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Polycyclic Aromatic Hydrocarbons (PAHs) and Heavy Metal Occurrence in Bed Sediments of a Temporary River

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Abstract The directive 2008/105/EC suggests the use of sediment or biota matrix for long-term monitoring of specific priority pollutants that tend to accumulate. But, the intermittent nature of flow in the majority of the Mediterranean rivers results in large variability of biological communities and especially fish, making advantageous the examination of pollution trend in sediment matrix and not in living organisms (biota). In this study, sediment environmental quality standards (EQSs) and sediment quality indicators (SQIs) were used to assess pollution by heavy metals (cadmium, nickel, lead, mercury, arsenic, chromium, copper, and zinc) and polycyclic aromatic hydrocarbons (PAHs) in Evrotas River, South Greece, monitored seasonally for 2 years (2009–2010) in five sampling sites. The results showed that, based on SQIs (geoaccumulation index (Igeo), enrichment factor (EF), and modified degree of contamination (mCd)), sediments of the Evrotas River can be classified as "low polluted," with some exceptions of "extreme pollution." EQS assessment revealed heavy metal pollution ranging from "low" to "medium high." Furthermore, based on the Hakanson's ecological risk index (RI) method, heavy metal potential risk was classified from "low" to "extreme." Cadmium showed the highest RI values, while mercury reached "moderate" pollution level. The average ΣPAH concentration (24.4 ng g^{-1}) was lower than both the reported EQSs and the values found in literature for unpolluted or moderately polluted river sediments. Increased heavy metal and PAH concentrations were found in sites where mixing of freshwater with reclaimed water occurred. EQSs are suggested to be supplemented with the RI or EF index that consider the natural background to assist a first ecorisk assessment and should be foreseen by 2008/105/EC directive. Sediments can be considered as a valuable matrix in assessing the spatial and temporal trends of several contaminants and should be included in the monitoring program of temporary river management plans. Special attention should be given when defining reference sites and the sampling period. Decreasing flow period at the beginning of the spring prevailed in order to diminish any disturbance by flash flood events.

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1 Introduction

Although temporary rivers drain all biogeographic regions and represent the dominant freshwater ecosystems in many areas, only recently have they received attention (Datry et al. 2014). Key driver for the aquatic community diversity and composition is the intense flow variability due to periodic flood and drought events. During the rainy season, the concentration of pollutants into the water column is highly variable, experiencing high peaks during the floods, because in a prompt way, sediments and pollutants are re-suspended and flushed out to the coastal area. But, in the low-flow period, temporary rivers are also vulnerable due to the higher pollutant deposition in stream-bed sediments and the slower surface water velocity that, in turn, enables a series of reactions to take place (Tzoraki et al. 2014). Moreover, often these river systems are characterized by small catchment areas that can be more vulnerable to anthropogenic activities for which there is a lack of systematic monitoring planning and environmental management.

In the framework of the Water Framework Directive (WFD 2000/60/EC), the MIRAGE-toolbox has been developed, consisting of a series of methodologies to guide the establishment of the ecological and chemical status of temporary streams (Prat et al. 2014). However, priority substances have received little attention in temporary river ecosystems, and only recently environmental quality standards (EQSs) for 41 priority substances (including PAHs and heavy metals) have been established through the Directive 2008/105/EC (EC 2008) (daughter directive of the WFD). Directive 2008/105/EC recognizes that traditional water quality–based controls are not enough to protect aquatic environments and suggests the use of sediment/biota as ultimate matrix for long-term monitoring of some priority pollutants that tend to accumulate in these matrixes. Special attention has been given to polycyclic aromatic hydrocarbons (PAHs) originating from pyrogenic and petrogenic sources that are characterized as environmentally stable, bioaccumulable, and toxics (Haritash and Kaushik 2009; Kaushik et al. 2012; Wang et al. 2012). Most PAHs, motivated by their strong hydrophobicity, bind to soil and sediment particles and, thus, are less available for biological uptake (Zhang and Wang 2010, Zhao et al. 2010). Especially in Mediterranean areas, where the majority of rivers experience intermittent flow (temporary rivers) leading to large variability of biological communities, it seems useful to monitor sediment matrix and not living organisms (biota), and to rely on these for long-term monitoring of pollutants. Changes of pollution in sediment column are not as fast as in the water column and long-term comparison can be made (EC 2010).

Since 1989, the US National Oceanic and Atmospheric Administration (NOAA) proposed screening values for 190 chemicals in sediment as a means of assessing the sediment quality in marine and freshwater environments. The effects range median and low (commonly referred to as ERM and effect range low (ERL), respectively) have been used as threshold criteria to initiate remediation actions to protect aquatic ecosystems from exposure to chemicals in sediments that have the potential to harm aquatic life (Violintzis et al. 2009). Updated NOAA's sediment quality guidelines (as new knowledge becomes) available have been used as the foundation for deriving sediment quality values in several countries around the world or have been adapted directly (MacDonald et al. 2000). Several thresholds has been suggested concerning heavy metals and PAH concentrations in sediments, where biological effects are unlikely to occur, such as the sediment quality guideline (SQG), the threshold effect level (TEL), the lowest effect level (LEL), the minimal effect threshold (MET), the consensus-based threshold effect concentration (TEC), the threshold effect level Environment Canada (EC-TEL), and the screening level contamination (SLC) (Chapman et al. 1999a; Chapman et al. 1987; Chapman and Mann 1999; Chapman et al. 1999b; MacDonald et al. 2000). All these screening values are based on bulk solid concentrations and neglect the mobile part of the metals that can partition into the water.

The use of the total concentration of a trace metal in sediment as a measure of its toxicity and its ability to bioaccumulate is not sufficient because metals can be partitioned into different chemical forms associated with a variety of organic and inorganic substances (Di Toro et al. 1992). Based on the observation that the divalent transition metals do not cause toxicity in sediment until their molar concentration in sediments exceeds the molar concentration of sulfide, an operation indicator for metals was developed, the "acid-volatile sulfide" (AVS) (Prica et al. 2008). Also, the speciation analysis by the use of sequential extraction procedures is a useful procedure to understand which metals are more associated with active and mobilizable fractions, which are transitional metals at relative high concentrations and may be toxic at high concentrations to the aquatic (Cui et al. 2014). Both AVS indicator and sequential extraction are used to extract first-order corrections to avoid the raw use of screening values (USEPA 2004). For the same reason, partitioning-based methods and biomimetic extraction methods have been developed in the last two decades to measure hydrophobic organic contaminant (i.e., PCBs and PAHs) bioavailability in soils and sediments (Cui et al. 2013).

The 2008/105/EC Directive allows EU Member States to set their own EQSs for sediment and/or biota, instead of water-based EQSs. Sediment EQSs can only be derived from a database of biological effects verified for sediment-dwelling organisms by a variety of methods that show the relationship between effects and contaminants. Given the lack of toxicity data on benthic organisms, Member States have not yet established sediment EQSs, despite the existence of quality criteria for water. For the purposes of this study, the sediment EQSs from national studies were adapted by a thorough investigation of the literature, and sediment quality indicators (SQIs) were used to assess heavy metal pollution.

The main objective of this study is the assessment of heavy metal and PAH contamination of river sediments under contrasting hydrologic conditions (high and low flow). The study was conducted in Evrotas River, Greece, a Mediterranean intermittent river mainly due to anthropogenic intervention. The ultimate goals are the improvement of the monitoring program scheme of the WFD and to identify possible pollutants that avoid reaching the objectives of the directives WFD and 2008/105/EC. We have focused on the following priority substances: heavy metals (cadmium, nickel, lead, and mercury), polycyclic aromatic hydrocarbons (PAHs), and some basin-specific substances (such as arsenic, chromium, copper, and zinc).

