Groundwater of Sicily (Italy) close to landfill sites: quality and human health risk assessment

Authors: Fabio D'Agostino[1*], Giuseppe Avellone[2], Leopoldo Ceraulo[2], Vita Di Stefano[2], Serena Indelicato[2], Leonardo La Pica [3], Sabina Morici[3], Salvatrice Vizzini[4,5], David Bongiorno[2*]

[1] Istituto per lo studio degli impatti antropici e sostenibilità in ambiente marino, Consiglio Nazionale delle Ricerche (IAS-CNR) di Capo Granitola, 91021 Campobello di Mazara (TP), Italy

[2] Dipartimento di Scienze e Tecnologie Biologiche Chimiche e Farmaceutiche, Università degli Studi di Palermo, via Archirafi 32, 90123 Palermo, Italy

[3] Istituto Nazionale di Geofisica e Vulcanologia (INGV), sez. di Palermo, Via U. La Malfa 153, 90146 Palermo, Italy

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

[5] Consorzio Nazionale Interuniversitario per le Scienze del Mare, CoNISMa, Piazzale Flaminio 9, 00196 Roma, Italy

(*) Corresponding authors:

PhD Fabio D'Agostino, email: fabio.dagostino@cnr.it

PhD David Bongiorno, email: david.bongiorno@unipa.it

Abstract

Groundwater close to three municipal solid waste landfill sites in Sicily (southern Italy) was sampled to determine the presence of contaminants and the risk associated with its possible use as drinking and sanitary water. Polycyclic aromatic hydrocarbons, polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans, and metals were investigated. These target compounds are the most common pollutants present in leachates. Risk Assessment Guidance for Superfund (RAGS, US EPA) was used to assess human health risk. Ingestion, dermal and total exposure to these xenobiotic contaminants in groundwater were evaluated, and the cancer and non-cancer risk indexes were calculated. The results revealed that, while the groundwater complied with Italian Drinking Water Directive 30/2001, it did not comply with the "good environmental state" criteria of Directive 30/2009 at two of the three sites investigated. Worrying results were revealed by the risk assessment at the investigated sites. Cancer and non-cancer risk indexes indicated a probable risk, mainly due to dermal exposure to groundwater. These results underline the importance of assessing the risk for all possible routes, evaluating not only ingestion but also dermal exposure, especially when organic pollutants are present. The results of this study show that human health risk has probably been underestimated in the past, as dermal exposure to organic pollutants has only rarely been evaluated in the literature.

Keywords: Human Health Risk, Polycyclic Aromatic Hydrocarbons, Polychlorinated Biphenyls, Dioxin PCDD/Fs, Toxic Elements, Environmental Quality Standard

Introduction

Groundwater is an important resource for the human population. Not only most extracted groundwater is destined for agriculture and irrigation, but it is also commonly used as a source of drinking water and domestic sanitary water. By its very nature, groundwater is recharged by the infiltration of surface water and rain through the ground (Egbueri et al. 2020). During the infiltration process, ideally, most impurities and pollutant residues are absorbed by the soil particles, and the resulting purified water is generally considered of very good quality (MacDonald and Calow 2009). However, the rapid spread of solid waste landfill sites in recent decades has created major environmental and public health concerns for cities around the world (Renou et al. 2008), and not only in developing countries. The waste in (legal or illegal) landfill sites is a major source of pollutant gases and wastewater (Pierucci et al. 2005; Orecchio et al. 2016; Egbueri 2018). The latter product is known as leachate and derives from the interaction of water with the mass of waste undergoing biological degradation. Leachate is a complex matrix containing several organic and inorganic pollutants: ammonia, humic and fulvic-like substances, trace metals, and persistent organic pollutants (POPs) such as polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs) (Orecchio et al. 2016; Christensen et al. 2001; Mavakala et al. 2016; Giuliani et al. 2019; Naveen et al. 2017). In addition, hundreds of other individual chemicals, from different classes, have been found in landfill leachate, including pharmaceuticals, fluorinated surfactants, phthalates, personal care products, polybrominated diphenyl ethers, and organotin compounds (Öman and Junestedt 2008; Pinel-Raffaitin et al. 2008; Eggen et al. 2010; Masoner et al. 2014). All these contaminants may alter the groundwater state when, for example, the rock below the landfill is permeable (Rizzo et al. 2008), and the leachate spills through defects in the geomembrane liners (Grugnaletti et al. 2016; Pantini et al. 2014). This process implies that a wider population may be insidiously exposed to pollution risks. The effects of landfill leachate in surface water and groundwater have been reported (Abu Qdais 2010; Guan et al.2014) but, as described above, the

composition of leachate is variable and therefore exposure to leachate constituents, above their recommended limits, could be associated with a plethora of acute symptoms and diseases. The POPs mentioned above are a severe concern for human health due to their environmental persistence, resistance to biodegradation, and carcinogenicity (IARC, 1987). For the same reason, these compounds are of interest to the scientific community for both basic (Karaborni et al. 1994; Bongiorno et al. 2014; Borra 2006) and applied studies (Haewell et al. 1999; Mulligan et al.2001; Paria 2008) and approaches (Cataldo et al. 2018) for the removal of such pollutants from soil,sediments, and water. However, the monitoring and evaluation of risks to human health remain central to broadening awareness among populations and policymakers (D'Agostino et al. 2020; Bagnato et al. 2020) and reducing or preventing groundwater contamination and instructing about its correct usage. Several studies have been published on groundwater contamination (Halwani et al. 2020; Downs et al. 1999; Wu et al. 2015; Egbueri 2018) but comprehensive (organic/inorganic pollutants and ingestion/dermal exposure) studies to assess human health risks are far less common. In some cases, evaluations have been carried out to establish the risk associated only with drinking groundwater. In contrast, a more significant risk is connected with its use as sanitary water and depends on the dermal absorption of several organic pollutants during bathing or showering. This study aims to fill this gap in knowledge by comprehensively evaluating the risks connected with these two possible routes of exposure (dermal and ingestion).

By exploiting the available dataset, it was possible to evaluate human health risks induced by the presence of organic and inorganic micropollutants of anthropogenic origin in aquifers subjected to the environmental pressure of human activities in addition to that of nearby landfill sites.

