with a potential environmental relevance are: TXIB, triacetine, isopropyl palminate, isopropyl myristate, tributyl-, triethyl- and trioctylphosphates, N,N-dibutyl formamide, methyl dihydrojasmonate, nonylphenols and bumetrizole. Nevertheless, all these organic contaminants could be regarded anthropogenic (originating from plasticizers, industrial pollutants, pesticides, etc.). It is remarkable that no coal-derived organic compounds have been detected; and therefore, no influence of the lignite deposits to the groundwater quality could be deduced.

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