2 Methodology

2.1 Study Area

The Evrotas River basin is described in detail by several studies (Skoulikidis et al. 2011; Tzoraki et al. 2013). Briefly, the basin expands between the mountain ranges of Taygetos (2407 m above sea level (a.s.l.)) and Parnon (1940 m a.s.l.), where numerous intermittent and ephemeral streams discharge into the main river course. Evrotas is originated by two major tributaries flowing out of Taygetos (Vivari mean annual flow 1.05± 0.9 $m^3\ s^{-1}$, 1974–2010) and Parnonas mountains (Oinountas Kladas mean annual flow 0.31± 0.31 $m^3\ s^{-1}$, 2008–2011) (Fig. 1). The population of the river basin is approximately 66,000 and the biggest town, Sparta, has 18,000 inhabitants. Most of the river basin's landscape is covered by semi-natural areas accounting for 61 % of the total river basin, followed by agricultural areas that cover 38 %, while urban areas account for approximately 1 %. The dominant anthropogenic pressures in the Evrotas River basin are derived mainly from agricultural activities and include overexploitation of water resources for irrigation, disposal of agro-industrial wastes, and agrochemical pollution. Almost 92 % of the Evrotas River network is composed of episodic flow streams, 4.3 % of intermittent flow, and only 3.5 % is composed of perennial (permanent flow) streams. The river hosts five native and two alien freshwater fish species, and three of the native species are range-restricted endemic cyprinids of outstanding conservation interest such as *Squalius keadicus* that is confined exclusively to this river. Evrotas River is one of the most biotically distinctive basins of the Ionian ecoregion due to its prolonged isolation from other river systems (Skoulikidis et al. 2011). River water is used for irrigation and recharge by river bed infiltration of the alluvial aquifer of Sparta plain.

2.2 Water and Sediment Sampling

Three sampling surveys (July 2009, April 2010, and October 2010) were performed in order to collect water and sediment samples in different sections of the river basin, representative of different hydrological conditions (Fig. 1). Sediment samples were collected in each site from the upper most oxic layer (0.5–2.0 cm) and kept refrigerated (+4 °C) until beginning of the analyses, within 24 h. Sediments were analyzed for heavy metal and PAH content and water samples for heavy metal content. Sampling sites were selected upstream and downstream from point sources. Kolliniatiko site was selected as a reference site with almost pristine conditions (free grazing animals, restricted agriculture, and hydromorphological alterations) that has good

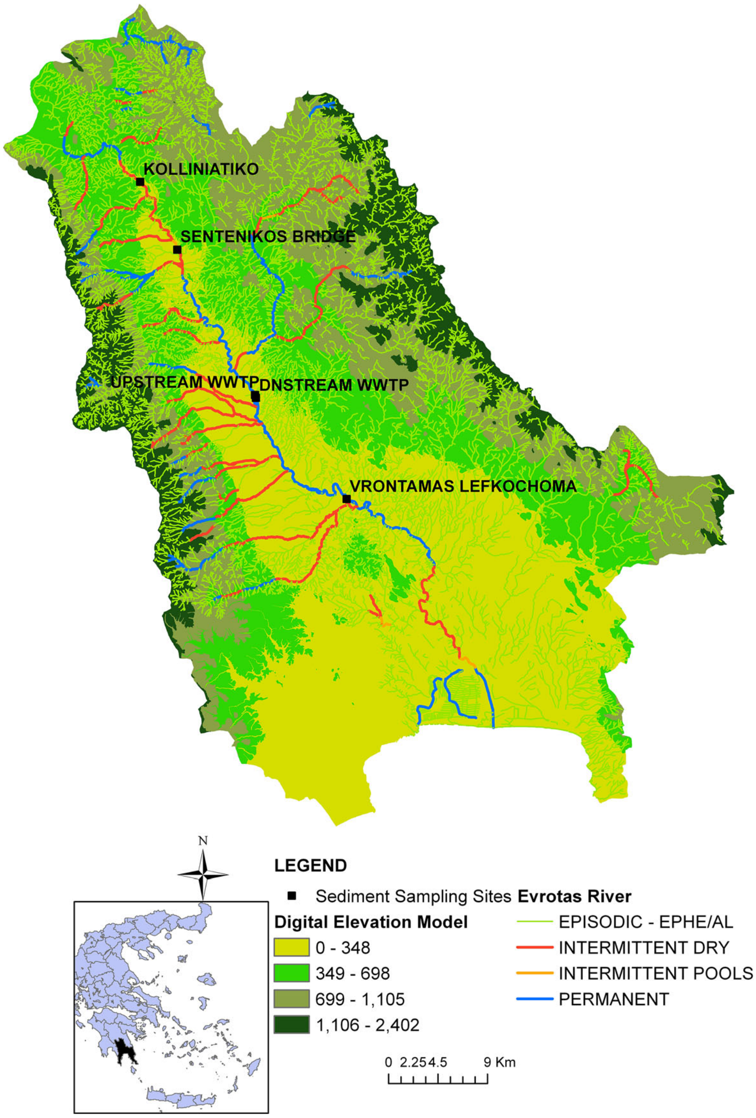

Fig. 1 Sampling network in Evrotas watershed

ecological quality (Skoulikidis et al. 2011). Sites upstream and downstream wastewater treatment plant (WWTP) effluents were sampled to evaluate the effect of reclaimed wastewater. Finally, Vrontamas site collects the flow of the permanent stream and numerous ephemeral flow tributaries (mean annual flow 3.62± 4.23 $m^3\ s^{-1}$, 1973–2011). In addition, monthly monitoring of river water for heavy metals was conducted at 2009 in order to estimate any seasonal variation in their concentration.

The sampling performed under "low-flow conditions" was characterized by a mean monthly discharge at Vrontamas site of 1.95 $m^3\ s^{-1}$ for the year 2009 (18 July 2009) and 0.84 $m^3\ s^{-1}$ for 2010 (26 October 2010) as calculated on a daily basis for the 30 days before sampling. Two months (13 February 2010) before the sampling campaign of "high-flow conditions," the river basin was hit by a flush corresponding to river bank full discharge (164.8 $m^3\ s^{-1}$) (Fig. 2) initiating sediment transport and inundating floodplain areas. The high-flow conditions were characterized by a mean flow of 8.2±2.2 $m^3\ s^{-1}$. Data by previous surveys in the area for the year 2007, which was

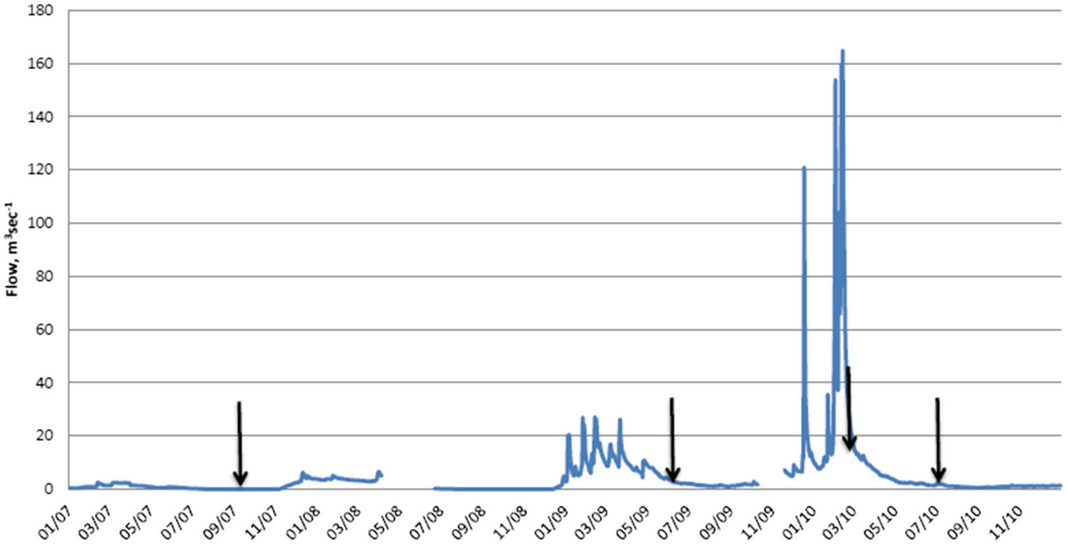

Fig. 2 Water flow in Vrontamas site of the Evrotas River

an extremely dry year, were used to validate the trends.

2.3 Chemical Analysis

Phenanthrene (Phen), anthracene (Anth), fluoranthene (Flu), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), benzo(g,h,i)perylene (BgP), and indeno(1,2,3-c,d)pyrene (InP) stock solutions in cyclohexane (100 mg L^{-1}) were supplied by Aldrich (98 % purity, Steinheim, Germany). Diluted working standard solutions (1 mg L^{-1}) in acetone were stored at 4 °C. The internal standard 1-methylpyrene was purchased from Lab Service Analitica s.r.l. (Bologna, Italy). Acetonitrile, hexane, and acetone at HPLC grade were from Merck (Darmstadt, Germany). Water for chromatography was purified (18MΩ cm^{-1}) by a Milli-Q system (Millipore, Bedford, MA, USA).

