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10 **Toxicity assessment of polycyclic aromatic hydrocarbons in sediments**

11 **from European high mountain lakes.**

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17

18   **Abstract**

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20   Sediment quality guidelines and toxic equivalent factors have been used for assessment

21   of the toxicity of sedimentary long-range atmospherically transported polycyclic

22   aromatic hydrocarbons (PAHs) to the organisms living in high mountain European

23   lakes. This method has provided indices that are consistent with experimental studies

24   evaluating in situ sedimentary estrogenic activity or physiological response to AhR

25   binding in fish from the same lakes. All examined lakes in north, central, west,

26   northeast and southeast European mountains have shown sedimentary PAH

27   concentrations that are above thresholds of no effect but only those situated in the

28   southeast lakes district exhibited concentrations above the indices of probable effects.

29   These mountains, Tatras, are also those having PAH concentrations of highest activity

30   for AhR binding. Chrysene+triphenylene, dibenz[a]anthracene, benzo[k]fluoranthene

31   and indeno[1,2,3-cd]pyrene are the main compounds responsible for the observed toxic

32   effects.

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35   **Key words**. Polycyclic aromatic hydrocarbons. High mountain lakes. Toxic effects.

36   Estrogenic effects. Activity to AhR binding. Sediment quality guidelines. Toxic

37   equivalent factors.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) occur in remote environments as consequence of incomplete combustion of fossil fuels or organic materials during industrial, urban or rural activities. Due to their continuous emission and chemical properties, i.e., semi-volatility and hydrophobicity, they occur ubiquitously in the environment and can be transported to long distances (Ding et al., 2007; Ravindra et al., 2008).

Recent reports have shown that remote ecosystems such as high mountain lakes may trap PAHs and other atmospherically transported pollutants (Fernández et al., 1999; Fernández et al., 2000; Barra et al., 2006). In these environments the PAH concentrations found in lake sediments are sometimes comparable to those found in soils or lake sediments located close to urban or industrial areas. These mountain ecosystems contain plant and animal communities of great ecological value that are sensible to external alterations by stressors such as pollutants (Sommaruga, 2001).

PAHs have well documented toxicity in a variety of organisms. However, the degree of understanding of the toxic effects of these pollutants in high mountain ecosystems is very limited. Garcia-Reyero et al. (2005) evaluated the estrogenic activity of surficial and bottom sediments from European mountain lakes using a recombinant yeast assay. They found that sediments showing highly estrogenic activity were significantly enriched in PAHs. This approach involved great technical and logistic efforts.

Other procedures encompass the use of sedimentary species that are sensitive to specific pollutant exposures and examination of their survival thresholds. Thus, *Chydorus sphaericus* had been proposed as test species for exposure to diverse metals

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63   (Koivisto et al., 1992; Dekker et al., 2002; Bossuyt and Janssen, 2005). This type of

64   toxicity information is generally limited to effects of metals.

65   Ecological risk assessment provides another framework for estimating the toxic

66   effect of sedimentary pollutants in lake organisms. Sediment quality guidelines (SQGs;

67   CCME, 1999) have recently been used for identification of zones with major

68   toxicological risk (Qiao et al., 2006; Colombo et al., 2005; Gomez-Gutierrez et al.,

69   2007). A procedure for toxicity estimation of high mountain lakes based on SQCs is

70   proposed in the present study. Additionally the dioxin-like toxicity ratios based on

71   binding to Ah receptor (Barron et al., 2004) and expressed in toxic equivalent factors

72   (TEFs) have also been used. This approach has allowed the comparison of the potential

73   toxicological effect of PAHs in sediment from European mountain lakes and the

74   identification of lakes and zones of highest toxicological risk.

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77   **2. Methods**

78   *2.1. PAH concentrations*

79   PAH concentrations (10 compounds) in surficial sediments of twelve high

80   mountain lakes (Figure 1) determined in Fernandez at al. (1999) have been used to

81   estimate sediment toxicity based on SQCs and TEFs methods. PAH concentrations in

82   surficial sediment of the lakes Negru and Bubreka have been analyzed additionally in

83   the present study because PAH data on high mountain lakes from southeast Europe

84   were not available.

