Effect of solid waste landfill organic pollutants on groundwater in three areas of Sicily (Italy) characterized by different vulnerability

Serena Indelicato, Santino Orecchio, Giuseppe Avellone, Sergio Bellomo, Leopoldo Ceraulo, Rossella Di Leonardo, Vita Di Stefano, et al.

ONLINE FIRST

Environmental Science and Pollution Research

Employ of Multivariate Analysis and Chemometrics in Cultural Heritage and Environment Fields
Guest Editors: Giovanni Visco, Pasquale Avino

and **Original Papers**

Editor-in-Chief
Philippe Garrigues

Official Organ of the
EuCheMS Division
of Chemistry and the
Environment (EuCheMS DCE)

Springer

Springer

CrossMark

Effect of solid waste landfill organic pollutants on groundwater in three areas of Sicily (Italy) characterized by different vulnerability

Serena Indelicato[1] · Santino Orecchio[2] · Giuseppe Avellone[2] · Sergio Bellomo[3] ·
Leopoldo Ceraulo[2] · Rossella Di Leonardo[1] · Vita Di Stefano[2] · Rocco Favara[3] ·
Esterina Gagliano Candela[3] · Leonardo La Pica[3] · Sabina Morici[3] ·
Giovannella Pecoraino[3] · Antonino Pisciotta[3] · Claudio Scaletta[3] · Fabio Vita[3] ·
Salvatrice Vizzini[1,4] · David Bongiorno[2]

Abstract The aim of this study was to obtain information on the presence and levels of hazardous organic pollutants in groundwater located close to solid waste landfills. Eighty-two environmental contaminants, including 16 polycyclic aromatic hydrocarbons (PAHs), 20 volatile organic compounds (VOCs), 29 polychlorinated biphenyls (PCBs), 7 dioxins (polychlorinated dibenzo-p-dioxins, PCDDs) and 10 furans (polychlorinated dibenzofurans, PCDFs) were monitored in areas characterised by different geological environments surrounding three municipal solid waste landfills (Palermo, Siculiana and Ragusa) in Sicily (Italy) in three sampling campaigns. The total concentrations of the 16 PAHs were always below the legal threshold. Overall, the Fl/Fl + Py diagnostic ratio revealed that PAHs had a petrogenic origin. VOC levels, except for two notable exceptions near Palermo landfill, were always below the legal limit. As concerns PCB levels, several samples were found positive with levels exceeding the legal limits. It is worth noting that the % PCB distribution differs from that of commercial compositions. In parallel, some samples of groundwater containing PCDDs and PCDFs exceeding the legal threshold were also found. Among the 17 congeners monitored, the most abundant were the highest molecular weight ones.

Introduction

At present, landfill is the most employed system for waste disposal around the world (Lou et al. 2009). Wastes produce mainly gases and wastewater (Pierucci et al. 2005; Orecchio et al. 2016). The latter, well known as leachate, is generated by the interaction of water into the mass of waste during its biological degradation. Modern landfills are built with a low permeability barrier layer to contain leachate that is collected and treated. Contrarily, the older ones do not have any waterproofing liners at the bottom or, when present, they are often damaged, with potential contamination of environmental matrices and consequent damages to people and animal health (Christensen et al. 2001). Leachate contains organic and inorganic pollutants: ammonia, trace metals, humic and fulvic-like substances and persistent organic pollutants (POPs) (Orecchio et al. 2016; Christensen et al. 2001). In particular, hundreds of single chemicals from different classes have been found in landfill leachate, including pharmaceuticals, fluorinated surfactants, phthalates, personal care products, polybrominated

✉ David Bongiorno
david.bongiorno@unipa.it

[1] Dipartimento di Scienze della Terra e del Mare, Università di Palermo, via Archirafi 18, 90123 Palermo, Italy

[2] Dipartimento di Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche, Università di Palermo, Viale delle Scienze, I-90128 Palermo, Italy

[3] Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo, Via Ugo La Malfa 153, 90144 Palermo, Italy

[4] CoNISMa, Piazzale Flaminio 9, 00196 Roma, Italy

🖄 Springer

diphenyl ethers, dioxins, furans and organotin compounds (Masoner et al. 2014; Eggen et al. 2010; Öman and Junestedt 2008; Pinel-Raffaitin et al. 2008). Leachate can reach and pollute groundwater through a break on the water-proof liner if the rock lying below the landfill is quite permeable.

Groundwater contamination is a growing problem in many areas near landfills. This leads to the reduction of water for human consumption and productive purposes (e.g., agricultural, industrial, farming etc). On the other hand, no information are available regarding the composition of groundwater interested by waste disposal activities, commonly located near to towns, especially in the Mediterranean areas.

Water pollutants include a group of toxic and carcinogenic chemical compounds, such as polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). Due to their presence in all environmental matrices, their resistance to biodegradation (especially in groundwater, soils and sediments) and susceptibility to bioaccumulation and carcinogenicity (IARC 1987), these compounds are of concern for healthcare and of interest for the scientific community. These worries are also legitimated by the difficult removal of such pollutants. Some base and applied research in the field are reported (Harwell et al. 1999; Mulligan et al. 2001; Paria 2008); in particular, bioremediation (Shao et al. 2015) and the segregation capability of surfactants (Karaborni et al. 1994; Bongiorno et al. 2016; Borra 2006) seem to be a promising tool in this respect.

On the other hand, prevention and monitoring are still the most important strategy to reduce or avoid groundwater contamination. The aim of this study was thus to investigate the actual effect of solid waste landfill on chemical quality of groundwater through the analysis of the above organic pollutants. In particular, areas surrounding three solid waste landfills (Palermo, Ragusa and Siculiana) in Sicily (Italy) and characterised by medium and high vulnerability were investigated in order to evaluate the eventual contamination of groundwater adjacent to landfills. The present work relies upon anthropogenic micro pollutant determination and does not include the research of markers of organic matter decomposition.

Experimental

Study areas

The three studied areas belong to different geological and hydrogeological regions in Sicily (South Italy); a short description of each area is presented in Table 1.

Bellolampo area (Palermo)

The Bellolampo area (Fig. 1) is located in the north-west part of the *Monti di Palermo* (Palermo, Sicily), which are a segment of the Maghrebid Apennine Chain and are the result of the superposition of different tectonic units derived from Miocene deformation of calcareous dolomitic deposits (Panormide carbonate platform), of calcareous dolomitic and

Table 1 Hydrogeological characteristics of the studied areas

Hydrogeologic basin	Aquifer	Hydrogeological description	Type of aquifer	Intrinsic vulnerability/land use
Palermo Mountains	Belmonte-P.zo Mirabella Mt. Castellaccio	Mesozoic carbonate, fractured and Karst,	Unconfined and confined	Very high/mixed
	Mt. Cuccio-Mt. Gibilmesi	unconfined and confined by		
	Mt. Kumeta Mt. Mirto	Oligo-miocene clays (Flysch Numidico)		
	P.zo Vuturo-Mt. Pellegrino			
Iblei Mountains	Lentinese	Miocene-Pleistocene volcanic		
	Siracusano nord-orientale	Mesozoic carbonate, fractured and Karst,	Unconfined and confined	High/mixed
	Ragusano	unconfined and confined by Tortonian and Pliocene clays		
	Vittoria Plain	Plio-pleistocenic alluvial coastal	Multi-layered	High/intensive agricolture,
	Augusta-Priolo Plain			petrolchemical industry
Caltanissetta basin	*Siculiana*	Clays	Unconfined and confined	Medium-high/mixed
		Evaporitic limestone and gypsum		
		Pliocenic and tortonian clays		

In italic the monitored aquifers

Fig. 1 Geological map of the Palermo mountains area. 1 = debris; 2 = alluvial deposits; 3 = Calcarenites; 4 = marly limestones; 5 = Numidian Flysch; 6 = limestone; *red area* = waste landfill area; *red dots* = water sampling points
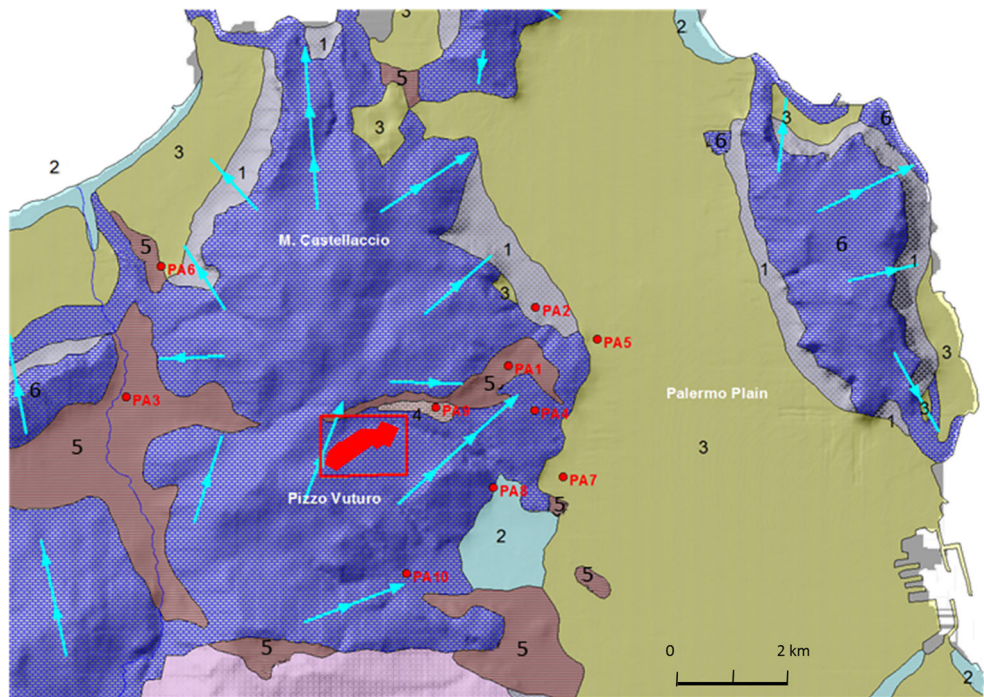
calcareous siliceous clastic terrains (Imerese Basin). The area of the waste landfill lies in the north-eastern of Pizzo Vuturo-Monte Pellegrino hydrostructure (Contino et al. 1998, 2003), constituted by dolomitic limestones with high fracture permeability and karst. For this reason, this hydrostructure is characterised almost by the absence of springs and by two main groundwater flow directions: one toward the sea at north, the other toward north-east, feeding the Palermo Plain calcarenitic aquifer. The vulnerability of this area is very high,

