

## ORGANIC POLLUTANTS IN THE GROUNDWATERS USED FOR IRRIGATION PURPOSE WITHIN A COAL-BEARING BASIN OF 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 ten groundwater samples were collected from this area. A sequential liquid-liquid extraction procedure was applied to approximately 1000 mL aliquots of the groundwater samples using dichloromethane as extractant. All extracts were analysed by Gas Chromatography (GC) 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 (TXIB), triacetine, isopropyl palmitate, isopropyl myristate, tributyl-, triethyl- and trioctylphosphates, N, N-dibutyl formamide, methyl dihydrojasmonate, nonylphenols and bumetizole. However, all these organic micro-pollutants 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:** organics, liquid-liquid extraction, GC-MS, Amynteo.

### Περίληψη

Σκοπός της παρούσας μελέτης είναι ο εντοπισμός τοξικών οργανικών ενώσεων στα υπόγεια ύδατα της υδρογεωλογικής λεκάνης Αμυνταίου και η έρευνα μιας πιθανής σύνδεσης αυτών των οργανικών ρυπαντών με τους λιγνίτες της περιοχής. Δέκα δείγματα υπόγειων υδάτων συλλέχθηκαν και υπέστησαν μία διαδοχική διαδικασία εκχύλισης υγρού-υγρού με διχλωρομεθάνιο. Όλα τα εκχυλίσματα αναλύθηκαν με αέρια χρωματογραφία-φασματομετρία μάζας (GC-MS). Οι οργανικές ενώσεις που προσδιορίστηκαν είναι: 2,2,4-τριμεθυλο-1,3-πεντανολόλη διισοβουτυρική (TXIB), τριακετίνη, ισοπροπυλική παλμιτική, ισοπροπυλική μυριστική, τριβουτυλ-, τριαιθυλ- και τριοκτυλ- φωσφορικά, N, N-διβουτυλ- φορμαμίδιο, μεθυλο- διυδροϊασμονικό, εννεύλοφαινόλες και μουμετριζόλη. Ωστόσο, όλες αυτές οι ενώσεις μπορεί να έχουν ανθρωπογενή προέλευση (πλαστικοποιητές, βιομηχανικοί ρύποι, παρασιτοκτόνα κλπ.)

ή να προέρχονται από επιμολύνσεις από τα δομικά μέρη της υδρογεώτρησης. Αξιοσημείωτο είναι ότι δεν προσδιορίστηκαν χαρακτηριστικές οργανικές ενώσεις που συνδέονται με γαιάνθρακες, όπως ανθρακένιο, φθορένιο, πυρένιο, φαινανθρένιο κλπ. Ως εκ τούτου, η επίδραση των λιγνιτικών κοιτασμάτων στην ποιότητα των υπόγειων υδάτων θεωρείται αμελητέα.

**Λέξεις Κλειδιά:** οργανικοί ρυπαντές, εκχύλιση υγρή-υγρής φάσης, αέρια χρωματογραφία.

## 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 (Vryzas *et al.*, 2012). A wide range of organic contaminants are present in groundwaters, which originate from many 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.

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% (Iordanidis *et al.*, 2014). 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 (Orem *et al.*, 1999, 2007). 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 this region and to investigate a possible link of the identified organic contaminants with the Pliocene Amynteo lignites, i.e. whether leaching of lignite seams transferred organic micro-pollutants in the groundwater. 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.