85   Sampling and analysis were as described in Fernandez et al (1999). Briefly,

86   sediment cores were divided in 0.25 cm sections (0.1-0.5 g), wrapped in aluminium foil

87   and stored frozen at –20ºC. They were extracted by sonication with methanol (1x20 ml;

88   20 min) and subsequently with dichloromethane-methanol (2:1; 3x20 ml; 20 min). The

89   combined extracts were spiked with perdeuterated PAHs: anthracene-d_{10}, pyrene-d_{10},

90   and benzo[*ghi*]perylene-d_{12}. Then, they were vacuum evaporated to 10 ml and

91   hydrolyzed overnight (20 ml of 6% KOH in methanol). The neutral fractions were

92   recovered with n-hexane (3x10 ml), vacuum evaporated and transferred to a glass

93   column (35 cm x 0.9 i.d.) packed with 2 g of activated aluminium oxide (120ºC

94   overnight). Two fractions were collected: 5 ml of n-hexane:dichloromethane (19:1) and

95   10 ml of n-hexane:dichloromethane (1:2; PAH). The PAH fractions were vacuum and

96   nitrogen concentrated and redissolved in iso-octane for instrumental analysis. Perylene-

97   d_{12} was added as internal standard for the injection.

98   The aromatic fractions were analysed by GC (Carlo Erba GC8000 Series)

99   coupled to a mass spectrometer (Fisons MD800). A 30 m HP-5MS column (0.25 mm

100   i.d. x 0.25 μm film thickness) was used. The oven temperature program was started at

101   90ºC (held for 1 min) and increased to 120ºC at 15ºC/min, and then to 300 ºC at

102   4ºC/min, held for 10 min. Injector, transfer line, and ion source temperatures were 280,

103   300, and 200ºC, respectively. Helium was the carrier gas (1.1 ml/min). The injector

104   operated in the splitless mode (48 s). Data were acquired in the electron impact mode

105   (EI, 70 eV ionization energy). PAHs were determined in selected ion recording mode.

106   The following diagnostic ions were chosen: m/z 166, 178, 202, 228, 252, 276, and 278

107   for PAH and 188, 212, 264, and 288 for perdeuterated standards (dwell time 40 ms per

108   single ion, mass windows defined according to the retention times of individual PAH in

109   the standard mixture). PAH identification was performed by m/z peak matching to

110   retention time to reference standards, and comparison to literature Lee retention indices

111   (Benner et al., 1995; Lee et al., 1979). Quantitative data were obtained by the external

112   standard method (EPA mix 16, Dr Ehrenstorfer). Compounds lacking reference

113   standard (acephenanthrylene, benzo[*e*]pyrene, and perylene) were quantified using the

114   response factor of the standard exhibiting the closest retention time. Reported values

115   were corrected by surrogate recoveries as follows: anthracene-d_{10} for compounds having

116   signals at ions m/z 166 and 178; pyrene-d_{10} for compounds at m/z 202 and 228; and

117   benzo[*ghi*]perylene-d_{12} for compounds at m/z 252, 276 and 278. Recoveries for the

118   overall procedure based on surrogate data were typically anthracene-d_{10} 62 ± 18 %,

119   pyrene-d_{10} 70 ± 18 %, and benzo[*ghi*]perylene-d_{12} 72 ± 12% (*n* = 37).

120   The whole analytical procedure was successfully calibrated with a standard

121   reference material with certified PAH values (marine sediment HS-4, Institute for

122   Marine Biosciences, Canadian National Research Council).

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124   *2.2. Sediment quality guidelines*

125   Ecological risk was assessed by comparison with SQCs of the Canadian Council

126   Minister of Environment (CCME, 1999). The concentration values of the interim

127   sediment quality guidelines (ISQGs) and probable effect levels (ng/g dw) for freshwater

128   sediment are shown in Table 1. According to this Table acephenanthrylene and

129   dibenz[*ah*]anthracene are the compounds with highest toxicity potential. Two toxicity

130   unit indices per lake sediment have been generated from these reference values. TU1

131   was calculated from the summed ratios between each individual PAH concentrations

132   and the corresponding ISQGs and TU2 from the summed ratios between individual

133   PAH concentrations and the probable effects levels (PELs). Summation gives a rough

134   estimate of the toxicity of the whole PAH distribution. This approach assumes that toxic

135   PAH effects are additive (DiToro and McGrath, 2000). While TU1 is measuring the

136   deviation of the distribution from a reference of no effect, the second is assessing

137   whether toxic effects will be observed according to the sedimentary PAH content.