due to the infiltration mode (directly in karst conduits) and the high speed of the groundwater flow.

Siculiana area (Agrigento)

The waste landfill of Contrada Materano (Siculiana, Sicily) is part of the Basin of Caltanissetta, consisting mainly of clay, conglomerate and sandstone sequences named "Gela Nappe" (Fig. 2). The tectonic units of the

Fig. 2 Geological map of the Siculiana area. a = alluvial deposits; df = debris; tm = marine terraces; QSG = sands with gypsum levels (Montallegro Formation); Pi = Trubi; Ma2a = sand-gypsum; Mg = gypsum; Mc = limestones ("Calcare di base"); Md = Tripoli; Maa = Terravecchia Formation Clays; *red area* = waste landfill area; *red dots* = water sampling points
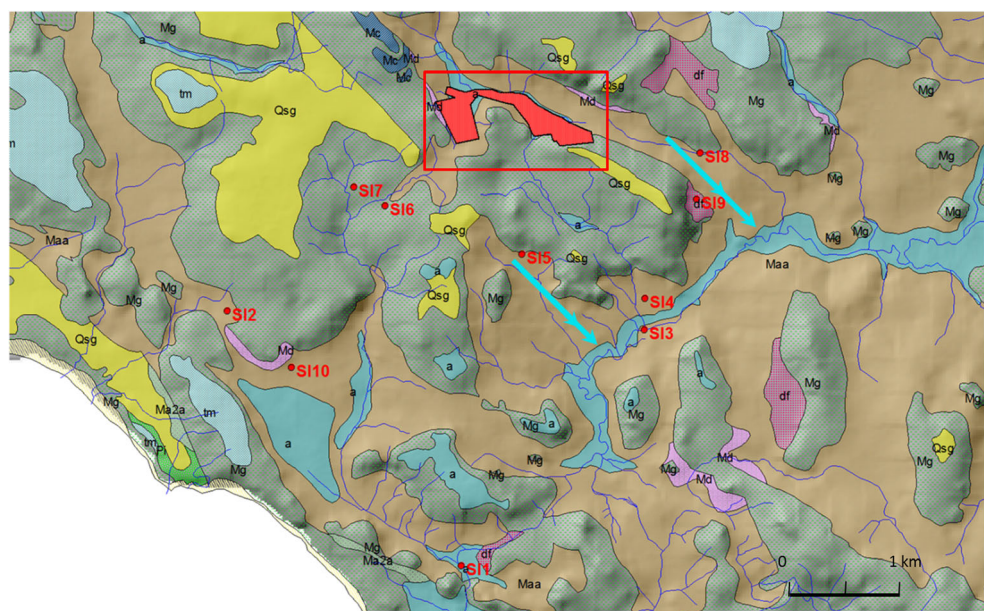
Gela Nappe consist of sequences of flysch type (Numidian Flysch) aged upper Oligocene-Miocene. These sequences are overthrusted by clayey successions (Sicilide units) of Cretaceous-Paleogene, followed by an unconformity by Tortonian conglomerate-sandy-clayey successions (Terravecchia Formation), Messinian evaporites and lower Pliocene carbonate-marly pelagic successions (Trubi).

Plio-pleistocenic clayey-sandy-calcarenitic successions unconformably overlain the Gela Nappe.

The waste landfill site is located on the clay of Terravecchia Formation. The sandy-conglomerate part of Terravecchia Formation and evaporite deposits have hydrogeological interest and are characterized by high permeability and vulnerability. The main groundwater flow direction is north-north west-south-south east.

Cava dei Modicani area (Ragusa)

The Cava dei Modicani waste landfill (Fig. 3) is located in the north-western area of the Iblei Mountains carbonate platform (Ragusa, Sicily) on the limestones and marlstones of the lower and median portion of the Irminio Member, belonging to the Ragusa Formation (upper Oligocene-Langhian). Groundwater flows in the Ragusa carbonate formation, where a first aquifer is partially confined in calcarenitic series of the Irminio Member, with an average depth between 100 and 150 m. This aquifer is followed, separated by a variable thickness of marly-clay terms, by a deeper and more productive confined aquifer in the marlstone series of the Leonardo Member of the Ragusa Formation. The permeability (from median to high) is due to fracturing and karst. For this reason, the

area presents a high degree of vulnerability. The main groundwater flow direction is NNW-SSE.
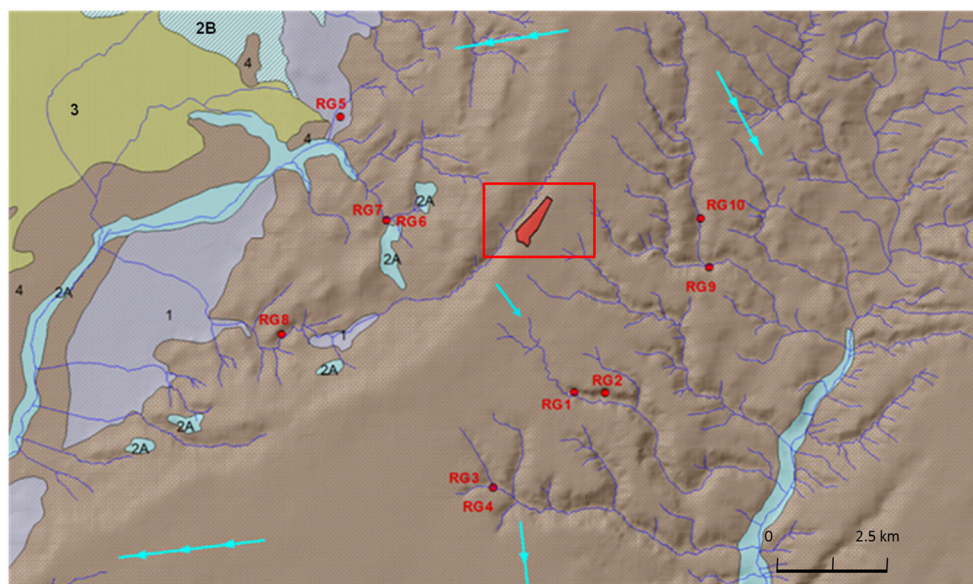
Sampling

In this study, 30 sampling stations distributed in areas close to each investigated landfill were selected on the basis of geological and hydrogeological criteria. The main characteristics of the sampling stations are summarized in Supplemental Information (Table 1SI).

Groundwater samples were collected in three sampling campaigns (1st = summer 2014, 2nd = autumn 2014, 3rd = spring 2015) during 2014 and 2015, at 3 months intervals, covering different seasons. Samples were collected from wells without water lifting device using a teflon Bailer type sampler. Spring samples were collected using sampling bottles without a further sampling device.

In the field, the chemical-physical parameters (pH, temperature, electrical conductivity and redox potential) have been acquired through a portable instrumentation. For each station, groundwater was collected using 1-L glass bottles for IPA, PCB, PCDD and PCDDF analysis, while 40-mL vials were used for VOC determination. The bottles were preventively cleaned with alkaline surfactant solutions and rinsed (in the following order) with tap water, distilled water and dichloromethane. The amber glass bottles were completely filled up to prevent air inclusion. Samples were stored at 4 °C until extraction.

For VOC analysis, HCl 6 M was added in amber 40-mL vials, in order to bring the solution's pH down to 2. Vials were then immediately plugged with PTFE/Silicone septa and preserved at 4 °C until analysis that was completed within 2 weeks. All the sampling procedures followed the guidance of EPA 441/2000 and APAT (IRSA-CNR 29/2003) protocols.

Fig. 3 Geological map of the Ragusa area. 1 = debris; 2A = alluvial deposits; 2B = lacustrine deposits; 3 = Calcarenites; 4 = marly limestones; *red area* = waste landfill area; *red dots* = water sampling points

In some cases, it was not possible to collect all the planned samples, mostly because the sampling station was dry. In the case of RG3 station, in the third campaign, an excessive water output prevented the sampling of the station.