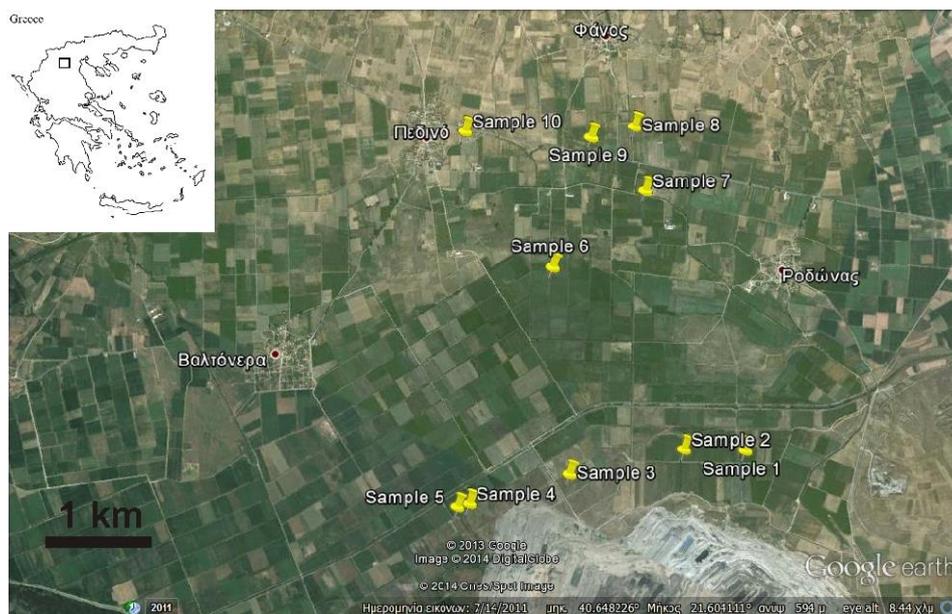
## 2. Description of study area

Most Greek lignite deposits are located in the Florina-Ptolemais-Kozani basin, a large intensively exploited area, in northern Greece. The elongated intermontaine 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 Serbia, 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 approx. 20 m (Iordanidis *et al.*, 2014).

The Amynteo hydrogeological basin has a total surface of 228 km<sup>2</sup> and belongs to the aforementioned coal-bearing basin (Gudulas, 2012). 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

Ten groundwater samples were collected from the study area (Figure 1) and were stored in glass bottles in the dark at a temperature of approximately 4 °C. The samples 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 pre-cleaned filters (0.45 µm pore size) in order to remove suspended particulate matter from the aqueous phase.



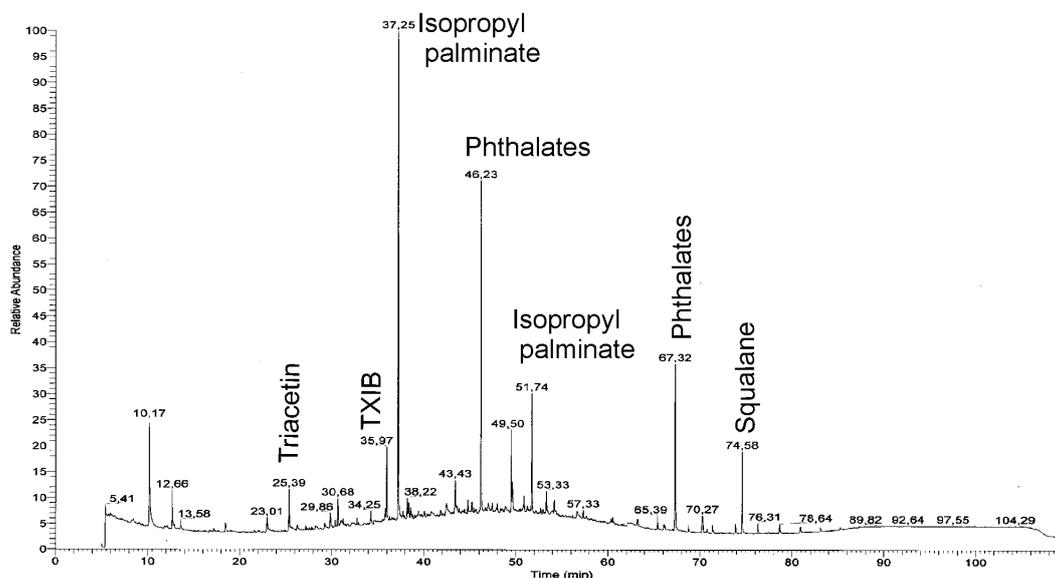
**Figure 1 - Sampling sites of groundwaters from ten wells within Amynteo coal-bearing basin of northern Greece. The Amynteo lignite mine is clearly observed at the lower bottom of the image.**

A sequential liquid-liquid extraction procedure was applied to approximately 1000 mL aliquots of the groundwater samples, dichloromethane (DCM) and dichloromethane after acidification to pH2 with hydrochloric acid. 50 mL of solvent were used for each extraction step. Thereafter, the organic layers were concentrated to approx. 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 non-polar and polar extracts are presented in this study. Prior to GC and GC/MS-analyses all extracts were further concentrated down to 50µL at room temperature under ambient pressure.

