

Passive samplers: Pollutant Monitoring on the European Continental Shelf Edge

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1. Introduction

Ireland lies within geographical **latitude** of 53° 00' N and **longitude** of 8° 00' W and is bounded by the continental shelf which runs along the edge of the Island, south west to north east. As a result the area is subjected to a variety of oceanic influences including the Gulf Stream, sub-Arctic intermediate waters, north Atlantic deep water and Mediterranean influences. Each of these water masses can contain different chemical signals (salinity, nutrients etc.) that can be used for source attribution purposes. The M6 weather buoy (53.07482°N 15.88135°W) is located approximately 400 miles off the west Irish coast in a depth of approximately 3000 metres of water above the Rockall Trough which is a perfect platform for monitoring in this remote environment. The Rockall Trough has been recognised as an important pathway for nutrient rich warm waters to enter Nordic seas. The upper 1000 m of water has been associated chemically with Eastern North Atlantic water (ENAW) which is characterised by warm saline water and formed in the Bay of Biscay.¹ At the Southern entrance of the trough between 400 – 800 m salinity values fall indicating a mixing line between ENAW water and Sub-Arctic intermediate water (SAIW). Other water masses present include Mediterranean water, Labrador Sea water (LSW) and Northeast Atlantic deep water (NEADW). It was the intention of this study to deploy two types of Passive Sampling Device (PSDs) at the M6 weather buoy (SPMD – semipermeable membrane device, PDMS – polydimethylsiloxane) to monitor contaminant levels (PAH – polyaromatic hydrocarbons, PCB – polychlorinated biphenyls and OCs – organochlorine compounds) at depth and to report on the loadings present. The buoy also has additional instruments deployed at depth (surface, 250, 500, 750 and 1040 m depth) with the samplers deployed in conjunction with these instruments for over 18 months.

2. Materials and Methods

PDMS passive samplers (9.5 – 5.5 cm) were placed in a soxhlet apparatus with ethyl acetate and extracted for 100 hours and were then spiked with Performance Reference Compounds (PRCs): naphthalene-₄₈, acenaphthene-₁₁₀, phenanthrene-₁₁₀, Chrysene-₁₁₂, perylene-₁₁₂ and PCB_{29, 30, 55, 78, 145, 155} and 204. SPMDs were prepared using low density polyethylene (LDPE) lay flat tubing following methods described previously by Booij *et al.*² Both passive sampler types were mounted on the deployment cages, covered in tinfoil and placed in air tight containers before being stored at -20°C during transport. Before they were deployed on the M6 mooring rope

they were brought on deck and had the tinfoil removed at the last minute before deployment to minimise atmospheric exposure. Field control samplers were exposed to the atmosphere for a similar time to estimate accumulation from the ambient air. After recovery the remaining samplers were placed into cleaned sample jars and stored in a freezer (-20°C) for transport to the laboratory. PDMS passive samplers were extracted using the method described by Smedes *et al.*,³ while the SPMDs were extracted using methods described by Booij *et al.*² Samples were analysed using an Agilent 5970N GC-MSD system using a DB5 60m x 0.22µm x 0.25 mm and a Varian GC3000 ECD using a HT8 50m x 0.22 µm x 0.22 mm and a CPSIL 19 60m x 0.25µm x 0.25mm columns.

Concentrations (pg/L) of dissolved contaminants in PDMS were estimated using the unweighted nonlinear least squares method described by Booij and Smedes,⁴ where PRC fractions were fitted as a function of the water sampler partition coefficient. Log K_{pw} values used are as per Booij and Smedes⁴ and recalculated to compensate for the salting out affect of marine water of samplers.⁵ In SPMDs the dissolved water concentrations (pg/L) were estimated using the Excel spreadsheet created by Alvarez *et al.*⁶ Of the samplers returned from the site, SPMDs fared better than PDMS with only 40 % lost while of the PDMS deployed 80 % were lost along with the Cage deployed at 500m. Concentrations found for all analytes in both SPMDs and PDMS are shown in Table 1.