Analyte determination

Eighty-two environmental contaminants (Tables 2SI–5SI), including 16 polycyclic aromatic hydrocarbons (PAHs), 20 volatile organic compounds (VOCs), 29 polychlorinated biphenyls (PCBs), 7 dioxins (PCDDs) and 10 furans (PCDFs) were monitored in groundwater potentially polluted by the three solid waste landfills.

The determination of such pollutants, especially when at trace concentrations, required sample manipulation and use of reliable techniques that are both sensitive and selective, as gas chromatography (GC) or liquid chromatography (LC) coupled to mass spectrometry (MS). This latter is a technique that provides both quantitative and qualitative information on several analytes after their ionization and is fairly applied in numerous scientific fields (Vogeser et al. 2007; Bongiorno et al. 2014; Nicosia et al. 2014). Determination of the analytes has been thus carried out according to the following MS-related US EPA methods: 3510 C (PAHs); 1668C (PCBs); 1613 (PCDDs and PCDFs); 5035A (VOCs). The description of analyte extraction and determination is detailed in supplemental information.

Chemicals, materials and methods

All the solvents were of HPLC grade. Anhydrous sodium sulphate (ACS reagent grade) and Alumina were purchased from Sigma-Aldrich (Germany). The alumina was activated by heating at 130 °C for 12 h. For dioxin and furan analyses, the water samples were filtered over Whatman filters (Whatman™ 1822-047 Grade GF/C; 1.2 μm pore diameter).

For PAH analysis, the internal and surrogate standards were perdeuterated compounds (Supelco, Milan), and the standard solution, containing each analysed compound at a concentration of 200 mg L^{-1}, was the standard PAH mixture (Ultra Scientific Inc., Italy).

Extraction, clean-up, labelled and syringe standards of PCBs and PCDDs and PCDFs were purchased from Cambrige Isoptope Laboratory (Tewksbury Massachussetts). The VOC standards in methanol for HPLC were from Dr. Ehrenstorfer (Germany) and later diluted in HPLC water.

Quality assurance/quality control (QA/QC)

All the vessels and flasks were cleaned before use by rinsing three times with hot HNO_3 (1%) and three times with water purified by Milli Q System. To evaluate the precision of each analysis, three replicates of the same sample were analysed for all compounds. The relative standard deviations of the replicates are in the range 5–15% which can be considered satisfactory for determinations at low concentration (ppb or sub ppb level).

To assess the reliability of the analytical procedures, several labelled standards were employed. For PAH analysis, according to US EPA Method 3510 C, the mean recoveries of surrogate standards ranged from 80 to 106%. For PCBs, PCDDs and PCDFs, the recoveries were determined according to their relative US EPA Methods. The average recovery rates were 89 ± 8, 60 ± 10 and $60 \pm 10\%$, for PCBs, PCDDs and PCDFs, respectively. The recoveries determined for VOCs, according to US EPA Method 5035A, were variable depending on the analyte and ranged from 84 to 90%.

Procedural blanks were analysed. The minimum detection limit (MDL) and the limits of quantification (LOQ) for all analysed compounds were determined as three times and ten times the noise level of the chromatogram in blank samples, respectively (IUPAC Criterion). ND (not detected) indicates a sample concentration below the LOQ.

Results and discussion

PAHs

PAHs include aromatic molecules containing fused aromatic rings and, because of their hydrophobic nature, they tend to become associated with particulates. Some PAHs, bioaccumulating in aquatic organisms, may induce the development of cancer in numerous organisms and adversely affect reproduction in other aquatic species (Al-Yakoob Saeed and Al-Hashash 1994). Accordingly, some PAHs have been included within the list of priority pollutants (EU Water Framework Directive 2000/60/EC) due to their genotoxicity and mutagenicity properties.

Total PAH concentrations in groundwater varied both among landfills in the same campaign and within landfills in different campaigns (Fig. 4).

The total concentrations of the 16 investigated compounds ($\sum PAH_{16}$), expressed as the sum of the individual concentrations, resulted quite comparable and ranged from 1.0×10^{-2} μg L^{-1} (MDL) to 7.0×10^{-2} μg L^{-1}, from 5.0×10^{-3} μg L^{-1} to 6.6×10^{-2} μg L^{-1} and from 3.0×10^{-3} μg L^{-1} to 5.2×10^{-2} μg L^{-1} at Palermo, Siculiana and Ragusa landfills, respectively (Fig. 4). In the first campaign, in the Palermo landfill, $\sum PAH_{16}$ concentrations were higher in the PA1 and PA2 stations (average 6.5×10^{-2} μg L^{-1}) than in all the other sampling stations (average 1.7×10^{-2} μg L^{-1}), while lower and similar concentrations were measured in all stations in second and spring

Fig. 4 $\sum PAH_{16}$ ($\mu g\ L^{-1}$) in the areas adjacent the three landfills in the different campaigns
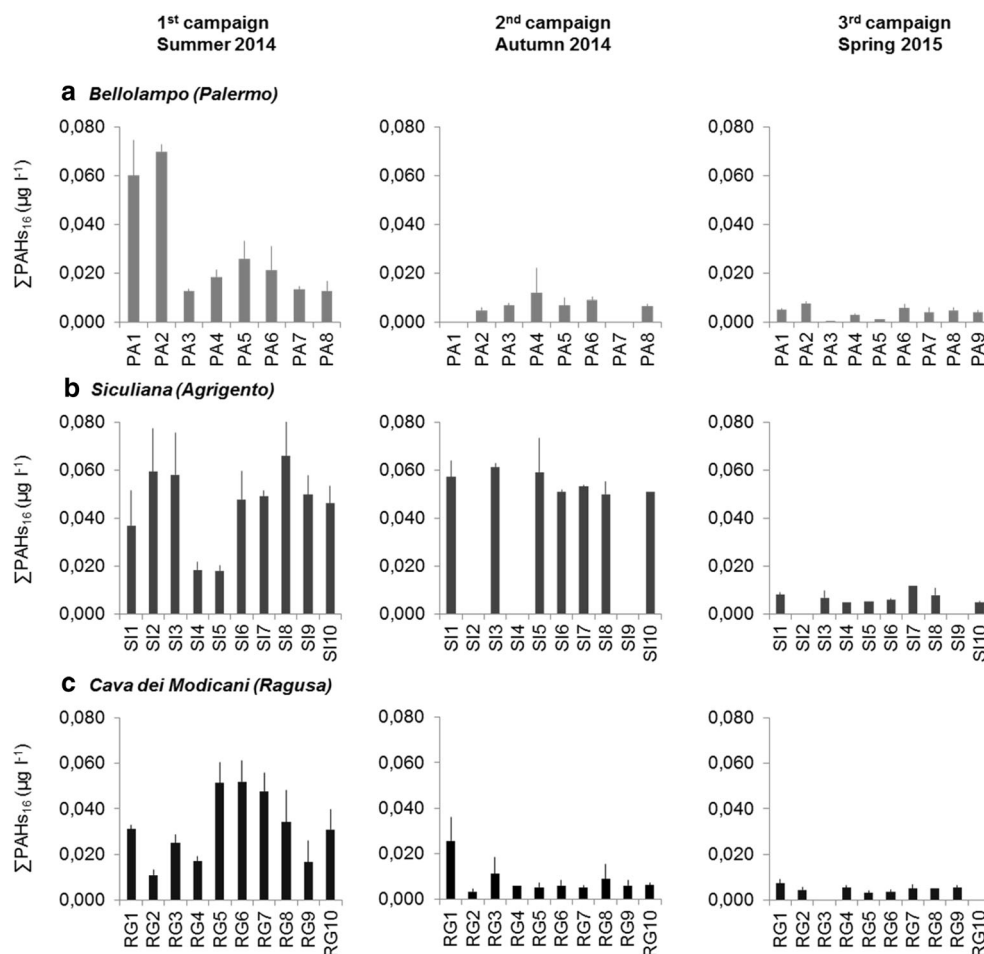
third campaigns (average 8.0×10^{-3} $\mu g\ L^{-1}$ and 5.0×10^{-3} $\mu g\ L^{-1}$, respectively). In the Siculiana landfill, in all sampling stations, during summer and autumn 2014, higher $\sum PAH_{16}$ concentrations were generally measured (average 4.5×10^{-2} $\mu g\ L^{-1}$ and 5.5×10^{-2} $\mu g\ L^{-1}$, respectively) than in spring 2015 (average 7.0×10^{-3} $\mu g\ L^{-1}$). In the Ragusa landfill, $\sum PAH_{16}$ concentrations showed a similar pattern between stations and periods to that of Palermo landfill: specifically, $\sum PAH_{16}$ concentration was higher in all stations in summer 2014 (average 3.2×10^{-2} $\mu g\ L^{-1}$) than in autumn 2014 and spring 2015 (average 8.0×10^{-2} $\mu g\ L^{-1}$ and 5.0×10^{-3} $\mu g\ L^{-1}$, respectively). This seasonal variability could be due to the typical Mediterranean climate where rainy weather is mainly in autumn-winter and dry period in summer. The effect of rain in groundwater is an increase of amount of water, which causes a dilution of pollutant concentration in spring (the opposite effect in summer). It must be also considered that some studies evidence that PAHs are strongly retained by soil even in vulnerable karst aquifers (Schwarz et al. 2011).

