

1 **Application of congener based multi-matrix profiling techniques to identify**
2 **potential PCDD/F sources in environmental samples from the Burrishoole**
3 **Catchment in the West of Ireland.**

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17 Identification of elevated PCDD profiles in fish, sediment and passive samplers from the Burrishoole
18 suggest a historic pentachlorophenol source.

19
20
21 **Abstract**

22 Homologue and congener profiles of PCDD/Fs in eels, passive sampler and sediment extracts
23 from the Burrishoole, a rural upland catchment on the western Irish seaboard were compared
24 with potential PCDD sources. Σ PCDD/F levels in eels ranged from 2.9 to 25.9 pg g⁻¹ wet
25 weight, which are elevated compared to other Irish locations. The OCDD congener
26 dominated the pattern of Σ PCDD/Fs in all matrices from Burrishoole. Passive samplers were
27 successfully deployed to identify for the first time the presence of PCDD/Fs and
28 dimethoxylated octachlorodiphenyl ether (diMeOctaCDE) in the water column, both of
29 which are impurities found in pentachlorophenol (PCP) production. Principal component
30 analysis (PCA) identified similarities between PCDD/F profiles in technical PCP mixtures
31 and environmental samples from the Burrishoole region. Results strongly suggest residual
32 PCDD contamination associated with historic local use of a dioxin contaminated product in
33 the catchment area, with pentachlorophenol a strong candidate.

34
35 **Keywords: PCDD/F; *Anguilla anguilla*; passive samplers; Principal component**
36 **analysis; pentachlorophenol**

37 **1.0 Introduction**

38 Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) are primarily formed as
39 unintentional by-products of a range of natural and anthropogenic processes including pulp
40 bleaching, and heating and/or combustion processes involving organic matter or chlorine
41 containing compounds (McLean., 2009). The presence of chlorinated organic compounds,
42 such as chlorophenols, chlorobenzenes, polychlorinated diphenyl ethers (PCDEs) or
43 polychlorinated biphenyls (PCBs) may further accelerate dioxin formation (Sanctorum et al.,
44 2011). Due to their extremely low water solubility, generally only trace concentrations of
45 dioxins are found in the water phase. However, because of their chemical nature, PCDDs are
46 highly liable to accumulate in sediments, fish and other aquatic organisms. This process
47 depends on various factors, such as species-specific accumulation and elimination processes,
48 diet, age and lipid content in conjunction with proximity to natural or pollution sources.
49 Despite recent phasing out of chlorine in many processes and other measures taken to reduce
50 contaminant emissions, levels of PCDD/Fs continue to be of ongoing concern in all
51 environmental compartments (Sundqvist et al., 2010).

52
53 A study on Persistent Organic Pollutants (POPs) in eels from Irish river systems found that
54 samples from the Burrishoole catchment in the West of Ireland, exhibited elevated Σ PCDD
55 levels relative to other Irish catchments (McHugh et al., 2010). The congener profile in
56 Burrishoole eels was dominated by higher molecular weight PCDDs, especially that of the
57 octachlorinated dioxin congener (OCDD). This unusual dioxin congener profile suggests a
58 specific and, given the persistence of these substances and the longevity of eels, possibly
59 historic source at this location. Historic production and application of certain chlorinated
60 chemicals, including pentachlorophenol (PCP), a halogenated compound which has primarily
61 been utilised in the timber processing industry, may result in the generation of a number of
62 impurities including polychlorinated diphenyl ethers (PCDEs), HO-PCDEs and
63 hexachlorobenzene (HCB), with OCDD suggested as being the most common dioxin
64 impurity formed (Geyer., 2000 and Masunaga et al., 2003).

65
66 Temporal, spatial and surveillance contaminant monitoring programmes generally focus on
67 the measurement and assessment of contaminant levels in sediment and in biomonitor
68 species, such as bivalve molluscs and/or fish to act as a proxy indicator of contaminant levels
69 in the water column and within the wider environment (Denier van der Gon et al., 2007 and

70 Geeraerts et al., 2011). Such approaches are possible as persistent contaminants accumulated
71 by biomonitor organisms represent the bioavailable fraction present in the sampled medium.
72 Passive sampling is a methodology which has been shown to provide dissolved water
73 concentrations of hydrophobic contaminants which can take into account seasonal changes as
74 well as point source influences and temporal/spatial trends (Allan et al., 2006, Huckins et al.,
75 1990, Kot-Wasik et al., 2007 and Stuer-Lauridsen, 2005). Passive samplers can accumulate
76 contaminants many times higher than background levels over the lifetime of the deployment
77 (Smedes and Booij, 2012), thus providing a means of improving analytical sensitivity,
78 especially as levels of POPs in the water column are generally low.