Study sites

The present monitoring study follows a previous one (Indelicato et al. 2017) based on the evaluation of POPs in samples collected around three solid waste landfill sites (Palermo, Ragusa, and Siculiana) in Sicily (Italy) that are characterised by moderate to high vulnerability. Briefly:

i) Palermo's solid waste landfill (Fig. 1a) has a surface area of about 180000 m^2 and is located in the hydrogeological basin of the "Monti di Palermo" at 480 m above sea level (4223499 N, 349028 E, UTM ED50). This study area, consisting of dolomitic limestone, is characterised by karst phenomena and permeability due to a network of fractures that determine a high level of vulnerability. The main directions of groundwater flow are one toward the sea to the north, the other toward the north-east, feeding the Palermo Plain calcarenite aquifer.

ii) Ragusa's solid waste landfill (Fig. 1b) has a surface area of about 28000 m^2 and is located in the hydrogeological basin of the Iblei mountains at 750 m above sea level (4092993 N, 473893 E, UTM ED50). The area is geologically made up of marl and limestone from the Irminio member of the Ragusa formation (Upper Oligocene-Langhiano). The permeability (from median to high) is due to fracturing and karst. For this reason, the area presents a high degree of vulnerability. The primary groundwater flow direction is toward the south-southeast.

iii) Siculiana's solid waste landfill (Fig. 1c) has a surface area of about 85000 m^2 and is part of the Caltanissetta Basin, consisting mainly of clay, conglomerate, and sandstone sequences named "Gela Nappe". It is located 250 m above sea level (4138254 N, 357882 E, UTM ED50). This sequence is composed of tectonic units consisting of flysch-type successions (Numidian Flysch) of the upper Oligocene-Miocene age dominated by predominantly clayey series (Sicilid units) of the Cretaceous-Paleogene age. Subsequently, there are discordant conglomeratic-arenaceous-clayey sequences (Terravecchia Formation) of the Tortonian age, Messinian evaporitic sequences, and pelagic carbonatic-marly sequences ("Trubi") of the lower Pliocene age. The presence of high permeability evaporite deposits implies medium-high vulnerability. The primary groundwater flow direction is toward the south-southeast.

Materials and Methods

Sampling

115 Twenty-nine sampling stations (coordinates and altitudes in Table 1) distributed around the
116 investigated landfill sites in Palermo, Ragusa, and Siculiana (9, 10, and 10, respectively) (Fig. 1) were
117 selected based on existing wells and natural springs, and according to hydrogeological flow (Indelicato
118 et al. 2017). Seventy-six groundwater samples were collected during three campaigns carried out in
119 summer (August–September 2014), autumn (October–November 2014), and spring (April–May 2015)
120 over a period of 12 months. Figures 1a, 1b, and c shows the sampling stations on a hybrid geographic
121 map. For each site, a sampling station putatively unaffected by landfill contamination (called the blank
122 sampling station) was selected *a priori*, upstream from the local hydrological flow and, when possible,
123 at a higher altitude with respect to the nearby landfill. These "blank" stations are indicated as PA9,
124 SI10, and RG10. The sampling procedures followed the EPA 441/2000 and APAT–IRSA/CNR
125 (29/2003) protocols.
126 One-litre glass bottles were used to collect groundwater samples for the analysis of PCB, PCDD,
127 PCDDF, and PAHs. All bottles were cleaned with alkaline surfactant solution and rinsed (in the
128 following order) with tap water, distilled water, dichloromethane, and distilled water. Samples were
129 stored at 4 °C until analysis.
130 It was not possible to collect all the planned samples in each campaign. In some cases, the wells had
131 run dry (specifically during dry seasons), and, in a few other cases, excessive water output prevented
132 the planned sampling.
133 Samples for the analysis of trace metals and minor elements were collected in high-density
134 polyethylene bottles (Nalgene). These bottles had previously been rinsed with 5% nitric acid solution
135 (with Ultrapure HNO_3) in the laboratory and were then washed several times with the water to be
136 sampled before the bottle was filled in the field. Samples were filtered through 0.45 μm pore filters and
137 acidified to a pH of ~2 with ultrapure HNO_3.
138

139 Analyte Determination

140 *Organic Pollutants*

141 Sixty-two organic environmental contaminants, including 16 PAHs, 29 PCBs, 7 dioxins (PCDDs), and
142 10 furans (PCDFs) were examined in groundwater potentially polluted by the three solid waste landfill
143 sites. The determination of such pollutants was carried out using gas chromatography coupled with a
144 triple quadrupole mass spectrometer as well as reported for other scientific fields (Vogeser et al. 2007;
145 Argo et al. 2010; Lebedev 2009). Briefly, liquid/liquid extractions with dichloromethane were
146 performed according to (i) U.S. EPA Method 3510C for PAHs, (ii) U.S. EPA Method 1668C, and EPA
147 Method 1613 for PCBs, PCDDs, and PCDFs, and (iii) U.S. EPA Method 1668C for PCBs. More details
148 are reported in the supplemental information (Tables S1I, S2I, S3I).
149
150 *Inorganic Pollutants*
151 Twenty-two trace metal elements were analysed by ICP-MS (Agilent 7500ce) equipped with a
152 Micromist nebuliser, Scott double pass spray chamber, one-piece quartz torch, and Octopole Reaction
153 System (ORS) to reduce molecular interferences on the masses of investigated analytes. The US EPA
154 method 200.8 for was used trace metals determination.
155 External calibrations were performed with standard solutions by mixing and diluting multi and single
156 element work solutions (100 and 1000 mg/L, Certipur ICP Standards Merck, Italy). Routine calibration
157 was accomplished on selected isotopes for each element with 11 calibration points prepared daily in
158 10 mL polyethylene tubes by dilution with 2% nitric acid solution, treated as the blank solution.
159 Sensitivity variations were monitored and corrected by ^{108}Rh, ^{111}In, and ^{185}Re at 10 µg/L concentration,
160 as the internal standard, added directly online. More details are reported in the supplemental
161 information.
162

Quality Assurance/Quality Control

All vessels and flasks were cleaned before use by rinsing three times with hot HNO_3 (1%) and three times with 18.2 MΩ water produced by an Elix System, Integral 5 by Milli-Q (Millipore, Molsheim France). The acids used were ultra-pure grade. For organic pollutants, three replicates of the same sample were analysed to evaluate the precision of each analysis, and the relative standard deviations were in the range 5–15%. Several labelled standards were employed to assess the reliability of the analytical procedures. For PAH analysis, according to US EPA Method 3510C, the mean recoveries of surrogate standards ranged from 80 to 106%. The recovery rates for PCBs, PCDDs, and PCDFs, determined according to their appropriate US EPA Methods, were 89% ±8%, 60% ±10% and 60% ±10%, respectively. Procedural blanks were analysed. The limit of detection (LOD) for all analysed compounds was determined as three times the noise level of the chromatogram in blank samples, respectively (IUPAC Criterion).

The precision of the toxic trace element analysis was checked by running five replicates, and it was always within 15%. Data accuracy was evaluated by analysing standard reference materials (Spectrapure Standards SW1 and SW2, NIST 1643e, Environment Canada TM-61.2, and National Research Council Canada SLRS-4) at regular intervals during sample analysis. The experimental concentrations determined were in accordance with these certified values (within 10%).

Assessment of Potential Risk to Human Health

The human health risk for the resident population, within the studied sites, and nearby populations that may use contaminated groundwater as a resource for drinking and/or washing, was assessed. Two routes of contaminant exposure according to Risk Assessment Guidance for Superfund (RAGS, US EPA 2004) were taken into account:

(1) Dermal absorption (during a shower);

(2) Ingestion by drinking water.