Generally, in terms of individual PAH composition, light compounds (2–3 rings) appeared dominant in samples from all the three landfills, accounting for 80 ± 21, 58 ± 30 and

$77 \pm 25\%$ of $\sum PAH_{16}$ concentrations at Palermo, Siculiana and Ragusa, respectively. Moreover, 4-ring compounds were the second more abundant fraction, while the most hydrophobic PAHs (5–6 rings) were rarely detected. An exception was the groundwater sampled in the station RG1 during autumn at Ragusa, where low, but detectable, concentrations of 5–6 ring PAH compounds were recorded. Therefore, the most abundant compounds in the investigated groundwater were naphthalene, phenanthrene and pyrene.

The ratio values of individual PAH are often employed as diagnostic tools to identify the origin of these compounds in environmental matrices (Budzinski et al. 1997). A Fluoranthene/fluoranthene + pirene (Fl/(Fl + Py)) ratio < 0.4 is generally characteristic of petrogenic sources (oil, diesel and coal), when between 0.4 and 0.5, it indicates liquid fossil fuel (crude oil and vehicle fuels) combustion, while a ratio over 0.5 is generally found in kerosene, grass, coal and wood combustion samples and creosote (Yunker et al. 2002).

Considering all the campaigns, Fl/(Fl + Py) mean ratio ranged from 0.12 to 0.53. In agreement with the values reported in the literature (Budzinski et al. 1997), PAHs in the investigated landfills can be considered of petrogenic, natural origin

with few exceptions (ratio between 0.4 and 0.5 in PA8, SI1, SI4 and SI5 in summer and in SI6 in spring; ratio equals to 0.504 in RG2 in summer). Considering the very low concentration of benzo[a]anthracene, chrysene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene, other isomeric ratios result inaccurate.

As aforesaid, the Water Framework Directive (Directive 2000/60/EC) identifies several PAHs as priorities or hazardous priority pollutants. For these compounds, two types of Environmental Quality Standards (EQSs) are established, with some differences for groundwater and surface ones: (i) the annual average concentration (AAC) of the compound over 1-year period and (ii) the maximum allowable concentration (MAC) of the compound measured in established points. In our case, none of the PAHs of interest exceeded the above limits in samples from all the three landfills, with the exception of station RG1 in autumn, where $\sum$(indeno[1,2,3-cd]pyrene + benzo[ghi]perylene) concentration was equal to the limit required by the WFD.

VOCs

VOCs constitute another important class of pollutants of current interest that can be transported to areas very far from their emission sources, thereby increasing their risky potential. Like other airborne pollutants, VOCs can indeed affect human health at concentrations above thresholds and the exposure to some VOCs has also been linked to cancer risks (Guo et al. 2004). VOCs are not often found in surface waters because of their high volatility, but they are the most common contaminants found in groundwater (Pecoraino et al. 2008). The acute toxicity of several volatile compounds has been well ascertained, as well as their distribution among the organs (Argo et al.

2010). However, the health risks associated with volatile compounds detected in environmental matrices from landfill and other common activities have not yet been assessed, even if in some cases a relationship between exposure to volatile anaesthetics and plasma and urine levels have been ascertained (Indelicato et al. 2014). During the processing of solid waste in landfills, VOCs are also generated as intermediate or end products (Sironi et al. 2007) and for this reason were traced in our monitoring campaigns.

Results of total and single VOC concentrations in groundwater sampled in the three landfill areas are reported in Tables 2, 3, 4.

The total concentrations of the 20 investigated VOCs are expressed as the sum of the single concentrations ($\sum VOC_{20}$). In the analysed groundwater samples ranged from 4.0×10^{-3} µg L^{-1} to 1.045 µg L^{-1}, from 1.0×10^{-2} µg L^{-1} to 3.6×10^{-2} µg L^{-1} and from 1.0×10^{-3} µg L^{-1} to 8.1×10^{-2} µg L^{-1} in Palermo, Agrigento and Ragusa landfills, respectively. Notably, during the autumnal campaign, in PA5 sampling station, chloroform was detected above (0.25 µg L^{-1}) the legal limit, which is 0.15 µg L^{-1}(Italian Legislative Decree 16 March 2009, n. 30; Ministerial Decree 8 November 2010 n. 260). In the spring campaign, elevated chloroform concentrations (0.63 and 0.96 µg L^{-1}) were found in two stations (PA5 and PA7), and also this time, above the legal limits. These findings are in good agreement with previous results (historical data of environmental monitoring collected from 2004 to 2013 by Qualified Laboratories and Agencies) that confirm the presence of chloroform (above 0.15 µg L^{-1}) in both stations since January 2011 (Mannino et al. in preparation).

In order to identify the sources of VOCs in the investigated groundwater samples, in a study (Orecchio et al. 2017), VOCs

Table 2 Total and single VOC concentration (µg L^{-1}) in the area adjacent to the Bellolampo (Palermo) landfill

Bellolampo (Palermo)

	2nd campaign AUTUMN 2014 (µg L^{-1})				3rd campaign SPRING 2015 (µg L^{-1})			
	Trichloroethylene	Tetrachloroethylene	Chloroform	Toluene	Trichloroethylene	Tetrachloroethylene	Chloroform	Trans 1,2-dichloroethylene
PA1	ND	ND	ND	ND	ND	ND	ND	6.0×10^{-3}
PA2	ND	3.0×10^{-3}	ND	4.0×10^{-2}	ND	ND	ND	8.0×10^{-3}
PA3	ND	4.0×10^{-3}	ND	9.0×10^{-3}	ND	8.0×10^{-3}	ND	ND
PA4	ND	5.5×10^{-2}	ND	2.2×10^{-2}	ND	1.1×10^{-1}	ND	5.0×10^{-2}
PA5	1.7×10^{-2}	1.6×10^{-1}	2.5×10^{-1}	1.1×10^{-2}	2.1×10^{-2}	1.2×10^{-1}	6.3×10^{-1}	ND
PA6	ND	4.0×10^{-3}	ND	1.1×10^{-2}	*	*	*	*
PA7	*	*	*	*	1.9×10^{-2}	7.0×10^{-2}	9.5×10^{-1}	ND
PA8	1.0×10^{-2}	2.8×10^{-2}	ND	7.0×10^{-3}	1.8×10^{-2}	5.8×10^{-2}	ND	ND
PA9	*	*	*	*	ND	ND	ND	ND

ND not detected indicates a sample concentration below the LOQ

Table 3 Total and single VOC concentration ($\mu g\ L^{-1}$) in the area adjacent to the Cava dei Modicani (Ragusa) landfill

Cava dei Modicani (Ragusa)

	2nd campaign AUTUMN 2014 ($\mu g\ L^{-1}$)				3rd campaign SPRING 2015 ($\mu g\ L^{-1}$)			
	Tetrachloroethylene	Toluene	Ethylbenzene	p-xilene	Trichloroethylene	Tetrachloroethylene	Chloroform	Trans 1,2-dichloroethylene
RG1	1.1×10^{-2}	6.0×10^{-3}	6.2×10^{-3}	2.0×10^{-3}	ND	1.1×10^{-3}	ND	ND
RG2	6.0×10^{-3}	6.0×10^{-3}	6.0×10^{-3}	1.1×10^{-3}	ND	1.0×10^{-2}	ND	ND
RG3	6.0×10^{-3}	5.4×10^{-3}	6.0×10^{-3}	2.0×10^{-3}	*	*	*	*
RG4	7.5×10^{-2}	3.0×10^{-3}	6.0×10^{-3}	1.0×10^{-3}	7.4×10^{-3}	7.2×10^{-2}	ND	ND
RG5	1.1×10^{-2}	8.1×10^{-3}	6.3×10^{-3}	1.8×10^{-3}	ND	1.0×10^{-2}	ND	2.1×10^{-3}
RG6	8.0×10^{-3}	7.0×10^{-3}	6.0×10^{-3}	2.0×10^{-3}	ND	8.1×10^{-3}	ND	2.0×10^{-3}
RG7	6.0×10^{-3}	7.0×10^{-3}	6.0×10^{-3}	1.6×10^{-3}	ND	6.9×10^{-3}	2.7×10^{-2}	1.9×10^{-3}
RG8	7.0×10^{-3}	4.0×10^{-3}	6.2×10^{-3}	1.6×10^{-3}	ND	7.0×10^{-3}	ND	3.0×10^{-3}
RG9	ND	4.0×10^{-3}	6.0×10^{-3}	2.2×10^{-3}	ND	ND	ND	ND
RG10	5.0×10^{-3}	1.0×10^{-2}	5.8×10^{-3}	2.1×10^{-3}	*	*	*	*

ND not detected indicates a sample concentration below the LOQ

were determined directly in the air near by the landfills and the leachate spillage points. None of the VOCs in groundwater was present in the gas phase. For a long time, chloroform has been considered only of anthropogenic origin, but, more recently, its presence in coniferous forest soil and groundwater has been demonstrated (Albers et al. 2008). Some authors (Hoekstra et al. 1998a) claimed that the detection of chloroform in groundwater, in absence of other anthropogenic contaminants, suggests that this carcinogenic compound may be formed naturally by biogeochemical processes. Several researches have suggested that enzymes (chloroperoxidase) produced by fungi could participate in biosynthesis of chlorinated organic compounds in soil (Hoekstra et al. 1998b). The current hypothesis is that enzymes explicate a chlorinating activity by forming HOCl or other oxidized chlorine species

(Hoekstra et al. 1998a). Other authors (Huber et al. 2009) have demonstrated that chloroform can also be formed abiotically, when organic matter is incubated with oxidants (Cl_2, Fe^{3+}, H_2O_2). Considering that the chloroform in groundwater of Siculiana and Ragusa is present only in trace amounts, and that in the mass of solid urban waste, there are no oxidizing conditions, the presence of $CHCl_3$, into Palermo groundwater, may be attributed to anthropogenic sources. In a previous paper (Pecoraino et al. 2008), $CHCl_3$ was found in all the vulnerable Sicilian aquifers. In particular, concentrations higher than the legal limits were found in wells located close to petrochemical industries, intensive agriculture areas and wastewater.