2.3. Dioxin-like toxicity approach

TEFs (Barron et al., 2004) have also been used to estimate dioxin-like toxicity expressed in toxic PAH equivalents (TEQs-PAHs). These factors have been calculated from the ratio between the activities of each individual PAH and that of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) as AhR agonists. Activity values were obtained from data on CYP1A induction or AhR binding for 74 PAHs in teleost avian or mammalian systems. The reference activity of TCDD was set to one (Barron et al., 2004). In each lake sediment TEQs-PAHs were calculated from the sum of the products of pollutant concentrations of each individual PAH and the corresponding TEFs.

3. Result

Lakes were grouped in European districts according to geographical location: west (Maam, Escura, Cimera, La Caldera and Redo), central (Noir, Schwarsee ob Solden and Gossenkollesee), northeast (Dlugi and Starolesnianske), southeast (Bubreka and Negru) and north (Øvre Neadalsvatn and Arresjøen) (Figure 1).

The PAH distributions are dominated by parent compounds, from phenanthrene to coronene, with a predominance of high molecular weight compounds of catacondensed structures (Fernandez et al., 1999; 2000).

3.1. Toxicity levels

The TU1 values for each high mountain lake included in Figure 1 have been calculated from the ISCQs (Figure 2). This index indicates the deviation of sedimentary PAH content from the level of no effect. All lakes had total TU1 values higher that one

164   indicating that PAH concentrations in these sediments exceeded the levels of no effect.

165   The TU1 values were lower in lakes from central, west and north lakes districts,

166   between 2 and 10. The highest values were found in the northeast lakes district, 132 and

167   173 for Dlugi and Starolesnianske Pleso, respectively. The lakes in the southeast lakes

168   district, Bubreka and Negru, exhibited intermediate values, 8 and 16, respectively.

169   The TU2 values for each high mountain lake included in Figure 1 have been

170   calculated from the PELs (Figure 3). This index reveals PAH contents for which effects

171   on organisms are likely. Total TU2 values in central, north and west lakes districts were

172   lower than 1 indicating unlikely PAH effects on organisms. The only lakes in which

173   total TU2 levels were higher than 1 were those in the northeast district, 7.8 and 10.0 in

174   Dlugi and Starolesnianske Pleso, respectively. In the southeast lakes district TU2 values

175   showed variable results between lakes, lower than 1 in Negru but nearly 1 in Brubeka.

176   These results indicate probable toxic PAH effects in the lakes from the northeast district

177   and possible toxicity related with these hydrocarbons in Brubeka.

178   Calculation of the TEQs-PAHs for the lakes included in Figure 1 shows that the

179   sediments from the lakes located in the northeast district are those with highest activity

180   for AhR binding (Figure 4). The lakes from the north, west, central and southeast

181   districts exhibit much lower values. Benzo[k]fluoranthene and indeno[1,2,3-cd]pyrene

182   are the compounds contributing the most to the activity for AhR binding in these lakes,

183   representing about 84% of total activity (Figure 4).

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186   **4. Discussion**

187   *4.1. PAHs concentrations in high mountain lakes.*

The uniform sedimentary PAH profile found in all lakes exhibits a high parallelism with the PAH composition in the atmospheric aerosols collected at these high altitude sites (Fernandez et al., 2003). This profile is quite ubiquitous and has been reported in sediments from remote/rural areas (Sanders et al., 1993) or in sites where organic pollutant inputs are mainly related to atmospheric transport and deposition (Simcik et al., 1996; Simo et al., 1997). The lakes with lower levels were those located at the periphery, e.g. Arresjøen, Cimera and La Caldera (150-210 ng/g). The lakes situated in more central sites, Pyrenees, Alps, Scandinavia, Retezat and also some of the periphery –Escura and Maam-, exhibited concentrations in the 430-910 ng/g range. These levels are significantly lower than those in the Tatra mountains, 13,000-18,000 ng/g. Brubeka, in the Rila mountains, exhibited intermediate values, 1,300 ng/g, among these two last groups (23 PAH, Fernandez et al., 1999).