Gas chromatographic analyses were carried out on a Carlo Erba 6000 vega series 2 gas chromatograph, equipped with a ZB5 capillary column (30 mX0.25 mm IDX0.25 µm film). Flow velocity of the carrier gas (hydrogen) was 25 cm s<sup>-1</sup>. The GC oven was programmed from 60 to 310 °C at a rate of 3 °C/ min, 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 (FID). GC/MS analyses were carried out with a Finnigan Trace MS mass spectrometer linked to a Carlo Erba HRGC 5160 gas chromatograph, employing the same conditions used for GC analysis.

### 4. Results and Discussion

The results of the GC and GC/MS analyses of the DCM extracts are presented in Figures 2, 3 and 4. It should be noted that in our study a non-target screening approach has been applied, hence only qualitative information are given.



**Figure 2 - Gas chromatogram of the DCM extract of the groundwater sample No 4. Specific organic compounds are assigned on the chromatogram (Triacetin, TXIB, Isopropyl palmitate, Phthalates and Squalane).**

Some of the identified organic compounds are shown in Figure 2, which is the gas chromatogram of the DCM extract of sample No 4. Very similar chromatograms were obtained by GC analyses of all other samples. The organic molecules presented in Fig. 2 are triacetin, 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 Figures 3 and 4. In particular, the TXIB, tributyl phosphates and N, N-dibutyl formamide are shown in Figure 3 and methyl dihydrojasmonate, bumetizole and nonyl phenols are encountered in Figure 4. A synopsis of the most significant compounds found in the DCM extracts of the samples of our study is shown in Table 1.

The identified organic compounds with a potential environmental relevance are: 2, 2, 4-trimethyl-1, 3-pentanediol diisobutyrate (TXIB), triacetine, isopropyl palmitate, isopropyl myristate, tributyl-, triethyl- and trioctylphosphates, N, N-dibutyl formamide, methyl dihydrojasmonate, nonylphenols and bumetizole.

TXIB is used as a plasticizer or the manufacture of PVC and vinyl plastics and its medium toxicity to fish was indicated in previous reports (Botalova *et al.*, 2011). Triacetin detected in most of the studied samples. It is a known contaminant in propellant and industrial wastewaters as well as in surface water (Botalova *et al.*, 2011). 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 water (Botalova *et al.*, 2011). Nonyl phenols, which are used as detergents and bumetizole, which is used in cosmetics, were detected only in sample No 9 and are indeed frequently found in groundwaters (Lapworth *et al.*, 2012).

**Table 1 - Abundance of organic pollutants in the groundwater samples of the present study.**

	sample 1	sample 2	sample 3	sample 4	sample 5	sample 6	sample 7	sample 8	sample 9	sample 10
TXIB	+	+	+	+	+	+	+	+	+	
Triacetin			+	+		+	+		+	+
Isopropyl palmitate		+	+	+	+	+	+			+
Isopropyl myristate						+				+
Tributyl-, triethyl- and trioctyl- phosphate		+			+				+	+
N, N-Dibutyl formamide			+			+	+			+
Methyl dihydro jasmonate						+				+
Nonylphenols									+	
Bumetrizole									+	

*Some 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*

Likewise, methyl dihydrojasmonate, which is used for flavours and fragrances and isopropyl palmitate and isopropyl myristate, which are used in cosmetics and personal care products were found in several samples of our study (Jurado *et al.*, 2012). Phthalates are very common organic compounds (Schwarzbauer, 2006) with a versatile use (plastics etc.) and while some authors have attributed them to lignite extractable compounds (Orem *et al.*, 1999), this could not be suggested in our study.

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 (McElmurry *et al.*, 2004; Orem *et al.*, 2007; Kapusta and Stanczyk, 2011; Iordanidis *et al.*, 2012). Many of these compounds have attached oxygen-based functional groups (hydroxy-, phenol-, keto-, 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 micro-pollutants 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. (Kapusta and Stanczyk, 2011; Iordanidis *et al.*, 2012). Hence, an influence of coal deposits to the groundwater quality is considered negligible.