Among chlorinate aliphatic compounds, tetrachloroethylene was the most frequent and widespread pollutant found in

Table 4 Total and single VOC concentration ($\mu g\ L^{-1}$) in the area adjacent to the Siculiana (Agrigento) landfill

Siculiana (Agrigento)

	3rd campaign SPRING 2015 ($\mu g\ L^{1}$)				
	1,2-dichloroethane	Trichloroethylene	Chloroform	Bromodichloro-methane	Dibromodichloro-methane
SI1	4.0×10^{-3}	ND	ND	ND	ND
SI2	*	*	*	*	*
SI3	4.0×10^{-3}	ND	ND	ND	ND
SI4	ND	4.0×10^{-3}	2.1×10^{-2}	ND	1.5×10^{-2}
SI5	ND	ND	ND	1.6×10^{-2}	ND
SI6	ND	ND	1.0×10^{-2}	ND	ND
SI7	ND	ND	ND	ND	ND
SI8	ND	ND	ND	ND	ND
SI9	*	*	*	*	*
SI10	ND	ND	ND	ND	ND

ND not detected indicates a sample concentration below the LOQ

Palermo and Ragusa groundwater (60 and 94%, respectively, of the sampled waters), while it was not found in Siciliana samples. Tetrachloroethylene is a volatile, non-flammable and colourless liquid. It is one of the most important solvent worldwide and widely used by dry cleaning facilities, and its origin is exclusively anthropogenic. For this latter reason, it has been chosen as a tracer in urbanised karst aquifers (Mahler and Massei 2007). On the other hand, levels recorded during our sampling campaign show no correlation between ground water fluxes originating nearby landflills and pollutant levels.

On the basis of the observations reported for other VOC pollution cases (Spayd 1985), the landfills could be hardly considered sources for such pollutants.

Looking at Table 3 and at Fig. 1, a clear relationship between chloroform and tetrachloroethylene cannot be ascertained even for PA5 and PA7 sampling stations; indeed, levels of these two contaminants were not well correlated as reported elsewhere (Minsley 1983; Giger and Molnar-Kubica 1978) and a more detailed investigation on the high chloroform concentration documented for these stations falls outside the scope of the present publication. Low VOC levels found in Siciliana stations could be related to the clayish/alluvial nature of the soil. This impermeable matrix could make a deep penetration of the water containing these volatile pollutants difficult, indirectly favouring their evaporation.

PCBs

PCBs, commercially produced as complex mixtures since 1929 for many industrial applications, represent a class of organic pollutants of high environmental impact. They have been used in capacitors and transformers, in pigments, as coolants, plasticisers and lubricants.

These pollutants include 209 congeners (persistent organic compounds), having 1–10 chlorine atoms bound to a biphenyl molecule with different biological activity and toxicity

(Tanabe et al. 1987). They cause in animals and people metabolic disorders, disturbances to the action of the endocrine system and are suspected to be carcinogenic (Safe 1984).

PCBs enter aquatic systems by atmospheric deposition, direct and indirect discharges, and river inputs. Landfills, open burning of materials containing PCBs, waste incineration and fires are the current main sources of PCB pollution in the environment (Pandelova et al. 2006). These synthetic organic compounds are very persistent (Hutzinger et al. 1974; Kimbrough et al. 2010). Indeed, although PCBs have been banned in most countries about 45 years ago, they are still ubiquitous. The monitoring of PCBs in the Mediterranean area has begun in 1970 and has been mainly focused on sediments and marine biota (Moret et al. 2005), while only few data are available for groundwater.

Our monitoring results on PCBs total concentrations ($\sum_{29}$ PCBs) were calculated as the sum of 29 congeners (Table 4SI). The $\sum_{29}$ PCBs concentrations varied considerably both among the three landfills in the same campaign and within the same landfill in different campaigns.

In the area adjacent to the Palermo landfill (Table 5), during the first monitoring campaign, in just two stations, PA6 and PA7 PCBs were found. In PA6 station, individual PCB ranged from 1.0×10^{-5} µg L^{-1} to 4.6×10^{-3} µg L^{-1} and the $\sum_{29}$ PCBs was 9.2×10^{-3} µg L^{-1}. In PA7 station, only PCB 180 non-dioxin like was found. In the second monitoring campaign, in all the monitored stations, except PA1, PCBs were detected. Only for PA8 station, the $\sum_{29}$ PCBs exceeded the legal limit of 1×10^{-2} µg L^{-1} (Italian Legislative Decree 16 March 2009 n. 30; Ministerial Decree 8 November 2010 n. 260). In the third campaign, the only sample that overcomes the legal limit is that arising from PA9 (monitored only in third campaign).

Relative abundances of individual PCBs in most of the investigated sampling stations were fairly similar. In

Table 5 The $\sum_{29}$ PCBs concentrations in Bellolampo (Palermo) stations in the monitoring campaigns

Bellolampo (Palermo)			
	1st campaign SUMMER 2014 $\sum 29$ PCBs (µg L^1)	2nd campaign AUTUMN 2014 $\sum 29$ PCBs (µg L^1)	3rd campaign SPRING 2015 $\sum 29$ PCBs (µg L^1)
PA1	ND	*	3.9×10^{-4}
PA2	ND	2.9×10^{-3}	8.5×10^{-4}
PA3	ND	1.9×10^{-3}	2.3×10^{-3}
PA4	ND	1.1×10^{-3}	ND
PA5	ND	6.5×10^{-3}	1.4×10^{-4}
PA6	9.2×10^{-3}	7.3×10^{-3}	ND
PA7	2.5×10^{-3}	*	ND
PA8	ND	1.3×10^{-2}	8.4×10^{-3}
PA9	*	*	1.2×10^{-2}

ND not detected indicates a sample concentration below the LOQ

*Indicates a sample not monitored

Table 6 The $\sum_{29}$ PCBs concentrations in Siculiana (Agrigento) stations in the monitoring campaigns

Siculiana (Agrigento)			
	SUMMER 2014 $\sum 29$ PCBs ($\mu g\ L^{-1}$)	AUTUMN 2014 $\sum 29$ PCBs ($\mu g\ L^{-1}$)	SPRING 2015 $\sum 29$ PCBs ($\mu g\ L^{-1}$)
SI1	1.0×10^{-2}	6.0×10^{-3}	7.0×10^{-3}
SI2	1.0×10^{-2}	*	*
SI3	ND	1.5×10^{-2}	2.6×10^{-2}
SI4	1.0×10^{-2}	*	1.5×10^{-2}
SI5	1.1×10^{-2}	2.4×10^{-3}	9×10^{-5}
SI6	1.8×10^{-2}	3.6×10^{-3}	5×10^{-5}
SI7	1.2×10^{-2}	1.2×10^{-2}	ND
SI8	7.9×10^{-3}	9.0×10^{-4}	9.0×10^{-3}
SI9	4.5×10^{-2}	*	*
SI10	6.5×10^{-2}	9.0×10^{-4}	1.4×10^{-2}

ND not detected indicates a sample concentration below the LOQ

*Indicates a sample not monitored

particular, in the second campaign, PCB128 and PCB151 (hexachlorobiphenyls) were dominant in PA2, PA3 and PA4 stations, while heptachlorobiphenyls (PCB180 non-dioxin like) were the compounds present in higher percentage in stations PA5, PA6 and PA7.

In the area adjacent the Siculiana landfill (Table 6), in the first monitoring campaign, all the samples (excepted SI3) showed $\sum_{29}$ PCBs close to or above the legal limit ($1 \times 10^{-2}\ \mu g\ L^{-1}$). In the second monitoring campaign, $\sum_{29}$ PCBs ranged from $9 \times 10^{-4}\ \mu g\ L^{-1}$ to $1.46 \times 10^{-2}\ \mu g\ L^{-1}$. Also for this campaign, SI3 and SI7 stations showed $\sum_{29}$ PCBs higher than the legal limits. In the last campaign, $\sum_{29}$

PCBs varied from $5 \times 10^{-5}\ \mu g\ L^{-1}$ (SI6) to $2.6 \times 10^{-2}\ \mu g\ L^{-1}$ (SI3). Three stations (SI3, SI4 and SI10) were found not complying with PCB legal limits.