PAHs in dried sediments were extracted by sonication with hexane/acetone 1:1 (*v*/*v*); the sonication was repeated for three times (Patrolecco et al. 2010). Briefly, the extracts were evaporated and reconstituted with acetonitrile/water 60:40 (*v*/*v*) to a final volume of 0.5–1.0 mL. Fifty microliters of final extracts were injected in duplicate in HPLC. Analytical determinations were performed by RP-HPLC (Varian 9012) coupled to a fluorescence detector (Perkin Elmer LS4) using a Supelco LC18-PAH column, 5 μm, 250×4.6 mm I.D. preceded by a guard column (4×3 mm I.D., 5 μm) of the same packing material for PAH analysis. The mobile phase for gradient elution was a mixture of acetonitrile and water delivered at a constant flow rate of 1.5 mL min^{-1}, passing from a ratio of 40:60 (*v*/*v*) to a final ratio of 0:100 (*v*/*v*) in 40 min. The excitation–emission wavelengths were automatically set by a time program, and the detection limits were in the range of 0.1–0.3 ng g^{-1} (dry weight) for all PAHs in the sediments.

Heavy metals were extracted from sediments with the procedure described by EPA method 3051A. Specifically, 9 mL HNO_3 was added to 0.2 g soil, followed by microwave digestion at 150–180 °C (Multiwave 3000 Digestor). Supernatant solutions were diluted with Milli-Q water and analyzed by ICP-MS (Agilent-CX).

2.4 SQIs

A variety of methods has been suggested to estimate the metal accumulation into the sediments. Analytical description of heavy metal pollution indicators can be found in the study of Hahladakis et al. (2012).

(a) A commonly used index is the geoaccumulation index (Igeo) that allows the assessment of contamination by comparing current and reference conditions using the equation

$$Igeo = \log_2\left(\frac{C_n}{1.5{*}B_n}\right) \tag{1}$$

where C_n and B_n are the measured concentrations of studied constituent in the studied sediment and in the background reference sediment respectively. The constant 1.5 is used to account for natural fluctuations of the environmental variables including possible minor anthropogenic inputs. The classification of the sediments varies from extremely polluted (>5), strongly polluted (3–5), moderately polluted (1–3), and unpolluted (<1).

(b) The modified degree of contamination (mCd) introduces a generalized approach to calculate the degree of contamination and is given by the equation

$$mC_d = \sum\left(\frac{C_n}{B_n}\right)\Big/n \tag{2}$$

where n is the number of analyzed sediments. Equation 2 allows the incorporation of as many metals as the study may analyze, even organic pollutants with no upper limit. Values lower than 2 indicate low degree of contamination, 2 to 4 moderate, and higher than 4 high degree of contamination.

(c) Enrichment factor (EF) approach normalizes the measured heavy metal content with respect to the background reference metal concentration such as Al, or Fe. Fe and Al have relatively high natural concentrations, and we do not expect that anthropogenic actions increase their concentrations in river sediments. The EF is calculated according to the equation

$$EF = \left(\frac{C_n{*}Fe_b}{B_n{*}Fe_s}\right) \tag{3}$$

where Fe_b and Fe_s are the Fe (or other normalizing elements) concentrations in background reference sample and in the studied sediment sample.

The above mentioned pollution indicators are not foreseen by the WFD but insist valuable methods especially for metal accumulation overcoming the problem with their high concentration variation from site to site.

(d) Hakanson's ecological risk index (RI) assessement method (Hakanson 1980) evaluates the potential ecological risks associated with the metal contaminant concentrations found in sediment samples. The index considers heavy metal concentrations in the soil and ecological toxicological effects and is calculated using the equation

$$RI = \sum\left(T^i_f\cdot\frac{C^i_s}{C^i_r}\right) \tag{4}$$

where T^i_f is the biological toxicity factor for a single metal, C^i_r is the background concentration of the metal in the sediments, C^i_s is the measured concentration of the metal in the sample, and RI is the potential ecological risk index for multiple metals. Metals used in this method are Cu, Ni, Pb, As, Zn, Hg, Cd, and Cr.

2.5 Sediment EQSs

The Guidance Document 27 (referred here as "GD-27") suggests for the deriviation of EQS for sediment three options: (i) ecotoxicity data from experiments with benthic organisms, (ii) water column ecotoxicity data used in conjunction with benthic organism, and (iii) empirical field or mesocosm data (e.g., co-occurrence of benthos and chemical contamination in the field) (EC 2011). GD-27 for the derivation of EQSs of WFD suggests the use of toxicity test or the Di Toro method (equilibrium partitioning (EqP) approach) based on K_d values for sediments from freshwater when sediment ecotoxicity data are not available. Preference is given to K_d values that are derived by field measurement instead of laboratory sorption or toxicity experiments. However, high variation in K_d values is observed even among different field-based measurements, and GD-27 recommends the use of WHAM model (Windermere Humic Aqueous Model). WHAM model uses organic carbon as solid phase receptor and neglects the rest of the components of sediment matrix. Natural sediments contain various binding ligands such as iron and manganese oxyhydrooxides which restrict the mobility of metals and consequently influence the availability and toxicity of metals to sediment-dwelling organism. Metals with high binding affinity are strongly influenced by the presence of ligand sites. For instance, for Evrotas sediments, only 0.78 % (average value of ten sediment samples) is the organic carbon content and the rest is calcite and ferrous oxide and other minerals. Evrotas sediments are poor in organic carbon in comparison to the European Union "standard sediment" that has a default organic carbon content of 5 % (EC 2011).

Due to low organic carbon content of Evrotas sediments and the absence of any ecotoxicological data, the third option, meaning the "empirical field or mesocosm data" is preferred for the purpose of EQS selection. Field thresholds may be selected referring to concentrations at which biological effects are unlikely to occur (referred to as "threshold effect level" (TEL) and "effect range low" (ERL)), and they are preferred in respect to thresholds associated with a significant biological impact (e.g., "probable effects level" (PEL)). ERL is defined as the tenth percentile of the distribution of concentrations (dry weight) associated with an effect in a database matching chemistry and ecotoxicological tests applied to sediments collected from the field. TEL is the geometric mean of the 50th percentile of concentrations (dry weight) associated with a biological effect and the 15th percentile of the no-effects set (EC 2011). TEL and ERL approaches should be used with a thorough assessment of the reliability of the data and their relevance, as recommended by GD-27. Sediment quality standards that have been developed and evaluated so far for reliability from field studies in various locations are the threshold effect concentrations (TECs) and "probable effect concentrations" (PECs) called as "consensus-based sediment quality guidelines" (CB-SQGs) (MacDonald et al. 2000). CB-SQGs are relevant for assessing freshwater sediments that are influenced by multiple sources of contaminants.

The use of international thresholds (CB-SQGs, ERL, and TEL) is an easy to use method of screening values, although they do not reflect the high site-specific variability as shown by the partitioning methods. The sediment quality criteria chosen in this study are shown in Table 1 and are derived by previous field studies by a series of empirical and statistical approaches to relate chemical concentrations to the frequency of biological effects (MacDonald et al. 2000; Long et al. 1995; Burton 2013). The comparison of the quality standards for marine and transitional water sediment established by the Italian Ministry of the Environment (10/12/2010-Legislative Decree 219) to the freshwater

Table 1 Environmental quality standards of sediments according to national thresholds

Priority substances	Metals (mg kg^{-1})		TEC[a]	PEC[a]	ERL[b,c]	TEL[b,c]
		Cadmium	0.99	4.98	1.2	0.68
		Mercury	0.18	1.06	0.15	0.13
		Nickel	22.7	48.6	20.9	15.9
		Lead	35.8	128	46.7	30.2
	PAHs (μg kg^{-1})	Benzo(a)pyrene (BaP)	150	1450	430	90
		Benzo(b)fluoranthene (BbF)	–	–	320	70
		Benzo(k)fluoranthene (BkF)	–	–	280	60
		Anthracene (Anth)	57.2	845	853	50
		Fluoranthene (Flu)	423	2230	600	110
		Phenanthrene (Phen)	204	1170	240	90
		ΣPAHs	1610	22,800	4000	–
Basin-specific substances	Metals (mg kg^{-1})	Arsenic	9.79	33	33	5.9
		Chromium	43.4	111	81	52.3

TEC threshold effect concentration, *PEC* probable effect concentration, *ERL* effect range low, *TEL* threshold effect level, *PAHs* polycyclic aromatic hydrocarbons

[a] (MacDonald et al. 2000)

[b] (Long et al. 1995)

[c] (Burton 2013)

sediment criteria of Table 1 revealed that the Italian thresholds are closer to the TEL values and even lower for some priority substances such as cadmium, benzo(b)fluoranthene (BbF), and benzo(k)fluoranthene (BkF).