79

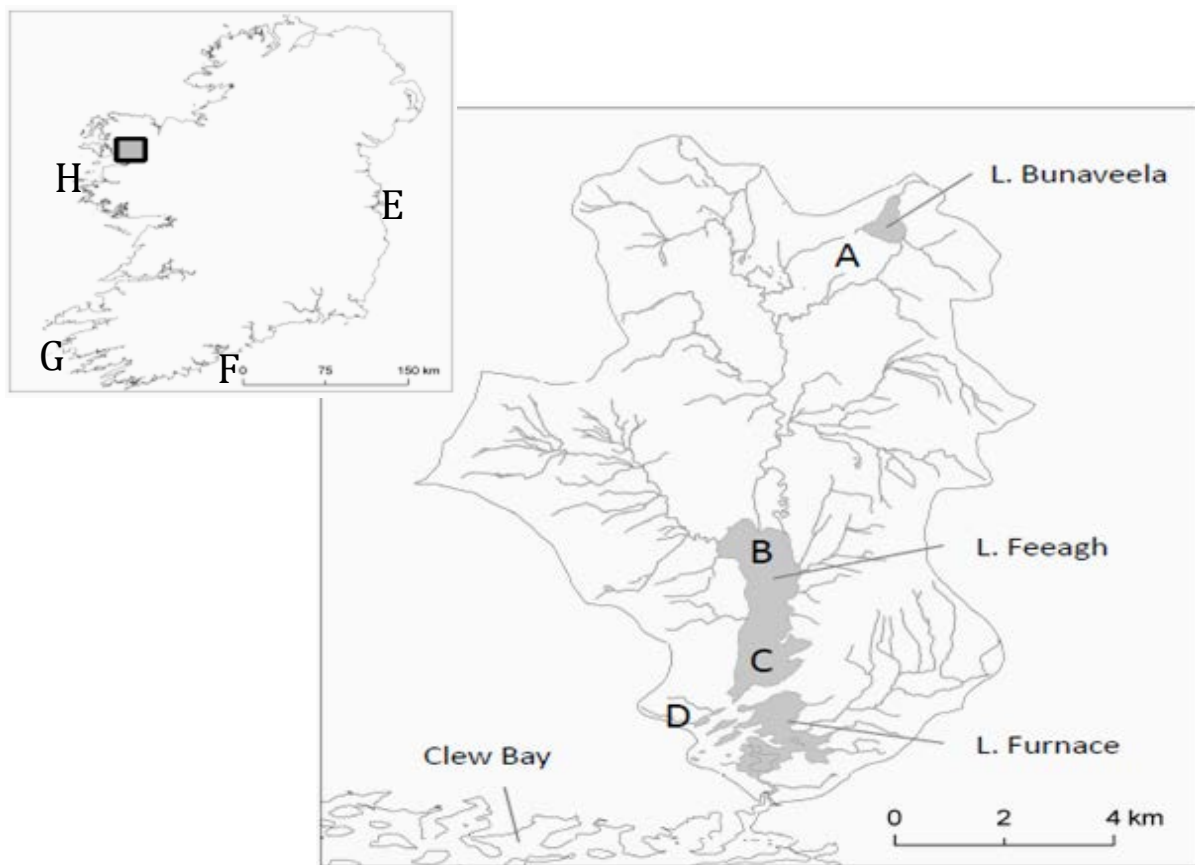
80 In recent years, the application of methodologies such as principal component analysis and
81 positive matrix factorization has been successfully employed to statistically identify
82 differences and similarities in congener patterns or "chemical fingerprints" observed in
83 environmental samples and those in potential sources (Masunaga et al., 2003, Sundqvist et
84 al., 2009 and Sundqvist et al., 2010) ultimately providing a means of discriminating between
85 contamination sources to trace the origin of pollution events. This study details the detection
86 of PCDD/F, PCDE, PCB, polyaromatic hydrocarbons (PAHs), organochlorine compounds
87 (OCs) and PCP (plus its primary metabolite pentachloroanisole - PCIA) in a variety of
88 matrices including sediment, biota (eels and trout) and polydimethylsiloxane (PDMS) passive
89 samplers from the wider Burrishoole region, this being further complemented by utilisation
90 of principal components analysis (PCA) to further characterise PCDD/F congener profiles
91 with reference to potential source inputs.

92

93 **2.0 Materials and methods: Sampling location, methodology and analysis**

94 The Burrishoole catchment is an oligotrophic and poorly buffered system ($53^{\circ} 55'.22N$, 009°
95 $34'.185W$, Fig 1), consisting of three main Lakes, the brackish Lake Furnace and the
96 freshwater Lakes Feeagh (sites B and C, Fig 1) and Bunaveela (site A, Fig 1). This rural
97 upland catchment area is drained by approximately 70 km of small shallow streams,
98 particularly to the west of the catchment. The largest Lake, Feeagh is joined to Lake Furnace
99 through two narrow turbulent channels; the Mill Race (Eel weir) and the Salmon Leap. The
100 waters of Lake Feeagh are neutral to acidic with pH ranging from approximately 6.3 to 7.0
101 with temperature and conductivity values ranging $3^{\circ}C$ to $20^{\circ}C$ and $80-90 \mu S cm^{-1}$
102 respectively (Poole and De Eyto, 2007). The sampling area is lowly populated with few

103 industrial influences apart from agricultural and forestry related activities, and is heavily
104 influenced by west to east flow of North Atlantic anticyclonic systems.



105
106 **Figure 1.** Ireland and the Burrishoole catchment, showing the sites for sediment collection
107 and passive sampler deployment, reproduced from Poole and De Eyto (2007).

108 Sediment samples were collected at sites; A (Lake Bunaveela), B (Black River), C (Eel weir)
109 and D (Gallagher's Lake – reference site) using a Van Veen sediment grab. Samples were
110 removed to solvent washed glass jars and placed in a cooler box for transport to the
111 laboratory. Particle size analysis was completed on a subsample prior to the samples being
112 wet sieved to $<63 \mu\text{m}$, placed in a solvent washed container and subsequently freeze dried in
113 preparation for analysis.

114 Eel and trout samples were collected from across the catchment using eel traps and fyke nets
115 and were then transported to the Marine Institute facility in Newport Co. Mayo. Otoliths were
116 removed for aging before eels were placed in a freezer and were transported to the laboratory
117 where they were allowed to thaw before being measured. Length classification was
118 completed on individual eels. Skinless muscle tissue was removed from between the pectoral
119 fin and tail, samples were pooled and then homogenised and frozen before analysis. Total
120 extractable lipid content (%) was then quantified gravimetrically on portions of solvent
121 extracted tissue.

122 Prior to deployment, passive samplers fabricated from PDMS sheets, were cleaned in a
123 soxhlet apparatus for 100 h using ethyl acetate to remove interfering oligomers. Calibration
124 was performed on the sheets by immersion in a methanol-water mixture containing
125 Performance Reference Compounds (PRCs) as described by Smedes and Booij (2012). The
126 passive sampling devices (PSDs) were transported to the Burrishoole sites shown in figure 1,
127 in a cool box and deployed approximately 2 m below the surface for a 4 month period
128 facilitating equilibration with the surrounding water column. Passive samplers from outside
129 the Burrishoole were deployed in a similar manner at Dublin (E), Cork (F), Bantry bay (G)
130 and Omey Island (H) (Shown fig 1). Once this period had elapsed, the sheets were removed
131 from the site and immediately frozen at -28°C prior to analysis. PDMS samplers were then
132 soxhlet extracted in methanol/acetonitrile (1:2 v/v) for 8 h prior to contaminant analysis.