Dermal Adsorbed Dose (DAD) and Average Daily Dose (ADD) for dermal and ingestion exposure (respectively) were calculated for each contaminant investigated. The human health risk posed by inorganic contaminants was calculated for each metal, while for organic contaminants it was calculated using the combined toxicity effect of each type of organic pollutant family, as demonstrated in Eqs. 1, 2, 3, 4. The toxicity of PAHs was calculated in terms of Toxic Equivalent Quotient (TEQ) (US-EPA 1993; Van De Berg et al. 2005; Akhbarizadeh et al. 2016) to benzo(a)pyrene_TEQ (BaPy_TEQ). The toxicity of dioxins was determined in terms of TEQ to tetrachloroparadibenzodioxin (TCDD_TEQ). The toxicity of dioxin-like polychlorinated biphenyl was determined as TEQ to TCCD (PCBdl_TEQ). The toxicity of non-dioxin-like polychlorinated biphenyl was calculated as a sum (PCBndl).

$$BaPy\_TEQ = \Sigma\, C_{PAH\_i} \times EF_{BaPy\_i} \quad (1)$$

Eq. 2 $$TCDD\_TEQ = \Sigma\, C_{Dioxin\_i} \times TEF_{TCDD\_i} \quad (2)$$

Eq. 3 $$PCBdl\_TEQ = \Sigma\, C_{PCBdl\_i} \times TEF_{TCDD\_i} \quad (3)$$

Eq. 4 $$\Sigma PCB\_ndl = \Sigma\, C_{PCBndl} \quad (4)$$

where C is the pollutant concentration in groundwater (µg/l) and TEF(i) is the Toxicity Effect Factor for the i-th compound. TEF(i) is indicated by the World Health Organization or US EPA, and they take into account the relative toxicity (ability to generate cancer or other acute and or chronic disorder) with respect to the most toxic congener of the pollutant family. The TEF is referred to benzo(a)pyrene

206 (BaPy) for PAHs, and to tetrachlorodibenzo-p-dioxin (TCDD) for both dioxins and PCBdl. Finally,
207 C_{PAH_i}, C_{Dioxin_i}, and C_{PCBdl_i} are the concentrations of each "i-th" congener's groundwater occurrence.
208
209 *Dermal Exposure Risk Assessment*
210 Assessment of Dermal Cancer Risk (DCR), Dermal Hazard Quotient (HQ_{Dermal}), and Dermal Hazard
211 Index, (HI_{Dermal}) were calculated according to the US EPA protocol, Risk Assessment Guidance for
212 Superfund (RAGS part E, US EPA 2004), following Eqs 5, 6, 7, 8, 9. The equations from 2.3 to 2.5
213 refer to each "i" contaminant.

214 Eq. 5 $$DA_{event\text{-}Water\ contact} = 2 \times FA \times Kp \times Cgw \times \sqrt{\frac{6 \times \tau\_event \times t\_event}{\pi}}$$

215 Eq. 6 $$DAD = \frac{DA_{event} \times EV \times ED \times EF \times SA}{BW \times AT}$$

216 Eq.7 $$DCR = DAD \times CSFo_{\_i}/ABS_{GI\_i}$$

Eq. 8 $HQ_{Dermal\_i} = DAD/(RfDo_{\_i} \times ABS_{GI\_i})$

Eq. 9 $HI_{Dermal} = \Sigma HQ_{Dermal\_i}$

Ingestion Risk Assessment

The Ingestion Cancer Risk (ICR), Ingestion Hazard Quotient ($HQ_{Ingestion}$), and Ingestion Hazard Index ($HI_{Ingestion}$) were calculated following Eqs 3.1 to 3.4 (US EPA 1991). Equations 10, 11, 12, 13 refer to each "i" compound.

Eq. 10 $ADD = C_{gw} \times IR \times EF \times ED/(BW \times AT)$

Eq. 11 $ICR = ADD \times CSFo$

Eq. 12 $HQ_{Ingestion\_i} = ADD/(RfDo_{\_i})$

Eq. 13 $HI_{Ingestion} = \Sigma HQ_{Ingestion\_i}$

In all the above equations: $(DA)_{event\text{-}Water\ contact}$ is Dose Adsorbed, FA is the fraction of the adsorbed water, K_p is dermal permeability, C_{gw} is groundwater pollutant concentration (ng/l or µg/l), τ_event is lag time per event (h/event), t_event is the duration of the event (h/event), EV is the frequency of the event (events/day), ED is the exposure duration (years), EF is the frequency of exposure (days/year), SA is skin surface area (cm^2), BW is body weight (kg), AT is average lifespan (years, AT=ED for non-cancer risk), CSFo is oral cancer slope factor (mg/kg/day), RfDo is oral Reference Dose (mg/kg/day), and ABS_{GI} is the fraction of contaminant absorbed in the gastrointestinal tract. IR is the Ingestion Rate. The values of these exposure parameters are shown in Table 2.

Risk Evaluation

According to the US EPA RAGS protocol, cancer risk should be assessed as follows: values less than 1E-6 indicate a no-risk level; values from 1E-6 to 1E-4 indicate an acceptable risk level; values higher than 1E-4 indicate a possible risk, in which case protective measures or actions to mitigate the risk should be taken.

241 The evaluation of risk level, using both the Hazard Quotient (HQ) and Hazard Index (HI), depends on
242 the calculated values. More specifically, there is no risk if HQ or HI values are lower than 1, a possible
243 risk if they are greater than 1, and a high risk if they are greater than 10.
244 *Uncertainty*
245 The human health risk assessment is based on a dose-response model that is subject to several
246 limitations: (i) the basic information obtained from the Integrated Risk Information System (IRIS), the
247 oral cancer slope factor (CSFo) and the Reference Dose (RfDo) are estimated values that are affected
248 by several uncertainty factors (UF). They are calculated from studies in living animals or organisms
249 other than humans, and ignore possible interactions among different xenobiotic compounds and
250 therefore, cancer and non-cancer risk levels could be overestimated; (ii) the dose calculated in this study
251 is only potential and cumulative during exposure (up to 30 years), assuming a constant contaminant
252 concentration in groundwater (determined in just one year of sampling), (iii) fixed exposure factors,
253 commonly used in risk assessment, may not adequately or accurately correspond to reality because of
254 their variability due to different life stages, life-style, and gender; (iv) some uncertainty should also be
255 attributed to the methods used to determine pollutant levels; the requirements of a method fit for
256 purpose, indicated in the Italian Directive (2001) for drinking water, set the LOD of the analytical
257 method to be six-times lower than the normative threshold limit. Taking into consideration the dermal
258 exposure risks, this LOD is probably still high.
259 Given these limitations, the risk level determined should be thought of as an estimate of groundwater's
260 dangerousness, correlated with the postulated exposure scenarios, and as an indication of which
261 contaminants could be riskier for human health.