3 Results

3.1 Hydrological Conditions

Water and sediment yield is highly influenced by the topography and the geomorphology of the area (Gamvroudis et al. 2015). The water yield for the whole catchment ranged from 246.6 mm (15.3 % of precipitation) in 2002–2003, hydrologic wet year, to 48.4 mm (7.9 % of precipitation) in 2006–2007, dry year, with a typical value of 167.8 mm (17.7 % of precipitation) in 2009–2010. The variability of the runoff coefficient is a combined effect of rainfall variability as well as the impact of water abstraction for irrigation purposes. The average sediment yield (2000–2011) for the whole watershed was estimated at 1.24 t ha^{-1} year^{-1}, which is lower than the reported erosion in Mediterranean areas (López-Bermúdez et al. 1998).

3.2 Reference Conditions

The reference conditions (RC) concept is defined as the condition in the absence of human disturbance which is used to describe the standard, or benchmark, against which the current condition of a stream has to be compared (Stoddard et al. 2006). This concept has been adopted by the WFD, since the latter requires the ecological status assessment, which may be expressed as a deviation from RC. The reference conditions protocol developed for temporary streams (Prat 2013) is used in this study for the characterization of Kolliniatiko site, which evaluates a total of 37 attributes and uses three additional validation criteria (Table SI-1) that are related to nutrient conditions. The examined attributes include land use pressures at basin scale and land use, morphological, hydrological, invasive species, and other pressures at river segment scale that should comply with specific thresholds. Koliniatiko site complies with the total 40 criteria of the suggested protocol and is used further in this study as reference site.

3.3 Sediment Chemical Characteristics

The total nitrogen content of Evrotas sediments at the riparian zone (seven surface-upper oxidized zone sediments) ranged from 0.03 to 0.18 g kg^{-1}, while organic matter from 0.5 to 2.4 %, organic carbon from 0.24 to 1.65 %, and total carbon from 1.25 to 7.29 %. Sediment pH ranged from 7.9 to 8.4, and electrical conductivity from 587 to 1075 μS cm^{-1}.

3.4 Concentration of PAHs in Sediment

PAHs have shown concentrations over the detection limits in all sediment samples with few exceptions concerning the InP and BgP (Table 2). The highest concentrations were always associated with the Flu (147.2 ng g^{-1}), followed by BbF (20.4 ng g^{-1}) and BgP (8.8 ng g^{-1}). The sum of the concentrations of the single compounds (ΣPAHs) ranged from 0.3 to 195.4 ng g^{-1}. The analysis of the contribution of the isomers to the PAH pool indicated that Phen and Anth (three-ring isomers) contributed 9–65 % to the whole PAH pool. Flu (four-ring isomer) was the predominant isomer, representing between 8 and 67 % of the total. The five-ring isomers (BbF, BaP) contributed to a similar extent to the whole pool (range 2–33 %) with the exception of BkF that showed higher variations (2–67 %). The six-ring isomer (BgP, InP) contribution was below 7 % with the minimum value observed in the dry period of 2010 (1 %).

A progressive reduction of ΣPAH concentration was observed, moving from the low-flow conditions in 2009, when a maximum value of 195.4 ng g^{-1} was found downstream from the WWTP, to the low-flow conditions in 2010, when a minimum value of 0.30 ng g^{-1} was found in Vrontamas (Table 2). Moreover, in the latter period, a drastic reduction of total PAH concentration (about 50 %) in the Kolliniatiko site was observed. Finally, a slight decrease in total PAH concentrations from the high- to the low-flow periods in 2010 was measured.

In our study, in all samples, ΣPAHs were below the TEC and ERL value, indicating that their levels in Evrotas River were within minimal effect ranges. The values of individual PAH congeners in all sediments were lower than the thresholds listed in Table 1, suggesting that most PAH levels in Evrotas River were in the minimal adverse effect range, with the exception of Flu in the site

Table 2 Concentration of PAHs in the sediments sampled from the Evrotas Basin during the surveys

Hydrological condition	Site	Phen (ngg^{-1})	Anth (ngg^{-1})	Flu (ngg^{-1})	BbF (ngg^{-1})	BkF (ngg^{-1})	BaP (ngg^{-1})	BgP (ngg^{-1})	InP (ngg^{-1})	ΣPAHs (ngg^{-1})
Low flow 2009	1-Kolliniatiko			15.8 (6)	6.8 (0.8)	2.9 (2.3)	1.04 (0.1)	<lod	<lod	26.6
	4-Downstream WWTP			147.2 (30.7)	20.4 (13.3)	8.4 (7.4)	4.5 (3.6)	8.8 (8)	6.1 (0.3)	195.4
	5-Vrontamas			14.4 (1.9)	3.1 (1.4)	2.9 (0.9)	1.1 (0.2)	<lod	<lod	21.5
High flow 2010	2-Sentenikos	0.9 (0.3)	<lod	2.9 (0.8)	3.0 (1.2)	0.9 (0.2)	1.6 (0.9)	0.3 (0.1)	0.5 (0.09)	10.1
	3-Upstream WWTP	1.4 (0.9)	<lod	2.7 (1.2)	<lod	<lod	0.5 (0.1)	<lod	<lod	4.7
	4-Downstream WWTP	<lod	1.0 (0.2)	0.4 (0.09)	<lod	<lod	0.2 (0.05)	<lod	<lod	1.7
	5-Vrontamas	2.3 (0.3)	<lod	1.7 (0.5)	0.9 (0.4)	0.1 (0.08)	0.1 (0.02)	<lod	<lod	5.3
Low flow 2010	1-Kolliniatiko	7.4 (0.6)	1.1(0.2)	1.1 (0.5)	1.2 (0.7)	0.3 (0.09)	0.4 (0.3)	0.3 (0.1)	0.1 (0.05)	12.0
	2-Sentenikos	4.6 (1.0)	<lod	1.0 (0.3)	1.5 (0.9)	0.3 (0.1)	0.5 (0.2)	0.6 (0.3)	0.4 (0.1)	8.9
	3-Upstream WWTP	1.2 (0.9)	<lod	1.6 (1.0)	<lod	<lod	0.9 (0.05)	<lod	<lod	3.7
	4-Downstream WWTP	<lod	1.7 (0.3)	0.9 (0.1)	<lod	<lod	<lod	<lod	<lod	2.6
	5-Vrontamas	<lod	<lod	<lod	<lod	0.2 (0.05)	0.1 (0.06)	<lod	<lod	0.3

Standard deviation in parentheses

lod limit of detection, *WWTP* wastewater treatment plant, *Phen* phenanthrene, *Anth* anthracene, *Flu* fluoranthene, *BbF* benzo(b)fluoranthene, *BkF* benzo(k)fluoranthene, *BaP* benzo(a)pyrene, *BgP* benzo(g,h,i)perylene, *InP* indeno(1,2,3-c,d)pyrene

downstream from the WWTP. However, the occurrence of BbF, BkF, BgP, and InP in the sediment suggests a possible ecotoxicological risk (Chapman and Mann 1999). In Evrotas River, BbF was present in 58 % of the samples, BkF in 67 %, and BghiP and InP in 33 %.