133 Quantification of PCBs, PAHs and a range of OCs on PDMS, eel tissue and sediment extracts
134 was performed using an Agilent 6890 gas chromatograph (GC) coupled to a 5973N mass
135 spectrometric detector (MSD) run in splitless mode with a 60 m 0.25 mm x 0.22 µm DB-5ms
136 column run in electron ionisation (EI) mode with helium as a carrier gas or on a Varian 3800
137 GC using a dual column system with a Ni⁶³ source electron capture detector run in dual
138 column mode with CPSil 19 (50 m 0.22 mm x 0.25 µm) and HT8 (50 m 0.25mm x 0.25 µm)
139 columns using helium as a carrier gas. Polymer/water partition coefficients as described by
140 Smedes and Beeltje (2010) were employed for quantitative measurement of dissolved
141 concentrations of hydrophobic contaminants on in situ PDMS samplers. There are no such
142 polymer/water partition coefficients for PCDD/F compounds and as such no quantification
143 took place rather PCDD/F profiles were used on a pg/sampler⁻¹ basis. The unweighted non-
144 least squares method (NLS) of determining the device sampling rate was employed and
145 dissolved water concentrations of PAHs/OCs and PCBs were calculated using methods
146 developed by Booij and Smedes (2010).

147 PCDD/F profile analysis of the PDMS extracts on a ng/sample⁻¹ basis and quantification of
148 biota and a composite sediment sample was completed under subcontract to Eurofins, GMBH
149 laboratories Germany, using a carbon on-glass fibre multi-column followed by quantification
150 on a Finnigan MAT 95 XL high resolution gas chromatograph with a DB-5 60 m column.
151 PCDD/F data in biota are reported on a concentration basis rather than using toxic
152 equivalency (TEQs) which are of greater relevance in food safety studies. A full quality
153 control programme underpinned all analysis and incorporated, where appropriate the use of

154 reference materials, fortified samples, solvent and method blanks, duplicate samples and
155 successful participation in internationally recognized proficiency exercises.

156

157 Total PCP/PCIA analysis of sediment and biota was completed under subcontract to the
158 University of Amsterdam using solvent extraction followed by gel permeation
159 chromatography (GPC) clean-up, diazomethane derivatisation, acidic silica clean-up with
160 analysis by GC-ECD. PDMS extracts were further analysed at the Toxicological Center,
161 University of Antwerp, Belgium, for additional organohalogen compounds (e.g. PCDE and
162 HO-PCDE derivatives) as described by Covaci et al (2012). Briefly, extracts were
163 concentrated to ~100 µL and analysed using an Agilent 6890-5793 GC-MS system operated
164 in the electron-capture negative ionization mode (ECNI) and equipped with a DB-5ms
165 column (15 m x 0.25 mm x 0.10 µm). Details on the acquisition parameters and ions are
166 reported by Covaci et al (2012).

167

168 **2.1 Statistical methods and principal component analysis**

169 For PCA, PCDD/F concentration data were scaled to unit variance/normalised, thereby all
170 variables have equal weighting. If such scaling is not performed, variables with high nominal
171 value/concentration will dominate and outweigh any important information in variables of
172 lower nominal value. This normalisation process was completed relative to the sum of a
173 number of individual congeners (n=17, Table 1) that were measured in all samples and in
174 prospective source samples. Data for the PCA were derived from the use of raw upperbound
175 PCDD/F concentration data from test samples (biota, sediment and PDMS Table 1) plus
176 those from prospective sources (Table S3 supplementary material). This technique enabled
177 concentration-independent congener profiles at test sites and between matrices to be
178 compared to potential sources. For source-based attribution purposes, the relative proportions
179 (%) of PCDD/F in PCP and in tetrachlorophenol (TeCP) technical mixtures as reported by
180 Sundqvist et al (2009) and in air emissions data from the Irish Environmental Protection
181 Agency (EPA, 2013) were collated and recalculated based on the 17 PCDD/F congeners
182 measured (See Table S3 supplementary material). In addition to samples collected in 2009,
183 data previously reported by McHugh et al (2010) are additionally included in this assessment.
184 PCA and graphical representations were performed using R (R Development Core Team,
185 2011).

186

187 **3.0 Results and Discussion**

188 The Burrishoole Catchment in western Ireland is sparsely populated with no industrial
189 influences. The predominant activities in the catchment are coniferous forestry and pastoral
190 agriculture. An examination of the Corine 2006 Land Cover Atlas (www.gis.epa.ie) (Figure
191 2 – supplementary material) shows most of the catchment area to consist of peat bog and
192 woodland primarily denoted as coniferous forest and transitional woodland. The west of
193 Ireland is heavily influenced by west to east flow of North Atlantic anticyclonic systems.
194 Consequently the initial finding of elevated dioxin concentrations in comparison to other
195 catchments was unexpected (McHugh 2010).