4.2. Toxicity Unit levels

Phenanthrene, chrysene+triphenylene and dibenz[*ah*]anthracene were the main PAH determining the TU1 values with average contributions of 14%, 17% and 22%, respectively. Comparison of PAH concentrations and TU1 values according to number of aromatic rings in all lakes (Figure 5) shows higher relative abundance of the PAHs with 3 rings but a more even contribution of all PAHs to the observed TU1 values. Dispersion between PAHs levels was lower than between TU1 values.

Comparison of PAH concentrations and TU2 values according to number of aromatic rings in all lakes (Figure 6) shows higher relative abundance of the PAHs with 3 rings but higher contribution of PAHs with four aromatic rings to TU2 values. The dispersion of values between PAH concentrations was lower than between TU2 levels.

212   The PAHs contributing the most to the high TU2 values in the northeastern lakes

213   district were chrysene+triphenylene (concentration/PEL 1.7 and 2.1 in Dlugi and

214   Starolesnianske Pleso, respectively), and dibenz[*ah*]anthracene (concentration/PEL 1.4

215   and 1.8 in Dlugi and Starolesnianske Pleso, respectively). These two hydrocarbons

216   exhibited concentrations above the PEL values (Table 1) in Dlugi. In Starolesnianske

217   Pleso other PAHs are also above this level such as pyrene and benz[*a*]anthracene

218   (concentration/PEL 1.5 and 1.1, respectively). The concentration of benzo[a]pyrene is

219   also very close to its PEL value in this lake. In Brubeka no individual PAH

220   concentration is above the corresponding PEL value. The highest concentration/PEL

221   ratios are found for pyrene, phenanthrene and chrysene+triphenylene.

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223   *4.3. TEQs-PAHs levels*

224   A study of the physiological response to dioxin-like compounds in fish

225   inhabiting in European high mountain lakes based on the analysis of Cyp1A gene

226   expression showed that among the PAH included in Table 1, chrysene+triphenylene,

227   benzofluoranthenes and indeno[1,2,3-cd]pyrene were those with highest correlation to

228   Cyp1A expression levels (Quiroz et al., 2007). Another study in which sediment

229   extracts were assayed by recombinant yeast analysis for estimation of estrogenic

230   activity (Garcia-Reyero et al., 2005) showed that benzofluoranthenes,

231   chrysene+triphenylene and indeno[1,2,3-cd]pyrene were the three PAHs in highest

232   concentration in the extracts with highest estrogenicity. The results of these two

233   previous independent experimental studies are in agreement with the estimations of the

234   present one based on TU2 and TEQs-PAH values.

235   Compilation of these TU1, TU2 and TEQs-PAHs indices has allowed to

236   identifying toxic marine hot spots due to PAH concentrations in the vicinity of

237   industrial and urban locations (Gomez-Gutierrez et al. 2007). Now, the present study

238   identifies the northeast lakes district in the Tatra mountains as a continental hot spot.

239   These results are consistent with previous reports showing high concentrations of these

240   hydrocarbons in the lakes from this area (Fernández et al., 1999; Fernández et al., 2000)

241   but now their toxicity to organisms is assessed. PAHs are long-range transported

242   through the atmosphere, mostly in association with particles (Masclet et al., 1988;

243   Aceves and Grimalt, 1993; Allen et al., 1996). Emissions of these compounds in the

244   vicinity of these mountains may be responsible for the probable toxic PAH effects

245   resulting from compilation of the TU2 and TEQ-PAH indices.

246   UV radiation in mountain areas can enhance PAH toxicity due to the formation

247   of polar derivatives that are more toxic than the parent compounds (Sommaruga, 2001).