262

263 Results

264 The TEQ values of each family of organic pollutants (Eq. 1, 2, 3, 4) and toxic metals are reported in
265 Tables 3 and 4, which show the minimum, maximum, and average TEQs for each site. Following the

266 Italian Directive on groundwater protection against pollution and deterioration, a concentration level
267 corresponding to half of its LOD (Directive 30/2009 Annex III) was attributed to each contaminant
268 below the LOD.
269 Each PAHs, PCBs, PCDD/Fs, congener and heavy metal concentrations in the groundwater samples
270 are reported in the Supplemental Information (Tables S4I, S5I, S6I, and S7I, respectively). The results
271 obtained for each pollutant at each site (Tables 2 and 3) were compared with the maximum acceptable
272 concentrations (MAC) set by Italian Directive (2009) to determine the environmental quality status
273 (EQS). Based on the average ΣPCB (sum of all PCB congeners) at Ragusa and Siculiana (1.0E-1 and
274 1.3E-2 µg/l, respectively), the EQS was considered unsatisfactory. Looking at the maximum values
275 determined at each site, Siculiana had a concentration of arsenic (11.21 µg/l) slightly higher than the
276 MAC (10.0 µg/l). The Italian Directive (2001) on drinking water does not report reference values for
277 very toxic compounds like dioxins, furans, and PCBs. Unfortunately, these dangerous pollutants were
278 found in some groundwater samples. A normative reference that can evaluate these results derives from
279 the US EPA recommendation (2018 Edition of the Drinking Water Standards and the Health Alert
280 Tables), which defines maximum contaminant levels (MCLs) for 2,3,7,8-TCDD and PCB in drinking
281 water (3.0E-5 and 5.0E-1 µg/l, respectively). The maximum and average values for all samples were
282 below the MCLs, demonstrating substantial compliance with normative levels, and the same applied
283 to metals (except for arsenic, which sometimes slightly exceeded the reference values), which were
284 well below the MCLs recommended for drinking water.
285 Comparison of the monitoring data with other groundwater monitoring results reported in the literature
286 (Table 4) highlighted that (i) the data fall within a comparable range, (ii) comprehensive monitoring to
287 extensively investigate POPs (Dioxins, PCBs, and PAHs) and toxic elements contamination is still
288 lacking, (iii) some studies have assessed human health risk: two studies were related to ingestion
289 exposure, one to PCB and the other one to cadmium (Chunfa Wu et al. 2015; Halwani et al. 2020,
290 respectively), and another two studies concerned both ingestion and dermal exposure, one to PCB and
291 the other one to metals (Downs et al. 1999; Bodrud-Doza et al. 2020, respectively).

292 A statistical approach was used to understand the possible correlation between contaminant
293 concentration detected at each sampling station, within the same site, for each sampling campaign and
294 their distances from the centre of the landfills. The Pearson correlation coefficient was calculated in
295 the matrices containing distances, the contaminant concentration (∑PAH, ∑PCB, ∑PCDD+PCDF,
296 each metal), and human health risk values. The test results did not show a strong or moderate
297 correlation, neither negative nor positive. According to these results, we can exclude the landfill as the
298 primary cause of groundwater contamination.

299 **Human Health Risk Assessment**

300 The use of groundwater, also through private wells, is widespread in the region studied. For these
301 reasons, hamlets, country houses, and farmhouses located in these areas may be at risk. In the absence
302 of routine and comprehensive monitoring of organic and inorganic pollutants in groundwater, human
303 health risk was assessed to verify the *status-quo*.

304 This evaluation was carried out using (i) the average values of each pollutant in the three surveys at
305 each station (assessment at the station level), and (ii) the average values of each pollutant in the three
306 surveys and the various stations at each site (assessment at the site level; Palermo, Ragusa, Siculiana).
307 The aims were also to evaluate the danger of any contaminant point to point and evidence of any
308 correlation with the landfill site, and to estimate the groundwater state's average quality on a site basis.
309 Geo-referenced distribution maps of the risks associated with each sampling station were created to
310 show our first objective results.

311 The study was performed using data referring to all contaminants occurring in groundwater with known
312 values of RfDo and/or CSFo. The non-cancer risks due to metal pollutant exposure were assessed
313 taking into account the following toxic elements: antimony, arsenic, barium, cadmium, chromium,
314 copper, lead, manganese, nickel, selenium, vanadium, and zinc (recognised as toxic metals), and the
315 carcinogenic risk took into account only arsenic and lead. The results of cancer and non-cancer risk
316 assessment are shown in Tables 5 and 6, respectively. The total cancer risk (ΣTCR) was calculated as
317 a cumulative additive model and based on an equal weight of evidence (WOE) of the study's

318 contaminants. In fact, PAH (as BaP_TEQ), PCBdl (as TCDD_TEQ), dioxins (as TCDD_TEQ), and
319 arsenic had the same weight of evidence (WOE) equal to 1 (EPA, 2005). ΣTCR represents the sum of
320 the risk due to dermal and ingestion exposure of all pollutants determined in groundwater.
321
322 **Cancer Risk Assessment at the Station Level**
323 The ΣTCR ranged from 6.2E-7 to 1.5E-4, from 1.5E-4 to 1.8E-2, and from 1.2E-4 to 1.1E-3 at Palermo,
324 Ragusa, and Siculiana, respectively. Furthermore, to show the risk at the station level a synthetic hot-
325 spot map of ΣTCR was elaborated per each site and showed in Figs 2a, b, c (Palermo, Ragusa,
326 Siculiana, respectively).
327 The risk map for Palermo revealed (i) no risk level at station PA9 (this station was selected as a blank
328 station *a priori*), (ii) an acceptable risk level at stations PA1 and PA7, and (iii) a possible risk at all the
329 other stations. The risk map for Ragusa showed a possible risk level for all the sampled stations, among
330 which RG9 was the most dangerous. This station experienced a high level of risk due mainly to PCBdl
331 contamination, like the groundwater at other Ragusa stations. The risk map for Siculiana showed a
332 possible risk level at all sampling stations, due mainly to PCBdl contamination and dioxin residues
333 present only at station SI7.
334
335 **Cancer Risk Assessment at the Site Level**
336 Table 6 shows the cancer risk assessment, based on the average value of each contaminant overall at
337 each site investigated, due to dermal absorption, ingestion, and total exposure. Risk values exceeding
338 1.0E-4 are reported in bold.
339 Focusing on cancer risk in relation to groundwater's hypothesised use (drinking and sanitary water)
340 close to the landfill highlighted the following points:
341 (i) The risk level at Palermo was acceptable for TCCD_TEQ and PCBdl_TEQ, both for dermal (7.0E-
342 5, 4.5E-5, respectively) and ingestion exposure (4.8E-6, 3.1E-6, respectively). The ΣTCR level was