Some ratios of selected PAHs found in the environment, such as Anth/(Anth+Phen), Flu/(Flu+Py), and InP/(InP+BgP), could be useful indicators of their possible origins. In general, a ratio of Anth/(Anth+Phen) >0.1 suggests a dominance of combustion, while a ratio <0.1 indicates petroleum origin (Okoro and Ikolo 2007). A InP/InP+BgP ratio <0.20 is consistent with petroleum source, intermediate ratios (0.20–0.50) imply petroleum combustion, and ratios >0.50 indicate combustion of coal and biomass (grass and wood) (Wang et al. 2012). In this study, the ratio Anth/Anth+Phenin Evrotas sediment was 0.12, revealing a slight predominance of combustion emission. The InP/(InP+BgP) ratio ranged between 0.25 and 0.63 implying both petroleum combustion and sewage, and biomass and coal combustion as PAH origin.

3.5 Concentration of Heavy Metals in Sediment and Water

The concentrations of heavy metals in stream sediments and in the water for the surveys of 2009 and 2010 are presented in Tables 3 and 4, respectively. Data from previous studies in the same area in 2007 are included for the evaluation of metal trend into water and sediment. The geoaccumulation index (Igeo) was used to estimate the contamination levels of priority (Ni, Cd, Hg, Pb) and non-priority (Cr, Zn, As, Cu) metals (Table 5). The mCd index showed that the degree of contamination varied from low to extremely high. Higher degree of contamination was observed during the low-flow period of 2009. The negative values of Igeo, shown in Fig. 3, are the result of relatively low levels of contamination for some metals while values higher than 2 reveal moderate to high degree of contamination. Especially in Sentenikos site, higher heavy metal contamination was observed.

The values of the Evrotas heavy metal enrichment factors (EFs) normalized by Fe and by Al for the period 2009–2010 are presented in Table 5. Generally, EF values between 1.5 and 3 represent

Table 3 Concentration of heavy metals in the sediments sampled from the Evrotas Basin during the surveys

Hydrological condition		Low flow 2007	Low flow 2009				High flow 2010	
	Site	3-Upstream WWTP	1-Kolliniatiko	3-Upstream WWTP	4-Downstream WWTP	5-Vrontamas	2-Sentenikos	3-Upstream WWTP
Na	g kg^{-1}	–	<lod	0.37	<lod	<lod	<lod	<lod
Mg	g kg^{-1}	–	6.28	2.85	4.15	7.51	371.8	16.7
Al	g kg^{-1}	–	15.56	9.9	11.22	17.78	783.9	36.9
Si	g kg^{-1}	–	<lod	1.25	<lod	<lod	<lod	<lod
K	g kg^{-1}	–	4.25	1.53	1.75	3.56	<lod	<lod
Ca	g kg^{-1}	–	195.7	19.12	25.41	55.3	2452.5	153.1
Fe	g kg^{-1}	11.63	12.09	23.68	17.83	20.79	1004.4	17.6
Cr	mg kg^{-1}	21.5	66.12	32.6	18.19	27.54	3247.3	52.67
Ni	mg kg^{-1}	22.43	80.53	17.13	32.61	36.31	3263.7	<lod
Cu	mg kg^{-1}	16	16.5	8.19	16.13	22.52	916.37	<lod
Zn	mg kg^{-1}	50.8	29.3	14.9	33.54	61.43	<lod	<lod
As	mg kg^{-1}	134.6	<lod	9.82	0.84	<lod	113.0	<lod
Cd	mg kg^{-1}	1.3	<lod	<lod	<lod	106.85	<lod	<lod
Hg	mg kg^{-1}	–	<lod	3.07	<lod	<lod	<lod	<lod
Pb	mg kg^{-1}	20	5.85	3.54	7.61	6.83	<lod	<lod

Hydrological condition	Low flow 2007	High flow 2010	Low flow - 2010		
	3-Upstream WWTP	4-Downstream WWTP	3-Upstream WWTP	4-Downstream WWTP	5-Vrontamas
Na	–	<lod	<lod	<lod	<lod
Mg	–	51.2	14.30	6.9	6.11
Al	–	69.1	29.02	23.8	8.22
Si	–	<lod	2.93	3.04	0.41
K	–	<lod	5.87	1.95	<lod
Ca	–	665.3	131.8	124.2	243.5
Fe	11.63	69.1	93.3	86.8	30.60
Cr	21.5	83.69	60.93	82.90	17.00
Ni	22.43	<lod	155.8	174.3	33.75
Cu	16	<lod	69.1	74.9	18.44
Zn	50.8	<lod	97.7	40.9	<lod
As	134.6	<lod	<lod	7.00	0.95
Cd	1.3	<lod	<lod	<lod	<lod
Hg	–	<lod	<lod	<lod	<lod
Pb	20	<lod	25.10	24.01	4.72

lod limit of detection, *WWTP* wastewater treatment plant

Table 4 Concentration of heavy metals in the water during the surveys

Hydrological condition		Low flow 2007	Low flow 2009				High flow 2010	
	Site	3-Upstream WWTP	1-Kolliniatiko	3-Upstream WWTP	4-Downstream WWTP	5-Vrontamas	2-Sentenikos	3-Upstream WWTP
Na	mg L^{-1}	–	7.63	7.31	10.07	11.04	0.41	0.83
Mg	mg L^{-1}	–	9.12	8.73	17.3	17.39	13.85	29.78
Al	mg L^{-1}	–	0.02	<lod	<lod	<lod	0.43	<lod
Si	mg L^{-1}	–	3.1	0.92	2.22	1.41	3.2	4.56
K	mg L^{-1}	–	<lod	<lod	0.42	0.99	0.65	1.13
Ca	mg L^{-1}	–	>20	>20	>20	>20	89.4	122.9
Fe	mg L^{-1}	–	<lod	<lod	<lod	<lod	0.17	0.11
Cr	μg L^{-1}	<lod	0.64	0.45	0.05	<lod	<lod	<lod
Ni	μg L^{-1}	18.38	1.76	1.04	1.39	1.53	<lod	<lod
Cu	μg L^{-1}	10.25	1.7	1.39	0.36	0.58	<lod	<lod
Zn	μg L^{-1}	4	7.72	12.51	0.97	0.45	42.67	36.76
As	μg L^{-1}	<lod	<lod	<lod	<lod	<lod	<lod	<lod
Cd	μg L^{-1}	<lod	<lod	<lod	<lod	<lod	<lod	<lod
Hg	μg L^{-1}	–	13.88	7.68	1.86	1.44		5.75
Pb	μg L^{-1}	6.5	0.13	0.2	0.16	0.04	<lod	<lod

Hydrological condition	Low flow 2007	High flow 2010	Low flow - 2010		
	3-Upstream WWTP	4- Downstream WWTP	3-Upstream WWTP	4- Downstream WWTP	5-Vrontamas
Na	–	0.7	<lod	<lod	<lod
Mg	–	23.72	22.60	19.87	20.48
Al	–	<lod	<lod	<lod	<lod
Si	–	3.9	3.37	2.97	1.78
K	–	1.15	<lod	0.10	<lod
Ca	–	103.3	98.37	100.99	57.13
Fe	–	0.11	<lod	<lod	<lod
Cr	<lod	<lod	<lod	<lod	<lod
Ni	18.38	<lod	<lod	3.23	5.44
Cu	10.25	<lod	<lod	1.30	<lod
Zn	4	41.03	17.12	115.68	20.14
As	<lod	<lod	<lod	<lod	<lod
Cd	<lod	<lod	<lod	<lod	<lod
Hg	–	<lod	8.08	<lod	<lod
Pb	6.5	<lod	<lod	<lod	<lod