248   Photoinduced PAH toxicity has not yet been studied in organisms from high mountain

249   lakes but it could enhance even further the environmental risk for the occurrence of

250   these compounds in these ecosystems (Oris et al., 1990).

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253   **5. Conclusions**

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255   The approach developed in the present study for risk assessment of the PAH

256   exposure in high mountain lake sediments provide indices that are consistent with

257   experimental studies evaluating in situ estrogenic activity in sediment extracts or

258   physiological response of fish inhabiting in these lakes to AhR binding. All examined

259   lakes in north, central, west, northeast and southeast European mountains have shown

260   sedimentary PAH concentrations that are above thresholds of no effect. However, only

261   those situated in the northeast lakes district exhibit concentrations above the indices of

262 probable effects levels. These mountains, Tatras, are also those having PAH
263 concentrations of highest activity for AhR binding.

264   PAH present in these environments have been incorporated from long-range
265 atmospheric transport. The high concentrations of these hydrocarbons in the northeast
266 lakes district may be originated from regional sources. Chrysene+triphenylene,
267 dibenz[a]anthracene, benzo[k]fluoranthene and indeno[1,2,3-cd]pyrene are the main
268 compounds responsible for these toxic effects.

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279 **References**

280

281 Aceves, M., Grimalt, J.O., 1993. Seasonally dependent size distributions of aliphatic
282   and polycyclic aromatic hydrocarbons in urban aerosols from densely populated
283   areas. Environ. Sci. Technol. 27, 2896-2908.

284 Allen, J.O., Dookeran, N.M., Smith, K.A., Sarofim, A.F., Taghizadeh, K., Lafleur, A.L.,
285   1996. Mesurement of Polycyclic Aromatic Hydrocarbons Associated with Size-
286   Segregated Atmospheric Aerosols in Massachusetts. Environ. Sci. Technol. 30,
287   1023-1031.

288   Barra, R., Popp, P., Quiroz, R., Treutler, H.-C., Araneda, A., Bauer, C., Urrutia, R.,

289   2006. Polycyclic aromatic hydrocarbons fluxes during the past 50 years

290   observed in dated sediment cores from Andean mountain lakes in central south

291   Chile. Ecotoxicol. Environ. Safety 63, 52-60.

292   Barron, M.G., Heintz, R., Rice, S.D., 2004. Relative potency of PAHs and heterocycles

293   as aryl hydrocarbon receptor agonists in fish. Mar. Environ. Res. 58, 95-100.

294   Benner, B. A., Wise, S.A., Currie, L.A., Klouda, G.A., Klinedinst, D.B., Zweidinger,

295   R.B., Stevens, R.K., Lewis, C.W., 1995. Distinguishing the contributions of

296   residential wood combustion and mobile source emissions using relative

297   concentrations of dimethylphenanthrene isomers. Environ. Sci. Technol. 29,

298   2382-2389.

299   Bossuyt, B.T.A., Janssen, C.R., 2005. Copper toxicity to different field-collected

300   cladoceran species: intra- and inter-species sensitivity. Environ. Pollut. 136, 145-

301   154.

302   CCME, 1999. Canadian Environmental Quality Guidelines. Canadian Council of

303   Minister of Canadian Environmental Quality Guidelines. http: //www.ec.gc.ca..

304   Colombo, J.C., Cappelletti, N., Lasci, J., Migoya, M.C., Speranza, E., Skorupka, C.N.,

305   2005. Sources, Vertical Fluxes, and Accumulation of Aliphatic Hydrocarbons in

306   Coastal Sediments of the Rio de la Plata Estuary, Argentina. Environ. Sci.

307   Technol. 39, 8227-8234.

308   Dekker, T., Krips, O.E., Admiraal, W., 2002. Life history changes in the benthic

309   cladoceran Chydorus piger induced by low concentrations of sediment-bound

310   cadmium. Aquat. Toxicol. 56, 93-101.