343 higher, rated as possible, due to the sum of risk values associated with each organic contaminant
344 (ΣCRorg = 1.2E-4); in all cases, BaPy_TEQ showed no risk level.
345 (ii) The risk level at Ragusa was acceptable for TCCD_TEQ and ΣPCBndl for ingestion (4.0E-6, 1.4E-
346 6, respectively) and for dermal exposure (5.7E-5, 1.1E-5, respectively). This rose to a risk level of
347 possible taking into account the PCBdl_TEQ for ingestion and dermal exposure (1.3E-4, 1.8E-3,
348 respectively); the risk level was considered acceptable for TCCD_TEQ and ΣPCBndl (6.1E-5, 1.2E-5,
349 respectively) for total exposure, and possible for PCBdl_TEQ for total exposure (2.0E-3); in all cases,
350 BaPy_Teq showed no risk level.
351 (iii) The risk level at Siculiana was acceptable for TCCD_TEQ and PCBdl_TEQ for ingestion exposure
352 (5.9E-6, 1.3E-5, respectively); the risk rose to possible when considering PCBdl_TEQ for dermal
353 exposure (1.8E-4) and was acceptable when considering TCDD_TEQ and ΣPCBndl (8.5E-5, 2.4E-6,
354 respectively) for dermal absorption; the risk was acceptable for TCCD_TEQ and ΣPCBndl (9.1E-5,
355 2.7E-6, respectively) and possible concerning PCBdl_TEQ for total exposure (2.0E-4); in all cases,
356 BaPy_Teq showed no risk level.
357 The cancer risk level for total exposure caused by arsenic contamination was acceptable at all sites
358 investigated (7.7E-6, 1.1E-5, and 8.5E-5 for Palermo, Ragusa, and Siculiana, respectively). In contrast,
359 the cancer risk level for total exposure due to lead contamination was classed as no risk at all sites.
360

361 Non-Cancer Risk Assessment at the Station Level

362 HI values ranged from 0.013 to 1.39, 1.5 to 169.0, and 1.1 to 9.9 for Palermo, Ragusa, and Siculiana,
363 respectively. The HI is represented in hot-spot maps in Fig. 3 (3a, 3b, and 3c for Palermo, Ragusa, and
364 Siculiana, respectively). A visual inspection of the map suggests the following:
365 (i) Palermo showed no risk level at PA9, and possible risk at all other stations. The most dangerous
366 zone was around station PA8.
367 (ii) Ragusa showed a possible risk level at all stations and a high level of risk at station RG9.
368 (iii) Siculiana showed a possible risk level at all stations and a high level of risk at station SI9.

369 Furthermore, where the HI was higher than 1 the most significant contribution was due to the HQ of
370 PCBdl_TEQ, calculated for dermal exposure.
371 It is also worth noting that stations RG9 and SI9, chosen as a *priori* blank stations for Ragusa and
372 Siculiana respectively, revealed a pollution level connected with a possible risk level for human health.
373 This result shows that groundwater contamination is not exclusively due to landfill pressure and is
374 probably caused by other anthropogenic activities. The HQ of BaPy_TEQ showed values much lower
375 than 1 at all stations at all sites. The HQ of each toxic element and relative HI_inorg (sum of the HQ
376 values of each toxic element) always showed values of less than 1 at all sites studied, both for ingestion,
377 and dermal and total exposure.
378
379 **Non-Cancer Risk Assessment at the Site Level**
380 The HQ and HI, based on the average of each contaminant across the whole area of each site monitored,
381 are reported in Table 7, where values higher than 1 are highlighted in bold.
382 Focusing on the HQ assessments, it is possible to conclude the following:
383 (i) A no-risk level was associated with Palermo, for all pollutant classes and all exposure typologies.
384 (ii) A possible risk level was associated with Ragusa, due to PCBdl_TEQ for all exposure typologies.
385 (iii) A possible risk level was associated with Siculiana for PCBdl_TEQ and dermal absorption, and
386 total exposure (1.7, and about 1.9, respectively).
387 (iv) The HQ for each metal at each site, and each exposure typology, was always much lower than 1.
388 With regards HI values related to Total Exposure (Table 7), the HI_inorg (the sum of the HQ of all
389 toxic metals) was always lower than 1 (5.9E-2, 8.5E-2, 5.0E-1 for Palermo, Ragusa, and Siculiana,
390 respectively), while HI_org (the sum of the HQ of all organic pollutants) was higher than 1 for all sites
391 (1.2, 20.0, 2.8, for Palermo, Ragusa, and Siculiana, respectively). These results show the greater danger
392 associated with Ragusa groundwater in comparison with Siculiana and Palermo, which were
393 characterised by similar and lower risk levels. Careful evaluation of the data shows that the calculated
394 risk levels are mainly due to the occurrence of appreciable amounts of PCBdl in Ragusa and Siculiana

395 groundwater (HQ 19 and 1.9, respectively). The major contribution to risk at the Palermo sites is due
396 to TCDD_TEQ and PCBdl_TEQ (0.71 and 0.46, respectively).
397

398 Discussion

399 Comparison of the sum of cancer risk values for organic (ΣCRorg) and inorganic pollutants (ΣCRinorg)
400 showed that organic contamination was vastly more dangerous than inorganic. The summed values
401 calculated for the cancer risk assessment referred to total exposure and all contaminants with the same
402 weight of evidence, equal to 1 (US EPA, 2005), led to ΣTCR values 1.3E-4, 2.0E-3, 3.7E-4 for Palermo,
403 Ragusa, and Siculiana, respectively. These values suggest that the carcinogenic risks due to
404 groundwater use were ranked in the following order: Ragusa > Siculiana > Palermo.
405 Looking at the results obtained in all cases, and consistent with the model parameters, dermal exposure
406 to groundwater was more dangerous than its ingestion. This behaviour is primarily due to organic
407 pollutants and depends on their high lipophilicity and high dermal permeability. These chemical
408 properties ease penetration into the human body, and are, for dermal exposure, also associated with the
409 large water volume to which everyone is exposed during a hypothetical shower. According to RAGS
410 parameters, this volume is two orders of magnitude higher with respect to water that is routinely
411 ingested.
412 The opposite behaviour was observed for metals, which showed higher toxicity in the "water ingestion"
413 scenario. Based on their contribution to the risk indexes, the most dangerous organic contaminants for
414 all the risky sites were PCBdl. In Palermo, dioxins and PCBdl contributed equally to generating the
415 overall cancer risk. Both pollutant classes impact human health, damaging the liver, endocrine, and
416 reproductive system (IRIS, 2007).
417 When comparing this study with others reported in Table 4 we found that (i) Chunfa Wu et al. (2015)
418 found a risk for ingestion exposure ranging from 1.49E-6 to 3.19E-3 and 3.09E-6 to 6.79E-3 for adults
419 and children respectively due to contamination by PCB dioxin-like (values comparable to those