196

197 **3.1 Assessment of PCDD/F in environmental matrices**

198 Total upperbound $\Sigma 7$ PCDDs measured in Biota (eels and trout) newly collected since the
199 McHugh et al (2010) study ranged from 2.7 to 25.2 pg g^{-1} w.w., while the $\Sigma 10$ PCDFs ranged
200 from 0.25 to 0.77 pg g^{-1} w.w. (Table 1). These values are similar to the results reported by
201 McHugh et al (2010) where eels from Burrishoole ranged from 22.3 to 77.6 pg g^{-1} w.w. and
202 0.26 to 1.01 pg g^{-1} w.w. for PCDDs and PCDFs, respectively. PCDDs contributed the
203 majority of the body burden present for Σ PCDD/F in the Burrishoole biota ranging from 89.2
204 to 97 % of the total PCDD/F contaminant burden. Results are similar to the results reported
205 by McHugh et al (2010) where PCDDs in 2005 to 2007 in eels from Burrishoole comprised
206 approximately of 99 % Σ PCDD/F compared to an average of 54 % in the eels measured from
207 other areas in Ireland. OCDD was still found to be the dominant congener relative to the
208 Σ PCDD/F contributing 65.2 to 71.4 % to the overall total contaminant burden, again similar
209 to that reported by McHugh et al (2010) where OCDD contributed 53.5 to 58.6 % of the total
210 body burden (Σ PCDD/F pg g^{-1} w.w.).

211 The Σ PCDD/F concentration totalled 2.6 ng g^{-1} d.w. in the composite Burrishoole sediment,
212 with OCDD again being the dominant congener comprising 90 % of Σ PCDD/F burden.
213 Sediment congener profiles closely resemble those reported by Birch et al (2007), Gaus et al
214 (2001) and Sanctorum et al (2011) who reported that PCDD/F levels in Australian and
215 French/Belgian sediments were strongly dominated by OCDD with potential input being
216 influenced by the presence of PCP.

217

218 With the exception of the Gallagher's Lake (reference location) PDMS sample, strong
219 correlations were evident between all Burrishoole catchment matrices for the percentage
220 contribution of each of the 17PCDD/F congeners (Table S2 - supporting material). Individual
221 PCDD/F contributions between Burrishoole sites are strongly correlated to those in biota
222 (ranging $r = 0.95$ to 1), between biota and PDMS (ranging $r = 0.91$ to 1), sediment to eels
223 (ranging $r = 0.93$ to 1) and sediment to PDMS (ranging $r = 0.98$ to 1). The Gallagher's Lake
224 PDMS profile showed correlations in the range (0.93 to 0.99) relative to the PDMS samplers
225 from outside the Burrishoole and were found to exhibit lower correlation (ranging $r = 0.50$ to
226 0.71) with PDMS, eels, trout and sediment from the Burrishoole catchment itself. Overall this
227 suggests that the contaminant profile in water, biota and sediment from the Feeagh,
228 Bunaveela, Furnace and Burrishoole test sites are similar to each other, but that the
229 Gallagher's Lake (reference site) while in the vicinity of the other Burrishoole test sites is
230 less affected by the PCDD/F loadings observed in the wider catchment. The nature of these
231 profiles is further explored by PCA (Fig 2).

232 PDMS extracts were screened in order to derive a PCDD/F profile (pg sampler^{-1}) for
233 comparison to profiles from other sampling locations and between matrices (Table 1). OCDF,
234 1,2,3,4,6,7-HpCDD and OCDD are the primary contributors to the total PCDD/F loading in
235 exposed samplers, however the relative proportion of PCDD to this burden is much greater in
236 Burrishoole samplers relative to those from other Irish urban and reference locations outside
237 the Burrishoole. The relative proportion of the higher chlorinated OCDD congener to
238 $\Sigma 1,2,3,4,6,7,8 \text{ HpD} + \text{OCDD}$ is 87.7 to 93 % in Burrishoole samplers (excluding Gallahers
239 Lake sampler) as against 69.4 to 78.4 % in samplers from the rest of Ireland. While the
240 feasibility of accurate quantification of PCDD/Fs in PDMS samplers is still under
241 development, it is clear that the percentage contribution of ΣPCDD (and especially higher
242 PCDD congeners) to the profile present was higher in the Burrishoole catchment samplers
243 compared to other Irish locations, while the ΣPCDF profile remained generally similar
244 between all samples tested. These findings of a higher percentage of OCDD in eel, sediment
245 and in the dissolved water phase are further suggestive of a specific local source of PCDD
246 (supplementary material Figure 1).

247 **3.2 PCP/PCIA in sediment, biota and PDMS**

248 The half-life of PCP in water is less than a few days due to photomineralisation and
249 adsorption to suspended solid matter, however at deeper levels sunlight is less available and
250 the degradation of PCP is completed by microorganisms in the sediment (Institute of
251 Environmental Protection, 2008). In soils and sediments, the half-life of PCP has been
252 calculated at <20 weeks, thus directly identifying historic PCP residues in the environment is
253 difficult. PCP and other chlorophenols are converted in the environment into numerous
254 different metabolites (e.g. pentachloroanisole) by O-methylation, hydroxylation,
255 dechlorination, or via a combination of these. While degradation of PCP residues is rapid, the
256 analysis of total pentachlorophenol and pentachloroanisole (Σ PCP/PCIA) in the <0.063 μ m
257 sieved fraction of sediment samples from the Burrishoole region in addition to those from a
258 further reference location (Kinvara, Co. Galway) was completed. PCP/PCIA in sediment was
259 highest at the Feeagh site (1.60 ng g⁻¹ d.w. Table 1) and Gallagher's lake (1.28 ng g⁻¹ d.w.)
260 with the lowest levels found in Lake Bunaveela (0.64 ng g⁻¹ d.w.), while levels of
261 Σ PCP/PCIA (0.51 ng g⁻¹ d.w.) were measured in sediment from Kinvara. While Σ PCP/PCIA
262 levels in Burrishoole sediments are not greatly elevated relative to the reference site, they do
263 exceed those from the reference location.

264 Biota from the Burrishoole were found to have similar Σ PCP/PCIA concentrations to those
265 from reference sites with Burrishoole trout (0.36 ng g⁻¹ d.w.), eels (1.12 and 1.17 ng g⁻¹ d.w.)
266 comparable to eels from a reference location (River Breagagh, Kilkenny, 1.31 ng g⁻¹ d.w.).
267 PCP has previously been measured at levels between not detected and 6.9 ng g⁻¹ d.w (n.d. -
268 1.39 ng g⁻¹ w.w) in eels from the River Liffey (Celbridge) and River Brosna in the Irish
269 midlands. In the majority of cases, OCDD concentrations measured in these eels was
270 correspondingly low (EPA, 2013). PCP/PCIA was not detected during screening of the
271 PDMS extracts.