In the Ragusa landfill area (Table 7) in the first monitoring campaign, $\sum_{29}$ PCBs ranged from $2 \times 10^{-3}\ \mu g\ L^{-1}$ to $6.2 \times 10^{-2}\ \mu g\ L^{-1}$. $\sum_{29}$ PCBs exceeded the legal limit for RG2, RG4, RG7, RG8, RG10. In the second campaign, the detectable concentration of $\sum_{29}$ PCBs ranged from $5 \times 10^{-5}\ \mu g\ L^{-1}$ to $6.6 \times 10^{-2}\ \mu g\ L^{-1}$. Even in this sampling campaign, the legal limit was substantially exceeded for several stations (RG1, RG2, RG4, RG7, RG9, RG10). In the third monitoring campaign, the legal limit was never exceed being the maximum $\sum_{29}$PCBs concentration $9 \times 10^{-3}\ \mu g\ L^{-1}$. All analysed Ragusa groundwater samples, during the first and second campaigns, showed elevated proportions of PCB123 and PCB183.

In this study, special attention was accorded to a group of the seven PCBs (28, 52, 101, 118, 138, 153 and 180) and to another one comprising the 12 dioxin-like PCBs (77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169 and 189). The former, identified by the International Council for the Exploration of the Seas (ICES PCBs) as markers of the degree of contamination, contains among the most frequently detected congeners in the environment. The dioxin-like PCBs are highly toxic to humans and persist in the environment (Kimbrough et al. 2010). The average concentrations of $\sum_{ICES}$ PCBs were 2.2×10^{-3}, 6.7×10^{-3}, and $1.5 \times 10^{-2}\ \mu g\ L^{-1}$ in the Palermo, Siculiana and Ragusa landfills, respectively. These concentrations represent the 64, 67 and 22% of the total PCB content.

The percentage PCB distributions (mean of all the samplings of the same area) did not show similarity with those

Table 7 The $\sum_{29}$ PCBs concentrations in Cava dei Modicani (Ragusa) stations in the monitoring campaigns

Cava dei Modicani (Ragusa)			
	1st campaign SUMMER 2014 $\sum 29$ PCBs ($\mu g\ L^{-1}$)	2nd campaign AUTUMN 2014 $\sum 29$ PCBs ($\mu g\ L^{-1}$)	3rd campaign SPRING 2015 $\sum 29$ PCBs ($\mu g\ L^{-1}$)
RG1	6.0×10^{-3}	4.0×10^{-2}	2.8×10^{-3}
RG2	2.0×10^{-2}	2.0×10^{-2}	3.9×10^{-3}
RG3	2.0×10^{-3}	7.0×10^{-3}	*
RG4	1.9×10^{-2}	6.6×10^{-2}	7.2×10^{-3}
RG5	30×10^{-3}	3.0×10^{-3}	3.6×10^{-4}
RG 6	4.0×10^{-3}	5×10^{-5}	8.8×10^{-3}
RG7	6.2×10^{-2}	2.4×10^{-2}	ND
RG8	1.3×10^{-2}	ND	2.5×10^{-4}
RG9	6.0×10^{-3}	1.4×10^{-2}	6.0×10^{-5}
RG10	2.9×10^{-2}	1.0×10^{-2}	*

ND not detected indicates a sample concentration below the LOQ

*Indicates a sample not monitored

Table 8 Total PCDDs and PCDFs contents reported as ∑PCDDs and PCDFs and as the toxic equivalent (TEQ) concentration, in the area adjacent the Bellolampo (Palermo) landfill

Bellolampo (Palermo)

	1st campaign SUMMER 2014		2nd campaign AUTUMN 2014		3rd campaign SPRING 2015	
	∑ PCDD/PCDF ($\mu g\ L^{1}$)	∑TEQ 17 PCDD/PCDF ($\mu g\ L^{1}$)	∑ PCDD/PCDF ($\mu g\ L^{1}$)	∑TEQ 17 PCDD/PCDF ($\mu g\ L^{1}$)	∑ PCDD/PCDF ($\mu g\ L^{1}$)	∑TEQ 17 PCDD/PCDF ($\mu g\ L^{1}$)
PA1	*	*	*	*	9.2×10^{-6}	1.4×10^{-7}
PA2	ND	ND	1.4×10^{-5}	1.1×10^{-7}	1.7×10^{-5}	1.7×10^{-7}
PA3	ND	ND	2.0×10^{-6}	3.0×10^{-8}	4.3×10^{-5}	1.9×10^{-6}
PA4	ND	ND	1.0×10^{-6}	3.0×10^{-10}	8.6×10^{-7}	8.6×10^{-8}
PA5	ND	ND	1.0×10^{-6}	3.2×10^{-10}	9.0×10^{-6}	1.3×10^{-6}
PA6	*	*	3.8×10^{-6}	4.0×10^{-7}	1.0×10^{-5}	1.0×10^{-7}
PA7	*	*	*	*	ND	ND
PA8	ND	ND	2.0×10^{-6}	$3.0\ 10^{-7}$	ND	ND
PA9	*	*	*	*	ND	ND

ND indicates a sample concentration below the LOQ

*Indicates a sample not monitored

of commercial mixtures (Aroclor 1016, 1242, 1248,1254, 1260, etc.). However, taking into account the eventual occurrence of PCB dechlorination processes (Rodenburg et al. 2010), groundwater contamination from the above indicated as PCB commercial mixtures cannot be excluded.

Further, in agreement with the literature (Ruiz-Fernández et al. 2012), PCB 153, measured at detectable concentrations only in Ragusa landfill in the autumn 2014 campaign, can be also originated by pyrolysis processes such as coal, wood, waste and peat combustion.

PCDDs and PCDFs

The formation of PCDDs and PCDFs from solid waste incineration facilities or from the fires of waste landfills is a well-documented phenomenon (Ruokojarvi et al. 1995; Vassiliadou et al. 2009; Sam-Cwan et al. 2013; Pandelova et al. 2006).

According to main results reported in the so-called "European Dioxin Emission Inventory", the composition of wastes and the constructive characteristics or the age of

Table 9 Total PCDDs and PCDFs contents reported as ∑PCDDs and PCDFs and as the toxic equivalent (TEQ) concentration, in the area adjacent the Siculiana (Agrigento) landfill

Siculiana (Agrigento)

	1st campaign SUMMER 2014		2nd campaign AUTUMN 2014		3rd campaign SPRING 2015	
	∑ PCDD/PCDF ($\mu g\ L^{-1}$)	∑TEQ 17 PCDD/PCDF ($\mu g\ L^{-1}$)	∑ PCDD/PCDF ($\mu g\ L^{-1}$)	∑TEQ 17 PCDD/PCDF ($\mu g\ L^{-1}$)	∑ PCDD/PCDF ($\mu g\ L^{-1}$)	∑TEQ 17 PCDD/PCDF ($\mu g\ L^{-1}$)
SI1	ND	ND	2.0×10^{-6}	6.0×10^{-10}	ND	ND
SI2	ND	ND	*	*	*	*
SI 3	ND	ND	8.1×10^{-6}	1.1×10^{-7}	ND	ND
SI 4	ND	ND	*	*	ND	ND
SI 5	ND	ND	8.0×10^{-6}	7.3×10^{-7}	1.6×10^{-6}	ND
SI 6	ND	ND	4.0×10^{-6}	4.0×10^{-8}	ND	ND
SI 7	ND	ND	5.9×10^{-6}	5.9×10^{-7}	ND	ND
SI 8	ND	ND	5.6×10^{-7}	1.0×10^{-7}	1.2×10^{-5}	3.6×10^{-9}
SI 9	ND	ND	*	*	*	*
SI 10	ND	ND	3.0×10^{-6}	9.0×10^{-10}	ND	ND

ND not detected indicates a sample concentration below the LOQ

*Indicates a sample not monitored

Table 10 Total PCDDs/F contents reported as ∑PCDDs/Fs and as the toxic equivalent (TEQ) concentration, in the area adjacent the Cava dei Modicani (Ragusa) landfill

Cava dei Modicani (Ragusa)

	1st campaign SUMMER 2014		2nd campaign AUTUMN 2014		3rd campaign SPRING 2015	
	∑ PCDD/PCDF ($\mu g\ L^{-1}$)	∑TEQ 17 PCDD/PCDF ($\mu g\ L^{-1}$)	∑ PCDD/PCDF ($\mu g\ L^{-1}$)	∑TEQ 17 PCDD/PCDF ($\mu g\ L^{-1}$)	∑ PCDD/PCDF ($\mu g\ L^{-1}$)	∑TEQ 17 PCDD/PCDF ($\mu g\ L^{-1}$)
RG1	ND	ND	ND	ND	ND	ND
RG2	ND	ND	ND	ND	ND	ND
RG3	ND	ND	$1.2\ 10^{-5}$	$1.2\ 10^{-7}$	*	*
RG4	ND	ND	$3.3\ 10^{-5}$	$3.3\ 10^{-7}$	ND	ND
RG5	$5.2\ 10^{-6}$	$5.2\ 10^{-9}$	$5.2\ 10^{-5}$	$3.6\ 10^{-7}$	ND	ND
RG6	$1.5\ 10^{-5}$	$3.3\ 10^{-7}$	$4.9\ 10^{-5}$	$4.0\ 10^{-6}$	ND	ND
RG7	$2.5\ 10^{-5}$	$2.5\ 10^{-8}$	ND	ND	ND	ND
RG8	ND	ND	$3.9\ 10^{-6}$	$3.9\ 10^{-7}$	ND	ND
RG9	$2.0\ 10^{-5}$	$2.0\ 10^{-8}$	ND	ND	$1.0\ 10^{-5}$	$1.0\ 10^{-6}$
RG10	ND	ND	ND	ND	*	*

ND not detected indicates a sample concentration below the LOQ

*Indicates a sample not monitored

municipal waste landfills strongly influence the content of PCDDs and PCDFs in the neighbouring environment, constituting an important potential source of emission of these compounds (Quaas et al. 2000). As for PCBs, their distribution and dispersion in the environment take place through air, water, soils and sediments, and in particular, their concentration in water is related to the sewage release. Human exposure to PCDDs and PCDFs has been related with injure to the liver and immune system, as well as undesirable action on reproduction and risk of cancer. In the landfills, there are the favourable conditions to promote their formation and accumulation and the leachate represents the medium where PCDDs and PCDFs are expected with the highest concentration.