3. Results and Discussion

Results shown (Table 1) can be considered useful as there is a relative paucity of data of this type present in the literature from such 'pristine' baseline sites. PAH PDMS concentrations (Table 1) were low with $\sum\text{PAH}_{15}$ ranging from 338 – 617 pg/L in the water column at 1040 and 5 m respectively. Phenanthrene was the major PAH found, contributing 62 – 74 % of the total $\sum\text{PAH}_{15}$ present in the samplers. Naphthalene was found at high levels in the PDMS and SPMD blanks and field controls and so excluded. PAH concentrations in the surface sampler were higher (particularly lower molecular weight PAHs) than those at depth indicating that perhaps aerial deposition and/or surface deposition from passing marine traffic may be a possible source of PAHs in the surface sampler. In SPMDs the $\sum\text{PAH}_{15}$ results were similar in concentration ranging from 342-438 pg/L. Major contributions to the $\sum\text{PAH}_{15}$ are noted from phenanthrene, fluoranthene and fluorine.

PCB results shown in Table 1 are at low levels with the $\sum\text{PCBs}$ ranging from 0.9 – 6.5 pg/L in PDMS and from 0.06 – 2 pg/L in SPMD. The levels of PCBs found are in agreement with those reported by Schulz-Bull *et al.*⁷ where PCBs in the North Atlantic were measured between 0.347 – 11.24 pg/dm³ and those reported in a Norwegian Institute for water research (NIVA) report using PDMS and SPMD samplers where the levels of upper bound $\sum\text{PCB}_{10}$ in PDMS PSDs were estimated at 29 pg/L.⁸ Overall $\sum\text{PCBs}$ increased slowly with depth up to and including 750 m samplers and then reduced at 1040 m. $\sum\text{OCs}$ were found at highest levels in the surface sampler and were found to reduce with depth. Aerial deposition of OCs at the surface would appear to be the primary route of transport to this site. For OC compounds major contributions were noted from α and γ -HCH which are in agreement with the NIVA report⁸ where these compounds were found in highest abundance in both

Table 5.3 C_w concentrations (pg/L) for PAH, PCB and OCs at different depths for SPMDs and PDMS passive samplers deployed at the M6 weather buoy.