272

273 **3.3 Supporting analysis**

274 To further assess the level of general anthropogenic impact on the Burrishoole region, a
275 broad suite of analyses was completed on each of the sampled matrices. The Σ 15PAHs in
276 Burrishoole sediment ranged from 376 ng g⁻¹ d.w. at Lake Feeagh to 799 ng g⁻¹ d.w. in the
277 high carbon, peaty sediment from Lake Bunaveela. Levels of the sum of Σ 14PAHs in Irish
278 lake soils have been reported by Scott et al (2012) in the range 52.2 to 1369 ng g⁻¹ d.w., thus
279 are similar to the current study. Levels are low in comparison to those in other freshwater

280 systems as reported by Cachot et al (2006) from the Seine – 12,210 ng g⁻¹ d.w. and by Hale et
281 al (2010) from the river Tyne for the USEPA Σ 16PAH, 16,400 \pm 7300 ng g⁻¹. The ratio of the
282 sum of low molecular weight PAHs (Σ LPAHs) (2-3 ring compounds) to the sum of higher
283 molecular weight PAHs (Σ HPAHs) (4–6 rings) is < 1 suggesting that PAHs in collected
284 Burrishoole sediments are mainly of pyrolytic origin (Webster et al., 2000 and Russell et al.,
285 2005) (Table S1 A Supplementary material)

286 The Dissolved water concentrations (Σ 15PAHs) determined in water from the Burrishoole
287 sampling sites by PDMS passive sampling ranged from 27.8 ng L⁻¹ in the Black river PDMS
288 to 67.1 ng L⁻¹ at the Eel weir site. Scott et al (2012) showed levels of PAHs in semi
289 permeable membrane devices (SPMDs) from five Irish lakes ranged from 125 to 577 pg L⁻¹
290 which are lower than the PAHs estimated in this study. PAHs reported from PDMS PSDs
291 deployed in four remote streams in Northeast Scotland ranged from 38 to 68 ng L⁻¹, which
292 are similar to results reported in this study (Emelogu et al., 2013). Overall, low molecular
293 weight PAHs dominate in water samples, while higher molecular weight compounds
294 dominate in lake sediments, thus supporting water/particulate partitioning theory and the low
295 levels as reported by Scott et al (2012).

296 Levels of the sum of seven marker PCBs (Σ 7PCBs) in eels from the Burrishoole catchment
297 ranged from 1.6 to 4.3 ng g⁻¹ w.w., while 1.9 ng g⁻¹ w.w. was recorded for the trout sample
298 from Lake Furnace. These data compare well with concentrations of marker PCBs in eels
299 reported by McHugh et al (2010) and are low in comparison to values ranging up to 1512 ng
300 g⁻¹ w.w. reported by Santillo et al (2005) in a composite eel sample from the Netherlands and
301 a mean of 1545 ng g⁻¹ w.w. recorded by Belpaire et al (2011) in eels from the River Meuse
302 basin, Belgium. Upperbound levels of dissolved PCBs determined in passive samplers in the
303 Burrishoole region were low with values for PCB 153 ranging from 0.11 to 0.6 ng L⁻¹
304 comparing well with other studies including O' Hara (2009), Smedes et al (2007) and
305 Monteyne et al (2013). PCB levels in the Burrishoole are generally low and the congener
306 profile is heavily dominated by lower chlorinated congeners, with similar profiles observed in
307 other Irish passive sampler data (O' Hara, 2009). This current study supports the findings of
308 McHugh et al (2010) who report low levels of a wide variety of pollutants measured in eels
309 from the catchment.

310 Analysis of eel and PDMS extracts from the Burrishoole detected a number of
311 chromatographic peaks characteristic for PCDEs, specifically dimethoxylated

312 octachlorodiphenyl ether (diMeO-octaCDE) which has been hypothesized as resulting from
313 the environmental hydroxylation, dechlorination, O-methylation of HO-PCDEs and PCDEs
314 (Covaci et al., 2012). These HO-PCDEs, together with the corresponding PCDEs, were
315 reported to be present as impurities in technical PCP up to 30,000 ppm (Environmental
316 Health Criteria (EHC), 1987), (Agency for Toxic Substances and Disease Registry (ATSDR),
317 2001). Electron capture negative ionisation (ECNI/MS) chromatograms resulting from
318 analysis of the PDMS extracts from Black river and Eel weir exhibited distinct signals for
319 negative ions with m/z 261 which are characteristic of diMeO-octaCDE, together with other
320 specific negative ions with m/z 244, 224 and 475, measured in the same ratios as those
321 previously observed in the eel samples, however at lower abundances (Covaci et al., 2012).
322 This indicates the unambiguous identification of diMeO-octaCDE in the PDMS extracts from
323 Burrishoole Black River and Eel weir sites and to a lesser extent, Lake Bunaveela. However,
324 due to the lack of authentic standards, no quantification was possible, hence analysis are of a
325 qualitative nature only. Similar to the eel samples from Burrishoole (Covaci et al., 2012, Mc
326 Hugh et al., 2010), the PDMS extracts from locations Black river, Eel weir and Lake
327 Bunaveela sites also identified trace levels of OCDD and HpCDD. The presence of PCDDs
328 was not identified in PDMS extracts from other locations outside the Burrishoole.

329 Due to the lower accumulation of organohalogen compounds in PDMS relative to eels, no
330 PCP or other PCDE derivatives (e.g. (di)MeO-monobromo polychlorinated diphenyl ethers or
331 (di)MeO-dibromopolychlorinated diphenyl ethers) as described by Covaci et al (2012) were
332 observed in the PDMS from Eel weir, Black river or Lake Bunaveela. PDMS extracts from
333 Gallagher's Lake and from locations outside the Burrishoole were not found to contain any of
334 the PCDE derivatives which have been reported in eel samples by Covaci et al., (2012).