420 reported in this study) and assessed the risk level as higher than acceptable; (ii) the results of Downs et
421 al. (1999) revealed that the concentration of PCB (seven congeners) was too low to require further
422 evaluation for human health risk (PCB concentrations were two orders of magnitude lower than in this
423 study).
424 Of those studies listed in Table 5, only Bodrud-Doza et al. (2020) performed a risk assessment for
425 ingestion and dermal exposure to the pollutants that they examined, concluding that the HQ due to
426 metal contamination (concentrations comparable with the present study) was much lower than 1,
427 indicating no risk for human health, at least with regards exposure to metals alone. However, Bodrud-
428 Doza et al. (2020) only assessed non-cancer risk (and not cancer risk), when calculating the risks to
429 determine HQ and HI.
430 Based on this study, the EQS of Ragusa and Siculiana groundwater was polluted by PCB. For this
431 reason, these water sources should be classified as unsatisfactory according to Italian Directive
432 (2009). The origin of these organic pollutants was investigated by comparing the relative
433 concentration of PCB congeners with commercial mixtures, such as Aroclor 1016, 1242, 1248,1254,
434 and 1260, and no matches were found. However, such an origin cannot be excluded due to the possible
435 dechlorination processes (Rodemburg et al. 2010) that could modify the relative abundance of the
436 congeners. In agreement with a previous study (Ruiz-Fernandez et al. 2012), PCB 153 may also
437 originate from pyrolysis processes and therefore may also be due to anthropic impacts on the
438 environment. The evaluation of the pollutant levels and the derived human health risk showed no direct
439 correlation with the presence of landfills, although their influence on sampled groundwater cannot be
440 excluded.
441 More specific studies, using some other molecular tracer, would be required to give a definite answer
442 on the impact of landfills on sampled groundwater. In this study, taking into account the direction of
443 the groundwater flow, the lack of correlation with municipal dumps indicates that the unequivocal
444 contamination found in the samples could also be attributed to improper and illegal waste disposal.

Unfortunately, illicit dumps linked to PCB pollution, plastic incineration (related to dioxins and PAH), or the release of wastewater from industrial sources into the environment, are not uncommon.

Conclusions

The risk assessment showed that most of the risks are related to the use of groundwater for sanitary purposes (showering) rather than drinking. Although the levels of contaminants were below the threshold limit of Italian Directive (2001) for drinking water, a possible cancer risk was found through dermal absorption mainly due to organic pollutants, namely PCB. Based on the level of groundwater contamination and human health risk assessment, the riskiest site was Ragusa, followed by Siculiana and lastly by Palermo. Although the size and the surface area of the landfills should play a role in pollutant generation there was no correlation between this and the results of the risk assessment. An evaluation of the HQ and HI for non-cancer-related risks revealed the same trend. The "probable risk" that was calculated for human health, both for acute and chronic stress in the hypothesised exposure scenarios, demonstrates that groundwater from the investigated sites should not be used either for drinking nor for washing, and proper pre-treatment to mitigate the presence of PCBs and dioxins should be carried out at the very least.

Looking at other sites' data on contaminants of groundwater in other locations around the world, pollutant concentrations were comparable with those found in our study, suggesting similar risk levels. Therefore, the scientific community should make an effort to assess the human health risks associated with the use of water when environmental monitoring is performed. Policymakers should promote the investigation of contamination levels in groundwater and try to mitigate any long-term risks for human health associated with its use as drinking and/or sanitary water.

Conflict of Interest Statement

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Funding

This work was funded through the SIGLOD *"Sistema Intelligente di Supporto alla Gestione e alla Localizzazione delle Discariche di rifiuti"* Operational Objective 4.1.1.1 project code: PON4a_2 - financed by The National Operational Programme for "Research and Competitiveness" 2007-2013 (NOP for R&C) PON Axis - Operational objective II - Integrated activities for sustainable development and dissemination of the information society. Action Integrated actions of research and competitiveness for sustainable development. Action line: Smart Cities. PON FESR 042a_F SIGMDL.

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Fig. 1 The study sites (a. Palermo, b. Ragusa, c. Siculiana): red dots indicate sampling stations while the landfill site surfaces are rendered in yellow/black colour. PA9, RG10, and SI10 are the wells chosen as "blank station". The light blue arrows indicate the groundwater flow direction.

Fig. 2 Cancer risk hot-spot maps (a. Palermo, b. Ragusa, c. Siculiana). Coloured hot spots identified the risks accordingly with the legend, and in yellow/black is evidenced the landfill

Fig. 3 Hazard Index hot-spot maps (a. Palermo, b. Ragusa, c. Siculiana). Coloured hot spots identified the risks accordingly with the legend, and in yellow/black is evidenced the landfill

661 **Table 1** PA, SI and RG indicate Palermo (Bellolampo), Siculiana (Agrigento), Ragusa (Cava dei
662 Modicani) stations respectively.
663

Sample	Type	Well Depth (m)	Elevation (m)	Coordinates	
				UTM ED50 E	UTM ED50 N
PA1	Spring		239	350835	4224684
PA2	Well	60	95	351234	4225537
PA3	Well	nd	107	345235	4224223
PA4	Well	20	233	351218	4224033
PA5	Well	60	75	352133	4225076
PA6	Spring		57	345742	4226148
PA7	Well	nd	76	351638	4223044
PA8	Well	nd	145	350615	4222892
PA9	Spring		488	349769	4224075
SI1	Surface water		15	357934	4134271
SI2	Spring		142	355724	4136678
SI3	Surface water		50	359659	4136505
SI4	Spring		85	359667	4136799
SI5	Spring		187	358506	4137216
SI6	Spring		219	357213	4137675
SI7	Spring		182	356919	4137852
SI8	Spring		196	360189	4138174
SI9	Spring		191	360152	4137738
SI10	Spring		122	356330	4136148
RG1	Spring		566	474678	4090096
RG2	Spring		567	475255	4090077
RG3	Spring		540	473176	4088318
RG4	Spring		540	473176	4088318
RG5	Spring		335	470335	4095215
RG6	Spring		445	471196	4093291
RG7	Well	53	445	471196	4093291
RG8	Spring		353	469257	4091165
RG9	Spring		477	477186	4092412
RG10	Spring		481	477028	4093323

nd = not determined

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667 **Table 2** Exposure parameters used for risk assessment

Variable (symbol)	Unit	Dermal exposure	Ingestion exposure	Reference
Fraction absorbed water (FA)	Unitless	Chemical specific		US EPA, 2004
Dermal permeability (Kp)	cm/h	Chemical specific		US EPA, 2004
Lag time per event (tau event)	h/event	Chemical specific		US EPA, 2004
Event duration (tevent)	h/event	0.30	//	
Event frequency (EV)	Event/day	1	1	
Exposure duration (ED)	year	30	30	US EPA, 2004
Exposure frequency (EF)	days/year	365	365	
Surface area (SA)	cm^2	18.000		US EPA, 2004
Body weight (BW)	kg	70	70	US EPA, 2004
Averaging time (AT)	year	70/9	70/9	US EPA, 2004
Cancer Oral slope factor (CSfo)	$(mg/kg\text{-}day)^{-1}$	Chemical specific		IRIS ,HC1, HC2,
Absorption fraction (ABSGI)	Unitless	Chemical specific		US EPA, 2004
Oral reference dose (RfDo)	mg/kg-day	Chemical specific		IRIS database
Ingestion Rate (IR)	l/day	//	2	US EPA 2011a