lod limit of detection, *WWTP* wastewater treatment plant

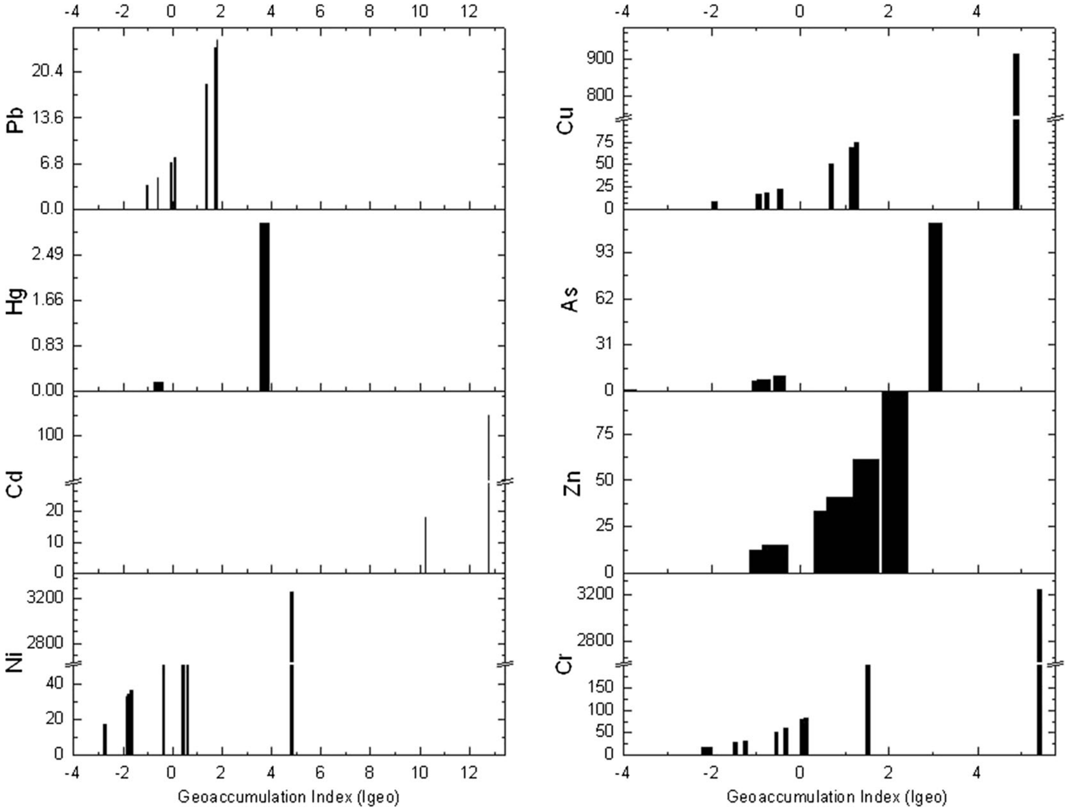

Fig. 3 Heavy metal geoaccumulation index (Igeo) in Evrotas sediments

minor enrichment, between 3 and 5 moderate, between 5 and 15 severe, between 15 and 40 very severe, and >40 extremely high enrichment. Similar characterization of river sediments was extracted by both normalizations. Evrotas stream sediments are subject to very low degree of contamination, with the exception of Vrontamas site during low-flow conditions of 2009 and Sentenikos of 2010. The EF index and RI produce similar results, and this confirms that the river is actually not deteriorated by any type of anthropogenic impacts.

Following Hakanson's ecological risk index method (ranging from 1 to 19,666), Evrotas sediment risk ranged from "low" to "extreme risk." The toxicity factors of the metals used in this method are 40 for Hg, 30 for Cd, 10 for As, 5 for Cu, Ni, and Pb, 2 for Cr, and 1 for Zn (Table 2SI). It was evident that Cd had the highest pollution coefficient, its degree of pollution reaching the "extremely high" level. The next highest pollution coefficient was found for Hg which reached the "middle" pollution level, and Cu, Ni, Pb, As, Zn, and Cr were found to be of low ecological risk. Index values were found to be the lowest after flood events, suggesting that rainwater washes out metal concentrations.

Pb and Hg concentration frequency value was 100 and 93 % for PEC and TEC criteria interval, respectively. Sediment samples exceeded 14 % of the PEC criteria for Cr, 50 % of the sediments for Ni, and 14 % for As. Sediment samples comply for 100 % with the TEC criteria for Pb, 14 % for Ni, and only 7 % for Cd. Concerning the non-priority heavy metals, 7 % of the samples comply with TEC criteria for As and 43 % for Cr. Heavy metal pollution classification is ranging between low and medium low and is consistent to one based on aquatic physicochemical and ecological parameters that classify the main river part (upstream and downstream of WWTP and Vrontamas) in the "moderate" quality class as regards the ecological quality. Lead concentrations of sediment did not overcome the TEL and ERL threshold (Fig. 4). Mercury and arsenic concentrations comply both with thresholds by 85.7 %.

Table 5 Heavy metal (Ni, Cd, Hg, Pb, Cr, Zn, As, Cu) enrichment factors in Evrotas sediments (contamination characterization in parenthesis)

		mCd	EF(FE)	EF(Al)	Igeo	RI potential ecological risk degree
Low flow 2009	3-Upstream WWTP	15.9(extremely high)	13.1(severe)	21.5(very severe)	0.89(unpoll.)	49(low)[a]
	4- Downstream WWTP	0.94(low)	1.0(unpoll.)	1.1(unpoll.)	0.0(unpoll.)	1(low)
	5-Vrontamas	8195(extremely high)	7686(extremely high)[b]	6170(extremely high)[b]	1.03(unpoll.)	19,666(extremely high)[b]
High flow 2010	2-Sentenikos	20.7(extremely high)	0.4(unpoll.)	0.4(unpoll.)	3.14(strongly polluted)	8(low)
	3-Upstream WWTP	0.88(low)	1.0(unpoll.)	0.3(unpoll.)	−1.06(unpoll.)	1(low)
	4-Downstream WWTP	0.95(low)	0.3 (unpoll.)	0.2(unpoll.)	−0.97(unpoll.)	1(low)
	5-Vrontamas	1.29(low)	0.2(unpoll.)	0.1(unpoll.)	−0.78(unpoll.)	1(low)
Low flow 2010	2-Sentenikos	1369(extremely high)	350(extremely high)[b]	565(extremely high)[b]	2.58(moderate)	3284(extremely high)[b]
	3-Upstream WWTP	2.54(moderate)	0.5(unpoll.)	1.2(unpoll.)	−0.05(unpoll.)	1(low)
	4-Downstream WWTP	2.25(moderate)	0.5(unpoll.)	1.3(unpoll.)	1.47(moderate)	1(low)
	5-Vrontamas	0.72(low)	0.5(unpoll.)	1.2(unpoll.))	−0.2(unpoll.)	1(low)

mCd modified degree of contamination, *EF* enrichment factor, *Igeo* geoaccumulation index, *RI* risk index, *WWTP* wastewater treatment plant

[a] Mercury had middle pollution degree and the rest of heavy metals low pollution degree

[b] Cadmium had extremely high pollution degree and the rest of heavy metals low pollution degree

Heavy metals exceeded the thresholds in the sediment in the order Ni>Cr>Cd>As>Hg>Pb.

Overall, levels of heavy metals in river water samples (Table 3) comply with the drinking water criteria with the exception of Hg (mean concentration 13.1 $\mu g\ L^{-1}$). Cd and As content was below the detection limit for the period 2009–2010 in all sites, and the mean concentrations of Ni, Pb, Cr, Cu, and Zn were 1.12, 0.05, 0.11, 3.68, and 32.2 $\mu g\ L^{-1}$, respectively. Moreover, heavy metal concentrations showed small seasonal variation and slightly increased following flood events, as it is shown in Fig. 5 for water samples taken in site downstream from the wastewater treatment plant.

4 Discussion

The nutrient and organic carbon content of the sediments sampled during different hydrological phases indicated a low trophic status, when compared to the values reported for other Mediterranean temporary river basins (Tzoraki et al. 2007). To date, there are limited field monitoring studies reporting the occurrence of PAHs (Zoppini et al. 2014) and heavy metals in temporary river sediments. Nevertheless, even the highest measured PAH concentration in our samples (ΣPAHs=195.4 ng g^{-1}) was within the lower range of values reported for sediments of permanent north European (6–96,000 ng g^{-1}) (Liu et al. 2013b) or Chinese rivers (Haihe River (259–11,297 ng g^{-1}) (Liu et al. 2013a) and Xiangjiang River (190–983 ng g^{-1}) and similar to PAH content in sediments of Czech rivers (1.2–15.2 ng g^{-1}). For Greece, this is the first study on PAHs in river sediments, and freshwater lotic data are not available for comparison. PAH data are available only in lentic environments, where concentrations were higher in Lake Pamvotis (34.7–1600 ng g^{-1}) (Daskalou et al. 2009) and Lake Koumoundourou sediments (280–3400 ng g^{-1}) (Hahladakis et al. 2012) in comparison to those in Evrotas River sediments. Furthermore, Evrotas