335 Overall, the extended additional analyses show that levels of POPs in sediments and water
336 and PCBs in Irish eels and trout from the Burrishoole catchment are generally low. PAH
337 ratios suggest that PAHs are generally of a pyrolytic nature. The OCDD congener dominated
338 profiles, with low PAH/PCB levels in all matrices, when further coupled with the detection of
339 PCDE derivatives strongly suggest the influence of a point source containing PCDDs in this
340 area. The application of profiling techniques in source characterisation is further described
341 below.

342

343 **3.4 Pollution sources and congener patterns**

344 Dioxin pollution may originate from a wide range of industrial point and/or diffuse sources.
345 Source tracing studies using a low number of congeners have in the past been used to indicate
346 that atmospheric deposition is a major contributor to total PCDD/F fluxes to regions such as
347 the Baltic Sea (Masunaga et al., 2003, Verta et al., 2007 and Armitage et al., 2009). These
348 studies further showed that comprehensive congener patterns have significantly higher
349 potential for identifying sources than using 2,3,7,8-substituted PCDD/F patterns or
350 homologue profiles alone, thus multi-congener based PCA is a beneficial technique when
351 attempting to elucidate the origins of PCDD/F compounds.

352

353 Unit variance/normalised PCDD/F profile data (n=17 congeners) from reference sources
354 including profiles from diverse combustion-related flue gas samples (n = 6 Irish locations
355 (EPA, 2013) and PCDD/F concentrations reported by Sundqvist et al (2009) for PCP and
356 TeCP technical mixtures (n=5) were evaluated against profiles in biota, PDMS and sediment
357 from the Burrishoole region and in other Irish samples (see Table S3 Supplementary
358 material). It should be noted that comparatively small amounts of PCP have been reportedly
359 used in Ireland (Denier Van der Gon et al., 2007), also the formulations in these instances is
360 unknown, therefore formulations as reported by Sundqvist et al (2009) are used for reference
361 purposes in PCA.

362

363 PCA of samples was restricted to three significant principal components (PCs). The first two
364 PCs (PC1 and PC2) were found to explain >86.9% of the variation in the data (58.5 and
365 28.4%, respectively). A bi-plot of sample scores and vector loadings (see *Fig 2*) suggest that
366 the ordinance of Burrishoole samples is strongly influenced by OCDD and 1,2,3,4,6,7,8-
367 HeptaCDD. It is additionally evident that the profile resembles that derived from PCDD/F
368 profiles of technical mixtures previously used in other countries, namely that of the PCP
369 technical mixture Sevarex granulate (100% PCP-Na) and TeCP technical mixture Sevarex
370 technical mix (ca 47% TeCP) (and to a lesser extent Santobrite D (100% PCP-Na)). Profiles
371 reported for other technical mixtures (TeCP/PCP mixtures KY-5 (ca 80% TeCP) and
372 Witophen N (100% PCP-Na)) were found to exhibit fewer similarities to those in the
373 environmental samples (See figure 1 – supplementary material).

374

375 Air emissions data from one sample SC(EM) derived from a wood chip facility in Scariff Co.
376 Clare > 150 Km south east of Burrishoole shows a similar profile to that observed in the
377 Burrishoole samples. The prevailing wind direction in the West coast of Ireland is between

378 West and South, thus historic emissions from this plant would not be expected to greatly
379 influence the profile obtained in Burrishoole samples. To support this, eels sampled from
380 Lough Corrib located mid way between Burrishoole and Scariff do not exhibit the same
381 higher chlorinated PCDD profile (McHugh et al., 2010).

382

383 As previously discussed, total concentrations of PCBs in Burrishoole samples were
384 comparable to those in samples from the rest of Ireland suggesting that PCBs are unlikely to
385 be a primary source of the PCDD/F profile. Greater proportions of OCDD and 1,2,3,4,6,7,8-
386 HeptaCDD in environmental samples has been suggested to be due to the sources originating
387 from chlorophenol related inputs (Masunaga et al., 2001), while greater proportions of
388 TCDFs suggest sources originating from PCB mixtures, chlorobenzenes, chlor-alkali
389 processes, or the incineration of PCBs and PVC (Hilscherova et al., 2003, Kannan et al.,
390 1998, Masunaga et al., 2001 and Rackwitz et al., 1991). Other sources, such as chlorophenol
391 and chlorobenzene production, incineration related activities, and/or chlor-alkali processes,
392 are often associated with changes in PCDD/F profiles. However, given the remote location of
393 the site and the absence of intensive industrial activity, these are not expected to contribute
394 greatly to the PCDD/F profile.

395

396 While PCP itself was not detected at high concentration in test samples, the concentrations
397 and uncharacteristic profile of PCDD/F congeners in biota, PDMS and sediment collected
398 from the Burrishoole, when compared with samples collected from other locations strongly
399 suggests historic local use of a PCDD-containing substance or product and although there is
400 no direct evidence of this, technical PCP is suggested as a good candidate.

401

402 **4.0 Conclusions**

403 A multi-matrix surveillance study incorporating data from a variety of sources and matrices
404 primarily focusing on PCDD/F levels in the Burrishoole region is reported. PAHs, PCBs and
405 HCB concentrations in all matrices were generally low relative to other similar studies further
406 emphasising low level anthropogenic impact in the Burrishoole region. PDMS passive
407 samplers have been demonstrated to be a useful screening tool for identifying the presence of
408 dissolved PCDD/F, PCDEs and the quantification of other POP residues in the aquatic
409 environment. However, further research is required to evaluate the potential for the future
410 application of PDMS PSDs in the provision of dissolved concentrations of PCDD/F or

411 PCDEs in the water column. Passive samplers and sediment PCDD/F profiles support
412 previous findings of McHugh et al (2010) and confirm the wider presence of higher
413 chlorinated PCDDs in a number of environmental compartments. PCA of PCDD/F profiles
414 suggests a chlorophenol based input, and in particular that of pentachlorophenol as a possible
415 point source influence in this location. The observed contamination patterns with higher
416 PCDDs and (HO-)PCDE derivatives have been associated with PCP contamination. While
417 PCP levels may be historic in origin, it is not uncommon for the parent PCP to be at low
418 concentrations in the environment (water and biota), with the more persistent by-products of
419 the manufacture of PCP (e.g. OCDD and PCDEs) being accumulated within biota. Literature
420 derived PCDD/F and HO-PCDE profiles in technical PCP mixtures suggest that the PCDD/F
421 and HO-PCDE profiles as measured in PDMS from the Burrishoole (apart from Gallagher's
422 Lake) better resembles that of PCP formulations than do the profiles from samples at other
423 Irish locations.