311   Di Toro, D.M.D., McGrath, J.A., 2000. Technical basis for narcotic chemicals and

312   Polycyclic Aromatic Hydrocarbon criteria. II. Mixtures and sediments. Environ.

313   Toxicol. Chem. 19, 1971-1982.

314   Ding, X., Wang, X.-M., Xie, Z.-Q., Xiang, C.-H., Mai, B.-X., Sun, L.-G., Zheng, M.,

315   Sheng, G.-Y., Fu, J.-M., Pöschl, U., 2007. Atmospheric polycyclic aromatic

316   hydrocarbons observed over the North Pacific Ocean and the Arctic area: Spatial

317   distribution and source identification. Atmos. Environ. 41, 2061-2072.

318   Fernandez, P., Carrera, G., Grimalt, J.O., Ventura, M., Camarero, L., Catalan, J.,

319   Nickus, U., Thies, H., Psenner, R., 2003. Factors governing the atmospheric

320   deposition of polycyclic aromatic hydrocarbons to remote areas. Environ. Sci.

321   Technol. 37, 3261-3267.

322   Fernández, P., Vilanova, R.M., Grimalt, J.O., 1999. Sediment Fluxes of Polycyclic

323   Aromatic Hydrocarbons in European High Altitude Mountain Lakes. Environ.

324   Sci. Technol. 33, 3716-3722.

325   Fernández, P., Vilanova, R.M., Martínez, C., Appleby, P., Grimalt, J.O., 2000. The

326   Historical Record of Atmospheric Pyrolytic Pollution over Europe Registered in

327   the Sedimentary PAH from Remote Mountain Lakes. Environ. Sci. Technol. 34,

328   1906-1913.

329   Garcia-Reyero, N., Piña, B., Grimalt, J.O., Fernandez, P., Fonts, R., Polvillo, O.,

330   Martrat, B., 2005. Estrogenic Activity in Sediments from European Mountain

331   Lakes. Environ. Sci. Technol. 39, 1427-1435.

332   Gómez-Gutiérrez, A., Garnacho, E., Bayona, J.M., Albaigés, J., 2007. Screening

333   ecological risk assessment of persistent organic pollutants in Mediterranean sea

334   sediments. Environ. Internat. 33, 867-876.

335 Koivisto, S., Ketola, M., Walls, M., 1992. Comparison of five cladoceran species in

336   short- and long-term copper exposure. Hydrobiologia 248, 125–136.

337 Lee, M.L., Vassilaros, D.L., White, C.M., Novotny, M., 1979. Retention indices for

338   programmed-temperature capillary-column gas chromatography of polycyclic

339   aromatic hydrocarbons. Anal. Chem. 51, 768-774.

340 Masclet, P., Pistikopoulos, P., Beyne, S., Mouvier, G., 1988. Long range transport and

341   gas/particle distribution of polycyclic aromatic hydrocarbons at a remote site in

342   the Mediterranean Sea. Atmos. Environ. 22, 639-650.

343 Oris, J.T., Hall, A.T., Tylka, J.D., 1990. Humic acids reduce the photo-induced toxicity

344   of Anthracene to fish and Daphnia. Environ. Toxicol. Chem. 9, 575-583.

345 Qiao, M., Wang, C., Huang, S., Wang, D., Wang, Z., 2006. Composition, sources, and

346   potential toxicological significance of PAHs in the surface sediments of the

347   Meiliang Bay, Taihu Lake, China. Environ. Internat. 32, 28-33.

348 Quiroz, L., Jarque, S., Lackner, R., Fernandez, P., Grimalt, J.O., Piña, B., 2007.

349   Physiological response to persisten organic pollutants in fish from mountain

350   lakes: analysis of Cyp1A gene expression in natural populations of *Salmo trutta*.

351   Environ. Sc. Technol. 41, 5154-5160.

352 Ravindra, K., Wauters, E., Van Grieken, R., 2008. Variation in particulate PAHs levels

353   and their relation with the transboundary movement of the air masses. Sci. Total

354   Environ. 396, 100-110.

355 Sanders, G., Jones, K.C., Hamilton-Taylor, J., Dorr, H., 1993. Concentrations and

356   deposition fluxes of polynuclear aromatic hydrocarbons and heavy metals in the

357   dated sediments of a rural English lake. Environ. Toxicol. Chem. 12, 1567-1581.