In our findings, the total PCDDs and PCDFs content varied considerably both between the different landfill areas in the same campaign and in the same area in different campaigns.

In the area adjacent the Palermo landfill, during the first monitoring campaign, PCDD and PCDF concentration was lower than the MDL ($1.0 \times 10^{-5}\ \mu g\ L^{-1}$) in all the samples. In the second campaign, the least toxic congeners were found almost exclusively (hepta- and octachlor-dioxins and furans). During the third monitoring campaign, the same congeners, accompanied by hexachlor-dioxins and furans, were found in all the stations excepted PA7, PA8 and PA 9 (Table 8).

In the autumn campaign, in three Siculiana stations (SI3, SI5 and SI7), the sum of the concentrations of the 17 congeners (∑PCDDs/Fs) was higher than the legal limit ($4.0 \times 10^{-6}\ \mu g\ L^{-1}$, Italian Legislative Decree 30/2009;

Ministerial Decree 260/2010). In the spring 2015 campaign, SI5 and SI8 stations were also found exceeding the legal threshold (Table 9).

ND indicates a sample concentration below the LOQ

*Indicates a sample not monitored

As concerns the Ragusa summer 2014 campaign, four stations (RG5, RG6, RG7 and RG9) showed the ∑PCDDs and PCDFs higher than the legal limit (Table 10). In the autumn campaign, RG3, RG4, RG5 and RG6 stations showed the highest concentrations. In the last campaign, all the samples were in accordance with the Italian law except for RG9 station.

Even though several stations showed ∑PCDDs and PCDFs exceeding the legal prescription, it must be taken into account that the intrinsic toxicity of different PCDDs PCDFs congeners is significantly different. World Health Organization (WHO) recommendation is to refer to toxicity equivalency factor (ITEF), which estimates the risk associated with exposures to complex mixtures of PCDDs and PCDFs referring the overall toxicity of the mixture to the most toxic congener, the 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD). A TEF equal to 1 has been assigned to this congener, while to the other 28 congeners, a corresponding TEF value (which generally ranges from 1.0×10^{-5} to 1) is assigned based on their toxicity relative to the toxicity of 2,3,7,8-TCDD. The toxic equivalent (TEQ) concentration is calculated by summing the multiplication of congener concentrations with congener-specific TEFs (Van den Berg et al. 2006). Many countries, including Italy (Kutz et al. 1990; Hickox and Denton 2003), use the TEQ approach for risk assessment and management. In TEQ terms, all of

the samples of the three sicilian landifills resulted well below the normative threshold limits (4.0×10^{-6} µg L^{-1}) (Van den Berg et al. 2006).

The concentrations of PCDDs and PCDFs in the landfill areas seem not to be directly influenced by waste depositions. A similar trend has been recently reported by Gworek et al. (2013).

Conclusions

In this study, a qualitative and quantitative control of groundwater in areas surrounding three Sicilian solid waste landfills was carried out. The landfills were featured by high permeability geological structures, which make them highly vulnerable. Indeed, pollution of groundwater in proximity of waste landfills might be facilitated in case of leachate loss. This risk is high in the areas of Palermo and Ragusa and medium in the Siciliana area. PAHs, VOCs, PCBs, PCDDs and PCDFs were chosen as indicators of potential contamination processes caused by landfills.

PAHs levels do not seem particularly alarming and their low concentration appears not to be related with the presence of the landfills, indeed almost all PAHs showed a petrogenic origin. Different VOC levels were recorded and may reflect the different vulnerability of the studied areas. VOC levels were lower in Siciliana (alluvial aquifer, medium vulnerability) than in Palermo and Ragusa (karst aquifer, high vulnerability). The area differences in the other pollutant levels are far less explainable by the aquifer vulnerability and are probably better linked to local pollutant charge. As regards PCBs, a certain seasonal variability was observed. In particular, their concentration tends to rise during the rainiest season, probably indicating a surface infiltration of the pollutants. A similar trend with the same seasonal variability was found for PCDD and PCDF concentrations. For these pollutants, several samples showed levels higher than the legal limits, even though in terms of TEQ, this aspect is scaled down well below any reasonable concern.

That said, even if the levels of the anthropogenic micropollutants could not be unequivocally related to landfill's pollution, they are still an evidence of the environmental impact of the human activities in the monitored areas.

References

Albers CN, Laier T, Jacobsen OS (2008) Vertical and horizontal variation in natural chloroform in two adjacent soil-profiles in a coniferous forest. Geo-Environment and Landscape Evolution 100:161–170

Al-Yakoob Saeed SN, Al-Hashash H (1994) Polycyclic aromatic hydrocarbons in fish: exposure assessment for Kuwaiti consumers after the Gulf oil spill of 1991. Environ Int 20:221–227

APAT-IRSA CNR, 2003. Metodi analitici per le acque. APAT Manuali e Linee guida 29/03.

Argo A, Bongiorno D, Bonifacio A, Pernice V, Liotta R, Indelicato S, Zerbo S, Fleres P, Ceraulo L, Procaccianti P (2010) A fatal case of a paint thinner ingestion: comparison between toxicological and histological findings. Am J Foren Med Path 31:186–191

Bongiorno D, Indelicato S, Giorgi G, Scarpella S, Turco Liveri V, Ceraulo L (2014) Electrospray ion mobility mass spectrometry of positively charged sodium bis(2 ethylhexyl)sulfosuccinate aggregates. Eur J Mass Spectrom 20:169–175

Bongiorno D, Ceraulo L, Indelicato S, Turco Liveri V, Indelicato S (2016) Charged supramolecular assemblies of surfactant molecules in gas phase. Mass Spectrom Rev 35:170–187. doi:10.1002/mas.21476

Borra JP (2006) Nucleation and aerosol processing in atmospheric pressure electrical discharges: powders production, coatings and filtration. J Phys D Appl Phys 39:R19

Budzinski H, Jones I, Bellocq J, Piérard C, Garrigues P (1997) Evaluation of sediment contamination by polycyclic aromatic hydrocarbons in the Gironde estuary. Mar Chem 58:85–97

Christensen TH, Kjeldsen P, Bjerg PL, Jensen DL, Christensen JB, Baun A, Albrechtsen HJ, Heron C (2001) Biogeochemistry of landfill leachate plumes. Appl Geochem 16:659–718

Contino A, Cusimano G, Frias Forcada A, (1998) Modello Idrogeologico dei Monti di Palermo. Proceedings 79° Congresso Nazionale della Società Geologica Italiana, Palermo 21–23 Settembre 1998, vol. A, 334–336

Contino A, Cusimano G, Di Cara A, Di Maggio C, Frias Forcada A, Hauser S (2003). Il ruolo del carsismo nella valutazione della vulnerabilità potenziale all'inquinamento degli acquiferi carbonatici dei monti di Palermo. Proceedings "Il Carsismo nell'area mediterranea", Castro Marina (Lecce), 14–15-16 settembre 2001, Dipartimento di Scienze e Tecnologie Biologiche ed Ambientali (Di.S.Te.B.A.), Università degli Studi di Lecce, vol. n. 26 supplemento di "Thalassia Salentina", 319–327

Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy OJ L 327, 22.12.2000, pp 1–73

Eggen T, Moeder M, Arukwe A (2010) Municipal landfill leachates: a significant source for new and emerging pollutants. Sci Total Environ 408:5147–5157

EPA, 2000. A Guide to the Sampling and Analysis of Waters, Wastewaters, Soils and Wastes. EPA Publication 441, 7th edition, Environment Protection Authority (Victoria).

Giger W and Molnar-Kubica E (1978) Bulletin of Enviromental Contamination and Toxicology 474–480

Guo H, Lee SC, Chan LY, Li WM (2004) Risk assessment of exposure to volatile organic compounds in different indoor environments. Environ Res 94:57–66

Gworek B, Hajduk A, Koda E, Grochowalski A, Jeske A (2013) Influence of a municipal waste landfill on the spatial distribution of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDDs/fs) in the natural environment. Chemosphere 92:753–759

Harwell JH, Sabatini DA, Knox RC (1999) Surfactants for ground water remediation. Colloids Surf A Physicochem Eng Asp 151:255–268

Hickox W, Denton J (2003) Proposal for the adoption of the Revised Toxicity Equivalency Factor (TEF WHO-97) Scheme. California Environmental Protection Agency and Office of Environmental Health Hazard Assessment. 1–37.