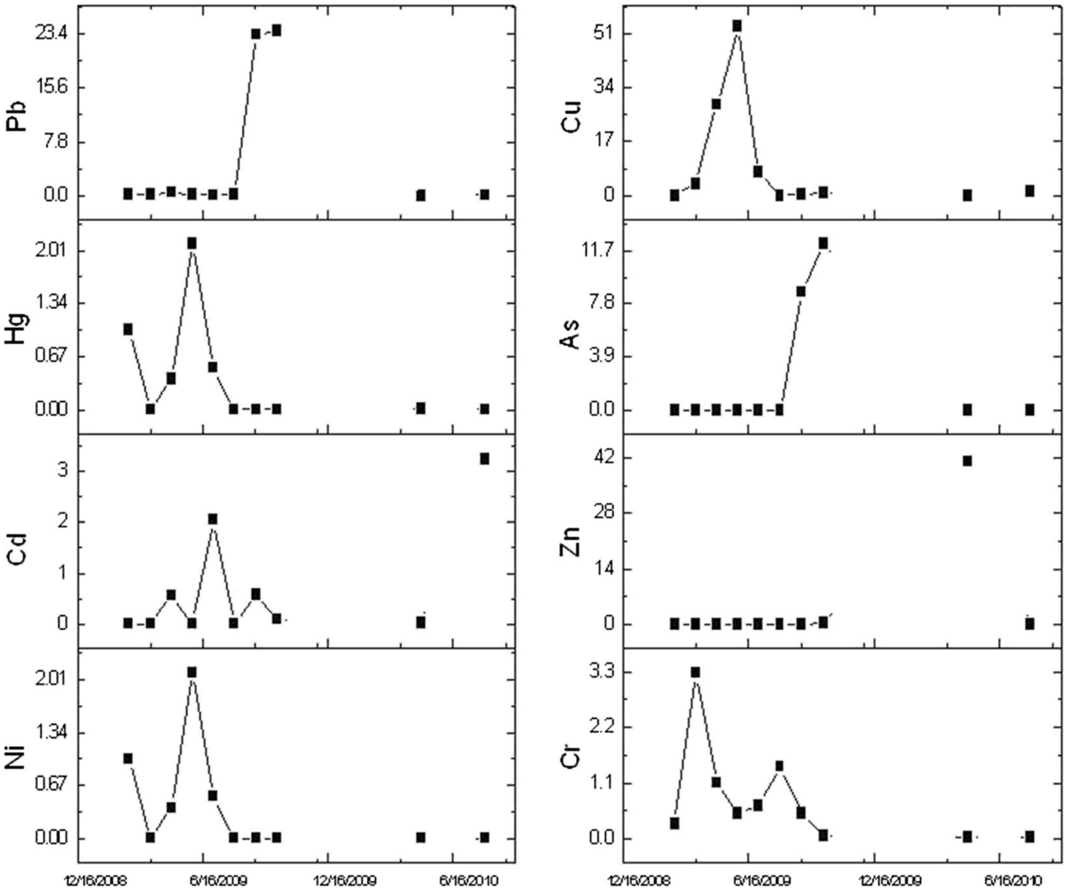

Fig. 4 Distribution of heavy metals (%) in all sediment samples complying with threshold effect level (TEL) and to effects range low (ERL) criteria

PAH content can be considered as low polluted when compared to that found in marine sediments of Greek coastal areas(44–26,000 ng g^{-1}) (Botsou and Hatzianestis 2012; Gonul and Kucuksezgin 2012; Hahladakis et al. 2012; Papadopoulou and Samara 2002). Similarly, the average ΣPAH concentration (ΣPAHs=24.4 ng g^{-1}) was lower than the limits reported for TEC (Table 1) and lower than the values found in unpolluted or moderately polluted river sediments (Yellow River in China, 11–252 ng g^{-1}) (Wang et al. 2012). The observed concentration of PAHs in the Evrotas basin was compared with ERL (threshold of total PAH concentrations 4000 ng g^{-1}). Results in this survey showed that the sum of PAH concentrations at all sites never exceeded 195.4 ng g^{-1}, with an average value of 24.4 ng g^{-1} significantly below all quality standard values reported in Table 1 also considering the concentrations of individual congeners; hence, we can classify Evrotas sediments as low polluted (Fu et al. 2011), indicating that their PAH content should not cause biological impairment. However, we must remember that some PAHs are of great concern due to their documented carcinogenicity and environmental persistence (i.e., BaP, BbF, BkF, and InP). The concentration of these compounds in sediments from the Evrotas River varied between <limit of detection (lod) to 20.4 ng g^{-1} and represented between 10 and 40 % of the total PAH concentrations. Currently, the only available references for freshwater sediment quality are the Canadian Quality Guidelines (CCME 2003) that report a list of substances and their interim sediment quality guidelines (ISQGs). On the basis of this list, the concentration of BaP observed in this survey was in all sites in the lower level of those recommended (threshold 31.9 ng g^{-1}), whereas Flu concentration exceeded the threshold value (TEL) of 110.0 ng g^{-1} only in the site downstream the WWTP (Flu=147.2 ng g^{-1}). However, the concentrations measured of these two compounds

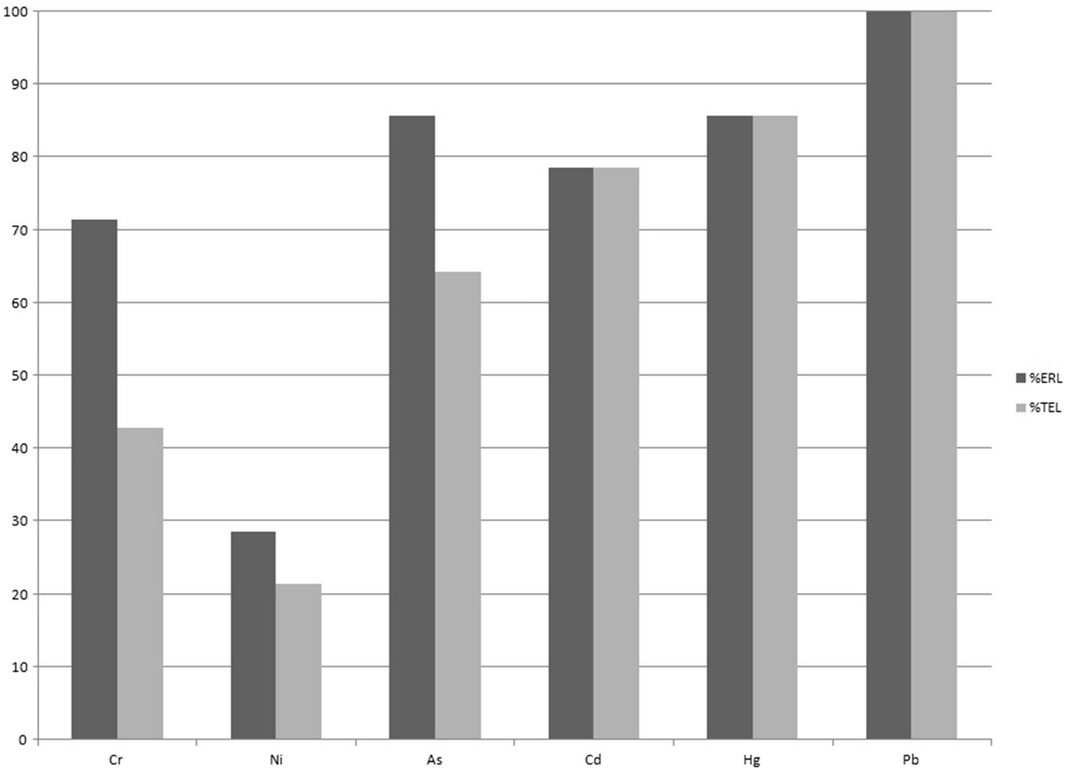

Fig. 5 Dissolved heavy metal concentrations (μg L^{-1}) in relation to time downstream from the wastewater treatment plant

are lower than the TEC (423 ng g^{-1} for Flu and 150 ng g^{-1} for BaP). Regarding the other PAH congeners, at present, there are no threshold limits in riverine sediments.