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669

670 **Table 3** Organic pollutant concentration in groundwater in µg/l (the n. of congeners in brackets), minimum, maximum, average and standard deviation
671 (st.dev). Average values higher than MAC are in bold

Organic pollutants	Palermo			Ragusa			Siculiana			MAC
	min	max	Average (st.dev)	min	max	Average (st.dev)	min	max	Average (st.dev)	
∑PAH (16)	1.0E-3	7.0E-2	1.4E-2 (1.7E-2)	3.5E-3	5.2E-2	1.6E-2 (1.5E-2)	5.1E-3	6.6E-2	3.5E-2 (2.3E-2)	
B(a)Py_TEQ (15)	1.17E-3	1.23E-3	1.18E-3 (1.6E-5)	1.17E-3	2.34E-3	1.23E-3 (2.4E-4)	1.17E-3	1.23E-3	1.21E-3 (1.3E-5)	1.0E-2
PCBdl_TEQ (12)	1.7E-6	1.9E-6	1.7E-6 (2.6E-8)	1.7E-6	1.8E-3	6.9E-5 (1.9E-4)	1.7E-6	5.2E-5	6.9E-6 (1.0E-5)	
∑PCBndl (17)	2.6E-4	1.2E-2	2.9E-3 (3.4E-3)	2.6E-4	2.8E-1	5.8E-2 (5.7E-2)	2.6E-4	5.1E-2	1.3E-2 (9.1E-3)	
∑PCB (29)	4,2E-4	1,7E-2	3,2E-3 (3.8E-3)	4,1E-4	7,4E-1	**1.5E-1** (1.2E-1)	4,2E-4	8,3E-2	**1.3E-2** (1.5E-2)	1.0E-2
∑PCDD+PCDF (17)	1.1E-5	7.1E-5	2.8E-5 (1.9E-5)	1.1E-5	1.9E-5	1.1E-5 (1.9E-6)	1.0E-5	2.3E-4	2.1E-5 (4.7E-5)	
TCDD_TEQ (17)	2.2E-6	4.0E-6	2.6E-6 (2.9E-7)	2.1E-6	3.0E-6	2.2E-6 (1.4E-7)	2.1E-6	2.8E-5	3.3E-6 (3.0E-6)	

MAC is the Maximum admissible concentration of the Directive 30/2009, in bracket is indicate the numbers of congeners

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673 **Table 4** Toxic metal concentration in groundwater in µg/l, minimum, maximum, average and standard deviation (st.dev). Average values higher than
674 MAC are in bold

Toxic metal pollutants	Palermo			Ragusa			Siculiana			MAC
	min	max	Average (st.dev)	min	max	Average (st.dev)	min	max	Average (st.dev)	
Antimony	0.02	0.11	0.04 (0.02)	0.04	0.13	0.07 (0.02)	0.01	0.44	0.27 (0.15)	5
Arsenic	0.11	0.76	0.42 (0.22)	0.38	1.17	0.63 (0.23)	0.39	**11.21**	4.62 (3.91)	10
Barium	9.31	43.86	21.10 (12.12)	20.67	52.68	33.63 (9.4)	6.24	164.25	47.09 (46.50)	
Cadmium	0.00	0.03	0.01 (0.01)	0.03	0.05	0.04 (0.01)	0.00	0.06	0.03 (0.02)	5
Chromium (III)	0.15	0.65	0.36 (0.16)	0.26	4.95	0.85 (1.03)	0.05	0.47	0.21 (0.14)	50
Copper	0.10	8.35	1.91 (2.97)	0.06	1.06	0.49 (0.33)	0.35	1.58	0.77 (0.53)	10000
Lead	0.01	0.52	0.13 (0.14)	0.01	0.12	0.05 (0.03)	0.01	0.10	0.05 (0.03)	10
Manganese	0.04	8.61	0.93 (1.58)	0.00	14.96	1.67 (3.84)	0.01	279.76	25.04 (53.56)	
Nickel	0.17	0.90	0.48 (0.26)	0.10	6.54	1.03 (1.56)	0.24	3.28	1.39 (0.9)	20
Selenium	0.13	0.69	0.29 (0.12)	0.17	1.35	0.74 (0.35)	0.31	3.32	1.29 (0.82	10
Vanadium	0.19	1.42	0.89 (0.37)	1.29	3.68	2.28 (0.6)	0.52	8.82	3.58 (2.9)	50
Zinc	0.34	232.32	44.88 (62.62)	0.33	4.38	1.53 (1.04)	0.85	19.32	7.52 (4.53)	
∑ Toxic Metals			69,88			42,82			92,63	

Note: MAC is the Maximum allowable concentration Directive 30/2009, LOD is the limit of detection

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Table 5 Study on contaminants of groundwater of other locations in the world. Mean value in µg/l, in round bracket (n. congeners), in square bracket [range values: min, max]

	ΣPAH	BaPy_TEQ	ΣPCB	PCB_TEQ	Σ PCDD/Fs	TCDD_TEQ	Σ Toxic Metals	Risk assessment Ing/Der	Author
Mount-Lebanon, Lebanon							[2.9E-2, 1,5E+2] (1)	Ing	Halwani (2020)
Taiwan					3.27E-6	1.7E-8		-	Ngo Thi Thuan (2011)
Japan						4.8E-8		?	Japan, MOE (2008)
Zhoukou, China	1.08E+0 (11) 3.3E-1 (11)							-	D. M. Han (2013)
Guozhuang, China	5.2E-3 (16)							-	Yixian Shao (2014)
Taizhou city, China			[6.2E-3, 9.7E-2] (21)	[2.9E-5, 6.5E-4] (12)				Ing	Chunfa Wu (2015)
Agra region, India	3.2E-2 (13)							-	Amit Masih (2008)
Cerro Colorado River, Mexico			[1.0E-5, 3.6E-5]				1.5E+2 (3)	Ing/Der	Downs (1999)
Tezeopentec de Almada, Mexico			[1.6E-5, 2.0E-5]				1.2E+2	Ing/Der	Downs (1999)
El Salto River Mexico			[0, 2.6E-5]				1.1E+2	Ing/Der	Downs (1999)
Salvador City, Bahia, Brazil	1.05E+0(6)							-	Santos (2017)
Guozhuang karst system, China	5.0E+0 (22)							-	Shao (2014)
Nanshan underground River, China			[3.0E-4, 3.0E-2]					-	Jahangir (2013)
Barcelona, Spain	[8.4E-3, 2.9E-2]						1.4E+1	-	Cabeza (2012)
Pingdingshan, China	[1.5E-1, 1.2E+0]					[1.2E-6, 6.6E-6]		-	Wang (2009)
Dhaka City, Bangladesh							2.8E+2 (3)**	Ing/Der	Bodrud-Doza Md. (2020)
Palermo, Italy	1.4E-2 (16)	1.18E-3(15)	3.2E-3 (29)	1.7E-6 (12)	2.8E-5 (17)	2.6E-6 (17)	6,9E+2 (12)***	Ing/Der	in this study
Ragusa, Italy	1.6E-2 (16)	1.23E-3 (15)	1.5E-1 (29)	6.9E-5 (12)	1.1E-5 (17)	2.2E-6 (17)	4,3E+1 (12)***	Ing/Der	in this study
Siculiana, Italy	3.5E-2 (16)	1.21E-3 (15)	1.3E-2 (29)	5.4E-6 (12)	2.1E-5 (17)	3.3E-6 (17)	9,3E+1 (12)***	Ing/Der	in this study