Hoekstra EJ, De Leer EWB, Brinkman UAT (1998a) Natural formation of chloroform and brominated trihalomethanes in soil. Environ Sci Technol 32:3724–3729

Hoekstra EJ, Verhagen FJM, Field JA, De Leer EWB, Brinkman UAT (1998b) Natural production of chloroform by fungi. Phytochemistry 49:91–97

Huber SG, Kotte K, Scholer HF, Williams J (2009) Natural abiotic formation of trihalomethanes in soil: results from laboratory studies and field samples. Environ Sci Technol 43:4934–4939

Hutzinger O, Safe S, Zitko V (1974) The chemistry of PCBs. CRC Press, Cleveland

Indelicato S, Bongiorno D, Indelicato S, Ceraulo L, Tranchina E, Avellone G, Arcadipane C, Giambartino F (2014) Halogenated anesthetics determination in urine by SPME/GC/MS and urine levels relationship evaluation with surgical theatres contamination. Journal of Analytical Methods in Chemistry 753237:1–8

IRC International Agency for Research on Cancer 1987, Monographs on the evaluation of the carcinogenic risk of chemicals to humans. In: Overall Evaluation of Carcinogenicity: an Updating of IAPC Monographs, 1–42 International Agency for Research on Cancer, Lyon, France (Suppl. 7)

Italian Legislative Decree, 2009, n. 30. "Implementation of Directive 2006/118 / EC on the protection of groundwater against pollution and deterioration. (09G0038)." Published in the Gazzetta Ufficiale no. 79 of 4 April 2009

Karaborni S, Esselink P, PAJ H, Smit B, Karthauser J, van Os NM, Zana R (1994) Simulating the self-assembly of gemini (dimeric) surfactants. Science 266:254–256

Kimbrough RD, Krouskas CA, Carson ML, Long TF, Bevan C, Tardiff RG (2010) Human uptake of persistent chemicals from contaminated soil: PCDD/fs and PCBs. Regul Toxicol Pharmacol 57:43–54

Kutz FW, Barnes DG, Bottimore DP, Greim H, Bretthauer EW (1990) The International toxicity equivalency factor (I-TEF) method of risk assessment for complex mixtures of dioxins and related compounds. Chemosphere 20:751–757

Lou Z, Zhao Y, Yuan T, Song Y, Chen H, Zhu N, Huan R (2009) Natural attenuation and characterization of contaminants composition in landfill leachate under different disposing ages. Sci Total Environ 407:3385–3391

Mahler B, Massei N (2007) Anthropogenic contaminats as tracers in an urbanizing karst aquifer. J Contam Hydrol 91:81–106

Masoner JR, Kolpin DW, Furlong ET, Cozzarelli IM, Gray JL, Schwab EA (2014) Contaminants of emerging concern in fresh leachate from landfills in the conterminous United States. Environ Sci – Processes Impacts 16:2335–2354

Ministerial Decree, 2010, n. 260. "Regulation regarding the technical criteria for the classification of surface water bodies". Published in the Gazzetta Ufficiale no.30 of 7 February 2011

Minsley B (1983) Tetrachloroethylene contamination of groundwater in Kalamazoo. American Water Works Association 75:272–279

Moret I, Gambaro A, Piazza R, Ferrari S, Manodori L (2005) Determination of Polychlorobiphenyl congeners (PCBs) in the surface water of the Venice lagoon. Mar Pollut Bull 50:167–174

Mulligan CN, Yong RN, Gibbs BF (2001) Remediation technologies for metal-contaminated soils and groundwater: an evaluation. Eng Geol 60:193–207

Nicosia A, Celi M, Vazzana M, Damiano MA, Parrinello N, D'Agostino F, Avellone G, Indelicato S, Mazzola S, Cuttitta A (2014) Profiling the physiological and molecular response to sulfonamidic drug in *Procambarus clarkii*. Comp Biochem Physiol C 166:14–23

Orecchio S, Amorello D, Barreca S, Pace A, Gambacorta S, Gulotta MG (2016) Analytical method for monitoring micro trace of landfill leachate in groundwater using fluorescence excitation–emission matrix spectroscopy. Anal Methods 8:3475–3480

Orecchio S, Fiore M, Barreca S, Vara G (2017) Volatile profiles of emissions from different activities by using canister samplers and GC/MS analysis: case studies. Int J Environ Res Public Health 14:195. doi:10.3390/ijerph14020195

Öman CB, Junestedt C (2008) Chemical characterization of landfill leachates – 400 parameters and compounds. Waste Manag 28:1876–1891

Pandelova M, Lenoir D, Schramm KW (2006) Correlation between PCDD/F. PCB and PCBs in coal/waste combustion Influence of various inhibitors Chemosphere 62:1196–1205

Paria S (2008) Surfactant-enhanced remediation of organic contaminated soil and water. Adv Colloid Interf Sci 138:24–58

Pecoraino G, Scalici L, Avellone G, Ceraulo L, Favara R, Gagliano Candela E, Provenzano MC, Scaletta C (2008) Distribution of volatile organic compounds in Sicilian groundwaters analysed by head space-solid phase micro extraction coupled with gas chromatography mass spectrometry (SPME/GC/MS). Water Res 42:3563–3577

Pierucci P, Porazzi E, Martinez MP, Adani F, Carati C, Rubino FM, Colombi A, Calcaterra E, Benfenati E (2005) Volatile organic compounds produced during the aerobic biological processing of municipal solid waste in a pilot plant. Chemosphere 59:423–430

Pinel-Raffaitin P, Amouroux D, Lehecho I, Rodriguez-Gonzalez P, Potin-Gautier M (2008) Occurrence and distribution of organotin compounds in leachates and biogases from municipal landfills. Water Res 42:987–996

Quaas U, Fermann M, Bröker G (2000) The European Dioxin Emission Inventory 2000. Stage II. vol. 1. Executive summary, North Rhine Westphalia State Environment Agency

Rodenburg LA, Du S, Fennel DE, Cavallo GJ (2010) Evidence for widespread dechlorination of polychlorinated biphenyls in groundwater, landfills and wastewater collection systems. Envirom Sci Technol 44:7534–7540

Ruiz-Fernández AC, Sprovieri M, Piazza R, Frignani M, Sanchez-Cabeza JA, Feo ML, Bellucci LG, Vecchiato M, Pérez-Bernal LH, Páez-Osuna F (2012) ^{210}Pb-derived history of PAHs and PCBs accumulation in sediments of a tropical inner lagoon (las Matas, Gulf of Mexico) near a major oil refinery. Geochim Cosmochim Acta 82:136–153

Ruokojarvi P, Ettala M, Rahkonen P, Tarhanen J, Ruuskanen J (1995) Polychlorinated dibenzo-p-dioxins and -furans (PCDDs and PCDFs) in municipal waste landfill fires. Chemosphere 30:1697–1708

Safe S (1984) Polychlorinated biphenyls (PCBs) and Polybrominated biphenyls (PBBs); biochemistry. Toxicology and Mechanism of Action CRC Crit Rev Toxicol 13:319–335

Sam-Cwan K, Geum-Ju S, Kwang-Seol S, Yun-Hwa K, Hans H (2013) Enrichment of PCDDs/PCDFs in peripheral utilities of the municipal solid waste incineration facility. Waste Manag 33:1158–1164

Schwarz K, Gocht T, Grathwohl P (2011) Transport of polycyclic aromatic hydrocarbons in highly vulnerable karst systems. Environ Pollut 159(1):133–139

Shao Y, Wang Y, Wu X, Xu X, Kong S, Tong L, Li B (2015) Biodegradation of PAHs by Acinetobacter isolated from karst groundwater in a coal-mining area. Environmental Earth Sciences 73:7479–7488

Sironi S, Capelli L, Céntola P, Del Rosso R, Il Grande M (2007) Continuous monitoring of odours from a composting plant using electronic noses. Waste Manag 27:389–397

Spayd SE (1985) Movement of volatile organics trough a fractured rock aquifer. Ground Water 23:496–502

Tanabe S, Kannan N, Subramanian A, Watanabe S, Tatsukawa R (1987) Highly ToxicCoplanar PCBs: occurrence, source, persistency and toxic implications to wildlife and humans. Evnviron Pollut 47:147–163

Van den Berg M, Birnbaum LS, Denison M, De Vito M, Farland W, Feeley M, Fiedler H, Hakansson H, Hanberg A, Haws L, Rose M, Safe S, Schrenk D, Tohyama C, Tritscher A, Tuomisto J, Tysklind M, Walker N, Peterson RE (2006) The 2005 World Health Organization re-evaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds. Toxicol Sci 93:223–241

Vassiliadou I et al (2009) Dioxin contamination after an accidental fire in the municipal landfill of Tagarades, Thessaloniki, Greece. Chemosphere 74:879–884

Vogeser M, Kobold U, Seidel D (2007) Mass spectrometry in medicine: the role of molecular analyses. Dtsch Arztebl 104:2194–2200

Yunker MB, Macdonald RW, Vingarzan RM, Regina H, Goyette D, Sylvestre S (2002) PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. Org Geochem 33:489–515