Compound (pg/L)	250 m		750 m		1040 m		PDMS PSD			
	SPMD 1	SPMD 2	SPMD 1	SPMD 2	SPMD 1	SPMD 2	5 m	250 m	750 m	1040 m
Acenaphthylene	32	41	35	24	29	33	36.8	5.56	4.22	2.89
Acenaphthene	22	23	17	15	15	12	42.0	7.54	4.20	3.54
Fluorene	61	65	53	51	44	43	50.0	20.4	11.2	10.9
Phenanthrene	176	184	174	162	133	143	406	308	328	210
Anthracene	11	12	12	11	10	11	10.2	16.5	19.2	10.9
Fluoranthene	23	23	92	87	66	83	38.9	37.5	95.6	78.9
Pyrene	5.7	5.3	15	14	12	15	14.0	6.16	10.8	8.68
Benz[a]anthracene	2.4	2.4	2.6	2.5	1.9	2.2	1.47	0.73	0.65	0.40
Chrysene	10	10	24	23	18	25	4.89	5.39	10.5	7.46
Benzo[b]fluoranthene	6.7	6.2	10	7.3	10	14	3.17	3.53	3.90	1.37
Benzo[k]fluoranthene	3.6	3.4	4.2	3.3	3.9	4.6	2.43	2.70	3.17	1.34
Benzo[a]pyrene	0.7	0.6	0.5	0.5	0.5	0.6	5.24	1.73	0.06	0.97
Indeno[1,2,3-cd]pyrene	0.3	0.1	0.3	0.1	0.4	0.8	0.64	0.15	0.02	0.08
Dibenzo[a,h]anthracene	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	0.08	n.d	n.d	n.d
Benzo[g,h,i]perylene	0	<0.01	0.3	0.2	<0.01	0.3	0.48	0.32	0.23	0.07
ΣPAHs	354	375	438	401	342	388	617	416	492	338
Ratio P/A	16	15	15	15	14	13	39.8	18.6	17.1	19.2
Ratio FL/PY	4.0	4.3	6.2	6.1	5.6	5.4	2.78	6.08	8.85	9.10
LPAH/HPAH	5.7	6.4	2.0	1.9	2.1	1.7	7.64	6.16	4.28	2.40
PCB 18	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	0.4	0.3	0.9	0.5
PCB 28	1.0	0.9	0.5	0.6	0.7	0.6	0.4	0.3	0.6	0.4
PCB 31	0.7	0.6	1.2	1.8	0.7	1.0	0.4	0.4	0.6	0.3
PCB 44	1.0	1.0	1.6	1.6	0.9	0.8	0.2	0.3	0.9	0.4
PCB 52	1.0	0.9	1.2	1.6	0.3	0.2	0.1	0.3	0.9	0.3
PCB 101	0.3	0.3	0.5	0.4	0.4	0.4	0.2	0.4	0.4	0.3
PCB 149	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	0.1	0.2	0.3	0.1
PCB 118	0.6	0.6	1.5	1.7	0.6	0.5	0.2	0.2	0.2	0.3
PCB 153	0.9	0.9	1.9	2.0	1.8	1.9	0.2	0.4	0.3	0.3
PCB 105	0.3	0.3	0.7	0.8	0.1	0.1	0.3	0.8	0.8	0.3
PCB 138	0.4	0.4	1.1	1.2	0.7	0.6	0.6	0.4	0.3	0.1
PCB 156	0.1	0.1	0.2	0.6	0.1	0.0	0.0	0.1	0.3	0.1
PCB 170	0.1	0.1	0.3	0.4	0.3	0.3	0.1	0.1	0.1	0.1
PCB 180	0.1	0.1	0.1	0.2	0.1	0.1	0.03	0.1	0.010	0.02
PCB 194	K	K	K	K	K	K	K	0.13	0.02	0.02
PCB 209	K	K	K	K	K	K	0.003	0.24	0.15	0.1
α-HCH	32.9	34.7	46.1	56.6	36.1	34.7	143	104	89	72.5
β-HCH	n.d	n.d	n.d	n.d	n.d	n.d	267	265	173	149
Endosulphane sulphate	26.6	26.9	30.7	41.0	26.4	n.d	n.d*	n.d*	n.d*	n.d*
Lindane	34.8	35.3	22.8	11.5	31.5	71.4	n.d	n.d	n.d	n.d
op-DDD	0.05	0.06	0.80	0.74	0.43	0.37	n.d	n.d	n.d	n.d
op-DDT	1.31	1.86	3.70	4.98	3.52	4.25	<0.02	0.4	0.1	<0.02
pp-DDD	0.44	0.43	2.55	3.02	1.01	1.13	5	3.1	1.4	1.38
pp-DDE	0.98	1.10	4.36	4.96	2.72	4.15	0.1	0.2	0.3	0.15
pp-DDT	1.88	1.99	7.08	8.84	6.23	7.83	2	0.5	0.8	2.19
Trans chlordane	0.91	1.13	1.68	1.94	1.25	2.30	n.d	n.d	n.d	n.d
op-DDE	0.33	0.50	3.77	4.77	4.21	2.57	0.6	0.3	0.1	0.15
cis-chlordane	1.39	1.65	4.56	4.79	2.32	2.59	0.4	0.7	0.5	0.16
Dieldrin	4.96	4.65	33.7	78.1	52.3	28.7	2.1	1.4	2.3	1.13
HCB	12.1	12.3	16.2	19.0	13.0	15.2	0.1	0.3	0.3	0.86
Heptachlor	0.68	0.75	0.85	2.34	0.52	2.74	K	K	K	K
Oxychlordane	21.0	21.1	12.0	34.7	73.2	35.5	K	K	K	K
Heptachlor Epoxide	9.7	7.37	5.48	7.47	4.09	3.23	K	K	K	K
Trans-Nonachlor	0.75	0.80	0.49	0.55	7.11	7.39	K	K	K	K
Endosulfan	26.6	26.9	30.7	41.0	26.4	28.4	n.a*	n.a*	n.a*	n.a*
Endrin	10.3	11.1	15.9	16.5	9.6	12.5	K	K	K	K

n.d – not detected, n.a – not analysed, n.a* – interferent in chromatogram, K – concentration calculated no K_{pw} value