424

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426

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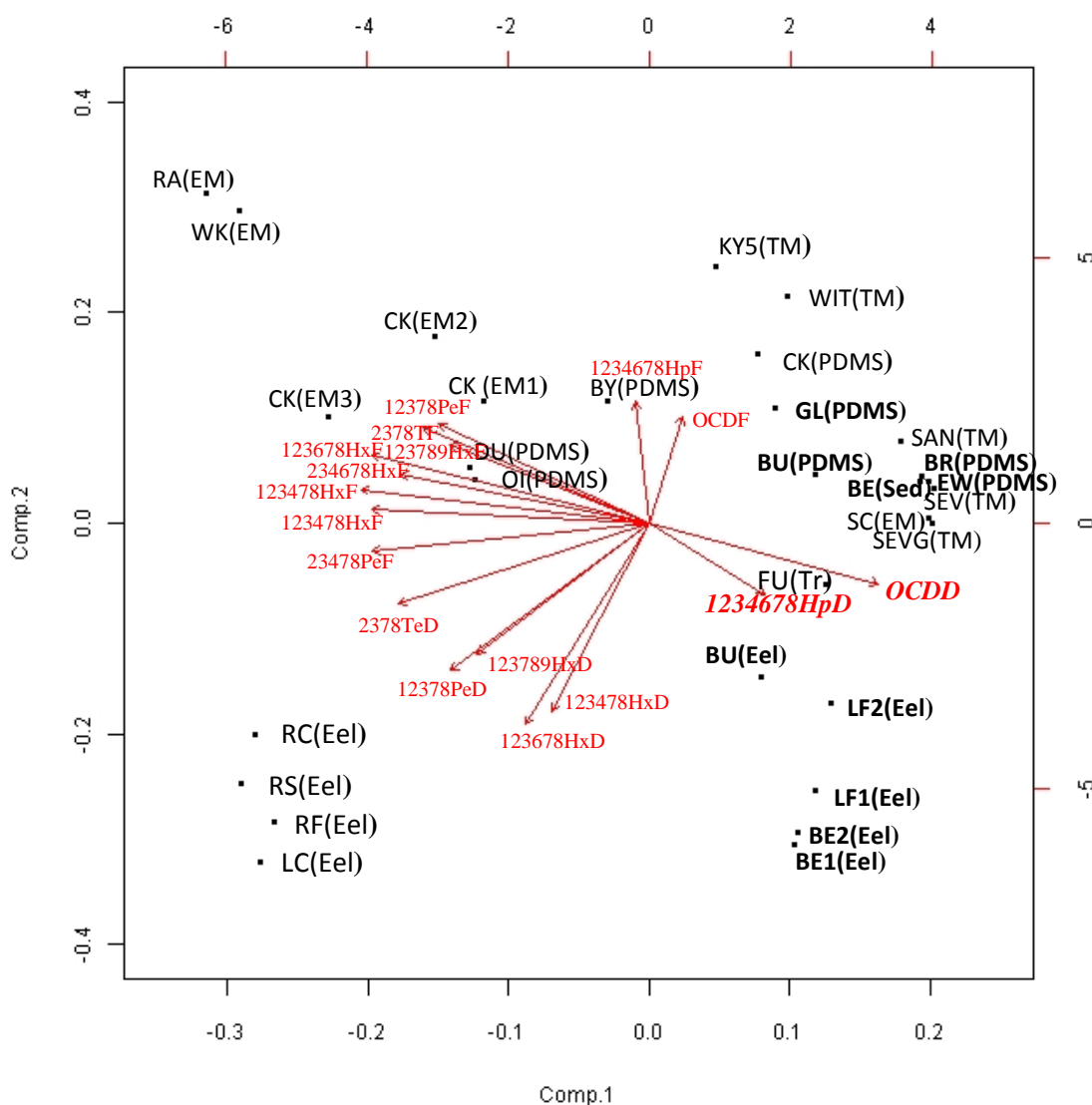
433 **Table 1:** Concentrations of PCDD/F in biota (pg g⁻¹ w.w.), in PDMS passive samplers (pg sampler⁻¹), sediment (ng g⁻¹d.w.). Total PCP/PCIA as
 434 ng PCP in sediment g⁻¹ d.w. and biota per g⁻¹ w.w. Σ7 PCBs and PCB153 in biota (ng g⁻¹ wet weight) and sediment (ng g⁻¹ d.w.), dissolved PAH
 435 and PCB concentrations in PDMS (ng/L⁻¹).