(*) Cadmium; (**) Iron, Manganese, Zinc; (***) Antimony, Arsenic, Barium, Cadmium, Chromium (III), Copper, Lead, Manganese, Nickel, Selenium, Vanadium, Zinc; Ing= Ingestion exposure; Der= Dermal exposure, TEQ as WHO-TEF

Table 6 Cancer risk assessed at the site level, values higher than 1E-4 are in bold

Pollutants	Ingestion			Dermal			Total Exposure		
	Palermo	Ragusa	Siculiana	Palermo	Ragusa	Siculiana	Palermo	Ragusa	Siculiana
BaPy_TEQ	3.3E-8	3.4E-8	3.4E-8	5.9E-7	6.1E-7	6.0E-7	6.2E-7	6.4E-7	6.3E-7
PCBdl_TEQ(TCDD)	3.1E-6	**1.3E-4**	1.3E-5	4.5E-5	**1.8E-3**	**1.8E-4**	4.8E-5	**2.0E-3**	**2.0E-4**
ΣPCBndl	7.2E-8	1.4E-6	3.1E-7	5.5E-7	1.1E-5	2.4E-6	6.2E-7	1.2E-5	2.7E-6
TCDD_TEQ	4.8E-6	4.0E-6	5.9E-6	7.0E-5	5.7E-5	8.5E-5	7.4E-5	6.1E-5	9.1E-5
ΣCRorg	8.1E-6	**1.3E-4**	1.9E-5	**1.2E-4**	**1.9E-3**	**2.7E-4**	**1.2E-4**	**2.0E-3**	**2.9E-4**
Arsenic	7.6E-6	1.1E-5	8.4E-5	2.2E-8	3.1E-8	2.4E-7	7.7E-6	1.1E-5	8.5E-5
Lead	1.4E-8	5.2E-9	5.2E-9	3.7E-11	1.4E-11	1.4E-11	1.4E-8	5.2E-9	5.2E-9
ΣCRinorg	7.6E-6	1.1E-5	8.4E-5	2.2E-8	3.1E-8	2.4E-7	7.7E-6	1.1E-5	8.5E-5
ΣTCR							**1.3E-4**	**2.0E-3**	**3.7E-4**

Table 7 HQ and HI for non-cancer risk assessed at the site level, values higher than 1 are in bold

Pollutants	Ingestion			Dermal			Total Exposure		
	Palermo	Ragusa	Siculiana	Palermo	Ragusa	Siculiana	Palermo	Ragusa	Siculiana
BaPy_TEQ	7.2E-4	7.5E-4	7.4E-4	1.3E-2	1.3E-2	1.3E-2	1.3E-2	1.4E-2	1.4E-2
PCBdl_TEQ	3.0E-2	**1.2E+00**	1.2E-1	4.3E-1	**1.7E+01**	**1.7E+00**	4.6E-1	**1.9E+01**	**1.9E+00**
ΣPCBndl	1.8E-3	3.5E-2	7.7E-3	1.4E-2	2.7E-1	5.9E-2	1.5E-2	3.1E-1	6.7E-2
TCDD_TEQ	4.6E-2	3.8E-2	5.6E-2	6.6E-1	5.4E-1	8.1E-1	7.1E-1	5.8E-1	8.7E-1
HI_organic	7.8E-2	**1.3E+00**	1.9E-1	**1.1E+00**	**1.8E+01**	**2.6E+00**	**1.2E+00**	**2.0E+01**	**2.8E+00**
Antimony	2.9E-3	5.0E-3	1.9E-2	5.1E-5	9.0E-5	3.5E-4	2.9E-3	5.1E-3	2.0E-2
Arsenic	4.0E-2	5.7E-2	4.4E-1	1.1E-4	1.6E-4	1.2E-3	4.0E-2	5.7E-2	4.4E-1
Barium	3.0E-3	4.8E-3	6.7E-3	1.2E-4	1.9E-4	2.6E-4	3.1E-3	5.0E-3	7.0E-3
Cadmium	8.0E-4	2.2E-3	1.4E-3	8.6E-5	2.4E-4	1.6E-4	8.8E-4	2.5E-3	1.6E-3
Chromium (III)	6.9E-6	1.7E-5	4.0E-6	1.4E-6	3.6E-6	8.3E-7	8.4E-6	2.1E-5	4.8E-6
Copper	1.4E-3	3.6E-4	5.5E-4	6.5E-6	1.7E-6	2.6E-6	1.4E-3	3.6E-4	5.5E-4
Lead	1.1E-3	4.1E-4	4.1E-4	2.9E-6	1.1E-6	1.1E-6	1.1E-3	4.1E-4	4.1E-4
Manganese	1.9E-4	3.5E-4	5.1E-3	8.5E-6	1.6E-5	2.3E-4	2.0E-4	3.6E-4	5.3E-3
Nickel	6.9E-4	1.4E-3	2.0E-3	9.3E-6	1.9E-5	2.7E-5	7.0E-4	1.4E-3	2.0E-3
Selenium	1.7E-3	4.0E-3	7.4E-3	1.5E-5	3.6E-5	6.6E-5	1.7E-3	4.0E-3	7.4E-3
Vanadium	2.8E-3	7.3E-3	1.1E-2	2.9E-4	7.5E-4	1.2E-3	3.1E-3	8.0E-3	1.3E-2
Zinc	4.3E-3	1.4E-4	7.2E-4	6.9E-6	2.3E-7	1.2E-6	4.3E-3	1.4E-4	7.2E-4
HI_inorg	*5.8E-2*	*8.3E-2*	*4.9E-1*	*7.1E-4*	*1.5E-3*	*3.5E-3*	*5.9E-2*	*8.5E-2*	*5.0E-1*
Hazard Index	1.4E-1	**1.4E+00**	6.8E-1	**1.1E+00**	**1.8E+01**	**2.6E+00**	**1.3E+00**	**2.0E+01**	**3.3E+00**