358 Simcik, M.F., Eisenreich, S.J., Golden, K.A., Liu, S.-P., Lipiatou, E., Swackhamer,

359   D.L., Long, D.T., 1996. Atmospheric loading of polycyclic aromatic

360   hydrocarbons to lake Michigan as recorded in the sediments. Environ. Sci.

361   Technol. 30, 3039-3046.

362 Simó, R., Grimalt, J.O., Albaigés, J., 1997. Loss of unburned-fuel hydrocarbons from

363   combustion aerosols during atmospheric transport. Environ. Sci. Technol. 31,

364   2697-2700.

365 Sommaruga, R., 2001. The role of solar UV radiation in the ecology of alpine lakes. J.

366   Photochem. Photobiol. B: Biology 62, 35-42.

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368   Table 1. Canadian Freshwater Sediment Quality Guidelines for polycyclic aromatic
369   hydrocarbons (PAH) in ng/g dw and Toxic Equivalent Factor (TEF) of PAHs

PAHs	Acronym	number rings	ISQGs[1] ng/g dw	PEL[2] ng/g dw	TEF[3]
Fluorene	Flu	3	21	144	-
Phenanthrene	Phe	3	42	515	-
Anthracene	Ant	3	47	245	-
Fluoranthene	Fla	4	111	2355	2.0E-09
Acephenanthrylene	Acy	4	6	128	-
Pyrene	Pyr	4	53	875	3.9E-07
benz[a]anthracene	BaA	4	32	385	2.0E-04
chrysene+triphenylene	Cry+T	4	57	862	5.6E-05
benzo[b+j]fluoranthene	Bb+jF	5	-	-	1.7E-04
benzo[k]fluoranthene	BkF	5	-	-	1.3E-03
benzo[e]pyrene	BeP	5	-	-	2.7E-05
benzo[a]pyrene	BaP	5	32	782	2.4E-04
Perylene	Per	5	-	-	2.3E-05
indeno[1,2,3-cd]pyrene	I123P	6	-	-	1.9E-03
benzo[ghi]perylene	BghiP	6	-	-	1.0E-05
dibenz[ah]anthracene	DahA	6	6	135	2.7E-04

370   1. Interim sediment quality guideline (ISQG); 2. Probable effect levels (PEL); 3. Barron et al., 2004

Figure captions

Figure 1. Studied lakes and PAH concentrations (Σ Flu+ Ant+ Phe+ Fla+ Acy+ Pyr+ (Cry+T)+BaP + DahA). Abbreviations in Table 1.

Figure 2. Total TU1 values from European high mountain lake sediments. 1, Maam; 2, Escura; 3, Cimera; 4, La Caldera; 5, Redon; 6, Noir; 7, Schwarsee ob Sölden; 8, Gossenköllesee; 9, Øvre Neadalsvatn; 10, Arresjøen; 11, Bubreka; 12, Negru; 13, Dlugi; 14, Starolesnianske Pleso.

Figure 3. Total TU2 values from European high mountain lake sediments. 1, Maam; 2, Escura; 3, Cimera; 4, La Caldera; 5, Redon; 6, Noir; 7, Schwarsee ob Sölden; 8, Gossenköllesee; 9, Øvre Neadalsvatn; 10, Arresjøen; 11, Bubreka; 12, Negru; 13, Dlugi; 14, Starolesnianske Pleso.

Figure 4. Toxic Equivalent values (TEQs-PAHa) from the European high mountain lake sediments. 1, Maam; 2, Escura; 3, Cimera; 4, La Caldera; 5, Redon; 6, Noir; 7, Schwarsee ob Sölden; 8, Gossenköllesee; 9, Øvre Neadalsvatn; 10, Arresjøen; 11, Bubreka; 12, Negru; 13, Dlugi; 14, Starolesnianske Pleso.

Figure 5. Triangular diagram of percentage of contribution for concentration and TU1 values for PAHs in high mountain lake sediment

Figure 6. Triangular diagram of percentage of contribution for concentration and TU2 values for PAHs in high mountain lake sediment