	Code	Year	2378TF	12378PeF	23478PeF	123478HxF	123678HxF	123789HxF	234678HxF	1234678HpF	1234789HpF	OCDF	2378TD	12378PeD	123478HxD	123678HxD	123789HxD	1234678HpD	OCDD	Σ7PCBs	ΣDL-PCBs	Σ15PAHs	PCP/PCIA	HCB	
L Feeagh (Eel)	LF2(Eel)	2009	0.03	<0.03	0.12	0.08	0.06	<0.03	0.07	0.09	<0.04	<0.22	0.04	0.67	0.75	2.14	0.7	3.96	16.9	4.34	0.28				
Furnace (Trout)	FU(Tr)	2009	0.03	<0.02	0.04	<0.02	<0.02	<0.02	<0.02	<0.03	<0.03	<0.14	<0.01	0.07	0.06	0.16	0.05	0.3	2.42	1.85	0.12		0.36		
Bunevella (Eel)	BU(Eel)	2009	0.03	<0.01	0.03	<0.01	<0.01	<0.01	<0.01	<0.02	<0.02	<0.12	<0.01	0.07	0.05	0.14	0.05	0.26	<2.07	1.56	0.11		1.17		
L Feeagh (Eel)*	LF1(Eel)	2007	<0.01	<0.01	0.06	0.05	0.04	<0.01	0.03	0.03	<0.01	<0.01	0.02	0.66	1.22	2.99	0.54	3.62	13.2	2.37	0.37				
R. Suir (Eel)*	RS(Eel)	2005	nd (0.03)	0.024	0.15	0.053	0.033	nd (0.02)	0.085	0.041	nd (0.03)	nd (0.05)	0.042	0.1	0.03	0.16	0.044	0.11	nd (0.3)	18.1	4.36			<0.5	
L. Conn (Eel)*	LC(Eel)	2005	0.01	0.014	0.1	0.059	0.035	nd (0.02)	0.086	nd (0.01)	nd (0.04)	nd (0.05)	0.029	0.083	0.08	0.17	0.037	0.11	nd (0.3)	3.63	0.92		1.12	<1	
R Corrib (Eel)*	RC(Eel)	2005	nd (0.03)	0.016	0.06	0.032	0.024	nd (0.02)	0.077	nd (0.01)	nd (0.04)	nd (0.07)	0.023	0.091	0.04	0.1	nd (0.02)	0.048	nd (0.3)	1.94	0.48		1.54	<0.8	
R Fane (Eel)*	RF(Eel)	2005	nd (0.04)	0.017	0.09	0.062	0.033	nd (0.02)	0.066	nd (0.01)	nd (0.04)	nd (0.07)	0.026	0.085	0.06	0.23	0.03	0.08	nd (0.3)	7.64	2.31			<0.9	
Burrishoole (Eel)*	BE1(Eel)	2005	nd (0.02)	0.085	0.12	0.22	0.12	nd (0.02)	0.25	0.088	nd (0.02)	0.07	0.055	2	5.3	13	2.2	13	42	6.77	1.81			<2	
Burrishoole (Eel)*	BE2(Eel)	2007	<0.02	0.02	0.1	0.1	0.06	<0.01	0.07	0.07	<0.01	<0.01	0.03	1.28	2.75	6.57	1.11	6.57	23.6	3.86	0.68				
Eel Wier (PDMS)	EW(PDMS)	2009	<0.64	<0.86	<0.86	<0.8	<0.8	<0.8	<0.8	1.05	<0.76	12.3	<0.36	0.92	0.98	1.07	<0.96	18.7	208	0.54		67.1		0.05	
Black river (PDMS)	BR(PDMS)	2009	<0.64	<0.86	<0.86	<0.8	<0.8	<0.8	<0.8	1.2	<0.76	13.6	<0.36	0.89	0.99	<0.96	0.96	17.7	235	0.11		27.8		0.03	
Bunevella (PDMS)	BU(PDMS)	2009	<0.64	<0.86	<0.86	<0.8	<0.8	<0.8	<0.8	<0.76	<0.76	7.27	<0.36	0.71	<0.96	<0.96	<0.96	4.89	34.9	0.47		48.9		0.52	
Cork (PDMS)	CK(PDMS)	2011	0.77	<0.86	<0.86	<0.8	<0.8	<0.8	<0.8	1.64	<0.76	31.6	<0.36	1.08	<0.96	<0.96	<0.96	3.44	9.51	0.14		150		0.51	
Dublin (PDMS)	DU(PDMS)	2011	<0.64	<0.86	<0.86	<0.8	<0.8	<0.8	<0.8	<0.76	<0.76	3.86	<0.36	<0.48	<0.96	<0.96	<0.96	1.7	<5.8	0.26		188		0.71	
Bantry (PDMS)	BY(PDMS)	2011	1.49	<0.86	<0.86	<0.8	<0.8	<0.8	<0.8	0.96	<0.76	9.45	<0.36	1.04	<0.96	<0.96	<0.96	3.13	7.09	0.02		39.8		0.02	
Omev Island (PDMS)	OI(PDMS)	2011	<0.64	<0.86	<0.86	<0.8	<0.8	<0.8	<0.8	<0.76	<0.76	4.28	<0.36	<0.5	<0.96	<0.96	<0.96	1.66	<5.8	0.02		15.5		<0.01	
Gallaghers (PDMS)	GL(PDMS)	2009	<0.64	<0.86	<0.86	<0.8	<0.8	<0.8	<0.8	1.8	<0.76	20.9	<0.36	0.97	<0.96	<0.96	<0.96	4.33	15.7	0.6		36.3	1.28	0.05	
Burrishoole (Sed)	BE(Sed)	2009	0.0005	0.004	0.005	0.006	0.005	<0.0009	0.004	0.03	0.003	0.03	0.0003	0.002	0.005	0.006	0.007	0.15	2.34	310				0.08	
Furnace (PDMS)		2012																		0.05					
Feeagh (Sed)		2009																				376	1.6		
Gallaghers (Sed)		2009																				494	1.28		
Bunevella (Sed)		2009																				799	0.64		
Kinvara (Sed)		2009																						0.51	
Kilkenny (Eel)		2007																						1.31	

436

437 *Supporting eel data from McHugh (McHugh *et al.*, 2010)

Figure 2: Principal Components Analysis score plot for PCDD/F congeners (n=17). Generated from contribution of individual PCDD/F congeners to the $\Sigma 17$ PCDD/F in sediment, passive samplers (PS), Air emissions (AE) (EPA, 2013) biota (eel and trout) and technical tetra- and pentachlorophenol mixtures (Sundqvist et al., 2009). Sample codes as per Table 1. Burrishoole samples indicated in bold



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