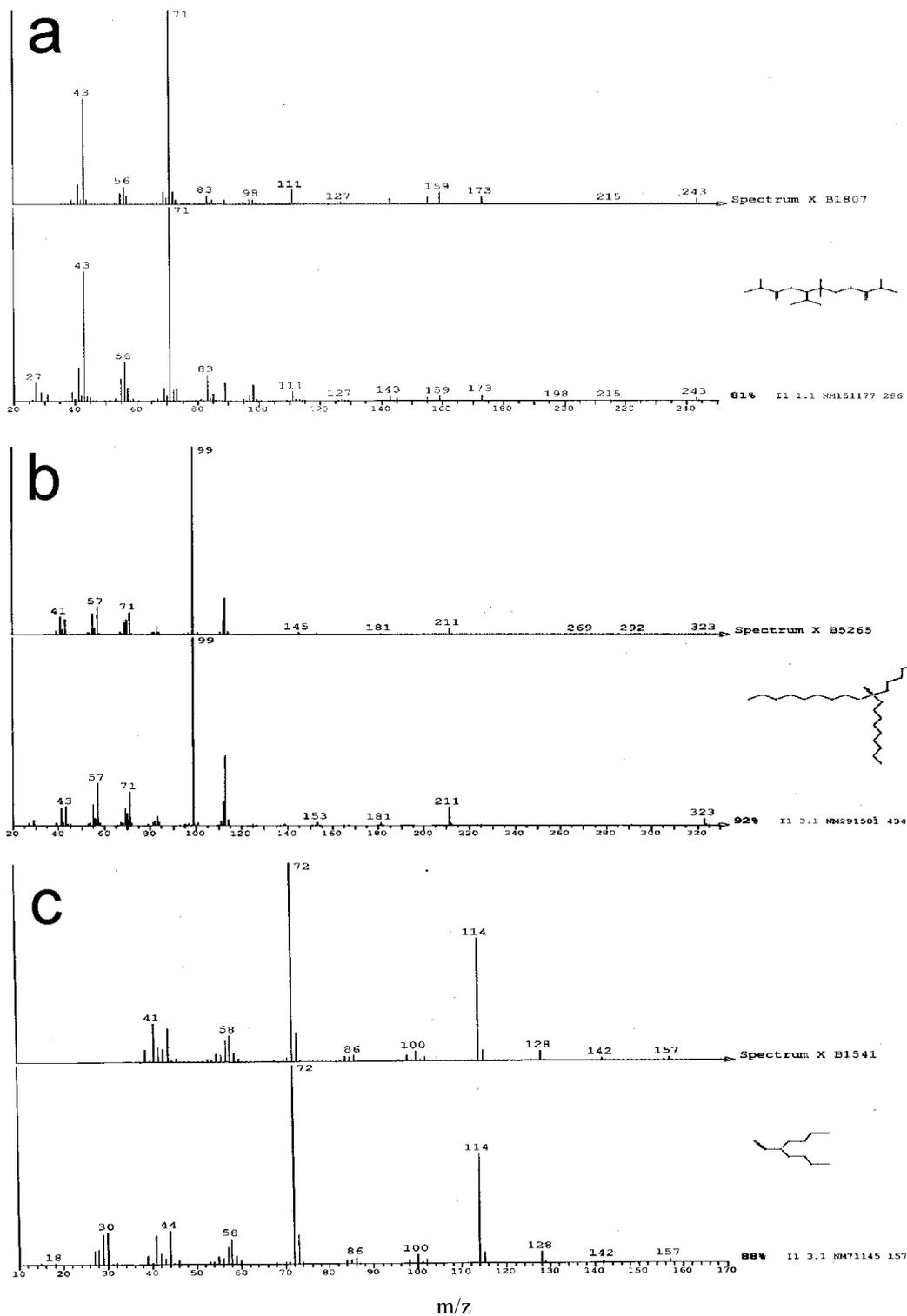
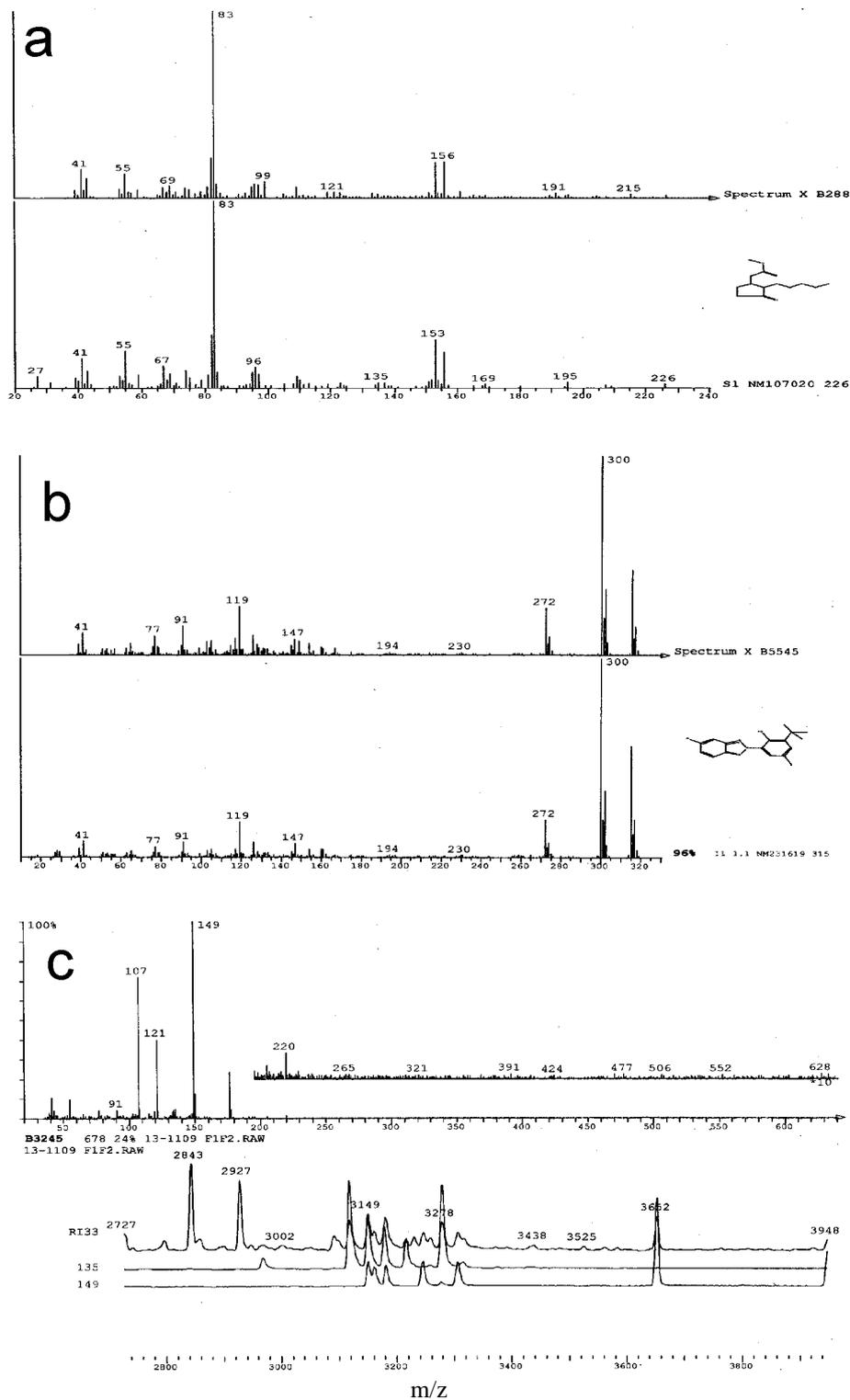


Figure 3 - Mass spectra assignment of specific organic molecules found in the GC-MS analysis of the DCM extracts of the groundwater samples: a) TXIB, b) Tributyl phosphate, c) N, N-dibutyl formamide.



**Figure 4 - 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, c) Nonyl phenols.**

## 5. Acknowledgements

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