SPMD and PDMS samplers deployed. Levels of PCBs and OCs present in the PDMS samplers were found to be low overall with levels similar to those reported by Allan *et al.*⁸ where HCHs were detected at low levels but higher than those of other OCs and PCBs. Overall OCs concentrations seem to be reduced at the lowest depth,

this may be as expected given the remote area under investigation as OC compounds are generally deposited at the surface and the freely dissolved water concentrations would be reduced at depth through sorption with particulate matter. Modelled PAH concentrations (normalised relative to the modelled concentrations determined in the SPMD sampler at 250 m) were evaluated in order to determine the level of correlation between devices at 3 sampling depths. Strong correlation (Using Pearson $R = 0.939$ to 0.948) for PAHs was shown to exist between the final concentrations measured by both sampler types irrespective of depth sampled. Lower correlation was calculated between PDMS and SPMD ($R = 0.42$ to 0.52) for PCBs and OCs. Increases in the concentrations of fluoranthene, pyrene and benzo(a)anthracene congeners, and decrease of acenaphthalene, fluorene and chrysene at depth indicate that the contaminant profile changes relative to sampling depth possibly due to a change in contaminant profile at ~ 750 m.

4. Conclusions

This study has provided valuable concentration and profile data for a variety of persistent pollutants, few such data are available in the literature. Such baseline dissolved water concentration data from pristine offshore waters are of great value in ongoing discussions regarding the relevance and applicability (and in the generation of legislative thresholds) of passive sampling in a wider monitoring context. Overall concentrations of PAH, PCBs and OC were low and comparable with the few studies available from open waters. Individual sampler types were shown to behave relatively similarly irrespective of depth but in the absence of sufficient replicates further research is merited to evaluate whether the major contributor to profile changes is related to different pollutant burdens associated with the relevant water mass or whether physico-chemical/adsorptive properties of the individual compounds is the main driver of the observed profiles. It will not always be possible to deploy and retrieve PSDs within closely stipulated timeframes especially in offshore often dynamic locations. It is clear however that while controlled deployment times are advisable it is still possible to derive valuable monitoring information with PSDs deployed over an extended period.

5. References

1. McGrath, T., Nolan, G. & McGovern, E. *Deep Sea Research Part I: Oceanographic Research Papers* **61**, 57–73 (2012).
2. Booij, K., Smedes, F. & Van Weerlee, E. M. *Chemosphere* **46**, 1157–1161 (2002).
3. Smedes, F., Bakker, D. & De Weert, J. *The use of Passive Sampling in WFD monitoring*. (Deltares, 2010).
4. Booij, K. & Smedes, F. *Environ. Sci. Technol.* **44**, 6789–6794 (2010).
5. Smedes, F. & Booij, K. *Guidelines for passive sampling of hydrophobic contaminants in water using silicone rubber samplers*. (ICES, 2012).
6. Alvarez, D. A. *Guidelines for the use of semipermeable membrane device (SPMD) and the polar organic chemical integrative sampler (POCIS) in environmental monitoring studies*. (USGS, 2010).
7. Schulz-Bull, D. ., Petrick, G., Bruhn, R. & Duinker, J. *Marine Chemistry* **61**, 101–114 (1998).
8. Allan, I. J., Aas, W. & Langford, K. *Passive air and water sampling at Andoya at andoya, Bjornoya and Jan Mayen*. (NIVA, 2012).