Considering the PAH isomer ratios observed in Evrotas sediments (see Sect. Concentration of PAHs in Sediment), a mixed pattern of PAH sources can be suggested. Most of the calculated indices point to a pyrolytic source for the PAHs in the studied area, where combustion of fossil fuels seems to be the principal input. The higher value of PAHs recorded in the site downstream from the WWTP especially in 2009 (see Table 2) is most probably due to urban runoff and the coal combustion in the power plant at the N-E boundaries of the basin. Much evidence has shown that PAHs, produced during anthropogenic combustion processes, appear to be delivered uniformly to remote sites via atmospheric particulate transport. Terrestrial runoff is also an important route of PAHs into the aquatic environment.

Sediments sampled at the same site but at different hydrological conditions showed differences in the ΣPAH concentrations (Table 2). The sediment analyzed in 2009 under low-flow conditions showed the highest ΣPAH concentrations, while in 2010, both at high- and low-flow conditions, a similar drastic decrease of concentrations was observed in all samples from the river stretch. The discrepancy between data collected in 2 consecutive years (2009 and 2010) under similar hydrological conditions (low flow) can be explained by the washing or diluting effects played by the high discharges measured on October 2010 (Fig. 2). This high flow peaks are connected with runoff events, as it is demonstrated by the deposition of elements connected with crustal particles (e.g., Ca, Fe, and Mn; see Table 3), but the runoffs did not bring PAH and, on the contrary, diluted or washed organic compounds already accumulated in the sediment. The occurrence of peak flow events implies a high presence of suspended solid matter from terrestrial origin, as well the re-suspension of sediments by turbulence and the transport of the associated PAHs downstream. On the contrary, when low-flow conditions are distant from previous flood events (as in the case of July 2009 sampling, Fig. 2), suspended matter settling and PAH particle–associated storage into the sediments are favored (Table 2).

The metal burden in the freshwater bodies in Greece is generally low (Lekkas et al. 2004). The heavy metal content of Evrotas was in the lower limits of other Greek rivers. For instance, the mean Pb value in Evrotas for the period 2009–2010 was 1.12 μg L^{-1}, which is in the lower limit of the 11 major Greek rivers (range 1.4–147.8 μg L^{-1}). Cu and Cr concentrations were 3.68 and 0.11 μg L^{-1}, lower than the values found in some Greek rivers (Cu 0.9–80.4 μg L^{-1}; Cr 0.5–137 μg L^{-1}) reported in the study of Lekkas et al. (2004). High Hg values were estimated in Evrotas River both in low- (1.44–>21.95 μg L^{-1}) and in high-flow period (5.75–94.3 μg L^{-1}) that exceed EQSs for freshwater (Hg EQS 0.05 μg L^{-1}). A slight increase in Hg water content was observed downstream the wastewater treatment plant, probably due to the mixing of freshwater with the reclaimed water. The overall contamination of heavy metals in the region is classified as low to moderate with significantly contaminated subareas in specific time periods. Crustal elements (i.e., K, Si, and Fe) show higher dissolved values in the high-flow period and lower values in the low-flow period.

Sediments revealed relatively variable distribution of heavy metals with higher hot spot pollution for Hg and Cd, which appear moderate and extremely high potential ecological risk accordingly, even though their concentrations exceed ERL and TEL criteria only 14.3 and 21.4 %. Both metals showed higher values in the sediment matrix during low-flow periods. Possible heavy metal sources could be insecticides and fungicides (source of Hg, Cd, Cu, Pb) since the area is intense cultivated, electrical batteries (Ni-Cd), lubricating and diesel oils (Cd), urban runoff (Cd, Zn), equipment (Hg), etc. (Bednarova et al. 2013).

Several studies used indexes estimated by bulk heavy metal concentration in combination with other assessing models. Li et al. (2013) combined SQGs with RI and cluster analysis to assess Hg contamination of Dongting Lake in Middle China. Cui et al. (2014) accompanied RI classification with speciation studies which are more associated with active and mobilizable fraction and principal component analysis and Pearson analysis to understand heavy metal origin and transport pathway of Wayer river in China. RI index classification was found reliable with measurement of anthropogenic origin metals on pheriphyton in natural ecosystems (Zhang and Liu 2014). RI index assessed the ecological risk of Evrotas River for Hg and Cd in comparison to Igeo and mCd.

EF index normalized by Al or Fe eliminates potential bias caused by the differences in grain size distribution. The EF for natural background concentration is equal to 1. EF index for Evrotas appeared as high values for Hg and Cd metals and is consistent with the potential ecological risk degree. The high values of EF for Hg and Cd identify the influence of anthropogenic sources. EF index is found reliable for Hg and Cd risk that their dissolved values exceed EQSs for freshwater. Important also is the pollution related to Zn downstream the WWTP and in Vrontamas area. EF index is significant in differentiating the pollution originated by human activities or background heavy metal occurrence in each area and should be used in conjunction to sediment quality standard criteria to prevent misinterpretation of the pollution assessment that could come from simple comparison of the measured metal concentrations to sediment quality guidelines.

For instance, Ni natural background concentration in the reference site (76.9 mg kg^{-1}) is very close to the sediment quality standard of Table 1 (15.9–48.6 mg kg^{-1}). Thus, when using the sediment EQS, about 86 % of the samples were identified as exceeding TEC criteria, despite the fact that there is very low enrichment of Ni compared to the natural background (EF(FE) average 0.91 and EF(AL) 0.85). This underlines the fact that quality indicator indexes, especially those that consider the natural background, should be taken into account together with the comparison to the sediment EQSs. Therefore, selecting to account the natural background, it is suggested the use of RI index which estimates the pollution degree in relation to the individual metals in comparison to the EF normalized index.

5 Conclusions

The pollution of Evrotas River from some priority substances and particularly heavy metals (cadmium, nickel, lead, mercury), polycyclic aromatic hydrocarbons (PAHs), and some non-priority substances (such as arsenic, chromium, copper, and zinc) was evaluated. Due to low organic carbon content of Evrotas sediments and the absence of any ecotoxicological data, the third option for EQS derivation of 2008/105/EC directive, meaning the “empirical field or mesocosm data,” was selected. Natural background level for heavy metals was estimated for pristine areas differentiated by the

Reference Conditions Protocol developed in MIRAGE-ToolBox. The concentrations of heavy metals and PAHs detected in Evrotas sediments were very low, whereas their concentrations ranged at low levels and were increased in a limited number of sites mainly due to human activities. This fact can be attributed also to the very low carbon content of the sediments. PAHs were detected in all sampling sites but can be considered as a low pollution regarding to values generally found in freshwater sediments. According to common sediment enrichment factors of heavy metal contamination, Evrotas can be characterized as "low polluted" with some exceptions of "extremely polluted." Heavy metal content in the sediments decreased during high-flow conditions, due to the high river washout behavior, but without any significant impact into the river water quality. Significant values of cadmium (106.8 ng g^{-1}) and mercury (3.07 ng g^{-1}) were found sporadically in river sediments most probably due to un-controlled disposal of human wastes. EQS classification of Evrotas sediments is not found consistent with the SQI classification. In order to consider the natural background heavy metal concentrations, EQS classification is suggested to be accompanied to the Hakansons' potential ecological risk index or EF index even that is not foreseen by 2008/105/EC directive. If EQSs and Hakansons' or EF index are used together, then a preliminary ecorisk assessment of various ecological units (i.e., rivers, lakes, and reservoirs) can be achieved. These indexes can be applied to distinguish patterns and classify the ecological risk in order to proceed in speciation studies accompanied with complementary studies (i.e., principal component analysis, Pearson analysis, and AVS) to understand pollutant interrelationship, origin, and transport pathways.

Sediments can be considered as a valuable matrix in spatial and temporal trends of several contaminants of temporary rivers. The representativeness of sediments strongly depends on the hydrological regime. Sampling period should be planned in the low-flow period in order to diminish any disturbance by flash flood events, but it is important also to take into account the hydrological conditions before the sampling period. As much as possible, it is better to plan the sampling campaigns in the same time window every year, under similar flow conditions. Frequency of sediment sampling can be maintained once per year, as minimum Water Framework Directive (Directive 2000/60/EC) requirement; however, one should take care to sample at the end of the winter or at the beginning of the spring before the summer dry period and autumnal rainfall, as thoroughly discussed in previous papers (Nikolaidis et al. 2013; Prat 2013). The high interannual sediment variability observed in this temporary river basin prevents also from using sediment as the matrix for trend monitoring.

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